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A Review of Australian Salt Lakes and Assessment of their Potential for Strategic Resources

Edited by T.P. Mernagh

With contributions by E.N. Bastrakov, J.D.A. Clarke, P. de Caritat, P.M. English, F.J.F. Howard, S. Jaireth, J.W. Magee, A.A. McPherson, I.C. Roach, I.F. Schroder, M. Thomas, and J.R. Wilford

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Executive Summary

Globally, salt lakes are major sources of lithium, potash, borates and other strategic mineral commodities. Salt lakes or 'salars' in the semi-arid to arid regions of Chile, Peru, Argentina and Bolivia contain most of the world's low-cost supply of lithium, while salt lakes in Jordan, Israel and China are significant sources of potash. Despite the large number of salt lakes distributed across Australia, public domain knowledge of saline lakes and their associated groundwater systems as potential sources for lithium, potash and other commodities is limited.

In this study we have reviewed the current, publicly available knowledge of Australian saline lakes and developed mineral systems models, which were used to assess the favourability of Australian salt lake systems for lithium, boron, potash and calcrete-hosted uranium deposits. Mineral systems methodologies have previously been applied to a range of hydrocarbon and mineral commodities (Magoon and Dow, 1994; Wyborn, *et al.*, 1994; Walshe, *et al.*, 2005; Barnicoat, 2009; Skirrow, *et al.*, 2009 and Huston, *et al.*, 2012). However, the application of mineral systems methodologies to economic deposits in salt lakes has not, to our knowledge, been previously attempted. Therefore, this report presents a new way to assess the economic potential of Australian salt lakes.

The critical features of salt lake mineral systems with potential for lithium, boron, potash and calcrete-hosted uranium are discussed in Chapter 4. Due to the limited data available for Australian salt lake systems, these models are based on examples of economic lake deposits from North and South America, China and western Asia. In Chapter 5, Australian salt lakes are assessed using the critical features of the above mentioned mineral systems. This has led to the development of preliminary favourability (prospectivity) maps (based on the limited data currently available) showing which Australian salt lakes have the highest potential for lithium, boron, potash and calcrete-hosted uranium or for combinations of these commodities. These maps have been designed for plotting on A0 sheets, and the GIS dataset from which the maps were derived is available for download at www.ga.gov.au.

The favourability assessment identified seven regions with salt lakes that have potential for lithium and/or boron and/or potassium and/or calcrete-hosted uranium. They are: the Lake Woods region of the Northern Territory and the central western region of the Northern Territory, the north east region of the Yilgarn Craton, the Paterson region, and the South Musgrave region (all in Western Australia) and the Lake Frome – Lake Eyre region and central Gawler region in South Australia.

Australia has considerable potential for salt lakes enriched in potash. This is indicated by historical production of potash from Lake Chandler, advanced potash projects at Lake Disappointment and Lake Mackay, and the discovery of new resources in the Karinga Creek region in the Northern Territory. This study has also identified a new greenfields area, the Lake Woods region, which is favourable for the production of potassium-rich brines. Another new finding from this study is that Lake Woods and other potash-enriched, Cenozoic salt lakes may be associated with nearby, older (Neoproterozoic to Paleozoic) evaporite-bearing successions. This suggests that the hydrochemistry of lakes in these 'halotectonic settings' differs from salt lakes whose chemical signatures are largely meteoric or, at most, reflect the geochemistry of their immediate catchments.

The Lake Frome region, the central Gawler region and the north east Yilgarn Craton were identified as areas having potential for lithium and/or boron but the potential is considered low relative to salt lakes

in the Americas and Asia. This may be due to Australia's arid climate and the older age of the geological units that host the Australian salt lakes. However, it is conceivable that other, as yet unrecognised, mineral systems, with alternative sources of lithium and boron may operate in some of these salt lakes.

Australia has many calcrete-hosted uranium deposits and prospects, including Yeelirrie, which is Australia's second largest undeveloped uranium deposit. Most of these deposits are spatially related to salt lake systems involving groundwater-bearing palaeochannels that drain into the salt lakes. Preliminary favourability analysis has identified the north east Yilgarn Craton, South Musgrave region and the Paterson Province in Western Australia, the central western region in the Northern Territory, and the central Gawler region in South Australia as having the highest potential for calcrete-hosted uranium deposits.

This preliminary assessment of Australian salt lakes has found that most of the data needed for a proper assessment of Australian salt lake mineral systems is either of inconsistent quality or severely limited in areal distribution. The available groundwater hydrogeochemical datasets are patchy at best, inconsistent and of variable quality. Many datasets in the vicinity of salt lakes only report salinity or total dissolved solids. There is a crucial need for a consistent and comprehensive national groundwater database that includes a comprehensive suite of elements as well as salinity, and other important parameters. Recommendations for further work that will improve our understanding of Australian salt lake mineral systems are given in Chapter 7.

1 Introduction

T.P. Mernagh and J.D.A. Clarke

Historically, salt lakes have been important sources of commodities such as halite, potash and borate. Salt lakes in Jordan, Israel and China contain significant resources of potash while lacustrine deposits and salt lakes in Turkey, South America, China and the USA contain most of the world's borate deposits. More recently, there has been an increase in the demand for lithium driven by green technology and the use of lithium-ion batteries. Salt lakes or 'salars' in the semi-arid to arid regions of Chile, Peru, Argentina and Bolivia contain most of the world's low cost supply of lithium. Despite the large number of salt lakes distributed across Australia, public domain knowledge of saline lakes and their associated groundwater systems as potential sources for potash, lithium, boron, uranium, and other commodities is limited. The ultimate aim of this project was to assess the favourability (prospectivity) of Australian salt lake systems for potash, lithium, boron, and calcrete-hosted uranium deposits. This was achieved by:

- Developing models for salt lake mineral systems using known global analogues to determine the key factors controlling element mobility and concentration in groundwaters and associated saline lakes, and the associated occurrence of relevant metals in geological materials (e.g. lake sediments, aquifer rocks, and regolith).
- Reviewing literature and compiling existing data on the concentrations of elements and minerals
 of interest in saline lakes, their associated groundwaters and geological materials.
- Applying a mineral systems concept in order to delineate salt lake systems in Australia favourable for forming economic concentrations of lithium, boron, and potash.
- Recommending future data acquisition and analysis requirements for more detailed mineral potential assessments of Australian salt lakes.

1.1 Strategic mineral production globally

In 2008 the US National Academy of Sciences produced a report entitled "Minerals, Critical Minerals, and the U.S. Economy", which generally defines 'critical minerals' (also known as strategic minerals) as those that are important in use and subject to potential supply restrictions (National Research Council, 2008). This has lead to increasing concern in many countries, including the USA, EU countries, Japan and South Korea, about security of supply of raw materials that underpin their industrial economies in the short to long terms (Skirrow *et al.*, 2013). As demand for metals and minerals increases, driven by the rise of hi-tech industries and growth in the emerging economies of Asia and South America, competition for resources is growing. This may be further compounded by political risks associated with the geographical concentration of the supply for certain strategic minerals. In this introductory chapter we consider some of the strategic mineral commodities that are produced from salt lake environments around the world, and which might be explored for and produced in Australia.

1.1.1 Potash

Potash is the common name for various mined and manufactured salts that contain potassium in water-soluble form. It usually refers to potassic fertilisers, which are potassium chloride (KCl or sylvite), potassium sulfate $[K_2SO_4$ or sulfate of potash (SOP), which usually is a manufactured product], and potassium-magnesium sulfate $[K_2SO_4 \cdot 2MgSO_4$ or either langbeinite or double sulfate of potash magnesia (SOPM or K-Mag)]. Muriate of potash (MOP) is an agriculturally acceptable mix of KCl (95% pure or greater) and sodium chloride (halite) for fertilizer use, which includes minor amounts of other nontoxic minerals from the mined ore and is neither the crude ore sylvinite nor pure sylvite (Geoscience Australia, 2012).

Potash can be considered as a strategic commodity as there are no substitutes for potassium as an essential plant nutrient and an essential nutritional requirement for animals and humans. More than 33 million tonnes per year of potash is currently produced worldwide, mostly for use in fertilisers (US Geological Survey, 2012). Various types of fertiliser-potash thus comprise the single largest global industrial use of the element potassium. In a report that considered the 10 major themes likely to emerge in the minerals space, Goldman Sachs have identified potash as the commodity for the next decade as the pressure to feed the world by achieving greater yields from nutrient deficient soils in China, India and elsewhere grows (Fitzgerald, 2013). Goldman Sachs reported that potash could be to the next decade what the boom commodity iron ore was to the last.

Potassium is considered a critical commodity for the Australian economy as Australia does not produce potash at present (Skirrow *et al.*, 2013). Currently, there are no published potash resources for Australia, but exploration for potash is continuing at Lake Disappointment, Lake Chandler and Lake Mackay, the south Carnarvon Basin, Perth Basin and Canning Basin in Western Australia, as well as the Adavale Basin in Queensland and in the Barrow Creek and Karinga Lakes areas in the Northern Territory (Geoscience Australia, 2012).

Canada is currently the world's largest producer of potash (10,160 million tonnes in 2011) with the largest reserves occurring in the Prairie Evaporite Deposit, which lies beneath the southern plains of Saskatchewan. The next largest producers are Russia (approx. 6,700 million tonnes) and Belarus (approx. 5,000 million tonnes; US Geological Survey, 2012). In Russia, the two existing potash mining companies concentrate their operations on a large deposit in the Urals, which has been mined since 1931. The Belarusian deposits near Minsk have been mined for potash crude salts since the early 1960s. Other producers include Germany, China, Israel, Jordan, Chile, Brazil, Spain, the USA and the United Kingdom (US Geological Survey, 2012, Figure 1.1). All these deposits are associated with buried evaporite basins rather than modern salt lakes.

The majority of potash mines still extract potash in solid form by conventional underground mining. The crude salt is dislodged using explosive charges or by cutting several hundred metres below the ground and is then brought to the surface via vertical shafts and processed in aboveground plants. Solution mining is an alternative method that involves extracting potash-bearing solutions from flooded underground mines or using well designs which access the potash with vertical drill holes. The potash-saturated salt solution is pumped to lined solar evaporation ponds, where salt and potash are concentrated through evaporation of the water.

Potassium-bearing salt solutions underground or in salt lakes represent a special form of natural potash deposit. However, recovering these resources is highly dependent on the climate, as sunlight is used to evaporate the solutions (solar evaporation). The world's largest salt lake resource of potash is the Dead Sea (up to 1 billion tonnes of K_2O), which has been used for potash production since the

beginning of the 1930s (Nissenbaum, 1993). Evaporation plants for potash recovery also operate in China, the USA and Chile. The brine used in China is mainly taken from Qarhan Salt Lake while producers in the USA use brine from the Great Salt Lake or the Bonneville Flats in the Great Salt Lake Desert. In Chile potash is extracted from salt solutions under the salt crust of Salar de Atacama (Orris, 2011). A summary of the major potash-bearing salt lakes is given in Table 1.1.

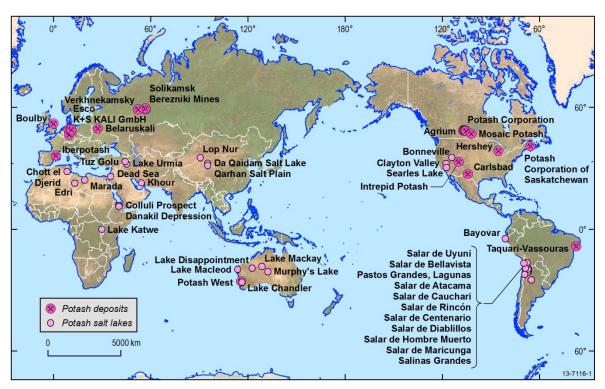


Figure 1.1 World map showing the distribution of hard-rock potash mines (dark pink circles with symbol) and potash-bearing salt lakes (light pink circles).

Table 1.1 Major potash-bearing salt lakes around the world

Name	Country	K ₂ O (mg/L in solution)	References
Salar de Cauchari	Argentina	3,480 to 8,328	Houston (2010), King (2010)
Salar de Centenario	Argentina	up to 10,000	Mining Exploration News (2011)
Salar de Diablillos	Argentina	5,270 to 6,600	Larrondo et al. (2011)
Salar de Hombre Muerto	Argentina	7,400	Garrett (1996)
Salar de Olaroz	Argentina	8,000	Orocobre (2012a), Houston and Ehren (2010), King (2010)
Salar de Rincón	Argentina	7,490	Mining Exploration News (2011), Sorentino (2004)
Salinas Grandes	Argentina	11,200	Houston (2010)
Pastos Grandes, Lagunas	Bolivia	14,200	New World Resource Corp. (2008)
Salar de Uyuni	Bolivia	8,640	Ballivían and Risacher (1981)
Salar de Atacama	Chile	22,200	Roberts (2008), Pueyo et al. (2001)

Name	Country	K ₂ O (mg/L in solution)	References
Salar de Bellavista	Chile		Ericksen (1963)
Salar de Maricunga	Chile	6,000 to >18,000	Li3 Energy (2011), Hains (2011)
Da Qaidam Salt Lake	China	25,700	Yu et al. (2001), Gao et al. (1993)
Lop Nur	China	5,400 to 11,000	Tse (2009), Wang et al. (2005)
Qarhan Salt Plain (Dabusun and others)	China	14,400 to 20,900	Yuan <i>et al.</i> (1996), Duan and Hu (2001)
Colluli Prospect	Eritrea		Orris (2011)
Danakil Depression	Ethiopia		Orris (2011)
Khour	Iran	1,450 to 4000	Geological Survey and Mineral Exploration of Iran (2007)
Lake Urmia (Rezayeh)	Iran	1,100	Notholt (1983)
Dead Sea	Israel/Jordan	7,200 to 9,000	Garrett (1996)
Edri	Libya	3,050	Goudarzi (1982)
Marada	Libya	22,600	Goudarzi (1982), Van Kauwenbergh (2006), Notholt (1983)
Bayovar	Peru	up to 13,670	Industrial Minerals (2010), GrowMax Agri Corp. (2013), Americas Petrogas (2013)
Chott el Djerid	Tunisia	1,830 to 5,200	Garrett (1996); Notholt (1983)
Tuz Golu (Salt Lake)	Turkey	8,900 to 46,000	Kilic and Kilic (2005)
Lake Katwe	Uganda	30,500	Kisitu (1991)
Bonneville (including Great Salt Lake)	USA	2,400 to 7,800	Gwynn (1996, 2001), Tripp (2001), Warren (1999)
Clayton Valley (Silver Peak)	USA	4,800 to 6,360	Garrett (1996), Papke (1976)
Searles Lake	USA	17,900 to 31,000	Smith (1976), British Sulphur Corporation (1984), Roskill Information Services (1989)
Lake Chandler	Australia	57,300 (reserves as solid alunite)	ASX Release (2009)
Lake Disappointment	Australia	Average 6583	Reward Minerals Ltd (2012c)
Lake Mackay	Australia	Not Available	Geoscience Australia (2012)
Lake Macleod	Australia	Not Available	Geoscience Australia (2012)
Murphy's Lake	Australia	Not Available	Geoscience Australia (2012)
Karinga Creek Project	Australia	3,550 to 8,688	Rum Jungle Resources (2012)

1.1.2 Lithium

Even though lithium products are widely used in households, factories, and laboratories, lithium's presence often goes unrecognized. Lithium may be as close to the average person as a medicine chest, a television, a swimming pool, or a mobile phone. For these reasons, the security of lithium supplies has become a top priority for Asian technology companies. Strategic alliances and joint ventures have, and continue to be, established with lithium exploration companies worldwide to ensure a reliable, diversified supply of lithium for Asia's battery suppliers and vehicle manufacturers.

One of the key technologies driving the green technology revolution is lithium-ion batteries. As a result of lithium-ion battery demand for hybrid-electric and electric cars, the increase in demand for lithium carbonate is expected to increase four-fold by 2025 (i.e. from ~129,000 tonnes in 2011 to ~500,000 tonnes in 2025, Figure 1.2, SignumBox, 2012).

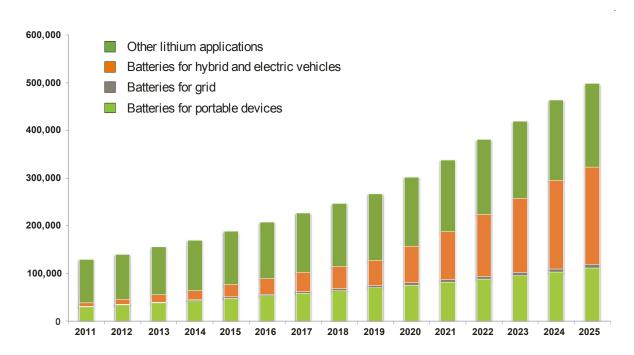


Figure 1.2 Global lithium (in tonnes lithium carbonate equivalent) demand forecast 2011 – 2025 (SignumBox, 2012).

Lithium carbonate is also an important industrial and medical chemical with numerous applications (Figure 1.3). In frits and glass, lithium carbonate is added to ceramics, enamels, and glass to reduce their melting point, reduce viscosity, and increase surface tension making lithium glasses suitable for ovenware (Ullmann's Encyclopedia of Industrial Chemistry, 2012).

Lithium hydroxide is used in the production of greases. The addition of lithium stearates maintains the viscosity of greases at high temperatures and makes them insoluble in water. Both of these properties are important for lubricants in vehicles, aircrafts, and heavy machinery (Ullmann's Encyclopedia of Industrial Chemistry, 2012).

Lithium bromide, lithium chromate, and lithium chloride are used in air conditioners operating on the absorption principle. Lithium hydroxide is also used to absorb carbon dioxide in submarines and spacecrafts (Ullmann's Encyclopedia of Industrial Chemistry, 2012).

Other uses of lithium include production of organic compounds and alloys. It is used as a coolant and shielding material in nuclear reactors, and for the production of tritium (for hydrogen bombs and biological research). Lithium metal is used in alloys with other metals; for example, it changes the hardness of aluminum and lead, and the ductility of magnesium (Ullmann's Encyclopedia of Industrial Chemistry, 2012).

Lithium compounds are employed in several applications. Lithium acetates are used in pharmaceuticals and in the production of polyesters. Lithium carbonate is added to cement to accelerate setting time and to molten salts used for electrolytic aluminum production. High purity lithium carbonate is used in pharmaceuticals to treat manic-depressive conditions (Ullmann's Encyclopedia of Industrial Chemistry, 2012).

The global lithium resource is estimated to be over 38 million tonnes (US Geological Survey, 2012). These resources are contained in three main types of lithium deposits: brines, pegmatites, and sedimentary rocks. In 2011, 78% of lithium production was from brines, primarily in Chile, Argentina and the USA, and 22% was produced from hard rock mines, primarily in China and Australia (SignumBOX, 2012).

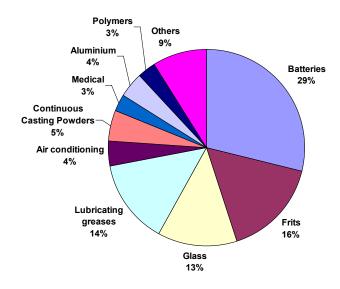


Figure 1.3 Pie chart showing the world consumption of lithium by application (SignumBOX, 2012).

1.1.2.1 Brines

Most lithium brine deposits are in geologically recent enclosed basins containing lacustrine evaporites that were produced by high rates of evaporation relative to precipitation. The most important deposits of this type are in the central Andes and China, with smaller deposits in the western USA (Figure 1.4; Vine, 1980; Kesler *et al.*, 2012). Lacustrine evaporates and associated brines have a wider range of composition than do marine evaporites and are more likely to be enriched in lithium particularly if there is a local source of lithium.

At present, the salt lakes in South America, China, and Tibet are the richest lithium sources of this type. The largest producing brine deposit in the world is the $3,000~\rm km^2$ Salar de Atacama, in northern Chile. Salar de Atacama has the highest known concentration of lithium, averaging 0.14% (or 1400 mg/L) lithium, and is the world's largest producer of lithium carbonate – 40,000 and 25,000 tonnes of $\rm Li_2CO_3$ in 2008 from operations owned by Sociedad Quimica y Minera (SQM) and Rockwood Holdings Inc., respectively (Tahil, 2008).

Bolivia's Salar de Uyuni has an average lithium concentration of 0.0532% and has yet to begin production. It is thought to be the largest salar in the world with a surface area of about 10,000 km². The brine at Salar de Uyuni varies from Na–Cl type to Mg–Cl type and Gruber *et al.*, (2011) have estimated a lithium resource of 10.2 Mt lithium. Exploration in other salars in the region has also encountered deep lithium-bearing brines indicating the potential for a large lithium brine resource in this region.

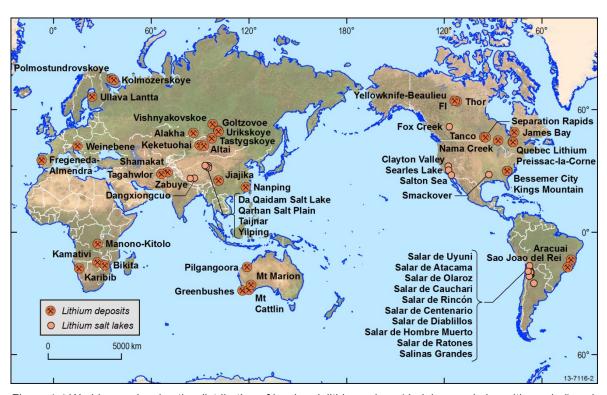


Figure 1.4 World map showing the distribution of hard-rock lithium mines (dark brown circles with symbol) and lithium-bearing salt lakes and brines (light brown circles).

Lithium-bearing lacustrine evaporites and brines are also found in the Qinghai–Tibet plateau. Lithium, is concentrated in many of these lakes, and is produced from two areas, a zone of magnesium-sulfate lakes in the Qaidam Basin, which is in the northern part of the plateau, and a zone of carbonate-rich lakes in the southern and southwestern part of the plateau. The most important lithium-bearing deposit in the zone of carbonate-type lakes is Zabuye (Zhabuye, Zabuye Caka) Lake for which the lithium carbonate mineral zabuleyite (Li_2CO_3) is named. Zabuye Lake, with a total surface area of 243 km², has an average lithium concentration of 0.068%, and an estimated lithium resource of 1.53 Mt (Research in China, 2009).

The brine at the Clayton Valley (Silver Peak) deposit in the USA has a lithium concentration of 0.02% and an estimated lithium resource of 0.3 Mt (Gruber *et al.*, 2011). The Clayton Valley basin, which is bounded on the east by a normal fault, has a relatively small area of 83 km² (Davis *et al.*, 1986).

Further evidence for deep penetration of brines in dry lakes comes from Searles Lake in California, which yielded by-product lithium until recently (Kesler *et al.*, 2012).

Brines are also found in deep oil reservoirs, and some of these are enriched in lithium. Best known of these are the brines in the Smackover Formation in the Gulf Coast region of the United States. The major unit in this Formation is a Jurassic marine limestone that occurs between evaporite units above and sandstones below, and it is a major hydrocarbon reservoir. The brines in the Formation are estimated to contain 0.75 Mt of lithium resource at an average lithium concentration of 0.0146% Gruber *et al.* (2012). The Smackover brines are also at depths of several thousand feet, which increases cost because of the need to pump the brine to the surface for processing (unless it is moved to the surface during oil production). Fox Creek in Canada also has a lithium-bearing oilfield brine. A summary of the major lithium-bearing brine deposits is given in Table 1.2. Therefore, oil field and deep geothermal brines are another potential source of lithium. Studies of geothermal fluids from the Cooper Basin in Australia have shown elevated concentrations of lithium which most likely reflects the increase in the solubility of lithium at higher temperatures (Uysal *et al.*, 2011).

Table 1.2 Major lithium-bearing salt lakes and brines around the world.

Name	Country	Average Li (mg/L in solution)	References
Salar de Cauchari	Argentina	380	Orocobre (2012b)
Salar de Centenario	Argentina	400	Rodinia Lithium (2012a)
Salar de Diablillos	Argentina	556	Rodinia Lithium (2012b)
Salar de Hombre Muerto	Argentina	520	Gruber et al. (2012)
Salar de Olaroz	Argentina	700	Gruber et al. (2012)
Salar de Rincón	Argentina	330	Gruber et al. (2012)
Salinas Grandes	Argentina	795	Orocobre (2012c)
Salar de Ratones	Argentina	600	Rodinia Lithium (2012a)
Salar de Uyuni	Bolivia	532	Gruber et al. (2012)
Salar de Atacama	Chile	1400	Gruber et al. (2012)
Da Qaidam Salt Lake	China	300	Gruber et al. (2012)
Qarhan Salt Plain (Dabusun and others)	China	62	Shengsong (1986)
Dangxiongcuo	China	400	Gruber et al. (2012)
Zabuye	China	680	Gruber et al. (2012)
Taijnar	China	500	Kesler et al. (2012)
Clayton Valley (Silver Peak)	USA	200	Gruber et al. (2012)
Searles Lake	USA	50	Gruber et al. (2012)
Salton Sea	USA	200	Gruber et al. (2012)
Jadar (sedimentary deposit)	Serbia	87	Gruber et al. (2012)
Smackover (oilfield brines)	USA	146	Gruber et al. (2012)
Fox Creek (oilfield brines)	Canada	88	Channel Resources (2012)

1.1.2.2 Pegmatites

Lithium is currently being extracted from at least 13 pegmatite deposits and more deposits are under development (Figure 1.4). The largest productive pegmatite operation is at Greenbushes, Western Australia. It is owned by Rockwood Holdings Inc. and has an estimated reserve of 2.4 Mt of lithium carbonate equivalent (LCE), with an average grade of 1.44% lithium (Talison Lithium, 2012). In the USA, Russia, and Australia, some pegmatite operations with lower lithium concentrations ceased operations when South American brine deposits came on line in the 1980s and 90s. For example, Kings Mountain, a pegmatite deposit in North Carolina with an average grade of 0.69% lithium, closed in 1991 when Chilean brine operations opened. Other Australian pegmatite resources include Mt Cattlin, Mt Marion and Pilgangoora, which are all in Western Australia.

Lithium in pegmatites is usually present as the mineral spodumene ($LiAlSi_2O_6$), which can be used directly in ceramics but must be processed to release lithium in a form, usually lithium carbonate, which can be used in the manufacture of batteries and other products. To produce lithium carbonate from spodumene, the material is pulverized, calcined at 1,100 °C, treated with sulfuric acid, dissolved in water, separated from aluminum, and precipitated with soda ash. The heating and dissolution in this process make it more expensive to extract lithium from pegmatites than to extract lithium from brines. The concentration of lithium in pegmatites is considerably higher than in brines, which offsets some of the costs.

1.1.2.3 Other deposit types

Lithium is also found in deposits of clay and lacustrine evaporites. In the clay deposits, lithium is part of clay minerals such as smectite, from which it must be separated by processing. The best known deposit of this type is in Kings Valley, Nevada, where deposits contain hectorite $[(Mg,Li)_3Si_4O_{10}(OH)_2]$, a type of smectite that is rich in magnesium and lithium. Estimates for Kings Valley are 14.937 Mt of proven resources grading 0.4% lithium and 12.198 Mt of probable resources grading 0.39% lithium (Western Lithium Corporation, 2012). The Jadar Valley, in Serbia, contains lacustrine evaporite deposits containing jadarite [LiNaB $_3$ SiO $_7$ (OH)], a new mineral that is a possible source of lithium and boron (Stanley *et al.*, 2007). An inferred resource of 125 Mt containing 0.84% lithium has been reported for this deposit (Rio Tinto, 2011). However, nothing is known about the economic feasibility of extracting lithium from these deposits.

1.1.3 Boron

On a global basis, boron moves naturally through the atmosphere at a rate of five to seven million tonnes per year. The element boron does not exist by itself in nature; it occurs in combination with oxygen and other elements in compounds called borates. Boron concentrations in soil are dependent on solubility of boron in the parent rock; the physical and chemical characteristics of the soil; and the amount of water moving through it. The available level of boron ranges from 0.1 mg/kg to 3 mg/kg of soil. However, most of the boron in soil remains part of insoluble minerals or is firmly attached to other components such as clay or organic matter. The total boron concentration (soluble and insoluble) in soil can be categorised as low-boron (less than 10 mg/kg soil) or high-boron (on the order of 100 mg/kg). The average overall concentration of boron in all soil ranges from 10 mg/kg to 20 mg/kg (Borax, 2012).

More than 150 minerals are known to contain boron but five of the most common forms of borate are:

Sassolite [B(OH)₃]

Sassolite is the mineral form of boric acid. It occurs in volcanic fumaroles and hot springs, as well as in bedded sedimentary evaporite deposits. It was originally found in Sasso Pisano, near Volterra in Italy.

The name borax comes from the Persian *burah*, a word that may have meant potassium nitrate or another fluxing agent. Borax was first discovered in dry lake beds in Tibet and was imported via the Silk Road to Arabia.

Kernite is named after Kern County, California, where it was first mined. Crystals of kernite more than 1.5 metres long have been found in the original mine.

This mineral takes on many different shapes. It can look like a mushroom, a cauliflower, a snowball or cotton ball. In fact, "cotton ball" is a common nickname for this mineral.

Colemanite gets its name from one of Borax's founding fathers, William T. Coleman.

The versatility of borates lies in their distinct bonding and structural characteristics. In living systems, these characteristics make borates vital to metabolism. In addition to being essential in living things, borates are important to many industrial applications including:

Biostatic: Sufficient concentrations of borates can inhibit the growth of bacteria and fungi and protect against damage by wood destroying insects. For this reason, borates are widely used to improve the durability of wood and wood based construction products. They are also used in the formulation of some insecticidal products.

Buffering: Borates can serve to balance acidity and alkalinity. This property is made use of in both industrial processes and consumer products.

Glass-Forming: Borates modify the structure of glass to make it resistant to heat, radiation, or chemical attack. They can also lower the melting temperature of glasses to facilitate the production of durable fiberglass, specialty glasses, and ceramic glazes. Borate glasses are important components in modern television, computer, and mobile device display panels (e.g. ultra-thin LCD screens).

Cross-linking: Borates react with suitable alcohols and carbohydrates to link them together. This effect is used to produce starch adhesives and fluids used in oil recovery. Related chemistry also provides the basis for the essential biological roles of boron.

Anticorrosion: Borates bond to ferrous and other metal surfaces to reduce their susceptibility to corrosion. This property is utilized in anticorrosive coatings, lubricants, industrial water systems, and automotive coolants.

Fire Retarding: Borates are used as fire retardants for polymers and cellulosic materials, such as cotton batting, wood, and cellulose insulation. Specialised borate compounds, such as zinc borates, are used as fire retardants and smoke suppressant additives in polymers.

Metallurgical: Borates are excellent fluxes used to remove oxide impurities from metals. Boron is also added to steel and aluminum to produce especially hard and corrosion-resistant alloys. Borates find many specialised metallurgical uses, including the production of super-strong magnets. Borates are also used to stabilise metallurgical slags to divert them from landfills into useful applications.

Detergency and Cleaning: Borates improve the performance of cleaning products by buffering and conditioning wash water. They inhibit the corrosion of washing machine parts. In addition, perborates can provide a convenient source of active oxygen for non-chlorine bleaching and stain removal.

Nuclear Shielding: Boron is unique among the light elements in its ability to capture neutrons, due to the natural presence of the ¹⁰B isotope of boron (~20% natural abundance). This radiation absorbing effect is utilized in the shielding, control, and safety of nuclear reactors and in medical therapeutics. Boron neutron capture therapy (BNCT) is an experimental treatment for cancers and other diseases in which neutron capture is harnessed to perform effective microsurgery.

Spectroscopic: Borates absorb infrared light. Incorporated into building products, such as insulation fiberglass, borates improve energy efficiency by preventing heat loss through infrared transmission. This effect can also be utilized in plastics, coatings, and other materials.

Synthesis: In addition to the above mentioned physical and chemical effects, borates are used as starting materials in the manufacture of a wide range of advanced materials and specialty chemicals. These include super-hard ceramics, boron halides, hydrides, and esters, to name only a few.

Major borate deposits around the world occur in tectonically active extensional basins associated with plate boundaries (Figure 1.5; Ozol, 1977). Most of the economic borate deposits in the USA, South America and Turkey are thought to be associated with continental sediments and volcanism of Neogene age. Older skarn deposits also appear to be related to continental volcanic sources. Marine deposits appear to be the product of seawater evaporation in restricted basins probably associated with a sea floor borate source and/or progressive decanting that lead to concentration of the borates.

Borates associated with igneous and metamorphic rocks are thought to be an end phase of specialised magmatic segregation, or leached from the intruded rocks by hydrothermal fluids (Kistler and Helvaci, 1994). A summary of the world's major boron-bearing salt lakes is given in Table 1.3.

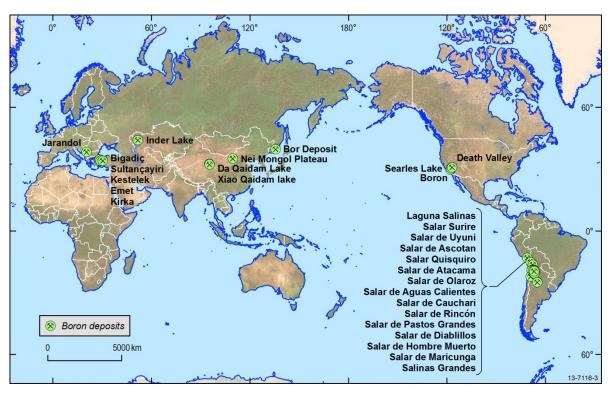


Figure 1.5 World map showing the distribution of major boron deposits (green circles with symbol).

Table 1.3 Major boron-bearing salt lakes around the world.

Name	Country	B (mg/L in solution)	References
Searles Lake	USA	1860	Smith (1976), British Sulphur Corporation (1984), Roskill Information Services (1989)
Laguna Salinas	Peru	n.a.	Kistler and Helvaci (1994)
Salar de Surire	Chile	1820	Kistler and Helvaci (1994), Garrett (1998)
Salar de Ascotan	Chile	89 - 1680	Kistler and Helvaci (1994), Risacher <i>et al.</i> (1999)
Salar de Uyuni	Bolivia	203 - 1059	Kistler and Helvaci (1994), Schmidt (2010)
Salar Quisquiro	Chile		Kistler and Helvaci (1994)
Salar de Atacama	Chile	61 - 440	Kistler and Helvaci (1994), Garrett (1998)
Salar de Maricunga	Chile	1810	Kistler and Helvaci (1994), Saenz (2012)
Salar de Cauchari	Argentina	421 - 547	Orocobre (2013)
Salar de Pastos Grandes	Argentina	87	Kistler and Helvaci (1994), Risacher and Fritz (1991)
Salar de Hombre Muerto	Argentina	40 - 250	Kistler and Helvaci (1994), Garrett (1998)
Salar de Aguas Calientes	Argentina	10 - 531	Orris (2011), Risacher et al. (1999)

Name	Country	B (mg/L in solution)	References
Salar de Diablillos	Argentina	540 - 691	Orris (2011), Rodinia Lithium (2012b)
Salar de Olaroz	Argentina	927 - 1100	Orris (2011), Orocobre (2012a)
Salar de Rincón	Argentina	275	Orris (2011)
Salinas Grandes	Argentina	>600	Orris (2011), Orocobre (2012c)
Da Qaidam Lake	China	470	Xiao et al. (1992)
Xiao Qaidam lake	China	278	Vengosh et al. (1995)
Dabusun Lake	China	182	Vengosh et al. (1995)
Zhacang Caka Lake	China	64	Vengosh et al. (1995)
Nei Mongol Plateau	China	2	Garrett (1998)
Inder Lake	Kazakhstan	198	Kistler and Helvaci (1994), Livingston (1963)

n.a. = not available

1.1.3.1 Other borate deposits

Most other borate mineral deposits are found interbedded with clays, mudstones, tuffs, limestones and similar lacustrine sediments. These deposits are summarised in Table 1.4.

Table 1.4 Other borate deposits around the world.

Name	Country	Major Boron-bearing Minerals	References
Boron (Kramer)	USA	Borax, kernite, ulexite	Kistler and Helvachi (1994)
Death Valley	USA	Borax, ulexite	Kistler and Helvachi (1994)
Bigadiç	Turkey	Colemanite, ulexite	Helvaci and Alonso (2000)
Sultançayiri	Turkey	Pandermite (priceite), howlite	Helvaci and Alonso (2000)
Kestelek	Turkey	Colemanite, ulexite, probertite, hydroboracite	Helvaci and Alonso (2000)
Emet	Turkey	Ulexite, teruggite, tunellite, veatchite-A, cahnite	Helvaci and Alonso (2000)
Kirka	Turkey	Borax, colemanite, ulexite, tincalconite, kernite, inderborite, inderite, kurnakovite	Floyd <i>et al</i> . (1998)
Khol-don (Hol-Kol)	North Korea	Ludwigite	Kistler and Helvachi (1994)
Raitakuri	North Korea	Ludwigite	Kistler and Helvachi (1994)
Magdalena	Mexico	Colemanite	Kistler and Helvachi (1994)
Jarandol Basin	Serbia	Howlite, colemanite	Erin Ventures (2012)

1.1.4 Valley and playa-type, calcrete-hosted uranium systems

Valley and playa-type, calcrete-hosted uranium systems are the most significant of the surficial uranium deposits. The host sediments are typically of Cenozoic age but uranium mineralistion is usually quite young, commonly less than 2 Ma. Calcrete-hosted uranium deposits have relatively large tonnages but very low grades with the average deposit size being 3000 t uranium at less that 0.05% uranium (Cuney and Kyser, 2008).

Valley and playa-type, calcrete-hosted uranium deposits comprise <1% of world uranium resources. Apart from Australia, uraniferous, valley-fill deposits also occur in Namibia, South Africa, Mauritania, Somalia, Argentina and China (Figure 1.6, Table 1.5).

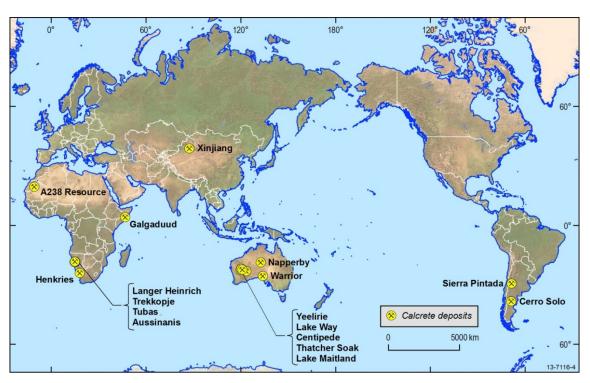


Figure 1.6 World map showing the distribution of major calcrete-hosted uranium deposits (yellow circles with symbol).

Most people are familiar with the use of uranium in nuclear power plants where it is used to fuel the nuclear fission reactors. It is also used to power nuclear powered submarines and ships and is used as the fissile explosive in nuclear weaponry. Depleated uranium is used to create high-density penetrators such as those projectiles used to piece heavily armoured targets and it is also used as shielding in containers that store radioactive materials despite the fact that it itself is radioactive. Before people knew that uranium was radioactive it was used as a yellow colouring for pottery and glassware and even kitchen and bathroom tiles. Uranium has been used in photographic chemicals, lamp filaments, to improve the whiteness of dentures and in the leather and wood industry as stains and dyes. Uranium is also mined to isolate radium for use in glow in the dark paints for clock faces and aircraft dials. Uranium metal is used as ballasts in yachts and aeroplanes and the radioisotopes from uranium are used in smoke detectors. Uranium metal is also used as a target for high-powered x-ray machines and uranium derivatives are used in biological science as stains to increase the interaction between virus and other cells. Some radioisotopes for scientific and medical purposes are also produced in nuclear reactors.

Table 1.5 Major calcrete-hosted uranium deposits around the world.

Name	Country	Reported Reserves/Resources	References
Yeelirrie	Australia	48Mt @ 0.13% U ₃ O ₈ for 63,820 t U ₃ O ₈	Geoscience Australia (2013)
Lake Way	Australia	9.95 Mt @ 0.045% $\rm U_3O_8$ for 5,280t $\rm U_3O_8$	Toro Energy Ltd., 2012a
Centipede	Australia	13.72 Mt @ 0.055% $\rm U_3O_8$ for 6,527t $\rm U_3O_8$	Toro Energy Ltd., 2012a
Millipede	Australia	7.28 Mt @ 0.047% $\rm U_3O_8$ for 3,663t $\rm U_3O_8$	Toro Energy Ltd., 2012a
Dawson Hinkler Well	Australia	13.09 Mt @ 0.031% $\rm U_3O_8$ for 4,077t $\rm U_3O_8$	Toro Energy Ltd., 2012a
Nowthanna	Australia	11.91 Mt @ 0.040% $\rm U_3O_8$ for 4,750t $\rm U_3O_8$	Toro Energy Ltd., 2012a
Thatcher Soak	Australia	16.1 Mt @ 0.017% U ₃ O ₈ for 2,800t U ₃ O ₈	Eleckra Mines Ltd. (2008)
Lake Maitland	Australia	31.2 Mt @ 0.038% $\rm U_3O_8$ for 11,430t $\rm U_3O_8$	Mega Uranium (2012)
Napperby	Australia	9.34Mt @ 0.036% $\rm U_3O_8$ for 3,351t $\rm U_3O_8$	Deep Yellow Ltd. (2010)
Langer Heinrich	Namibia	102 Mt @ 0.54% $\rm U_3O_8$ for 77,980t $\rm U_3O_8$	Cuney and Kyser (2008), Paladin energy (2012)
Trekkopje	Namibia	340Mt @ 0.015% $\rm U_3O_8$ for 26,000t $\rm U_3O_8$	Cuney and Kyser (2008)
Tubas	Namibia	87 Mt @ 0.015% $\rm U_3O_8$ for 12,876t $\rm U_3O_8$	Cuney and Kyser (2008)
Aussinanis	Namibia	34.6 Mt @ 0.024% $\rm U_3O_8$ for 8,203t $\rm U_3O_8$	Cuney and Kyser (2008)
Henkries	South Africa	0.044% U ₃ O ₈ for 2,041t U ₃ O ₈	Cuney and Kyser (2008)
A238 Resource	Mauritania	45.2Mt @ 0.024% U ₃ O ₈ for 10,614t U ₃ O ₈	Forte Energy (2012)
Galgaduud	Somalia	8,800t U ₃ O ₈	Hawthorne (2009)
Cerro Solo	Argentina	0.15% U ₃ O ₈ for 4,536t U ₃ O ₈	Wealth Minerals Ltd. (2012)
Sierra Pintada	Argentina	0.12% U ₃ O ₈ 13,608t U ₃ O ₈	Maple Minerals (2005)
Xinjiang	China	Not available	Cuney and Kyser (2008)

1.2 Economic potential of Australian salt lakes

Australian inland salt lakes have been the sites for extraction of a number of commodities, with halite and gypsum being the main ones to date. Halite has been mined at Lake Tyrrell in Victoria, Lake Deborah East and Lake Lefroy in Western Australia, and Lake Bumbunga in South Australia.

Gypsum has been extracted from the following Western Australian inland salt lakes: Lakes Moore, Cowan, and Hillman, Cowcowing Lakes South, and also Lakes Brown, and Wandell. In South Australia gypsum has been extracted from the Blanchetown Clay, deposited by the Bungunnia megalake, Lakes Everard and Malata, and Gordon Lagoon. Gypsum deposits in Victoria have been mined from many locations with the Raak Boinka and deposits at Nypo, Jerapit South and to west of Hopetoun being the most significant. In New South Wales, gypsum is extracted from a number of groundwater-fed lakes in the Murray Basin, particularly in the vicinity of Ivanhoe.

Very small amounts of potash were mined in the 1940s at Lake Chandler in Western Australia in the form of potassium sulfate. Exploration for potash in the form of alunite is just commencing in South Australia, but may have considerable promise in Western Australia, South Australia, and Victoria.

1.2.1 Halite

The only inland playa lake in Western Australia that is currently being used for salt extraction is Lake Deborah East, located near Koolyanobbing, 65 km north of Southern Cross and 450 km east of Perth. Salama *et al.* (1992) showed that the Yilgarn Palaeovalley has a basement-rock constriction at the down stream end of Lake Deborah East. This feature combines with impermeable lacustrine clays underlying the playa to restrict groundwater throughflow down the palaeovalley and has greatly enhanced long-term accumulation of salts due to evaporative discharge. At Lake Deborah East WA Salt Supply Pty Ltd produces over 200 000 tpa salt following evaporation of water collected in the lake during winter rains. The crystallised salt is washed on-site and then railed in containers to the company's Hamilton Hill refinery in Perth. Most of the company's high-quality, refined salt is supplied to the domestic salt market while around 20% of production is exported to countries such as Singapore, Fiji, Mauritius, Reunion, Brunei, and the United Kingdom (Fetherstone 2008).

Halite was harvested from Lake Lefroy in Western Australia from evaporation ponds. Major production ceased in 1982. Total amount produced was 1.24 Mt (Griffin, 1989).

Lake Bumbunga in South Australia is a small inland saline lake (1500 ha) that has produced salt since 1912. The salt is dissolved from saline mud produced when winter rain fills the lake. Lake Bumbunga is the largest of a system of saline lakes draining an area to the east of the Barunga Range and extending ~30 km north of the town of Lochiel, locaked on the shores of Lake Bumbunga. The resultant brine is pumped into evaporation ponds for refining. Uses include manufacturing of water softeners, tanning, butchering, snow clearing, paper making and metallurgy. Two companies are involved in the harvesting, Ocsalt Pty Ltd., a subsidiary of Cheetham Salt, with an average production of 10,000 tpa. Burnsfield Pty Ltd also has a salt operation at Lochiel, producing ~400 tonnes per annum.

Lake Tyrrell is the main inland production site for halite in Victoria. Cheetham Salt Ltd. harvests halite from both evaporation ponds and directly from the lake surface. Active harvesting sites are on the middle-western shores. The lake and the ponds fill from winter rains when water tables are high and evaporate over summer. Very minor intermittent production occurs at various small salt lakes, some 25 in total, in the Mildura, Horsham and Kerang areas. Production from these sites amounted to no more than 622 tonnes in the 1978-1982 period. Total production of halite from all sources in Victoria averaged 130,000 tpa between 1989 and 1994 (McHaffie and Buckley, 1995).

1.2.2 Gypsum

Western Australian gypsum is largely produced from either coastal evaporation ponds or Lake McLeod. Production from inland playa lake systems is more limited and is mostly from playas located in the southwest region. Of these, 13 have reserves in excess of 1 Mt. In addition, there are about 16 smaller agricultural-grade gypsum producers mining from playa lakes that extend through the agricultural region from north of Esperance on the south coast, almost to Dongara, south of Geraldton (Fetherstone, 2008).

Gypsum is being mined from a number of inland playa systems in South Australia where gypsum deposition is largely thought to have ceased ~17.5 ka (calibrated radiocarbon, DMITRE, 2012). Those occurring within the Murray Basin are mostly associated with the Yamba Formation (Brown and Stephenson, 1991). The lakes are all in enclosed depressions in relatively impermeable sandy clay, and at the time of deposition were closed basins subject to rapid seasonal variation in volume and

salinity of the associated brine pool. These are the conditions favouring seasonal development of new sand-sized prismatic crystals and deposition of laminated gypsarenite. The largest of these playas is at Blanchetown in the Murray Basin, which is mined predominantly for plaster and cement manufacture. Lunettes developed on the leeward side of continental playas are the sources of much of the State's agricultural gypsum (DMITRE, 2012). Other locations are at Everard (east of Lake Bumbunga), Gordon Lagoon (Murray Basin) and at Lake Malata on Eyre Peninsula.

Gypsum deposits in Victoria are found associated with active and inactive saline lakes, in particular those associated with groundwater discharge zones or boinkas (Macumber, 1980). Gypsum occurs both as massive crystalline gypsum associated with the capillary fringe of such systems, and as fine-grained (kopi) or seed gypsum associated with lunettes and gypsum dunes derived from nearby playas. Historic production of gypsum in Victoria has occurred at 67 locations in the Mallee and Wimmera regions. Between 1979 and 1993 an average of 220,000 tpa was produced. Crystalline gypsum from locations such as the Raak Boinka, was used mostly for the building industry while kopi and seed gypsum from places such as Nypo, Jerapit South and to west of Hopetoun were used for agriculture (McHaffie and Buckley, 1995).

1.2.3 Potash

There has been an increase in potash exploration in Australia in recent years. Current exploration for potash is occurring at three locations in Australia. Reward Minerals Ltd. has exploration licences at Lake Disappointment and Lake Mackay in Western Australia and a Joint Venture with Rum Jungle Resources at Karinga Lakes in the Northern Territory (Reward Minerals 2012a).

The Lake Disappointment project comprises nine Exploration Licenses, one Miscellaneous Licence, one Mining Lease and two applications covering approximately 3,327 km² of the playa lake. Global Groundwater Pty Ltd were contracted to conduct the hydrogeological assessment of the Lake using a purpose-built 'Geoprobe rig' transported over the Lake by helicopter in conjunction with trenching and pump testing, to enable a JORC standard resource estimate to be generated. The lake sediments vary from 3 m to at least 10 m in thickness, averaging 4.1 m. Heavy brines were encountered in every pumptested hole. The resource estimates for total contained sulfate of potash (SOP) were between 7,705 Mt at 3.17 kg/t for 24.43 Mt SOP and 8,635 Mt at 3.17 kg/t for 27.37 Mt SOP. The difference between the upper and lower figure relates to depth and area assumptions for the lake margins. The average SOP content per tonne of lakebed sediment is derived from the analysis of the whole drill core. The average of 3.17 kg/t translates to 6.17 kg SOP/m³ of lakebed material. Higher grade areas of the lake reported 10.40 kg SOP/m³. In practice the recovery of SOP will be via the (solar) evaporation of the entrained brines. Brine samples drawn from drill holes have returned SOP values as high as 20.01 g/L. Of significance is the average (arithmetic mean) SOP value of 12.56 g/L for all brine samples collected. Vigorous brine flow was encountered in all of the holes drilled (Reward Minerals, 2012a, b, and c).

Lake MacKay is a modern, playa lake with a surface area of over 2,250 km². It is situated in the Gibson Desert, straddling the Western Australia–Northern Territory border, 50 km north of the Tropic of Capricorn. Reward Minerals Ltd has delineated a JORC compliant, Inferred Resource at Lake Mackay of 4,780,400,000 Bulk Cubic Metres (BCM) at 4.3kg of SOP per BCM for a total of 20.56 million tonnes of SOP. The resource estimate was calculated on the basis of lakebed sediment volume (BCM) from surface to a depth of two metres and the water soluble potassium sulfate content of these sediments located within the Company's tenement holdings at Lake Mackay. The next stage of development at Lake MacKay will involve infill drilling, construction of pilot ponds and pump testing as well as flow sheet development for the preparation of a project feasibility study (Reward Minerals, 2012a and d).

Rum Jungle Resources has also recently signed an agreement with Toro Energy Limited to explore for potash in the southern sections of Lake Mackay (Rum Jungle Resources, 2013). Previous shallow drilling by Toro Energy confirmed the recovery of brine containing potassium, magnesium, and sulfur. Rum Jungle Resources state that the brine has the potential to produce schoenite, epsonite and sulfate of potash, similar to the Karinga Lakes Project (see below). Rum Jungle Resources has also acquired the Lake Hopkins project which is strategically located between Lake Mackay and the Karinga Lakes project to explore for the possibility of potash-bearing brines in this region.

The Karinga Creek lakes in the Northern Territory occur along the Karinga Creek drainage which lies in a palaeovalley that extends east from Lake Amadeus and is tributary to the Finke River system flowing towards Lake Eyre. Evaporative concentration increases down the length of the palaeovalley (Jacobson *et al.* 1988). This has resulted in extreme concentration of brines and the only published example of bittern salt precipitation in Australia with both sylvite and schoenite being reported (Arakel and Cohen, 1991, Arakel and Wakelin-King, 1991) and also epsomite, glauberite and mirabalite (Arakel and Hongjun, 1994). The Karinga Creek Potash Joint Venture between Rum Jungle Resources Ltd and Reward Minerals Ltd includes six granted exploration licenses totaling 2,310 km² along the Karinga Creek system. The companies are exploring for sulfate of potash and schoenite in sub-surface lake brine in up to 26 dry salt lakes on pastoral leases adjacent to the Lasseter Highway. Rum Jungle Resources Ltd announced a maiden JORC total resource of 1.2 Mt of schoenite, which is equivalent to 530,000 tonnes of SOP. The resource is derived from brine to an average depth of 3.2 m. This resource consists of inferred resources in nine lakes containing brines with 52,000 tonnes SOP and indicated resources in a further seven lakes of 447,000 tonnes SOP, for a total of 530,000 tonnes of SOP in 16 lakes (Rum Jungle Resources, 2012).

Lake Barlee is a large palaeovalley salt lake in Western Australia. Jervois Mining (2011) reported that brine samples from the lake contained up to 8% potassium on Exploration Licence 77/1332. Sulfate samples from Central Barlee tenements range between 2.18 to 13.8% sulfate in brine. Lake Barlee surface waters have near neutral brine pH (Mann 1983), suggesting that the potassium would form a sulfate phase on evaporation.

1.2.4 Alunite

Deposition of the potassium-bearing sulfates, alunite and jarosite may result in the sequestering of significant amounts of potash in acid lake systems. Exploration programs for potash in alunite have been carried out at Lake Chandler and Lake Campion in Western Australia and at Lake Ifould in South Australia. Exploration of these resources is at an early stage, but given the widespread extent of alunite in Australian salt-lake sediments in Western Australia, South Australia, and Victoria, the potential may be considerable. This section reports only the known exploration projects up to the time of writing.

Lake Chandler, the lake with a previous production history of potash in the form of glaserite derived from alunite (Bayliss 1980), is part of the Lake Brown system of saline lakes within the Deborah Palaeovalley, 300 km east of Perth. It has been the site of an exploration program by ActivEX Ltd. (ActivEX, 2013a) now at the scoping and pre-feasibility study stage (ActivEX, 2013a) that has identified a JORC-compliant inferred resource of 5,779,025 Mt at 5.73% $\rm K_2O$ in alunite (ActivEX, 2009). At Lake Chandler the alunitic clay accumulation is 6 m thick. Extensive drilling of the lake in the 1980s outlined the deposit and showed that the potassium content of the clay is consistent over the deposit. Additional drill testing is required to improve this estimate to measured and indicated status. The resources study also identified the potential for additional mineralisation peripheral to the current resource but within the confines of the Lake Chandler. No drilling has been carried out on Reward Lake but records show potash contents at the surface similar in grade to Lake Chandler (ActivEX, 2013b).

Reserves of K_2O in alunite at Lake Campion, 6 km west south west of Lake Chandler, were estimated by Edwards (1953) to total 1.8 Mt. Considerable interest was shown in the 1940s in this deposit, but the end of World War II appears to have precluded its development (see history of the project by Bayliss, 1980).

Lake Ifould (formerly known as Lake Pidinga in older literature) is a palaeovalley saline lake along the margin of the Eucla Basin in South Australia. Potash deposits have been known to occur in the area since at least 1948. The South Australian government drilling outlined a body of alunitic clay at least 700 m long by 150 m wide, with a mineralised zone is about 3 m thick lying within a few metres of the surface. The mineralised zone is open to the south and east. The intersections contained up to 7.24 % potash. Other holes drilled away from Lake C also returned potentially ore-grade intersections (Proactive Investors, 2012). Exploration is being carried out through Southern Potash Pty. Ltd., a wholly owned subsidiary of WPG Resources Ltd (WPG Resources, 2012).

1.2.5 Lithium

Several companies have already begun exploration for lithium-bearing salt lakes in Australia. AmeriLithium has taken out three exploration leases in Western Australia which cover over 174 km² around and abutting Lake Dumbleyung (AmeriLithium Press Release February 2012). The leases are as follows:

- Bare Rocks Project: immediately east of and abutting Lake Dumbleyung, covers a salt lake system expected to have significant potential for lithium;
- Hoffman Hills Project: approximately 25 km south of Lake Dumbleyung, covers a salt lake system expected to comprise the same brine drainage outlets as those found in the Bare Rocks Project; and,
- *Normans Lake Project*: 25 km north of Lake Dumbleyung, represents another salt and drainage lake system expected to have high lithium potential.

The Company intends to execute a staged exploration program comprising remote sensing desktop studies, initial field reconnaissance, sampling of the brines and saline crusts, and analysis for lithium and a basic set of elements including potassium, calcium, sodium, magnesium, boron, chlorine and sulfate. Additionally, the Company intends for the exploration plan to be tailored for the identification of any potential gold mineralisation.

ERO Mining Limited is exploring for brine-hosted lithium in the Wertaloona Project (Lake Frome) and Lake Torrens areas in South Australia. Previous exploration by Comalco at Lake Frome included broad scale testing of the surface and subsurface brines for trona [Na₃(CO₃)(HCO₃)•2H₂O] and other associated salts for industrial purposes and they also reported significant lithium concentrations in the southwestern corner of Lake Frome and the adjacent lowlands. ERO proposes to undertake systematic close spaced drilling, on the Wertaloona Project area focusing where lithium values are known to be highly anomalous, and test sediments, local, shallow and deeper aquifers and brines for lithium, potassium, magnesium, boron, calcium and sodium (ERO, 2011). They have also commenced analysing shallow groundwater sources (including established wells and water bores) at Wertaloona Station.

1.2.6 Boron

Although boron is commonly associated with potassium- and lithium-rich brines, there is no publically available data on the boron contents of Australian salt lakes.

1.2.7 Valley and playa-type, calcrete-hosted uranium systems

There is no current production of uranium from valley and playa-type, calcrete-hosted uranium systems in Australia. In August 2012, BHP Billiton signed an agreement to sell the Yeelirrie uranium deposit (Australia's second largest undeveloped uranium deposit) to Cameco Corporation for US\$430 million. The sale is subject to relevant approvals from the Australian Foreign Investment Review Board and the Government of Western Australia. In June, 2012 BHP Billiton released a resource estimate for Yeelirrie giving measured and indicated mineral resources of approximately 48 Mt of U_3O_8 , with an average grade of approximately 0.13% U_3O_8 and inferred resource of 2.4 Mt at 0.10% U_3O_8 . Cameco plans to review the gamma logs and the grade-radiometry relationship, and revisit the criteria used to classify the BHP Billiton estimate (Geoscience Australia, 2013).

The Wiluna project in Western Australia is operated by Toro Energy Limited (2012b). The project comprises two shallow (less than 8 m deep) calcrete hosted deposits, Lake Way and Centipede, which are 15 km south and 30 km south of Wiluna respectively. At December 2011, Lake Way had Indicated + Inferred Resources of 9.95 Mt averaging 530 mg/kg U_3O_8 (5,280 tonne contained U_3O_8) and Centipede had total Measured + Indicated + Inferred Resources of 11.31 Mt averaging 493 mg/kg U_3O_8 (5,58 kt contained U_3O_8). Toro also owns three other calcrete deposits in the Wiluna region (Millipede, Dawson Hinkler Well and Nowthanna deposits). These have total Indicated + Inferred Resources estimated to be 30.98 Mt averaging 382 mg/kg U_3O_8 (11,782 tonnes contained U_3O_8 , Geoscience Australia, 2013). Toro has also announced the discovery of the Theseus uranium prospect located just south of Lake Mackay in Western Australia (Toro Energy Ltd., 2012c).

The Lake Maitland project also in Western Australia is a calcrete hosted uranium deposit 100 km south east of Wiluna and occurs as a single horizontal layer 1 metre to 3 metres thick with the top of the mineralised zone 1 to 2 metres below the surface. During 2011 Mega Uranium Ltd advanced its feasibility studies of the Lake Maitland project. The program was completed in early 2012 and Mega Uranium Ltd reported an updated resource of 31.2 Mt at 0.038% U_3O_8 for 11,430t U_3O_8 (Mega Uranium Ltd., 2012).

Eleckra Mines Limited's Thatcher Soak uranium project is located approximately 150 km northeast of Laverton in Western Australia. The Thatcher Soak uranium mineralisation is principally carnotite with the mineralised zones elongated parallel to the drainage and largely coincident with a playa lake system. The mineralisation is usually shallow and 1 m to 2 m thick. Eleckra Mines Limited have reported a resource of 16.1 Mt at $0.017\%~U_3O_8$ for $2.800t~U_3O_8$ for Thatcher Soak (Eleckra Mines Ltd., 2008).

Zeus Resources Ltd. has also taken out a single tenement in the north Musgrave region in central-eastern Western Australia (Zeus Resources Ltd., 2012). The tenement covers a portion of the van der Linden palaeochannel that flowed from north to south across prospective rocks of the Amadeus Basin. Other Zeus Resources projects include the Percival Lakes Project in the Paterson Region of Western Australia. Here exploration is focused on the Percival palaeochannel that flowed from the east across sediments of the Canning Basin, then was diverted south by a palaeotopographic high. The palaeochannel appears to be enriched in uranium as it passes across the eastern flanks of the palaeotopographic high.

Toro Energy is continuing exploration at the Napperby deposit which is in the northeast part of the Ngalia basin in the Northern Territory. The mineralisation occurs within a 20 km palaeochannel, trending approximately east-northeast. Carnotite mineralisation resides mostly in sands and sandy clays as finely disseminated particles and concretions up to 5 cm long; it can also be found in overlying calcrete as joint coatings. Energy Metals Limited is continuing feasibility studies at the Cappers deposit in the Ngalia basin where mineralisation is associated with calcareous alluvium (Energy Metals Ltd., 2012).

UraniumSA is conducting research and development work on the extraction of uranium from saline solutions and has subsequently identified a number of resins which warranted evaluation. Test work carried out by the Australian Nuclear Science and Technology Organisation using mineralisation from UraniumSA's Samphire project confirmed the suitability of 4 of these resins for potential commercial use. UraniumSA signed a Memorandum-of-Understanding (MoU) with uranium-extraction specialist Clean TeQ. Under the MoU, the companies will test the suitability of Clean TeQ's U-HiSAL process to extract uranium from acidified saline solutions at Samphire project in South Australia (Geoscience Australia, 2013).

1.3 Energy from salt lakes

All lakes absorb heat from the sun. Normally, heat is lost as warm water rises to the surface and cools by evaporation. But water is a very poor conductor of heat and if this circulation can be stopped, the heat can be trapped in the bottom of the lake. A salt lake, (ideally about 3 m deep), managed so that the water on top is of (relatively) low salinity and the water on the bottom is of very high salinity, will not circulate to release heat because the water on the bottom is so dense it cannot rise. The deeper water gets very hot (over 100 °C in the right circumstances), 80 °C is common in the tropics and in southern Australia 60 °C is easily achievable. Such ponds are called 'Salt Gradient Solar Ponds' or just 'Solar Ponds'. Effectively, the pond acts as a very large, low cost, collector of solar heat. Seasonal natural examples of this exist at Lake Hayward and on Rottnest Island, Western Australia, (Rosen *et al.*, 1995). Temperatures in the hypoliminion get up to 45 °C in the winter.

Solar brine pond technology is well established (Figure 1.7) and Israel is currently using the Dead Sea as a solar pond to make electricity. One method of generating electricity from solar ponds uses a convertor called an 'Organic Rankine Cycle Engine' or ORC engine (Solar Ponds, 2012). The ORC engine works by using the hot water to evaporate a low boiling point chemical, such as those used in refrigerators. The vapour then becomes a high pressure gas which can be used to drive a turbine and produce electricity. Once used, the gas is recirculated, cooled, condensed and recycled (same as in a refrigerator). This technology was used at several remote sites in Australia in the 1970s. Australian Solar Ponds P/L (now disbanded) built an experimental 0.5 ha solar pond system at Alice Springs which produced electricity (net 15 kW) on and off for several years. Enreco P/L built conversion units in the 1970s (powered by hot water from the Great Artesian Basin) of up to 150 kW - one of these is still functional at Birdsville (Solar Ponds, 2012).

Basic resources essential for solar pond sites include an availability of sealing clays, high density brines, seawater, brackish or fresh-water, and a large area for the solar pond. Potash or magnesian brines are preferable because of their increased density. Although solar ponds may only generate electricity on a relatively small scale they could be ideally co-located with brine extraction operations or other industrial plants in isolated areas, thus alleviating the need to obtain power from more distant sources.



Figure 1.7 A solar pond at Pyramid Hill (near Kerang in Northern Victoria) showing the mesh of pipes running down the wall of the pond. These run across the bottom of the pond and up the other side. Fresh water (or radiator coolant) is circulated through them, and is heated by the saline pond water. This hot fluid is then used to heat air to flash dry gourmet salt products. The plastic rings visible on the surface of the water are used to reduce water movement caused by wind (http://soilwater.com.au/solarponds/).

2 Review of Australian Continental Salt Lakes

P.M English, J.W. Magee, J.D.A. Clarke

2.1 Review of Australian continental salt lakes

This chapter summarises Australian salt lake research. De Deckker (1983) recognised four types of Australian salt lakes: large closed basins with (often) extensive internal drainage areas, small closed basins with small internal drainage areas, crater lakes, and coastal lakes. Small enclosed basins and crater lakes will not be considered here, because of their size, coastal lakes will be the subject of Chapter 3. It is the large, inland lakes that are the subject of this chapter.

Here we review previous work, the distribution and settings of Australian salt lakes, summarise their characteristics, compare them with salt lakes occurring on other continents, and overview their economic significance. The distribution of some of the major Australian salt lakes is shown in Figure 2.1.

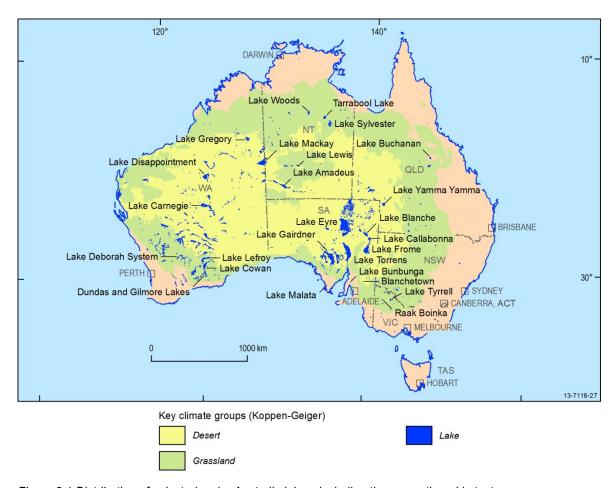


Figure 2.1 Distribution of selected major Australia lakes, including those mentioned in text.

The sedimentary record and diagenetic features of salt lake basins provide evidence of hydrological change across time and space. Records of interest include lake level fluctuations, siliciclastic sediments and chemically-precipitated minerals in respective basins and palaeovalley settings. The variables or controlling factors involved in their genesis and modes of occurrence include geology, climate, groundwater, geological setting, basin morphology, hydrochemistry and pedogenesis. Early investigations of and research on Australian salt lakes proceeded independently of possible corollary salt lake work in other continents. Australian salt lakes, at the outset, seemed unique in their temporal and spatial contexts. It was perhaps not until the work of Hardie and Eugster (1970), Eugster and Hardie (1978) and Hardie *et al.* (1978) on the hydrochemistry of brines in salt lakes in the western United States that comparisons could be drawn and the distinctiveness of Australian systems elucidated in an analytical sense (e.g. Bowler, 1986a), although, Australian work was not referred to by overseas workers.

2.2 Australian salt lakes: Previous work

Australian salt lake research is regarded to have occurred in three phases, with the Salt Lakes, Evaporites and Aeolian DepositS (SLEADS) program representing a significant benchmark or watershed in the discipline. The first is the early, or pre-SLEADS, phase prior to 1980, followed by the SLEADS project of the 1980s, and finally, the post- SLEADS work.

2.2.1 Early work (pre-SLEADS)

The earliest geological observations on salt lakes, or playas, in Australia were recorded by early European explorers. Examples include Mitchell's 1836 descriptions and topographic sketch of a lunette in western Victoria (Mitchell, 1839; reproduced in Bowler, 1983); Lewis' (1876) survey and mapping of Lake Eyre that included descriptions of a lake floor traverse; and Carnegie's (1898) recognition of the significance of chains of playas and salt lakes as elements of remnant palaeodrainage in Western Australia. Early professional geologists also undertook detailed studies of the nature and origin of playas/salt lakes including observations and conclusions that continue to resonate and are still relevant today. Jutson (1934), in a major treatise on the geomorphology of Western Australia, summarised the results of many years of study of playas/salt lakes including their origins in palaeovalley systems and details of deflation and playa migration controlled by salt-weathering and other processes associated with saline groundwater. Similarly, Jack (1921, 1923) studied the nature and origin of a number of inland and coast-marginal salt lakes in South Australia and elucidated novel and accurate observations concerning their origin and sedimentary characteristics which included an early interpretation of the cyclic-salt or marine-aerosol origin for the salts in the lakes. Details of Jack's work featured prominently in the local media (The Register, 1921). These and other results were incorporated into broad-scale geological syntheses (David, 1932; Browne 1945) including the first comprehensive continental-scale geological summary by David and Browne (1950).

Lake Eyre, Australia's largest salt lake, provides a case study of this early geological investigation. Lake Eyre is the lowest point on the Australian landmass, at approximately 15 m below sea level and, on rare occasions that it fills, is the largest lake in Australia. The lake was named after the first European explorer to sight it in 1840, Edward John Eyre, whose attempt to cross the continent was blocked by the "impassable barrier". This very early expedition was followed in the 1860s and 1870s by the surveying and mapping expeditions of Warburton and then Lewis (1876). Dedicated geological studies commenced from the 1880s with stratigraphic description and fossil collection by Debney (1882), Brown (1892) and the famous and popularised Gregory expedition of 1901-1902, the account

of which coined the term 'Dead Heart of Australia' (Gregory, 1906). Following Halligan (1924), who flew over the lake in 1922 and reported the presence of water, Madigan conducted aerial surveys and ground visits during the 1930s including traversing the eastern shoreline as the last phase of his famous 1939 camel crossing of the Simpson Desert (Madigan, 1944). Madigan investigated the lake sediments by hand-augered holes located at distances of up to 19 km from the shoreline in Central Madigan Gulf, where he measured a halite crust thickness of 43 cm, and reported sediment, salt and groundwater brine analyses. Madigan believed that Halligan's report of water in the lake was mistaken and that the lake never held substantial water in the modern climatic regime. However, the historically unprecedented great flooding of 1949-50 (Peake-Jones, 1955) filled Lake Eyre North to a depth of 4.9 m and a water volume of 21 km³. This event heralded a co-ordinated research effort to study flooding and other aspects of the lake's geology and hydrology through the 1950s, 1960s and 1970s. Bonython was a key figure in these efforts and made the first detailed assessment of the nature, volume and origin of the halite salt crust (Bonython, 1956), noting that the salt budget did not balance and the quantity of salt stored could be accounted for by only a few thousand years input. This 1950s research also included very early geo-biological investigations of the origin of sulfur nodules discovered in sediments on the shoreline of Madigan Gulf (Bonython and King, 1956; Baas-Becking and Kaplan, 1956). That research phase culminated in studies of a second, greater historical flooding event, in 1974, which united Lake Eyre South and Lake Eyre North to a maximum depth of 6.1 m and a combined volume of 32.5 km³ (Bonython and Fraser, 1989).

The 1960s saw the first detailed and systematic investigations of Lake Eyre with a 32 km drilling transect conducted by the South Australian Geological Survey in 1961, consisting of four boreholes extending to the north west across Madigan Gulf from its shore at Level Post Bay; an additional bore was drilled in Lake Eyre South. Most of these bores reached depths of 60-90 m and penetrated below the lacustrine Etadunna Formation (Oligo-Miocene), although the deepest bore extended to 300 m and penetrated a thick sequence of non-marine Eyre Formation (Eocene) and Winton Formation (Cretaceous) sediments. Detailed sedimentology, mineralogy, geochemistry and brine chemistry analyses were acquired along each retrieved core and a chronology was derived from palynological information (Johns and Ludbrook, 1963). In the 1970s, Dulhunty (1982, 1986, and 1990) initiated a decade of intense study of the modern Lake Eyre depositional environment including detailed mapping of the nature and extent of the halite salt crust before, during and after the 1974 flooding event (Dulhunty, 1974, 1977, and 1978). In 1982 and 1983 the SLEADS group (see below) included Lake Eyre in its drilling program. These more detailed investigations from the 1960s were complemented by regional geological mapping at 1:250,000 scale by the Geological Survey of South Australia (Williams, 1975) and regional stratigraphic studies carried out in association with vertebrate palaeontological research (Stirton et al., 1961; Tedford et al., 1986; Tedford and Wells, 1990).

Elsewhere in Australia, detailed and systematic investigations of salt lakes began in the 1960s and 1970s. Regional geological mapping at 1:250,000 scale extended to detailed mapping of unconsolidated Cenozoic sediments in addition to mapping bedrock geology. This extension included mapping of salt lakes and their precursor depositional systems and began in South Australia with the Frome Sheet (Callen and Tedford, 1976). In Victoria, Bowler commenced a long-term study of Australian playas/salt lakes with initial work on Lake Keilambete, a volcanic maar lake in western Victoria (Bowler, 1981), and fault-dammed lakes near Echuca on the Murray River (Bowler, 1978, 1986b). Bowler's research included the study of fluvial and aeolian landforms and aimed to constrain past climates and environments by studying geomorphology, stratigraphy, sedimentology and evaporite geochemistry. After moving to the Australian National University (ANU) his research focus extended to the iconic Willandra Lakes of south-western NSW (Bowler, 1998; Bowler *et al.*, 2003, 2012), Lake Tyrrell in north-western Victoria (Bowler and Teller, 1986; Teller *et al.*, 1982), Lake Frome

in northern South Australia (Bowler, 1986a, Bowler *et al.*, 1986) and Lake Gregory (Bowler, 1990, Bowler *et al.*, 2001) in northern Western Australia. Bowler's research eventually led to the SLEADS project (see Section 2.2.2 below) but his pre-SLEADS work was integrated into a conceptual scheme that summarised hydrological evolution and spatial variability of Australian arid-zone lakes by relating catchment area/lake area ratios to climate and runoff functions (Bowler, 1981, 1986a). Bowler's classification illustrates the factors controlling the palaeoclimatic sensitivity of lakes as well as the controls on sedimentary processes and the resulting sediment records (see Section 2.2.3 below).

Also in the 1970s, Macumber (1991) began a long-term investigation of the interaction between groundwater and surface water systems in the Murray Basin of Victoria. The aim of this investigation was to interpret and quantify processes of basin salinisation in association with changes in highland recharge and ongoing irrigation practises down gradient within the basin. As part of this long and detailed study, Macumber greatly enhanced understanding of the evolution, movement and discharge of saline groundwaters at local and regional scales as well as the processes and the history of salt lakes and so-called 'boinkas', or groundwater discharge areas, of the basin (see Section 2.4.4 below).

2.2.2 SLEADS project

The Salt Lakes Evaporites and Aeolian Deposits (SLEADS) Project (Chivas and Bowler, 1986) was a multi-disciplinary ANU project which commenced in 1981 and expanded previous salt lake research that had been conducted at ANU by Dr J. M. Bowler and others. The project aimed to systematically sample salt lake/playa and aeolian depositional systems in transects across different Australian climatic zones. Drill core samples from the project were subjected to a variety of analyses with a wide interdisciplinary focus. These included the study of Cenozoic and Quaternary climate change, evaporite sedimentology, groundwater-surface water interactions, geochemical and biological evolution and vegetation history.

A light-weight drill rig capable of push-tube and piston-sampler coring inside hollow augers to 15 m depth was used to sample individual playa/salt-lake systems with multiple core sites, rather than minimal cores from a larger number of lakes. Considerable problems were met in terms of access to and across the surface of remote playa/salt lakes as well as remote-site drilling logistical issues. Coring transects were successfully recovered over a four-year drilling programme from Lakes Eyre. Frome and Callabonna in South Australia; Lakes Woods, Lewis and Amadeus in the Northern Territory; Lake Buchanan in Queensland; and Lakes Tyrrell and Terang in Victoria. Cores were returned to ANU, logged and archived in cold storage to minimise moisture loss and chemical alteration. Analyses of most sites began during the active field phase of the project but some core transects were archived and studied later including substantial contributions to post-field-phase PhD projects. The SLEADS project activity at Lake Eyre provides a specific example. In 1982 and 1983 the SLEADS group drilled transects of shallow cores through the Quaternary sediments in Madigan Gulf and a connected playa inlet to the east. Analysis was aimed at elucidating palaeoenvironments and palaeoclimates but included detailed stratigraphy, sedimentology, mineralogy, chemistry and geochronology (Magee et al., 1995). The SLEADS Lake Eyre coring program was extended to a PhD project (Magee, 1998; Magee et al., 2004) with a similar focus.

Yearly project workshops brought together most Australian researchers with an interest in arid zone research and abstract volumes from these meetings for most years from 1981 to 1991 exist in the literature. More substantial workshops in 1984, 1988 and 1991 had international participation and papers from those meetings were published as special issues of Palaeogeography, Palaeoclimatology, Palaeoecology (Volumes 54, 84 and 113) and included SLEADS results alongside other Australian and international arid zone studies.

Two major reviews stemming from this period provided conceptual frameworks for salt lake research and remain touchstones today: De Deckker (1983) reviewed the history, chemistry and biota of Australian salt lakes; and Bowler (1986a) provided a spatial context for the variability of Australian salt lakes and their evaporites. DeDekker (1983) classified Australian salt lakes into four major types based on geomorphological grounds: (a) Large closed basins with (often) extensive internal drainage, e.g. Lake Eyre, (b) Small closed basins with small internal drainage areas, typically with lunettes, (c) Crater lakes, such as the well-studied saline lakes in western Victoria, and (d) Coastal lakes. Bowler (1986a), in addition to conceptualising the spatial and mineralogical aspects of Australian salt lakes, also considered the Pleistocene to contemporary time frame involved in their hydrological evolution.

2.2.3 Recent work (post-SLEADS)

Salt lake research continued in Australia subsequent to SLEADS, albeit in a less formally coordinated manner.

Between 1988 and 1991, Arakel and co-authors investigated calcrete and playa lithofacies in central Australia (Arakel, 1986, 1987; Arakel and McConchie, 1982; Arakel and Wakelin-King, 1991; and Arakel and Hongjun, 1994). Additional research focussed on the occurrence of carnotite mineralisation in playa setting (Arakel, 1988), playa glauberite (Arakel and Cohen, 1991), and silicification of calcrete in palaeodrainage basins (Arakel *et al.*, 1989).

Jacobson and co-authors also investigated hydrogeological aspects of central Australian salt lake systems (e.g. Jacobson, 1987), which included a focus on Lake Amadeus (Jacobson *et al.*, 1989), and on calcrete and gypcrete (Jacobson *et al.*, 1988; Jacobson and Arakel, 1986). This work encompassed hydrochemical evolution and groundwater discharge processes (Jankowski and Jacobson, 1989; Jacobson and Jankowski, 1989), high nitrate groundwaters in Australia's arid zone basins (Jacobson *et al.*, 1990), brine dynamics (Fergusson *et al.*, 1992), and investigations of groundwater discharge playas in the Mallee region of the Murray Basin (Jacobson *et al.*, 1994). The latter work set the scene for work by the Australian Geological Survey Organisation (AGSO, forerunner of Geoscience Australia), on salt disposal basins in the Murray Basin in response to salinisation of lands and waterways from agricultural practices (Jacobson *et al.*, 1990, Fergusson *et al.*, 1992, 1995).

2.2.3.1 Willandra Lakes

Since the 1990s, work at the Willandra Lakes, particularly Lake Mungo, has continued. This has mainly focussed on detailed refinements of the chronology of the stratigraphic sequence by both filtering of incorrect radiocarbon dates (due to sample contamination with younger carbon) and the application of luminescence dating techniques (Bowler, 1998; Bowler and Price, 1998; Bowler *et al.*, 2003; Bowler *et al.*, 2012). These studies elucidated a complex history of wetting and drying cycles between 60 ka and 15 ka (Figure 2.2) and provided an environmental and chronological context for the associated archaeology, the most recent summary coming from Bowler *et al.* (2012).

Older, generally poorly dated, phases of lake activity are preserved as mostly buried sedimentary units on lake floors and as basal lunette units capped by well-developed soils. Luminescence dates from the youngest of these, the Golgol lunette unit, indicate an age in the range 100–130 ka. Soon after 60 ka the lakes refilled and the system was full, fresh, and overflowing depositing quartz-rich beach and foredune lunette sediments of the Lower Mungo unit throughout the system.

The first drying is evident at about 45 ka and after about 40 ka, the onset of significant drying and clay-pellet rich lunette building, due to deflation controlled by saline groundwater, marks the transition to the

Upper Mungo unit. The Mungo unit is followed by the Arumpo and Zanci units, which also record wetter, surface water-dominated conditions followed by lake-floor deflation under drier conditions. The trend is toward increasingly effective dry phases and culminates in a thick sequence of gypseous pelletal clay deposited during the Zanci unit saline groundwater-deflation stage (21–18 ka). This intense dry phase at the glacial maximum and its preceding wet phase are now recognised as having diachronous expression from upstream to downstream lakes in the overflow system, whereby high lake levels last longer in the upstream Lake Mulurulu and coincide with the onset of drying and deflation in downstream Outer Arumpo Lake (Bowler *et al.*, 2012). This recognition has led to abandonment of a previously described separate final wet phase (Mulurulu Unit) restricted to the upstream lakes. Since about 18 ka the lakes have remained dry, with regionally low water tables, and soils have formed over the landscape.

This revised stratigraphy and chronology places the archaeological record into a firm palaeoenvironmental and chronological context with the oldest stone artefacts dated to 49 ka and the oldest burials, Mungo I and III, dated to 41 ka (Figure 2.2).

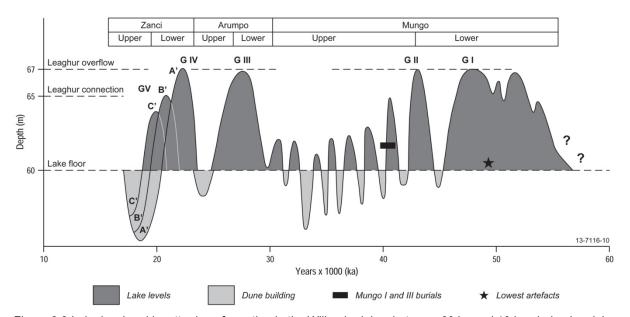


Figure 2.2 Lake level and lunette dune formation in the Willandra lakes between 60 ka and 10 ka, derived mainly from the Lake Mungo record. The overflow and lake-lake floor levels and gravels deposited at high stands at Lake Mungo are shown. The wet event and subsequent drying at the LGM (23-18 ka) is diachronous between basins. A, B and C represent progressive reduction in levels from Outer Arumpo Lake to Lake Mungo to Lake Mulurulu respectively. A', B' and C' indicate progressive initiating of drying and gypseous clay-pellet deflation from the basin floors of Outer Arumpo Lake then lake Mungo and finally Lake Mulurulu respectively. The location of significant archaeological features in the sequence is shown.

2.2.3.2 Lake Eyre

Lake Eyre has a complex suite of deep-water, nearshore, playa, beach, lunette, and inflowing stream sediments that provide a detailed sedimentary history and palaeoenvironmental record of the Australian monsoon. Following the SLEADS Project, Magee has used the archived SLEADS Lake Eyre cores, combined with new drilling and examination of playa- and river-marginal cliff exposures to derive a lake-level and sedimentary record over the past 150 ka, constrained by multiple dating techniques (Figure 2.3; Magee *et al.*, 1995; Magee, 1998; Magee and Miller, 1998; Magee *et al.*, 2004). Prior to 130 ka, in marine isotope stage (MIS) 6, the lake was dry, with the basin floor lowered by deflation to levels at least 4.3 m below today's playa floor.

At around 130 ka (early MIS 5), there was an abrupt change to a perennial salinity-stratified lake, 25 m deep with a shoreline at about +10 m AHD (Australian Height Datum). At least 6 m of finely laminated, millimetre-scale gypsum-clay and calcite-clay couplets were deposited in a salinity-stratified water body with strongly-reducing bottom conditions. The calcite laminae occur in the zone of strongest reducing conditions and were deposited as gypsum but altered by sulfate-reducing bacteria, a process previously reported from the Dead Sea (Neeve and Emery, 1967). This perennial saline lake was fed by enhanced monsoon-associated flow from the Diamantina and Cooper systems and included overflow from a combined Frome—Callabonna—Blanche—Gregory megalake at ~15 m AHD, fed by the Strzelecki Creek, a distributary from the Cooper (DeVogel *et al.*, 2004; Leon and Cohen, 2012).

After a brief drying episode apparently without deflation, lower-level perennial lacustrine conditions returned between about 100 ka and 75 ka, with considerable variation in water level and salinity. Interbedded lacustrine deep-water clays, calcareous nearshore and beach sands, and clastic gypsum evaporites were deposited at this time and beaches constructed at about +5 m AHD.

Drying and deflation of the basin occurred again between about 75 ka and 70 ka, followed at about 65 ka to 60 ka by the last, relatively short, high-level lacustrine conditions, which constructed a beach, rich in the brackish-water gastropod *Coxiellada gilesii*, at -3 m AHD. Between 60 ka and 50 ka, the lowering of water table associated with the transition from the previous high-lake events of MIS 5 resulted in a major deflation event that effectively excavated the modern Lake Eyre playa basin.

A low-level (-10 m AHD), poorly dated lacustrine event occurred around 40 ka and was followed by prolonged dry conditions with episodic deflation from about 35 ka to 14 ka and deposition of a now-buried last glacial maximum (LGM) halite salt crust. At about 12 ka low-level, semi-perennial lacustrine conditions (below -10 m AHD) returned to the basin, with deposition of shallow-water laminated gypsiferous clays. This indicates reinvigorated monsoon, but with less impact on Lake Eyre than in the previous interglacial (early MIS 5).

The modern ephemerally flooded playa conditions were established at about 3–4 ka, indicating a change to a drier monsoon regime marked by more extreme events. Older lacustrine sediments, similar to those of the last glacial cycle, occur east and north east of the current playa and have luminescence dates indicating an enhanced monsoon and lake occurred during MIS 7 and earlier interglacials. However, it is not possible to compare the lake area and relative monsoon strength through time due to migration of the depocentre and the destruction of pre-MIS 5 shorelines and beach ridges.

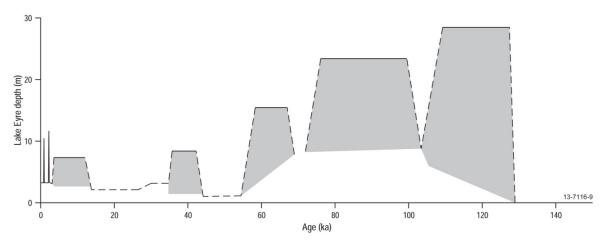


Figure 2.3 Lake-level record from Lake Eyre, northern South Australia. Modified from Magee et al. (2004)

2.2.3.3 Lake Amadeus

Following the SLEADS project, Chen examined the Lake Amadeus sequence, using archived SLEADS cores, additional drilling, numerous shallow pits and hand auger holes and geomorphic mapping combined with palaeomagnetic reversal and luminescence dating (Chen, 1989; Chen and Barton, 1991; Chen *et al.*, 1991a, 1991b, and 1993). The Cenozoic sequence in the lake Amadeus basin contained two major units. The basal Uluru Clay is at least 60 m thick, overlies Proterozoic basement and consists of uniform clay horizons with minor intercalated gypsum deposited in shallow lacustrine and fluviatile environments, which were periodically saline and often dry. Deposition of the Uluru Clay, dated by palaeomagnetic reversal stratigraphy, was thought to have commenced prior to 5 Ma.

The Winmatti Beds comprise the top few metres of the sequence and consist of aeolian sand, gypsum-clay laminae and gypsum sands, which represent deposition in a saline groundwater discharge playa system. The basal Winmatti Beds appear to coincide with the Jaramillo palaeomagnetic subchron (0.91 Ma) but may be as old as 1.6 Ma (Chen and Barton, 1991). The lake is ringed by an older gypsum dune system that may have formed soon after Uluru Clay deposition and a younger inner gypsum dune with luminescence age constraints of 45–50 ka. These gypsum dunes were formed by deflation of near-shore gypsum deposited in the groundwater seepage zone during a period with a high regional watertable due to a wetter climate.

Regional quartz dune activity, including an aeolian sand deposit on the playa floor and thick mantling of the gypsum dunes represents a drier period that followed the gypsum dune-building phase. The sequence is capped by deposition of a shallow-water gypsum layer, which represents a return to relatively high groundwater levels and now forms playa-marginal terraces and low terrace islands. Gypsum ground, a distinctive gypsum-rich playa surface type, was defined and described from Lake Amadeus (Chen *et al.*, 1991b) and is formed by degradation of gypsum-rich sands by differential dissolution, overgrowth and leaching in the vadose zone.

2.2.3.4 Lake Lewis

A PhD on the Cenozoic geology and hydrogeology of Lake Lewis basin in central Australia, Northern Territory, was completed by English (2002), based initially on the foregoing work of the SLEADS project, including analysis of archived refrigerated drill core that had been retrieved in the 1980s. The SLEADS work referred to the salt lake as 'Lake Napperby' or 'Napperby Lake', as it is located on Napperby Station, on the Tanami Track, north of the West MacDonnell Ranges; the gazetted name is 'Lake Lewis'. New drill holes were sunk, both in Lake Lewis and within its broad, heterogeneous playa margins. Multi-disciplinary analyses and syntheses were carried that included palaeolake reconstruction, magnetostratigraphy, hydrogeology, hydrochemistry and groundwater dating, outlined elsewhere and below (English, 2001; 2002; English *et al.*, 2001).

2.2.3.5 Australian salt lakes at the continent scale

As part of the SLEADS project, Australian salt lakes were conceptualised in terms of the relationship between catchment/lake areas (Ac/Al) and climatic parameters and the hydrological threshold separating perennial surface water lakes and dry, groundwater lakes across the continent (Bowler, 1981). This conceptualisation was subsequently elaborated by Magee (1998) and English (2002) as is shown in Figure 2.4. The classification scheme is based on the ratio of catchment area to lake area (Ac/Al) plotted against a climatic function (Fc) that takes into account evaporation, precipitation and a runoff coefficient (f), which is the percentage of rainfall that reaches a lake. For example, f = 0.1 where 10% of rainfall in the catchment that reaches the lake. The groundwater flux is not taken into account in the calculations.

The plot for Lake Lewis is based on the following parameters: 14,000 km² catchment area, 250 km² lake area, 280 mm rainfall, 3,065 mm evaporation per annum, and a runoff coefficient of f=0.1. English (2002) further plotted the evolution of palaeolake phases at Lake Lewis from a perennial lake with Ac/Al = 10 and a humid climate, to an intermediate perennial-ephemeral palaeolake when chemical precipitation was well underway at the lake (Ac/Al = 20; Fc = sub-humid), to the present position on the 'dry lake' side of the Hydrological Threshold, with a negative hydrological balance and semi-arid to arid climate Figure 2.4.

Bowler (1986a) refined conceptualisation of the characteristics of Australian salt lakes and playas and the range of geomorphic features and sedimentary deposits they contain in a gradational sequence of environments from surface-water- to groundwater-dominated systems. The classification scheme, shown in Figure 2.5, is based on a disequilibrium index (Δ el) which is a measure of how far the modern climatic setting of the basin (for example, Lakes Keilambete to Amadeus) has deviated from that required to maintain steady-state, surface-water cover.

The disequilibrium index is calculated from Evaporation/Precipitation (E/P) ratios and the catchment to lake area ratios modified by an efficiency coefficient.

$$\Delta el = \frac{(E/P)el - E/P}{(E/P)el} \times 100$$

Where E/P are the mean annual evaporation and precipitation of the modern climate and (E/P)el are the mean annual evaporation and precipitation required to maintain steady-state, lake-full conditions. The data used for the calculation of this index are detailed in Bowler (1986a).

Salt lakes are at the groundwater-dominant end of Bowler's continuum and are characterised by irregular shorelines, common residual islands and low, irregular lunettes on the downwind margin. These playas rarely hold surface water and lack well-defined, smooth constructional shoreline deposits or landforms produced by a combination of wave and wind energy. Instead the playas are dominated by active geomorphic processes due to groundwater discharge and outcrop. Groundwater bevelling, whereby the horizontal watertable acts as a base level to deflation and salt weathering, commonly forms almost perfectly flat basin-floors in many groundwater playas. This process was first recognised from palaeovalley playas in the Yilgarn Craton by Jutson (1917, 1918, and 1934). Aeolian deflation from the exposed playa floor can also occur in basins subject to seasonal, or drought-cycle oscillations of groundwater level, where the evolution of groundwater reaches saturation of the controlling salts, mostly halite and some sulfates. Lake-floor clayey sediments are disrupted by efflorescence of salts and deflated by saltation as sand-sized aggregates on the down-wind margin, with construction of characteristic transverse dunes (lunettes). Sub sand-sized sediment and salts are also removed from the basin by the same process and transported downwind as dust.

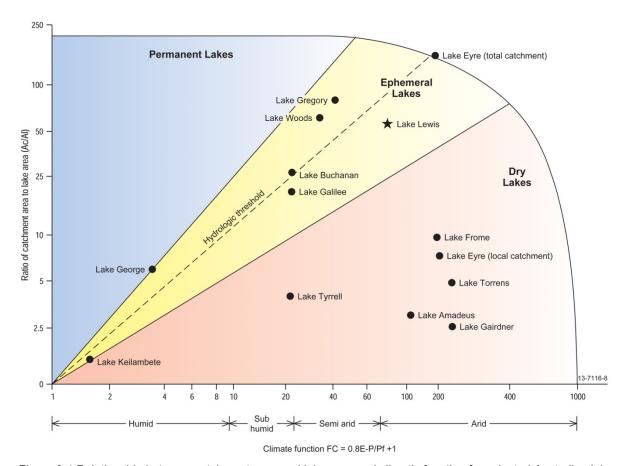


Figure 2.4 Relationship between catchment area and lake area and climatic function for selected Australian lakes across a broad climatic range (after Bowler, 1981, Figure 30.5, with additional data from Magee, 1998, and English, 2002). Ac = area of catchment (including lake), Al = area of lake (water) surface, Fc = climatic function, P = mean annual precipitation, E = mean annual evaporation, Pf = run off coefficient of 0.1 (10%) x P. Lake Gregory is located immediately south of Lake Buchanan, Queensland (the latter shown on Figure 2.1); Lake Keilambete is in western Victoria and Lake George, NSW, is located near Canberra, ACT.

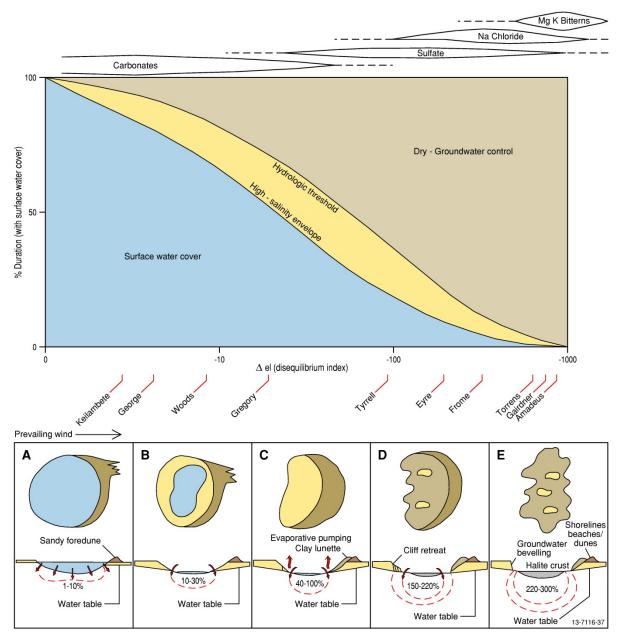


Figure 2.5 Classification of Australian lake/playa basins across a climatic gradient which extends from humid to arid conditions. Five lake/playa basin types, A to E, are differentiated by morphological and sedimentological features, which reflect successive stages in a hydrological series from surface-water to groundwater dominated systems including the evolution of a sub-playa brine pool. Figure is modified from Figures 2 and 5 of Bowler (1986a). Lake George, NSW, near Canberra, ACT, and Lake Kielembete, western Victoria, both located in the humid climate zone, are endorheic lakes, i.e., closd basins with no outflow.

2.2.3.6 Other Lakes

Palaeovalley salt lakes in the Yilgarn Craton, WA, were subject to several studies in the 1990s. Work undertaken on Lake Deborah East near Southern Cross (Salama *et al.*, 1992) and Salama (1997) are of particular note. Salama *et al.* (1992) investigated Lake Deborah East as a prototype palaeodrainage salt lake, while its broader context in the Salt River palaeodrainage system was studied by Salama (1997). Lake Deborah East is somewhat atypical in that it has a thick salt crust, underlain by up to 2 m of interbedded evaporates and clastic sediment. The halite crust has formed from mixed groundwater

and surface water sources leading to high bromide and bittern salts in the brines. Mudstone beds underneath the salt lake sediments were interpreted as a permeability barrier preventing brines from migrating downward (Salama *et al.*, 1992).

Lake Lefroy is a significant salt lake near Kambalda (Clarke, 1994b), typical due to its palaeovalley setting and stratigraphy being similar to other salt lakes in the region (c.f. Clarke 1994b, Salama, *et al.*, 1992, Salama, 1997), but unusual because of its well-developed salt crust. The evaporitic succession is up to 9 m thick and was deposited episodically since the earliest Pliocene, based on palynological evidence (Clarke, 1994b). The palynologically–derived depositional model was disputed on palaeomagnetic grounds by Zheng *et al.* (1998) who concluded that evaporite deposition occurred from the middle part of the Pleistocene onwards. Surface water in Lake Lefroy is supplied largely by surface runoff, with a limited contribution from near-surface aquifers. As is the case with Lake Deborah East (Salama *et al.*, 1992), the surface brine pool is partly isolated from the main palaeodrainage aquifers and regional basement groundwater by essentially impermeable underlying sediments, probably the Miocene Revenge Formation strata (Clarke 1994a). Lake brines are of sodium chloride type and salinities are as high as 462,000 mg/L total dissolved salts, with the salts being interpreted as being of marine origin (Clarke, 1994b).

Between 2007 and 2012, a team lead by Brenda Bowen (Purdue University, USA) and Kathleen Benison (West Virginia University, USA) carried out a number of studies on the acid salt lakes of the south western Yilgarn Craton. The primary purpose of this work was to gain an understanding of modern analogues for the Permian evaporites of the United States, which they postulated may also have been deposited under acid conditions (Benison *et al.*, 2007), and for Martian evaporite minerals (Benison and Bowen, 2006). This research group published a number of papers detailing the sedimentology (Benison *et al.*, 2007), geochemistry (Bowen and Benison, 2008), deposition of haematite (Bowen *et al.*, 2008), microbiology (Mormile *et al.*, 2009), authigenic clays (Story *et al.*, 2010), and diagenesis (Bowen *et al.*, 2012). Collectively these studies are the most detailed to date of acid salt lake characteristics and processes in Australia.

2.3 Distribution, settings and mode of occurrence of Australian salt lakes

2.3.1 Role of climate change and climate regimes

2.3.1.1 Cenozoic climate change

During the period from 65 Ma to 35 Ma (Paleocene – Eocene epochs) the Australian continent lay well south of its current position. There was no Antarctic sea ice; sea-levels were up to 60 m higher than present and atmospheric CO₂ concentrations were more than three times that of modern levels. Australia was vegetated dominantly with warm to cool temperate rainforest, even across the inland. Perennial rivers and lakes were widespread and these early Cenozoic valleys and depressions later became the sites of the thousands of salt lakes that characterise the contemporary continent. The Antarctic ice sheet progressively increased in size from the late Eocene onwards, temperatures decreased and sea levels fell. Central Australia became more arid as the continent moved northward to the subtropical high pressure zone, which is characterised by mid-latitude deserts. Notwithstanding, large freshwater lakes persisted through much of the Neogene, and desert conditions were not fully established until the late Pliocene, around 3 Ma (Pain *et al.*, 2012).

With the increase in Antarctic ice, the subtropical, high-pressure system migrated northwards to the latitudes of Australia's continental interior and aridity increased as a consequence. Rivers began to dry up because of the lack of rainfall and the increase in evaporation. Post-Miocene tectonism commenced as the north eastern part of the Indo-Australasian Plate began to subduct beneath the edge of the Pacific Plate and tilted much of the Australian continent, which had varying degrees of effect on drainage systems. Some rivers in parts of the continent were unable to adjust to the new, occasionally reversed gradients and became disaggregated lakes and swamps, which subsequently contracted in response to climate change.

Quaternary glacial cycles, commencing from about 2.6 Ma, brought alternating wetter and drier conditions related to glacial and interglacial periods, which greatly affected the flow of inland water. During dry glacial periods, when much of the global water budget was bound up in polar ice caps and high altitude glaciers, the rivers and lakes contracted, and the lakes dried and became saline, and desert dunefields formed elsewhere across the inland.

Many salt lakes retain palimpsest landforms that are a testimony of former lakewater high stands, or palaeolake extents. For example, concentric beach ridges many kilometres from the present playa, such as at Lake Woods, Northern Territory (Bowler *et al.*, 1998) and Lake Gregory, Western Australia (Bowler *et al.*, 2001) are well-documented examples of such landforms. Palaeo-shorelines around other major inland lakes are sometimes less conspicuous because of relatively recent precipitation of broad calcrete aureoles (described in Section 2.5.3.1) that have overprinted pre-existing features (e.g. as at Lake Lewis; English, 2002). Elsewhere, dense encircling dunefields have encroached upon the salt lake shorelines to completely cover any underlying palaeolacustrine landforms that may have predated dunefield development. Lake Amadeus (Bowler *et al.*, 1986; Bowler, 1986a; Chen *et al.*, 1993), which is at the centre of the continental-scale, anti-clockwise dunefield whorl (Wasson *et al.*, 1988; Hesse *et al.*, 2004; Hesse, 2013), is a noteworth example of this scenario.

Arid-zone lakes, particularly closed or terminal lakes, are important and sensitive palaeoclimatic archives. The lake level and the nature of the sedimentary processes and sediment types therein is directly controlled by the balance between inflows (direct precipitation plus surface water and groundwater inflow), and outflows (evaporation, groundwater outflow and surface-water outflow). In the simplest case, with minimal groundwater interaction and a small catchment, a lake can act as a palaeo-rain gauge, such as for some maar crater lakes (Bowler, 1981; Jones et al., 1998, 2001). Bowler (1981, 1986a) examined the controls on the palaeoclimatic sensitivity of lakes and related catchment amplification of inflow to a moisture-availability function which incorporated rainfall, evaporation and a catchment runoff efficiency coefficient. At the wet end of the spectrum, lakes are permanent and have fresh or brackish water and little potential for evaporite deposition or concentration of soluble ions. At the dry end of the spectrum, the Australian arid zone has abundant extremely large groundwater-dominated salt lakes, with very low catchment to lake ratios. These lakes are insensitive to climate change because they lack the required amplification of a large catchment area and evaporation always exceeds inflow, even if the climate becomes significantly wetter. However, this domination of the hydrology by evaporation leads to a high probability of significant evaporite deposition and soluble ion concentration. In between these extremes, lakes close to the equilibrium line in this relationship have water budgets almost in balance and tend to be ephemeral with the highest sensitivity to climate change. Even modest changes of climate can have dramatic impacts on the sedimentary processes and the preserved sediment records of these basins. These sensitive ephemeral lakes can oscillate between low and high salinity deposition and have complex stratigraphic sequences with alternate clastic- and evaporite-dominated facies.

Bowler (1986a) extended this concept to recognise the characteristics typical of each lake type in the sequence from surface-water dominated basins to groundwater dominated basins. These characteristics included lake plan form which changes from smooth and circular to highly irregular with abundant islands; the lunette lithology and geomorphology which changes from quartz-dominated through clay-dominated, to gypsum-dominated; and chemical sediment and evaporites which change from carbonates through sulfates then chlorides to magnesium, potassium and bitterns.

2.3.1.2 Desert settings

At the continent-scale, most of Australia's major and most highly-evolved salt lakes occur within the desert dunefields and aeolian sand plains, and can be viewed as co-evolving with the dunefields. During the late Neogene and Quaternary, rivers and lakes dried up and evolved to salt lakes, as described above. Exposed alluvium also dried up in response to aridity and became remobilised and redeposited down-wind to either form dunefields or to be lost further afield as dust. The loss of vegetation during the most arid periods exacerbated the effectiveness of wind action to remobilise large volumes of sediment from across the continent. Moreover, during the Quaternary glacial periods, when sea levels were low, sediment was sourced from the exposed continental shelves to contribute to the aeolian sediment load and to the development of down-wind dunefields and dust plumes (Wasson et al., 1988; Hesse et al., 2004; Hesse, 2013). The process of desertification involves a loss of the productive soil forming clays by wind erosion, which progressively leaves an increasing amount of winnowed residual quartz sand that is subsequently reworked into dunes by further wind action. Australia's sandy deserts are typical of this evolution, and their contemporary status quo, along with potential future changes, are easily observed by using the ASTER "Silica Index" product (Figure 2.6).

Increased aridity and increased windiness during the glacial periods thereby promoted the evolution of dunefields and salt lakes, the former ultimately developing into the continental-scale, anti-clockwise dunefield whorl that is a major characteristic of the contemporary Australian landscape (Hesse, 2013). Formation of the dunefields, further, blocked many prior surface drainage systems which effectively increased groundwater influence in catchments whilst impeding surface water flow to topographically lower-lying areas, or depocentres, even after the last glacial period when climatic conditions became less arid. The present-day status quo in Australia of innumerable salt lakes, groundwater dominance of hydrological processes, and the persistence of the dunefields across the continent would require massive climate change and very long periods of time to revert to perennial rivers and freshwater lakes and for the dunefields to diminish and economic clayey soils to be established.

2.3.1.3 Climate regimes

Climate zones of present-day Australia are classified into the extremes of hot humid summers in the north, and wet winters and dry summers in the south. The northern zone is associated with the summer monsoon system, including tropical cyclones, and the southern zone is dominated by the prevailing winter westerlies. Elsewhere, rainfall is uniform throughout the year or very low such that it cannot be classified seasonally (Figure 2.7).

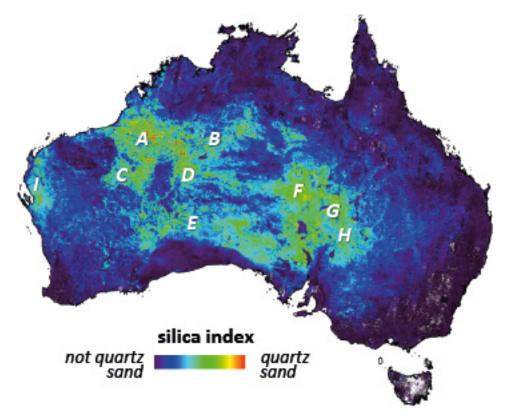


Figure 2.6 ASTER "Silica Index" map which is sensitive to both the SiO₂ content (primarily quartz) and the surface particle size. This product highlights the distribution of Australi's sandy deserts. Deserts shown: A – Great Sandy; B – Tanami; C – Little Sandy; D - Gibson; E – Great Victoria; F – Simpson; G – Sturt Stony; H – Strzelecki; and I – Gascoyne (after Cudahy et al., 2013).

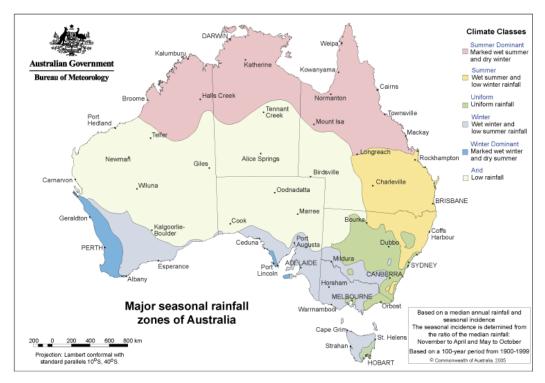


Figure 2.7 Australian seasonal rainfall zones (Source: Bureau of Meteorology, 2005).

The rainfall seasonality regime influences salt lake development and dynamics and is, in large part, responsible for the distribution of salt in the Australian landscape. Whilst major salt lakes and extensive networks of playas occupy the arid zone, many also occur in the southern winter rainfall zone where large volumes of marine-derived salt are brought onto the coastal regions and hot dry summers exacerbate evaporative processes. In contrast, summers in the northern and eastern parts of the continent experience relatively high rainfall and lower evaporation/precipitation (E/P) ratios, and salt lakes are scarce. Where they do occur across the north, saline lakes tend to be ephemeral and display a mixture of surface water and groundwater influence. Strong prevailing westerly winds that affect the southern part of the continent serve not only to bring marine-sourced aerosols onshore but also to promote drying and evaporation. In the arid zone and the southern winter rainfall zone, groundwater domination of salt lakes is more prevalent and intense because of the long periods of high E/P ratios. A Mediterranean climate is attributed to the extreme south-western part of Western Australia (mean rainfall 600-1000 mm pa).

The gradational boundary at approximately 30° S, the east-west Menzies Line, across southern Western Australia (Butt *et al.*, 1977) marks a change in interrelated climatic, vegetation, regolith and groundwater characteristics (Figure 2.8 and 2.9).

North of the Menzies Line, rainfall is influenced by sporadic cyclonic storms over summer. Groundwater calcretes, or 'valley calcrete', form in palaeovalleys whereas pedogenic carbonates are less common. Groundwater calcretes are tabular bodies up to 30 m thick and 1–2 km wide and tens of kilometres in length. They are important aquifers and can also host uranium mineralisation (Chapters 4 and 5). There is generally more relief north of the Menzies Line, with erosional scarps (breakaways), silcrete armouring granite terrain and ferruginous duricrust on greenstones. North of the Menzies Line groundwater quality is reasonable, commonly potable or stock quality (Figure 2.9; Commander, 1989; Gray, 2001).

South of the Menzies Line, the rain falls dominantly during winter, declining from about 450 mm/year in the west to ~225 mm/year in the east. The region has low relief with broad, sediment filled valleys with extensive playas. Soils are characterised by widespread pedogenic carbonates, 'pedogenic calcrete', which has precipitated in the unsaturated zone, in contrast to valley calcretes north of the Menzies Line that relate to the water table. Lateritic gravels are common, overlain by brown to red clay soils with a high proportion of hematite- and maghemite-rich gravels. Groundwater is generally acidic and saline to hypersaline (Figure 2.9).

Some of the contrasting features of the Yilgarn to the north and south of the Menzies Line are conveyed in ASTER mineral maps of Australia by Cudahy *et al.* (2013). Figure 2.10 shows the iron oxide (a) and clay mineral (b) ASTER mineral maps; the Menzies Line is clearly depicted in the Clay (AlOH) mineral map in particular. A continuation of the Menzies Line further eastward from its former mapped extent on the Yilgarn, across much of the continent, is also indicated in the AlOH index (Thomas Cudahy, pers. comm., 2012) in Figure 2.10(b). This may suggest that the manifestation of contrasting climatic regimes and its impact on landscape attributes north and south of the Menzies Line may be more extensive than previously thought across the continent.

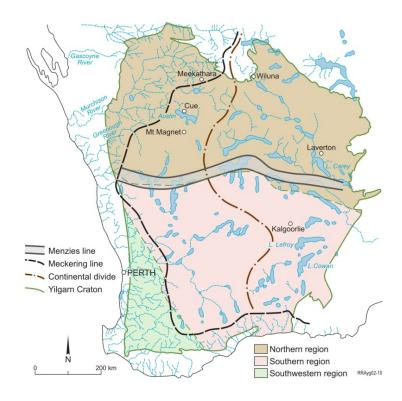


Figure 2.8 Map of the Yilgarn Craton with drainages (from Anand and Butt, 2010). The Menzies Line is described in Section 2.3.1.3, and the Meckering Line in Section 2.3.3.3.

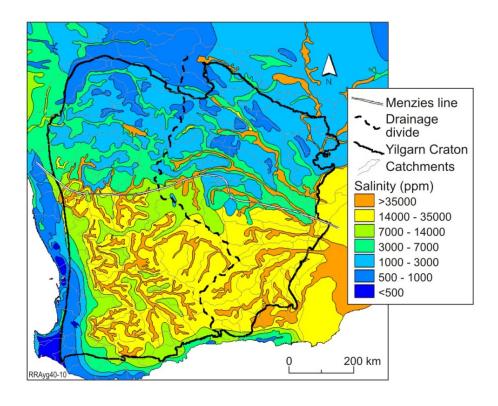


Figure 2.9 Groundwater salinity distribution in the Yilgarn Craton (from Commander, 1989; Gray, 2001; Anand and Butt, 2010).

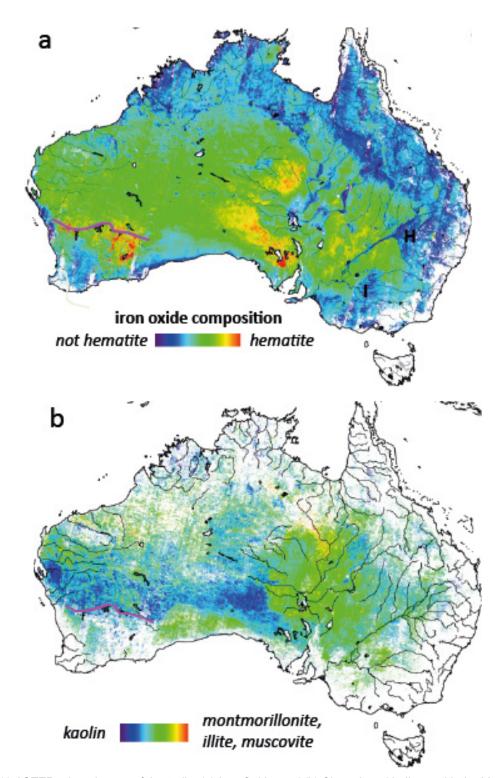


Figure 2.10 ASTER mineral maps of Australia: (a) Iron Oxide, and (b) Clay mineral indices, with the Menzies Line overlain in pink (after Cudahy et al., 2013).

2.3.2 Role of Groundwater

Hardie et al. (1978) stated that to form a saline or playa lake two conditions must be met: (a) evaporation must exceed inflow, and (b) the basin should be hydrologically closed, or at least with flow greatly restricted. A subsequent review of playa classifications by Rosen (1994) focussed on the relationship between sedimentology and hydrology, and emphasised the importance of hydrological closure and groundwater.

Rosen (1994) defined a playa as an intracontinental basin where the water balance of the lake is negative for more than half the year, and the annual water balance is also negative, with the playa surface acting as a local or regional discharge zone where evaporite minerals are present. The 'classic' western USA basin-and-range depositional model provided a framework for Rosen (1994), i.e., a concentric sequence of deposits: coarse alluvial fan sediments, mud-flat sediments, carbonates, followed by gypsum and halite in the surface crust in the lakebed. The degree to which basins are hydrologically open or closed systems is fundamental to Rosen's 1994 scheme, and indeed, Sanford and Wood (1991) had previously emphasised the critical significance of basin leakage on the suite and magnitude of evaporite minerals deposited. The earlier work of Hardie and Eugster (1970) and Eugster and Hardie (1978), e.g. Figure 2.18, below, wherein the brine chemistry of closed basins is seen as substantially influenced by the lithology of the sediments and bedrock within the playa catchment, was also central to Rosen's (1994) review.

Rosen (1994) conceptualised all possible configurations for the relationship of groundwater flow to playas: (a) through-flow of groundwater substantially beneath a lakebed, not interacting with the playa, (b) lake full conditions where there is recharge from the lake to the underlying groundwater system and no evaporite formation, or at most, only minor evaporites form from the final solution in the lakebed and these are deflated, (c) water table intersection and groundwater discharge to the lakebed, with displacive evaporite minerals and surface crusts precipitating in response to evaporation, and, (d) the groundwater table being above the surface of the deepest part of a closed basin playa so that groundwater input is constant and subaqueous evaporites accumulate, a scenario which may also apply to through-flow basins. In the case of some of the western USA basin-and-range playas exemplified by Rosen (1994), the possibility that basins are actively subsiding and thereby promoting progressive accumulation and preservation of evaporites, seems an implicit likelihood, although one that is less applicable to the Australian context.

In Australian salt lakes, the dominance of groundwater and the intensity of climatic parameters, such as illustrated by Bowler (1986a) and in Figure 2.5, are more important in salt lake evolution than the question of hydrological closure of the lake basins. DeDeckker (1983), on the other hand, classified Australian salt lakes more on geomorphological grounds.

Although most Australian salt lakes occur in flat-lying areas, with limited relief in their catchments and poorly defined watersheds, they typically function as hydrologically closed systems, even in large sedimentary basins where numerous through-flowing aquifers may exist. This is because of the high groundwater levels in the Australian arid and semi-arid zones that promote intersection of the watertable in lakebeds and topographic hollows, which sustain discharge of groundwater around the edges of the lakes under prevailingly dry climatic conditions. Progressive deflation of evaporites and clays from the lakebed creates a topographic depression which, in turn, influences surface drainage patterns. Subsequent development of centripetal surface drainage networks around the salt lakes has commonly occurred, even if only incised into saline aeolian landforms, such that prior through-flow of rivers and creeks no longer applies.

Commonly, Australian salt lakes are underlain by aquitards in the form of palaeolacustrine strata such that through-flow beneath the salt lakes does not proceed or is very sluggish. Through-flow is not necessarily the main groundwater flow regime even within the extensive linear Cenozoic palaeovalleys of the Eastern Goldfields of the Yilgarn, Western Australia, which are characterised by chains of salt lakes that have expanded over hundreds of kilometres of valley floors and contain shallow hypersaline groundwater. In these Yilgarn palaeovalleys, the basal palaeochannel aquifer, the Eocene Wollubar Sandstone is incised into Archean bedrock and is typically overlain by dense intervening clay, the Perkolilli Shale, which attains thicknesses of up to 40 m (Commander *et al.*, 1991). The latter clay deposits reflect waning surface water conditions and deposition of fine-grained swamp deposits later in the Cenozoic. Both the basal sandstone and overlying shale within the palaeovalleys are nowadays saturated with hypersaline groundwater, the watertables of which intersect the Quaternary salt lakes. Hydraulic gradients are low, reflecting the widespread flat topographic gradients, and most groundwater discharges by evaporation from the salt lakes; in places, reversal of flow direction occurs due to the flat gradients. Groundwater flow towards the salt lakes and upward deflection of deeper groundwater is commonly exacerbated near bedrock outcrops, or at faults, and as a result, contributes groundwater discharge to nearby salt lakes.

The association of chains of salt lakes within a palaeovalley does not implicate the presence of through-flowing groundwater within that valley, but rather, the importance of groundwater discharge at the salt lakes leading to centripetal groundwater flow around each salt lake and a distinct self-perpetuating flow regime dominated by evaporative pumping. Karinga lakes, east of Lake Amadeus, in central Australia, presents a case in point. In this case, palaeovalley groundwater flow might be construed to flow in an east-southeasterly direction, between Lake Amadeus and Lake Eyre, based on topography and broad-scale physiography, an assumption that is not supported by more intrinsic evidence. A large assemblage of evaporite minerals occur in the Karinga system of salt lakes, including: micrite, dolomite, amorphous silica, gypsite, sepiolite, aragonite, halite, epsomite, thenardite, mirabilite, zeolites and glauberite [Na₂Ca(SO₄)₂] (Arakel and Cohen, 1991). It is unlikely that such a suite of evaporite minerals could form and accumulate in a system that was exposed to through-flowing groundwaters.

Thick Cenozoic palaeolacustrine clays commonly underlie Australian Quaternary salt lakes that have a lacustrine, rather than a fluvial, origin, such as many of the central Australian and Lake Eyre Basin salt lakes. These extensive Australian salt lake systems may not be perceived as hydrologically closed with respect to encompassing topographic divides nor in the idealised conceptualisation of Rosen (1994). However, they have evolved from full, commonly overflowing, lakes to terminal lakes with no outlets, to dry terminal lakes, to groundwater lakes in which surface water is rare. These salt lakes fundamentally function as hydrologically closed entities that are dominated by groundwater discharge, regardless of where or whether there is a regional groundwater flow component within the basin. The notion of terminal lakes, rather than hydrologically closed lake basins, *per se*, and the dominance of groundwater, have been elucidated by Bowler (1986a, 1990) and Bowler et al. (1998, 2001), see Section 2.2.3.5, above, and 2.4.4, below.

Bowler (1986a) further emphasised that the concept of 'closed' systems for terminal lakes, while satisfactory for analysis of surface-water budgets, is quite inapplicable to the evolution of brines where surfacewater-groundwater exchange during the high-salinity drying stages becomes an arbitrating factor affecting all salt budgets. Regardless of hydrological gradients and magnitude of closure of a basin, the controlling influence of the frequency of drying on the evaporitic evolution of interstitial and local groundwaters is paramount; it is these processes that ultimately control the deposition and preservation of evaporites. Evaporite salts deposited on a hydrologically closed lake basin floor would not be preserved until such time as the interstitial waters in the underlying sediments have evolved to near-saturation levels for the salt involved (Bowler, 1986a).

2.3.3 Role of tectonics and neotectonics in salt lake evolution

2.3.3.1 Continent-scale tectonic setting

The Australian continent is generally characterised by extremely low relief topography, which particularly dominates much of the arid zone. This low relief can result in significant impacts on groundwater flow systems, even for modest tectonic deformation, with important consequences for salt lake systems. Australia is relatively stable tectonically, compared to other plates, due to its location as a stable continent in an intraplate position. Notwithstanding, as the fastest moving continent on a large diverse tectonic plate, Australia is relatively highly stressed, which has resulted in three distinct Cenozoic deformation modes (Sandiford, 2007; Sandiford *et al.*, 2009; Pain *et al.*, 2012):

- At the longest wavelengths (1000 km-scale), 300 m amplitude continental-scale northeast-down, southwest-up tilting, which is attributed to dynamic topographic response (variations in vertical stress transmission between convective upper mantle and the lithosphere) to the northward motion of the continent. This process has influenced the long-term evolution of the sedimentary infill of palaeovalleys of the southern Yilgarn with implications for modifications of gradients influencing the formation of saline groundwater and playa salt lake systems.
- At intermediate wavelengths (100 km-scale), undulations of 100 m amplitude are the least wellunderstood but are believed to reflect lithospheric buckling due to high levels of intraplate stress arising from plate-boundary forcing. Examples include the ~400 m uplift of the Flinders Ranges relative to surrounding basins in South Australia and deformation south west of Lake MacKay, where the upper Throssell Palaeovalley is now ~80 m lower than sections of the palaeovalley immediately downstream (Sandiford et al., 2009), discussed further in Section 2.3.3.6. The Flinders Ranges scenario has provided accommodation space in the form of the 'Horseshoe Lake' ring of playas, comprising Lakes Frome, Callabonna, Blanche, Gregory, Eyre and Torrens, girdling the northern Flinders Ranges. Continued sagging of these basins, currently at or below sea level in the case of Lakes Eyre and Frome, despite large effective sediment transporting fluvial inputs, has resulted in their ongoing hydrological closure and maintenance of groundwater discharge, both essential for large playa development. The second process is an example of how post palaeovalley infill tectonics (or halotectonics, as postulated in Section 2.3.3.6, below), can disrupt groundwater throughflow and force local dominance of evaporative discharge, resulting in concentration of soluble ions and deposition of evaporites in large playas.
- At short wavelengths (10 km-scale) undulations of 10–100 m are associated with cumulative fault movements which are also generally associated with intraplate stress related to plateboundary forcing. Such faults have probably also disrupted groundwater flow paths and promoted local dominance of evaporative discharge.

Thus active faults are widespread and seismic activity is significant. Tectonism during the Cenozoic has greatly contributed to the shaping of the landscape that now contains the present-day array of salt lakes. Many of the faults are ancient in origin, associated with major orogenies of the Precambrian and Phanerozoic, and have been reactivated during the Cenozoic. New ruptures are less common than reactivated ancient structures in the present stress regime of the continent. Australia has migrated more than 3000 km to the north-northeast at a rate of 6–7 cm per annum over the past 45 million years, making it the fastest moving continent since the Eocene (Sandiford, 2007). Thus, although much of the Australian landscape is low, flat and ancient, features reflecting relatively recent landscape rejuvenation in response to Neogene to Recent plate motion and associated intraplate

deformation are widespread (Sandiford 2003a, b; Sandiford *et al.*, 2009). Some of these structures as well as neotectonism and seismicity have influenced salt lake evolution in parts of the continent.

2.3.3.2 Neotectonic basin-and-range salt lake basins

Structural and stratigraphic evidence suggests that the modern intraplate stress field in Australia was firmly entrenched by the mid- to late-Miocene (Dickinson *et al.*, 2001; Sandiford *et al.*, 2004; Hillis *et al.*, 2008), driven principally by the pull force associated with subduction zones in the Indonesian region. The modern stress field, as inferred from earthquake focal mechanism solutions, borehole breakouts and fracture arrays (Hillis *et al.*, 2008) has been extrapolated to the terminal Miocene - early Pliocene (10–6 Ma). Geological and geomorphological studies in recent years have identified several hundred faults across the continent with demonstrable Pliocene and Quaternary activity (Clark *et al.*, 2011; Quigley *et al.*, 2010). Recent faults can be linked to the modern tectonic stress regime and, within this context, Australia can be perceived as having experienced a dynamic Neogene to Recent tectonic history (Quigley *et al.*, 2010). This neotectonism has substantially influenced the evolution of palaeoriver valleys and palaeolakes, including more recent phases of salt lake development.

Several Cenozoic basin-and-range basins have been mapped in and around the uplands of central Australia, around the MacDonnell Ranges in the Northern Territory, by Senior *et al.* (1995); Langford *et al.* (1995), English (2002), and Bell *et al.* (2012). These include the Ti-Tree, Burt, Lake Lewis, Whitcherry and Mount Wedge basins, among others (Figure 2.11). The Lake Lewis Basin contains Lake Lewis, and the Mount Wedge Basin contains Lake Ngalia and Lake Bennett; an extensive calcreted palaeovalley (Figure 2.14) connects the Mount Wedge Basin with Lake Mackay on the Northern Territory-Western Australia border.

These central Australian Cenozoic basins, surrounded by steep ranges or ridges of Proterozoic and Paleozoic rocks, represent a distinctive province that provides the setting for palaeolake and salt lake evolution at relatively high elevations, around 500 m AHD, in the centre of the continent. These are lake basins, rather than more typical infilled palaeo-river valleys that became disaggregated into salt lake chains. Whether there was a major east-west flowing precursor river in the pre-Cenozoic period is unknown. It seems more likely that early drainage from the MacDonnell Ranges was to the south east, towards the present position of Lake Eyre, rather than to the west, towards Lake Mackay. English (2002) presented evidence to suggest subsidence north of the MacDonnell Ranges on the Redback Thrust Zone, an ancient east-west fault zone, possibly during a Cenozoic period of tectonic relaxation, initiated formation of the Lake Lewis and Mount Wedge basins. Several hundred metres of sediments infilling the basins indicate dominantly lacustrine depositional settings, with alluvial fans at the range fronts, flowing towards the lake depocentres. English (2002) regarded the region as a tectonically-initiated Cenozoic basin-and-range province, with basin formation attributed to minor tectonic or epeirogenic processes involving reactivation of ancient structures. Basement rheological modelling by Beekman et al. (1997) of fault-bounded Arunta Complex basement blocks provides a basis for understanding intermontane basin development while the sedimentation patterns and geomorphological configuration are strongly structurally-controlled (English, 2002; Woodgate et al., 2012).

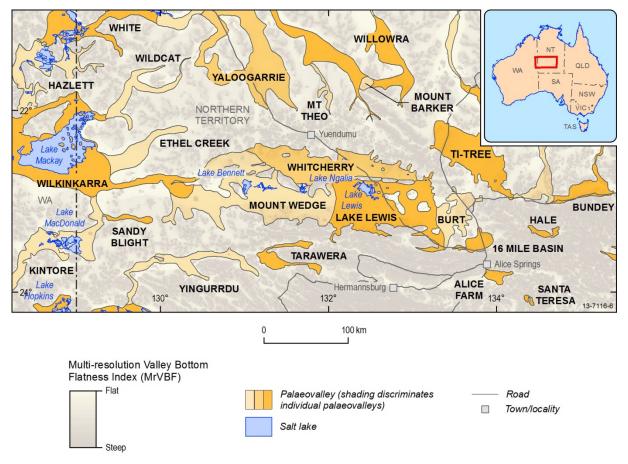


Figure 2.11 Central Australian Cenozoic basin-and-range province, including basin and palaeovalley names (after Bell et al., 2012). Lake Ngalia is an ungazetted salt lake name, ascribed in various unpublished reports (English, 2002). The grey-toned background is a derived DEM, the Multi-resolution Valley Bottom Flatness Index (MrVBF) described in English et al. (2012).

2.3.3.3 The Australian continental plateau

The Australian continent comprises an extensive inland plateau surrounded by an escarpment, typical of other post-Gondwanan continents. The escarpments mark a major boundary between low rates of geomorphological processes on the inland side and more active processes on the seaward side. Whilst the most dramatic of the Australian escarpments is on the eastern side of the continent, other escarpments extend for hundreds of kilometres across the northern, western and southern parts of the continent (Pain, 1985; Pain *et al.*, 2012). Salt lakes are, for the most part, located on the relatively inactive plateau that extends across most of the continent, inland from the more erosionally active coastal zones. An exception is south of Lake Eyre and other major salt lakes in this part of South Australia, such as Lake Frome, which occur in the lowest-lying part of the continent. This is explained by the possibility that Lake Eyre has only been at such a low point for a few million years and that such dynamic topography may reflect flow instabilities in the underlying upper mantle (Pain *et al.*, 2012). Comparable low points occur in the middle of other post-Gondwanan continents, between uplifted edges, although Lake Eyre constitutes an extreme example.

In Western Australia, the arcuate Darling Escarpment extends from the Great Australian Bight, east-west along the Jarrahwood Axis in the south, before curving north-westward near Perth, and continuing northward for hundreds of kilometres. East of Perth the 'Darling Scarp' closely corresponds with the position of the Darling Fault, which separates the ancient, dissected Archean basement of the

Yilgarn Craton to the east (along with its panoply of salt lakes) and the down-faulted Phanerozoic Perth Basin to the west of the scarp. The Yilgarn Craton is partitioned by a meridional continental divide that separates the rivers draining east from those draining west and south. Post-Eocene uplift led to rejuvenation of the latter drainages. The upstream limit of rejuvenation of the westward-flowing rivers is termed the Meckering Line (Mulcahy, 1967; Figure 2.8). The Meckering Line converges on the Darling Fault north of Perth. From this location, the edge of the Darling Escarpment follows the north east trending Meckering Line across the Murchison Province of the northwest Yilgarn. The scarp tracks a few hundred kilometres inland onto the Northern Yilgarn where it demarcates old weathered Yilgarn regolith in the east, and rejuvenated granite greenstone terrain in the west, as depicted in Figure 2.8. Neotectonic faults are numerous in this rejuvenated western part of the Northern Yilgarn Craton. The scarp maintains an inland position as it extends northward across the Capricorn Orogen and the Pilbara where it meets the coast at the edge of the Canning Basin.

Salt lakes in the Murchison Province are confined to the plateau, 400 km inland from the Indian Ocean, with none occurring westward where there is considerable seismic activity and numerous neotectonic faults (Clark et al., 2011). The latter are illustrated in Figure 2.12. Elsewhere salt lakes occur closer to the coast where the plateau approaches the coastline. The main salt lakes in the Murchison Province are Lake Austin and Lake Annean, located on the Yilgarn Plateau. West of these salt lakes, the Yilgarn landscape has been eroded and scoured. Radiometric imagery (Figure 2.12) reveals relatively fresh granite, disclosed by high total gamma radiation (white) and high potassium radiation (pink), corresponding with major drainage systems that ultimately reach the base level of the ocean. Elsewhere, weathered granite-greenstone terrain displays high thorium concentrations (green) associated with iron oxides in ferruginous regolith, whilst the salt lakes show high uranium concentrations (blue), where there is no external drainage. The concentration of uranium in and around salt lakes is common in Precambrian provinces of Australia, and is discussed in Sections 1.1.4 and 5.5. Figure 2.12 includes DEM-derived long profiles for two of the Murchison Province rivers, showing the gradient to the coast for the Murchison River (left), and from the headwaters of the Sanford River to its confluence with the Murchison River (right). The profile of the Sanford River highlights the hydrological closure of Lake Austin, perched on the Yilgarn plateau, and of the salt lake from its host palaeovalley, the Sanford River, which has apparently been rejuvenated and subject to neotectonic activity.

Numerous small scattered saline lakes are associated with palaeovalleys across the southern coastal zone of Western Australia. This zone is the onshore western Eucla Basin (Clarke *et al.*, 2003), also known as the Bremer Basin (Hocking, 1995), comprising numerous small sediment-filled depressions rather than a continuous basin, which may be a legacy of the break-up from Antarctica. Southward and south eastward flowing drainage systems were already established in the Yilgarn Craton and the Albany-Fraser Orogen by the Late Mesozoic. The southern reaches of these palaeovalleys are filled with fluvial and swamp deposits of the Werillup Formation, which forms a significant palaeovalley aquifer, during the Eocene. Marine transgression drowned the valley system in the Late Eocene and led to deposition of marine sediments of the Pallinup Formation, Which represent the overlying palaeovalley aquiclude (English *et al.*, 2012). Quaternary salt lakes and brackish swamps subsequently developed in these palaeovalleys, as shown on the coastward portions of the Mount Barker, Bremer Bay and Esperance 1:250,000 geological map sheets. These numerous small saline lakes are circular, oval or crescent shaped and apparently surface water dominated. They are no doubt in receipt of large salt loads in rainfall and sea spray from the Southern Ocean. These fall into the coastal salt lake category, described in Chapter 3 .

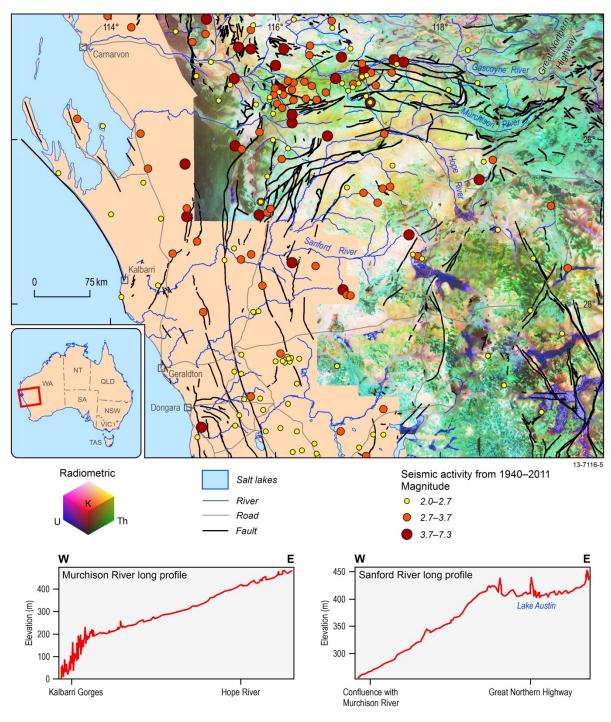


Figure 2.12 Airborne gamma radiometric Ternary RGB image of the Murchison region, in the northwest Yilgarn Craton, with salt lakes, faults, seismic activity sites (earthquake centres) shown. Red is potassium, Green is thorium, and Blue is uranium (from English et al., in prep). Large salt lakes are associated with uranium, sourced from weathering of Archean granites (blue to purple in image). The evolution of many of the Yilgarn salt lakes has been influenced by faults and neotectonism. Insets show the long profiles for two rivers in the region, the Murchison, which debouches to the coast, and the Sanford, which has been disrupted to isolate Lake Austin near its headwaters.

2.3.3.4 Sag basins

From at least 20 Ma, the Lake Eyre Basin may have been an intra-continental basin subsiding as result of tectonic post-rift sag following separation of Australia and Antarctica (Drexel *et al.*, 1993; Waclawik, 2003). The crust beneath the Lake Eyre Basin is one of the thinnest parts of the Australian continental crust, along with the Pilbara, at around 30 km thick (Salmon *et al.*, 2013). Weathering and erosion prevailed during the late Mesozoic and Late Paleocence. Late Paleocence tectonic subsidence in north eastern South Australia produced a large shallow basin in which episodic fluvial and lacustrine sedimentation has taken place up to the present.

Lake Eyre today, is very different environmentally and spatially, compared to the Pliocene lakes evidenced by the Tirari Formation and the Oligo-Miocene Etadunna-Namba Formation lake(s). The basin as a non-marine depocentre has existed over a long period of Cenozoic time although the evolution of the contemporary Lake Eyre is essentially a Quaternary manifestation. During the Quaternary, at Lake Eyre, deflation has been more important to lowering the topographic level, and intersection with the groundwater table, than tectonism. Thus, the Lake Eyre Basin and the evolution of the lake itself represent a different scenario from more active Cenozoic large sag basins such as the East African Rift.

2.3.3.5 Halotectonics and salt lake formation

Halotectonic deformation, distinct from other forms of modern tectonism, in some of Australia's major sedimentary basins involves relatively recent movement of ancient evaporites in the form of salt diapirs and salt domes that have intruded to shallow levels and which can cause deformation of the surface and near surface environments. Ancient evaporite deposits, including the Neoproterozoic Bitter Springs and Browne formations of the Amadeus and Officer basins, respectively, and the Paleozoic Carribuddy Formation of the Canning Basin, have been identified as the main ancient salts involved in halotectonic deformation. In addition to the Amadeus and Officer basins, the Ngalia and Georgina basins and the Adelaide Rift Complex were actively receiving sediment during deposition of the Bitter Springs Formation at ~0.8 Ga (Lindsay, 1987). Pain *et al.* (2012) suggested the following scales of neotectonic deformation for the Australian continent: (a) long wavelengths of thousands of kilometres, (b) intermediate wavelengths of hundreds of kilometres and undulations of 100 – 200 m amplitude, and (c) low wavelengths of tens of kilometres or less represented by fault scarps that have ruptured in response to seismicity. Halotectonic deformations are classified as intermediate scale according to the above definitions.

The Proterozoic Browne Formation in the Officer Basin, which contains halite, gypsum, anhydrite, dolomite, among other sedimentary rocks, attains a thickness of 4000 m (Carlsen *et al.*, 1999). These extensive salt deposits represent the oldest preserved NaCl-dominant salt deposits in the world. The Madley Diapirs and other salt diapirs of the Browne Formation are known to crop out in the Officer Basin. Halotectonic features in the Amadeus Basin have been reviewed by Lindsay (1987) and Marshall and Dyson (2005), and in the Officer Basin by Jackson (1976), Jackson and van de Graaff (1981), and Simeonova and Lasky (2005). Of interest to the present project are salt structures that crop out at the land surface or that have deformed the near-surface landscape to influence salt lake formation and evolution. This may include the ESE-WNW-striking array of diapirs through the Officer Basin that have been penetrated by the Yowalga, Browne, Hussar, Madley and Dragoon (Woolnough Diapir) series of petroleum exploration wells (Simeonova and Lasky, 2005), and possibly Lake Breaden in the Throssell Palaeovalley, west of the Browne Diapir, on the Gunbarrel Highway, northwest of Warburton in the Gibson Desert, referred to in Section 2.3.3.6.

2.3.3.5.1 Lake Disappointment

Palaeovalley mapping by Bell *et al.* (2012) and English *et al.* (2012) which utilised the Multi-resolution Valley Bottom Flatness (MrVBF) index of Gallant and Dowling (2003) applied to the 9 second Shuttle Radar Topography Mission (SRTM) Digital Elevation Model (DEM) and complementary datasets. This output has highlighted anomalous topographic features and geological associations that may point to more widespread halotectonism within major Australian basins than previously documented. For example, Figure 2.13 shows Lake Disappointment in Western Australia, and features that are attributable to halotectonism. Severe deformation of Proterozoic bedrock, namely the Yeneena Group of sediments, in the form of "cauliflower structures" surrounding Lake Disappointment is regarded as halotectonic in origin (R. Hocking, GSWA, pers. comm., 2011). These intensely folded sandstones, of the Neoproterozoic arkosic Karara Formation, cropping out east of Lake Disappointment, are depicted in topographic data (Figure 2.13) by waves of Cenozoic alluvium between tight bedrock folds. Both the proximity to the salt lake and the disposition of the folds in the form of "cauliflower structures" support the interpretation of halotectonism.

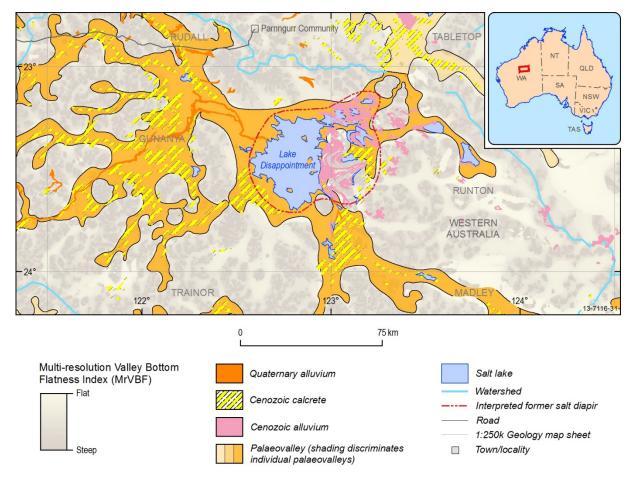


Figure 2.13 Lake Disappointment, Officer Basin, WA, showing interpreted centripetal palaeovalley drainage network (pink outlines), valley calcrete and playa-fringing calcrete aureole within the palaeovalley drainage system (yellow hatched polygons), and "cauliflower structures" to the east of the salt lake, depicted by Cenozoic alluvium (pink) between bedrock folds, namely the Neoproterozoic Karara Formation, attributed to underlying salt structures. Image background is the MrVBF DEM index of Gallant and Dowling (2003).

Lake Disappointment is interpreted to have been the site of a large salt diapir that intruded not only into overlying Proterozoic sediments, but also to the land surface where the salt subsequently dissolved, and the site consequently subsided. These dynamics created a void, and produced a large depression, with an associated centripetal internal drainage network as the resultant salt lake developed. The data suggest a Cenozoic, and possibly a Quaternary, evolution for Lake Disappointment, even though diapiric rise to upper levels of the crust may have occurred throughout the Paleozoic and Mesozoic eras. Outflow from the Lake Disappointment catchment to the north east, to link with the Percival Palaeovalley of the Canning Basin is discerned in airborne electromagnetic imagery (Roach *et al.*, 2010). Notwithstanding, when compared with the size of Lake Disappointment, this conduit for hypersaline groundwater from Lake Disappointment is relatively minor and tenuous, and seen to follow fractures in deformed Proterozoic Karara Formation outcrops. The interpretation of a former salt diapir here may, moreover, resolve issues with earlier attempts to reconstruct drainage patterns for Lake Disappointment by Beard (1973), Bunting *et al.* (1974), Van de Graaff *et al.* (1977) and Beard (2002) that have been reviewed by Magee (2009).

2.3.3.5.2 Lake Mackay and Lake MacDonald

Lake Mackay, on the Northern Territory-Western Australia border, lies in the western parts of the Paleoproterozoic Arunta complex and Neoproterozoic Amadeus and Ngalia basins. The Proterozoic Bitter Springs Formation of the Amadeus Basin basal sequence crops out to the immediate south west of Lake Mackay (Webb 1:250,000 geology map sheet), and may occur at shallow depth elsewhere beneath dunes of the Great Sandy Desert.

Palaeovalley reconstruction by Bell *et al.* (2012) and described in English *et al.* (2012) supports a proposition that Lake Mackay, (Figure 2.1 and Figure 2.14) may represent an ancient salt lake basin composed of Bitter Springs Formation evaporites (Gillen Member in particular). It is proposed that a former diapir rose to the landscape surface where it dissolved and created a hydrologically-closed depression in which a large Cenozoic salt lake developed. The topographic depression is depicted in the MrVBF DEM in Figure 2.14. Its connectivity with surrounding regional palaeovalleys is not straightforward. The large salt lake does not unequivocally relate to any particular ancient throughflowing palaeovalleys or palaeoriver courses, but rather to disaggregated internal-drainage. Accordingly, on the WASANT Palaeovalley Map (Bell *et al.*, 2012), Lake Mackay was depicted as a circular depression and assigned a unique classification, the 'Wilkinkarra Palaeovalley', as shown in Figure 2.11 and Figure 2.15, prior to the realisation that Lake Mackay may have once been the site of an emerged salt diapir or a cluster of diapirs.

Lake MacDonald lies south of Lake Mackay (Figures 2.11 and 2.14) and displays comparable criteria: (a) an anomalous palaeovalley pattern (Bell *et al.*, 2012), disconnected from other major palaeovalley systems, and (b) outcrops of deformed Proterozoic Bitter Springs Formation surrounding the salt lake (MacDonald 1:250,000 geology sheet). Lake Hopkins, south of Lake MacDonald (Figure 2.14), is similarly co-located near Bitter Springs Formation outcrops (Rawlinson and Bloods Range 1:250,000 geology sheets). The latter is apparently located in the exposed core of the Amadeus Basin and is part of the Katiti Palaeovalley delineated by Bell et al. (2012) that connects Lake Hopkins, Lake Neale, Lake Amadeus (Figure 2.1) and the Karinga chain of playas (Bloods Range and Lake Amadeus 1:250,000 geology sheets).

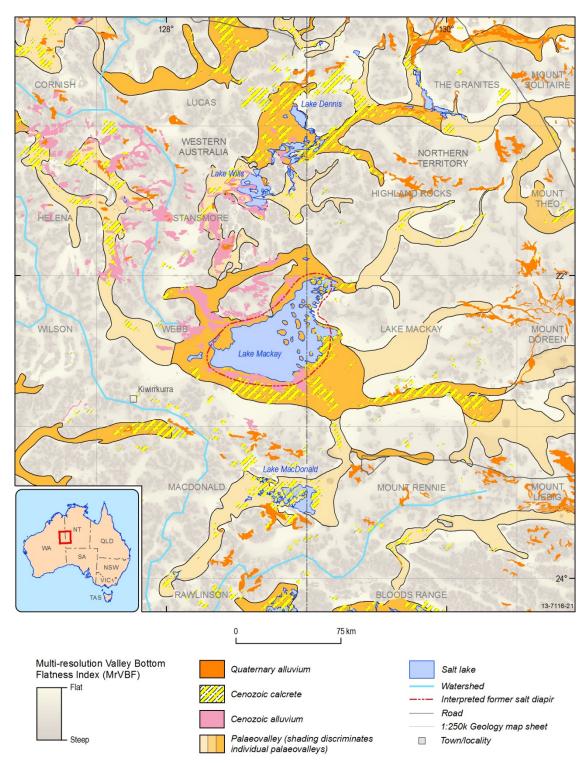


Figure 2.14 Lake Mackay on the WA-NT border showing a 150 km diameter topographic depression in which the salt lake is located (based on Bell et al., 2012; English et al., 2012). The background is the MrVBF DEM overlain by polygons for salt lakes, alluvium, calcrete (from Raymond, 2012) and interpreted palaeovalleys. See also, Figure 2.15, below, that shows the distribution of individual palaeovalleys and the interpreted hydrological closure of Lake Mackay. The interpretation of Lake Mackay being the site of a former salt diapir of Bitter Springs Formation that relatively recently reached the landscape surface is an outcome of the present study.

Intersection of the interpreted Bitter Springs Formation diapir with the landscape surface at Lake Mackay may have been a recent development, <15 ka. It has recently been observed that a salt lake

was evidently not present at Lake Mackay during the Last Glacial Maximum (LGM), around 20-12 ka, but rather, the area was covered with east-west linear dunes and vegetation (John Magee, pers. comm., 2013). This may suggest that the postulated underlying diapir may have intersected the surface within the past 12,000 years whereupon dissolution of the ancient salts and collapse of the structure created a shallow void, and a Quaternary salt lake evolved as the water table became exposed through subsidence and as centripetal drainage developed in the newly-formed depression to contribute to the underlying groundwater body. It is conceivable that, prior to exposure of a salt diapir at the ground surface, the overlying terrain had been elevated or forced into a broad anticlinal or domal structure, thereby raising the landscape elevation relative to its present-day elevation. If such a hypothesis is tenable, this may account for the existence of a broad dry, dune covered and vegetated area that was raised above the watertable. Salt lake development would have been delayed until such time as the diapir became exposed and began to dissolve, with subsequent subsidence of a shallow depression in which salt concentration in the brine pool became concentrated under contemporary climatic conditions. Subsequent topographic lowering would have proceeded through deflation of salts and lakebed sediments.

The hypothesis that Lake Mackay may have been a former diapir of Proterozoic salts that reached the landscape surface relatively recently, to create a shallow depression over the diapir crest and a modern salt lake, may have had wider impacts in central Australia. These may include promotion of westward flow of drainage through the Mount Wedge Basin and the contiguous eastern arm of Wilkinkarra Palaeovalley (Figure 2.11), along the gentle topographic gradient to the Lake Mackay depocentre. Several salt lakes, including Lake Ngalia and Lake Bennett (locations in Figure 2.11), plus extensive calcrete deposits have formed within the broad, low-lying tract east of Lake Mackay. A recent drilling program in this eastern arm of the east-west trending Wilkinkarra Palaeovalley, west of Lake Bennett and east of Lake Mackay, reveals that the original landscape surface sloped down from the west to the east, based on the disposition of the buried weathered basement surface, whilst the present day surface and subsurface flow direction on and within overlying Cenozoic sediments is the opposite, east to west (Figure 3.13 in Woodgate et al., 2012). This represents a 180° change in the topographic gradient during the Cenozoic when Lake Mackay was or became the regional depocentre. Up to 18 m thicknesses of calcrete, 10 km wide, north-to-south, and covering up to 200 km east-west, accumulated at the surface of the westward-sloping palaeovalley tract leading to Lake Mackay. Dense sand dunes obscure information, if present, about former lake phases of salt lakes such as Lake Bennett and Lake Ngalia. At Lake Bennett and Lake Ngalia, cursory mapping of "palaeolake extents" by English (2002) was mainly based on the distribution of calcrete aureoles rather than more intrinsic evidence for palaeolacustrine phases. These salt lakes and numerous satellite salt lakes along the broad Mount Wedge – Wilkinkarra palaeovalley tract may be relatively young, evolving penecontemporaneously with Lake Mackay, i.e., very recently, in the latter part of the Quaternary, as inferred above. In contrast, available evidence for Lake Lewis further east suggests greater topographical or hydrological closure during the Neogene and more definite palaeolacustrine phases (English, 2002).

The suggestion that Lake Disappointment, Lake Mackay and possibly other salt lakes in Australia's major basins evolved at locations where former salt diapirs penetrated the landscape surface in relatively recent times, may account for the apparent absence of palaeo-shorelines in the landscape surrounding Lake Disappointment and Lake Mackay. Bowler (1986; 1990) and Bowler *et al.* (1998; 2001) described palaeo-shorelines for terminal lakes that have evolved from large rounded surface water lakes to contracted shallow lakes to dry playas, leaving palimpsest concentric imprints of sequential former shorelines. In comparison, lakes Disappointment and Mackay appear to have merely evolved as salt lakes in large, shallow crater-like depressions without evidence for major precursory perennial freshwater lake phases that merely responded to the onset of aridity.

2.3.3.6 Other halotectonic salt lakes

Among intermediate-wavelength deformations, Sandiford *et al.* (2009) note a substantial undulation in a major palaeovalley south-southwest of Lake Mackay, which those authors referred to as the 'Lake Mackay palaeodrainage' although the 'Throssell Palaeovalley', variously spelled 'Throssel' in the literature, is the more accepted name. The profile of the palaeovalley that Sandiford *et al.* (2009) produced showed the upper, northern reaches draining internally to depths at least 80 m lower than southern, or formerly downstream, reaches of the palaeovalley. Sandiford *et al.* (2009) proposed that derangements within Australian Cenozoic basins of an order of 100 m amplitude undulation and intermediate wavelengths of 100 km, are attributable, at least in part, to lithospheric buckling due to relatively high levels of intraplate stress arising from plate-boundary forcing. At shorter wavelengths, on the order of 10 km, topographic variations are associated with cumulative fault movements up to the order of 100 m (Sandiford *et al.*, 2009). In the case of the Throssell Palaeovalley topographic anomaly, the possibility of salt diapirism was not broached by those authors.

The Throssell Palaeovalley was reinterpreted during reconstruction of palaeovalleys for the WASANT Palaeovalley Map (Bell *et al.*, 2012; English *et al.*, 2012) using high resolution DEMs, long profiles along palaeovalleys and geological data. The Throssell Palaeovalley was found to be completely disrupted near the Clutterbuck Hills and Iragana Fault on the Cobb 1:250,000 map sheet. Salt lakes have formed both to the north and south of the outcropping fractured and faulted Proterozoic and Permian bedrock that make up the Clutterbuck Hills: Lake Cobb to the north and Lake Newell to the south. The segregation is so complete that the respective parts of the palaeovalleys were assigned separate names: Cobb Palaeovalley in the north and Throssell Palaeovalley in the south (Figure 2.15). Near surface salt diapirs have been interpreted to account for the topographic and salt lake anomalies (English *et al.*, 2012).

In addition, a neotectonic divide in the major east-to-west trending Disappointment Palaeovalley, in the Little Sandy Desert, is interpreted from the WASANT Palaeovalley mapping, shown near the top left-hand corner of Figure 2.15. This is attributed to near-surface intrusion of salt diapirs during the Cenozoic, disrupting the Disappointment Palaeovalley by 50 vertical metres. This site, circled in Figure 2.15, is less than 10 km west of the exposed Madley Diapirs of Proterozoic Browne Formation (Madley 1:250,000 geology sheets) and 30 km southwest of Woolnough Hills Diapir (Warri 1:250,000 geology sheet).

Several salt diapirs have been interpreted from deep seismic reflection data acquired along Geoscience Australia's Yilgarn-Officer-Musgrave (YOM) seismic traverse (Carr *et al.*, 2012; Neumann, 2013). This 487 km long seismic line (11GA-YO1) includes one diapir that has intruded the landscape surface, in the Baker Palaeovalley immediately west of the township of Warburton (Figure 2.15). Substantial disruption of strata that the diapir intruded on its rise to the surface is apparent in the seismic section (Figure 2.16).

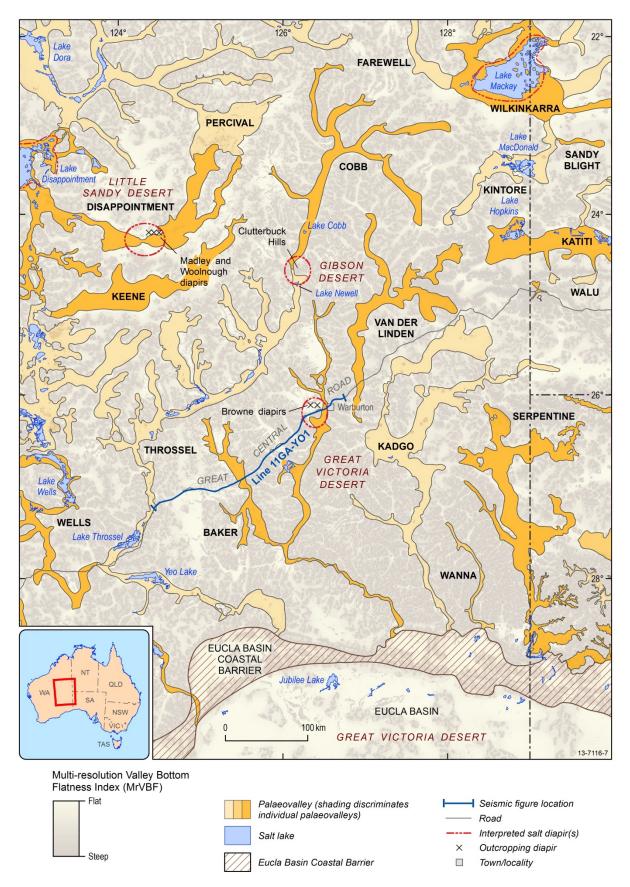


Figure 2.15 A section of the WASANT Palaeovalley Map over the Officer Basin, WA, with ascribed palaeovalley names (after Bell et al., 2012), showing the Throssell and Cobb palaeovalleys trending southward from near Lake

Mackay to the Eucla Basin, once a continuous valley but subsequently dismembered by an inferred near-surface salt diapir (red dashed circle in the Gibson Desert). The association of Lake Mackay with a former large salt diapir is interpreted from the present study. Other interpreted salt diapirs, circled, are inferred to have disrupted some palaeovalleys and greatly influenced salt lake formation or, have reached the landscape surface and dissolved to create a depression and hydrologically closed salt lake. Examples include: the eastern arm of the Baker Palaeovalley, near Warburton on the Great Central Road, Great Victoria Desert (most likely associated with the Yowalga - Browne diapirs), based on seismic data; and in the Disappointment Palaeovalley, east of Lake Disappointment, close to the outcropping Madley – Woolnough diapirs, Little Sandy Desert, which appears to have influenced the evolution of both the Disappointment Palaeovalley and the Percival Palaeovalley, the latter based on topographic anomalies and evidence for the development of new watersheds.

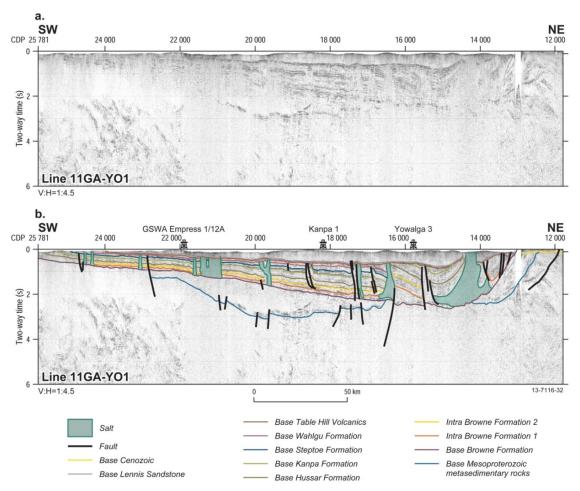


Figure 2.16 Salt diapirs interpreted from Geoscience Australia's Yilgarn-Officer-Musgrave seismic section (from Neumann, 2013). The north eastern diapir, near station 14000 in Figure 2.16b, has reached the land surface in the Baker Palaeovalley, immediately east of Warburton community (this community is located at ~13000 NE where no seismic data were obtained - blank on section). This near-surface salt structure is most likely associated with the Browne – Yowalga complex of diapirs, labelled in Figure 2.15.

Proterozoic marine evaporites occur in the Tomkinson Province, in the central part of the Northern Territory (Ambrose and Putnam, 2005; Hussey *et al.*, 2001). The Tomkinson Province is likely to be contiguous with the McArthur and Birrindudu basins. These ancient evaporites crop out in the vicinity of Lake Woods (Figure 5.16), namely the Proterozoic Tomkinson Creek, Namerinni and Renner groups. Similarly, Cambrian evaporites, of the Barkley Group, crop out in the adjacent Georgina Basin, close to lakes Tarrabool and Sylvester on the Barkley Tableland. Whether ancient salts have contributed to the large ephemeral lakes at Lake Tarrabool and Lake Sylvester and other lakes east of Lake Woods, is yet to be determined (Section 5.4.4.1).

2.3.3.7 Ancient salts versus Quaternary salts

Salt compositions in the world's large ancient evaporite basins (saline giants) are dominated by halite and/or anhydrite, along with varying amounts of evaporitic carbonates and potash salts. When mega-evaporite settings were active in the past within appropriate arid climatic and hydrological settings then huge volumes of seawater were drawn into the sub-sea level evaporitic depressions. Large, thick and extensive deposits dominated by rock-salt (mega-halite) or anhydrite (mega-sulfate) deposits tend to be marine evaporites and can be associated with substantial deposits of potash salts (mega-potash) (Warren, 2010). These criteria appear to have been met in major Australian basins, such as the Late Precambrian Bitter Springs Formation of the Amadeus Basin and the Browne Formation of the Officer Basin, and the Paleozoic Carribuddy Formation of the Canning Basin. Accordingly, these extensive ancient evaporite deposits may contain elevated concentrations of potash and be particularly prospective where these salt deposits have risen to near-surface levels as diapirs or other salt structures, or where the landscape has been eroded down to expose diapirs.

In contrast to these ancient sub-sea level evaporites, economic salt lake deposits of borate, sodium carbonate (soda-ash) and sodium sulfate (salt-cake) salts, along with evaporitic sediments hosting lithium-rich brines, require continental-meteoric hydrologies, as opposed to marine-fed hydrologies. Warren (2010) elaborates that beds rich in salt-cake, soda-ash, borate and lithium salt deposits tend to be Neogene and mostly occur in supra-sea level hydrographically-isolated (endorheic) continental intermontane and desert margin settings that were subject to pluvial-interpluvial oscillations of Neogene glacial-interglacial climates. When compared to ancient marine evaporites, today's marine-fed sub-sea level deposits tend to be smaller sea-edge deposits. Their distribution and extent is limited by post-glacially-driven eustasy and a lack of appropriate hydrographically isolated sub-sea level tectonic depressions (Warren, 2010). An exception, in Australia, may be the large Lake McLeod, adjacent to the Indian Ocean on the Western Australian coast (Logan, 1987), which formed in a structurally controlled low lying area through tectonic activity that commenced in the Miocene and continued into the Quaternary and caused 90–120 m of subsidence.

As an example, Lake Eyre has been located relatively close to the coast only since the break-up of Gondwana. Shallow marine and paralic sedimentation occurred during the Early Cretaceous (~115 Ma) at the edge of the Eromanga Basin, when there was crustal extension prior to rifting between Australia and Antarctica, but evaporites did not accumulate. Fluviolacustrine sedimentation had resumed in the Lake Eyre region by the Late Cretaceous ~95 Ma (Krieg, 1991). It is dubious whether marine mudstones of that age, e.g. the Bulldog Shale, could store connate salts to contribute to latter day Quaternary salts at Lake Eyre (J. Magee, pers. comm., 2013). Although Lake Eyre is below the present-day sea level, it has not been connected to the ocean during its evolution as a salt lake in the Neogene and Quaternary. Its present depressed elevation is the result of deflationary processes, so it is excluded from the above discussion of the role of sea level and ancient evaporite deposits to Quaternary salt lake evolution.

Warren (2010) notes that, for the past forty years, Quaternary continental lacustrine deposit models have been applied to the interpretation of ancient marine evaporite basins without recognition of the time-limited nature of this type of comparison. Ancient mega-evaporite deposits (platform or basin-wide deposits) require conditions of epeiric seaways (greenhouse climate) or continent—continent proximity. Basin-wide evaporite deposition is facilitated by continent—continent proximity at the plate tectonic scale, for example, an incipient opening rift that becomes sub-sea level and hydrographically isolated (a marine evaporite drawdown basin) and yet replenished with seawater by a combination of ongoing seepage and occasional marine overflow. Diverse tectonic settings can promote development

of basin-wide evaporite deposits, as outlined by Warren (2010), although beyond the scope of the present overview of Australian salt lakes. It is also implicit that the latitude of salt lake basins, ancient and modern, plays an important role in their evolution.

The prodigious volumes of evaporite salts in the large ancient basins require a mother brine source that could only have been supplied via connections to a large NaCl-rich reservoir of seawater (Warren, 2010). The fact that ancient salts sourced from former great depths in major Australian basins have emerged to generate or contribute to Cenozoic salt lakes in substantial parts of the continent raises the question of whether the hydrochemistry of the salts and brines in the 'halotectonic settings' or what could be termed 'ancient salt lake basin deposits' differs measurably from those salt lakes whose chemical signatures are largely meteoric or, at most, reflect the sum of the geochemistry of their immediate catchments.

It is noted that other major ancient salt deposits occur outside the Amadeus, Officer and Canning basins that are not associated with contemporary salt lakes but which complement our understanding of the nature of ancient salts in inland Australia generally. Proterozoic salt in the Adelaide fold belt, noted above, contemporaneous with the Bitter Springs Formation, has largely dissolved (Warren, 2010). The coarsely crystalline Boree Salt in the Adavale Basin was deposited under conditions of saline reflux in a restricted marine basin environment during the Devonian (McKillop *et al.*, 2005). These underground salt deposits are mined, especially for potash and economic bromine minerals, and explored for potential safe underground storage caverns for hydrocarbons or waste materials. Reward Minerals, for example, hold ~790 km² in the Adavale Basin, seeking potash in a 900m thick occurrence of the Boree Salt Member (Reward Minerals, 2012f).

The chloride-bromide (Cl/Br) ratio has been used as a tracer to determine the origin and evolution of groundwater, surface water and brines, and has become an effective aid in hydrogeological studies of surface and groundwater with low-to-moderate salinity (Fontes *et al.*, 1986; Cartwright *et al.*, 2006). The Cl/Br ratio has been used to differentiate between salinity from seawater or residual brines or from dissolution of halite or halite-rich gypsum in more ancient sediments, or from trapped seawater in large basins or crystalline aquifers. It may also be applicable to distinguishing between ancient marine evaporites (such as those contained in outcropping salt diapirs in the present-day centre of the Australian continent and contemporary salt lakes that have evolved at these sites) and Quaternary terrestrial salt lakes that have evolved above sea level. Similarly, strontium-calcium ratios, Sr/Ca, in calcium minerals may provide information about the conditions that may have favoured strontium replacement of calcium and about the antiquity of such minerals. Moreover, strontium isotopes, ⁸⁷Sr/⁸⁶Sr, in calcium-rich minerals such as gypsum and anhydrite are expected to have different signatures in ancient and modern evaporite deposits respectively, as well as contrasting with basement ⁸⁷Sr/⁸⁶Sr signatures.

Isotopic analysis, such as chlorine isotope values in halite, sulfur isotopes in gypsum and oxygen isotopes in crystalline water of gypsum, have, elsewhere helped distinguish between a marine or continental origin for salt lakes. For example, Hongbing *et al.* (2006) showed that the sulfur isotope composition of gypsum can be used to distinguish between a marine and continental origin and chlorine isotopes of salt and oxygen isotopes of crystalline water in gypsum can be used to assess the sedimentary stage. Hongbing *et al.* (2006) fingerprinted Tethyan seawater that had repeatedly flooded sub-basins in China, attributing contemporary salt lakes with a marine origin and representing a later stage of marine evaporite sequences compared to other evaporites in the regions, and making these basins prospective for potash deposits. In Australia, however, much can initially be achieved by understanding the origin of respective salt lakes, and discovering whether there was a possible ancient marine connection, as described above, or whether evaporites in Australian salt lakes have a much more recent and terrestrial evolution with a largely meteoric origin for salts.

Whilst Lake Mackay is possibly prospective for potash (Section 7.4.6), that may be associated with ancient marine evaporites, it is also prospective for secondary uranium mineralisation although the latter is not related to marine origins, but rather, to more recent terrestrial mineralisation processes in uranium-bearing catchments. Toro Energy Limited (2012c) holds an exploration licence over the Theseus Project, on the southern edge of Lake Mackay. A radiometric anomaly attracted exploration to the lake and subsequent drilling intersected sandstone-hosted uranium mineralisation in palaeovalley sediments. Uranium mineralisation is taken to be a separate process to the marine-origin postulated above for potash concentration (see Chapter 4).

Lake Disappointment, Lake Mackay, Lake Cobb, Lake Newell and salt lakes in the Baker Palaeovalley, among other salt lakes in both the Western Australian and South Australian parts of the Officer, plus the Canning and Amadeus basins, may be underlain by salt structures and are of particular interest to the present project. These salt lakes may be worthy targets for sampling brines, salts and sediments for detailed hydrochemical and mineralogical analysis for regionally comparisons and synthesis. It needs to be established:

- whether Australian salt lakes that are associated with ancient evaporites, or which may be associated thus by inference, are ubiquitously potash-rich;
- whether potash deposits occur in Australian Cenozoic salt lakes and how these deposits compare with 'halotectonic salt lakes' that have ancient salt sources;
- concentrations of lithium and boron in Australian brines need to be assessed and correlations
 drawn with corresponding salt lake settings. This will test the more global observation of Warren
 (2010) that lithium- and boron-rich brines require continental—meteoric hydrologies, not marinefed regimes, and Neogene periods of salt lake evolution and solute concentration in supra-sea
 level hydrographically-isolated (endorheic) continental intermontane and desert margin settings.

The above recommendations are reiterated in context with other considerations for the present project in Chapter 7 to establish understanding of and models for Australian salt lake mineral systems.

2.4 Hydrology and the role of groundwater

2.4.1 Patterns and hydrochemical criteria

The sedimentation patterns of salt lakes have been very well studied, and dominated by chemical precipitation of soluble minerals, deposition of which occurs sequentially from the least to the most soluble, as described by Hardie and Eugster (1970), Eugster and Hardie (1978) and Hardie *et al.* (1978). As seawater concentration increases, carbonates are deposited first, followed by sulfates, halite and finally complex potassium and magnesium salts (bitterns). Australian salt lakes differ from this pattern in many respects.

The unique characteristics of Australian salt lakes are encapsulated in the major reviews of the hydrogeology of Australian salt lakes by Bowler (1986a) and De Deckker (1983), despite these being written between 25 and 30 years ago. The salt lakes studied are hydrogeological features formed from a combination of surface water and groundwater, and vary between being surface water dominated to being dominated by groundwater. For a lake to become saline it must be hydrologically closed such that water loss through evaporation exceeds water loss through outflow. Once lakes become hydrologically closed, salts can accumulate, with waters changing from being fresh to saline. Commonly used definitions of salinity terms with respect to dissolved solids are shown in Table 2.1.

Regardless of differences in water chemistry, from weakly alkaline to acidic, all Australian salt lakes become dominated by sodium and chloride brines (see Figure 2.18). Bittern salts are very rare in Australia, the only published naturally occurring examples being found in the Karinga Lakes system (Arakel and Cohen, 1991; Arakel and Wakelin-King, 1991; Arakel and Hongjun, 1994). Examples of salinities of some of Australian salt lakes are shown in Table 2.2.

Table 2.1 Salinity limits for commonly used terms.

Salinity (mg/L) TDS	Quality
up to 1,000	Fresh
1,000 to 3,000	Fresh to brackish
3,000 to 5,000	Brackish
5,000 to 35,000	Saline (seawater 35,000)
35,000 and above	Hypersaline (brine)

Table 2.2 Salinities of selected salt lakes.

Lake	Salinity (mg/L) TDS	Reference
Lake Gregory, WA	<24,100	Bowler, (1990)
Lake Woods, NT	45,600	Williams and Buckley (1976)
Lake Buchanan, Qld	87,600	Williams (1984)
Lake Lewis, NT	210,000	English (2002)
Lake Amadeus, NT	228,300	Jankowski and Jacobson (1989)
Lake Bennett, NT	274,000	Jacobson (1998) in English (2002)
Lake Ngalia, NT	280,000	Jacobson (1998) in English (2002)
Lake Tyrrell, Vic	250,000 - 330,000	Macumber (1992)
Lake Frome, SA	308,900	Draper and Jensen (1976)
Lake Eyre, SA	310,000	Johns and Ludbrook (1963)
Lake Gairdner, SA	313,200	Johns (1968)
Spring Lake, NT	353,300	Jankowski and Jacobson (1989)

N.B. Spring Lake is part of the Karinga chain of salt lakes in the Amadeus Basin, southern NT; the locations of other lakes are shown on Figure 2.1 or Figure 2.11.

Bowler (1986a) defined lakes by a set of numerical parameters (Section 2.2.3.5). These consisted of the catchment area to lake-surface area ratio (Ac/Al) and the climatic setting, specifically the ratio of potential evaporation to precipitation (E/P), Figure 2.4. From these, and a standard runoff coefficient, a number of additional hydrological parameters can be derived, especially the amplification factor and the disequilibrium index. The amplification factor is derived from basin catchment area, lake water surface area, and the run-off coefficient. The disequilibrium index is calculated from the amplification factor and the evaporation and precipitation values. The higher the index the greater the evaporative concentration and groundwater contribution are to the lake hydrology (Table 2.3). These data were plotted graphically by Bowler (1986a) and are shown above in Figure 2.5.

Table 2.3 Disequilibrium index values for selected Australian salt lakes (modified from Bowler 1986a)

Basin	Disequilibrium index
Buchanan	+3.4
Keilambete	-1.8
George	-4.1
Woods	-8.6
Gregory	-17.9
Tyrrell	-92
Eyre	-194
Frome	-332
Torrens	-629
Gairdner	-771
Amadeus	-798

Two additional non-numeral parameters were also mentioned by Bowler (1986a). These were the tectonic-physiographic setting as expressed by topographic relief, and hydrochemistry, which for Australian lakes are sulfate-chloride dominated brines depositing sulfates and halite.

2.4.2 Palaeovalley lakes

Australian salt lakes are typically located in palaeovalley settings, in palaeoriver valleys and palaeolake depressions. The salt lakes have evolved from former perennial river systems or precursor perennial lakes in response to climate change, namely the onset of aridity, most likely during the Miocene and Pliocene, with accelerated evolution to salt lakes during the Quaternary. As rivers became ephemeral and then dry in response to aridification, their water courses became dissected, commonly forming disaggregated chains of playas along the former river valley. Perennial lakes responding to aridity commonly contracted progressively leaving distinctive concentric lacustrine landforms, such as palaeo-shorelines and residual beach ridges, as testimony to palaeolake levels.

Salt lakes associated with palaeovalleys vary greatly in size, shape and pattern (Table 2.4). An implicit assumption in many earlier palaeovalley studies is that the playas either reflect the dismembered palaeovalley channel or are relict of valley-lakes after reduced levels of flow resulted in the channel or lake being occluded by aeolian sands (due to aridity). This assumption erroneously regarded the playas as relict or defunct landscape elements of the palaeovalley fill. The playas are a dynamic and active part of the modern landscape and a product of a new hydrological regime involving saline palaeovalley groundwater interaction with the landscape surface. Playas are also an important component of the groundwater flow system, being a major site of groundwater discharge from palaeovalley aquifers. This aspect of the playas was evident to some early researchers who recognised that the playas were dynamic landscape elements and that they migrated upwind due to a combination of salt weathering and deflation (Jutson, 1914, 1917, 1918; Blatchford, 1917; Honman, 1914, 1917; Talbot, 1920).

Table 2.4 Summary of main playa types associated with arid zone palaeovalleys (Magee, 2009).

Туре	Description	Examples
1	Chains of small disconnected basins with variable, often large, spacing	South-west Yilgarn palaeovalleys (WA); eastern Eucla Basin palaeovalleys (SA); Officer Basin to western Eucla Basin palaeovalleys (SA, WA)
2	Elongated chains of closely spaced playas, some with connecting channels	Serpentine Lakes Palaeovalley (WA), Percival Lakes/Lake Auld section of the Canning Palaeovalley (WA)
3	Groups of very large and irregularly shaped playas	Moore-Monger Palaeovalley (WA) and Lake Deborah section of Yilgarn-Salt River Palaeovalley of the eastern Yilgarn (WA); all eastern Yilgarn and western Eucla Basin margin palaeovalleys (WA)
4	Very large irregular single playas	Lake Disappointment and Lake Mackay

In the case of disaggregated palaeorivers valleys, calcrete commonly precipitated around contracting waterbodies and evolving salt lakes along the playa chains. Similarly, calcrete aureoles precipitated around contracting palaeolakes, exacerbating both disconnection of surface water flow-lines and enhancing chemical evolution of shallow groundwaters flowing to the new depocentres.

Deflation of exposed lakebeds along palaeovalleys has lowered the topographic elevation of lakebeds (and continues to do so), thereby effectively bringing the underlying water table closer to the surface. The surface of dry or salt lake beds is progressively lowered such that it appears that the water table has been elevated, although the key aspect is that the watertable becomes exposed to solar radiation and thereby to evaporative concentration of solutes. Thus, evaporative pumping promotes groundwater discharge at the lake, augmenting flow that is driven by the hydraulic head that the water inherited from recharge further up-gradient.

This process progressively promotes groundwater flow towards salt lakes, with evaporative pumping becoming a driving mechanism for persistent lakeward groundwater flow and groundwater discharge at the salt lakes. Hydrochemical evolution of shallowing groundwaters is intensified and salt efflorescence and progressive accumulation of brine are fostered. This combination of factors and processes tends to exacerbate hydrological closure of groundwater flow paths leading towards salt lakes, at least with respect to local shallow groundwater flow. Deeper or more regional groundwater flow systems may remain unaffected, although it is generally more difficult to assess the behaviour of deeper aguifers in catchments or groundwater provinces in which salt lakes are contained. Valley calcrete around palaeovalley salt lakes and calcrete aureoles around palaeolacustrine salt lakes serves to further bolster hydrological closure of the surface and near-surface settings. Hydrological closure of catchments around salt lakes can result in not only shallow groundwater flow to the respective salt lake because of evaporative pumping, but also in the development or intensification of centripetal drainage patterns around the evolving lakes during episodic surface water flow towards the ever-lowering depocentres. Deeper flow in palaeovalley aquifers, in basal palaeochannels for example, may continue to follow the gradient of the original drainage and of concomitant aguifers and not effect or be impacted by the overlying salt lake or shallow aguifers.

2.4.3 Salt lake evolution and age

The age of Australian salt lake systems is unclear and its determination difficult. As shown by Bowler (1986a), sedimentation has been marked by alternation of more and less saline conditions, with lake beds that were in turn permanently inundated, ephemerally flooded, or completely dry. This results in a highly episodic record. A further complication is that the oldest sediments can only be dated by either palynology, which suffers from poor zone control in the Plio-Pleistocene or palaeomagnetic reversal stratigraphy, which is complicated by the episodic sedimentary record.

Four possible constraints of the onset of saline lake processes in Australia are provided by Lake Lefroy in Western Australia, palaeolake Bungunnia in Victoria, South Australia and New South Wales, Lake Eyre precursors in northern South Australia and Lake Amadeus in the Northern Territory. Clarke (1994b) suggested that deposition of gypsum in Lake Lefroy commenced in the Pliocene, based on palynology. Zheng *et al.* (1998) however, used palaeomagnetic reversal chronologies and interpolation to interpret gypsum deposition as occurring more recently, from about 500 ka in the middle Pleistocene.

The age of Lake Bungunnia is similarly disputed. An *et al.* (1986) and Bowler *et al.* (2006) concluded that deposition in this weakly saline megalake commenced at about 3.2 Ma or 3.5 Ma, in the middle Pliocene, based on magnetostratigraphy. McLaren *et al.* (2009), using similar methods but more complete sections, concluded that deposition may have commenced as late as 2.4 Ma in the early Pleistocene.

The Tirari Formation at Lake Eyre is a late Cenozoic unit which includes saline lacustrine facies with primary gypsum evaporites (Tedford and Wells, 1990). Initial palaeomagnetic studies indicated initiation of deposition in the latest Pliocene and most deposition occurring through the early and medial Quaternary (Tedford *et al.*, 1986). However, subsequent and more extensive palaeomagnetic analysis (Tedford *et al.*, 1992) suggested that an equivocal but mostly reversed interval from the upper part of the unit could be biostratigraphically constrained to the youngest reversed interval in the Gilbert Chron (3.9–3.4 Ma). Though these palaeomagnetic data are somewhat inconclusive the age estimate is consistent with the degree of pedogenesis (redness and secondary gypsum development) affecting the upper part of the unit.

At Lake Amadeus (Chen and Barton, 1991; Chen *et al.*, 1993) the gypsum-rich, Winmatti Beds playa deposits associated with the existing lake overly the Uluru Clay, which was deposited in a fluvial and shallow lacustrine environment with thin intercalations of primary gypsum evaporites. The palaeomagnetic reversal stratigraphy indicates that the transition between these units occurred before or about 0.91 Ma and perhaps as old as 1.6 Ma. This demonstrates that the onset of evaporite deposition occurred in the early Pleistocene.

Given these uncertainties, at present the onset of saline lake deposition can only be said to have occurred some time between the mid Pliocene to mid Pleistocene, probably diachronously across the continent and occurred episodically under highly variable climatic regimes. This contrasts with the situation in the Atacama Desert where a combination of factors has resulted in evaporite-depositing conditions persisting since the Triassic (Clarke, 2006).

2.4.4 Geomorphology

Arid and semi-arid Australia is characterised by low elevation, low gradients and negative water budgets, resulting in abundant, variably sized ephemeral lakes which can be subdivided into four geomorphic categories:

Flood-out lakes are the most common type in the semi-arid zone peripheral to the arid core where connected, often ephemeral, drainage occurs. These lakes are connected to an adjacent low-gradient fluvial system by either single or multiple channels and are flooded by river floods higher than the feeder-channel sill level. After the flood peak has passed, flow is reversed in the feeder channel, and the lake is partially emptied until the sill level is reached. Lowering of the lake level then continues more slowly, by evaporation and infiltration to groundwater, until the lake dries or is replenished by the next flood. Regular deflation of sediment from the floor during dry periods prevents infilling of the basin by sediment. Flood-out lakes can thus contain long but discontinuous lake-level records that reflect the flood history of the adjacent fluvial system. However they rarely have significant evaporite deposits, because they are essentially surface-water systems, are not hydrologically closed and do not have shallow saline groundwater pools. The Darling Lakes near Menindee in south western New South Wales and the Anabranch Lakes on the Great Darling Anabranch further south are examples of flood-out lakes.

Overflow lakes are rare in arid Australia, certainly much less common than flood-out lakes. They consist of a connected series of lakes along a fluvial channel that fill successively as each basin overflows along the chain. Therefore the effects of changing hydrology in the catchment can differentially impact the system from upstream to downstream. Evaporites can be deposited in overflow lakes when hydrological budgets become negative and are usually more abundant and occur first in the downstream lakes. The Willandra Lakes including Lake Mungo, in south western New South Wales on the Willandra Billabong Creek, a distributary of the Lachlan River, are a classic example of an overflow system. The Willandra Lakes have a complex history of episodic wetting and drying with deposition in the system varying spatially and temporally from freshwater to evaporite facies. The lake system is currently inactive with no flow in the Willandra Billabong Creek and groundwater lying well below the lake floor levels (Bowler, 1998, Bowler *et al.*, 2012).

Terminal lakes are basins that occur at the end of a drainage system and have no surface outlet channel. Water is lost by infiltration to groundwater or by evaporation and they are frequently saline with abundant evaporite deposits and a well-developed groundwater brine pool. Examples in Australia are Lake Eyre, in northern South Australia; Lake Tyrrell, in north western Victoria; and Lake Gregory in northern Western Australia. Some lake basins that are closed for surface water may not be continuously closed for groundwater and this may lessen their potential to form evaporite minerals particularly their potential to concentrate highly soluble ions. Macumber (1991) has demonstrated that Lake Tyrrell, in addition to being a terminal lake with respect to surface drainage, is a groundwater window to the regional saline aguifer, the marine Pliocene Parilla Sand, which extends down-gradient from the lake towards the Murray Basin centre. Under current hydro-climatic conditions, evaporative pumping from the lake induces a local groundwater divide in the Parilla Sand aquifer down gradient of the lake which limits groundwater loss and enables the development of a brine pool and concentration of soluble ions. However, both wetter and dryer climatic conditions can result in removal of the local groundwater divide and consequent loss of the sub-playa brine pool. Many playas in palaeovalley tracts across the continent are effectively closed for surface drainage but may be hydraulically connected to underlying palaeochannel aguifers that can flow down gradient in the palaeovalley. Lake Gregory in the Paraku Palaeovalley and connected down gradient to the Mandora Palaeovalley (English et al., 2012) is an example. As with Lake Tyrrell, these palaeovalley lakes may be temporily closed for groundwater due to local groundwater divides produced by evaporative pumping.

Groundwater discharge lakes have no connection to surface-water drainage and occur where saline groundwater discharges at the surface by evaporation. The suite of associated landforms is complex and includes highly irregular outlines; salt lakes with halite crusts; sand and clay plains; and sand-, clay- and gypsum-rich lunettes and islands. These landforms were termed *boinkas* by Macumber (1980, 1991) based on Murray-Basin examples in northern Victoria with the Raak Plain being a typical example. Lake Gairdner (South Australia) is another example of large a groundwater discharge system in Australia. Because groundwater discharge lakes have often been sites of long-term evaporative concentration of saline regional groundwater systems they have a high potential for evaporite deposition and concentration of soluble ions.

Lunette dunes on downwind shorelines are characteristic of all four geomorphic lake categories, and Australian arid-zone lakes are very commonly referred to as lunette lakes because of the almost universal occurrence of lunettes. The lunette facies and lithology depends on the sedimentary conditions in the lake. Quartz-rich lunettes containing abundant biogenic carbonates occur when surface water dominates as lunettes are derived from beach foredunes. As hydrological budgets become more negative and saline groundwater dominates, lunettes become clay- and gypsum-rich (Bowler, 1973, 1983; Magee, 1991). Lake-floor sediments are disrupted by efflorescent salt crystallisation at the water table capillary fringe and disrupted sand-sized clay aggregates and salts are deflated across the lake floor to accumulate in the lunette. This strong genetic lake-lunette association ensures that lunettes are high-quality archives of the lake environmental history and associated prehistoric human occupation. Lunette lakes are indicative of a regime with a predominant wind direction, which results in upwind wave-eroded erosional cliff margins. Sediment produced by this erosion, or brought into the basin from external sources, is reworked around the lake margin by long-shore transport when the lake is wet or across the lake by wind when it is dry and deposited in beaches or lunettes on the downwind margin. Over 10s to 100s of thousand years the lake basin migrates with the direction of the dominant wind by this process.

Deltaic settings: Salt lake deltas have been described for Lake Buchanan, Queensland, by Wakelin-King (1984), and at Lake Lewis, Northern Territory, by English (2002). Lake deltas are distinctive sedimentary and hydrological environments, not only in perennial lakes, where a mix of fluvial and lacustrine processes prevail, but especially when lakes become ephemeral and contract during arid periods when new deltas form on the surface of exposed former lake beds. Delta morphologies change in response to differing regimes. Geomorphological features that may include strandlines from former high-lake stands, terraces, spits, lagoons, islands of gypsiferous aeolian landforms, playa-fringing dunes and encroaching linear sand dunes may be indicative of such changes. These features may be combined with the impact of sporadic high magnitude run-off events that typify desert hydrological processes and the influence of the build-up of calcrete bodies around a playa. The complexity is exacerbated when contracted lakes become saline and incoming fresh fluvial waters intermix with shallow brines in the delta setting, promoting intense physical and chemical responses and reactions.

English (2002) described hybrid sediments characteristic of deltaic fluvial-lacustrine successions, along with several distinctive features at Napperby Delta at the terminus of Napperby Creek, Lake Lewis. Immature, poorly-sorted, fluvial bedload sands are interstratified with lacustrine clays that are variably reduced (green) and oxidised (red), indicative of alternating fluvial flow regimes, subaerial and subaqueous deposition. Complex, multi-phase and intense chemical overprinting has altered or obliterated sedimentary structures. CaCO₃ replacement of sediments around the zone of inferred water table fluctuation at 3–6 m depth, is intense, no doubt exacerbated by the porosity of fluvial sediments. CaCO₃ in turn has been overprinted by SiO₂, displacive gypsum crystals appear to have been dissolved and replaced by acicular gypsum. Diagenetic processes are complicated and calcretisation and silicification, ferrolysis, zeolitisation and secondary uranium mineralisation are all apparent in the delta setting.

2.4.5 Sedimentation and diagenesis

Sediment deposition in Australian inland salt lakes is controlled by four factors, size of the surface catchment, amount of groundwater discharge, precipitation, and evaporation (Bowler 1986a). Clastic sediments, comprising sand- to silt-sized quartz and detrital clays are washed into the lakes from the surrounding catchments or blown in by the wind. The degree of lake bed accretion is controlled by the water table. Unless the water table is actively rising, the lake bed is a deflation surface, with the depositing sediments only transitory in the lake before being exported to the lake margins as dunes, lunettes and downwind of the lake as dust blankets.

Most Australian saline lakes have near neutral to weakly alkaline chemistries and sodium chloride-rich waters. There are a few exceptions to this generalisation (De Deckker, 1983). They include volcanic crater lakes in Victoria and small lakes in the Monaro region of New South Wales, also associated with mafic volcanics. Larger alkaline lakes are rare, examples including Lakes Bathurst and Jillamatong in New South Wales and Lake Gregory in northern Western Australia where high pH values are believed to be the result of photosynthetic activity by aquatic vegetation during periods of high water level (De Deckker, 1983).

Many lakes are acidic, but as summarised by Bowen and Benison (2008), the formation and evolution of natural acid saline brines are poorly understood (Section 2.5.4). In addition, acid saline lakes show some significant differences from better studied neutral to alkaline ephemeral saline lakes documented in standard works such as Eugster and Hardie (1978) and Lowenstein *et al.* (1989). The brines in neutral to alkaline, non-marine saline lakes typically evolve from relatively dilute rivers and groundwaters with composition of the resulting brines largely dependent on the lithology of the surrounding drainage basin. However, those in the acid lakes of southern Australia are fed by diffuse seepage of concentrated groundwater brines, and meteoric and surface waters play a minimal role. The acidic regional groundwater brines appear to be quite ancient and have evolved by evaporation past the carbonate divide through consumption of alkalinity and have acquired a low pH and unusual compositions through a combination of several processes (Section 2.5.4).

Australian salt lakes rarely show the classic bullseye pattern of evaporite deposits, with concentric distribution of increasingly soluble salts towards the centre of the lake (e.g. Rosen et al., 1991). These tend to occur in small coastal salt lakes such as those described by Warren (1982). Instead, Australian inland salt lakes are floored by sulfate-rich muds, a central zone with an ephemeral surface halite crust may be present in some lakes, but this often dissolves when the lakes are fully flooded (e.g. Clarke, 1994b; Macumber, 1992; Jacobson et al., 1989; Draper and Jensen, 1976). Lake Eyre is the only Australian salt lake known to have a permanent buried halite layer (Johns and Ludbrook, 1963; Magee et al., 1995). Evaporitic minerals deposited in these lakes are predominantly gypsum and halite, with alunite $[KAl_3(SO_4)_2(OH)_6]$ and jarosite $[KFe_3(SO_4)_2(OH)_6]$ in the more acidic lakes (Section 2.5.4) and minor carbonate in those that are more alkaline (Macumber, 1992; Bowler, 1986a; De Deckker, 1983). Efflorescent salt crystallisation can also include sodium sulfates (thenardite) and magnesium silicates (palygorskite) (Bowler, 1983). Authigenic minerals reported in the sediments include clays and haematite from the more acidic salt lakes (Story et al., 2010; Bowen et al., 2008), and zeolites and silica in alkaline lakes (English, 2001; 2002). Dolomite is a common mineral in the Miocene sediments of the Lake Eyre basin, but is only a minor component of the sediments of modern inland lakes (Alley 1998). Celestite (SrSO₄) has formed as a product of the dissolution and re-precipitation of gypsum and carbonate in the Lake Eyre Basin (Williams, 1972) and occurs as nodules. Celestite has also been reported as an accessory primary precipitate in association with primary gypsum evaporites in the Prungle Lakes, downstream from the Willandra Lakes, south western New South Wales (Magee, 1991).

2.5 Summary of Australian salt lake characteristics

2.5.1 Origin of salts

The origin of salts within the Australian landscape was investigated very early, by Jack (1912) and Teakle (1937), who used rainfall data to indicate that the known accession of salt to the land surface could be accounted for in relatively short periods of 100,000–1,000,000 years. This contention was supported by Hingston and Gailitis (1976). The prevailing south westerly winds, in particular, carry large amounts of sea salt onto the Australian continent. The sea salt content of rainwater at Cape Grim, Tasmania, which is regarded as extremely 'clean air' with negligible anthropogenic input, is up to an order of magnitude greater than measured at Pacific Ocean sites, and some 95% of total sulfate is marine in origin (Andreae, 1982; Ayers and Ivey, 1988).

Isotopic analysis of gypsum from salt lakes across Australia shows little relationship with underlying bedrock. Chivas *et al.* (1991) showed that δ^{34} S values of surficial gypsum from salt lakes across the continent, from the coast to 1000 km inland, have a regular pattern, from ~21 % near the coast, decreasing to δ^{34} S values of ~14 % further inland. Sea-salt gypsum is the dominant source of sulfur to the lakes, although the proportion decreases from ~100 % near coastlines to ~50 % inland. A secondary source of sulfur is also airborne, derived from volatile sulfur compounds of marine origin, whilst sulfur from rock weathering is generally a minor component, except where ancient evaporites occur in salt lake catchments. For example, the δ^{34} S measurements of Chivas *et al.* (1991) firmly traced the salt accessions in salt lakes to sea-salt and marine aerosols that have followed established wind patterns inland.

Keywood *et al.* (1997) measured chloride concentration in precipitation from 18 sites in remote areas of Australia over a 2 year period and demonstrated a relationship with distance from the coast. A map of chloride accession was constructed to reveal a maximum chloride deposition in Western Australia coastal localities of 60–70 kg/ha decreasing to <1 kg/ha in the interior of the continent. Chloride deposition from the south of the continent (70 kg/ha) to the north (<5 kg/ha) reflects the greater importance of subpolar marine air masses in the supply of salts to Australia (Keywood *et al.*, 1997).

2.5.2 Salinity and brine evolution

Rainwater in equilibrium with atmospheric CO_2 ideally has a pH of 5.7, although this varies with location. In addition to dissolved CO_2 species (H_2CO_3 and HCO_3) rainwater contains significant amounts of other solutes including common cations, Na^+ , Ca^{2+} , Mg^{2+} , K^+ and anions, Cl^- , SO_4^{-2-} and NO_3^- (Eugster and Hardie, 1978). Rainwater chemistry for Alice Springs is given in Table 2.5, where it is compared with the chemistry of seawater and of groundwaters and brine from Lake Lewis.

Rainwater that has infiltrated into soils and regolith often shows lower pH values than rainwater having absorbed additional CO₂ through bacterial decay of organic matter in the root zone. Acid soil waters in turn are effective weathering agents, more so than fresh rainwater. Weathering reactions at the soil-bedrock interface depend on the pH of reacting waters and mineral constituents encountered. Selective removal of ions from soils, regolith materials and rocks contributes to the solute load of groundwater.

The evolution of the chemical composition of salt lakes requires the accumulation of solutes in groundwater, both atmospheric accessions of dissolved salts in rainwater that has percolated to the water table, and ions derived from chemical weathering reactions. Subsequent evaporative

concentration proximal to or at the groundwater discharge zone leads to precipitation of minerals which, in turn, affects the composition of remaining waters.

Chloride ions tend to be the most conservative ions in a groundwater system. This is because chloride is rarely precipitated under dilute conditions and remains in solution along the hydraulic gradient, increasing in concentration towards the groundwater discharge zone. Chloride concentration, or "chlorinity", can therefore be used to map where the freshest (low chloride) input waters and older, more evolved (high chloride) waters reside in a system. Input of most chloride in Australian salt lake basins can be taken to be by rainfall and dry fallout from resuspended regional continental dust, with negligible contributions from weathering of bedrock that may contain chloride in micas and amphiboles. The chloride concentration in rainfall near Alice Springs is around 0.70 mg/L (Hutton, 1983), and around 19,000 mg/L in seawater. For comparison, chloride in Lake Lewis brine is 212,680 mg/L and in groundwaters from across the Lake Lewis Basin is 1,384 mg/L (average of 10 samples; Table 2.5).

Table 2.5 Rainfall chemistry data for Alice Springs, average of 22 samples (from Hutton,1983); Analyses of groundwater from 10 bores across Lake Lewis Basin and brine from Lake Lewis (from English, 2002); Seawater chemistry from Goldberg et al. (1971). TDS: Total Dissolved Salts. All values are in mg/L.

	TDS	Са	Mg	Na	K	HCO ₃	SO ₄	CI	NO ₃	SiO ₂
Rainfall	6.91	1.60	1.89	1.22	0.23	0.64	0.62	0.71	ND	ND
Groundwater	1,383.9	69.0	61.9	304.9	21.6	473.7	179.2	373.1	24.0	51.0
Brine	212,680	659	1,812	7,725	2,789	75	21,260	111,115	18	4
Seawater	35,000	410	1,350	10,500	390	142	2,700	19,000	1	6

ND = not detected

In central Australia, taking the Lake Lewis basin as an example, bicarbonate and sulfate ions dominate over chloride in fresh groundwater (<1,000 mg/L TDS). The basinal trend suggests that water-rock and water-sediment interactions are a more dominant process than evaporative concentration in the vicinity of up-catchment mountain ranges and beneath adjoining alluvial plains, where water tables are moderately deep, to tens of metres. The dominant mineral species change along the ~50 km flow gradient (Figure 2.17) from HCO₃-SO₄-Na groundwaters near the mountain ranges and creeklines, to CI-SO₄-Na basin-ward in the silicified calcrete aureole (where available HCO₃ has been used to form CaCO₃) and finally to Cl-Na-SO₄ waters at the salt lake, where all available Ca has been utilised in precipitation of gypsum. Thus, there is excess SO₄ in the playa brine, which may hypothetically form rare ephemeral sulfates, such as BaSO₄, RaSO₄, or SrSO₄, depending on available cations after all Ca is utilised for gypsum and depending on pH and evaporative conditions at the salt lake. Salinity, in the form of Total Dissolved Solids (TDS), depends on the position in the basin, some groundwaters being occluded from through-flow because of buried basement highs such that TDS is moderately high even near the ranges. From the mid-plain position, the salinity gradient is steep, increasing from fresh, 800 mg/L TDS HCO₃-rich water, to hypersaline 210,000 mg/L Cl-rich brine over a distance of 40 km.

With increasing salinity, chloride progressively becomes the more dominant ion, indicative of cumulative effects of sediment-water reactions along the flow path and, more importantly, evaporative concentration of shallowing groundwaters down-gradient (English, 2002). A chloride concentration factor of 36 is represented along a 50 km gradient, from the freshest groundwater, with the lowest

chloride concentration, to Lake Lewis where the playa brine contains 111,115 mg/L CI. In the Lake Lewis basin the distribution of fresh recharge waters on the basis of their HCO_3/CI ratio can be mapped. Recharge areas correspond with sites where the HCO_3/CI ratio (in milliequivalents) is >1, found to be close to the mountain ranges and along creeklines and their ephemeral floodout zones. Brine at Lake Lewis has 5.86 times the chloride concentration of seawater (English, 2002), most of the chloride being sourced from rainfall and dryfall, such as dust (including aeolian salts deflated from playas), from the atmosphere.

Hardie and Eugster (1970) and Eugster and Hardie (1978) distinguished several major water types in hydrologically closed continental evaporite basins. Proportions of sodium, calcium, magnesium, and bicarbonate ions in brackish inflow waters determine the subsequent evaporation pathway of closed basin brines, a modified version of which is shown in Figure 2.18.

Path II continental waters (Figure 2.18) are commonplace in arid saline settings in the modern interiors of the cratonic regions of Australia. Initial waters have $Ca + Mg >> HCO_3$ then, after initial evaporative carbonate precipitates, typically $CaCO_3$. The brines become enriched in alkaline earths but depleted in HCO_3 and CO_3 . If the relative volume of HCO_3 is low, as in Australian deserts, carbonate precipitation attenuates and brine evolution follows Path II whereby excess Ca combines with sulfate to form gypsum (Warren, 2010). This path is not dissimilar to proportions derived from precipitation of seawater, reflecting the marine origin of Australian inland salts (Section 2.5.1).

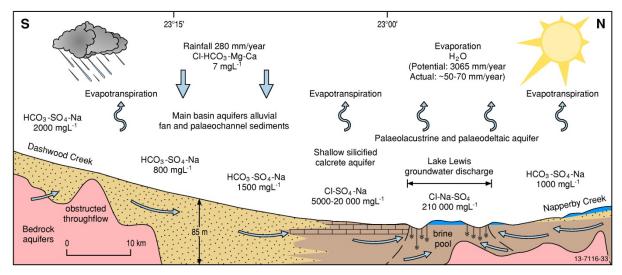


Figure 2.17 A hydrochemical gradient and groundwater flow system through Lake Lewis Basin in central Australia. Solute loads (mg/L) and the main groundwater chemical types are indicated, based on dominant anion and cation compositions. Downward arrows beneath Lake Lewis represent salt plumes or fingers of brine produced by evaporation at the playa surface sinking into the underlying brine pool that infuses the palaeolacustrine clay (from English, 2002).

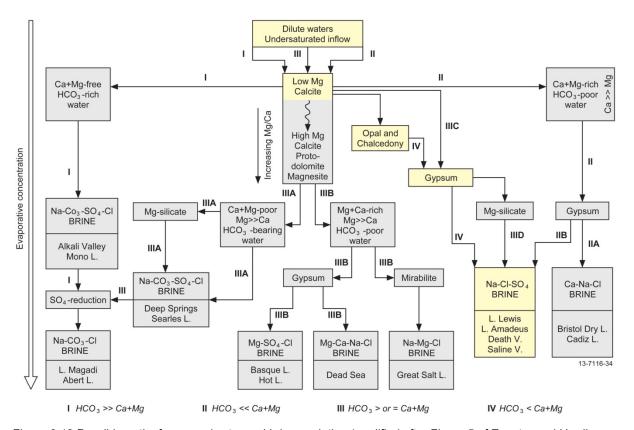


Figure 2.18 Possible paths for groundwater and brine evolution (modified after Figure 5 of Eugster and Hardie, 1978). Solid rectangles represent critical precipitates; rectangles with dashed borders are typical water compositions; evolved brine types, together with examples of representative salt lakes, are surrounded by double rectangles. The evolution of Lake Amadeus and Lake Lewis groundwaters is shaded (from English, 2002).

The evolution of groundwaters at Lake Amadeus (Jankowski and Jacobson, 1989) and Lake Lewis (English, 2002), for example, is highlighted in the scheme of Eugster and Hardie (1978) in Figure 2.18. These central Australian lake basins follow a saline, but lower alkalinity path (shaded), in which calcite and gypsum have formed or are forming as major minerals through evaporative concentration, and HCO_3 then Ca are lost from solution. Saline Valley and Death Valley in the USA also share Path II evolution. After selective removal of HCO_3 and Ca ions to precipitate $CaCO_3$ as calcrete, the groundwaters proceed to precipitate gypsum, with only minor loss of Mg from solution en route. Precipitation of chalcedony and opal precludes down-gradient precipitation of Mg-silicates. The final brine composition is $Na-CI-SO_4$ -rich. This residual brine yields some halite in the form of efflorescent crusts upon dehydration of interstitial brine in the capillary fringe, but Na and CI are mostly retained in solution, along with whatever SO_4 is not required for gypsum precipitation.

Large silica deficiencies are noted in many concentrated brines of closed basins, even though aqueous SiO_2 concentrations are substantial in up-gradient groundwaters. At Lake Lewis, for example, SiO_2 concentrations in basinal groundwaters average 100 mg/L, decreasing in saline groundwaters near the salt lake and leaving less than 10 mg/L in the brine (English, 2001; 2002). This trend reflects the magnitude of silica precipitation in the form of opal and chalcedony in the calcrete aureole surrounding the Lake Lewis (English, 2001; 2002); illustrated in the box between calcite and gypsum precipitation in the evolutionary flow path in Figure 2.18. Precipitation of silica is widespread in the Australian salt lakes context, as described in Section 2.5.3

2.5.3 Sedimentation and diagenesis

Salt lakes commonly exhibit a bulls-eye facies distribution. Low gradient alluvial or palaeolacustrine sediments typically ring the salt lake, overprinted with calcrete (CaCO₃) in the down-gradient reaches, towards the depocentres or the groundwater discharge zone. Basin-ward in the playa margin facies, gypsum is commonly abundant in Australian settings because of large volumes of atmospherically-derived SO₄. Gypsum can occur as displacive gypsum crystals forming in muds in the sub-surface, as 'gypsum mush' from shallow CaSO₄-saturated lakewaters, or as hummocky 'gypsum ground' such as described by Chen *et al.* (1991b). Very large volumes of gypsum are also present in aeolian landforms down-wind from the salt lakes, attesting to substantial periods of evaporative pumping and favourable gypsum-forming chemistries and conditions in the past. Efflorescent halite on lacustrine muds is typical in the centre of Australian salt lakes, forming from brine-saturated muds in the flat lakebed. Rarely, halite crusts form from ponded ephemeral surface water in the lake, intermingled with SO₄ from the brine pool. Bitterns that are characteristic of the centre of many salt lakes on other continents do not occur in the Australian setting.

2.5.3.1 Calcrete

The occurrence of 'valley calcrete' bodies in palaeovalleys and 'calcrete aureoles' surrounding salt lakes was discussed above (Section 2.3.1 and Section 2.4.2) with respect to the distribution, settings and mode of occurrence of Australian salt lakes, and the Menzies Line in Western Australia in particular. Both are groundwater calcretes, or 'phreatic calcretes' formed at or above the water table, and typify not only the Yilgarn north of the Menzies Line, but most palaeovalleys and salt lake settings across the continent (Figure 2.19). As such, they differ from pedogenic calcretes, or 'vadose calcretes' that form from soil moisture above the water table to produce calcareous soils, also described above, south of the Menzies Line. Chen et al. (2002) has compiled a summary of information on calcretes in Australia including their morphological features, distribution, classification, genesis, role in landform evolution and their relevance to mineral exploration.

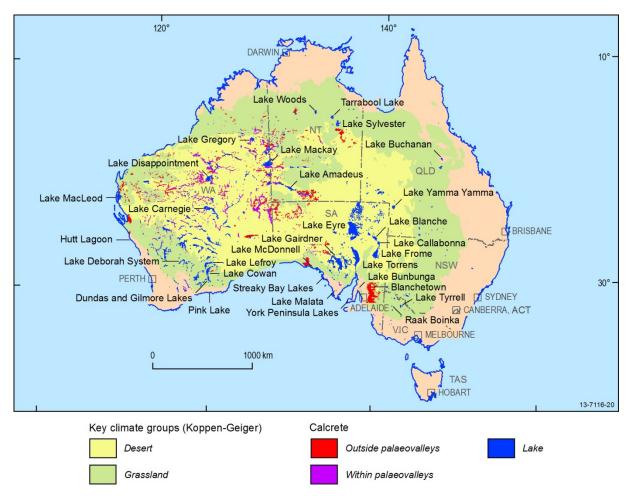


Figure 2.19 Distribution of calcrete in Australia, from the Geoscience Australia 1:1 million scale Surface Geology map (Raymond, 2012).

Mann and Deutscher (1978) indicated that the optimum conditions for formation of groundwater calcrete involved low rainfall, high evaporation, active weathering, low gradients, and high permeability of upper soil or sediment strata over large catchment areas. Butt *et al.* (1977) suggested that, in Western Australia, groundwater calcretes preferentially occur in summer rainfall regions in contrast with the prevalence of pedogenic calcretes in winter rainfall zones. The latter are associated with the longer growing season with consequent greater root respiration, evolution of CO_2 and higher CO_2 content in soil moisture. With respect to regional variations in the distribution of calcretes, Anand *et al.* (1997) regarded rainfall patterns as less important than the nature of and proximity to carbonate rocks, topography, drainage, infiltration rates and soil type.

The calcrete aureole surrounding Lake Lewis typifies this mode of occurrence. The calcrete aureole is approximately 10 km wide and approximately 10 m thick, illustrated in Figures 2.20 and 5.7). Calcrete occupies topographically low, flat-lying parts of the landscape and is well-exposed around the eastern and southeastern part of the playa and to the west and northwest. In the processed Landsat TM scene (Figure 2.20), the calcrete has a distinctive pale blue colour, which corresponds with a high-albedo spectral signature. The surface is pockmarked and disrupted with karstic hollows (10 - 30 m diam.) and small, minor closed basins – resembling shallow dolines – indicating subsurface solution. The calcrete aureole corresponds approximately with the 560 m topographic contour. South of the playa, the aureole is covered with an aeolian sand sheet and to the north by sheetwash deposits fanning

from Stuart Bluff Range. The calcrete aureole largely delimits a 'lacustrine plain' sub-division of the basin physiography and coincides with the outer limit of a high water table associated with groundwater shallowing towards the salt lake, where it occurs a few to several metres beneath the ground surface (English, 2002).

The age of calcrete in palaeovalleys and surrounding salt lakes is conjectural. Calcification and silicification of fluvial-lacustrine sediments in the Neogene in central Australia was described and discussed by English (2002). The Miocene – Pliocene Waite Formation is widely distributed across plains near the central Australian ranges. The dolomitised and silicified Etadunna Formation in Lake Eyre Basin is Miocene in age. Notwithstanding these older occurrences, calcrete is probably presently precipitating in numerous areas in arid Australia where Ca and HCO₃ ions are available in shallow groundwaters. Karstic solution of calcrete bodies also appears to be a contemporary process, where moderately acidic rainfall and surface waters percolate into and dissolve the carbonate.

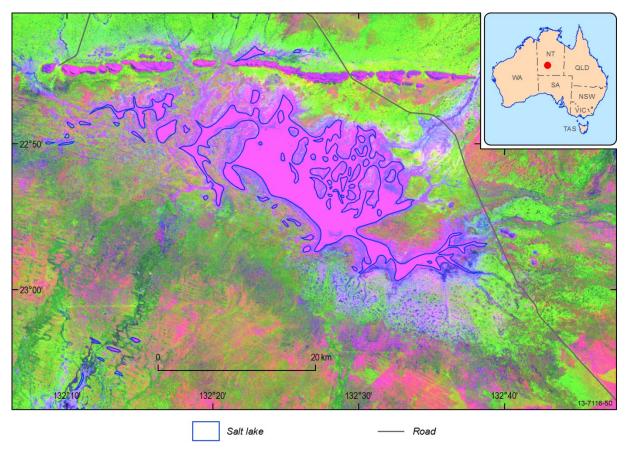


Figure 2.20 Processed RGB Landsat TM image highlighting the calcrete aureole around Lake Lewis. Spectral unmixing processing of 6 non-thermal TM bands (Bierwirth, 1990). RED = clay, water, carbonate; GREEN = iron oxides; BLUE = quartz. Calcrete is represented by high albedo mauve reflectance = CaCO₃ and silica. The 'pockmarked' karstic hollows in the surface of the calcrete aureole are typical for Australian playa settings. The mapped extent of calcrete outcrop around Lake Lewis is shown in Figure 5.8, although is more extensive beneath aeolian sand cover.

2.5.3.2 Secondary silica

Weathering of silicate minerals in bedrock within catchments and drainage basins can lead to supersaturation of groundwater with respect to silica. Hydrolysis of albite, for example, produces kaolinite or smectite, consumes hydrogen and releases sodium, bicarbonate and silica (Garrels and McKenzie, 1971) by the following reaction pathway (solid phases underlined, variable interlayer cations in smectite excluded):

$$2NaAlSi_3O_8 + 2CO_2(g) + 11H_2O(l) = Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4(aq)$$

As incongruent dissolution converts feldspars and micas to clay minerals and increases the aqueous concentrations of cations and silicic acid $[H_4SiO_4^{\ 0}, \text{ or }SiO_2(\text{aq})]$, the weathering of extensive areas of granites and felsic metamorphic rocks produces large quantities of dissolved SiO_2 [aq] in groundwaters, resulting in widespread and intense silicification of the regolith.

High silica concentrations enhance precipitation of poorly-crystalline silica species from shallow groundwaters when a suitable host substrate is encountered along the flow path and when evaporation is significant. Calcrete bodies are an ideal host, particularly karstic calcrete that provides vughs and cracks for silica to infill (English, 2001; 2002). In the absence of an 'inert' host substrate such as CaCO₃, dissolved SiO₂ would be likely to form new clay minerals. Evaporation and evapotranspiration processes appear to be important to, if not the driving mechanism for, silica precipitation from supersaturated waters. Thin layers of silica sequentially build up and consolidate from pockets of groundwater in available voids in the calcrete host material (English, 2001, 2002).

Silica initially precipitates at or near the groundwater table as opal-CT¹ and chalcedony polymorphs, and these metastable species can subsequently mature into microcrystalline quartz. The transformation from poorly ordered SiO₂ mineraloids to quartz is by means of sluggish, progressive solution and reprecipitation where there is space for crystal growth (Figure 2.21e, f).

¹ Opal-CT has been interpreted as consisting of clusters of stacking of cristobalite and tridymite over very short length scales. The spheres of opal in opal-CT are themselves made up of tiny microcrystalline blades of cristobalite and tridymite.

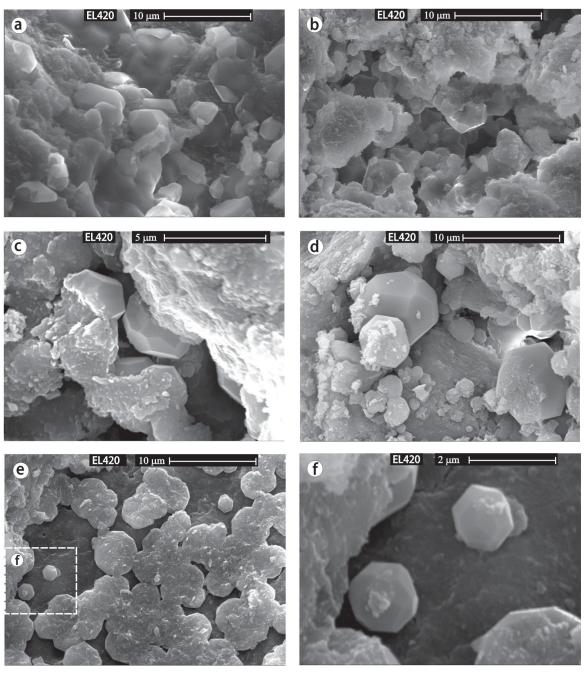


Figure 2.21 Scanning Electron Microscopy micrographs of SiO₂ polymorphs from the silicified calcrete aureole at Lake Lewis, Northern Territory: (a) Opal-CT in the form of spherical aggregates (lepispheres) composed of thin crystal blades; (b) Close-up of opal-CT aggregates in (a). (c) Chalcedony, showing feint plate-like microstructure; (d) Chalcedony laths showing acute angles, feint chevron microstructural elements, and typical waxy lustre. (e) Microcrystalline palisadic quartz prisms growing in a fine-grained matrix of micritic Mg-calcite rhombs; (f) Microcrystalline quartz crystals on the surface of poorly-crystalline silica (from English, 2001; 2002).

2.5.3.3 **Zeolites**

Zeolites are hydrated aluminium silicates that most commonly occur in volcanic rocks and, rarely, authigenically in sediments. As a mineral group, zeolites are characterised by high ion-exchange properties and by their capacity to readily hydrate and dehydrate. Generally, analcime may form by reaction between saline solutions and volcanic glass in pyroclastic sediments. Less commonly, analcime occurs in non-volcaniclastic sediments, from feldspar and clay-rich detrital sediments, in comparable saline aqueous environments. The occurrence of zeolites in an Australian salt lake setting was recorded by Arakel (1987) and Arakel and Wakelin-King (1991) from the Karinga playa system at Curtin Springs in the Northern Territory. Authigenic analcime [Na(AlSi₂)O₆·H₂O] and other authigenic zeolites: mordenite [Ca,Na₂,K₂)Al₂Si₁₀O₂₄·7H₂O], chabazite [Ca,Na₂,K₂,Mg)Al₂Si₄O₁₂·6H₂O] and wairakite [Ca(Al₂Si₄O₁₂)·H₂O] were identified by XRD analysis of palaeolacustrine mud from a delta from Lake Lewis (English, 2001, 2002). The formation of authigenic zeolites in central Australia is significant in that no volcanic rocks or pyroclastic sediments are involved. Key processes involved in zeolite formation in this environment include solute acquisition, brine evolution, evaporative concentration, diagenesis and authigenic crystallisation (English, 2001, 2002).

Although not well understood, the occurrence of zeolites in Australian salt lake settings appears to be related to the silica deficiency in groundwaters reaching the brine pool down-gradient from the silicified calcrete aureole. All dissolved silica is precipitated from groundwater in the calcrete aureole, so long as sufficient host material is available and evaporative conditions persist. Down-gradient at the salt lake, clays that make up the palaeolacustrine sediments become metastable in the presence of silica-deficient brines and begin to form zeolites, utilising cations from the brine pool (English, 2001, 2002). Available information suggests that the palaeolacustrine clays initially form amorphous to gelatinous masses prior to crystallising zeolites (Figure 2.22).

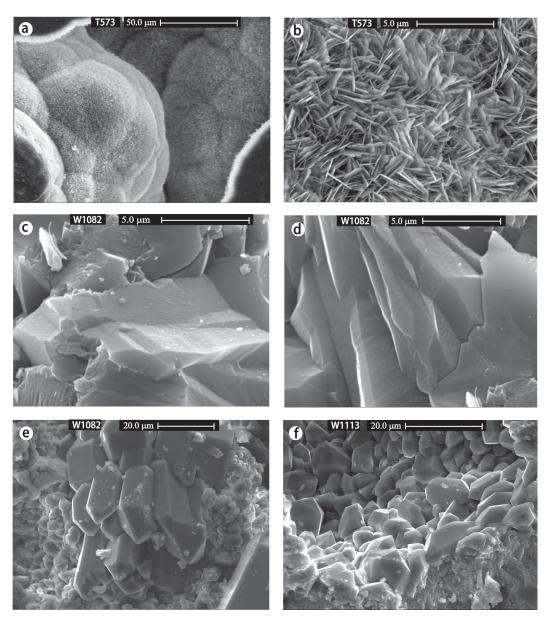


Figure 2.22 SEM micrographs of the zeolite mineral, analcime, crystallising from amorphous aluminosilicate material in palaeolacustrine clay from Lake Lewis, NT: (a) to (d) Euhedral analcime to 9 mm diameter in pore spaces, crystallising from amorphous clay/gel. Energy Dispersive X-ray spectroscopic analysis of the analcime crystals gives Si-Al-Na peaks; the matrix clays having a similar composition but with some K and/or Fe peaks. (e) Irregular and subhedral masses of impure analcimic material, with isolated euhedral analcime crystals occupying pore spaces in the centre left and upper right. The aluminosilicate matrix "globules" resemble frogs' eggs or thick gelatin. (f) Close-up of two well-formed trapezohedron analcime crystals in the outlined area in Figure (e); the crystals are almost 2 µm in diameter. (f) shows the emerging analcime crystallinity of the isochemical subhedral matrix material. The structure of analcime deviates within cubic symmetry from (pseudo)cubic trapezohedron to icositetrahedron crystal forms, as represented here (from English, 2001, 2002).

2.5.4 Acid salt lakes

2.5.4.1 Background

Australian salt lakes are, for the most part, near neutral with respect to pH. This contrasts to continental lakes in many other parts of the world which tend towards higher pH with increasing salinity (Brodine and Jones, 1986; Hardie and Eugster, 1970). Moreover, many salt lakes in southern Australia (e.g., those in the Eyre Peninsula; Lock, 1988; Giblin, 1987), south western Western Australia (Mann, 1983; MacArthur *et al.*, 1991) and parts of the Mallee region of Victoria and South Australia (most notably Lake Tyrell, see Macumber, 1992; Long *et al.*, 1992b) are acidic. A consequence of saline acidic conditions is the occurrence of distinctive sulfate minerals, namely alunite $[KAl_3(SO_4)_2(OH)_6]$ and jarosite $[KFe_3(SO_4)_2(OH)_6]$ which are much more abundant relative to other global and Australian salt lake environments (McArthur *et al.*, 1991). The most detailed studies of acid lakes in Australia have been those of Lake Tyrrell and the lakes in southern Western Australia. These have led to a reappraisal of the abundance of acid lake systems in the geological past as well as at present (Long *et al.*, 2009).

2.5.4.2 Case studies

Lake Tyrrell is a groundwater-fed lake with minor surface-water contributions from Tyrrell Creek. Springs along the western side of the lake have a pH range of 4.0 to 2.6, and salinity in the main part of the lake is almost always above 250,000 mg/L TDS (Macumber, 1991; 1992). The system has been studied in considerable detail, with many papers published in a special issue of Chemical Geology (e.g. Alpers et al., 1992; Fegan et al., 1992; Giblin and Dickson, 1992; Hines et al., 1992; Lyons et al., 1992; Long et al., 1992a, b, and Macumber, 1992). Highly complex interactions are occurring in the lake groundwater system leading to the formation of the acidic conditions, including oxidation of anoxic regional groundwaters in spring discharge zones (Macumber, 1992), reflux of evaporatively concentrated brines (Long et al., 1992a), fluid mixing (Hines et al., 1992), and biogeochemical processes (Hines et al., 1992; Welch et al., 2004). Long et al. (2009) proposed a model for the evolution of the acid brines of Lake Tyrrell (Figure 2.23) and noted that they are not easily classified according to the classic Hardie and Eugster (1970) model which described the evolution of so-called "continental" rather than "marine solutions", as defined by North American lake chemistries. However Lake Tyrrell, in common with most Australian continental lakes, has a marine-like chemical signature. Starting with the deposition of cyclic salts of marine composition in rainfall, Ca and HCO₃ are removed in the vadose zone through precipitation of calcite in calcretes prior to entering the regional aquifer. Ferrolysis and sulfide oxidation in groundwater initiates the acidification process that progresses down the flow path until it reaches the spring zone area, or the groundwater discharge zone, where ferrolysis becomes the dominant processes. During acidification, HCO₃ is removed and the water becomes relatively enriched in Mg as well as in Al and Fe. When the groundwater is discharged into Lake Tyrrell from springs, Ca is removed during evaporation through precipitation of gypsum. The resulting brine is a Na(Mg)–Cl(SO₄) solution with low pH and high concentrations of Al, and Fe. The Fe–Al–SO₄–K assemblage precipitates alunite, jarosite and iron oxides on evaporation. The evolution of Lake Tyrrell brine is summarised in Figure 2.23.

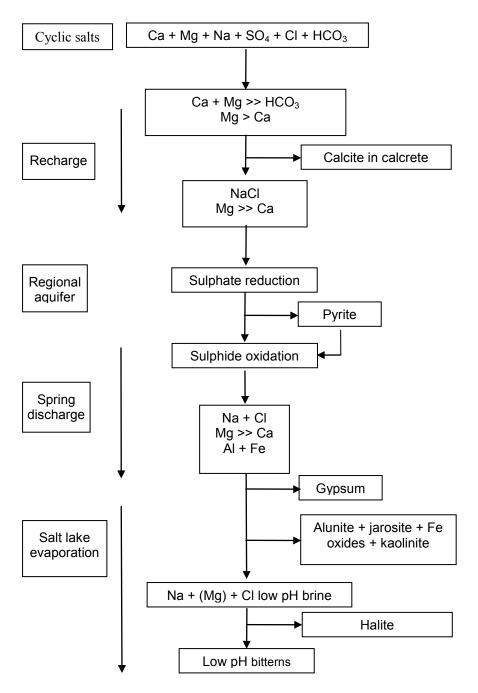


Figure 2.23 Evolution of Lake Tyrrell-style acid brines from a cyclic marine salt source (modified from Long et al. 1992a, 2009)

Alunite and subordinate jarosite have also been identified in 22 evaporitic lakes on Eyre Peninsula, South Australia by Lock (1988), where occurrences are related to highly acidic groundwaters and lakewaters in a granite province. Lock (1988) briefly described a large number of medium to small acid salt lakes associated with the Narlaby and Yaninee palaeovalleys on the peninsula. Salinities were not documented but pH varied between 2.8 and 3.7. Water in the deep palaeovalleys had pH values of around 3.0 (Giblin, 1987). These lakes are formed by groundwater discharge with little or no surface runoff, as defined by the geomorphic classification of Bowler (1986a). A study of Pinjarra Lakes, the most distal of those in the Narlaby Palaeovalley, by Kimber (2002) showed that these lakes had surface water pH values as low as 3.6 and surface salinities (calculated from electrical conductivity) up

to 92,000 mg/L TDS at the time of measurement. The geomorphology of the Pinjarra lakes is complex, with numerous small lakes and sub-basins set within larger lakes, each with a distinctive patterning of evaporitic lacustrine facies. Groundwater discharge into the lakes occurred through point sources (springs and seeps) and by diffuse flow through lakebed sediments.

A contrasting mode of occurrence is no doubt attributable for alunite formation in clay pellets in gypseous lunettes in the Yilgarn (Lock, 1988: pers. comm. from J. Bowler to D. Lock), and an even more unusual occurrence of near-surface alunite has been documented in the Lake Lewis basin, central Australia (English, 2002). Within the calcretised aureole surrounding Lake Lewis, the presence of alunite in sediments above the present-day water table was detected by XRD analysis whilst subsequent petrographic analysis indicated "alunitised feldspar". The alunite formed or is forming in situ directly from weathering of detrital K-feldspar grains and exhibiting excess silica as films around the reaction sites. Diagenesis appears to be occurring at ambient conditions. The underlying groundwater is brackish, 3,200 mg/L TDS, not hypersaline, and circum-neutral pH 6.5, so is incapable of transporting Al³⁺ or Fe³⁺. Thus, pedogenic processes were attributed because, even if groundwaters had been involved, their chemistry is unsuitable as key ions could not have been in solution (English, 2002).

A somewhat enigmatic occurrence of alunite is in the Oligo-Miocene lacustrine Namba Formation of the Frome embayment of the Lake Eyre Basin. The Namba Formation is a lateral equivalent of the Etadunna Formation at Lake Eyre (Callen and Tedford, 1976). As for the Etadunna Formation, the Namba Formation is interpreted as dominantly deposited in alkaline brackish lakes and is dominated by cyclic sand/clay clastic sequences and montmorillonite-dolomite-palygorskite associations. Alunite is frequently developed as lustrous white particles or patches within black iron-rich montmorillonite clay at the top of the lower unit of the Namba Formation. Callen and Tedford (1976) describe the alunite as a series of nodular horizons that resemble soil carbonate hard pans. They imply an origin as a modified pedogenic horizon, but provided no explanation for the formation of alunite mineralogy in an otherwise alkaline mineral chemistry dominated unit. Shallow drilling north east of Lake Frome between the main lake and Lake Cootabarlow has established the presence of significant deposits of similar nodular white alunite in black montmorillonitic clays in the Namba Formation at depths of less than 15 m (Bowler and Magee, pers. comm.)

Mann (1983) documented 48 groundwater samples across the Yilgarn; most were associated with lakes. Of these, 35 had pH values below 7.0, with the lowest being 3.0. McArthur *et al.* (1991) listed 42 water analyses from across the Yilgarn, only one had a pH above 7.0 and the lowest pH was 2.8. The studies reveal groundwater salinities almost invariably exceeding >35,000 mg/L TDS (MacArthur *et al.*, 1991) and occasionally exceeding 400,000 mg/L TDS (Clarke, 1994b). Based on a study of 59 ephemeral lakes in southern Western Australia, Bowen and Benison (2009) reported approximately 40% of the lakes and 84% of the measured groundwaters were extremely acidic (pH < 4) with the lowest measured pH being 1.7. The salinity of these lake waters and groundwaters ranged from fresh (rare) to brines with >280,000 mg/L TDS.

Chemical and isotopic compositions of lake water and shallow groundwater from 21 acid lakes in the Yilgarn Craton led Bowen *et al.* (2008) and Bowen and Benison (2009) to conclude that Western Australian acid saline lakes did not evolve from surface evaporation of dilute inflow waters, but rather were fed by acidic and saline groundwaters. The lake waters subsequently diversified through interaction with a range of processes including surface flooding, evapo-concentration, mineral precipitation and dissolution, and fluid mixing. These studies indicate that the brine evolution pathways and evaporitic divides of Hardie and Eugster (1970) are robust for neutral to alkaline lake systems, but

do not always apply to acid lakes. The sediments deposited by these lakes (Bowen *et al.*, 2008) consist of a mix of quartz sand and silt plus mineral precipitates, including halite, gypsum, kaolinite, and haematite. Interstitial brines result in halite, gypsum, haematite, kaolinite, jarosite, and alunite cements in the sediments of the lake mudflats, sandflats and channels, as well as associated dunes. The variable long-term preservation potential of these minerals suggests that the older sediments are likely to be composed mostly of bedded red siliciclastic and reworked gypsum sand, alternating with less common bottom-growth gypsum and halite, overprinted by early acid diagenetic features such as jarosite and alunite.

As at Lake Tyrrell (Fee *et al.*, 1992), several studies have used rare earth elements (REEs) to trace the evolution of acid brines. Johannesson *et al.* (1994) studied brines from Lake Gilmore (the same sites investigated by McArthur *et al.*, 1991) near Norseman and identified two separate water compositions on the basis of REE concentrations, pH and salinity. The highest concentrations of REEs occurred in shallow groundwaters discharging along western playa margins; these waters also had the lowest pH (2.86 – 3.55) and salinity (39,000 – 197,000 mg/L TDS). More saline brines (up to 208,000 mg/L TDS) that occur further toward the middle of Lake Gilmore had higher, but still acidic, pH values (4.52 – 5.31) and the lowest concentrations of REEs. The data suggest that acidic shallow groundwaters remove REEs from surrounding granitic rocks and introduce them into Lake Gilmore where they are precipitated as pH increases. Evaporative concentration alone does not appear to have a significant effect on REE concentrations, but rather, increasing pH and scavenging of REE by ferric oxyhydroxides which precipitate with increasing pH, appears to be more significant.

2.5.4.3 Generation of low pH brines

A number of hypotheses have been proposed for the formation of acid saline brines in these lakes. Most commonly they are attributed to undefined modern-day weathering processes active in granitic regions (e.g. Lock 1988). Mann (1983) argued that acidity was generated by iron ferrolysis, the oxidation of ferrous to ferric ion according to the reaction:

$$4\mathrm{Fe}^{2^+} + 6\mathrm{H_2O} + \mathrm{O_2} \rightarrow 4\mathrm{FeOOH} + 8\mathrm{H}^+$$

This reaction was proposed to occur at the weathering front with, by implication, both basement sulfides and ferrous iron-bearing silicates involved.

However a study by McArthur *et al.* (1989) based on chloride ratios and isotopes of S and Sr showed that weathering of basement had a comparatively minor contribution to the brine chemistries. Developing on these data, McArthur *et al.* (1991) suggested microbial reduction of ferric ion to ferrous coatings in surficial sediments in aquifers, the sequestering of alkalinity in near-surface calcrete deposits, and the formation of acidity by ferrolysis of groundwater following discharge into the near-surface environment were key processes in the development of low pH brines.

Acidity in Lake Tyrell has been attributed to the oxidation of diagenetic pyrite which is plentiful in the Pliocene Loxton/Parilla Sands sedimentary aquifer that underlies the lake (Macumber, 1992, Long *et al.*, 1992a, b). Although the source of ferrous iron is different, the reaction is still essentially the same equation as shown above. Mineral chemistry studies of alunite and jarosite from Lake Tyrrell (Alpers *et al.*, 1992) show that the sulfate is derived largely from aerosols, with only minor contributions from pyrite oxidation; this is consistent with the Western Australia data from McArthur *et al.* (1991).

More recently Worrall and Clarke (2004) suggested an alternative hypothesis for acid lakes to those of Mann (1983) and McArthur *et al.* (1991), this being the oxidation of pyrite in Eocene sediments that occur in palaeovalley sequences overlying basement in both southern Western Australia and on Eyre Peninsula. The Worrall and Clarke (2004) hypothesis has not been tested by detailed geochemistry or isotopic studies. However, this model would provide a common hypothesis to account for the acidity that occurs in the Murray Basin, Eyre Peninsula, and southern Western Australian lakes through oxidation of sedimentary pyrite.

Another mechanism was proposed by Peiffer *et al.* (2009), based on mathematical modelling. They suggested that weathering-generated alkaline fluid reacts with gypsum to form calcite. A further consequence of this reaction is the spatial separation of acid and alkaline fluids.

2.5.4.4 Consequences and implications of acid lakes

The most obvious consequence of low pH brines is the absence of carbonate minerals from the precipitated sediments. Carbonate may occur close by, for example as calcrete, just above the water table, along the lake margins and in the catchments (McArthur *et al.*, 1991; Peiffer *et al.*, 2009; Long *et al.*, 1992a, 2009) and sequestering of carbonate ions in calcretes may be an important prerequisite to the development of acid lakes. The absence of carbonate buffering in the lake brines precludes the precipitation of zeolites and results in the pH eventually falling so that jarosite and alunite are deposited.

Deposition of the K, Al and Fe sulfates, alunite and jarosite, may be a significant reaction for sequestering of potassium found in brines, with both Alpers *et al.* (1992) and Long *et al.* (1992b) reporting that the alunite in Lake Tyrrell was the potassium-rich end member and that little or no sodium was present (no natroalunite). In Western Australia alunite is particularly widespread and abundant in the Lake Brown system of playas, near Merredin, 300 km east northeast of Perth. In one of these, Lake Chandler, part of the Deborah Palaeovalley, alunite constitutes 60% of the sediments to a depth of 6 m (Hall, 1978). McArthur (1991) measured alunite as comprising 13–29 % of samples from Lakes Gilmore and Swann, south and south east of Norseman, Western Australia. In South Australia, Lock (1988) reported a number of small (2 – 10 hectare) lakes in the Minnipa-Kyancutta area that contained over 50% combined alunite and jarosite to depths of up to 2.3 m below lake surface. Radiocarbon dating of the lake sediments indicates that these have accumulated in approximately the past 5,000 years. The consequences of potassium deposition as alunite and jarosite as potential potash resources is a field that warrants more research given the much greater known extent of acid lakes than was the case fifty years ago. Equally, the potential for acid brines to downgrade the possibility of significant dissolved potash reserves in other mineral phases, through precipitation of alunite and jarosite, is also a topic for further research.

Acid brines are highly effective in the mobilisation of REEs. Several papers have been published examining the REE mobility in Australian acid-lake brines and natural laboratories for REE mobilisation for both insight into mineralisation processes and for analogues of the leaching of radionuclides for nuclear waste (Johannesson *et al.*, 1994, 1996). REEs appear to be carried into lakes by discharging groundwater whereupon they are rapidly bound in the lake sediments. REE grades are below what are generally considered economic (<0.1%), although the possibility of new technologies to access and extract REEs transforming future economies of scale cannot be excluded.

McArthur *et al.* (1991) suggested that the strong silicate leaching associated with acid brines may explain the formation of silcrete. This appears unlikely as the areas associated with acid brines have only minor silcrete in spite of the fact that there is potentially abundant aqueous silica derived from weathering granites in respective regions and because silcrete and other secondary silica deposits (such as opal and chalcedony) are widespread across areas not noted for acid conditions.

2.5.5 Brine pool characteristics and dynamics

The presence of a Ghyben-Herzberg interface (Herzberg, 1901; Ghyben, 1888) creates a physical barrier between fresh and saline groundwater around a salt lake margin. When lake waters reach the halite saturation point they become very dense and are thought to form a descending plume beneath the lake. Additional to this vertical downward movement of highly saline water, lateral migration in the subsurface can occur away from the playa (Figure 2.17). Because of the higher mineral content, greater density and higher water pressure of saltwater relative to fresh or less saline water, hypersaline waters or brines can push inland, shoreward, beneath the fresher groundwater that is flowing to the discharge zone. Mixing of brines with lower-salinity groundwater along the margins of the lake may result in the development of a subsurface convection cell that leads to the brines being returned to the lake (Warren, 1983). Because the fluids are of a different density and viscosity the flow patterns which emerge are more complex than those caused only by diffusive mixing. A potentially unstable situation pertains in which fluid of a higher density lies on top of fluid of a lower density and may lead to convective motions within the aquifer system, particularly in a homogeneous medium. Convection rolls can become steady state and circulate over the entire depth of the aguifer, assuming hydrological closure of the basin, sufficient rainfall to maintain a flux of water (recharge) in the basin leading to the salt lake (discharge), and arid climate conditions with high potential evaporation (Holzbecher, 2005).

Sediment input to groundwater-controlled playas via surface water is limited by the small area of effective catchment and removal of sediment by deflation. It is also irregular and is of relatively small magnitude due to the stability of the water table level at the playa surface. Thus, as evaporation continues through time, the evolution of the groundwater chemistry produces an enlarging brine pool which can expand both vertically and laterally to form a relatively deep structure that can affect local groundwater flow systems and the chemical compositions and the densities of groundwater bodies. Brine pool characteristics in Australia have been investigated by Bowler (1986a), Barnes *et al.* (1990) and Fergusson *et al.* (1992), among others, who documented mixing processes between saline groundwater and evaporation brines near groundwater discharge zones, including advection and diffusion of brines in both ancient and modern salt lakes.

Bowler (1986a) stated that the evolution of playa groundwater towards higher salinity and the formation of a sub-playa brine pool is controlled by a combination of the proportion of time that the playa floor lacks surface water and is exposed to evaporation from the capillary fringe of the water table and the evaporative strength of the prevailing climate. The effectiveness of this process also depends on other factors such as:

- The thickness of the capillary fringe or the depth to the saturated zone, controlled by sediment grainsize, porosity and permeability characteristics;
- The hydraulic conductivity of the sub-playa sediments and the groundwater pressure gradients;
- The nature of the connectivity to the underlying aquifer; and,
- The salinity of the groundwater.

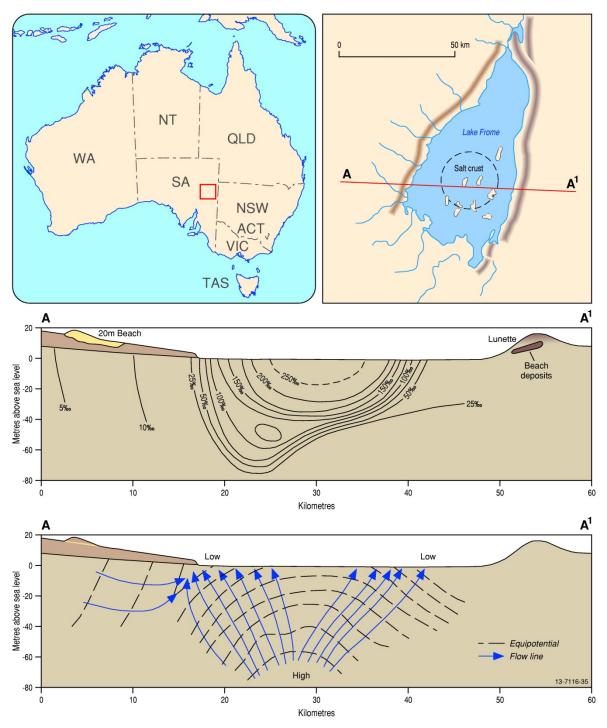


Figure 2.24 Plan and cross-section of Lake Frome illustrating the relationship between the surface salt crust and the structure of the underlying brine pool. The equipotential isolines indicate how the surface high-density brine pool refracts groundwater discharge flow away from the halite salt crust zone towards the playa margins. Figure is modified from Magee (2009) after Bowler (1986a; Figure 2.4).

The evolution of sub-playa groundwater salinity in inland Australia has been examined by a number of studies which include the Lake Amadeus–Curtin Springs area of central Australia (Jacobson *et al.* 1988, 1989; Jacobson and Jankowski, 1989; Jankowski and Jacobson, 1989; Chen, *et al.* 1991a, 1993), Lake Frome, South Australia (Bowler, 1986a), Lake Tyrrell (Teller *et al.* 1986; Macumber, 1992) and Lake Lewis (English, 2002).

At Lake Frome, South Australia, Bowler (1986a) demonstrated the evaporative concentration of shallow interstitial water immediately underlying the basin floor. Highly saline shallow groundwater, with TDS in excess of 200,000 mg/L occurs in the centre of the basin, along with a halite salt crust (Figure 2.24). This grades laterally and vertically to lower salinity groundwater (25,000 mg/L TDS) near the basin margin, with the lowest salinity (<10,000 mg/L TDS) located over 5 km to the west. The brine pool that extends 60 m below the playa floor acts as a large refracting lens, concentrating groundwater flow towards the margins of the halite crust and maintaining pressure discharge which concentrates flow towards the playa margins. West of the playa, where alluvial and colluvial sediments extend from the Flinders Ranges the lowest salinity regional groundwaters (<10,000 mg/L TDS) are located beyond 5 km from the playa. This brine-pool structure, characterised by density reversal, concentrates groundwater flow towards the margins of the halite crust and the playa margins (Figure 2.24).

Macumber (1991; 1992) investigated evaporative brine-pool formation by groundwater reflux at Lake Tyrrell, which is a window to the saline regional Loxton-Parilla Sands aguifer. This situation has been shown to induce a local groundwater divide in the regional aquifer that prevents groundwater loss from the playa and down-valley throughflow (Figure 2.25), a process analogous to a stagnation point and groundwater divide induced by pumping a bore on a sloping water table. This occurs even where there is no surface-water topographic divide and both surface-water and groundwater potentiometric gradients are low. The playa acts as an evaporative pump and the induced groundwater divide is located about 6 km from the lake (Macumber, 1991). A Ghyben-Herzberg interface between the sharply contrasting regional aquifer salinity and the high-density, high salinity brine pool beneath the lake diverts lower-density regional groundwater into the playa system. Extension of the high-density reflux brines vertically through the aquifer precludes down gradient regional groundwater underflow beneath the playa (Figure 2.25). Macumber (1991) has demonstrated that this situation of closed outseepage from the playa basin is a self-perpetuating metastable equilibrium. Under existing climatic conditions, the low regional groundwater gradients preclude the formation of a sufficiently high hydraulic head upgradient of the playa to flush the aquifer by down gradient throughflow. However, even relatively small changes in the climate and water budget can induce enhanced groundwater throughflow and out-seepage from the playa system. This change can be achieved by two contrasting hydrological regimes:

- by increased aridity which would lower the regional water table and groundwater divide and permit outseepage and throughflow but in minimal amounts due to the reduced groundwater flow budgets; or
- by wetter climates whereby increased surface-water accumulation in the lake increases the hydrostatic head of the lake brine.

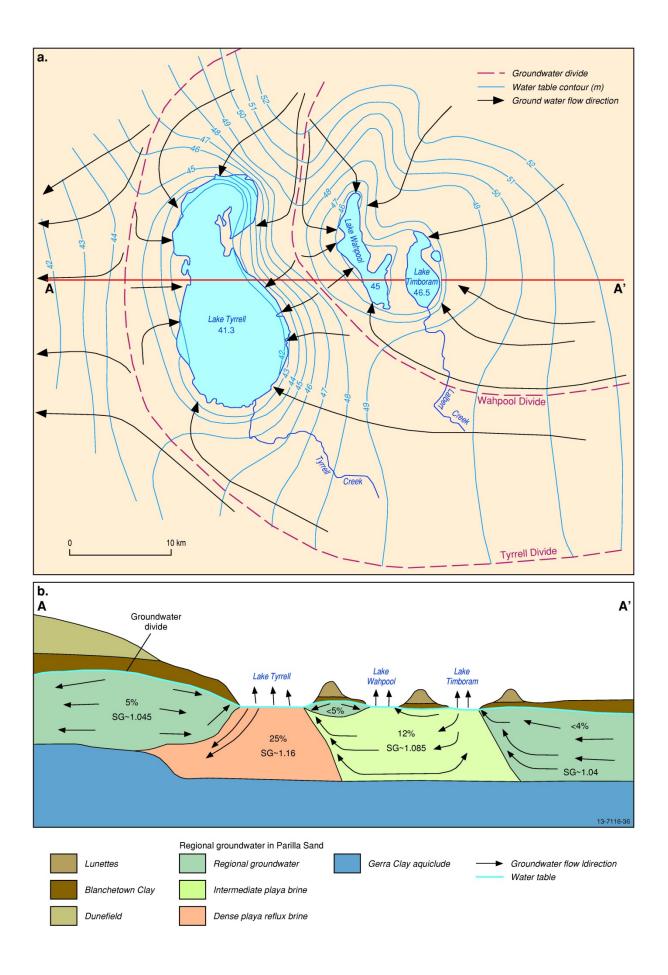


Figure 2.25 (A). Potentiometric surface and groundwater flow lines for the Pliocene Loxton-Parilla Sand aquifer in Victoria's Tyrrell Basin. The water table contours are strongly affected by the three discharge lakes, Tyrrell, Wahpool and Timboram. The floor of each lake intersects the regional water table. The closed contours around Lake Tyrrell and Lake Wahpool indicate groundwater inflow from all directions, whereas Lake Timboram (without similar contour closure) only receives inflow from the east. The groundwater flowlines demonstrate that regional groundwater flow only enters Lake Tyrrell from within the Tyrrell groundwater divide, excluding groundwater within the Wahpool divide which is captured by Lakes Timboram and Wahpool. However, groundwater underflow passes from the Wahpool–Timboram system to Lake Tyrrell. Macumber (1991) estimated that this process contributes about 33% of the Wahpool–Timboram inflow to Lake Tyrrell. (B). East–west cross-section of the Tyrrell Basin showing groundwater flow and salinity variations of the regional Parilla Sand aquifer (3,000–5,000 mg/L TDS), the Lakes Timboram–Wahpool reflux brine pool (9,000–12,500 mg/L TDS), and the Lake Tyrrell reflux brine pool (20,000–29,000 mg/L TDS). Groundwater underflow from the Lakes Wahpool–Timboram system to Lake Tyrrell is also indicated. Figure is modified from Magee, 2009, after Macumber (1991).

Bowler (1986a) pointed out that playa sediment sequences cannot preserve solid evaporite phases of highly soluble salts, such as halite, until the groundwater brine pool that underlies the playa and saturates the sediments has evolved to near saturation levels for those salts. Macumber (1991) argued that the lack of significant salt accumulation at Lake Tyrrell was due to periodic flushing of the reflux brine pool by changes to both wetter and drier climates during Quaternary glacial-interglacial climate cycles. This implies that only those lakes with long-term hydrological closure for groundwater, where discharge is dominated by evaporation, have a high potential for the formation and preservation of evaporites and soluble-ion concentrations. This will include terminal lakes and groundwater discharge zones or boinkas and palaeovalley playas where groundwater throughflow is occluded post valley infill tectonics. The proposition that the majority of palaeovalley playas are subject to loss of solutes to downgradient throughflow seems probable given that most have only thin discontinuous and/or ephemeral efflorescent deposits of soluble salts such as halite, but requires further investigation.

In addition to the development of a groundwater divide down-gradient to a playa, Macumber, (1991) listed other important controls over playa outseepage and regional down-gradient groundwater throughflow including:

- The geometry, stratigraphy and connectivity of regional aquifers beneath the lake;
- The ratios between vertical and horizontal hydraulic conductivities beneath the lake; and
- The potential water depth in the lake.

Subsurface brine descent beneath salt lakes has been experimentally and theoretically investigated by Wooding *et al.* (1997a; 1997b), as well as in the Murray Basin saline wastewater disposal basins, where brine dynamics have been studied by Barnes *et al.* (1990), Ferguson *et al.* (1992) and Jacobson *et al.* (1994). Chambers *et al.* (1995), also as part of saline disposal basin work, used chemical equilibrium models to characterise groundwaters by predicting their evaporative evolution pathways, further predicting that some of the evaporites may have commercial possibilities. Although all groundwaters considered in the Murray–Darling Basin have sodium and chlorine as their dominant ions, none are similar to seawater in their predicted evaporative brine evolution.

The work of Wooding *et al.* (1997a) focussed on the onset of gravitational instability in near-surface groundwater beneath an evaporating salt lake and the development of convective groundwater motion that strongly controls the subsurface distribution of salts and the formation of saline minerals. Convection is driven by the evaporative concentration of salts at the surface leading to an unstable distribution of density aquifer permeability and the evaporation rate from the lake bed (Wooding *et al.* 1997a). Convection will dominate in an aquifer with permeability above an empirically estimated threshold whereas salts will accumulate at the land surface in a system below this aquifer permeability threshold.

Further experimental and numerical work by Wooding *et al.* (1997b) investigated downward convection of salt fingers or plumes that coalesced with time and which simulated field-scale brine pool behaviour.

The Murray–Darling Basin investigations of Ferguson *et al.* (1992) and Jacobson *et al.* (1994) identified two main hydrodynamic systems operating within the same climatic regime and the same general environment, with the differences determined by the type of sediment underlying the saline basins. Where permeable sand aquifers are present, salt sinks advectively downward. Where less-permeable clays are present, slow diffusional transport of salt downward occurs. At Spring Lake, east of Lake Amadeus, diffusive sinking of accumulated salt occurs despite continuous upward flow of groundwater (Jacobson and Jankowski, 1989).

Cartwright *et al.* (2001) investigated the trend for increasing salinity along groundwater flow paths in the Murray–Darling Basin where dramatic salinity variations from 650 mg/L to >100,000 mg/L TDS occur over distances of a few kilometres in both shallow and deep aquifers. Using hydrochemical data, particularly Br/Cl ratios, they showed that limited dissolution of salt from the aquifer is occurring. Stable isotope data and $Mg/Ca/SO_4$ ratios indicated that brines produced in the saline lakes reflux into underlying aquifers to depths of up to 180 m, implying that there is significant vertical interconnection within the basin.

Carey et al. (2003) describe a complex brine flow regime at Lake Lefroy, Western Australia, where regional brines flow to the salt lake and are evaporated to produce hypersaline (playa) brines that sink and flow away from Lake Lefroy and beneath the regional brines. Density-driven, convective mixing of these two fluids forms a zone of brines with transitional compositions located near the edge of Lake Lefroy. Knowledge of the groundwater flow regime was used to interpret the distribution of elements around bedrock gold mineralisation. No anomaly was identified in deep brines associated with the nearby gold ore body, however, shallow regional brines showed elevated gold values overlying and down-gradient from the mineralisation. The lack of elevated gold concentrations in deeper groundwater associated with the gold deposit is due to the hypersaline playa brines being sourced from Lake Lefroy, and not having been exposed to the mineralisation (Carey et al., 2003).

A distinctive brine pool dynamic is described by Chen *et al.* (1991a) at Lake Amadeus, where so-called 'gypsum ground' has formed on the playa surface which relates to changes in water table levels during the Holocene. Gypsum ground is a slightly elevated, rough and patterned surficial crust that has a 'gilgai' texture and is underlain by gypsum. Chen *et al.* (1991b) proposed that initial gypsum deposits formed when the water table was high, probably during wetter climatic conditions, causing active seepage and more frequent surface exposure of brine in the playa. A later decline in the water table, most likely during drier times, caused degradation of the gypsum deposit by dissolution and leaching processes. In this case, brine dynamics have had a direct geomorphological influence in forming distinctive salt lake crusts that have also been recognised in Lake Lewis (English, 2002).

Figure 2.17 illustrates interpreted groundwater flow and brine pool dynamics at Lake Lewis in cross-section, where considerable hydrodynamics occur at the playa margin, at the Ghyben-Herzberg interface. Saline basinal groundwaters meet brines and are deflected upwards at the edges of the salt lake and while density driven descent of brine occurs beneath the lakebed, in this case exacerbated by the presence of subsurface granite inselbergs (English, 2002).

Advection and diffusion processes at Lake Lewis resulted in downward advection of salt in sandy layers of the uppermost 0.5–1 m, and also in Napperby Delta, on the northeast side of Lake Lewis (English, 2002). These processes potentially facilitated rapid initial infiltration of ephemeral saline lakewaters beneath the playa. English (2002) also proposed that diffusion of salt was the main

dynamic process below 1 m depth, i.e., within the bulk of the brine pool, because of poor hydraulic conductivity in the thick, dense palaeolacustrine Anmatyerra Clay beneath the playa. Salt movement downward occurs despite the upward pressure gradient of discharging basinal groundwaters. The arrival of up-gradient saline groundwaters at the discharge zone at Lake Lewis is concentrated along spring zones near the playa margins, with the less-dense basinal groundwaters deflected upwards along the interface with brines. This is analogous to the situation at Lake Tyrrell (Macumber, 1992), and as illustrated above in Figures 2.17 and 2.25. The role of buried and outcropping granite highs at Lake Lewis may complicate the movement of both basinal groundwaters and brine.

2.6 Recommendations

The fact that ancient salts originating from great depths have, in places, emerged to generate or contribute to Cenozoic salt lakes raises the question of whether the hydrochemistry of the salts and brines in these 'halotectonic settings' and what could be termed 'ancient salt basins', differs from those salt lakes whose chemical signatures are largely meteoric or, at most, reflect the geochemistry of their immediate catchments. For this reason the following salt lakes are suggested targets for sampling brines, salts and sediments for detailed hydrochemical and mineralogical analysis: Lake Disappointment, Lake Mackay, Lake MacDonald, Lake Hopkins, Lake Neale, Lake Amadeus, Karinga lakes, Lake Cobb, Lake Newell and salt lakes in the Baker Palaeovalley.

3 Review of Australian Coastal Salt Lakes

J.D.A. Clarke

Australian salt lakes fall into two distinct settings, continental and coastal (de Deckker, 1983). Continental salt lakes, covered in the previous chapter, occur inland and are characterised by water supplied by runoff, rainfall, and groundwater discharge, with salts entering the lakes from regional groundwater and cyclic salts. Coastal salt lakes are characterised by a coastal setting and are fed by coastal saline groundwater. Salts are directly marine in origin, either from seawater seepage through coastal barriers, and from spray.

This chapter summarises Australian coastal salt lake research. It will review previous work, the distribution and settings of Australian coastal salt lakes, summarise their characteristics, compare them with coastal salt lakes occurring on other continents, and overview their economic significance.

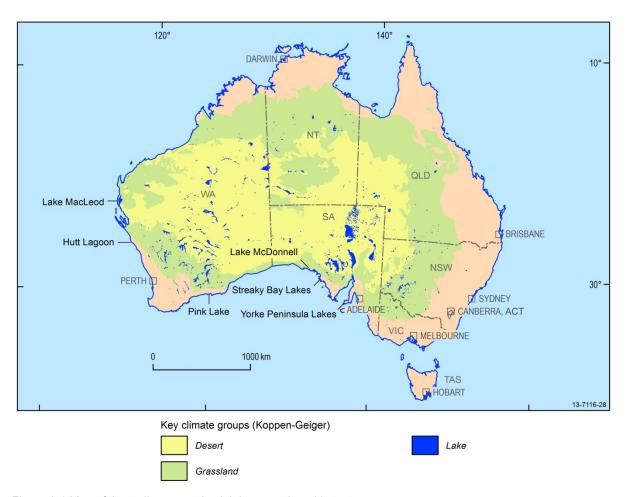


Figure 3.1 Map of Australian coastal salt lakes mentioned in text.

3.1 Factors controlling occurrence of Australian coastal salt lakes

Almost all Australian coastal salt lakes are associated with barrier systems along depositional coasts that have been established during Quaternary transgressions (Gostin *et al.*, 1988) and are therefore comparatively young features. Major Australian coastal salt lakes are associated largely with carbonate depositional provinces and are thus not found in Heggie *et al.*'s (2002) classification of Australian clastic depositional coasts. The exception to this is the largest Australian coastal salt lake, Lake MacLeod (Figure 3.1), which is controlled by the Cenozoic warping that led to the formation of the Bullara Sunkland (Logan *et al.*, 1970; Caldwell, 1977) and records deposition, albeit not necessarily evaporitic, as old as Pliocene.

3.1.1 Role of climate change and climate regimes

Australian coastal salt lakes are all associated with the semi-arid to arid zone of Australia. Surface runoff and rainfall plays only a minor role in the hydrology of these systems, minimising dilution of seep seawater and saline groundwater. The exception to this is the Coorong (Warren, 1994) which receives river water from the lower Murray lakes and is thus a brackish rather than saline lake system. Because coastal salt lakes are Late Pleistocene to Holocene features, climate changes have played a minimal direct role in their evolution, unlike continental salt lakes. Indirect influences of climate change, expressed by climate-driven sea level change has, however been vital in the development of these coastal systems.

3.1.2 Role of sea level change in coastal salt lake evolution

Gostin *et al.* (1988) illustrated the coastal environments in southern Australia and how these evolved following the peak of the Holocene transgressions. Examples of these systems include those of Yorke Peninsula (Warren, 1982a), Streaky Bay on Eyre Peninsula (Olliver *et al.*, 1988), Lake MacDonnell (Warren, 1983), and Pink Lake near Esperance (Galloway, 1986). The Coorong is another, albeit non-evaporitic example of a coastal lake system formed by the peak of the Holocene transgression (Warren, 1994). Coastal embayments and archipelagos formed by the transgression have been converted into lagoons and salt lakes by coastal progradation, the best studied examples being those at the foot of Yorke Peninsula (Olliver and Warren, 1979; Warren, 1982a; b), but equally applying to lakes on Eyre Peninsula (Olliver *et al.*, 1988), Lake MacDonnell (Warren 1983), and Pink Lake (Galloway, 1986).

3.1.3 Role of tectonics

Lake MacLeod (Logan, 1987) formed within the Bulla Sunkland (Logan, 1970; Caldwell, 1977), a tectonically controlled low-lying area with an approximately north-south axis lies landward of the Indian Ocean coast of Western Australia. Tectonic flexures mark its margins: to the west lie the Cape Range, Warroora, Cuvier and Dirk Hartog anticlines, and to the east lie the Giralia-Marrilla, Chargoo, and Minilya uplifts. Tectonic activity commenced in the Miocene and continued into the Quaternary with 90-120 m of subsequent subsidence. Infill of the sunkland includes aeolian sands, thin marine sediments and, in the Lake MacLeod Basin, evaporites. In the Lake MacLeod area the sunkland is expressed as a graben (Logan, 1987). As a result of subsidence in the graben, the floor of Lake MacLeod is up to 4.3 metres below sea level, the head difference between the lake floor and the sea on the other side of the Quobba Barrier is the main driver for the hydrology. Another consequence of

the tectonics is that the Quobba Barrier between the lake and the sea is composed of mostly the highly-permeable Miocene Trella Limestone, which also occurs beneath Lake MacLeod at a depth of more than 70 m, rather than Quaternary calcarenites and Holocene barriers as in other coastal salt lakes.

3.1.4 Role of groundwater

Groundwater is the dominant force in coastal salt lake systems in Australia. All coastal lakes are close to sea level (e.g. von der Broch *et al.*, 1977; Warren, 1982a, b; Olliver and Warren, 1988) or, in the case of Lake MacDonnell and Lake MacLeod (Warren, 1983; Logan *et al.*, 1987), below sea level. In most cases they are separated from the sea by a permeable barrier of Miocene limestone to the west and Quaternary sediments to the south, which allows seawater to seep into the lakes, discharging as springs along the shorelines and beneath the lake bed. The presence of a Ghyben-Herzberg lens (Herzberg, 1901; Ghyben, 1888) in the barrier results in the presence of both fresh and brackish water springs along the lake margin, the later arising from mixing between seawater and freshwater. When lake waters reach the halite saturation point they become very dense and are thought to form a descending plume beneath the lake (Warren, 1983), preventing the precipitation of bitterns. Mixing with lower-salinity groundwater along the margins of the lake may result in the development of a convection cell that leads to the brines being returned to the lake (Warren, 1983).

3.1.5 Sedimentation and diagenesis

Sedimentary facies vary markedly from lake to lake but, as described by von der Broch *et al.* (1977), Warren (1982a, b; 1983), Galloway (1986), and Oliver *et al.* (1988), in general the pattern more closely approximates the classic bull's eye distribution of evaporite deposits reported in the literature (e.g. Rosen, 1991). In Australian coastal salt lakes carbonates, which are often aragonitic, are deposited on the lake margins by springs (von der Borch *et al.*, 1977; Warren, 1982b; Warren, 1983; Logan *et al.*,1987). A central core of gypsum is present in most lakes, and may be composed of either loose crystals (gypsarenite) or massive gypsum (selenite). During periods of maximum salinity halite may precipitate towards the centre of the lake. Halite, however, appears to be a permanent deposit in the case of Lake MacDonnell (Warren, 1983), Pink Lake (Galloway, 1986), and Lake MacLeod (Logan *et al.*, 1987), unlike in continental salt lakes, where halite almost never persists.

In such an environment, with diverse mineralogy, active groundwater, and actively-changing conditions, diagenesis is both rapid and complex. Carbonates, whether biogenic in the less-saline parts of the lakes, or direct precipitates, undergo rapid cementation (von der Borch *et al.*, 1977; Warren, 1982b). Mouldic porosity develops in many cases, for example aragonite forms overgrowths on gypsum in Marion Lake (Warren, 1982b) with subsequent dissolution of the gypsum. Halite forms infill within similar mouldic porosity in gypsum in Lake MacDonnell (Warren, 1983).

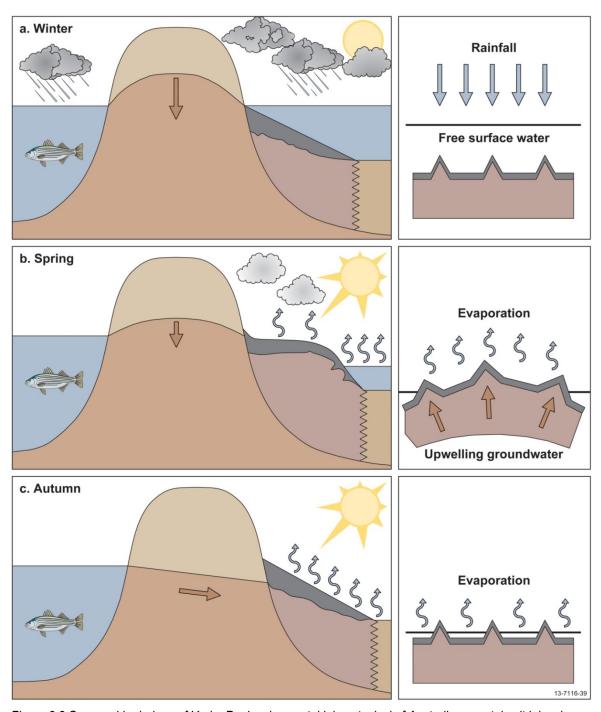


Figure 3.2 Seasonal hydrology of Yorke Peninsula coastal lakes, typical of Australian coastal salt lakes in general (after Warren 1982a).

3.2 Significant Australian coastal salt lakes

Working in a clockwise direction round Australia the major coastal lakes include a number on Yorke and Eyre peninsulas, Lake MacDonnell, Esperance, Hutt and Leeman lagoons, and Lake MacLeod. Only areas with known evaporite deposition (gypsum or halite) that have been described in the scientific literature are discussed herein; there are many small coastal saline lakes with no literature or large weakly evaporitic systems (such as the Coorong, Warren, 1994) that are not described. All share common features with respect to hydrology (Figure 3.2).

3.2.1 Yorke Peninsula

The foot of Yorke Peninsula contains a large number of small coastal salt lakes. These formed when depressions between porous calcarenite dunes of the Bridgewater Formation were flooded by the Holocene transgression (Warren, 1982a), forming a complex coastline of inlets and islands. The sediments consist of skeletal grainstone and seagrass (Posidonia) bank deposits. Subsequent build up of coastal deposits isolated the inlets from the sea and joined the islands to the mainland. The resulting lakes, including Marion Lake, Spider Lake, Snow Lake and Deep Lake, continued to receive saline influx from the sea and evaporation has raised lake water salt concentration to halite saturation. The first sediments in the lake basins were brackish to saline water carbonates, with evolution of the lake system, carbonate deposition became restricted to the lake margins (von der Borch et al., 1977; Warren, 1982b). In Marion Lake the sedimentary succession in the basin centre consists of carbonates overlain by prismatic gypsum, massive selenite, and finally by gypsarenite. In Spider Lake and Snow Lake only gypsarenite formed as the rate of salinity change was too rapid and the bottom brine salinity too unstable for the formation of selenite. The exposed gypsarenite has been deflated by prevailing winds during periods of low-water table into gypsum lunettes along the leeward margins. Surficial gypsum dissolved by rainwater in these lunettes was reprecipitated in the zone of soil moisture as silt-sized gypsum (gypsite) (Warren, 1983). Halite is common in the central parts of the lakes, but does not accumulate. Marion Lake has been extensively mined for gypsum (see below) and the hydrology has been disturbed.

3.2.2 Eyre Peninsula

Oliver *et al.* (1988) summarised the geology of a group of small coastal salt lakes near Streaky Bay on Eyre Peninsula. They described the evolution of these lakes, which include the Purdilla, Toorna, and Calpatanna lakes, as being similar to those on Yorke Peninsula studied by Warren (1982a, b). The lakes occur in interdune corridors in Bridgewater Formation calcarenites. These corridors were flooded by the sea during the peak of the Holocene transgression and then isolated by coastal progradation. Seawater seepage continued through the porous barriers and calcarenite ridges. Aragonitic limestone was deposited first and continued to be deposited around the lake margin, gypsum was precipitated in the core of the lake. Defilation of the lake beds during low water periods has resulted in the formation of downwind gypsum dunes.

3.2.3 Lake MacDonnell

Lake MacDonnell occurs in a northwest-trending trough between calcreted Pleistocene calcarenites of the Bridgewater Formation (Warren, 1983). During the last interglacial highstand at ~125 ka this trough was flooded by the sea. It was again flooded at the peak of the Holocene transgression ~7 ka. By ~6 ka a coastal barrier had cut off the trough from the open sea, establishing the evaporitic lake system. Reflux of seawater through this barrier forms the lake water which is then evaporated. The surface of the lake is currently 0.6-1.2 m below sea level. The lake bed is composed of silt to fine sand-sized gypsum, grading down into sand-sized gypsum crystals. This in turn passes down into massive crystalline gypsum. Mixed with the gypsum are calcite and aragonite grains from ostrocod valves, cyanobacterial activity, and wind-blown skeletal grains. Halite occurs as a 1 m thick layer in the centre of Lake MacDonnell proper.

3.2.4 Esperance

A number of lakes occur behind the coastal barrier along the Western Australian coast near Esperance, ranging from near fresh to hypersaline in chemistry. Very little work has been done on these lake systems. At Esperance itself, Pink Lake (Figure 3.1) is the most saline and one of the largest, getting its name from the common blooms of halophytic microorganisms that colour its waters. Salt production occurs from Pink Lake. Salt inflow into the lake is conservatively estimated to be about 800 tonnes per year from surface stream flow, and approximately 5500 tonnes per year from groundwater flows. An estimated 1.1 million tonnes of salt occurs on the surface of the lake as halite, and is thought typical of the season-to-season surface salt-store. Drilling indicates that up to 18 million tonnes of salt could be contained in the subsurface sediments (Galloway *et al.*, 1986).

3.2.5 Hutt and Leeman lagoons

Two relatively small salt lakes on the west Australian coast are Hutt and Leeman lagoons. Hutt Lagoon occurs near Port Gregory and Leeman Lagoon near Port Leeman, north and south of Geraldton, respectively. Like the coastal salt lakes of South Australia, these lagoons have formed through the isolation of former marine environments, in this case occurring in interdune swales in the Tamala Limestone, the Western Australian equivalent of the Bridgewater Formation (Arakel, 1980; 1981). Initial sediments were of shallow marine carbonates, these pass up into lagoonal carbonate and gypsum. Current gypsum and carbonate deposition is through vadose zone precipitation; halite is also precipitated in ephemeral ponds. The lakes formed at ~6 ka at the peak of the Holocene transgression. Sediment surfaces are still ~4 m below sea level, and seepage occurs through the barrier into the coastal lakes, supplying water and salts.

3.2.6 Lake MacLeod

Lake MacLeod (Caldwell, 1977; Logan, 1987) is Australia's largest and most complex coastal salt lake. It is atypical in that its origin is due to tectonics, rather than through isolation of an embayment through coastal progradation. The Lake MacLeod Basin has an area of ~2000 km² and is up to 4.3 m below sea level. The lake is about 130 km long and is 40 km across at its widest point. Lake MacLeod is separated from the Indian Ocean by the Quobba Barrier. The MacLeod Basin has been flooded several times by the sea entering from the south, across the Texada Sill, which occurred three times in the Quaternary. The following is summarised from Logan (1987), unless otherwise attributed.

The earliest phase of sedimentation in the MacLeod Basin was the Westphal Clay, an inferred Pliocene succession of red claystone and siltstone typically between 20 and 40 m thick. The depositional environment for the Westphal Clay was lacustrine but non-evaporitic. This unit is overlain by the Early Pleistocene Dampier Formation, a thin marine limestone that occurs both in the MacLeod Basin and on the Quobba Barrier. The Dampier Formation averages about 3 m in thickness and U-Th dating indicates that it was deposited between 118 ka – 134 ka. In the MacLeod Basin the Dampier Formation is overlain by the Little Creek Formation, which is up to 18 m thick. The Little Creek Formation is composed of red claystone and siltstone with thin (0.2 – 0.5 m thick) sandstone beds. It is interpreted as a fluvial, deltaic, and lacustine deposit. The Little Creek Formation is capped by a second, thin limestone of marine origin, the Bibra Formation. This unit is composed of marine limestone up to 3 m thick that occurs as a sheet across the basin. Uranium-thorium and calibrated radiocarbon ages of this formation of 42 ka and 43.3 ka, respectively (Logan *et al.*, 1970). Unaltered molluscs have yielded calibrated radiocarbon ages as young as 33.5 ka (calibrated radiocarbon).

These Pleistocene units are overlain by the MacLeod Evaporite Formation, which consists of up to 12 m of halite, gypsum and limestone. The base of the Formation is the Coolan Member, which represents the third Quaternary marine flooding event. The Coolan Member is 0.5 m thick, yields calibrated radiocarbon ages of 8.9 – 6.6 ka, and was deposited during the peak of the Holocene transgression. It is overlain by the Cygnet Carbonate Member, 1 m of laustrine aragonite and gypsum. The Cygnet Carbonate Member has calibrated radiocarbon ages of 6.6–5.8 ka. The main Holocene fill of the Lake MacLeod Basin is taken up by two members, the Texada Halite and the Ibis Gypsite. The Texada Halite is 3–5 m of halite and minor gypsum, dated to 6.1–4.2 ka (calibrated radiocarbon). It is thickest in the southern and eastern parts of the basin. This is the thickest deposit of Holocene halite in Australia and one of the few examples of halite persistence in the Quaternary. The 2-6 m thick Ibis Gypsite is well bedded clastic and massive gypsum, with minor clay and aragonite mud. It is thickest to the north and the west. Deposition of the member began at 6.6 ka (calibrated radiocarbon), with most deposition occurring from 4.2 ka (calibrated radiocarbon) to the present. The Ibis Gypsite is thus coeval with and ultimately overlying the Texada Halite, forming much of the floor of Lake MacLeod. Lastly the Egret Carbonate Member occurs at select locations along the western margin of Lake MacLeod where seepage rates are high enough to support standing water and aragonite mud and minor peat are deposited. The member is up to 1 m thick and covers ~200 km², about 10% of the floor of Lake MacLeod. The Boolathanna Formation, which is up to 8 m thick, is the equivalent to the MacLeod Evaporite Formation across the Texada Sill and comprises the Holocene Bejaling Barrier. It consists of the marginal-marine to marine Arthur Member, composed of skeletal guartz sand with minor carbonate mud and peat, the Pilot Member, a transition between the MacLeod and Boolathanna Formations composed of quartz sand, carbonate mud, gypsite, skeletal sand, and peat. Both these members are overlain by the coastal dune deposits of the Bejaling Sands.

Brine is stored in the unconfined MacLeod Evaporite and is separated from Pleistocene aquifers by an aquitard formed by the Cygnet Carbonate Member. The strong control the member exerts on the shape of the drawdown cones of brine pumping shows that it is an effective aquitard where it is present. Underlying Pleistocene and Cenozoic limestone aquifers are semi-confined.

Lake MacLeod hydrology is driven by seawater seepage into the basin, mostly through the Cenozoic limestones of the Quobba Barrier, and evaporation. Seepage is strongest in the central part of the western margin of the basin, where it forms the Cygnet Marsh with two large pools of standing water, the Cygnet and Ibis Ponds.

3.3 Comparison with overseas coastal salt lakes

Coastal saline basins were reviewed by Babel (2004), who introduced a series of integrated hydrological and sedimentary qualitative models for evaporite deposition in ancient drawdown saline basins. The type example of saline drawdown basins is Lake MacLeod, however, all Australian coastal salt lakes are essentially of this type. Drawdown saline basins (Figure 3.3), characterised by salt lake surfaces at or below sea level and separation from the sea by a permeable barrier, can be distinguished from the older barred evaporite basin model (Woolnough, 1972), where there is an open channel, albeit hydrologically restricted, to the sea. Following is a brief description of some coastal salt lakes elsewhere in the world that can be compared and contrasted with those of Australia. It is not intended to be exhaustive.

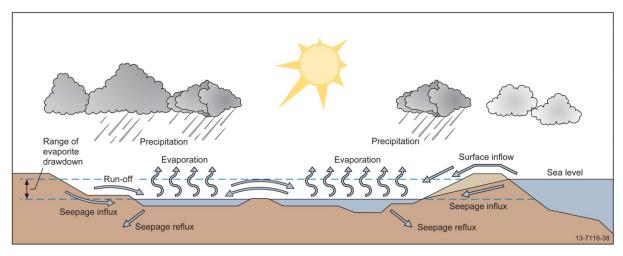


Figure 3.3 Drawdown basin model for coastal evaporite basins, after Babel (2004).

The largest and most significant modern coastal salt lake is Kara Bogaz Gol in Turkmenistan. This varied basin on the eastern shores of the Caspian Sea has an area of about 18,000 km² (Kosarev *et al.*, 2008; Kosarev and Kostianoy, 2005). Caspian Sea water flows into Kara Bogaz Gol and is removed by evaporation, leaving the salts behind. Evaporation is so intense that the surface of Kara Bogaz Gol is several metres lower than that of the Caspian Sea. Hydrology is dynamic through both natural fluctuations and via human intervention. Halite precipitated from 1939 onwards. In addition to halite, sodium sulfate (thenardite), bischofite (MgCl₂·6H₂O), magnesium sulfate (epsomite), and Glauber's salt (mirabalite) are being harvested. Kara Bogaz Gol differs from the Australian coastal salt lakes in that it has a direct open connection to the sea through which seawater enters the basin, unlike its Australian counterparts which are isolated from the sea by permeable barriers. In this respect Kara Bogaz Gol resembles the classic barred basin for the formation of ancient evaporates (c.f. Woolnough, 1972; Stewart, 1979). It also differs in that the salts being deposited include highly evolved bitterns, more characteristic of inland playas of North America than coastal lagoons. This may be due to the waters of the Caspian Sea having different ionic ratios to the world ocean (see Tuzhilkin *et al.*, 2005, for analyses).

Kjerfve *et al.* (1996) described Lagoa de Araruama in Brazil, which is one of a series of coastal salt lakes east of Rio de Janeiro. The Lagoa has a number of sub-basins, some of which are effectively closed and recharged only by ocean seepage and adjacent salt lakes. As a whole, however, Lagoa de Araruama is fed by a narrow channel to the sea, and can be considered a type of barred basin, albeit with some drawdown basin characteristics like those of Australian coastal salt lakes. The Lagoa has been continuously hypersaline for at least 4·5 centuries, but the mean salinity has varied substantially. It has recently decreased due to increased discharge of waste water from surrounding communities. Halite is being harvested from evaporation ponds. Elsewhere waters are hypersaline but still able to support communities of aquatic molluscs. Nearby is Lagoa Mermelha (Vasconcelas and McKenzie, 1997), which precipitates modern dolomite, analogous to coastal lagoons associated with the Coorong (Warren, 1994).

The Ojo de Liebre Lagoon of Baja California and the nearby Guerrero Negro Lagoon (Pierre *et al.*, 1984; Phleger, 1969) are coastal barred basins with extensive modification by the construction of salt pans. Aspects of the geomorphology resemble those of tidal flats (Fryberger *et al.*, 1990). Halite is being deposited in the pans and the parts of the lagoon most distant from the sea, with gypsum and dolomite in the subsurface through brine seepage and reflux.

3.4 Economic aspects

Australian coastal salt lakes have been the sites for extraction of a number of commodities, with halite and gypsum being the only major examples to date. Some potash has been reportedly mined at Lake MacLeod, but no production recorded.

3.4.1 Halite

Salt has been produced at Lake MacDonnell on the Eyre Peninsula since 1920 by solar evaporation of brine that seeps into a shallow lake through porous coastal dunes. Brine is also pumped into the lake from nearby gypsum operations. Production from the 72 ha of crystallising pans is either processed and bagged on site, or railed in bulk to Thevenard (64 km away) for shipment to markets in South East Asia and New Zealand or to the company's Geelong refinery. Average production is 100,000 tonnes per annum (tpa), (Hough, 2008).

Esperance (WA Salt Supply, 2012) has a history of salt production from Pink Lake. However none appears to be occurring at present and there are no listed JORC reserves. Maximum production was 14,000 tpa (Galloway *et al.*, 1986).

The Lake MacLeod salt works have a current production capability of 2.9 million tpa. The current operating area is 764 ha with plans to expand operations to 1000 ha by 2016. The brine is collected from Lake MacLeod by a collection ditch that has been cut to the halite layer. Lake MacLeod brine is pumped at an average rate of 55 cubic metres per minute from the collection ditch to a common collection point before being pumped into the crystallisers. Deposition of halite is stopped by draining the remaining brine when about three quarters of the sodium chloride has been deposited and before other dissolved salts come out of solution in significant quantities. The residual brine called bitterns contains high concentrations of potassium, magnesium and other salts and is a potential source of these minerals (Dampier Salt, 2012).

3.4.2 Gypsum

The cluster of gypsum-bearing lakes at the lower end of Yorke Peninsula near Stenhouse Bay have been historically mined for gypsum, most notably at Marion Lake where 6 Mt of gypsum was extracted between 1905 and 1973. At the time of the most recent assessment (1974), at least 1 Mt of gypsum remained. None, however, has been extracted to date. Two other lakes, Snow Lake and Spider Lake, had resource estimates published in 1979. Snow Lake had an indicated geological reserve of 2.8 Mt of gypsum to an average depth of 0.92 m with and average grades of 76.3%. This is well below that found in Marion Lake, which was >91%. Spider Lake contained indicated geological reserves of 2.4 million tonnes of gypsum to an average depth of 1.18 m and an average grade of 91.6%, comparable to that found in Marion Lake. Extraction from Marion Lake was facilitated by a hard bed, however the bed of both Spider and Snow lake are soft, which was thought to be a hindrance (Olliver and Warren, 1979). No subsequent extraction has been recorded.

Reserves of Holocene gypsarenite in the Streaky Bay area were recalculated by Oliver *et al.* (1988) for two small lakes and adjacent areas. In Lake Purdilla, 44 Mt of proven gypsum reserves of a grade of >88.4% gypsum or a probable resource of 48 Mt at a grade of >87.8%, was defined for parts of the deposit having a thickness of greater than 1 m. At Lake Tooma, 6 Mt of proven reserves at >85.9% gypsum, included within 48 Mt of probable resources at 85.9% gypsum were defined based upon a

minimum gypsum thickness of 1 m. Marginal dunes to the two lakes contained a further 0.5 Mt and 0.17 Mt of possible gypsum reserves at Lakes Purdilla and Tooma, respectively, although the grade was not specified. None of these deposits had been mined at the time of writing.

The Lake MacDonnell mine, owned by Gypsum Resources Ltd. (MiningLink, 2013), is Australia's largest gypsum mine, containing a resource of 500 Mt. Operations started at the site in 1919, with 1.34 Mt produced in 2002. The deposit has been operated by Gypsum Resources since 1984 when CSR and Boral combined their separate operations. The deposit comprises 1 m of gypsarenite at 93% gypsum, overlying 5 m of selenite grading between 94% and 96% gypsum. Reserves at Lake MacDonnell are between 250 Mt and 300 Mt of gypsum. Unconsolidated (seed) gypsum occurs up to 0.5 m above the water table, including in dunes, with crystalline (rock) gypsum is up to 6 m below the water table.

In 1997, Dampier Salt Ltd. commissioned a gypsum project next to the Lake MacLeod solar salt fields. The product was exported to the wall board and cement industries in Japan and other parts of Asia, Africa and Australia. However gypsum is no longer mined at Lake MacLeod.

3.4.3 Potash

In 1973, Texada Mines Pty Ltd. was reportedly working towards becoming Australia's first local potash producer in the form of langbeinite $(K_2Mg_2(SO_4)_3)$ at Lake MacLeod. The planned capacity of the plant was variously reported to be from 80,000 tpa to 200,000 tpa (Wells and Richter-Bernburg, 1973). There is, however, no record of production of potash from the proposed operation and no JORC-compliant reserve was ever released (Australian Mines Atlas, 2012).

3.4.4 Biological products

Hutt Lagoon (Handford, 1991) is the site of both carotene production and the aquaculture of *Artemia* brine shrimp. Both take advantage of the natural hypersaline water of the coastal salt lake to sustain growths of the producing organisms. Carotene is produced by the micro-algae *Dunaliella salina*. This organism can grow at very high salt concentrations and temperatures where few other organisms can survive. Large shallow ponds of several hundred hectares in area and 30–60 cm deep are used to grow the algae. Dried *Dunaliella* powder is also sold as a feed additive for aquaculture to pigment crustaceans (e.g.prawns, BEAM, 2012) to improve colour. "Several thousand" tpa of *Artemia* were produced in 2010 (Baird Maritime, 2010) and used as a feed stock in the aquaculture of fish and prawns. There is considerable potential for expanding the conjunctive production of these products from other artificial and natural saline systems in Australia.

4 Salt Lake Mineral Systems

E.N. Bastrakov, S. Jaireth and T.P. Mernagh

4.1 Introduction to mineral systems

The petroleum industry adopted the concept of the "Petroleum System" as 'a pod of mature source rocks and all its generated oil and gas accumulations, and includes all the geological elements and processes necessary for oil and gas to exist' (Magoon and Dow, 1994). This concept was later applied to ore deposits by (Wyborn *et al.*, 1994) and expanded upon by Walshe *et al.* (2005), Barnicoat (2009), Skirrow *et al.* (2009) and Huston *et al.* (2012).

The same general model can also be applied to salt lakes which form by a series of hydrological processes that result in the enrichment of chloride and other elements within a catchment. In some respects, salt lakes are more complex than petroleum systems, as they involve meteoric precipitation, weathering, surface water, groundwater, hydrothermal fluids, precipitation-dissolution reactions, evaporation, and biotic activity. The composition of salt lakes is also affected by the climate and lithology of source rocks and host sediments, which control the initial chemistry of aqueous fluids flowing into the catchments. Brine evolution along different flowpaths is controlled by the molar ratio of solutes, which eventually produces diagnostic mineral assemblages. Preservation of these saline fluids and minerals depends on the amount of closure in the system. The ratio of subsurface water outflow to inflow, or "leakage ratio", can have a significant effect on evaporate precipitation and solute fractionation (Sanford and Wood, 1991; Rosen, 1994). Other processes such as deflation may also remove some mineral components, especially sodium carbonates, which are usually porous and easily eroded. Despite the above complexities, we consider that all these factors can be incorporated into the following major components of a salt lake mineral system:

- Geological setting
- · Sources of fluids and elements
- Drivers/migration pathways
- · Brine evolution/enrichment mechanisms
- Preservation

Salt lakes in endorheic (closed drainage) basins typically contain the potential for extraction of multiple commodities including potash, lithium, boron, and uranium. The purpose of the current chapter is to briefly review the major components of the salt lake mineral system outlined above and then derive sets of critical features that can be used to assess the potential of Australian salt lakes for lithium, boron, potassium and calcrete-hosted uranium deposits.

4.2 Features of salt lakes with economic potential for potash, lithium and boron

In this section we discuss in detail five categories of salt-lake mineral systems with economic potential for potassium, lithium, and boron. Systems economic with respect to uranium will be discussed separately (Section 4.3) due to the fundamental differences between the chemistry of uranium compared to potassium, lithium, and boron.

4.2.1 Geological setting

Salt lakes are found in all the continents (Figure 4.1). The processes that lead to salt build-up may occur on the flanks of continental uplifts, within extensional basins, in endorheic basins, and in glaciated terrains. The majority of salt lakes are found in the semi-arid to arid regions of the world as evaporation in excess of precipitation plays a critical role in the development of salt lakes.

Three basic conditions are needed to form salt lakes (Eugester and Hardie, 1978). First, outflow must be absent or severely restricted to ensure hydrological closure. Second, evaporation must exceed inflow, and thirdly, inflow must be sufficient to form a body of water (that may be ephemeral) at or very close to the surface. Therefore, favourable locations for the formation of salt lakes are arid basins in the rain-shadows of mountain ranges or highland areas, which provide the catchment for precipitation. In areas of lower relief, shallow basins may act as the focus of local discharge and evaporation from regionally extensive groundwater systems. Important features of the world's major lithium-bearing salt lakes are given in Table 4.1.

Some of the world's largest salt lakes are found at elevations exceeding 1000 m, such as Salar de Uyuni (Bolivia), Salar de Atacama (Chile), Qinghai Lake (Tibet), and the Great Salt Lake (USA). This reflects the tendency for these systems to form in tectonically active regions. Even some large saline lakes nearer to sea level (e.g. the Caspian and Dead seas) are associated with active tectonism. The occurrence of lithium and boron in salt lakes is also correlated with recent or concurrent volcanic activity and/or areas that have a higher than average geothermal gradient. Borate deposits, in particular, appear to be associated with long-lasting, high-boron geothermal springs with a long-lasting volcanic period or a high underlying magmatic temperature (Garrett, 1998).

By their nature, lakes are not permanent features in earth's history; they form, gradually fill up and finally disappear. In Australia, the salt lakes occupy features of the landscape that have changed little tectonically and have not been transgressed by seawater since at least the Paleogene (De Deckker, 1983). The playa lakes in Western Australia have been the sites of periodic lacustrine deposition since the mid-Miocene (Van de Graaff *et al.*, 1977). Lake Torrens and Lake Frome have existed since the Eocene (Callen, 1977; Johns, 1968). In more tectonically active parts of the world the lakes have formed in more recent times. In the Mojave Desert, California, salt lakes such as the Bristol Dry Lake may have existed for 4 Ma (Rosen, 1991). However, in the Clayton Valley, Nevada, lithium-enriched, tuffaceous, lacustrine sediments were deposited in the Late Miocene or Pliocene (Munk *et al.*, 2011) and the oldest lacustrine sediments at Searles Lake, California are of Pleistocene age (Smith, 2009). The precursors to the giant salars in Bolivia and Chile have estimated ages of ~73 ka ~ ~30 ka from carbon isotopic dating (Fornari *et al.*, 2001). In comparison the borate deposits (Helvaci and Alonso, 2000) range in age from Early Miocene (Turkey) to Late Miocene (Argentina). Therefore, most lake systems appear to be of Paleogene age or younger while the surrounding lithologies can be of any age but most economic mineral systems are in Mesozoic or younger units.

Table 4.1 Important features of lithium-bearing salt lakes around the world.

Important Features	Clayton Valley (Nevada, USA)	Searles Lake (California, USA)	Chile	Bolivia	Argentina	China (Qaidam Basin)
Resources (Mt)	~0.12 to 0.38	0.032	~4.4 to 6.3	~ 5 to 10.2	0.8 to 4.6	3.3
Type examples salt lake containing lithium resources	Clayton Valley playa	Searles Lake	Salar de Atacama	Salar de Uyuni	Salar de Hombre Muerto	Xi Taijnar, Dong Taijnar, Lake Chaka
Grade Li (mg/kg)	100 to 800	~50 to 80	82 to 1570 (130 to 1570 for Atacama)	210 to 1640 (320 to 700 for Uyuni)	97 to 1020 (914 for Hombre Muerto)	20 to 310; Lake Chaka: 660
Lake size (km²)	100	100	0.55 to 3000 (3000 for Salar de Atacama)	150 to 480 (9000 to 10500 for Uyuni)	565	East Taijnar (116); West Taijnar (82); Zubuye Caka (up to 600); Da Qaidam (310)
Drainage basin size (km²)	1300	~ 25000	280 to 18100 (18100 for Salar de Atacama)	220 to 2240	~ 2000	Qaidam Basin (100,000); catchment area of the basin (250,000)
Setting	Intermontane basin; regions with elevated geothermal gradient (Walker Lane province with elevated geothermal gradient of (100°C/km to 800°C/km)	Intermontane basin; region with caldera and thermal springs	Intermontane basin filled with continental clastic and evaporitic sediments. Rhyolitic ignimbrite and andesitic stratavolcanoes along the eastern margin of the basin.	Intermontane basin rimmed with regions containing Cenozoic andesitic to rhyolitic volcanics	Intermontane basin filled with continental clastic and evaporitic sediments. Rhyolitic ignimbrite and andesitic stratavolcanoes along the eastern margin of the basin.	Intermontane basin with felsic rocks in the areas feeding the lake system.
Climate: Precipitation (mm/y); Evaporation (mm/y)	Arid: 99 to 127; 760 to 1370	Arid: ~100;	Arid: 100 to 379; 1000 to 1800	Arid: 100 to 400; 1000 to 1500	Arid: 60 to 80; 1500	Arid: 25 to 50; 3000 to 3200
Thermal springs	Present	Present (Long Valley caldera with thermal springs)	Present; Hot springs in the lake and in the Western Cordillera (at least 10 to 25°C hotter than surface water). El Tatio geyser field (47 mg/L Li); Active volcano (Cerro Miniques) to SE of the lake	Present. Several thermal springs feed Rio Grande rive and the salar and contain between 4 to 30 mg/L Li and B)		Present (water in the Yangbajing well reaches temperature of 159°C)
Total salinity (mg/L)	~200,000	~10,000 to 12,000	113,000 to 400,000	240,000 to 370,000	260,000 to 340,000	68,520 to 436,000
Brine type	Na-Cl	Sulfate-rich and calcium-rich	Sulfate-rich and calcium-rich	Alkaline, sulfate-rich, calcium-rich;	Sulfate-rich, calcium-rich	Na-Cl; Mg-Cl (locally)
рН	7.1 to 7.3	9.2 to 9.5	6 to 10.4	6.3 to 7.2	6.5 to 7.2	Neutral to slightly alkaline; Dabson Lake acidic (pH 5.3)
Type of salt lake	Not zoned; silty halite crust	Not zoned; silty halite crust	Zoned: interior halite zone surrounded by sulfate zone	Zoned: halite crust with minor gypsum in muddy margins	Zoned	Zoned (?)
Thickness and zoning of salt layers	From top to bottom: mud with halite; Halite; gypsum-rich beds separate with mud layers; total thickness of salt-rich beds of 50 to 80 m	Halite crust (up to 8m); underlain by salt and mud to a depth of ~270 m (Li brine extracted from upper and lower salt layers)	Thickness of salt layer varies (average ~800 m). Depth controlled by faulting in the salt-lake basin	Average thickness of salar is 121 m (11 halite beds with average thickness of 3 m to 6 m) interlayered with mud and sand	Salt (halite)-clay surface underlain by halite, sulfate and/or borate layers (> 50 m thick in Salar de Hombre Muerto	Lake Chaka: Halite crust. Thickness of halite rich layer locally up to ~600 m underlain by gypsum-rich layer (~100 m thick)
Age and duration	At a 35 m depth salt bearing sediment age is 26.9 ka ^a	Halite at the base is 6 ka old; halite at the surface 3.5 ka old. The succession of dry and wet periods continued for ~ 150 ka.	At 200 m depth salt age ~325 ka and at 5 m depth age ~5 ka	Age of the top layer ~3.5 ka. Lake part of a large lake formed between 22 ka to 44 ka)	For Salar de Hombre Muerto: Bottom of the layer dated to about 82 ka; at the depth of 6.4 m the age about 8 ka. Between 64 and 82 ka it was saline lake and weather was wet; between 8-26 ka weather was relatively dry	Lake Chaka: detrital siliciclastics began depositing at ~17 ka; gypsum + halite at ~12 ka

Important Features	Clayton Valley (Nevada, USA)	Searles Lake (California, USA)	Chile	Bolivia	Argentina	China (Qaidam Basin)
Source of Lithium	Intermediate to felsic tuffs and flows with volcanic glass (Esmeralda Formation); Cenozoic Li-bearing pegmatite; Li-bearing clays and lake sediments; Thermal springs.	Thermal springs; Tuffs in the Christmas Canyon Formation	Ignimbrites (ash flow, tuff) within and at the edges of salt lake (tuffs contain up to 89 mg/kg Li); thermal springs (El Tatio geyser contains 28 to 46 mg/L Li)		Three sources: Paleozoic basement (especially for B); Neogene-Pleistocene ignimbrites; and Cenozoic andesite; Mesozoic limestones (for B)	Felsic rocks at the margins of the basin; thermal springs (Yangbajin spring contains up to 25 mg/L Li)
Major references	Garrett (2004); Davis et al. (1986); Munk and Chamberlain (2011)	Garrett (2004); Smith (1976)	Garrett (2004); Jordan <i>et al.</i> (2002); Ericksen (1987); Risacher <i>et al.</i> (2003); Ide and Kunasz (1989); Kesler <i>et al.</i> (2012)	Garrett (2004); Risacher and Fritz (1991); Ericksen (1977); Schmidt (2010); Kesler <i>et al.</i> (2012)	Garrett (2004); Lowenstein <i>et al.</i> (1998); Helvaci and Alonso (2000); Alonso (1999); Kaesmann <i>et al.</i> (2004); Kesler <i>et al.</i> (2012)	Kesler et al. (2012); Chen and Bowler (1986b); Tan et al. (2012); Guo et al. (2012)

^a ka = 1000 years before present.

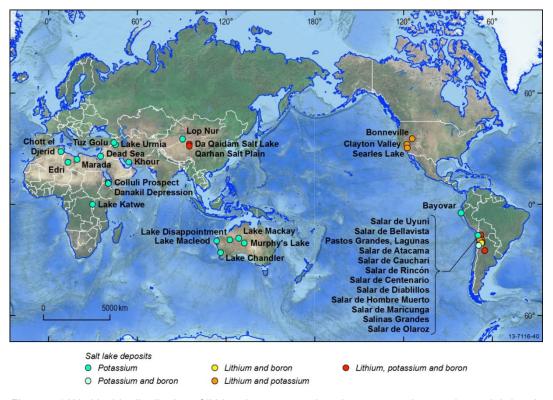


Figure 4.1 World-wide distribution of lithium-boron-potassium, boron-potassium, and potash brine deposits associated with salt lakes. Modified and amended from Orris (2011). The deposits are characterised based on the presence of three commodities (lithium±boron±potassium), including the major element and co- and by-products.

4.2.2 Sources of fluids and elements

4.2.2.1 Fluids

The sources of fluids are mainly direct precipitation, associated surface flow, and/or groundwater. Groundwater may be derived from a local or regional meteoric system, interstitial water from sediments, or deep basinal or hydrothermal fluids. Hydrothermal discharge (e.g. from geothermal springs), though often small in volume can be significant in terms of solute contribution.

4.2.2.2 Elements

As in all natural waters, the composition of salt lakes is dominated by Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{-2-} , dissolved inorganic carbon as $HCO_3^{-2-} + CO_3^{-2-}$ and rarely SiO_2 . This results in the three major salt lake systems discussed in Section 4.3.4. However, of more importance to the present study is the source of the strategic elements lithium, boron and potassium.

Lithium can be sourced from volcanic glasses and felsic rocks, particularly andesitic to rhyolitic tuffs and ash flows. Another source is lithium-bearing clays (e.g. hectorite) formed from the weathering of feldspars and micas.

Boron can be mobilised from different sources, depending on the drainage system and host lithologies. In South America demonstrated ($\delta^{11}B$) sources include the Paleozoic basement and Cenozoic volcanic and sedimentary rocks (including Neogene-Pleistocene ignimbrites). Borate deposits are also associated with long-lasting, geothermal springs associated with a prolonged volcanic period or a high underlying geothermal gradient (Garrett, 1998).

Sources of potassium are most commonly acidic to intermediate volcanic rocks, but also include older evaporites and continental sedimentary rocks (Alonso and Risacher, 1996; Risacher and Fritz, 2009). Sources of potassium in these rocks are weathered minerals, such as orthoclase, microcline, biotite, leucite, and nepheline. Studies have found a positive correlation between potassium, lithium, and boron in brines (Carmona *et al.*, 2000; Orris, 1997; Zheng, 1984), which is probably indicative of the fact that many salt lakes occur in volcaniclastic terranes that typically are associated with convergent plate boundaries (Orris, 1997) (Figure 4.2). This correlation implies that during evaporation these elements largely behave in a similar way. Salt lakes with potassium can have lithium and/or boron only if leachable lithium and boron are available in the system.

Availability of lithium for acquisition by groundwaters and hydrothermal solutions is controlled by three factors:

- Concentration of lithium in the source rock and distribution of lithium between the host phases (i.e., volcanic glass, primary and secondary minerals)
- Landscape evolution in the last 100 to 200 thousand years (because most economic salt lake systems are formed within this time span; Table 4.1)
- Hydrogeological system connecting leachable source with the lake system. In the Yilgarn
 Craton this connection is through systems of palaeochannels which may or may not contain
 felsic source rocks. Hence although absolute concentration of lithium in this rock is as high as
 100 mg/kg and more, only a fraction of it is available to the salt lake system.

The liberation of lithium and boron or chloride from protolithic rocks to aqueous solutions, and possible sequestration by an alteration or weathering mineral, are dependent on a number of factors including the composition of circulating fluids, temperature, permeability and alteration intensity.

Reyes and Trompetter (2012) provided an in-depth study of lithium and boron partitioning during the hydrothermal alteration of volcanic rocks and greywackes of the Taupo Volcanic Zone (TVZ). For fresh volcanic rocks, concentration of lithium and boron increases from basalts to andesites to rhyolites (e.g., for the TVZ from 10 to 19 to 38 mg/kg foir lithium; from 7 to 18 to 22 mg/kg, for boron; Reyes and Trompetter, 2012). Boron behaves as an incompatible element both in andesite and rhyolite. In contrast, lithium occurs mostly in glass in andesite, but is preferentially partitioned into phenocrystic phases such as hornblende and biotite in rhyolites; all rhyolitic minerals have higher lithium contents than the glassy mesostasis.

In the process of hydrothermal alteration (important for the source of boron), the proportion of boron lost from the protolith during hydrothermal alteration varies with lithology: highest in rhyolite and lowest in basalt. In andesite and rhyolite containing hydrothermal mineral assemblages formed at temperatures below 200°C±20°C, Reyes and Trompetter (2012) documented a lithium decrease irrespective of the rock type, though high temperature hydrothermal assemblages might be enriched in lithium.

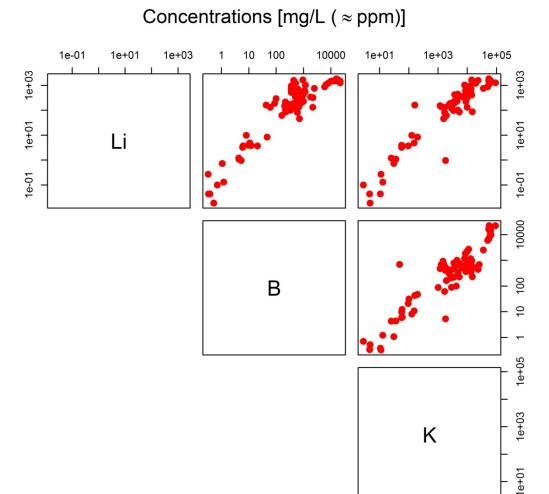


Figure 4.2 Correlation between lithium (Li), boron (B), and potassium (K) for productive lithium-boron-potassium salt lake mineral systems from South America and China. Data from Ericksen (1987), Garrett (1992; 1998), and Risacher and Fritz (2009).

1e+01

1e+03

1e+05

Because the glassy mesostasis of a volcanic rock is more readily altered by hydrothermal fluids, boron, which is more incompatible than lithium, would be expected to be more readily extracted from andesite and rhyolite; and lithium from andesite would be more readily released into the aqueous solutions than from rhyolite. The extracted proportion of lithium for andesite and rhyolite is generally lower than for boron. Experiments by Ellis and Mahon (1964, 1967) suggested that, at a given temperature, lithium is extracted from andesite ~3 times faster than from rhyolite (Reyes and Trompetter, 2012).

Regardless of the composition of the protolith and reacting aqueous solutions, the fluid mobility of lithium during hydrothermal alteration is substantially decreased at temperatures >200 °C with the widespread formation of quartz±chlorite±illite that change lower temperature smectite- and crisobalite-bearing mineral assemblages (Reyes and Trompetter, 2012). Common hydrothermal chlorite, quartz, and illite may contain appreciable concentrations of lithium (3.6 to 210 mg/kg; Reyes and Trompetter,

2012) and control lithium distribution in the process of water–rock interaction at higher temperatures and greater depth. To a limited extent, an uptake of boron by smectite, illite-smectite and chlorite at higher temperatures also restricts the fluid mobility of boron. However, the boron concentrations incorporated in the hydrothermal minerals are rather low (e.g., 1.8 mg/kg to 35 mg/kg; Reyes and Trompetter, 2012), limiting a temperature effect for the latter.

Availability of lithium, boron, and potassium in productive salt-lake systems results in readily detectable elevated concentrations of these elements within the whole hydrodynamic system feeding the salt lake(s). Figures 4.3 to 4.5 illustrate the degrees of incipient enrichment of waters in these elements in economic salt-lake systems, as well as their further accumulation during brine evolution (from dilute inflows to salt-saturated brines).

4.2.3 Drivers/migration pathways

4.2.3.1 Drivers

Climate plays a critical role in the water balance of salt lakes. The amount of inflow to a closed basin, including precipitation, must be closely balanced by evaporative loss in the basin in order to produce elevated salinities.

Ambient temperature is also an important climatic control on lake systems, not only with respect to effects on local biota, but also on changes in mineral thermodynamics that may produce different mineralogies in concentrated sulfate-carbonate waters (Last, 1999). The sensitivity of closed basins salt lake systems to climate makes them important indicators of climate change and important sedimentary archives of past climates.

Most of the surface and groundwater is dominantly controlled by gravity-driven fluid flow. Gradients in potential energy (hydraulic head) drive fluid flow from regions of higher hydraulic head to regions of lower hydraulic head. Capillary forces may also affect fluid flow in the capillary fringe (a saturated zone above the water table).

Geothermal gradients may lead to the discharge of hydrothermal fluids into the system. These higher temperature fluids not only add thermal energy to the system but potentially carry higher concentrations of solutes than other fluids.

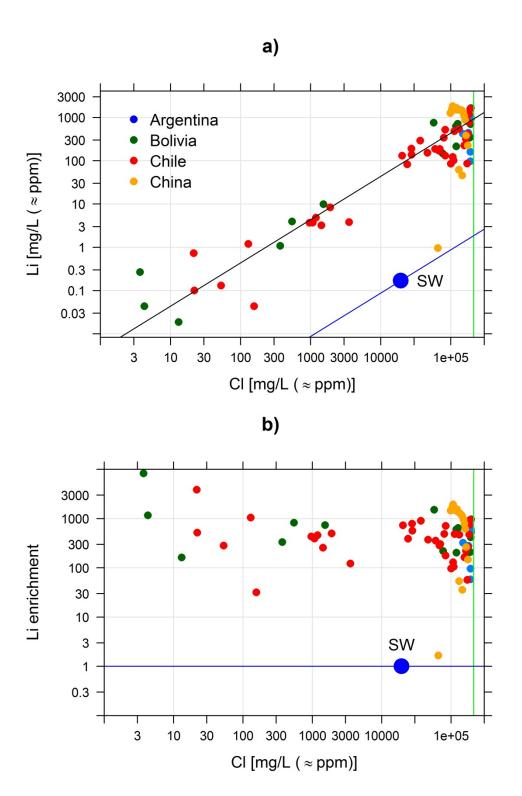


Figure 4.3 Lithium concentrations (a) and enrichment factors (b) as function of chloride for productive lithium-boron-potassium salt-lake mineral systems. The large blue dot and the blue line represent composition and evaporation/dilution trends for average sea water, respectively. The black line outlines 500 times enrichment in lithium compared to evolved seawater. The green vertical line represents the approximate chloride concentration at which water becomes saturated with halite (NaCl). Data from Ericksen (1987), Garrett (1992; 1998), and Risacher and Fritz (2009).

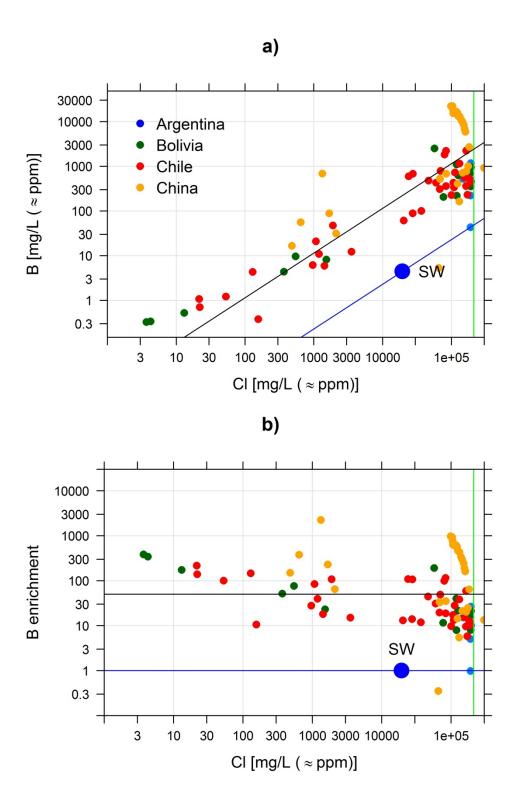


Figure 4.4 Boron concentrations (a) and enrichment factors (b) as function of chloride for productive lithium-boron-potassium salt-lake mineral systems. The large blue dot and the blue line represent composition and evaporation/dilution trend for average sea water, respectively. The black line outlines 50 times enrichment in boron compared to evolved seawater. The green vertical line represents an approximate chloride concentration at which water becomes saturated with halite (NaCl). Data from Ericksen (1987), Garrett (1992; 1998), and Risacher and Fritz (2009).

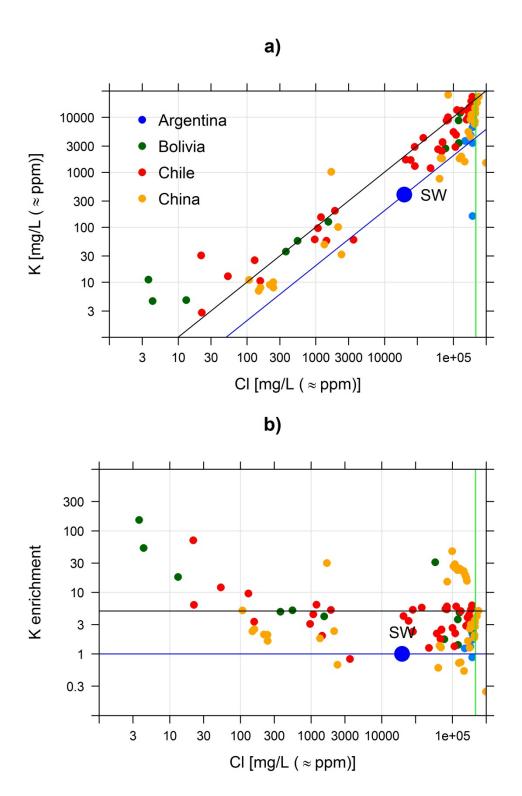


Figure 4.5 Potassium concentrations (a) and enrichment factors (b) as function of chloride for productive lithium-boron-potassium salt-lake mineral systems. The large blue dot and the blue line represent composition and evaporation/dilution trends for average sea water, respectively. The black line outlines 5 times enrichment in potassium compared to evolved seawater. The green vertical line represents an approximate chloride concentration at which water becomes saturated with halite (NaCl). Data from Ericksen (1987), Garrett (1992; 1998), and Risacher and Fritz (2009).

In density-stratified lakes, small-scale turbulence is essential for energy and mass transfer. Although the energy is brought into the system at much larger scales, it is the small-scale turbulent motion that brings different density layers in close enough contact for mixing by viscosity and diffusivity to occur (Imboden and Wuest, 1995). Waves play a crucial role in energy storage and also act as the link between the input of energy and the production of turbulence. Waves are activated by the wind and lead to horizontal currents and, therefore, to internal mixing. The subsequent small-scale (eddy-type) turbulent diffusion also affects the exchange through the sediment-water interface.

4.2.3.2 Migration pathways

Migration pathways include surface flow, which results mainly from direct precipitation, and groundwater migration in aquifers and fault zones. Groundwater may be derived from the local meteoric water system, interstitial water from sediments, or deep basinal or hydrothermal fluids (Rosen, 1994).

The presence of deep aquifers and/or faults may also lead to leakage from some salt lakes. The ratio of subsurface water outflow to inflow, or "leakage ratio" can have a substantial effect on evaporate precipitation and solute fractionation by delaying salinity development (Wood and Sanford, 1990; Wood and Sanford, 1995).

The composition of migrating fluids in endorheic basins is dominated by the reaction of natural waters with the lithologies of the surrounding drainage basin. However, although lithological composition is very important, the hydraulic conductivity, aquifer residence times, dissolution rates, and leakages in the salt lake systems will all affect the hydrochemistry of the salt lakes.

4.2.4 Brine evolution/enrichment mechanisms

The evolution of salt lake waters begins with the acquisition of solutes in dilute inflow, primarily through chemical weathering reactions and atmospheric input. The composition of these waters is dictated by the major lithologies of the endorheic basin and their relative distribution; these lithologies control which constituents are concentrated in the brines and the relative amounts of each constituent. On the lake side of the Ghyben-Herzberg interface water-rock reactions are superseded by other processes. Evaporative concentration is normally the major process leading up to mineral precipitation but other factors such as fluid mixing, basin leakage, degassing (particularly of CO₂) and temperature changes may also affect brine evolution.

The outcome of these processes is the generation of three main groups of brines (e.g., Risacher *et al.*, 2003): alkaline (Na/HCO $_3$ – CO $_3$ – CI), sulfate-rich (Na/SO $_4$ – CI) and calcium-rich (Na – Ca/CI) brines. For the sake of brevity, waters where SO $_4$ >Ca are referred to as sulfate-rich and those where Ca>SO $_4$ are referred to as calcium-rich. These pathways are summarised in the flowchart diagram shown in Figure 4.6.

As indicated in Figure 4.6 calcite is usually the first mineral to precipitate. This also illustrates a major geochemical factor in brine evolution known as the "chemical divide" (Eugster and Hardie, 1978). When a fluid evaporates, the concentration of its dissolved components increases and a sequence of minerals precipitate in the order of their increasing solubility. Typically, only a few minerals actually control the evaporative pathways. The first mineral to precipitate is usually calcite (Figure 4.6). This is the first chemical divide and it leads to two evolutionary pathways: the alkaline path where CO_3^{2-} increases and CO_3^{2-} decreases and the neutral path where CO_3^{2-} increases and CO_3^{2-} decreases. When

a fluid follows the neutral pathway, the concentration of Ca^{2+} increases and the next critical mineral to precipitate is gypsum (Figure 4.6). This new chemical divide then defines two more evolutionary pathways: a calcium-rich/sulfate-poor path and a sulfate-rich/calcium poor path. Eventually, two main brine types are produced: sulfate-rich (Na–SO₄–CI) and calcium-rich (Na–Ca–CI) brines.

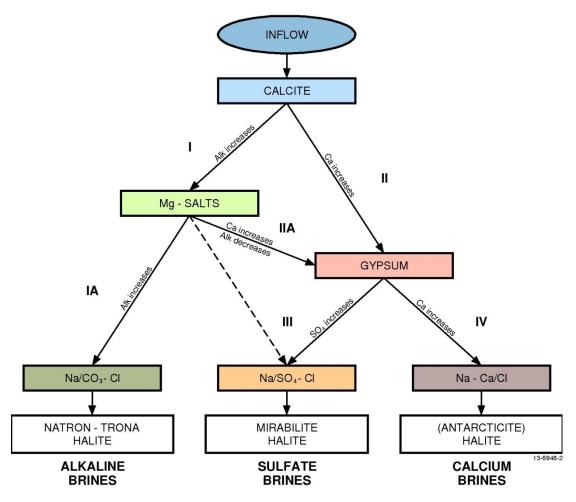


Figure 4.6 Flowchart diagram for evaporative concentration of dilute waters (from (Risacher et al., 2003). path numbers are those of (Hardie and Eugster, 1970): alkaline (I-IA); sulfate-alkaline (I-IIA-III); sulfate-neutral (II-III) and calcic (II-IV). The dashed line shows the rarely observed path from the Mg divide to the sulfate-rich brine, bypassing the gypsum divide.

In the alkaline pathway (Figure 4.6), the increase of pH favours the precipitation of Mg-salts (silicates or carbonates). The decrease of carbonates may be important enough to reverse the alkaline path to the neutral path. Thus, the magnesium salts control another chemical divide with one pathway producing alkaline (Na–CO $_3$ –CI), while the other produces sulfate-rich (Na–SO $_4$ –CI) brines. So in summary, there are four possible evaporative pathways which lead to three major brine compositions (Figure 4.6): alkaline brines, SO $_4$ -rich brines, and Ca-rich brines.

Probably the simplest way of applying the "chemical divide" concept to the prediction of evolution pathways is through the use of the "Spencer Triangle" (Spencer, 2000) (Figure 4.7). This plot uses the fact that in a triangular diagram of the system $Ca - SO_4 - Carbonate$ alkalinity (HCO $_3 + CO_3$), a line connecting a point representing a particular solute distribution and precipitate composition will define, in

terms of a three-component system, the direction of chemical evolution of the fluid. The join between calcite and SO_4 apex represents the "calcite divide", and the join between calcite and gypsum represents the "gypsum divide". Waters will move away from these divides as the respective minerals precipitate. Sodium and chloride are considered ubiquitous. Each field is labelled according to the principal solutes left in the final fluid.

The above discussion indicates that there does not appear to be a close correlation between the three major salt lake systems and the occurrence of potash, lithium and boron. From a geochemical viewpoint, closed basin lakes and their surface or groundwater inflow are dominated by the reaction of natural waters with the lithologies of the surrounding drainage basin. Hydrological setting and processes, however, affect secondary modifications, including simple mixing of two or more chemically different inflow waters, and pore-water reactions and residence times. Seasonal variations, meromictic stratification, and multiple inflow sources from variable lithologies all affect the mixing processes within the salt lake environment.

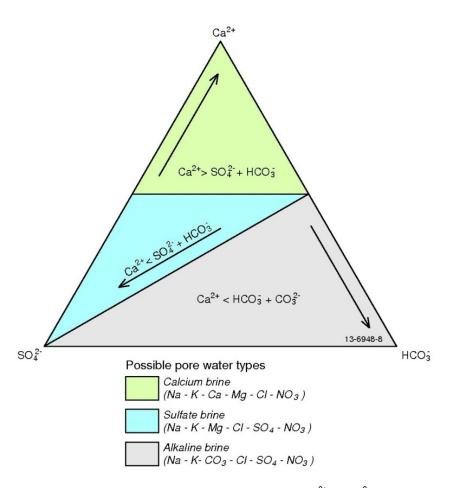


Figure 4.7 The "Spencer Triangle" ternary phase diagram in the system $Ca^{2+} - SO_4^{2-} - HCO_3^{-}$ (Spencer, 2000).

Figure 4.8 shows the distribution of lithium in salt lakes from South America plotted in a Spencer Triangle (data from Risacher *et al.*, 2003). Although lithium occurs in all three major brine systems, Figure 4.8(b) indicates that higher concentrations of lithium occur in alkaline lakes.

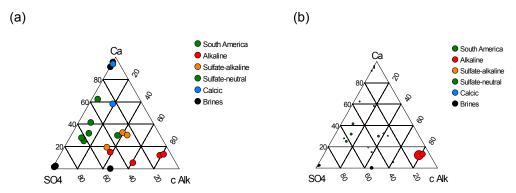


Figure 4.8 A "Spencer Triangle" plot of Li/Cl concentration infor brines from salt lakes in South America. (a) Plot showing brine compositions the distribution of Li/Cl according to lake type, and (b) a similar plot where the size of the circle is proportional to the concentration of Li/Cl ratio in brines.

Depending on the resulting composition of the salt lake, potassium, lithium and boron may be present as carbonate, bicarbonate, sulfate, chloride and/or other complexes. The incipient enrichment of the inflow waters in lithium and boron is paramount for economic lithium—boron systems. Economic lithium systems are characterised by \sim 100- to 1000-fold enrichment in lithium content relative to the values that can be expected from concentrated or diluted seawater with the same chloride concentrations; and by \sim 10- to 100-fold enrichment in boron, respectively. An important factor in lithium-enrichment is repeated cycles of evaporation of freshly introduced waters in the lake system. The lithium and boron enrichment reaches its maximum level at halite-saturation level. The total salinity of economic lakes is > 100,000 mg/L TDS.

4.2.5 Preservation

As mentioned previously, climate plays a critical role in the preservation of salt lakes. Either an excess or insufficiency in precipitation compared to evaporation will prompt a hydrological response that will either dilute the contained brines or cause the lake to dry up.

Similarly, groundwater discharge is important in many arid regions. It is only in the discharge phase that the chemical evolution of the groundwater can effectively proceed (Bowler, 1986a). Australian data (Bowler, 1986a) suggest that the evolution of shallow interstitial waters, eventually extending to affect local groundwaters, is a critical factor in controlling many features of basins subject to hydrological change. Bowler (1986a) suggests that for the preservation of evaporates, taking halite as an example, the prerequisite salinity of the underlying interstitial waters needs to be in excess of 250,000 mg/L.

Deflation may also remove some mineral components of salt lakes, especially sodium carbonates, which are usually porous and easily eroded (Bowler, 1986a).

4.2.6 Summary

The evolution of any salt lake is associated with a few fundamental lithologies, their mode of reaction with the dilute inflow waters, and the resulting relation of major cations and anions (Figure 4.9). In most cases evaporative concentration is the main mechanism for brine evolution and mineral precipitation. The result of evaporative concentration is the generation of three main groups of brines: alkaline (Na/HCO $_3$ – CO $_3$ – CI), sulfate-rich (Na/SO $_4$ – CI) and calcium-rich (Na – Ca/CI) brines.

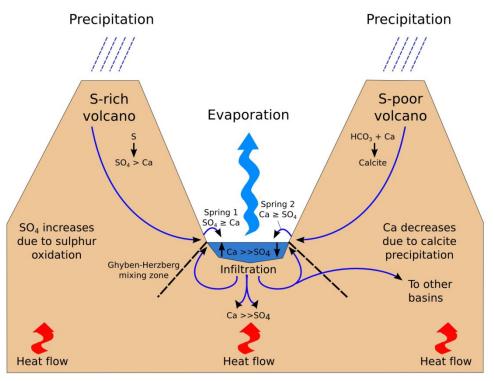


Figure 4.9 A cartoon outlining the mineral system features of the economic (lithium, boron, potassium, uranium) salt-lake based on Andean mineral systems (Risacher et al., 2003).

As a consequence of brine evolution, potassium, lithium and boron enrichment in salt lakes mainly results from two processes: (1) enrichment in potassium, lithium, and boron prior to the evaporation process due to water–rock interaction (i.e. leaching), and (2) evaporative concentration of the inflow water. In some cases lithium and/or boron enrichment is also related to long-lasting, geothermal springs associated with prolonged volcanic activity or a high underlying geothermal gradient.

Based on the Andean salt lake system, Tables 4.2 to 4.4 list the critical features of salt lake mineral systems economic with respect to lithium, boron, and potassium, respectively.

Table 4.2 The critical features of salt lake mineral systems economic with respect to lithium.

Geological Setting

Intermontane basins (often closed) with salt lakes

Climate: arid (evaporation > 10 times precipitation)

Size of lakes: few km² to 9000 km² (large size preferable)

Size of feeder basins: up to 18000 km² (large size preferable)

Lakes underlain by basins with good aquifers

Higher than average geothermal gradient

Source

Fluids

Meteoric water, lake water, shallow to deep (~400 m) groundwater

Salinity: From ~40 000 mg/L to 400 000 mg/L TDS. Salinity results from a convective hydrological system involving meteoric, lake, ground and geothermal waters

Chemically waters can be either alkaline type (Na/CO₃ – CI) or SO₄ and Ca brines; pH > 7

Lithium

Felsic rocks: Volcanic rocks (andesitic to rhyolitic tuffs and ash-flows) contain more leachable material. Source rocks in the aquifers underlying salt lakes and in areas feeding the lake system

Lithium-bearing clays formed from weathering of feldspars and micas

Locally geothermal springs (especially important for boron)

Energy

Dominantly gravity-driven fluid-flow

Geothermal

Fluid pathways

Aquifers underlying the lake system

In some lake systems (e.g., Clayton Valley, Nevada) brines move along fault zones

Trap

Brines contain lithium in the form of soluble sulfate, carbonate and chloride complexes. Brine fills interstitial spaces in aquifers.

Age

Lake systems of Cenozoic age. Rocks surrounding and underlying the lake system can be of any age but known economic systems are in relatively younger rocks (Mesozoic and younger)

Relative timing of mineralisation

Most known economic lakes are within active hydrological system. However recharge rates and residence time of brines can vary from region to region

Preservation

Not critical in active systems. In general preservation will depend on factors which control hydrological drivers of the system

References

Risacher and Fritz (2009); Garrett (2004); Risacher et al. (2003); Davis et al. (1986).

Table 4.3 The critical features of salt lake mineral systems economic with respect to boron.

Examples

Western Asia (Western Anatolia region of Turkey)

South America (Argentina, Bolivia, Chile, and Peru)

North America (United States: Oregon, California, Nevada)

China (Tibet)

Geological Setting

Closed intermontane basins with internal drainage leading to the formation of salt lakes and playas (an uplifted rift environment)

Arid climate (evaporation >> precipitation)

Recent or concurrent volcanic activity

Host rocks:

Immediate: variable lacustrine sediments

Proximal associated volcanics: calc-alkaline series (from basic to acidic)

Basement rocks: variable, from Precambrian-Mesozoic metamorphic rocks (Turkey) to Paleozoic rocks with low metamorphic grade (South America)

Geothermally active areas with long-lasting high boron geothermal springs

Source

Fluids

Meteoric water, lake water, shallow to deep (~400 m) groundwater, geothermal waters

Salinity: Variable, up to ~400 000 mg/L TDS in salt-saturated brines

Waters of variable hydrochemical types, from neutral to alkaline (sulfate-neutral, sulfate-alkaline, alkaline; pH >=7)

Boron

Mobilised from different sources, depending on the drainage system and local country rocks. For South America, demonstrated sources (δ¹¹B) include the Paleozoic basement and Cenozoic volcanic and sedimentary rocks (including Neogene-Pleistocene ignimbrites)

Geothermal springs/hydrothermal solutions

For lithium and lithium/boron deposits, high boron-lithium correlation in source fluids, (?)suggesting some commonality in terms of the commodity sources

Energy

Dominantly gravity-driven fluid-flow

Geothermal

Fluid pathways

Aquifers underlying the lake system

Fault zones supplying boron in hot water springs/geothermal fluids

Traps

Lakes and playas characterised by:

Ample basin depth or subsidence for a thick accumulation of salts

Often broad shallow margins with a deep centre

Sufficient seepage and/or periodic flashing to remove nonborate salts

Chemical deposition due to evaporation of waters enriched in boron (waters of mixed origin, hot water springs)

Principal mineralisation:

Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), ulexite ($NaCaB_5O_9 \cdot H_2O$), borax ($Na_2B_4O_7 \cdot 10H_2O$) or inyonite ($Ca_2B_6O_{11} \cdot 13H_2O$) (borate deposits in playa and perennial lakes)

Brines (as by-product of lithium production)

Special local geochemical or mineralogical features:

Gypsum is common in evapofacies in the sections of some Argentine deposits

Common association with arsenic minerals in Turkey (realgar and orpiment)

Age

Deposits age: Early Miocene (16-20 Ma, Turkey) to Late Miocene (5-7 Ma, South America), Pleistocene-Holocene (China)

Rocks surrounding and underlying the lake system can be of any age but known economic systems are in relatively younger rocks (Mesozoic and younger)

Relative timing of mineralisation

Most known economic lakes are within active hydrological system. Recharge rates and residence time of brines can vary from region to region

Preservation

Not critical in active systems. In general preservation will depend on factors which control hydrological drivers of the system

References

Boschetti (2007), Garrett (1998), Helvaci and Alonso (2000), Kasemann (2004).

Note: essential features are shown in bold

Table 4.4 The critical features of continental salt lake mineral systems economic with respect to potash.

Examples

North America (Great Salt Lake in Utah)

South America (Chile, Salar de Atacama)

China (Qaidam Basin, Tibet)

Western Asia (the Dead Sea)

Geological Setting

Closed basins with internal drainage leading to the formation of salt lakes and salars or playas (an uplifted rift environment)

Frequently: structural basins that formed in volcaniclastic terranes; sub-basins may exist and have distinctly different characteristics, such as chemistry or grade

Arid climate (evaporation >> precipitation)

Most of the productive basins have some surface or near-surface evaporites and salts (e.g., include the presence of Cenozoic continental evaporates)

Basins with young volcaniclastic sequences

Host rocks:

Immediate: variable lacustrine sediments, gypsum and(or) halite

Proximal associated rocks: volcanic rocks, siltstones, sandstones, and mudstones

Source

Fluids

Meteoric water, seawater, groundwater, geothermal waters (hydrothermal springs)

Salinity: Variable, up to ~400 000 mg/L TDS in salt-saturated brines

Waters of variable hydrochemical types, from neutral to alkaline (sulfate-neutral, sulfate-alkaline, alkaline; $pH \ge 7$)

Potash

Scavenged from the local country rocks

Commonly acidic to intermediate volcanic rocks

Older saline rocks (common: Cenozoic continental evaporites)

Continental sedimentary rocks

Energy

Dominantly gravity-driven fluid-flow

Geothermal

Fluid pathways

Surficial run-off

Aquifers underlying the lake system

Fault zones

Traps

Brines containing potash in the form of soluble chloride, sulfate, carbonate and nitrate complexes Halite and other evaporates hosting disseminated potash minerals and stratoid lenses

Age

The duration of this process can extend from hundreds of years to tens of thousands of years, and in some cases, over a million years.

Relative timing of mineralisation

Most known economic lakes are within active hydrological systems. Recharge rates and residence time of brines can vary from region to region

Preservation

Not critical for active systems. In general preservation will depend on factors which control hydrological drivers of the system

References

Orris (2011), Ericksen and Salas (1989), Casas *et al.* (1992), Bryant *et al.* (1994), Garrett (1996), Carmona *et al.* (2000), Duan and Hu (2001), Jones and Deocampo (2003), Jones *et al.* (2009), Risacher and Fritz (2009).

4.3 Features of salt lakes economic with respect to calcrete-hosted uranium systems

Most calcrete-hosted uranium deposits in Australia are spatially and genetically related to salt lake systems involving groundwater-bearing palaeochannels draining into salt lakes. This setting is different from the calcrete-hosted uranium deposits in Namibia (e.g. Langer-Heinrich) where the hydrogeological system is driven by the gradient created between coastal areas in the west and the escarpment in the east (Hartleb, 1988). All deposits are closely associated with calcrete formed from drainage systems in palaeochannels.

4.3.1 Types of calcrete-hosted uranium deposits

Butt *et al.* (1984) classified calcrete-hosted uranium deposits by their geomorphological setting into three main types: valley, playa and terrace. Valley deposits, such as Yeelirrie, Hinkler-Centipede, Lake Way and Lake Raeside in the Yilgarn Craton, occur in calcretes and associated sediments in the central channels of major (palaeo)drainages, and in the platforms and chemical deltas where the drainage enter playas. The calcretes generally change vertically downwards into an alluvial clay-quartz unit. Uranium mineralisation is not limited to the calcretes but transgresses into underlying units, with the greatest concentration located in the vicinity of the groundwater table. Mineralisation occurs almost entirely as carnotite, generally as a late-stage precipitate in cavities, lined by thin coatings of minerals such as calcite, dolomite, silica and/or sepiolite. Carnotite may also form fine disseminations in the clay-quartz units.

The playa deposits, such as the Lake Maitland and Lake Austin deposits in the Yilgarn Craton, occur in near-surface evaporitic and alluvial sediments. The calcretes near playas act as principal aquifers to the playas. In the Yilgarn, mineralised playas are usually closely associated with calcretes in the

channels, often enriched in uranium. Mineralisation is generally concentrated near the groundwater table in sediments consisting of gypsiferous clays and muds. The sandy and silty clays locally contain calcareous nodules. In some deposits, such as Lake Maitland, the mineralisation occurs in thin calcretes in the playa itself.

The terrace deposits are less common and occur in calcrete terraces in dissected valleys mainly in the Gascoyne Province.

4.3.2 Geological setting

Geologically significant uranium is associated with non-pedogenic calcrete or dolocrete formed within Cenozoic drainage systems incised into rocks containing leachable uranium and vanadium. Non-pedogenic calcrete (also known as groundwater or valley calcrete) is formed predominantly near the water table from groundwater moving along extremely low gradients (Carlisle, 1978). The formation of non-pedogenic calcrete is generally controlled by climate and the type of soil. In the Yilgarn Craton, the distribution of non-pedogenic and pedogenic calcretes is defined by the Menzies Line (Butt *et al.*, 1984). North of the Menzies Line, the zone dominated by non-pedogenic calcretes, the soils are generally neutral to acid and the groundwaters are less saline and neutral to alkaline. South of the Menzies Line, dominated by pedogenic calcretes, the soils are neutral to alkaline and the groundwaters are saline and neutral to acidic. The southern zone is characterised by higher annual rainfall (> 225 mm), which is winter-dominated, and lower annual evaporation (< 2500 mm) with average temperatures below 19°C. The northern zone is characterised by summer-dominated rainfall, lower total rainfall, and higher annual evaporation in comparison with the southern zone.

4.3.3 Source of uranium, vanadium and potassium

One of the main components of the system is shallow-level groundwater in the palaeochannels. The groundwater is generally of variable salinity, ranging between 3000 mg/L and 6790 mg/L chloride in the Langer-Heinrich region in Namibia (Table 4.5). The pH varies between 6.6 and 7.8. The pH of calcrete groundwater in Australia is very similar to those in Namibia. However the variation in salinity (chloride concentration) is large ranging between 136 mg/L and 95,160 mg/L (Table 4.5).

Locality	рН	CI (mg/L)	Source
Langer Heinrich, Namibia	6.6. to 7.8	3000 to 6790	Bowell et al. (2009)
Hinkler Well drainage, Yilgarn, WA	4.3 to 8.2	138 to 95,160	Mann and Deutscher (1978)
Northern goldfields, Yilgarn, WA	7.6 to 8.2	610 to 2900	Johnson et al. (1999)
Paterson region, WA	7.4	136	CSIRO GW data (Giblin, 2001)
Napperby, Lake Lewis, NT	7.2 to 7.7	718 to 1600	English (2001)
Calcrete Tarcoola, Gawler, SA	6.0 to 7.7	1600 to 87,000	SA GW data

All known calcrete-hosted uranium deposits are located in palaeochannels incised into potential source rocks of potassium, uranium and vanadium. Felsic rocks in the Yilgarn Craton contain up to 20

mg/kg uranium (Schofield, 2009) and a granite in the upstream area of Lake Way deposit contains up to 25 mg/kg uranium (Mann and Deutscher, 1978). Intensive weathering and erosion of such felsic rocks can provide uranium as well as potassium to the calcrete system. High uranium concentrations (up to 400 ppb) in groundwaters in the Lake Way area supports leaching of uranium from the felsic rocks (Mann and Deutscher, 1978).

Mafic igneous rocks, sediments with vanadium-rich clays, ironstone such as banded iron-formation and ferricrete are often enriched in vanadium (Bastrakov *et al.*, 2009). Such rocks are generally present in the vicinity of calcrete-hosted uranium deposits (Mann and Deutscher, 1978; Karner and Becker, 2009) and can provide vanadium.

4.3.4 Drainage system

The calcrete-hosted uranium system is driven by shallow groundwater drainage in extremely low gradients, ca. 10 m/km (Karner and Becker, 2009), established in permeable sediments infilling palaeochannels. Groundwaters in mineralised areas are generally neutral to alkaline with maximum median salinity of ca. 10 wt. % (Mann and Deutscher, 1978; Gray, 2001). The high salinities are more common along palaeovalley axes (Gray, 2001). The drainage in the region is controlled by a recharge area upstream and a system of playa lakes in the discharge area. In addition of the infill sediments, calcretes formed near the water table also function as aquifers which allow groundwaters to actively interact with the calcretes. The presence of playa lakes creates conditions where groundwaters in the palaeovalleys can mix with relatively more saline waters in the playas.

4.3.5 Geochemical factors controlling precipitation of carnotite in calcrete-hosted uranium deposits

Carnotite is a hydrated uranium- and potassium-bearing vanadate with the formula $K(U^{+6}O_2)(V^{+5}O_4).xH_2O$.

Its solubility and precipitation depend on:

- The concentration/activity of potassium, uranium and vanadium in the fluid;
- The oxidation state of the fluid, because in oxygen-saturated, low-temperature surficial fluids, uranium and vanadium form aqueous complexes of uranyl (U⁺⁶O₂) and V⁺⁴ and V⁺⁵ respectively; and,
- The type of oxidation-reduction reaction. As the valence state of uranium and vanadium in carnotite is +6 and +5 respectively, oxidation-reduction reactions are important with respect to vanadium only in conditions where vanadium forms complexes containing V⁺³ and V⁺⁴. In such cases, precipitation of carnotite will require oxidation and not reduction of the fluid (see discussion below).

Calculations on speciation of uranium and vanadium and on the stability of carnotite in shallow-level groundwaters show that geologically realistic concentrations of uranium and vanadium (> 0.01 mg/L each of uranium and vanadium) can be transported in oxidised fluids (Bastrakov *et al.*, 2009). In such conditions, uranium forms aqueous uranyl complexes and vanadium forms complexes containing either V^{+4} or V^{+5} . The calculations also show that precipitation of carnotite can occur due to changes in any of the following:

- pH; decrease in pH if the groundwater is alkaline (pH >8) or increase in pH if the groundwater is acidic:
- 2. Oxidation state. At oxidation states where vanadium is transported as complexes of V⁺³ and/or V⁺⁴, an increase in the oxidation state is essential to form carnotite;
- 3. Concentration of dissolved potassium. An increase in the concentration of potassium will cause precipitation of carnotite;
- 4. Partial pressure of CO₂, which controls the concentration of carbonate complexes in the groundwater. As uranium in these conditions is transported as a uranyl-carbonate complex, any decrease in the concentration of carbonate ions in groundwater will favour precipitation of carnotite;
- Concentration of dissolved calcium in the groundwater. As addition of calcium to the groundwater can cause precipitation of carbonate, the associated decrease in the concentration of dissolved carbonate ion in the groundwater can cause precipitation of carnotite; or,
- 6. Concentration of dissolved sulfur in the groundwater. In oxidised groundwater sulfur is dissolved to form sulfate ions which control the solubility of uranium as uranium forms uranyl-sulfate complexes. A decrease in the concentrations of sulfate ions caused often by the deposition of gypsum and barite can thus favour precipitation of carnotite.

The formation of carnotite in valley calcretes is closely related to the seasonal fluctuation of the groundwater table. The fluctuation is associated with evaporation of groundwaters which can lead to an increase in the concentration of dissolved potassium, vanadium and uranium (Butt *et al.*, 1984). It can also change the concentration of carbonate ions in the water affecting the solubility of uranium.

Evaporation is also important in the playa deposits where it can control the salinity of lake waters and the precipitation of gypsum-bearing sediments. However, mixing of more saline lake waters, relatively enriched in potassium and calcium, and the incoming groundwaters from the drainage channel can be equally important in the formation of carnotite. Such mixing can cause an increase in the concentration of potassium and calcium in groundwater which may lead to the precipitation of carnotite. In a similar way, an increase in the concentration of calcium can destabilise uranyl carbonate or uranyl sulfate complexes by precipitating calcite and gypsum, respectively, and thereby facilitate the formation of carnotite (Mann and Deutscher, 1978).

According to Mann and Deutscher (1978), redox process can also contribute to the formation of carnotite in some calcrete-hosted uranium deposits. In this model the interaction of mildly-reduced groundwaters with mafic rocks in the greenstones can cause dissolution of vanadium to form V^{+4} -bearing complexes. Vanadium from these groundwaters mixes with overlying uranium-bearing fluids either through diffusion and/or by upwelling of the waters caused by a subsurface hydromorphic barrier. Mixing causes oxidation of vanadium from V^{+4} to V^{+5} to form carnotite. The presence of darkgreen coloured (relatively reduced with V^{+4}) carnotite deep in the calcrete profile, and of more yellow-coloured (relatively oxidised, with V^{+5}) carnotite towards the surface in some deposits is cited in support of this model.

The formation of calcrete-hosted uranium deposits can be illustrated in a three-stage model (Figure 4.10). The first stage represents the filling of palaeovalleys with coarse-grained sediments of high permeability (Figure 4.10a). This is followed by the initiation of an active groundwater drainage system. In arid zones dominated by intensive evaporation the drainage system generates calcrete zones near the water table (generally in the vadose zone, Figure 4.10b). Intensive evaporation in the

playa lakes causes deposition of evaporites and calcrete. Like other infill sediments, calcrete also begins to act as aquifers and is affected by chemical processes caused by evaporation and a fluctuating water table. Potassium and uranium are leached from felsic rocks (located upstream or in the incised bedrock of the palaeochannel) by saline and oxidised groundwaters, whereas vanadium is extracted from sources such as mafic rocks or iron-rich (meta)sediments. Evaporation of groundwaters can cause changes in the concentration of dissolved potassium, uranium, vanadium and carbonate triggering precipitation of carnotite. In the vicinity of playa lakes, precipitation of carnotite can occur due to mixing of valley groundwaters with more saline lake waters.

Critical features of calcrete-hosted uranium mineral system are summarised in Table 4.6. These features will be used to comment on the prospectivity salt-lake systems to form calcrete-hosted uranium deposits in Australia (Chapter 5).

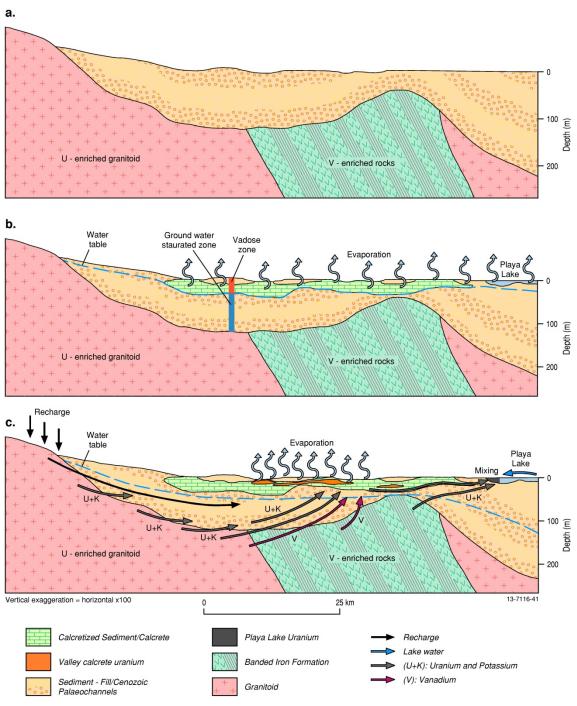


Figure 4.10 Model depicting the formation of calcrete-hosted uranium deposits.

Table 4.6 The critical features of calcrete-hosted uranium associated with salt lake systems.

Geological Setting

Cenozoic salt lakes and connected palaeochannels in arid zones

Palaeochannels filled with sediments containing non-pedogenic calcrete

Source

Fluids

Meteoric water, lake water, shallow to deep (~400 m) groundwater

Salinity (chloride): variable ranging between 136 mg/L and 95160 mg/L. High salinity waters can transport more uranium and vanadium; pH varies between 6.0 and 8.2. pH is not considered important for the transport of uranium and vanadium

Potassium, Uranium, and Vanadium

Felsic rocks for uranium (rocks with > ~20 mg/kg uranium).

Mafic rocks and banded iron formations for vanadium. Average abundance (in mg/kg) of vanadium in major rock types (Krauskopf, 1982): Basalt (250); Shale (130); Granite (50)

Potassium from felsic rocks

Energy

Dominantly gravity-driven fluid-flow. Seasonal variation of groundwater table is considered important

Fluid pathways

Permeable sands in palaeochannels

Efficient hydrological system involves a good connection between aquifers in palaeochannels and salt lakes (discharge areas)

Traps

For valley-type calcrete deposits: changes in pH and concentration of potassium,vanadium and uranium, and dissolved CO₂ due to evaporation of upwelling groundwater

For playa-type deposits: mixing of groundwater with saline lake water and changes in the concentration of potassium, Ca, CO_3 and SO_4 .

Less frequently: mixing of relatively reduced waters carrying vanadium with more oxidised waters carrying uranium

Age

Cenozoic.

Relative timing of mineralisation

Timing of the system depends on the timing of establishing hydrological connection between palaeochannels and salt lakes

Preservation

Not critical. In general preservation will depend on factors which control hydrological drivers of the system

References

Bastrakov et al. (2010), Dahlkamp (1993), Butt et al. (1984).

5 Preliminary Favourability (Prospectivity) Analysis of Australian Salt Lakes

5.1 Introduction

In Chapter 4 we discussed the main features of salt lakes prospective for lithium, boron, and potassic brines. The chapter also summarised features of salt lakes favourable to form calcrete-hosted uranium deposits. In this chapter mapable elements of these features are used to comment on the favourability of salt lakes in Australia to generate economic brines and calcrete-uranium deposits. We commence with a discussion on the feasibility of using ASTER geoscience maps of Australia for identifying and mapping Australian salt lakes and then discuss the statistical robustness of the geochemical data collected during the National Geochemical Survey of Australia (NGSA). We finish with the principal aim of the chapter, which is to generate a list of favourable salt lake systems (shown on national and regional scale maps) for further more detailed geological and geochemical data acquisition and analysis.

5.2 Feasibility of ASTER geoscience maps of Australia for identifying and mapping Australian salt lakes

F.J.F. Howard, M. Thomas and P.M. English

The multispectral satellite ASTER (Advanced Spaceborne Thermal Emission and Reflectance Radiometer) Geoscience Maps of Australia (Cudahy, *et al.*, 2012) and accompanying product notes (http://c3dmm.csiro.au/Australia_ASTER/index.html), released in August 2012, provide unprecendented information on surface mineralogy across Australia, at a spatial resolution of 30 m x 30 m to 90 m x 90 m pixels across the whole of the continent. The 17 geoscience products map a variety of mineral group signals at the surface and are readily integrated with other datasets, such as GIS (Cudahy, 2012) or Geoscience Australia's WorldWind viewer (www.ga.gov.au/aster-viewer).

Salt lakes, because of their negligible vegetation cover (with the exception of lichen crusts in some areas), and high reflectivity, are excellent candidates for the application and interrogation of this type of surface-reflectivity multispectral data.

In this section we assess the potential of the new national-scale ASTER geoscience products as a source of new information on Australian salt lake distributions, spatial patterns and surficial geochemical compositions, along with implicit groundwater/surface interactions in these unique environments.

5.2.1 Using ASTER for salt lake characterisation

Presented below are case studies undertaken for the present project to highlight some of the different capabilities and limitations of the ASTER products for the characterisation of salt lakes, based on their surface geochemistry and morphologies, and for the identification of anomalous mineralogical targets for further investigation.

5.2.1.1 Gypsum

The ASTER gypsum index product has a 90 m x 90 m pixel size and a range of geoscience applications including the identification of acid waters invading carbonate-rich materials and hydrothermal systems (Cudahy, 2012). It is particularly effective at mapping gypsum in modern evaporite environments because most other environments in Australia do not have a gypsum spectral response. Consequently this ASTER product could prove a very powerful tool for the characterisation of salt lakes and their mineralisation potential.

An initial trend evident from the ASTER gypsum index product is the stronger signal and more abundant surface coverage of gypsum in salt lakes close to the coast (Figure 5.1). This is probably a consequence of sea-salt sulfate being the most dominant source of sulfur; a key component and potentially limiting factor for gypsum mineralisation in Australian salt lakes (see Section 2.2 and Chivas et al., 1991). Further inland, the marine influence and the amount of sulfur available to salt lake settings decreases, limiting the amount of gypsum that can be formed. Local zones of gypsum response in inland lakes are interpreted to be restricted mainly to where the water table intersects the land surface. Inland salt lakes displaying a high gypsum signal in the ASTER product could therefore provide a preliminary indication of a greater relative contribution of rock weathering constituents for its down-gradient salts, particularly sulfate. Such lakes could, potentially, also have a higher prospectivity for elements such as lithium, boron, potash and uranium sourced from the same catchment rocks.

In the case of Lake Amadeus, in central Australia, the geomorphology and major lithological units of the lake and its surroundings were sampled and mapped in detail by Chen *et al.*, (1991a), who found that the lake surface has an extensive coverage of a distinctive gypsum-rich unit (~16 %), which they termed "gypsum ground" (Figure 5.2 and Chapter 2). Additionally the margins of the playa were found to be outlined by predominantly gypsiferous dunes. This makes Lake Amadeus a particularly suitable candidate to examine the potential applications of the ASTER gypsum index for mapping salt lake mineralisation.

The ASTER Gypsum product, in Figure 5.3, over Lake Amadeus in Central Australia, shows a correlation between the distribution of gypsum across the lake and areas identified and mapped as "gypsum ground" in Figure 5.2. This provides an indication of the efficacy of using ASTER data to map gypsum.

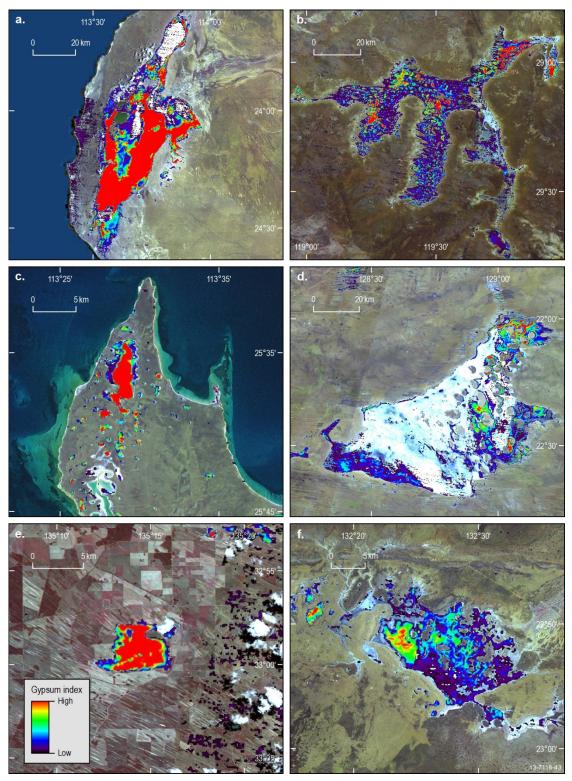


Figure 5.1 The ASTER gypsum index product for a series of coastal (a-c) and inland (d-f) salt lakes across Australia. Red indicates relatively high levels of gypsum, blue relatively low levels of gypsum and null values were masked to reveal the underlying image, the ASTER false colour product. The name and location of the lakes are: (a) Lake Macleod, WA; (b) Lake Barlee, WA; (c) Lake Montbazin, WA; (d) Lake Mackay, WA-NT border; (e) Lake Yaninee, SA; and, (f) Lake Lewis, NT. Notice that gypsum distribution is much more uniform and ubiquitous in coastal salt lakes (a,c,e), while in inland salt lakes its distribution is generally lower and occurs in more discrete patches (b,d,f).

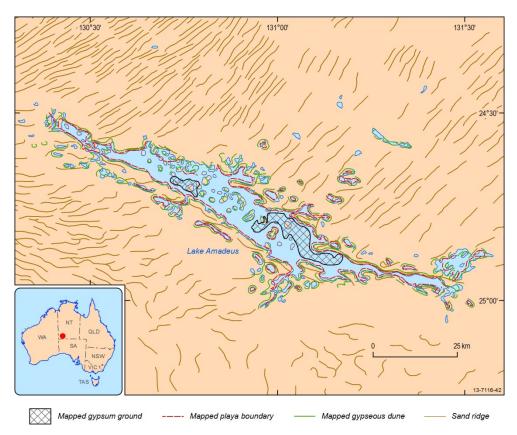


Figure 5.2 Geomorphological map of the Lake Amadeus region after Chen et al. (1991a).

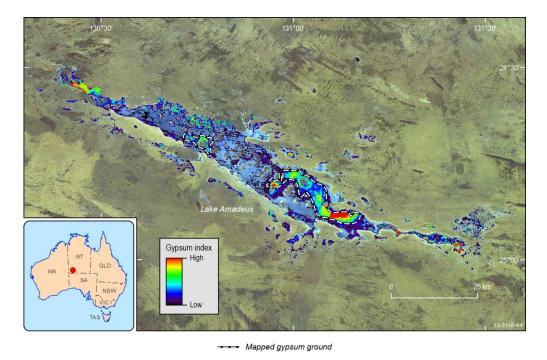


Figure 5.3 ASTER Gypsum index product for the Lake Amadeus region showing discrete areas of gypsum abundance. The dashed line shows the gypsum ground mapped by Chen et al. (1991a). NB. Null values are mapped as transparent, revealing the underlying image, the ASTER false colour product, for reference.

Figure 5.3 identifies three additional regions of high surface abundance of gypsum in the northwest and southeast corners along with the northern margins of the lake. This may be a reflection of the difference in time when the two datasets were captured (possibly a 15-20 year gap) with the potential for the formation or uncovering of new surface gypsum deposits since the initial study. However, given the large size of the lake (~800 km²) and difficulty of access, these newly-identified gypsum ground areas could also have been missed by the original field sampling program. Thus ASTER products can provide a useful tool for identifying chemical variation on the lake surface, and could be used to make quick regional assessments prior to field work to assist in obtaining representative data that captures the variability of the area of interest, particularly where access might be restricted.

The gypsum product, however, was unable to identify the gypsiferous dunes that had been mapped by Chen *et al.* (1991a) and which run parallel to the edges of the lake. While this could reflect the different times the two datasets were collected, it could also be the consequence of an aeolian quartz sand veneer masking the gypsum signal in the dunes (as described by Chen *et al.*, 1995), leaching of surface gypsum that has left residual silica dominating the dune surfaces (Chen *et al.*, 1991b), or simply that the scale of the lake edge dunes were not large enough to be detected by the 90 m x 90 m cell resolution of the ASTER gypsum index product. This example highlights that although the potential for mapping gypsum deposits on salt lakes is high, the ASTER maps only identify what is occurring in the top few microns of the surface, rendering them unable to map near-surface mineralisation on salt lakes in areas where there is watercover or significantly thick or extensive veneers of dust, silica sand or charcoal obscure them.

5.2.1.2 Differentiating lake floor materials

The ASTER opaque index product and ASTER false colour product used in combination could provide a method for mapping muddy lake floors and the absence of a salt crust. The ASTER opaque index, with a 30x30 m cell size, identifies targets based on contrasting albedos and thus is complicated by factors such as shadow and fire scars (Cudahy, 2012). These, however, are of little concern in salt lakes which are generally very flat and have little green vegetation. The opaque product has been masked for "sun glint" which removes most deep water bodies such as water-filled lakes, dams, flooded ground etc. (Cudahy, 2012).

Salt crusts appear as bright white features in the ASTER false colour product. Areas with a deeper blue colour (in the false colour product) that also contain high values in the opaque index product are hypothesised to correspond with sulfide-rich muds at the surface, Figure 5.4 This hypothesis has been supported by John Magee (pers. comm., 2012) who conducted some fieldwork at Lake Amadeus in the late 1980s although systematic ground truthing is necessary to confirm this hypothesis.

5.2.1.3 Halite

Examination of the ASTER products has identified two potentially different methods to identify and map halite distribution in Australian salt lakes. The method which is appropriate appears to depend on which stage of the hydrogeological cycle each lake was at when the ASTER data were collected.

The first method employs the ASTER false colour, gypsum index and opaque index products. As described in Section 5.2.1.1, bright targets within playa boundaries correspond with salt crusts. The gypsum index product is used to identify areas of gypsum salt crust, as seen in Figure 5.5 where bright targets in the the northwest and southwest of the false colour product (Figure 5.5a) had medium to high gypsum responses (Figure 5.5b). The gypsum index product was then overlain with the opaque index to distinguish and mask out areas that were dominated by putative sulfide muds. The

remaining bright target areas are interpreted as halite crusts, highlighted by the pink arrow and dashed line in Figure 5.5c. Other salts could be present but numerous studies have shown that there are few exceptions in the Australian context to sodium-chloride rich (halite forming) or calcium-sulfate rich (gypsum forming) waters (Williams, 1967; De Deckker, 1983). It is highly unlikely therefore that the flat, white, high albedo areas identified through this methodology represent salt deposits other than halite, but ground truthing studies are needed to test this.

Some cases were observed of areas that were bright targets in the false colour product and gypsum poor but contained strong opaque signals. Areas with both a high opaque index response, an absent or low gypsum index response, and which were very bright, could correspond to slushy, wet but still halite-dominated crust. Although surface water is generally masked out of the opaque product, using a sun glint removal method, very low amounts of water at the time of the ASTER satellite overpass that were insufficient to dissolve the crust entirely could result in this contradictorary 'opaque' yet 'bright' signal.

5.2.1.4 Brine evolution/mineral zonation

The ASTER MgOH group content and the ASTER MgOH group composition products have potential to trace brine evolution and map consequential mineral zonation halos deposited. The MgOH group content product over salt lake environments was found to be useful for mapping carbonate-rich rocks; with the warmer the colour corresponding to the greater the amount of carbonate material present. Figure 5.6a of Lake Mackay, located on the WA-NT border, shows an interpreted increase in surficial carbonate towards the centre of the playa depocentre in the south-west corner of the playa. This increase in concentration is most likely due to carbonate enrichment as the brine evolves. It is important to note that this signal is only visible in bare lake areas where there is no halite or gypsum crusts dominating and/or covering the carbonate signal.

The MgOH group composition product, on the other hand, reveals information about the chemistry of the carbonate distinguishing between calcitic (red/warm colours) and dolomitic end members (blue/cool colours). As Figure 5.6b shows, carbonate deposited outside the playa and on its edges being more calcium-rich and accumulations further lake-ward from the shore being more magnesium-rich carbonate. This pattern is probably the consequence of a progressive calcium deficiency relative to magnesium as calcium is consumed with brine evolution. This corresponds to modelled increasing alkalinity. The calcium-rich strip at the edge of the playa could be the consequence of biological accretion of calcite skeletons (by ostracods for example) at the margin of the playa, creating a discrete band of high calcite concentrations that may have been readily wind-borne in dry conditions and accumulated at the edge of the playa.

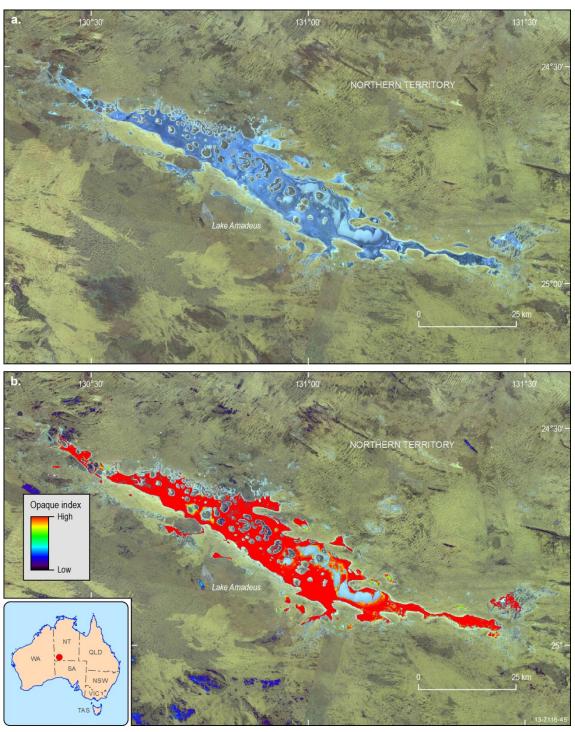


Figure 5.4 Maps of Lake Amadeus, NT, using different ASTER products. (a) is a map using the ASTER false colour product, and (b) is a map using the ASTER opaque index product with null values masked to reveal the ASTER false colour product. Deeper blue areas within the salt lake in the ASTER false colour correspond closely with high values in the ASTER opaque index product.

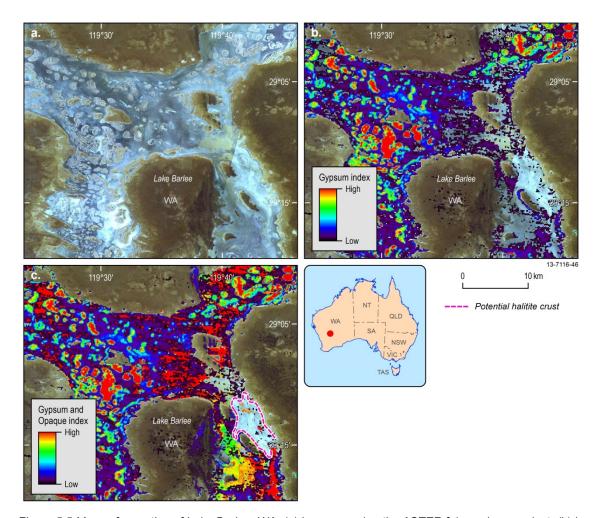


Figure 5.5 Maps of a section of Lake Barlee, WA. (a) is a map using the ASTER false colour product; (b) is a map using the ASTER gypsum index product with null values masked revealing the ASTER false colour product; and, (c) is a map of the ASTER gypsum index product over the ASTER opaque index product with null values masked to reveal the false colour product; an area of 'salt crust' that is evidently not gypsiferous is outlined in pink.

Similar evolution of brines and deposition of a calcrete or dolocrete halo around a salt lake is evident at Lake Lewis, in the Northern Territory (Figure 5.7a). This ASTER map corresponds quite closely to a map of calcrete deposits surrounding Lake Lewis produced by English (2002) from field studies (Figure 5.7b). The close correlation between the two maps highlights that this use of the ASTER MgOH group content and composition products to map carbonate halos around and within salt lakes is probably valid, although further field studies to test this are required.

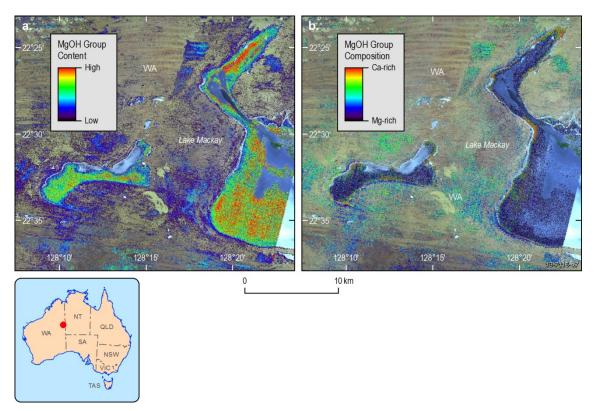


Figure 5.6 Maps of Lake Mackay, WA-NT border. The diagonal line towards the southeast side of the images is a scene boundary, where adjacent scenes that make up the mosaic are from different dates/seasons and show contrasting wetness and sun angles. (a) shows a map of the ASTER MgOH group content product identifying the relative abundance and distribution of surficial carbonate deposits, null values were masked revealing the ASTER false colour product. (b) shows a map of the ASTER MgOH group composition product which distinguishes whether carbonate material identified by the MgOH group content product was more calcium-rich (warm colours) or more magnesium-rich (cool colours). Null values were masked revealing the ASTER false colour product.

5.2.1.5 Uranium deposits

Investigation of the ASTER gypsum index product and the uranium radiometric map of Australia revealed an intriguing inverse relationship between the two products at Yeelirrie in the Yilgarn Craton, WA. Figure 5.8a shows the distribution of gypsum deposits in this area, outlined roughly by the white dashed line. In this region, salt lake deposits are generally along palaeovalley drainage channels (Bell *et al.*, 2012). When these gypsum deposition zones are compared with the uranium channel of the radiometric map for the same region (Figure 5.8b) it is clear that they are relatively uranium poor, while the adjacent segments of the palaeovalley are generally uranium rich.

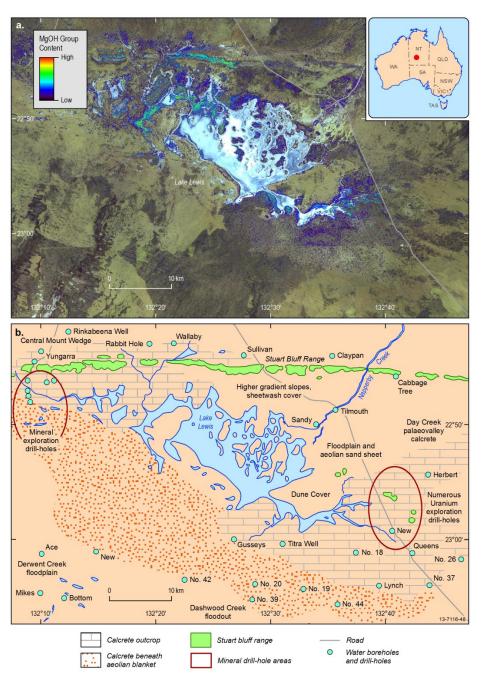


Figure 5.7 Maps of carbonate deposits around Lake Lewis, NT. Map (a) shows the ASTER MgOH group content map of Lake Lewis, NT, which detects and maps the relative abundance of surficial carbonate deposits (Cudahy, 2012). Null values have been masked revealing the underlying image, the ASTER false colour product. Exposed carbonate deposits are concentrated largely around the perimeter of the lake, although there is a large surficial deposit in the northwest areas of Lake Lewis and another large surficial carbonate deposit in the southeast arm of the lake. Map (b) shows the extent of thick contiguous calcrete outcrop and subcrop around Lake Lewis, NT, from English (2002), mapped from existing geological data, Landsat imagery and field observations. The mapped surficial calcrete corresponds well with the pattern of carbonate material found identified around the margins of the lake using the ASTER MgOH group content product with large deposits in the northwest and southeast. The area mapped using ASTER is patchier than that produced by English (2002) possibly as a result of dry vegetation, or aeolian deposits masking the carbonate signal.

The inverse relationship between gypsum and uranium deposits along the same palaeochannel suggests that the mutual exclusion of the two deposits types have an interrelated cause. Whether this relationship is a direct one, or is a consequence of variations of a separate component in the system (that independently affects both) is presently unknown and warrants further investigation and elucidation. Uranium is present as the mineral carnotite and is sequestered preferentially in calcrete, which is typically located up-gradient from gypsum in given systems or parts of systems. The general observation of an inverse correlation highlights the potential to use the ASTER products in conjunction with other geoscience datasets to increase our understanding of the distribution of mineral deposits in salt lake systems and also may be used as a rapid exploration method.

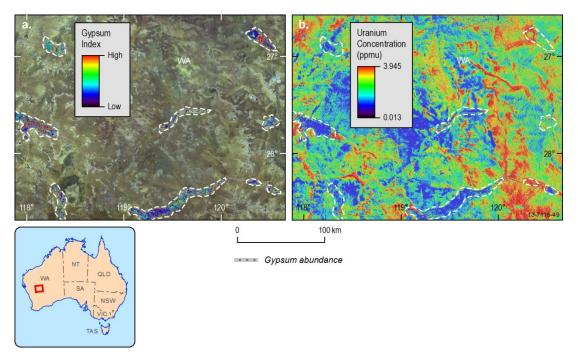


Figure 5.8 Maps of gypsum and uranium in the Yeelirrie region, Yilgarn Province, WA. Map (a) is the ASTER gypsum index for the area, showing discrete areas of gypsum abundance, with dashed lines highlighting these enriched areas. Null values were masked revealing the underlying image, the ASTER false colour product. Map (b) is the uranium concentration map for the Yeelirrie region from radiometric data, with warm areas corresponding with high concentrations of uranium and cool colours corresponding with low concentrations of uranium. Dashed lines are the location of the surficial gypsum deposits identified in Figure 5.8a.It can be seen that there is generally an inverse relationship between the occurrence of gypsum along the palaeochannels in this region and areas of high uranium concentrations.

5.2.2 Conclusions on the potential of ASTER geoscience mineral maps

The new ASTER geoscience mineral maps of Australia have been found to have significant potential as a reconnaissance tool for characterising and mapping variations in the surface chemistry and mineralogy of Australian salt lakes at a broad-scale to support a national assessment of salt lakes with the greatest mineral prospectivity. A combination of the ASTER gypsum index, and ASTER opaque index products was successful at identifying and mapping broad patterns and changes in the surface chemistry of salt lakes, particularly in distinguishing between gypsum and halite crusts, bare lakebeds without a salt crust, and aeolian silica blown onto the lakebed surface. The ASTER MgOH group content and MgOH group composition products also show some potential in identifying carbonate deposits in and around salt lakes and to distinguish more calcium-rich from more magnesium-rich

carbonates, although substantiating field data are lacking. Carbonate deposits though were generally only detectible in areas that were not covered by salt crust, *i.e.* in bare lakebed sections, and not covered by aeolian sands in the playa margins.

It is noted that limitations exist in the ASTER products, largely due to the time differences in adjacent scenes used in the composite mosaic, and these inconsistencies must be considered and acknowledged when interpreting the imagery to map the surface geochemistry of salt lakes. Important considerations include, but are not limited to:

- Adjacent scenes within a basin being captured over a period of 10 years, usually at different times of the year and stages of a lake's hydrological cycle;
- Cloud and vegetation cover can affect the ASTER products;
- Scenes represent the lake at the moment the information was captured and cannot necessarily represent the present-day lake conditions or the more prevailing conditions;
- Products have only been ground-truthed in small study areas, although the spectral signal of each pixel does represent an actual response; and,
- ASTER products only reveal the chemistry of the top few microns of the surface, be that rock, soil or plant or other material. Essentially this means these products alone cannot be used for quantitative or 3-dimensional calculations, rather they can indicate a presence or absence of a material. Some relative abundances can be inferred, using an understanding of the landscape and by taking into account the likely influences on pixel values, as has been done for the purpose of this preliminary investigation.

5.3 An assessment of geochemistry data collected during the National Geochemical Survey of Australia

P. de Caritat

In the following section, geochemical data analysis will be developed for lithium in the Australian regolith as an exemplar of what insights can be obtained from low-density geochemical mapping. The case of lithium was selected because, contrary to boron, it is available after both Aqua Regia and Mobile Metal Ion digestion in the National Geochemical Survey of Australia dataset. Uranium and potassium data have been analysed in Caritat *et al.* (2011b) and Wilford *et al.* (2011) and are thus not discussed further here.

5.3.1 Distribution and concentration of lithium in Australian regolith

Lithium concentration in catchment outlet sediment samples was measured as part of the National Geochemical Survey of Australia (NGSA; www.ga.gov.au/ngsa). For this project, samples were collected at or near the outlet of 1186 catchments covering ~81% of Australia (Caritat and Cooper, 2011). Including quality control duplicates, a total of 1315 sites were sampled during 2007-2009. At each site a top outlet sediment (TOS) sample was collected from 0-10 cm depth, and a bottom outlet sediment (BOS) sample was collected from ~60-80 cm depth; each of these samples was split into a coarse grain-size fraction (<2 mm) and a fine grain-size fraction (<75 μ m) thus yielding a total of 5260 samples for analysis, as detailed in Caritat *et al.* (2010).

Because the aliquots analysed for total element content were mixed with a lithium borate flux (for X-ray fluorescence analysis), neither lithium nor boron could be analysed on these aliquots. Consequently, lithium data are only available for the Mobile Metal Ion (MMI®) and Aqua Regia (AR) digestion techniques. Neither of these digestions is Total. The MMI® digestion is very weak and only mobilises ions loosely bound on the surface of minerals (Mann, 2010). MMI® data are available only for TOS coarse (Tc) samples. The AR digestion is quite a strong digestion method: it dissolves sulfides, carbonates, some sulfates, the oxides of some elements (e.g., uranium), some metal hydrates (e.g., Fe, Mn), but leaves most silicates untouched or partially leached and resistates unaltered (e.g., Church *et al.*, 1987; Snäll and Liljefors, 2000; Chen and Ma, 2001; Xu *et al.*, 2012). AR data are available for all four sample types: TOS coarse (Tc), TOS fine (Tf), BOS coarse (Bc) and BOS fine (Bf). Lithium data from large regional-scale geochemical surveys are rare because of the flux problem mentioned above; the ratio of median AR to median Total lithium concentrations is ~50% in soils and sediments of Spain (Otros and Locutura, 2012).

Censored data (reported to be below the Lower Limit of Detection, LLD) accounts for 32% of the MMI[®] data (LLD = 0.005 mg/kg) and <1% of the AR dataset (LLD = 0.1 mg/kg). Censored data was imputed using a nearest neighbour method (Hron *et al.*, 2010) as explained in Caritat and Grunsky (2013). Table 5.1 gives a statistical summary of the datasets.

Table 5.1 Statistical summary of lithium concentrations (mg/kg) from the National Geochemical Survey of Australia (NGSA) after Mobile Metal Ion[®] (suffix M) or Aqua Regia (suffix A) digestion and imputation (suffix i) of censored data. Abbreviations are as follows: TOS (top outlet sediments) coarse (Tc), TOS fine (Tf), BOS (bottom outlet sediments) coarse (Bc) and BOS fine (Bf).

	Li_Mi Tc	Li_Ai Tc,Tf,Bc,Bf	Li_Ai Tc	Li_Ai Tf	Li_Ai Bc	Li-Ai Bf
Count Numeric	1309	5252	1313	1313	1313	1313
Count Null	5	1	1	0	0	0
Minimum	0.0013	0.1	0.1	0.2	0.1	0.2
Maximum	0.788	88	67.4	88	56	86.5
Mean	0.0213	10.0258	7.6133	10.7689	8.8313	12.8896
Median	0.011	7.9	5.6	8.7	7.1	10.7
Variance	0.0020	74.9208	48.3117	73.6133	57.9204	103.7330
Standard Deviation	0.0446	8.6557	6.9507	8.5952	7.3601	9.5845
Kurtosis	124.7332	11.1749	8.8987	13.8274	7.3051	9.5845
Skewness	9.7067	2.4698	2.2331	2.6532	2.1653	2.3861
Coefficient of Variation	209.7940	86.3345	91.2964	79.8148	86.1773	79.0170
Robust Coefficient of Variation	87.6083	88.2054	99.2814	80.9467	85.6151	71.0125
Interquartile Range	0.013	9.4	7.5	9.5	8.2	10.25
Range	0.7867	87.9	67.3	87.8	55.9	86.3

From Table 5.1 it can be seen that the median MMI[®] value is three orders of magnitude lower than the median Aqua Regia concentration. Further, there is an increase in median lithium for the Aqua Regia digestion following the order Tc < Bc < Tf < Bf; in other words the deep or fine samples have higher lithium concentrations than their surface or coarse counterparts. Compared to the lithium values reported from Spain (median values of 18.4-22.3 mg/kg in sediments, topsoils and subsoils after Aqua Regia digestion), the lithium concentrations in Australia are two to three times lower (median values of 5.6-10.7 mg/kg in sediments after Aqua Regia digestion).

The statistical summary also shows elevated positive skewness for all datasets, especially MMI[®], indicating asymmetric or non-normal (non-Gaussian) distributions. This is illustrated in the histograms of Figure 5.9. Non-Gaussian distribution precludes the meaningful use of parametric (classical) statistics, such as mean, standard deviation or regression analysis, without suitable transformation (e.g., Filzmoser *et al.*, 2009). If the data are log-transformed (base 10), the distributions become closer to normal, as illustrated by the histograms of Figure 5.10 and the probability distribution curves of Figure 5.11. The probability distribution curves are particularly useful to demonstrate departures from Log-normality (non straight lines) and multiple populations (kinks). Figure 5.11 shows that even after Log transformation the distributions are not completely Log-normal (MMI[®] data still positively skewed; Aqua Regia data now negatively skewed) or unimodal. It is clear, however, that the Log transformation significantly improves the distribution, allowing further data analysis to proceed meaningfully.

With lithium data available in Australia from two different digestions, it is informative to compare the relationship between them. Even after Log-transformation, the correlation between MMI[®] and Aqua Regia lithium concentrations is visually poor. Figure 5.12 shows the scatter plot and the above robust regression line.

Robust regression (i.e., regression unaffected by outlying or unusual samples) between the two datasets yields the following equation:

Log Li Ai =
$$(0.5308 * Log Li Mi) + 1.7389 (R^2 = 0.2533; N = 1308)$$

The R^2 value of 0.25 (correlation coefficient r = 0.5) is significant at the p < 0.0001 level for the size of population at hand. Thus we can have confidence in stating that both lithium concentrations are positively correlated according to the above equation, but with scatter.

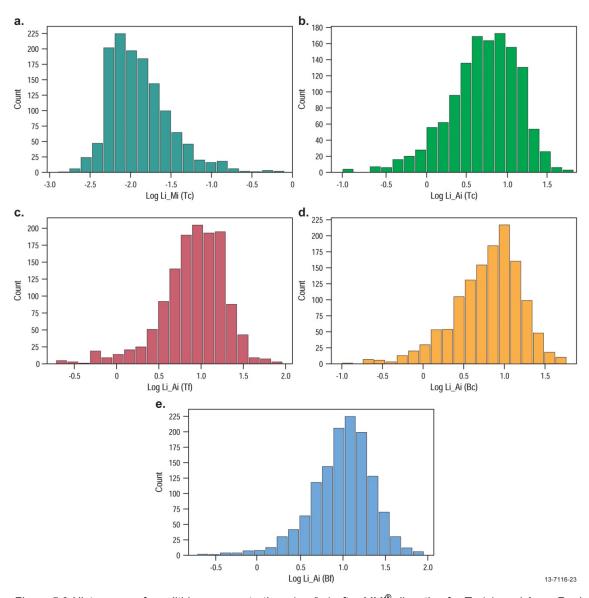


Figure 5.9 Histograms of raw lithium concentrations (mg/kg) after MMI^{\otimes} digestion for Tc (a), and Aqua Regia digestion for Tc (b), Tf (c), Bc (d) and Bf (e).

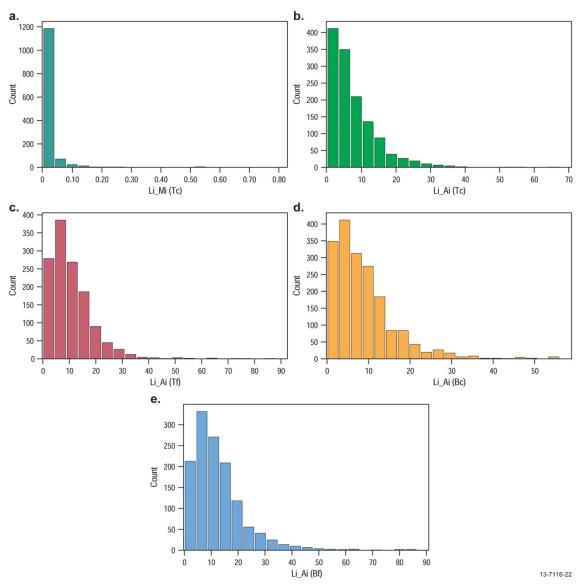


Figure 5.10 Histograms of Log(10)-transformed lithium concentrations (mg/kg) after MMl $^{\otimes}$ digestion for Tc (a), and Aqua Regia digestion for Tc (b), Tf (c), Bc (d) and Bf (e).

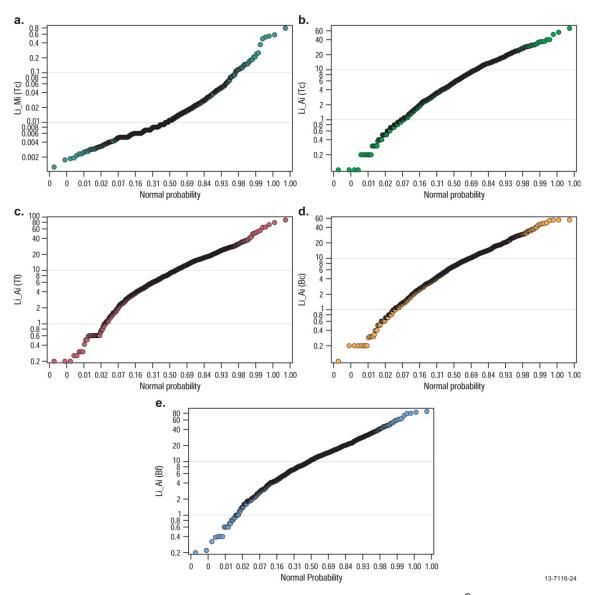


Figure 5.11 Probability distribution curves of lithium concentrations (mg/kg) after MMl^{\otimes} digestion for Tc (a), and Aqua Regia digestion for Tc (b), Tf (c), Bc (d) and Bf (e).

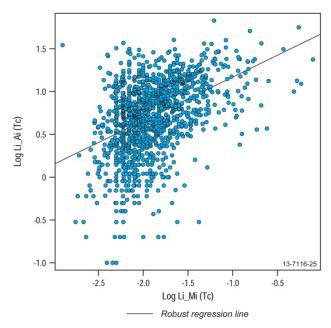


Figure 5.12 Scatter plot of Log Li by Aqua Regia versus Log Li by $\mathit{MMl}^{@}$ for Tc superimposed by a robust regression line.

Next, we investigate the spatial distribution of lithium concentrations in Australia based on the NGSA data. Figure 5.13 shows bubble plot maps of the various lithium datasets.

The most obvious distinction between the MMI[®] and the Aqua Regia maps is that the Eucla Basin (Great Australian Bight), straddling the coastal regions of southeastern Western Australia and southwestern South Australia, presents more elevated values (relative to the data range) in the MMI[®] than in the Aqua Regia concentrations. This area is underlain mainly by limestone of which the dominant constituents, carbonate minerals, can provide adsorbing surfaces for metals in arid soils (Jurinak and Bauer, 1956; Cavallaro and McBride, 1978; McBride, 1980; Dudley *et al.*, 1991).

All the lithium maps show elevated concentrations in areas where salt lakes are present, such as near the border between Western Australia and the Northern Territory (Lake Mackay, etc.), the southernmost Northern Territory (Lake Lewis, etc.), the Yilgarn Craton in south central Western Australia, eastern South Australia (Lake Eyre, Lake Gairdner, etc.) and western New South Wales and Victoria (Lake Tyrell, etc.).

In order to assess not the concentrations but the 'availability' of Li, we can calculate and plot the ratio of MMI® to AR Li (Li_Mi/Ai). A statistical summary of that variable is presented in Table 5.2. Li 'availability', as defined above, ranges from almost non-existent up to 14%. The Li_Mi/Ai ratio has a near unimodal Log-normal distribution (Figure 5.14a-c), apart from a few high values (> 0.025) that deviate from this behaviour. The map of Li_Mi/Ai (Figure 5.14d) shows that the regions of high Li 'availability' correspond to the Yilgarn Craton, much of eastern South Australia, the southernmost, westernmost and central Northern Territory, south and western Queensland, western New South Wales and Victoria and a few coastal areas. These commonly are regions where salt lakes occur (Figure 5.13), including coastal areas (though here the ratio is elevated probably because of low pH values, see Caritat *et al.*, 2011a).

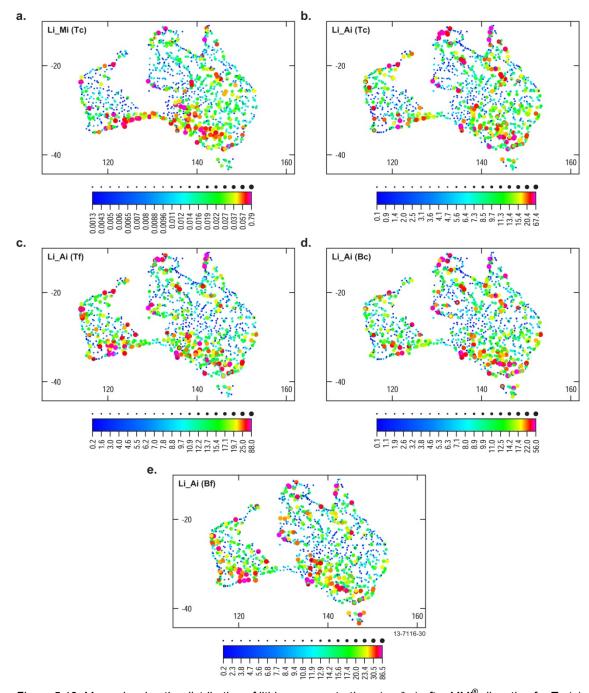


Figure 5.13. Maps showing the distribution of lithium concentrations (mg/kg) after MMI^{\otimes} digestion for Tc (a), and Aqua Regia digestion for Tc (b), Tf (c), Bc (d) and Bf (e).

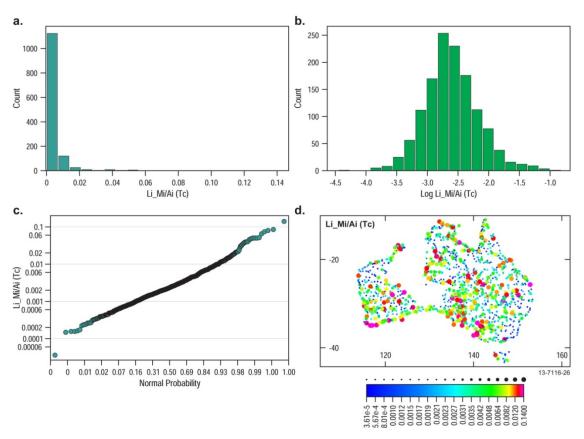


Figure 5.14 Histogram of raw Li_Mi/Ai ratio (a), histogram of Log(10)-transformed Li_Mi/Ai ratio (b), probability distribution curve of Li_Mi/Ai ratio (c), and map showing the distribution of the Li_Mi/Ai ratio (d).

Table 5.2 Statistical summary of Li_Mi/Ai ratio (dimensionless) from the National Geochemical Survey of Australia (NGSA) based on Mobile Metal Ion[®] (suffix M) and Aqua Regia (suffix A) digestion and imputation (suffix i) of censored data.

Sample Type	Li_Mi/Ai Tc
Count Numeric	1308
Count Null	6
Minimum	3.61 x 10 ⁻⁵
Maximum	0.14
Mean	0.0044
Median	0.0023
Variance	6.53 x 10 ⁻⁵
Standard Deviation	0.0081
Kurtosis	86.3849
Skewness	7.5879
Coefficient of Variation	181.8536
Robust Coefficient of Variation	101.0858
Interquartile Range	0.0032
Range	0.1400

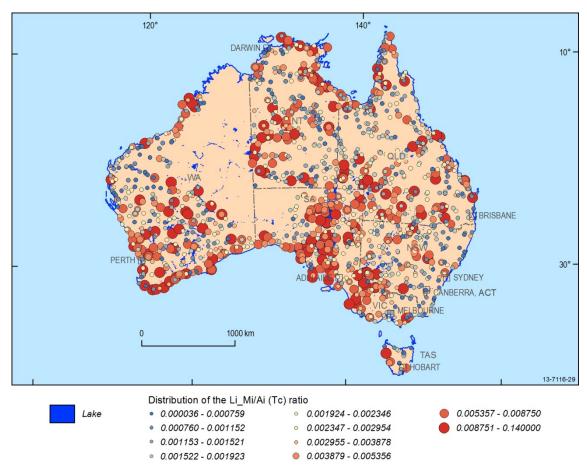


Figure 5.15 Map showing the distribution of the Li_Mi/Ai ratio overlain on lake distribution.

5.3.2 Conclusions from the National Geochemical Survey of Australia dataset

Lithium in surface and near-surface transported regolith in Australia is present at low concentrations (median values of 5.6-10.7 mg/kg after Aqua Regia digestion). These levels are two to three times lower than in Spain for example. The median MMI[®] value is three orders of magnitude lower than the median Aqua Regia concentration. Lithium concentrations after Aqua Regia digestion are higher in the sub-surface than at the surface, and in the fine grain-size fraction relative to the coarse.

The distribution of lithium is heavily skewed and non-unimodal, for both the Mobile Metal Ion[®] and Aqua Regia datasets. Log transformation of the data improves the distribution (closer to normal or Gaussian).

Maps of lithium distribution appear to show more elevated concentrations in southern and central Australia, regions where salt lakes tend to occur. The map of lithium 'availability' (ratio of Li MMI[®]/Li Aqua Regia) also highlights these areas, but perhaps with greater contrast. Areas of elevated lithium 'availability' include: Yilgarn Craton, much of eastern South Australia, the southernmost, westernmost and central Northern Territory, south and western Queensland, and western New South Wales and Victoria. These areas tend to correspond to regions were lakes are common in Australia.

5.4 Critical features of lithium, boron and potassium salt lake systems

S. Jaireth, E.N. Bastrakov, A.A. McPherson and J.R. Wilford

Critical features of salt lake systems prospective for lithium, boron and potash are described in Chapter 4 . A preliminary comparison of mineralised salt lakes in the Andes, Nevada, Tibet and Turkey shows that the geological setting of economic salt lakes is characterised by the presence of (a) closed or semi-closed salt lakes in basins surrounded by an uplifted highland area (an altitude difference of greater than ~ 1000 m. This ensures an active hydrogeological system of groundwater flow; (b) geothermal systems providing not only additional sources of boron and lithium but also enabling the establishment of active convection between shallow groundwater (salt lake brines and associated inflow) and deeper geothermaly heated groundwater; and of (c) felsic to intermediate volcanic containing volcanic glass which provides a readily leachable source of lithium, potassium, and boron.

The above three critical features have not been mapped in regions with salt lake systems in Australia, which limits potential of these systems to form economic grade concentration of lithium and boron. The favourability of salt lake systems in Australia is assessed using two critical features:

- Presence of a leachable source of lithium, boron and potassium. Volcanic glass in felsic and intermediate volcanics is thought to be the best leachable source of lithium and boron. The presence of volcanic glass is also important because most economic brines are known to have formed in less than ~ 100 ka to 150 ka (see Chapter 4 for discussion). Most salt lakes in Australia are located within regions where source rocks are much older (Archean and Proterozoic) and hence volcanic glass in them has not been preserved. In these settings, the presence of evaporate sequences and salt diapirs may be an important source of potassium and other elements.
- Active hydrogeological connectivity between leachable source of lithium, boron and potassium and salt lakes.

The selection of potentially favourable salt lake systems for more detailed studies has been carried out in two stages. In the first stage broad regions of salt lake systems were selected based on above mentioned criteria. In the second stage available groundwater data were used to comment on their potential to generate enriched brines by plotting the data on lithium (boron or potassium) vs chloride-diagrams and comparing them with the evaporative trends of groundwater data from mineralised regions (Andes, Nevada, China and Turkey).

5.4.1 Datasets used for the favourability analysis of Australian salt lakes

The favourability of salt lake systems to generate lithium, boron and potassic brines and to form uranium-bearing calcretes is assessed using a number of national- and regional-scale datasets. A complete list of the datasets used in the favourability analysis of Australian salt lakes is given in Appendix A.

5.4.2 First stage selection

The selection was based on the presence of favourable source rock in the catchment containing salt lakes. The following datasets used for the selection (see Appendix A for details):

- Concentration of lithium, boron, and potassium in rocks from Ozchem (Appendix A.1.3). An
 average value of lithium, boron and potassium was estimated for each catchment and assigned
 to the salt lake located in the catchment.
- Concentration of lithium, boron, and potassium in overbanks sediments (NGSA survey). See section 5.3 for details.
- Concentration of lithium, boron and potassium in groundwater dataset. Mean values of lithium, boron, and potassium in a catchment were calculated and assigned to the lake located in the catchment.
- In many salt lake systems evaporites (outcropping as well as undercover) are known to provide significant quantities of potassium to waters inflowing into salt lakes. For instance in the Karinga Lake system potassium is thought to be sourced from pre-existing evaporites in the basement rocks (Rum Jungle Resources, 2012). In this study we have used the distribution of evaporites and evaporite-bearing rock units from Geoscience Australia's 1:1 million surface geology database.

The concentrations of lithium, boron and potassium assigned to salt lakes were derived from three datasets: Ozchem (for whole-rock analysis); NGSA samples in the catchments (catchment outlet sediments); and groundwater datasets. The mean values of concentration were derived by averaging of values in samples (separately for each of the three datasets) located in the catchment. These mean values were assigned to salt lakes located in the catchment. In those cases where values from the three datasets overlapped, the highest value was assigned to the overlapping part of the salt lake. Hence the maps delineating favourable salt lake systems (Appendix B) do not show concentrations of lithium, boron and potassium in the salt lakes but represent concentrations of these elements in rocks, overbank sediments and groundwaters in the catchment.

More detailed hydrogeological studies are essential to determine precisely the nature of hydrogeological connection between the source rocks of lithium, boron and potassium in the catchment and the salt lake in the catchment. In this study we have assumed that most salt lakes are predominantly fed by groundwaters controlled by aquifers in the palaeovalleys. Hence the shape, size and nature of infill sediments in the channels would largely determine the quantity of lithium, boron and potassium inflowing into salt lake systems.

5.4.3 Second stage selection

Second stage selection is carried out by analysing the chemistry of groundwater data in proximity to salt lake systems delineated in the first stage. For each region of selected salt lake systems concentrations of lithium, boron and potassium in groundwaters are plotted against concentration of chloride ions. The significance of these plots has been described in Chapter 4. These plots help to compare evaporative trends of groundwater feeding Australian salt lake systems with the groundwaters from salt lakes containing economic concentrations of these elements in brines outside Australia (e.g. Andes, Nevada, China and Turkey). The evaporative trends can also provide rough estimates of the maximum concentrations of lithium, boron and potassium that can be achieved by evaporation of lake waters.

5.4.4 Salt lake systems favourable for lithium, boron and potassium

Salt lake systems favourable for lithium, boron and potassium were identified from the above two stage selection process. The following regions were identified as having salt lakes with the highest favourability for these elements. However, due to the non-uniform national coverage of the available datasets, there may be other regions that have not yet been identified.

In the following sections, lithium and boron are considered together due to the similarity of their mineral systems criteria (see Tables 4.2 and 4.3). Potassium is considered separately because of differences in Source criteria (Table 4.4) and valley and playa-type, calcrete-hosted uranium systems will be considered in Section 5.5 due to the many differences in criteria for this mineral system (Table 4.6).

5.4.4.1 Lake Woods Northern Territory

Major lakes in the area: These are Lake Woods, Tarrabool Lake, and Lake Sylvester (Figure 5.16).

Hydrogeological connectivity: No major palaeovalleys have yet been mapped in the area (see inset on Map 2). The salt lakes are thought to be fed predominantly by surface inflow and from groundwater sampled in several bores.

Lithium and boron in the catchments: Currently there are no available data on the concentrations of lithium and boron in groundwater in the catchments. Therefore, the economic potential of these elements cannot be assessed.

Maximum concentration of potassium in the catchments: The catchments to these lakes contain up to 1.6 wt. % K₂O, with potassium possibly sourced form evaporites in the Proterozoic Namerinni and Renner groups (Figure 5.16). These evaporites crop out along the eastern margin of Lake Woods. Evaporitic units are also present in close proximity to Tarrabool Lake and Lake Sylvester.

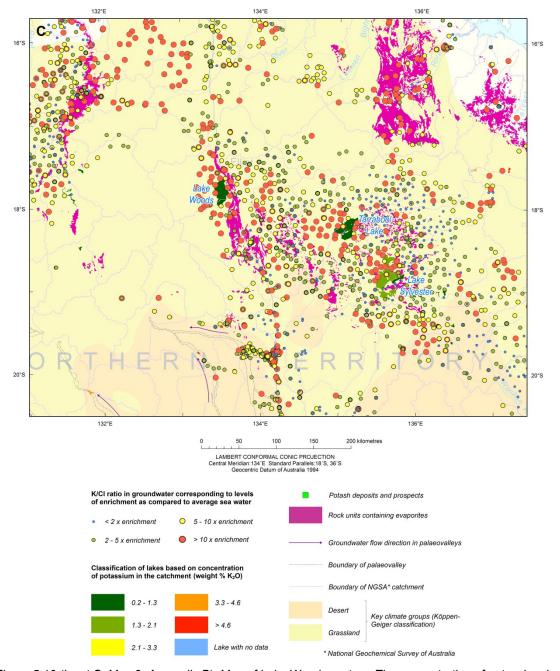


Figure 5.16 (Inset C, Map 3, Appendix B). Map of Lake Woods system. The concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. Potassium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in K/Cl compared to an evolved sea water of the same chloride concentration.

K/Cl ratio of groundwaters: A large number of bore waters record K/Cl values above the 10 times enrichment threshold (Figure 5.17). These values show that these waters are capable of forming economic-grade concentrations of potash in the salt lakes. Bore waters in proximity to Lake Woods and Tarabool Lake show K/Cl values greater than 50 times enrichment threshold. These values also demonstrate a close spatial association with outcropping evaporitic rocks suggesting that potassium and other salts could have been derived from these rocks.

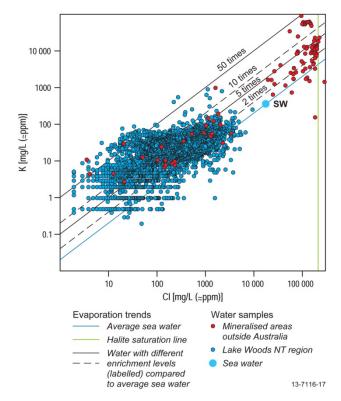


Figure 5.17 K-Cl plots of groundwaters in salt lake systems in Lake Woods region NT. Red dots and lines represent groundwater and evaporation trend respectively from salt lakes with economic-grade concentration of potassium outside Australia. Large blue dot and line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of lake systems near Lake Woods (inflow and lake waters). Sloping lines show enrichment in K/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. Green vertical line represents the chloride concentration at which water becomes saturated with halite (NaCl).

Conclusions: The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for the formation of salt lakes with economic concentrations of potash. More detailed geochemical analysis of the lake and groundwater is required in order to assess the potential for lithium and boron. Evaporites in the Namerinni and Renner groups are possible sources of potassium and other salts in the groundwater but we need to more accurately map their distribution (in outcrop as well as under cover). The hydrogeological setting of these lake systems is still poorly understood.

5.4.4.2 Central Western Northern Territory

Major lakes in the area: Lake Mackay, Lake MacDonald, Lake Hopkins, Lake Bennett, Lake Lewis, Murphy's Lake, Lake Amadeus, and Lake Neale are the main lakes in this region (Figure 5.18).

Hydrogeological connectivity: Most salt lakes in the area are located within Cenozoic palaeovalleys, suggesting that the lakes may be fed predominantly by groundwaters flowing through the palaeochannels (English *et al.*, 2012). The infill sediments in the Wilkinkarra and Kintore palaeovalleys, spatially associated with Lake MacDonald and Lake Bennett, are dominated by weathered and oxidised sandy alluvial facies, interbedded with fine-grained sediments such as clay and silt (English *et al.*, 2012).

Lithium and boron in the catchments: Currently there are no available data on the concentrations of lithium and boron in groundwater in the catchments. Therefore, the economic potential of these elements cannot be assessed.

Maximum concentration of potassium in the catchments: The maxium concentration of potassium in the catchements is 5.6 wt. % $\rm K_2O$, and the potassium is possibly sourced from felsic rocks in the Arunta region (Figure 5.18). It can also be sourced from evaporites in the Bitter Springs Formation (both outcropping as well as under cover). A number of salt lakes (such as Lake MacDonald, Lake Hopkins, and Lake Neale) lake are located in close proximity to the outcropping Bitter Springs Formation.

K/Cl ratio of groundwaters: A large number of bore water geochemical data are available in the area. A large number of analysis show K/Cl values greater than 50 times enrichment threshold (Figure 5.19). Some values with greater than 50 times enrichment plot in areas in proximity to salt lakes such as Lake Lewis. The K/Cl data illustrate that these waters can generated economic-grade concentrations of potash in most salt lakes in the area. Economic-grade concentrations have been reported from both Lake Mackay and Murphy's Lake. Rum Jungle Resources is actively exploring for potash deposits in the area (Karinga Creek Potash project located near Murphy's Lake).

Conclusions: The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for the formation of salt lakes with economic concentrations of potash. Some salt lakes (such as Lake Mackay, Lake Lewis and Murphy's Lake) have been drilled and sampled but a large number still remain unexplored. More information about the nature of lake sediments and waters (lithology and geochemistry) will help assessing their potential to form potash deposits. More detailed geochemical analysis of the lake and groundwater is required in order to assess the potential for lithium and boron. The hydrogeochemistry of groundwaters feeding some of the major salt lakes (such as Lake Mackay, Lake MacDonald and Lake Hopkins) in the area remains largely unknown. If evaporites in the Bitter Springs Formation are acting as sources of potassium and other salts, it is important to more accurately map their distribution (in out crop as well as under cover). Although some work has been carried out on the shape, size and evolution of palaeovalleys in the area (English *et al.*, 2012) more work is needed to understand hydrogeological setting of salt lake systems in the area.

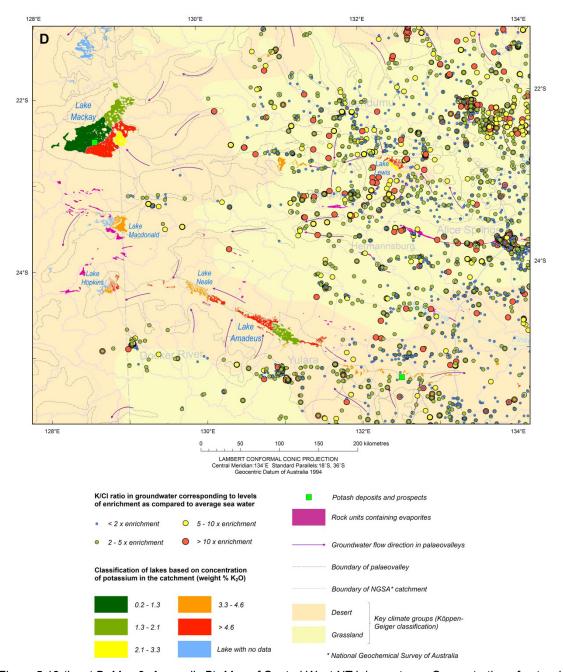


Figure 5.18 (Inset D, Map 3, Appendix B). Map of Central West NT lake systems. Concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. potassium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in K/Cl compared to an evolved sea water of the same chloride concentration.

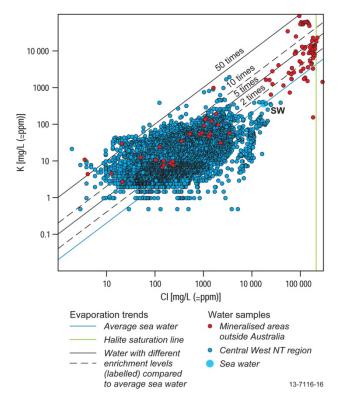


Figure 5.19 K-Cl plots of groundwaters in salt lake systems in Central West NT. Red dots and line represent groundwater and evaporation trend respectively from salt lakes with economic-grade concentration of potassium outside Australia. Large blue dot and blue line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of central lake systems in central-west NT (inflow and lake waters). Sloping lines show enrichment in K/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. Green vertical line represents the chloride concentration at which water becomes saturated with halite (NaCl).

5.4.4.3 Lake Disappointment

Major lakes in the area: Major lakes in this region include Lake Disappointment, Lake Dora, Lake Waukarlycarly, and Ten Mile Lake (Figure 5.20). Lake Disappointment is one of the largest potash prospects in Australia (Reward Minerals, 2012c) but very little is publicly known about its lake and groundwater geochemistry. Potash occurs in the lake sediments as well as in the brine (see Section 1.2.3 for details).

Hydrogeological connectivity: A well-developed system of Cenozoic palaeovalleys has been mapped in the region and all salt lakes are located within them (Bell *et al.*, 2012). It is likely that salt lakes are fed by groundwaters in the aquifers within these palaeovalleys. The palaeovalleys are often filled with tillitic clay, gravel and conglomerate (Bell *et al.*, 2012).

Lithium and boron in the catchments: Currently there are no available data on the concentrations of lithium and boron in groundwater in the catchments. Therefore, the economic potential of these elements cannot be assessed.

Maximum concentration of potassium in the catchments: The catchments to salt lakes in this region contain up to 5.8 wt. % K₂O (Figure 5.20). The bulk of the potassium is possibly sourced from Proterozoic felsic rocks in the Rudall Complex and Mount Crafton and associated granites. Minor evaporites are also present in the Proterozoic Wonyulgunna Sandstone which locally crops out in the

area. A number of salt diapirs (Madley and Woonlnough) have been mapped in the Officer Basin sediments and may be present (undercover) in proximity to salt lakes in the area (Carlsen *et al.*, 1999)

K/Cl ratio of groundwaters: K/Cl values of bore water cluster close to the 2 times the enrichment trend (Figure 5.21), favourable for generating economic grade concentrations of potassium (Figure 5.21). Bore waters with higher K/Cl values show spatial association with evaporite-bearing units (see inset on Map 3, Appendix B).

Conclusions: The above discussion is based on very limited hydrogeochemical data. There are no hydrogeochemical data available in the proximity of Lake Disappiontment (the largest known potash prospect in Australia). More comprehensive groundwater data are essential in order to assess the potential of salt lakes in this area for potash, lithium and boron. It is also important to determine more precisely the hydrogeological setting of these lake systems. More information about the nature of lake sediments and waters (lithology and geochemistry) is also needed. A number of under cover salt diapirs have been mapped in the Officer Basin not far from the salt lakes (see Section 2.3.3.6). It is critical to map the distribution of the salt diapirs because potassium and perhaps also lithium and boron may be sourced from them.

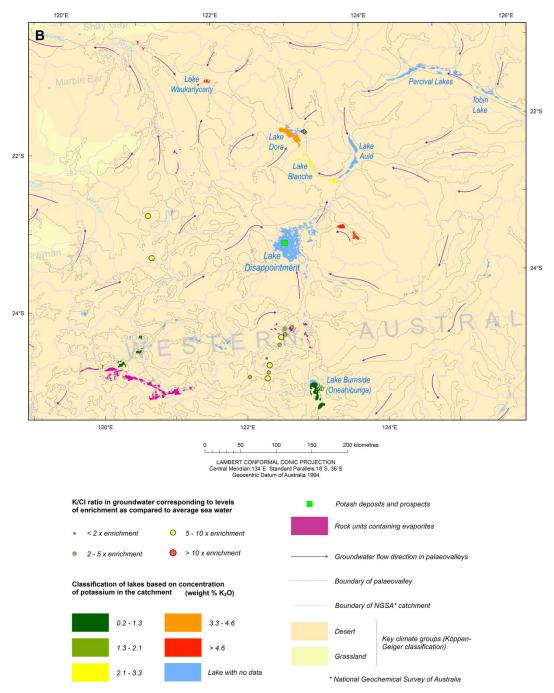


Figure 5.20 (Inset B, Map 3, Appendix B). Map of lake systems in near Lake Disappointment, WA. Concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. Potassium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in K/Cl compared to an evolved sea water of the same chloride concentration.

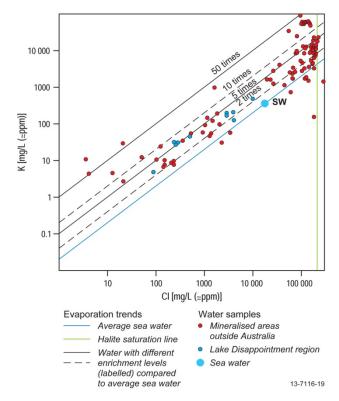


Figure 5.21 K-Cl plots of groundwaters in salt lake systems in lake systems near the Lake Disappointment region. Red dots and lines represent groundwater and evaporation trend respectively from salt lakes with economic-grade concentration of potassium outside Australia. Large blue dot and line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of lake systems near Lake Disappointment (inflow and lake waters). Sloping lines show enrichment in K/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. Green vertical line represents the chloride concentration at which water becomes saturated with halite (NaCl).

5.4.4.4 North East Yilgarn

This region contains a number of large non-perennial salt lakes such as, Lake Nabberu, Lake Way, Lake Darlot, Lake Irwin, Lake Carey, Lake Carnegie, Lake Raeside, Lake Mason, Lake Barlee, Lake Noondie and Lake Austin (Figure 5.22).

Hydrogeological connectivity: Most salt lakes in the area are located within Cenozoic palaeovalleys, indicating that the lakes are fed predominantly by groundwater flowing through the palaeochannels. In addition to calcretes, the channels are filled with alluvial clay-quartz units (Butt *et al.*, 1984).

Geothermal and mound springs: No geothermal or mound springs have been reported in the area. Bore water temperatures in some bores reach up to 40°C (Dickson and Giblin, 2006).

Maximum concentration of lithium and boron in the catchments: Archean felsic and intermediate intrusive and volcanic rocks metamorphosed up to greenschist and amphibolite facies are enriched in lithium and boron to values of 52 mg/kg and 29 mg/kg, respectively (Figures. 5.22, 5.23). However it is not clear how much lithium and boron is readily leachable.

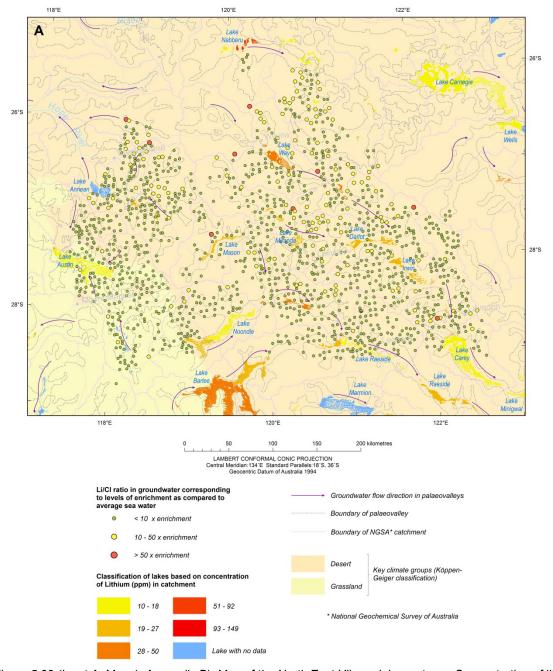


Figure 5.22 (Inset A, Map 1, Appendix B). Map of the North East Yilgarn lake systems. Concentration of lithium in a lake represents the average concentration of boron in rocks in the catchment in which the lake is located. Lithium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in Li/Cl compared to an evolved sea water of the same chloride concentration.

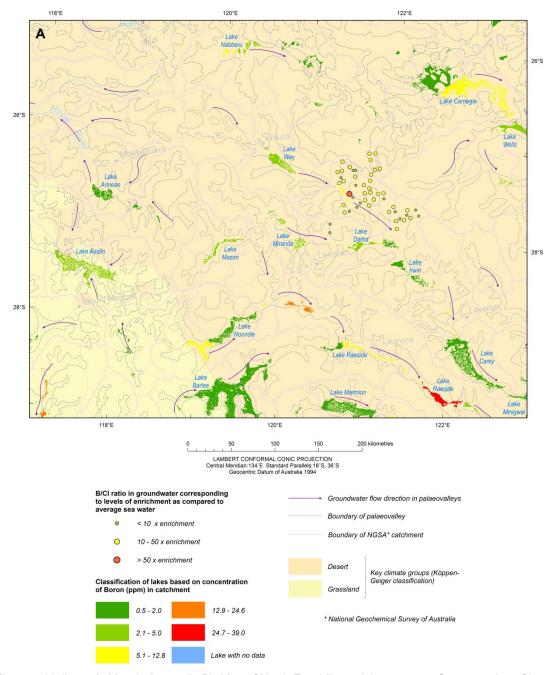


Figure 5.23 (Inset A, Map 2, Appendix B). Map of North East Yilgarn lake systems. Concentration of boron in a lake represents the average concentration of boron in rocks in the catchment in which the lake is located. Boron and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in B/Cl compared to an evolved sea water of the same chloride concentration.

Li/Cl and B/Cl ratio of groundwaters: A large number of bore water geochemical data are available in the area. More than 90% of analyses show Li/Cl values below 50 times the enrichment threshold (Figure 5.24a). In a few bore waters the Li/Cl ratios are higher. Evaporation of these waters in salt lakes may be able to form economic-grade concentrations of lithium. Most B/Cl values cluster around 10 times enrichment threshold trend (Figure 5.24b). These relatively higher values are concentrated in proximity to Lake Maitland. The evaporation trend of these bore waters in salt lakes indicates that they have the potential to generate economic-grade concentrations of boron.

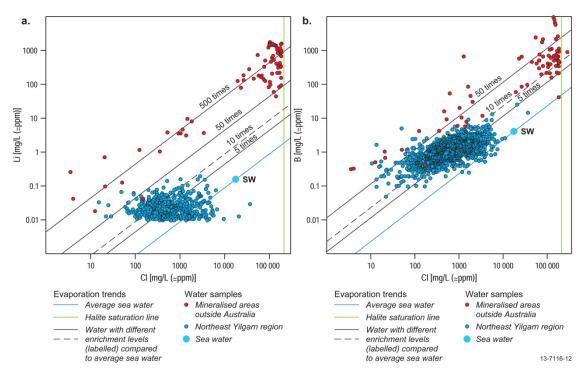


Figure 5.24a and b. Li-Cl (a) and B-Cl (b) plots of groundwaters in North East Yilgarn lake systems. Red dots and lines represent groundwater and evaporation trends respectively from salt lakes with economic-grade concentration of lithium and boron outside Australia. Large blue dot and line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of lake systems in North East (inflow and lake waters). Sloping lines show enrichment in Li/Cl and B/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. Green vertical lines represents the chloride concentration at which water becomes saturated with halite (NaCl).

Maximum concentration of potassium in the catchments: The highest potassium concentration in the catchements was 3.4 wt. % K₂O (Figure 5.25). Potassium is mostly likely to be sourced from Archean felsic and intermediate intrusive and volcanic rocks as described above.

K/Cl ratio of groundwaters: The K/Cl ratio of bore water clusters is close to two times the enrichment trend (Figure 5.26). On evaporation, some of these values may produce economic grade concentrations of potassium. In proximity to Lake Maitland, K/Cl values showing more than 10 times enrichments are recorded.

Conclusions: The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for the formation of salt lakes enriched in potash and perhaps also lithium and boron. Although a significant number of bore waters have been analysed in the area, a more rigorous check is required to determine the quality of groundwater data. It is also important to understand the hydrogeological setting of the salt lake system (lithology and geochemistry of sediments infilling palaeochannels) and gather more information on lithology of lake sediments and geochemistry of lake waters.

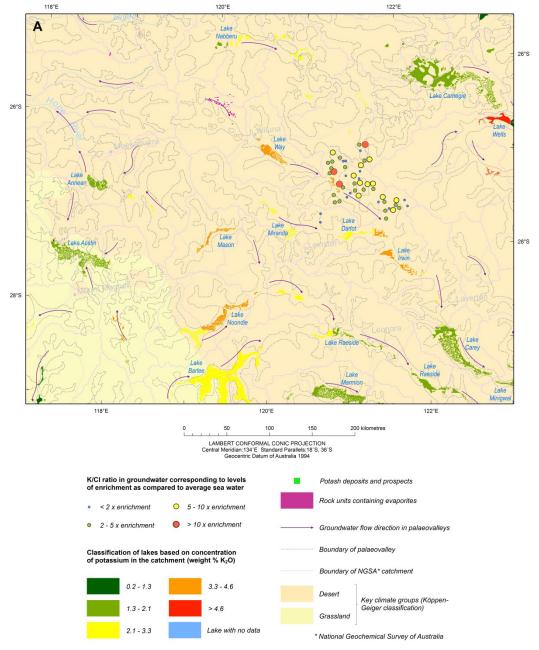


Figure 5.25 (Inset A, Map 3, Appendix B). Map of lake systems in North East Yilgarn. Concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. Potassium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in K/Cl compared to an evolved sea water of the same chloride concentration.

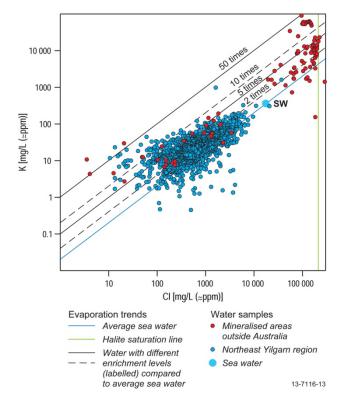


Figure 5.26 K-CI plots of groundwaters in salt lake systems in lake systems in North East Yilgarn region. Red dots and line represent groundwater and evaporation trends, respectively, from salt lakes with economic-grade concentration of potassium outside Australia. Large blue dot and line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of lake systems in North East Yilgarn (inflow and lake waters). Dashed red lines show enrichment in K/CI (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. Green vertical line represents the CI concentration at which water becomes saturated with halite (NaCI).

5.4.4.5 South East Yilgarn

The region contains a number of large non-perenial salt lakes such as, Lake Cowan, Lake Deborah, Lake Dundas, Lake Gilmore, Lake Hope, Lake Johnson, and Lake Lefroy, Lake Moore and Lake Yindarlgooda (Figure 5.27). This region also hosts the Lake Chandler potash deposit (see Chapter 1).

Hydrogeological connectivity: Most salt lakes in the area are located within Cenozoic palaeovalleys, formed during Jurassic to Middle Eocene incision, suggesting that the lakes may be fed predominantly by groundwaters flowing through the palaeochannels (Bell *et al.*, 2012; Bowen and Benison, 2009). Palaeovalley sediments consist of Eocene lignites, siltstones, sandstones and marine limestones formed in at least two marine transgressions (Clarke *et al.*, 1996). River flow in the palaeodrainage is thought to have ended in the late Eocene caused by the uplift of the Darling Range in the western part of the Yilgarn Craton. The uplift dammed westward flow of the palaeodrainage which led to the formation of individual closed lake basins from the accumulation of surface waters (Bowen and Benison, 2009).

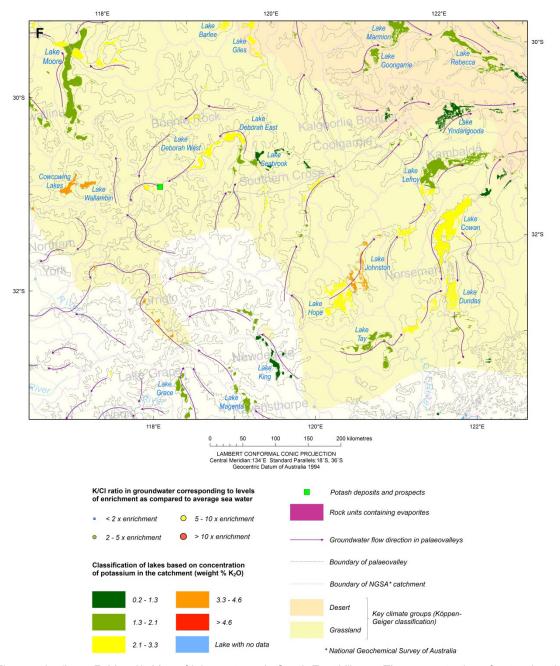


Figure 5.27 (Inset F, Map 3). Map of lake systems in South East Yilgarn. The concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. No potassium or chloride concentrations in groundwaters are shown because reliable hydrogeochemical data for bore water in the region was not available at the time this report was compiled.

Maximum concentration of lithium and boron in the catchments: Unfortunately, no comment can be made about the concentration of lithium and boron in this region at present due to lack of publicly available data.

Maximum concentration of potassium: Catchments to lakes in this region have maximum concentrations of 3.7 wt. % K₂O. Potassium is mostly likely to be sourced from Archean felsic and intermediate intrusive and volcanic rocks which have been metamorphosed up to greenschist and amphibolite facies.

K/Cl ratio of groundwaters: The chemistry in the region is virtually unknown due to a lack of publicly available data. However major ion concentrations in waters from some salt lakes (8 out of 65 salt lakes) suggests K/Cl ratios in some lakes show some enrichment compared to the mean sea water (Jankowski and Jacobson, 1989; Bowen and Benison, 2009).

Conclusions: The preliminary analysis shows that this region has potential to host brine- and alunite-type potash mineralisation. This is supported by the fact that salt lakes in this region are generally more saline than the lakes in northeast Yilgarn with TDS values in some lakes reaching values greater than 200,000 mg/L (Jankowski and Jacobson, 1989; Bowen and Benison, 2009). Some salt lakes are relatively more acidic than the lakes in northeast Yilgarn with pH in some lakes reaching values of four and less (Jankowski and Jacobson, 1989; Bowen and Benison, 2009) indicating conditions favourable for forming alunite-type potash mineralisation. However more detailed work on the hydrology and hydrogeochemistry of salt lake systems can provide significant information to assess their potential to form economic-grade concentrations of potash.

5.4.4.6 Lake Frome and Lake Eyre regions

The Lake Frome salt lake system consists of four major salt lakes (Lake Frome, Lake Callabonna, Lake Blanche and Lake Gregory, Figure 5.28) and is described in detail in Chapter 6.

Hydrogeological connectivity: The non-perennial lake system is fed by surface waters and groundwaters. The groundwater flow is dominantly controlled by Paleogene and Neogene palaeovalleys filled by sands and shales which locally contain abundant plant material (Roach, 2012). Some infill sediments show high values of lithium (up to 250 mg/kg; ERO Mining, 2011).

Geothermal and mound springs: The Paralana Hot Spring System is located at the eastern margin of the Mount Painter Inlier (Brugger *et al.*, 2005). Temperatures up to 60°C have been measured in the hot spring pool (Brugger *et al.*, 2005). Several mound springs are reported in the Lake Frome region. These are interpreted to be related to groundwaters in the Great Artesian Basin (Sheard *et al.*, 1995) and discharge waters with temperatures ranging between 20°C and 46°C.

Maximum concentration of lithium and boron in the catchments: These are 20 mg/kg and 1.25 mg/kg, respectively (Figures 5.28, 5.29). Salt lakes in the Frome system are located in catchments which contain felsic rocks with up to 20 mg/kg lithium. Mount Painter and Mount Babbage inliers, which are located to the west and southwest of the lakes, are known to contain an abundance of felsic and intermediate intrusive and volcanic rocks for which no lithium values have yet been reported. It is likely that these rocks may have even higher concentrations of lithium. Lithium-rich felsic and intermediate intrusive and volcanic rocks are located to the south and east of the lake system (units in the Olary Block and especially the Benagerie Volcanics). The rocks are of Proterozoic and Paleozoic ages and have been largely deformed and metamorphosed, hence volcanic glass in the volcanics (the most readily leachable source of lithium) has been destroyed.

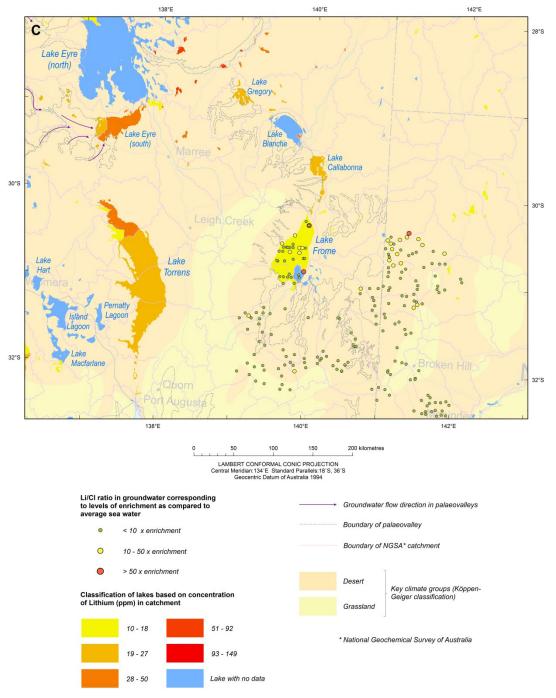


Figure 5.28 (Inset C, Map 1, Appendix B). Map of the Lake Frome salt lake system. The concentration of lithium in a lake represents the average concentration of lithium in rocks in the catchment in which the lake is located. Li/Cl ratios in groundwaters show different levels of enrichment compared to an evolved sea water of the same chloride concentration.

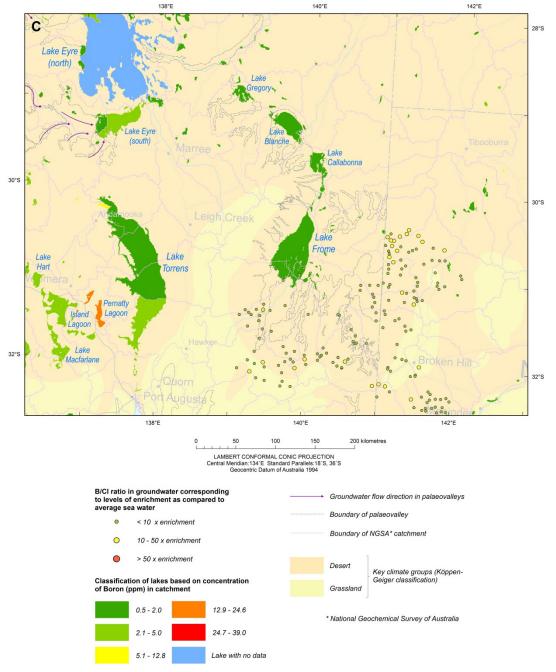


Figure 5.29 (Inset C, Map 2, Appendix B). Map of the Lake Frome region. The concentration of boron in a lake represents the average concentration of boron in rocks in the catchment in which the lake is located. Boron and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in B/Cl compared to an evolved sea water of the same chloride concentration.

Li/Cl and B/Cl ratio of groundwaters: Limited lithium and boron analysis of available groundwater in the salt lakes and of the groundwaters feeding the lakes show that most values of Li/Cl ratio fall below the 50 times enrichment (compared to mean sea water) trend (Figures 5.30a, b) The highest values (> 50 times enrichment) are recorded in groundwaters discharging from known mound springs and may be related to their relatively higher temperatures. Evaporative trends of these waters indicate that maximum concentration reached (at halite-saturation shown by the green vertical line on Figure 5.30a) will be ~ 100 mg/kg lithium or less.

For boron, a large number of sites report groundwaters showing enrichment between 10 times to 50 times compared to mean sea water (dots plotting above red dashed line labelled 10 in Figure 5.30b). The evaporation trend-line shows that some of these waters on evaporation can reach concentrations similar to those observed in many salt lake systems with economic grade concentrations.

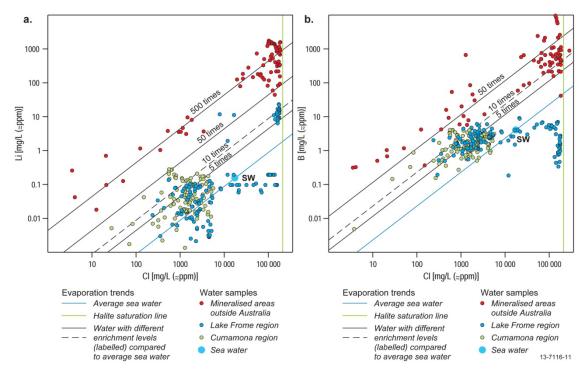


Figure 5.30a and b. Li-Cl (a) and B-Cl (b) plots of groundwaters in Lake Frome region lake systems. The red dots and line represent groundwater and evaporation trend respectively from salt lakes with economic-grade concentration of lithium and boron outside Australia. The large blue dots and lines represent composition and evaporation trend respectively of average sea water. Blue and green dots represent groundwater of Lake Frome and Curnamona systems (inflow and lake waters). Sloping lines show enrichment in Li/Cl and B/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. The green vertical lines represents the chloride concentration at which water becomes saturated with halite (NaCl).

Maximum concentration of potassium in the catchments: Maximum K_2O concentrations of rocks in the catchment are 5.8 wt.%. The bulk of the potassium is possibly sourced from felsic rocks in the Mount Painter and Mount Babbage inliers and in the Curnamona province (Figure 5.31).

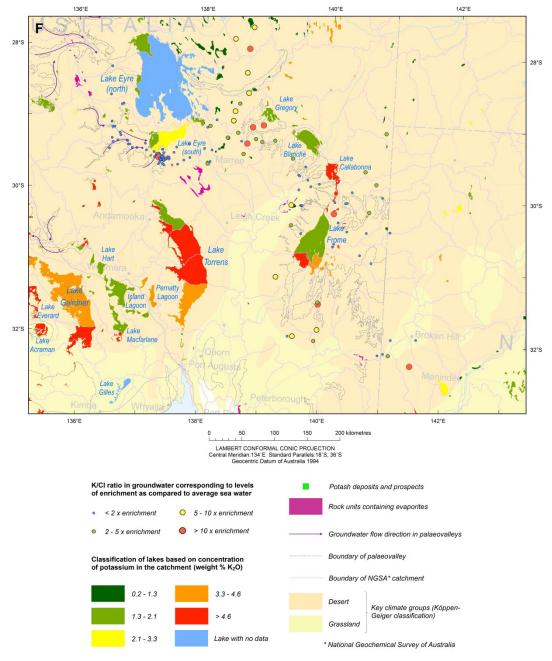


Figure 5.31 (Inset F, Map 3, Appendix B). Map of Lake Frome and Lake Eyre systems. The concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. Potassium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in K/Cl compared to an evolved sea water of the same chloride concentration.

K/Cl ratio of groundwaters: K/Cl values of bore water feeding the Lake Frome system (which includes bore water from Curnamona region) are generally lower than the seawater trend (Figure 5.32). Some values, however, show higher values favourable for generating economic-grade concentrations. Out of the two sites with high K/Cl value, the one at the northeastern end of Lake Frome samples water of the Great Artesian Basin aquifer (well depth of ~ 400 m). The second site in the Curnamona region represents a sample of shallow (palaeovalley aquifer) groundwater.

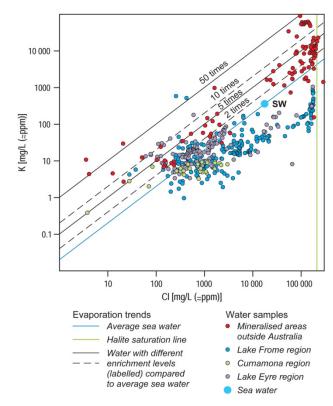


Figure 5.32 K-Cl plots of ground waters in salt lake systems in Lake Frome and Lake Eyre systems. Red dots and lines represent groundwater and evaporation trends, respectively, from salt lakes with economic-grade concentration of potassium outside Australia. Large blue dot and line represent composition and evaporation trend respectively of average sea water. Dots in other colours represent groundwater of Lake Frome, Lake Eyre and Curnamona systems (inflow and lake waters). Sloping lines show enrichment in K/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. Green vertical line represents the chloride concentration at which water becomes saturated with halite (NaCl).

Evaporation of such highly potassium-enriched groundwater can form economic grade concentrations. A similar observation can be made for bore waters in proximity to Lake Eyre. Relatively high potassium concentrations around Lake Eyre are recorded in waters of the Great Artesian Basin aquifers. In comparison, groundwaters from shallower bores have much lower K/Cl values. Groundwater (with high K/Cl values greater than five times the enrichment threshold) can, on evaporation in salt lakes, attain concentrations well above 1 wt. % potassium. The K/Cl values are low compared to those observed in the Lake Woods area and in the salt lakes in the Central and Western NT (compare with Figures 5.16 and 5.18). This is possibly explained by the presence of evaporates enriched in potassium in the latter two areas.

Conclusions: The Lake Frome and Lake Eyre regions are favourable for generating economic concentrations of potassium and/or lithium and/or boron. An assessment with higher certainty will require the acquisition of more reliable data such as: the chemical analysis of groundwater including mound springs; hydrogeological setting of the salt lake system (lithology and geochemistry of sediments infilling palaeochannels); lithology of lake sediments and geochemistry of lake waters.

5.4.4.7 Central Gawler

This region contains a number of large non-perennial salt lakes including Lake Torrens, Pernaty Lagoon, Island Lagoon, Lake Gairdner, Lake Harris, Lake Acraman, Lake Gilles, Lake Younghusband and Lake Labyrinth (Figure 5.33).

Hydrogeological connectivity: A well-developed system of Cenozoic palaeovalleys has been mapped in the Central Gawler region (Hou et al., 2013) and it is likely that salt lakes are fed by groundwater in the aquifers within these palaeovalleys. Cenozoic sediments within palaeovalleys are dominated by sands, shales (locally enriched in lignitic material) and calcareous sediments (Hou et al., 2013). Lake Gairdner and Lake Torrens likewise are dominantly fed by groundwaters with little surface water influence (Bowler, 1986a).

Geothermal and mound springs: No geothermal or mound springs have been reported in the area. Bore water temperatures recorded in the area vary between 15°C and 30°C. On the OZTemp map (Gerner, 2010), part of Lake Torrens plots in a relatively high geothermal area. However, the temperature measured in a drill hole at a depth of ~ 220 m is 35°C (Gerner, 2010).

Maximum concentration of lithium and boron in the catchments: Felsic intrusive rocks belonging to the Hiltaba Supersuite and felsic to intermediate Gawler Range Volcanics constitute the dominant source rocks of lithium and boron, with concentrations to 22 mg/kg and 16 mg/kg, respectively (Figure 5.35a, b). The region also has shaly units that can be good sources of boron. Most felsic and intermediate intrusive and volcanic rocks are Proterozoic ruling out availability of volcanic glass as source material for lithium.

Li/Cl and *B/Cl* ratio of groundwaters: Very few lithium and boron analyses are available for groundwater in these salt lake areas. The groundwater feeding the lakes usually have Li/Cl ratios below the 10 times enrichment trend compared to mean sea water (Figure 5.35a). Evaporative trends of these waters indicate that maximum concentration reached (at halite-saturation as shown by green vertical line on Figure 5.35a, b) will be ~ 10 mg/kg lithium or less).

B/Cl ratios are also less than 10 times the enrichment values (compared to mean sea water, Figure 5.35b). However, the evaporation trend line of some waters may reach values of boron similar to that observed in mineralised salt lake systems. Some of the highest values are recorded in groundwaters feeding the salt lake systems of Lake Younghusband and Lake Labyrinth.

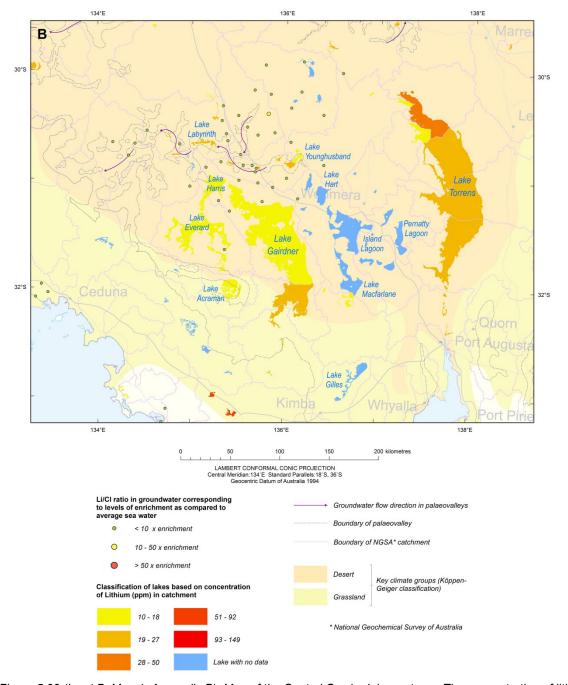


Figure 5.33 (Inset B, Map 1, Appendix B). Map of the Central Gawler lake systems. The concentration of lithium in a lake represents the average concentration of lithium in rocks in the catchment in which the lake is located. Lithium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in Li/Cl compared to an evolved sea water of the same chloride concentration.

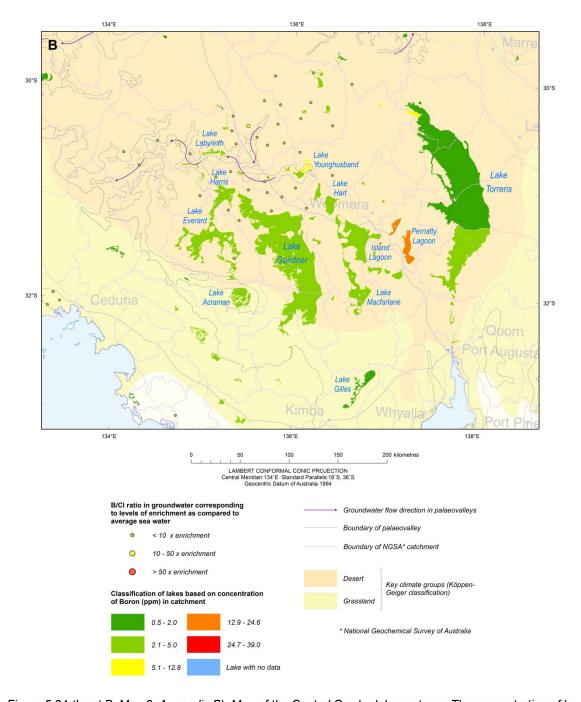


Figure 5.34 (Inset B, Map 2, Appendix B). Map of the Central Gawler lake systems. The concentration of boron in a lake represents the average concentration of boron in rocks in the catchment in which the lake is located. Boron and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in B/Cl compared to an evolved sea water of the same chloride concentration.

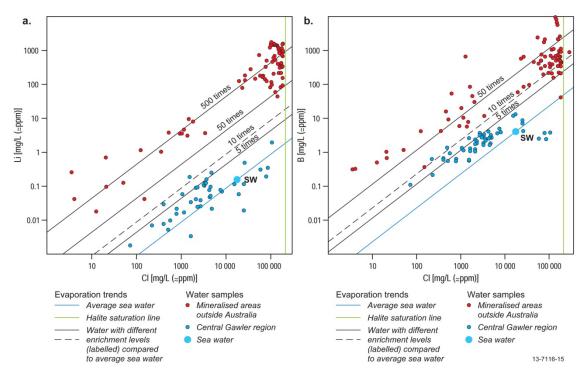


Figure 5.35a and b. Li-Cl (a) and B-Cl (b) plots of groundwaters in Central Gawler lake systems. The red dots and lines represent groundwater and evaporation trend respectively from salt lakes with economic-grade concentration of lithium and boron outside Australia. The large blue dot and line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of lake systems in Central Gawler region (inflow and lake waters). Sloping lines show enrichment in Li/Cl and B/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. The green vertical line represents the chloride concentration at which water becomes saturated with halite (NaCl).

Maximum concentration of potassium in the catchments: The highest potassium concentration in catchments is 6.2 wt. % $\rm K_2O$ (Figure 36). The bulk of the potassium is possibly sourced from Proterozoic felsic intrusive and volcanic rock in the Gawler Craton (such as Hitlaba Supersuite and Gawler Range Volcanics). It is possible that some potassium and other salts are also sourced from evaporitic units (Callana Subgroup) located to the northeast of Lake Torrens.

K/Cl ratio of groundwaters: Most bore waters record K/Cl values close to the sea water trend, with only a few samples plotting close to the 5 times enrichment trend favourable for generating economic grade concentrations of potassium (Figure 5.37).

Conclusions: The favourability analysis indicates that this region may have potential for salt lakes enriched in potassium and perhaps also lithium and boron. However, the analyses are based on very few groundwater and lake water analyses. More data are required on potassium, lithium and boron concentrations in groundwater and lake waters. More information is also required on the hydrogeological setting of the salt lake systems (lithology and geochemistry of sediments infilling palaeochannels) and on the lithology of lake sediments and geochemistry of lake waters.

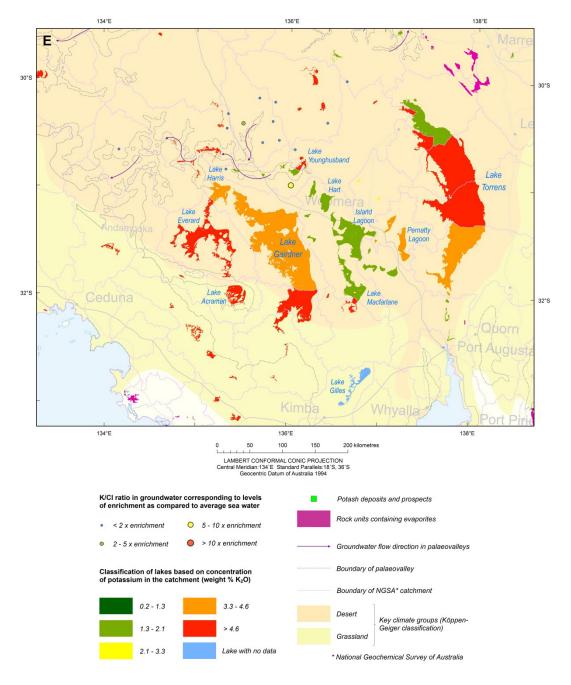


Figure 5.36 (Inset E, Map 3, Appendix B). Map of lake systems in Central Gawler region. Concentration of potassium in a lake represents the average concentration of potassium in rocks in the catchment in which the lake is located. Potassium and chloride concentrations in groundwaters are shown as ratios at different levels of enrichment in K/Cl compared to an evolved sea water of the same chloride concentration.

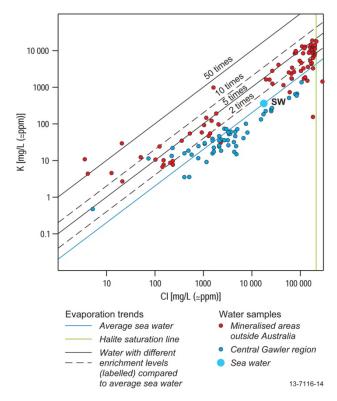


Figure 5.37 K-Cl plot of groundwater in salt lake systems in lake systems in Central Gawler region. Red dots and lines represent groundwater and evaporation trends, respectively, from salt lakes with economic-grade concentrations of potassium outside Australia. The large blue dot and line represent composition and evaporation trend respectively of average sea water. Blue small dots represent groundwater of lake systems in Central Gawler region (inflow and lake waters). Sloping lines show enrichment in K/Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. The green vertical line represents the chloride concentration at which water becomes saturated with halite (NaCl).

5.5 Critical features of salt lake systems with valley and playa-type, calcrete-hosted uranium

S. Jaireth, E.N. Bastrakov, A.A. McPherson and J.R. Wilford

Critical features of salt lakes systems favourable to form calcrete-hosted uranium deposits are described in Chapter 4 and summarised in Table 4.6. As discussed in Section 4.3, to generate an economic salt lake system capable for forming calcrete-hosted uranium deposits it is essential to have, (a) leachable source of uranium and vanadium in the catchment, (b) an active hydrogeological connection between the source rock and calcretes in the palaeovalleys (for valley-type deposits) and salt lakes (for playa-type deposits).

The selection of potentially favourable salt lake systems studies has been carried out in two stages. In the first stage broad regions of salt-lake systems were selected based on the above mentioned criteria. The second-stage selection uses (a) groundwater uranium concentration data, and (b) U²/Th values (as described in Appendix A).

5.5.1 First stage selection

The selection was based on the presence of favourable source rock in the catchment containing salt lakes. The following datasets were used for the selection (see Appendix A for details):

- 1. Concentrations of uranium and vanadium of rocks in Ozchem. An average value of uranium and vanadium was estimated for each catchment and assigned to that catchment.
- 2. Distribution of non-pedogenic calcretes extracted from Geoscience Australia's 1:1 million surface geology database.
- 3. A map of known and interpreted palaeovalleys in WA, SA and NT. An important feature of this map is the interpreted flow direction of groundwater in palaeovalley aquifers. Most calcrete-hosted uranium deposits occur in systems where groundwater flow connects the leachable source of uranium and vanadium with the calcretes in the palaeovalleys and/or with the margins of salt lakes. In some regions such as in Namibia, which hosts some of the largest deposits in the world, such as Langer Heinrich, the regional groundwater flow is toward the coast line.

Map 4 (Appendix B) shows results of the first-stage selection. It identified regions with known calcrete-hosted uranium deposits and prospects such as North East Yilgarn in WA, Central Gawler in SA, and Napperby and Lake Mackay in the NT. The map also identifies new favourable areas which need additional studies to assess their potential.

5.5.2 Second stage selection

In the second-stage selection process we include more detailed descriptions of the most favourable areas and recommend detailed studies which need to be undertaken to assess the potential of calcrete-hosted uranium deposits in these areas.

5.5.3 Salt lake systems favourable for calcrete-hosted uranium deposits 5.5.3.1 North East Yilgarn

Most major known deposits and prospects of calcrete-hosted uranium are located in the north east Yilgarn (Map 4, Appendix B). The region (Figure 5.38) contains all features considered critical for calcrete-hosted uranium deposits. It has uranium-enriched felsic rocks from which potassium can also be sourced. The region has Archean greenstone lithologies containing mafic and ultramafic rocks and also banded iron formations which are known to be good source of vanadium. A well developed system of Cenozoic palaeovalleys provides an effective hydrogeochemical connection between source rocks (which may be present also in the basement incised by the palaeovalleys) and calcretes and the margins of salt lakes.

The groundwater analysis shows that they are enriched in uranium (up to 700 mg/L) and vanadium (250 μ g/L). Palaeovalleys which contain calcrete-hosted uranium deposits invariably show high U²/Th values indicating that U²/Th values can be used as an indicator of uranium mobility in the palaeovalley aquifers.

Conclusions: This region is one of the most prospective areas for calcrete-hosted uranium deposits. However not all palaeovalley calcretes have been adequately explored. A more detailed hydrogeochemical study in areas with limited previous data will help assess the potential of the region.

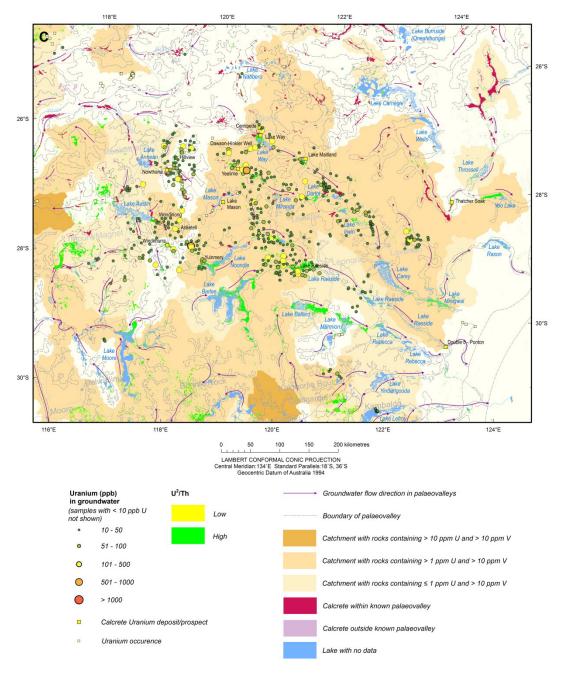


Figure 5.38 (Inset C, Map 4, Appendix B). Map of lake systems in North East Yilgarn. The lake systems host a large number of valley- and playa-type calcrete-hosted uranium deposits. Note the spatial correlation between high U^2/Th values and palaeovalleys hosting uranium deposits and prospects.

5.5.3.2 Arunta

The western Arunta region (Figure 5.39) contains known calcrete-hosted uranium prospects, including the Napperby prospect, which is located in the palaeovalleys south of the Ngalia Basin. Calcrete-hosted uranium mineralisation is also being explored in the Lake Mackay area by Toro Energy.

Source of uranium, vanadium and potassium: Felsic rocks in the Arunta region represent leachable sources of uranium and potassium. The region has a large number of sandstone-hosted uranium

deposits and occurrences and uranium-bearing pegmatites and fluoro-apatite veins with readily leachable uranium. The region also contains an abundance of mafic rocks which can provide vanadium.

Non-pedogenic calcretes: Non-pedogenic calcretes have been mapped in most palaeovalleys in the regions. The palaeovalleys also contain salt lakes creating a setting similar to the North East Yilgarn region.

Hydrogeochemical data: The hydrogeochemical dataset in the region is limited and patchy. However, locally high uranium values (up to 2,350 μ g/L) have been recorded. The concentration of vanadium in the groundwaters is relatively low (less than 190 μ g/L).

 U^2/Th values: High values are recorded in the region. However only a limited number are present within interpreted palaeovalleys. Calcrete-bearing palaeovalleys near Lake Lewis and Lake Bennett also show high U^2/Th values. Similarly high values are also recorded in a northwest-trending palaeovalley in the Amadeus region. Groundwaters in the aquifers of this palaeovalley drain into Lake Hopkins. High U^2/Th values are also seen at the margins of Lake Mackay, Lake MacDonald and Lake White (see inset on Map 4, Appendix B).

Conclusions: This region already contains the Napperby and Lake Mackay prospects. In addition to these prospects, several other calcrete-bearing palaeovalleys need more detailed hydrogeochemical studies to assess their potential. The areas of interest include: palaeovalleys associated with Lake Lewis and Lake Bennett; palaeovalleys associated with Lake Amadeus and Lake Neale; palaeovalleys running south from the Tennant Creek region and palaeovalleys to the northeast end of the Ngalia Basin where available hydrogeochemical data suggest a cluster of high uranium and vanadium concentrations.

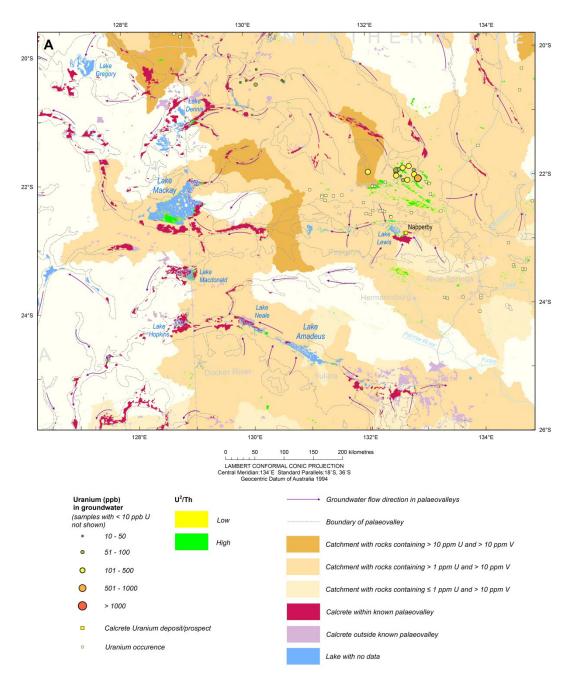


Figure 5.39 (Inset A, Map 4, Appendix B). Map of lake systems in Arunta region. The lake systems host a few valley- and playa-type calcrete-hosted uranium deposits and prospects. Note the spatial correlation between high U^2/Th values and palaeovalleys hosting uranium deposits and prospects.

5.5.3.3 Central Gawler

No calcrete-hosted uranium deposits or prospects have as yet been found in the Central Gawler region (Figure 5.40). However, a number of sandstone-hosted prospects (such as Warrior) are located within Cenozoic palaeovalleys.

Source of uranium, vanadium and potassium: Felsic rocks in the Gawler Craton (such as the Hiltaba Supersuite and Gawler Range Volcanics) represent leachable sources of uranium and potassium. The region also contains an abundance of mafic rocks (the Lake Harris Greenstone) which can provide

vanadium. Vanadium can also be sourced from ferruginous units in the Archean-Proterozoic basement rocks.

Non-pedogenic calcretes: Non-pedogenic calcretes have been mapped in most palaeovalleys (such as Kingoonya, Garoford, and Tallbaringa) in the region (Bell *et al.*, 2012). The palaeovalleys also contain salt lakes creating a setting similar to North East Yilgarn region.

Hydrogeochemical data: The hydrogeochemical dataset in the region is limited and patchy. However, the highest concentration recorded in the groundwater is 20 μ g/L for uranium and 29 μ g/L for vanadium.

 U^2/Th values: High values are recorded in all major palaeovalleys in the regions. High U^2/Th values are also seen at the margins of many lakes such as Lake Antony, Wilkinson Lake, Lake Bring, and Lake Labyrinth and Lake Younghusband (see inset on Map 4)

Non-pedogenic calcretes: Non-pedogenic calcretes have been mapped in most palaeovalleys (such as Kingoonya, Garoford, and Tallbaringa) in the region (Bell *et al.*, 2012). The palaeovalleys also contain salt lakes creating a setting similar to North East Yilgarn region.

Hydrogeochemical data: The hydrogeochemical dataset in the region is limited and patchy. However, the highest concentration recorded in the groundwater is 20 μ g/L for uranium and 29 μ g/L for vanadium.

 U^2/Th values: High values are recorded in all major palaeovalleys in the regions. High U^2/Th values are also seen at the margins of many lakes such as Lake Antony, Wilkinson Lake, Lake Bring, and Lake Labyrinth and Lake Younghusband (see inset on Map 4, Appendix B).

Conclusions: A proper assessment of this region requires more robust and widespread hydrogeochemical data. There are no uranium and/or vanadium analysis of groundwaters in the Garford and Talbaringa palaeovalleys which also contain Lake Antony. The Kingoonya palaeovalley has been explored relatively more intensively for both gold and uranium deposits but no exploration on that scale has been carried out in the Garford and Talbaringa palaeovalleys.

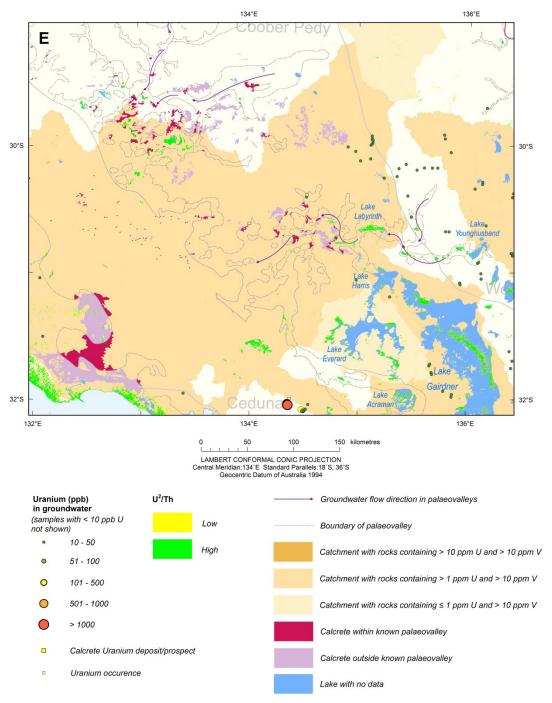


Figure 5.40 (Inset E, Map 4, Appendix B). Map of lake systems in Central Gawler region. The lake systems host a large number of valley-type calcrete-hosted uranium prospects. Note high U^2/Th values in a number of palaeovalleys and at lake margins.

5.5.3.4 Paterson

One calcrete-hosted uranium prospect (Lamil Hills) is known to exist in the Paterson region (Figure 5.41) near Lake Waukarlycarly. The region has a well-developed system of Cenozoic palaeovalleys containing valley calcretes and salt lakes. A more comprehensive mineral potential assessment of this area was conducted earlier which showed high and moderate to high levels of potential for Lake Waukarlycarly and Lake Winfred (Liu and Jaireth, 2012).

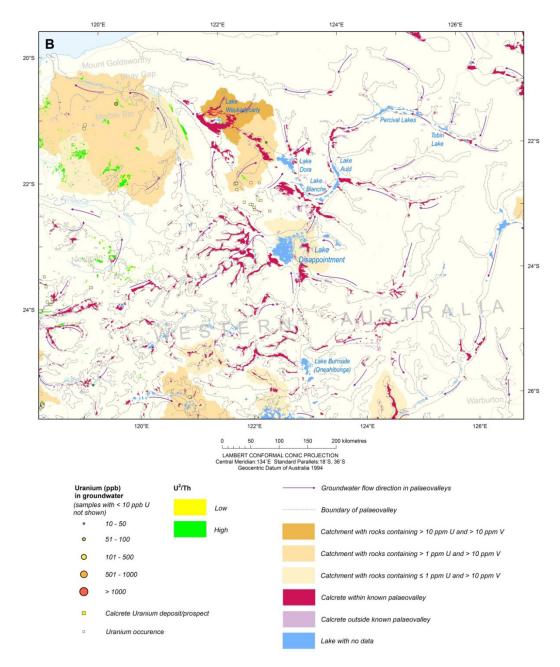


Figure 5.41 (Inset B, Map 4, Appendix B). Map of lake systems in the Paterson region. The lake systems host a playa-type calcrete-hosted uranium prospect (Lamil Hills). Note high U^2/Th values in a number of palaeovalleys.

Conclusions: This region needs a more detailed hydrogeochemical study with systematic analysis of groundwaters in the palaeovalley aquifers. This will help to assess the potential of other lake systems such as Lake Dora, Lake Disappointment, Lake Auld and Percival Lakes.

5.5.3.5 South Musgrave

No calcrete-hosted uranium deposits or prospects have as yet been discovered in the South Musgrave region (Figure 5.42).

Source of uranium, vanadium and potassium: Proterozoic felsic rocks (granites, gneisses and pegmatites) in the Musgrave regions can include leachable sources of uranium and potassium. The

region also contains an abundance of mafic rocks (Giles Complex, Table Hill Volcanics) which can provide vanadium. Vanadium can also be sourced from ferruginous units in the Archean-Proterozoic basement rocks.

Non-pedogenic calcretes: Non-pedogenic calcretes have been mapped in most palaeovalleys (such as Baker, Van del Linden, Serpentine, Kadgo, Wanna) in the region (Bell *et al.*, 2012). They generally run north to south and contain salt lakes (such as Baker and Serpentine Lakes).

Hydrogeochemical data: The hydrogeochemical dataset of Dickson and Giblin (2006) does not include samples from this region. The available bore water analyses contain information only on total salinity and the concentration of major cations and anions.

 U^2/Th values: The Airborne Radiometric dataset (Minty et al., 2009) does not cover a significant part of the palaeovalleys in the region. As a result U^2/Th values are available only for selected parts. However high values are locally recorded in the Serpentine, Kadgo and Van der Linden palaeovalleys. (see inset on Map 4, Appendix B).

Conclusions: The region is favourable for calcrete-hosted uranium deposits. However, more detailed hydrogeochemical studies are required to assess mineral potential of individual palaeovalleys in the region. Most palaeovalleys are probably incised into basement felsic and/or mafic rocks, however more information is needed on the aquifers and other sediments infilling palaeovalleys.

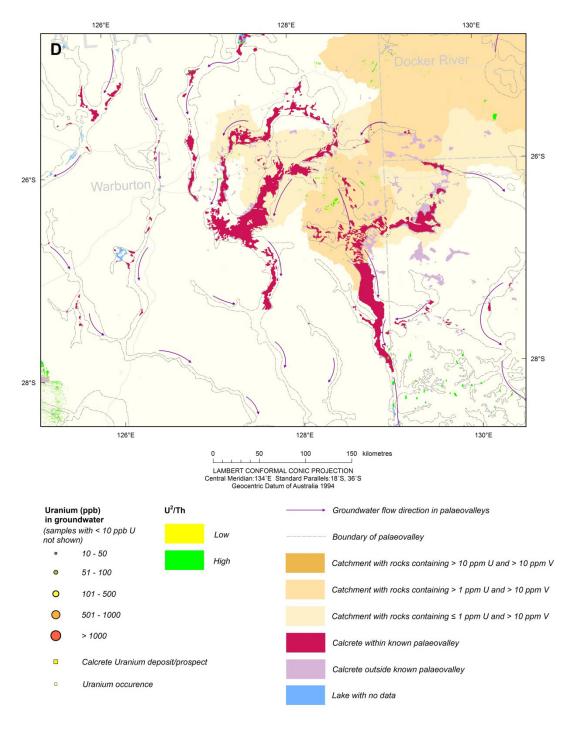


Figure 5.42 (Inset D, Map 4, Appendix B). Map of lake systems in South Musgrave region. No calcrete-hosted uranium mineralisation has as yet been reported in the area. The radiometric data only are available only for a limited part of the area. Note presences of high U^2/Th values in some palaeovalleys.

6 A Case Study: Lake Frome, South Australia

I.F. Schroder, E.N. Bastrakov, S. Jaireth, T.P. Mernagh, and I.C. Roach

6.1 Introduction

As part of Geoscience Australia's broader interest in the mineral potential of salt lakes, this chapter assesses Lake Frome's prospectivity for strategic elements such as lithium and potassium using spatial Geographic Information System (GIS) analysis coupled with geochemical modelling of the source waters. Lake Frome was chosen because it has been extensively researched in the past, thus providing a large number of samples and well understood evolution history. Lake Frome's prospectivity will be assessed using the mineral systems concept developed by Geoscience Australia and adapted for salt lakes (Chapter 4).

6.2 Geological setting

Lake Frome is a large playa, covering an area of ~2700 km² in eastern South Australia (Figure 6.1). It is the terminal lake within the Callabonna sub-Basin; an endorheic basin that covers ~40,000 km². The Frome region currently has a semi-arid to arid environment, with an annual rainfall of ~150 mm in the basin, increasing to ~300 mm in the western and southern ranges (Callen and Tedford, 1976). The annual potential evaporation for the area is greater than 2000 mm, resulting in Lake Frome being largely devoid of surface water (Draper and Jensen, 1976). Most of the lake is covered instead with a thin halite crust, with several isolated groups of clastic and carbonate mound springs to the east. Below the halite crust, interstitial discoidal gypsum crystals along with traces of pyrite and carbonates abound within the dark brown clay-rich sediments (Draper and Jensen, 1976; De Deckker *et al.*, 2011). Underlying Lake Frome, at depths ranging from 10 cm to greater than 10 m, is a brine pool, characteristically NaCl-enriched, with salinities exceeding 250 g/L (Draper and Jensen, 1976).

Lake Frome is bounded to the west by the Flinders Ranges, which comprise highly deformed Neoproterozoic to Early Cambrian metasedimentary and volcanic rocks of the Adelaide Fold Belt. These are underlain by Mesoproterozoic metasediments and granites, which crop out to the north in the Mt Painter Inlier (Preiss, 1987; Drexel *et al.*, 1993; Sheard, 2009). Bounding Lake Frome's drainage basin to the south is the Olary Spur, which consists of Neoproterozoic metasediments of the Adelaide Fold Belt underlain by Paleo-Mesoproterozoic rocks of the Curnamona Province (Campana, 1957).

Proximal to the lake, the Cenozoic fill consists of Late Paleocene to Eocene fluvial sands and gravels of the Eyre Formation, which underlie Oligocene to Late Miocene fluvio-lacustrine sands and clays of the Namba Formation. Pliocene fluvial and lacustrine deposits of the Willawortina Formation reach greater than 100 m thickness between Lake Frome and the Flinders Ranges (Callen and Tedford, 1976).

Inflow into Lake Frome comes mostly from surface tributaries and groundwater sourced from the Flinders Ranges to the west, groundwater following palaeovalleys to the south, and minor ephemeral streams to the east. (Bowler, 1986a; De Deckker *et al.*, 2011). To the north a salt creek connects Lake Frome with the playas Lake Blanche and Lake Callabonna, which during extreme wet periods can discharge water into Lake Frome from the Cooper Creek catchment to the north (De Deckker *et al.*, 2011).

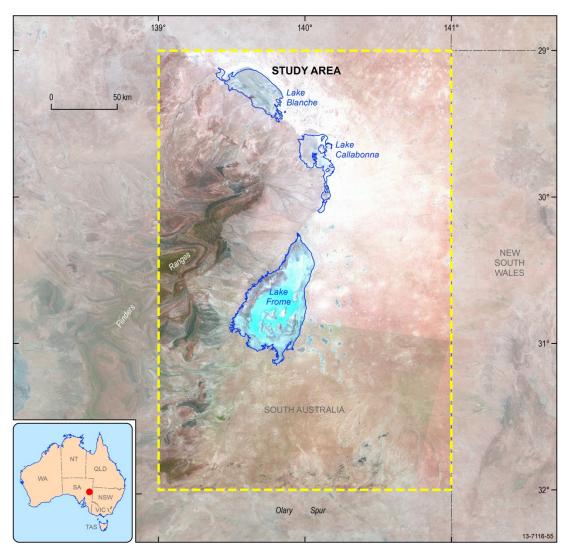


Figure 6.1 A Landsat image of Lake Frome, showing surface coverage and location for the study area (Geoscience Australia, 2010). The yellow box, from 139-141°E longitude and 29-32°S latitude, defines the boundaries for the study area.

Lake Frome first formed during the Middle Miocene as an alkaline lake associated with the middle Namba Formation (De Deckker, 1983). Over its history Lake Frome has undergone significant changes in volume, associated with changes in climate and sea level. The timing of filling events for Lake Frome has been established using radiocarbon, optically stimulated luminescence and thermoluminescence dating techniques of palaeo-shoreline deposits (Ullman and McLeod, 1986; Cohen *et al.*, 2012). During filling events that produced water depths of greater than 6 m, Lake Frome merged with the three lakes to the north (Lakes Gregory, Blanche and Callabonna) to form a single water body, termed Lake Mega-Frome. When filled to over 15 m Lake Mega-Frome drained via the Warrawoocara channel to Lake Eyre. Drainage into Lake Eyre has occurred as recently as the mid-Marine Isotope Stage (MIS) 3 (~ 45 ka). Over the last 100 ka Lake Mega-Frome phases have occurred at least seven times, with three of those overtopping into Lake Eyre (Cohen *et al.*, 2012). However, palaeohydrological records suggest there has been a progressive shift to more arid conditions since 45 ka, with Lake Frome returning to playa-dominated conditions with the onset of the modern El Niño Southern Oscillation from ~4 ka (De Deckker *et al.*, 2011; Cohen *et al.*, 2012).

The composition of a salt lake is affected by the climate and the lithology of source rocks and host sediments, which control the initial chemistry of aqueous fluids flowing into the catchments (Eugster and Hardie, 1978). Lake Frome has undergone significant hydrochemical changes from its formation in the Late Miocene to now. Lake Frome began with carbonate-rich waters, as indicated by the dolomite-rich sediments of the Namba Formation. The lake since changed to chloride/sulfate-dominated waters (De Deckker, 1983; 1988), the timing of which is not known. Lake Frome has undergone several flushing periods, when Lake Mega-Frome phases discharged into Lake Eyre (Cohen *et al.*, 2012). At these times the Frome mega-lake was not a closed terminal basin, meaning any accumulated salts and trace elements were vulnerable to dissolution and flushing from the basin. De Deckker *et al.* (2011) suggested that Lake Frome's brine pool (and current geochemical signature) formed much more recently, during deglaciation following the Last Glacial Maximum, and prior to that the lake maintained slightly saline to freshwater conditions.

6.3 Lake Frome - A salt lake mineral system

Assessment of Lake Frome's prospectivity was conducted using the mineral systems concept for ore deposits discussed in Chapter 4 . The major components considered in the Lake Frome - salt lake mineral system are:

- · Sources of elements and fluids;
- · Drivers / Migration pathways;
- · Depositional setting; and,
- Brine evolution or enrichment mechanisms.

Other components which have not been included in this simple mineral system but will be discussed later in the chapter, are: brine preservation; transportation pathways; and the depositional site.

6.3.1 Datasets and processing

Data used for analysis of Lake Frome were restricted to a rectangular box of latitude 29°S to 32°S and longitude 139°E to 141°E (Figure 6.1), encompassing the Lake Frome catchment with an added buffer. The datasets used in this study are described in detail in Appendix A. All datasets were imported into a GIS, and used to graphically assess each component of the Lake Frome salt lake mineral system.

The study was complicated by the fact that most of the accessible water and rock geochemical data did not include lithium analyses. Based on the fact that in all lithium-enriched salt lake systems lithium and potassium behave proportionally in solution (Chapter 4), potassium has been used as a proxy for lithium. This assumption can be applied to Lake Frome, which does not precipitate potash, and therefore is expected to exhibit a correlation between potassium and lithium.

6.3.1.1 Rock geochemistry

Rock geochemistry was used to represent the source using a mineral systems approach. An effective source rock requires elevated concentrations of lithium and or potassium, as well as the presence of these elements in an appropriate mineral phase to allow leaching. For most rock samples, the lithology of the sample was not identified, thus mineral phases incorporating lithium and potassium could not be identified.

For the GIS analysis, samples were restricted to depths of less than 150 m below surface. This was to ensure that deeper rocks, unlikely to play a role in Lake Frome's geochemistry, would not be included in the GIS analysis.

Rock geochemistry was obtained from:

- SARIG South Australian Resources Information Geoserver (SARIG)—accessible online at https://sarig.pir.sa.gov.au
- Ozchem Geoscience Australia's Ozchem database—accessible online at https://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=65464

During this process, stream sediment, soil and calcrete samples were removed from the rock geochemistry data and put into a new spreadsheet. A separate feature class containing these samples was prepared, as these surface materials may also contribute to Lake Frome's chemistry as contemporary sources.

6.3.1.2 Water chemistry

Water chemistry was used in the geochemical modelling to help validate whether there was an effective source rock by identifying; whether appreciable leaching had occurred, and whether this could evolve to compositions seen in Lake Frome. It was also used in the mineral systems framework to highlight transportation pathways and enrichment components.

All water samples were converted to a template that Geoscience Australia uses for input into the AquaChem[®] software package (Schlumberger Water Services). The datasets were then combined into a single spreadsheet for GIS analysis. Although AquaChem differentiates between dissolved and total quantities of species, as the state of the sampled species were not known, values were transcribed into the total columns.

Water chemistry datasets were named after their originators or the geographical area they describe:

DEWNR – South Australia's Department of Environment, Water and Natural Resources (DEWNR) groundwater database, WaterConnect – accessible online at https://www.waterconnect.sa.gov.au/GD;

- Giblin A Commonwealth Scientific and Industrial Research Organisation (CSIRO) dataset (Dickson and Giblin, 2006);
- Curnamona A CRC LEME/Geoscience Australia dataset (Caritat et al., 2005); and,
- COMALCO An exploration report prepared by Commonwealth Aluminium Corporation Limited (Chaku, 1980).

A problem prevalent in all but the Curnamona dataset is that a good portion of the samples are legacy data, having been taken over 40 years ago. Thus the reliability of the sampling and analysis techniques for legacy data are often below today's standards and should be treated with greater caution.

Another issue was that, except for the COMALCO dataset, water samples did not have a sampling depth described. This made it difficult to assess whether these were surface or groundwater samples and, if the latter, what groundwater unit they were derived from. Thus, some of the included water samples may well be derived from units below the Namba Formation, which do not feed into Lake Frome. As it was not possible to categorise water samples by their aquifer unit or depth, the results from multiple groundwater and surface sources were combined during GIS analysis. Consequently, chemical trends such as changes in TDS associated with a single source are obscured within a cloud of scatter, meaning only general, broad patterns have been inferred.

6.3.1.3 The Frome airborne electromagnetic survey

An airborne electromagnetic (AEM) survey of Lake Frome was used to help validate fluid transportation pathways, especially in the near sub-surface, for Lake Frome (Roach, 2012). The AEM survey measures the electrical conductivity of the surface and subsurface (up to ~200 m depth below the surface), and has the potential for mapping salinity differences in groundwater in the near-surface. Using the Geoscience Australia layered earth inversion algorithm (GA-LEI), conductance maps for a range of depths and elevations were prepared, as well as east-west cross-sections of electrical conductivity through Lake Frome.

The depth of penetration of the AEM survey, referred to as the depth of investigation (DOI), varied based on the conductance (the summed conductivity of all layers in the inversion) but was highly correlated to the electrical conductivity of the surface layer. Where the surface was highly conductive, such as over the Lake Frome playa, the signal saturated close to the surface and the DOI was much shallower (~60 m). This limits our understanding of how deep the brine pool extends, and as a consequence, what stratigraphic units are contributing to Lake Frome's water chemistry.

6.4 The geochemical modelling process

Chemical characterisation and modelling of Lake Frome's inflow waters was conducted to establish geochemically distinct groups within the catchment, and what role they have on the overall composition of Lake Frome's brine.

Modelling tracked the fluid's evolution by simulating evaporation in equilibrium with the atmosphere. Several different models were tested in order to find the most appropriate method for simple modelling of saline fluids to predict provenance pathways.

Geochemical modelling was conducted using The Geochemist's Workbench v. 8 (GWB) (Bethke, 2007).

6.4.1 Data processing

To generate valid results, GWB required the complete analyses of the groundwater in terms of the major components (anions, ${\rm CO_3}^2$ -/HCO₃ or alkalinity, Cl , ${\rm SO_4}^2$; cations, Na⁺, K⁺, Mg²⁺ and Ca²⁺), and pH. Of the 1070 water samples, only 149 contained all the required variables. The GWB program was then used to calculate the charge balance and charge balance error; samples with greater than 5% error were discarded. A total of 124 samples were retained for geochemical modelling.

6.4.2 Modelling methods

Several methods exist for modelling fluid evolution, which vary depending on what assumptions and restrictions are placed on the system. For this study, simple evaporation models were used, which assumed that groundwater evaporation was the only process for brine enrichment. Complex mixing and leaching processes were ignored, as these require an intimate knowledge of the transportation paths, host rock chemistry and water chemistry. Minerals which reached saturation were allowed to precipitate out, following the method of Bethke (2007).

Modelling was done using the two programs SpecE8 and React within GWB. As only a single sample could be run at a time, it required that representative samples were chosen, and often a second analysis

of a similar sample was conducted to verify results. The SpecE8 program was used to show how elements are speciated in solution at equilibrium, and which minerals are supersaturated. The React program was then used to model fluid evolution as water was removed through evaporation. Since the temperature of the water samples was not known it was assumed all reactions occurred at 25°C.

There are many decisions to make when setting up the geochemical model; these can affect the evolution path of the starting fluid. Two main methods were trialled, and variations experimented with, based on some of the major decisions required, which include:

- Set Charge Balance for Cl⁻: This fixes the charge balance to neutral by adjusting the Cl⁻ concentration. This is done because we assume the solution is electrically neutral, and any charge imbalance is because of the charge of species not included in the model. As Cl⁻ does not factor into mineral formation until very high concentrations (with the precipitation of halite), changing the concentration of Cl⁻ will not significantly affect the initial Li⁺:Cl⁻ ratio;
- Fixing CO₂ fugacity: If the water samples are assumed to be evaporating in equilibrium with the atmosphere, CO₂ log fugacity was set to atmospheric levels (-3.5);
- Selecting 'Flow-through configuration': This option prevents the fluid from back-reacting with precipitated minerals. Effectively it assumes that the fluid is moving and precipitated minerals are left behind;
- Selecting 'Precipitation': This option allows minerals to precipitate once saturation is reached;
- Changing 'delxi' and 'dxplot': These are variables which control the maximum step in each iteration of the reaction to provide increased detail near the end of the reaction path (Bethke, 2007); and,
- Suppressing dolomite precipitation: Dolomite is a highly ordered mineral which does not precipitate at 25°C except in saline brines (Garrels and Mackenzie, 1967) and no evidence for appreciable dolomite formation has been found in the Lake Frome area.

Varying the input controls can have a marked effect on the fluid evolution path. This is shown in Figure 6.2, where the brine evolution of sample BV3 (from Giblin, 1987), in the upper Flinders Ranges, was modelled using both methods as well as a range of different conditions.

6.4.3 Discussion of modelling methods

Two approaches were modelled to reflect conditions where the sample was not in equilibrium with the atmosphere; however these approaches were quickly abandoned. Fixing the sample's current fugacity, rather than equilibrating to atmosphere (green line in Figure 6.2), is inadvisable, as in the time between sampling and analysis it is highly likely the sample's CO_2 fugacity would have changed through interaction with the atmosphere. Similarly, when CO_2 fugacity is not fixed (red line in Figure 6.2), CO_2 concentrates in solution, rather than exsolving, causing carbonate species in solution to increase in turn, generating erroneous evolution paths.

The two approaches to modelling the fluid in atmospheric equilibrium, involve either setting the sample's CO_2 fugacity to the atmospheric value (Method 1), or linearly changing the CO_2 fugacity from the sample to atmospheric value over many iterations (Method 2). Both approaches change the starting composition of the fluid prior to modelling evaporation. This is because CO_2 is forced to exsolve, causing carbonate species in solution to compensate and produce more CO_2 (decreasing the solution's carbonate concentration), however the two methods produce slightly different starting

compositions. The advantages of sliding the fugacity are that: the composition of the solution can be tracked graphically; minerals that become saturated are allowed to precipitate out, meaning the solution doesn't become super-saturated in several mineral phases for the start of evaporative modelling; and this is part of the recommended method put forward by Bethke (2007).

The effect of dolomite suppression is most significant during equilibration with the atmosphere, favouring calcite and magnesite precipitation instead. At the low salinities and non-elevated temperatures typical of Lake Frome's headwater samples, Garrels and Mackenzie (1967) assert that dolomite would not precipitate. Further, no evidence for appreciable dolomite formation has been found in the Lake Frome area. Both these points support the suppression of dolomite during modelling.

Following this analysis, Method 2 was selected as the favoured approach for modelling evaporative concentration.

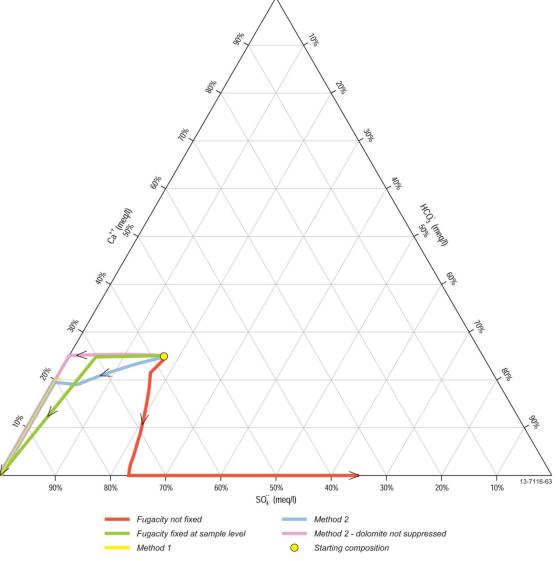


Figure 6.2 A Ca²⁺-HCO₃⁻-SO₄²⁻ ternary diagram for sample BV3 in the upper Flinders Ranges west of Lake Frome. Each coloured line represents different geochemical evolution paths during evaporation using different modelled conditions.

6.4.4 Geochemical groupings in the Lake Frome study area

The composition of the water samples imported into GWB were categorised by location, and plotted in Figure 6.3 to identify any broad geochemical groupings based on geographical source.

Water samples from the Flinders Ranges exhibited the most variability in composition (green circles in Figure 6.3), ranging between sulfate and alkaline brine types. Samples to the south from the Olary Spur were more tightly grouped (blue circles in Figure 6.3), typically depleted in HCO_3^- and yielded mostly sulfate brines. Samples within Lake Frome itself were similarly clustered with very low HCO_3^- , but were more enriched in SO_4^{-2} (red circles in Figure 6.3) characteristic of Lake Frome's sulfate-rich brine. Surface samples from the north and east have a very distinct composition dominated by HCO_3^- (grey circles in Figure 6.3). Based on their different chemical composition to other Lake Frome water, it is likely these surface samples do not contribute significantly to Lake Frome in either inflow or geochemistry.

The low salinity samples (Total Dissolved Solids - TDS<5000 mg/L) exhibited most of the variability seen in water compositions of the Lake Frome region, producing most of the scatter seen in the centre of Figure 6.3. At higher salinities samples are clustered to the left of Figure 6.3 with low HCO_3^- , with a general trend towards increasing SO_4^{-2-} (and decreasing Ca^{2+}) as TDS increases.

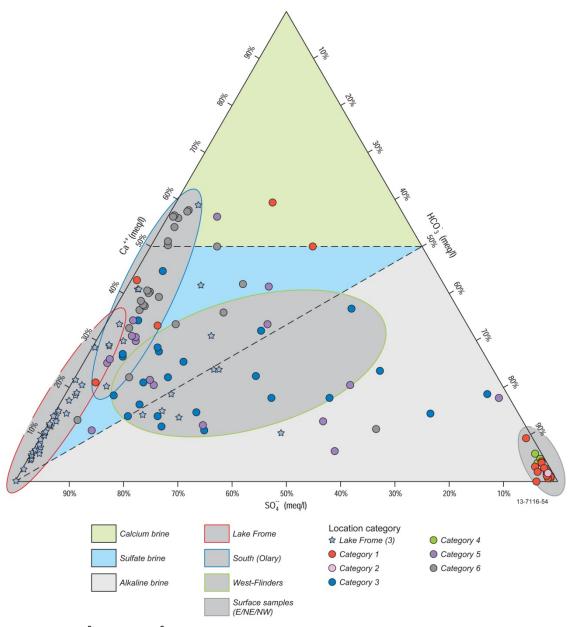


Figure 6.3 A Ca^{2+} -HCO $_3^{-}$ -SO $_4^{-2-}$ ternary diagram showing the composition of water samples by location in the Lake Frome region. Major geochemical groups are circled. For reference, the geochemical divides for the three dominant brine types have been included. See Table 6.1 for the colour key for each location.

Table 6.1 Colour key for water sample locations. Samples are divided into 1 degree grid squares.

Latitude (S)	Longitude (E)	Category	Colour
29 to 30	139 to 140	1	Red
	140 to 141	2	Pink
30 to 31	139 to 140	3	Blue
	140 to 141	4	Green
31 to 32	139 to 140	5	Purple
	140 to 141	6	Grey

6.4.5 Modelling of saline fluid evolution

As the most common waters flowing into Lake Frome are sulfate brines, a representative sample was modelled to highlight the typical geochemical evolution pathway for these fluids. A low salinity sample from near the headwaters of the Flinders Ranges (sample 6736-78 from DEWNR), was modelled using Method 2. During equilibration to atmospheric CO_2 (g) fugacity, calcite and magnesite became super-saturated, precipitating out and removing much of the HCO_3^- from solution. Evaporative concentration caused further precipitation of these minerals, but the dominant precipitating species was gypsum (Figure 6.4). In solution, during evaporation modelling, species such as K^+ , which do not associate with the precipitating minerals, are predicted to increase in concentration (Figure 6.5). This modelling does not however factor in ion exchange processes likely to deplete K^+ from solution. There were some exceptions, where K^+ decreased in concentration during modelling, when GWB predicted the precipitation of K-bearing minerals such as polyhalite.

Assuming that sub-surface groundwater follows a similar path to surface channels, water similar to sample 6736-78 should outflow in central west Lake Frome, based on the 1:250 K Australian watercourses dataset. When the compositions of the nearest Lake Frome water samples (boreholes CF7 and CF8) are plotted on the ternary plot (Figure 6.6), they overlap well with the calculated path of fluid evolution. Similar compositional agreement is seen between Lake Frome brines and the evolution pathway of samples modelled from the Olary Spur. This supports the conclusion that geochemical modelling of evaporative concentration using Method 2 in GWB can predict the provenance pathways of Lake Frome brines.

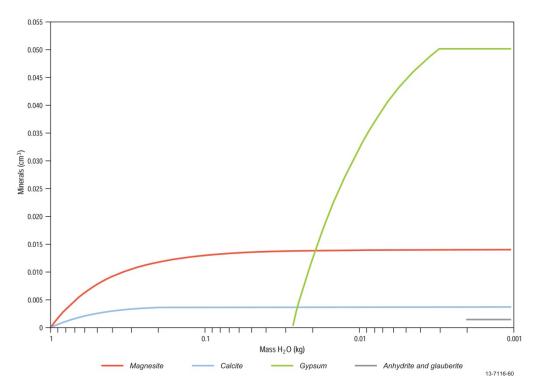


Figure 6.4 A plot showing mineral precipitation for the chemical evolution of Sample 6736-78 in the Flinders Ranges. Evaporation is modelled following Method 2, with the amount of water remaining in solution, starting from a 1 kg solution, along the x-axis.

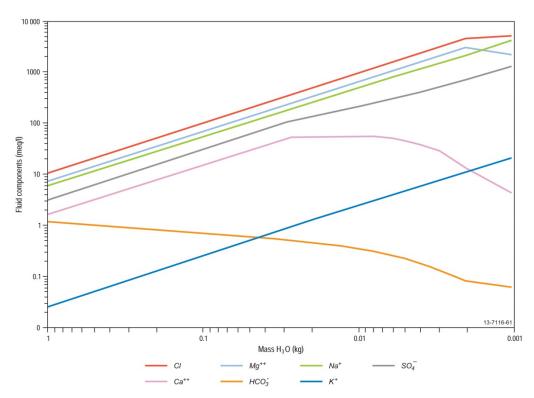


Figure 6.5 A plot showing concentration of major species in solution during the chemical evolution of Sample 6736-78 in the Flinders Ranges. Evaporation is modelled following Method 2, with the amount of water remaining in solution, starting from a 1 kg solution, along the x-axis.

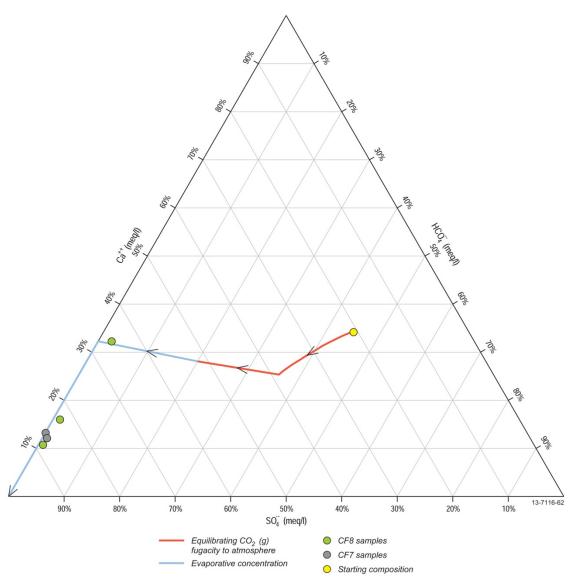


Figure 6.6 A Ca²⁺-HCO₃-SO₄²⁻ ternary diagram showing the modelled chemical evolution of Sample 6736-78 in the Flinders Ranges, west of Lake Frome, during equilibration with the atmosphere and subsequent evaporation following Method 2. The composition of the closest Lake Frome samples are included for reference.

6.5 Results

6.5.1 Assessing the salt lake mineral system

6.5.1.1 Source rocks

Potential source rocks, rich in potassium, have been identified in the Flinders Ranges and Olary Spur (Figure 6.7). Restricted to shallower than 150 m depth below the surface, potassium concentration of rock samples reach up to 85,318 mg/kg in the northern Flinders Ranges, and 90,600 mg/kg in the Olary Spur. Sparse lithium analyses support the assertion that the Flinders Ranges and Olary Spur are valid potential source rocks (Figure 6.8). It also highlights that the sediments below Lake Frome are highly enriched in lithium, reaching levels of 250 mg/kg (Chaku, 1980), representing a source hydrologically connected with Lake Frome.

A sampling bias is also evident in Figure 6.7, where rock samples (in yellow) are strongly correlated with the shorter wavelength, high intensity anomalies in the magnetic data. These areas correspond to exposed hard rock (Proterozoic basement) at surface or under shallow cover, reflecting a mineral exploration-driven approach to sample acquisition. Because of this bias, far fewer samples exist within the sedimentary fill of the Callabonna Sub-basin. As these sedimentary units represent the major rock facies that groundwater comes into contact with, an accurate assessment of the source potential of Lake Frome cannot be established.

6.5.1.2 Transport

Several fluid transportation pathways from lithium-potassium-rich source rocks to the depositional site of Lake Frome have been identified over the course of GIS analysis. These pathways largely mirror the accepted inflow sources for Lake Frome described earlier, consisting predominantly of surface tributaries and groundwater from the Flinders Ranges and Olary Spur.

Transportation pathways into Lake Frome are evident from the elevated TDS values loosely constrained to channels and increasing towards the Lake (Figure 6.9). Similar trends are seen for lithium in water samples south of Lake Frome, where higher lithium values correlate well with surface drainage features (Figure 6.8).

Surface and near sub-surface channels can also be identified surrounding Lake Frome using AEM data. In the 0-5 m depth slice, higher conductivities are associated with channels carrying more saline fluids (Figure 6.9; Roach, 2012), and again correlate well with known drainage pathways. Thus the AEM can be used to highlight potential transportation pathways in less sampled areas, such as the lower slopes of the Flinders Ranges, where several channels can be identified through elevated conductivity.

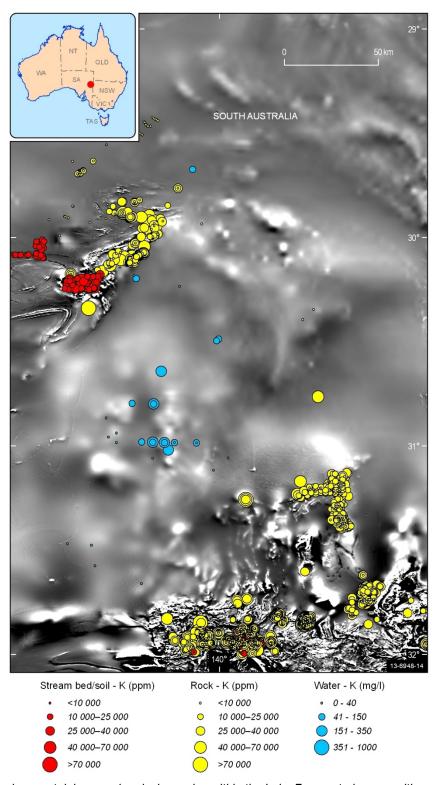


Figure 6.7 Potassium containing geochemical samples within the Lake Frome study area, with symbol size proportional to potassium content. Datasets include: Stream bed and soil geochemistry (red); Rock geochemistry (yellow) - restricted to shallower than 150 m depth, and water geochemistry (blue). These are displayed over the magnetic anomaly map of Australia (Milligan et al., 2010).

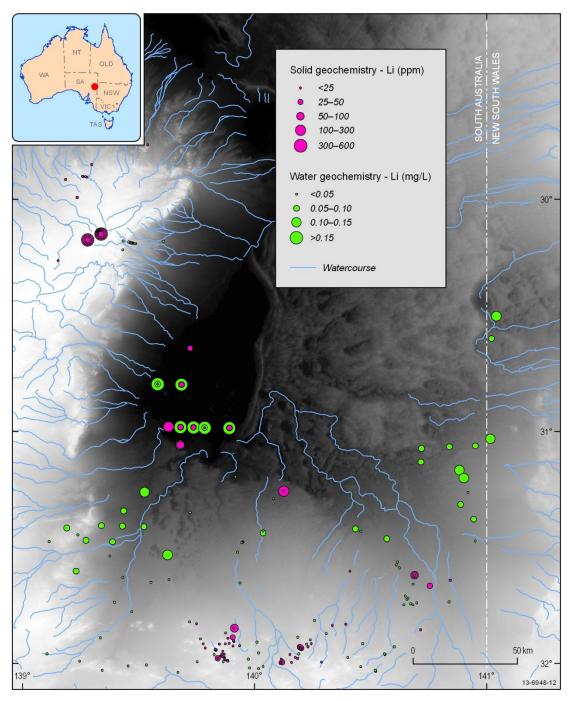


Figure 6.8 Lithium containing geochemical samples within the Lake Frome study area, with symbol size proportional to lithium content. Datasets include: Rock geochemistry (pink) - restricted to shallower than 150 m depth, and water geochemistry (green). These are displayed over the 1 second SRTM DEM (Shuttle Radar Topography Mission Digital Elevation Model) of Australia.

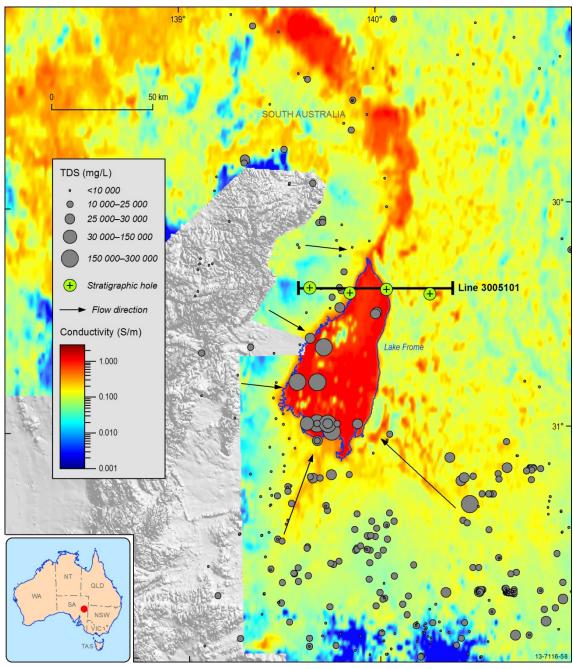


Figure 6.9 Water samples in the Lake Frome study area, sized proportional to total dissolved solids (TDS) content, for samples with TDS >5000 mg/L. The general flow direction of surface and near-surface waters are indicated by arrows. A section of flight line 3005101 (from the Frome AEM Survey), along with proximal stratigraphic holes, have been indicated to show the location of the cross section in Figure 6.8. These are displayed over the 0-5 m conductivity depth slice from the Frome AEM Survey (Roach, 2012).

6.5.1.3 Enrichment

The enrichment of saline fluids and subsequent brine evolution has been identified for Lake Frome. Given that fluid flow is towards the lake, enrichment of the inflow waters through evaporative concentration is evident in Figure 6.10, with Total Dissolved Solids (as well as lithium and potassium) increasing towards the Lake.

Another facet of brine evolution in the lake itself is evaporative pumping, where evaporation near the surface draws up deeper saline fluids. Geomorphological evidence for evaporative pumping has been identified in field surveys of Lake Frome through polygonal ridges in the halite crust (De Deckker, 1988). Evaporative pumping is also evident in AEM cross-sections across Lake Frome (Figure 6.10), which displays a draw-up cone of conductance extending from the margins of the lake, cutting across aquifer units.

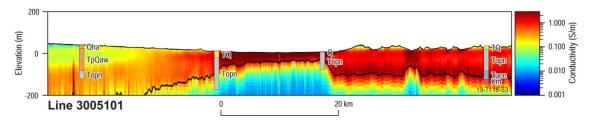


Figure 6.10 A west-east electrical conductivity cross section across Lake Frome (see Figure 6.7 for location) from the Frome AEM Survey (Roach, 2012). This has been prepared using sample by sample inversion of AEM data, with a logarithmic stretch applied. The black line indicates the depth of investigation (DOI). Proximal stratigraphic holes are displayed to show the broad correlation between conductance and facies. Note the draw-up cone of conductance into the centre of the lake, which is characteristic of evaporative pumping

6.6 Geochemistry of Lake Frome

Samples from Draper and Jensen (1976) and Chaku (1980) highlight that the Lake Frome brine is highly enriched in Na-Cl, with subordinate levels of SO_4^{2-} and only minor HCO_3^- and trace elements. The species Ca^{2+} , Cl^- and HCO_3^- are enriched in salt crust relative to brine, while Mg^{2+} and SO_4^{2-} are conversely enriched in the brine (Draper and Jensen, 1976).

The present strontium isotope ratio (⁸⁷Sr)⁸⁶Sr) of Lake Frome brines and modern halite crust (0.71126 - 0.71206) are of similar composition to the shallow Willawortina Formation (0.71171 – 0.71223) (Ullman and Collerson, 1994). This suggests that the major source for Lake Frome brines is from the west, as tributaries and groundwater associated with this Pliocene unit have similar strontium isotope ratios. Strontium isotope ratios increase with depth in preserved gypsum deposits in Lake Frome's sediment, which reflect either increasing groundwater input from the older Namba Formation, or greater groundwater residence times in the past (Ullman and Collerson, 1994).

6.7 Commercial viability of Lake Frome brines

In the sub-surface brines, lithium and potassium attain a maximum concentration in central east Lake Frome, reaching > 20 mg/L and > 750 mg/L respectively (Draper and Jensen, 1976). However these concentrations fall far below the levels required for economic development. Current or recently producing lithium-bearing salt lakes contain brines with lithium concentrations ranging from 50 mg/L to 1,400 mg/L, although the lowest productive grade for assessing prospectivity is currently 200 mg/L lithium (Gruber *et al.*, 2011). The cut-off grade for extraction of potassium brines is variable, and historically, development has not been based on true economic merit (Garrett, 1996). Current commercial potassium brines range in concentration from 1,500 mg/L up to 40,000 mg/L (Garrett, 1996; Kilic and Kilic, 2010).

Another way to assess Lake Frome's potential is to evaluate what the lithium concentration would be if the saline waters were evaporated to the point of halite precipitation (Figure 6.11). Samples within Lake Frome itself, collected by Draper and Jensen (1976), show the highest lithium concentrations (~5-25 mg/L) (Figure 6.11). However, these are grouped right at the boundary of halite saturation, and thus have no potential for further concentration during the extraction process. The three samples of inflow water apart from the cluster in Figure 6.11 correspond to mound spring samples. These mound springs have greater economic potential as they have capacity for further evaporative concentration, which would produce lithium levels of ~100 mg/L. This contrasts markedly to samples taken by COMALCO (Chaku, 1980) within Lake Frome, which show no lithium enrichment, and frequently lie below the enrichment curve for sea water. Samples from the Lake Frome catchment cluster around the sea water enrichment curve, and at best would reach concentrations similar to those found by Draper and Jensen (1976) if the fluids were evaporated to halite saturation.

When the Li:Cl evaporative trends of Lake Frome's brines and inflow waters are compared to major international lithium deposits and sea water, it is evident that Lake Frome is not much more enriched in lithium than sea water, and is well below the grades present in major deposits. Further, as the ratio of lithium to chloride is so low, future potential remains low as even evaporation modelling suggests that the brine will not reach economic concentrations.

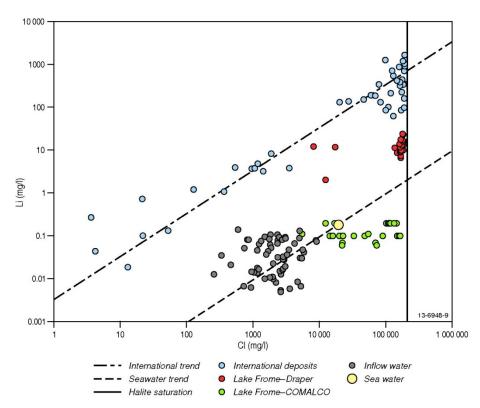


Figure 6.11 A plot of Li versus CI for lithium-bearing water samples in the Lake Frome study area compared with international lithium deposits and the sea water enrichment line during evaporative concentration. Data for international deposits obtained from: (Ericksen, 1987; Garrett, 1992; Garrett, 1998; Risacher and Fritz, 2009).

6.8 Reliability of potassium as a proxy

Based on the limited lithium data available it is worth establishing the validity of our assumption that potassium can be used as an effective proxy for lithium. When lithium is plotted against potassium (Figure 6.12), we would expect broadly a linear relationship.

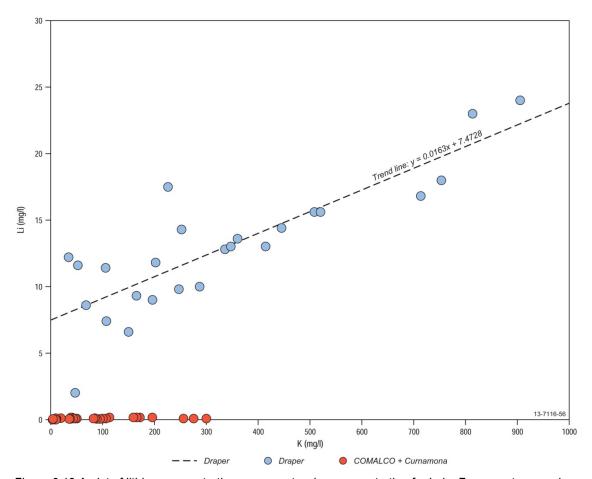


Figure 6.12 A plot of lithium concentration versus potassium concentration for Lake Frome water samples, separated by sample source. Draper samples (Draper and Jensen, 1976) in blue have a linear trend line fitted.

The Lake Frome waters, however, exhibit two distinct trends;

- A broadly linear relationship; and,
- No relationship where lithium remains ~0 mg/L as potassium increases.

The fact that a significant portion of the lithium-bearing samples do not exhibit a linear relationship with potassium suggests Lake Frome may behave as a potassium-bearing system. In such a system potassium increases independent to lithium and the use of potassium as a proxy for lithium breaks down.

However, these two relationships are complicated by the sample data. The only points to show the linear relationship are from Draper and Jensen (1976), while COMALCO and Curnamona data show depleted lithium at all levels of potassium. This is further complicated by the fact that the Draper and Jensen (1976) and COMALCO datasets consist of legacy data, using outdated sampling and analysis methods. Nonetheless, this raises doubt as to the validity of using potassium as a proxy.

6.9 Conclusions

Based on the current data available for Lake Frome, the modelling suggests there are not sufficient concentrations of lithium (or potassium) being supplied to Lake Frome for economic brines to form.

6.10 Mineral systems summary

6.10.1 Hydraulic connectivity

The major issue which has been identified through the course of this study is whether the source rocks, transportation pathways and depositional site are hydraulically connected.

The volcanic and metamorphic source rocks identified in the Flinders Ranges and Olary Spur are at the margins of the Callabonna Sub-basin, where contact with recharge waters is minimal. The high source rock potential, identified from rock samples, is likely not representative across the whole Callabonna sub-Basin, as rock samples were biased to hard rock units. In contrast, during transit, the surface and groundwater is mostly in contact with the Cenozoic units of the Namba Formation and Willawortina Formation. Although only a small number of rock samples were taken from these units, it is clear that these sedimentary units have low concentrations of potassium and lithium, and thus are not effective source rocks.

Extremely high lithium values of 100-250 mg/kg were measured below Lake Frome in sediment samples taken by COMALCO (Chaku, 1980), which represents a potential source material with clear hydraulic connectivity. However, water samples from the same depths do not reflect this enrichment, with lithium values between 0.1 – 0.2 mg/L. The fact that the brines have very low concentrations of lithium indicates that either lithium is not present in a readily leachable phase under current conditions or that the dataset is flawed.

6.10.2 Preservation

Another component that could explain the lack of lithium and potassium enrichment in brines is if a lack of brine preservation has been a problem. The climate, and as a result, water levels of Lake Frome have varied frequently during its history. During wet periods the brine pool rises above the surface, becoming a lake, with the potential to re-dissolve much of the precipitated salts and dilute the lithium and potassium in the brine (Li *et al.*, 1996). When lake levels recede, the lithium and potassium is largely retained in the brine pool. However, during some of Lake Frome's wet periods, it reached heights such that the Lake discharged into the Eyre Basin (Cohen *et al.*, 2012), losing a portion of the accumulated lithium and potassium. As Lake Frome last flushed as recently as 47 ka, for mass balance and geochemical purposes it can only be considered a closed basin since then.

Another potential factor that could affect brine preservation is groundwater leakage. Unless the salt lake base is sealed by an impermeable layer, brine infiltration out through bottom sediments can lose lithium and potassium from the system (Wood and Sanford, 1990). Brine leakage eventually produces a steady state-system, where inflow is balanced by outflow and the concentration of conservative species such as lithium and potassium in solution does not change (Risacher *et al.*, 2003). No prior research has suggested leakage is a concern for Lake Frome's brine, however, without sampling the base of the brine pool and below, this cannot be confirmed.

6.10.3 Drivers

If Lake Frome were to be considered a closed basin only for the last 47 kyr, this is still of a similar time-scale to salt lake lithium deposits worldwide, which have generally been active over the last 10-100 kyr (Chapter 4). The difference, however, is that although high levels of lithium have been identified in source rock within Lake Frome itself, there is a lack of geochemical or geothermal drivers in the Lake Frome region to facilitate the leaching, dissolution and transport of lithium. Because the solubility of lithium increases with temperature, most of the present lithium salt lake deposits are situated in active volcanic areas with strong geothermal gradients (Risacher *et al.*, 2003).

6.11 Study limitations

There are several problems identified in this study which limited the GIS analysis and modelling.

Without a depth or hydrological context for the water samples, it was not possible to identify which samples actually flow into Lake Frome, nor the relative contribution of groundwater sources to Lake Frome's chemistry. Further, it has not been clearly established to what depth groundwater feeds into Lake Frome. As Lake Frome formed in the upper Namba Formation, this suggests lateral groundwater drainage into Lake Frome can occur from only the upper Namba Formation and above (the Willawortina Formation). Evaporative pumping however may be drawing groundwater from deeper aquifers (Eyre Formation and below) below Lake Frome as indicated by AEM data. Thus water samples are needed of deeper units from the margins and within Lake Frome to identify salinity variations indicative of these units feeding Lake Frome.

A similar problem exists with rock samples. Most of the rock samples (excluding OzChem) do not give a stratigraphical or lithological descriptor. Furthermore, the sedimentary units which transport much of the groundwater have been under-sampled, with most of the rock samples consisting of hard rock units at the periphery or underlying the Callabonna sub-Basin. This has given a disproportionate view of the source potential of the Frome region, as the lithium- and potassium-poor sedimentary units are under-represented in the GIS analysis.

Another limitation for this study was that the available geochemical water and rock samples only rarely contained lithium analysis. This meant judgement of the potential of Lake Frome for hosting lithium deposits could only be based on potassium values, using the assumption that potassium was an effective proxy for lithium. However, comparing lithium with potassium in water samples for Lake Frome suggested that potassium may not necessarily be appropriate as a proxy for lithium.

7 Summary and Recommendations

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The preliminary favourability analysis of Australian salt lakes (see Chapter 5) is based on limited data that is sometimes inconsistent and patchy (see Appendix A). Most datasets used in this assessment were not available at the national scale. For example, currently, salinity data exists for only approximately 100 lakes out of over 1,200 salt lakes in Australia. There is also severely limited information on the concentration of lithium, boron, potassium, uranium and other elements in groundwater feeding salt lake systems. Furthermore, in most cases, very little is known about the hydrogeological connectivity between leachable source rocks and salt lakes. This is an important control on the potential of salt-lake systems to form economic grades of lithium, boron, potassium, and uranium and needs to be better defined.

Given the limitations imposed by the publicly available data, our assessment of the potential of Australian salt lakes for strategic resources has identified seven regions with salt lakes that have potential for lithium, boron, potassium and/or calcrete-hosted uranium. They are the Lake Woods region and the central western region of the Northern Territory, the north east Yilgarn Craton, the Paterson region, and the south Musgrave region in Western Australia, the Lake Frome – Lake Eyre region and the central Gawler region in South Australia. The conclusions and recommendations for each region are discussed below. However, other favourable areas for exploration may be discovered if more data can be collected and analysed.

7.1 Salt lake systems favourable for lithium and boron

Based on examples from North and South America, China and western Asia, the mineral systems for salt lake-hosted lithium and boron are very similar (see Tables 4.1 and 4.2), and the potential for similar mineral systems in Australia is considered to be low to moderate. Most of the world's productive salt lakes occur in intermontane basins at elevations exceeding 1000 m, whereas the majority of Australia's salt lakes occupy relatively flat, low-lying parts of the landscape. Furthermore, in other parts of the world, most of the lithium and boron is sourced from felsic to intermediate volcanic rocks containing volcanic glass, which provides a readily leachable source of lithium, potassium and boron, with additional lithium and boron also sourced from springs in geothermally active areas. These sources of metals are rare in Australia but other sources are likely to be present as indicated in the results of the National Geochemical Survey of Australia (Caritat and Cooper, 2011).

Australia also has an arid climate that has resulted in the formation of a plethora of salt lakes and it is conceivable that other, as yet unrecognised, mineral systems, with alternative sources of lithium and boron may operate in some of these salt lakes. In fact, several companies have already begun exploration for lithium-bearing salt lakes in Australia. AmeriLithium has taken out three exploration leases in Western Australia around and abutting Lake Dumbleyung (AmeriLithium Press Release February 23, 2012) and ERO Mining Limited is exploring for brine-hosted lithium in the Lake Frome and Lake Torrens areas in South Australia (ERO, 2011). Furthermore, the preliminary favourability analysis of Australian salt lakes (see Chapter 5) has shown that the evaporation trends for some groundwaters (particularly those associated with mound springs) in the Lake Frome – Lake Eyre and central Gawler regions may approach economic concentrations.

7.2 Salt lake systems favourable for potash

The potential for Australian salt lakes enriched in potash is much higher than lithium as there are many more potential sources of potassium. Based on examples from North and South America, China and western Asia (see Table 4.4), the most productive basins globally, are those with some surface or near-surface evaporites or basins with relatively young volcaniclastic sequences. However, Australia also possesses the critical factors needed for the formation of salt lakes enriched in potash and the preliminary analysis of Australian salt lakes (see Chapter 5) has identified the Lake Woods and central western part of the Northern Territory, the Lake Frome, Lake Eyre and central Gawler regions of South Australia, the Paterson region and the north east Yilgarn region in Western Australia as areas with potential for salt lakes enriched in potash.

There are already a number of active potash projects within Australia. Reward Minerals Limited has announced that they intend to bring the Lake Disappointment project into production as soon as possible (Reward Minerals, 2012c) and they are also currently assessing the potential of Lake Mackay for the production of potash (Reward Minerals, 2012d and f). Rum Jungle Resources in partnership with Reward Minerals Limited have also identified a significant salt lake potash resource in the Karinga Creek region in the central western region of the Northern Territory (Reward Minerals, 2012e) and, historically, potash was also produced from the Lake Chandler deposit in the Yilgarn Craton in Western Australia.

7.3 Critical features of salt lake systems with valley and playa-type, calcrete-hosted uranium

Australia has many calcrete-hosted uranium deposits and prospects, including Yeelirrie, which is Australia's second largest undeveloped uranium deposit. Most calcrete-hosted uranium deposits in Australia typically form in palaeochannels that drain into salt lakes, and hence, are spatially related to salt lake systems. The preliminary analysis of Australian salt lakes (see Chapter 5) has identified the north east Yilgarn Craton, South Musgrave region and the Paterson Province in Western Australia, the central western region in the Northern Territory, and the central Gawler region in South Australia as having the highest potential for calcrete-hosted uranium deposits.

Apart from the Yeelirrie deposit, other already known calcrete-hosted uranium deposits include the Lake Way, Centipede, Lake Maitland and Thatcher Soak deposits in the Yilgarn Craton, the Lamil Hills prospect in the Paterson region, and the Napperby deposit in the central western region of the Northern Territory.

7.4 Recommendations

The following recommendations are based on the evaluation of the salt lake data and geological, geochemical, and hydrological interpretations of that data presented in previous chapters:

Recommendation 1: The identified high potential for Australian salt lakes enriched in potash needs to be followed up with additional studies in prospective areas to improve the quality of hydrogeochemical and geological data in these regions and fill in gaps in the existing datasets. Potash is essential for the production of fertilisers, and hence, essential for Australia's agriculture industries. As there is no current production of potash in Australia (although some is planned), a mineral systems based prospectivity analysis would identify areas with potential for economic production of potash and also encourage further interest in potash exploration in Australia.

Recommendation 2: This study has shown that salt in some Cenozoic salt lakes was derived from older (Neoproterozoic to Paleozoic) evaporite-bearing successions. This raises the question of whether the hydrochemistry of the salts and brines in these 'halotectonic settings' differs from those salt lakes whose chemical signatures are largely meteoric or, at most, reflect the geochemistry of their immediate catchments. For this reason Lake Disappointment, Lake Mackay, Lake MacDonald, Lake Hopkins, Lake Neale, Lake Amadeus, Karinga lakes, Lake Cobb, Lake Newell and salt lakes in the Baker Palaeovalley are worthy of further study. Both deep and shallow wells are required for sampling the brines, salts and sediments for detailed hydrochemical, isotopic and mineralogical analysis.

Recommendation 3: Although not in the scope of this report, higher temperature, oil field and deep geothermal brines are also potential sources of potash and/or lithium and/or boron. Therefore, further studies of Australia's oil fields and the deep geothermal fluids in the Great Artesian Basin are required in order to assess their potential for these strategic commodities.

7.4.1 Recommendations to improve data quality

The preliminary favourability analysis of Australian salt lakes has also found that most of the data needed for a proper assessment of Australian salt-lake systems are either of inconsistent quality or severely limited in areal distribution. Some general recommendations needed to rectify this situation are given below:

Recommendation 4: There is a significant need to collect a consistent and comprehensive suite of chemical analyses (including salinity) from selected salt lakes. The salinity of salt lakes undergoes seasonal and spatial variation, and hence, a robust methodology of measuring salinity needs to be developed before undertaking sampling and analysis. Continuous pH/TDS/temperature monitors could be used for this purpose. In addition, airborne electromagnetic (AEM) data can provide rough estimates of conductivity (hence salinity) of salt lakes which may then be applied to any remaining lakes not previously sampled.

Recommendation 5: The available groundwater hydrogeochemical datasets are patchy at best, inconsistent and of variable quality. Many datasets in the vicinity of salt lakes only report salinity or total dissolved solids. There is a crucial need for a consistent and comprehensive groundwater database that includes a comprehensive suite of elements as well as salinity, pH, Eh, etc. Given that there are more than 1,200 salt lakes in Australia, detailed hydrochemical and hydrological datasets should initially be obtained from those lakes that are likely to be economically significant. New wells equipped to sample at multiple depths and different aquifers in the groundwater are recommended to fill data gaps and assess flow of saline water to the playas. Instrumentation to record evaporation on playa surfaces and evapotranspiration near playa margins is also essential for modelling brine evolution.

Recommendation 6: An important control on the potential of salt-lake systems to form economic deposits of lithium, boron, potassium and calcrete-hosted uranium is the existence of hydrogeological connectivity between leachable source rocks and salt lakes. Thus, it is essential to map the hydrogeological system in catchments of prospective salt lakes and the rocks and sediments infilling any palaeochannels feeding salt lakes in combination with the hydrochemical data available in order to understand the evolution of the brine and the pathways of fluids to the salt lakes.

Recommendation 7: Geoscience Australia's (Ozchem) whole-rock geochemistry dataset was used to delineate the distribution of source rocks with lithium, boron, potassium, uranium, and vanadium.

However, the number of rock samples analysed for lithium and boron is severely limited due to the analytical methods of analysis. Therefore, rock powders from areas near salt lakes that are available in Geoscience Australia's rock store need to be re-analysed to fill the existing gaps in the elemental analyses in this dataset.

Recommendation 8: The National Geochemical Survey of Australia (NGSA) dataset only reports boron and lithium concentrations obtained in aqua regia and MMI extracts, which represent only minimum estimates of the total concentration of these elements in samples. Once again, these samples need to be re-analysed for total boron, lithium and other elements. In addition, the NGSA survey did not cover some important catchments in South Australia and Western Australia.

Recommendation 9: The occurrence of evaporites and evaporite-bearing rocks was obtained from Geoscience Australia's 1:1 000 000 surface geology map. It would be highly desirable to map the distribution of evaporitic rocks under cover but this would require a consistent national-scale solid geology map of Australia.

More detailed recommendations for future work in the areas of potential for salt lake-hosted lithium, boron, potash or calcrete-hosted uranium are given below. The areas with potential to host all four commodities are listed first followed by those with fewer commodities. However, it should be noted that in many of these areas there is no data available on the other commodities.

7.4.2 Recommendations for the north east Yilgarn Craton in Western Australia

The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for the formation of salt lakes enriched in potash and/or lithium and/or boron and/or calcrete hosted uranium. Major lakes in this area include Lake Nabberu, Lake Way, Lake Darlot, Lake Irwin, Lake Carey, Lake Carnegie, Lake Raeside, Lake Mason, Lake Maitland, Lake Barlee, Lake Noondie and Lake Austin (see inset on Map 3, Appendix B).

- Although a significant number of bore waters have been analysed in the area, a more rigorous check is required to determine the quality of data and its implications for the aquifers in this region.
- More studies are needed to understand hydrogeological setting of the salt lake system (i.e., lithology and geochemistry of sediments infilling palaeochannels).
- More information is also needed about the nature of lake sediments and lake water compositions to help in assessing their potential.

7.4.3 Recommendations for the Central Gawler region in South Australia

The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for potash and/or lithium and/or boron and/or calcrete-hosted uranium deposits. The major lakes in this area are Lake Torrens, Pernaty Lagoon, Island Lagoon, Lake Gairdner, Lake Harris, Lake Acraman, Lake Gilles, Lake Younghusband and Lake Labyrinth. A well developed system of Cenozoic palaeovalleys has been mapped in the Central Gawler region (Hou *et al.*, 2013) and it is likely that salt lakes are fed by groundwaters in the aquifers within these palaeovalleys.

- A more comprehensive geochemcial groundwater dataset is essential to properly assess the potential of salt lakes in this area. Currently, there are no publicly available hydrogeochemcial data in the proximity of Lake Torrens.
- Although some work has been carried out on the shape, size and evolution of palaeovalleys in the area (Hou *et al.*, 2013), more work is needed to understand the hydrogeological setting of palaeovalleys and salt lake systems in this region.

7.4.4 Recommendations for Lake Frome – Lake Eyre regions in South Australia

The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for potash and/or lithium and/or boron deposits. The major lakes in this area are Lake Frome, Lake Callabonna, Lake Blanche, Lake Gregory and Lake Eyre (see inset on Map 3, Appendix B).

- A more detailed hydrogeochemical survey of the Lake Frome and Lake Eyre region is required, including lithium, boron and potassium analyses, and with information on the unit or depth the sample was taken from.
- Samples of lake waters at multiple depths are needed, to assess the depth of the brine pool and risk of groundwater leakage, as well as for testing the validity of evaporation models and to allow more complex processes including mixing of separate sources to be modelled.
- Rock samples are needed from the Cenozoic cover to better assess their source potential.
- More studies are needed to understand the hydrogeological setting of the salt lake system and in particular the hydraulic connectivity, preservation and geothermal and geochemical drivers (past or present).
- Additional temperature data are needed from groundwater systems.

7.4.5 Recommendations for the Paterson region in Western Australia

The preliminary favourability analysis of Australian salt lakes indicates that this region has considerable potential for salt lakes enriched in potash and the formation of calcrete-hosted uranium. Major lakes in the area include Lake Disappointment, Lake Dora, Lake Waukarlycarly, and Ten Mile Lake (see inset on Map 3, Appendix B).

- A more comprehensive hydrogeochemical groundwater dataset will be essential for the proper assessment of the potential for calcrete-hosted uranium and potash deposits. Currently, there are no data publicly available in the proximity of Lake Disappointment itself.
- A number of undercover salt diapirs have been mapped in the Officer Basin not far from these salt lakes. It will be critical to better map the distribution of the salt diapirs because they may be the source of potassium and other salts.

7.4.6 Recommendations for the central western region of the Northern Territory

The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for salt lakes enriched in potash and the formation of calcrete-hosted uranium deposits. Major lakes in the area include Lake Mackay, Lake MacDonald, Lake Hopkins, Lake Bennett, Lake Lewis, Murphy's Lake, Lake Amadeus, and Lake Neale (see inset on Map 3, Appendix B).

- A major requirement is for the collection of hydrogeochemical data on the composition of groundwater feeding into the above lakes as there is a paucity of data at present, particularly for Lake Mackay, Lake MacDonald and Lake Hopkins.
- If evaporites (e.g. the Bitter Springs Formation) are the source of potassium in this region, it will be necessary to more accurately map their distribution both from surface outcrops and subsurface mapping from drilling new wells or from new seismic surveys.
- Although some work has been carried out on the shape, size and evolution of palaeovalleys in
 the area (English et al., 2012), more work is needed to understand the hydrogeological setting
 of salt lake systems in this region. Further studies are needed on: (1) the palaeovalleys
 containing Lake Lewis and Lake Bennett; (2) the palaeovalleys containing Lake Amadeus and
 Lake Neale; (3) the palaeovalleys running south from the Tennant Creek region; and (4) the
 palaeovalleys to the north east end of the Ngalia Basin where hydrogeochemical data indicates
 a cluster of high uranium and vanadium concentrations.
- More information is also required on the local geology and sediment lithology near the lakes of interest.

7.4.7 Recommendations for the Lake Woods region of the Northern Territory

The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for the formation of salt lakes enriched in potash. The major lakes in this region are Lake Woods, Tarrabool Lake, and Lake Sylvester (see inset on Map 3, Appendix B). The salt lakes are thought to be fed predominantly by surface inflow and groundwater. No major palaeovalleys have as yet been mapped in the area.

- If evaporites are the source of potassium in this region, it will be necessary to more accurately map their distribution (outcrop as well as under cover).
- It will be also necessary to collect more hydrogeochemical data on the composition of groundwater and lake water.
- More information is also required on the local geology, sediment lithology, and on any palaeovalleys (if present) near the lakes of interest.

7.4.8 Recommendations for the south Musgrave region in Western Australia

The preliminary favourability analysis of Australian salt lakes indicates that this region has potential for the formation of calcrete-hosted uranium deposits (see inset on Map 4, Appendix B).

- A comprehensive geochemical groundwater dataset will be essential for the proper assessment of the potential for calcrete-hosted uranium deposits.
- More information is also needed on the aquifers and on the other sediments infilling the palaeovalleys to check for sources of uranium and vanadium.

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Appendix A Datasets used for the favourability (prospectivity) analysis of Australian salt lakes

The favourability of salt lake systems to generate Li, B and K brines and to form uranium-bearing calcretes was assessed using a number of national- and regional-scale datasets. These datasets are listed below in two categories; (A.1) datasets that have already been published, and (A.2) additional datasets that were developed during this project or datasets that are not readily accessible. The latter are supplied in digital form with printed copies of this report or alternatively they may be downloaded from the Geoscience Australia website http://www.ga.gov.au/products-services/data-applications.html.

A.1 Published datasets

A.1.1 Salinity of salt lakes

There is limited information on the salinity of waters in salt lakes. This is because salinity undergoes seasonal variation and also varies spatially. We have compiled salinity data for one hundred salt lakes documented in published and unpublished reports (e.g. Jankowski and Jacobson, 1989; Bowen and Benison, 2009).

A.1.2 National Geochemical Survey of Australia (NGSA) geoochemistry dataset

This dataset provides concentration of Li, B, K, U, V in four soil samples collected in each NGSA catchment (For detailed description of the dataset and methodology see https://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=71973). However, the NGSA survey did not cover some important catchments in South Australia and Western Australia. In addition the dataset reports concentrations for lithium and boron only in aqua regia and MMI extracts which represent minimum estimates of total concentration of these elements in samples. However they also provide good estimates of leachable concentrations these elements. In this work concentrations in coarse BOS and TOS fractions are combined to estimate mean values in the coarse fraction. Similarly mean values of fine fractions of BOS and TOS samples are also estimated.

A.1.3 Ozchem whole rock geochemistry database

Geoscience Australia's whole rock geochemistry data (Ozchem) is available from http://www.ga.gov.au/products/servlet/controller?event=PRODUCT_SELECTION&theme=Geochemistry&keyword=Ozchem. This dataset is important to delineate the distribution of source rocks of leachable Li, B, K, U, and V. However number of rock samples analysed for lithium and boron is relatively limited. Hence this dataset cannot be used to prepare a national-scale favourability map of lithium and/boron-rich brines in salt lake systems. In this work concentrations of elements in Ozchem samples within a catchment are combined to give mean value for the catchment.

A.1.4 U²/Th Dataset

This dataset was used for selecting calcrete-bearing palaeochannels with anomalous values of uranium. Previous studies have shown a close spatial correlation between high U²/Th values and uranium-bearing valley calcretes (Wilford *et al.*, 2009). Airborne gamma-ray spectrometry measures gamma-rays from potassium, thorium and uranium that emanate from the uppermost 30 cm to 40 cm of soil and rock in the crust. Variations in the concentrations of these radioelements largely relate to bedrock and regolith geochemistry

(https://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=70791). Uranium and thorium abundances are derived indirectly by measuring gamma-ray emissions associated with the daughter radionuclide's bismuth (214Bi) and thallium (208TI), respectively. Uranium is generally more mobile than thorium. Thorium mobility is generally low and its concentration in the regolith is typically associated with stable weathering products including clays and iron oxides and resistate minerals such as zircon. High U/Th or U²/Th rations values can therefore indicated preferential mobilisation and concentration of uranium compared to lower ratios values of the original bedrock.

A.1.5 Evaporites and Evaporite-bearing Rocks

The rocks were extracted from Geoscience Australia's 1:1 million surface geology map (http://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=74619). The selected rocks include units which contain in the lithological description attributes such as evaporites, gypsum, halite, and salt. They represent rocks mapped as outcropping. It will be important to map distribution of evaporitic rocks under cover but this would require a consistent national-scale solid geology map of Australia

A.1.6 WASANT Palaeovalley map of WA, SA, and NT

The spatial distribution of palaeovalleys, which are regarded as significant in influencing groundwater system flow to salt lakes, was sourced from the WASANT Palaeovalley Map (Bell *et al.*, 2012: https://www.ga.gov.au/products/servlet/controller?event=FILE_SELECTION&catno=73980). This map covers only WA, SA and the NT although most salt lake systems of interest to the present study are located in these states. Generation of the WASANT Palaeovalley Map, its limitation and caveats are described by English *et al.*, (2012): http://archive.nwc.gov.au/library/waterlines/86. The map extends across the arid and semi-arid zones of the three states, as defined by the Köppen-Geiger climatic classification scheme (http://www.bom.gov.au/climate/environ/other/koppen_explain.shtml), in which zones virtually all Australian salt lakes are located. The map was compiled using national-scale datasets, including Digital Elevation Models (DEMs), particularly NASA's Shuttle Radar Topography Mission (SRTM) data, plus existing geological maps and expert knowledge. The mapped distribution of palaeovalleys includes those buried beneath desert dunefields disclosed through an innovative DEM, the Multi-resolution Valley Bottom Flatness (MrVBF) index of Gallant and Dowling (2003), with other data datasets.

A.1.7 Map of Calcrete Distribution in Australia

The map showing the distribution of calcrete is based on the digital 1:1 million Surface Geology of Australia (Raymond (2012);

http://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=74619). The map shows where calcrete dominates the unit and does not include polygon units where calcrete and other carbonate materials (e.g. calcareous soils) are described as a component in the lithological description.

A.1.8 Calcrete-hosted Uranium Deposits and Prospects

Calcrete uranium deposits and prospects and other uranium occurrences. Known calcrete uranium deposits and prospects and other uranium occurrences were extracted from Geoscience Australia's Ozmin database

(http://www.ga.gov.au/products/servlet/controller?event=PRODUCT_SELECTION&theme=Geology&k eyword=Ozmin).

A.1.9 The South Australian Resources Information Geoserver (SARIG)

SARIG (http://www.pir.sa.gov.au/minerals/sarig2) is a portal created by the Government of South Australia that provides free access to all state and company rock samples. Rock samples included in SARIG comprise drill cores, drill cuttings and rock outcrops/floats. Using the SARIG application, an advanced rock sample search was conducted. The search was restricted to rock samples with "Geochemistry Analysis", "Geochemistry" under 'Analysis Type', and "Potassium" under 'Analyte'. As SARIG is limited to a 2° by 2° search window, the data was collected using multiple "Geographic Search Extents" and aggregated at the last step. The results of the search were obtained by "Download results data package", where both files; "rock sample details" and "geochemistry results" were downloaded. This yielded 8682 samples. Of these samples, only 446 had Li values.

The "geochemistry results" data was not presented in a useable format, requiring significant data reformatting, which matched each sample (row) in "rock sample details" with the geochemistry of each element, converting all measurements into consistent units. This was done for each spreadsheet, and aggregated at the end. Where negative values where encountered (likely indicating the detection limit had been reached) the value was halved and made positive.

A.1.10 Groundwater hydrogeochemical data

A.1.10.1 Department of Environment, Water and Natural Resources dataset

WaterConnect

(https://www.waterconnect.sa.gov.au/GD/Pages/default.aspx#ctl00_m_g_21d79c5a_22e5_4930_b0f6 _e8db1335a1f2_ctl00_tabber:713bb3b5-4b73-46d9-954c-716214bcd793) is a portal created by the Government of South Australia that provides free access to State and company groundwater samples. Using the WaterConnect application, Lake Frome and a wide surrounding area were highlighted on the graphical user interface. The search was restricted to samples with "Salinity" values (under the "Parameters" heading). The selected samples were obtained using "Download Data" as a series of files; 'Well Summary', 'Water Chemistry', 'Lithological Logs', 'Hydrostratigraphic Logs' and 'Stratigraphic Logs'.

To process the data, samples beyond the boundaries of the study area were deleted. The data from "Well Summary" and "Water Chemistry" were then collated into the AquaChem template. The geochemical data was presented without units, but were assumed to be in mg/L. All salinity values were taken from the 'Well Summary' file. For samples also containing 'Water Chemistry', all values except salinity were transferred, and the sampling date of the water chemistry was used.

A problem prevalent in the WaterConnect water samples is that none of them gave the depth the sample was taken from. Without depth, further information on lithology and stratigraphy from the accompanying log files could not be incorporated. This was because within these logs, multiple units (hydrological, stratigraphic and lithological) were the identified over the depth of the bore for each sample number, with no way of knowing which of the units was sampled. A rough sample depth was assumed for WaterConnect samples, where applicable, from the water table depth (swl) given in the "Well Summary" file. A further problem for this study was that none of the WaterConnect samples contained Li analyses.

A.1.10.2 The COMALCO dataset

During the 1970s, the Commonwealth Aluminium Corporation Limited (COMALCO) drilled nine holes within Lake Frome, taking rock and water samples at several depths for geochemical analysis. The geochemical analyses of COMALCO's water samples were transcribed into the AquaChem template from the well completion reports (Chaku, 1980).

Samples within each well were assumed to correspond to the logged aquifer units, starting at number 1 nearest the surface and increasing with depth. Wells CF2 and CF3 had more water samples than identified intersected aquifer units. Thus an additional aquifer unit was assumed in the log based on facies and the samples attributed depths accordingly. Due to these assumptions there is some doubt associated with the depths of each sample.

Where COMALCO water geochemistry was below detection limits, i.e < 0.05 mg/L, these were represented as 0.05 mg/L.

A.1.10.3 Northern Territory hydrochemistry

This hydrochemistry dataset can be obtained from the Northern Territory Department of Land Resource Management (http://www.lrm.nt.gov.au/nrmapsnt).

A.1.10.4 Hydrochemistry for the Lake Disappointment region

A small amount of hydrochemical data for the Lake Disappointment region was obtained from the Western Australian Department of Water (http://www.water.wa.gov.au/).

A.2 Additional datasets developed or used during this project

A.2.1 Distribution of Australian Salt Lakes

Australian salt lakes showing distribution, size and nature (perennial and non-perennial) of salt lakes. Lakes were derived from the Australian 1:250,000 digital topographic dataset (https://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=64058). The topographic dataset comprises of over 128,000 water bodies including perennial and non perennial lakes. Several filters were applied to derive the 1,200 lakes used in this investigation. Only non-perennial

lakes were selected which essentially limited the analysis to lakes in arid and semi-arid regions of Australia. We also applied a size threshold with lakes less than 4.9 km² removed from the analysis. This filter largely removed smaller bodies that corresponded to drainage lines and flood plains.

A.2.2 Groundwater hydrochemical data

A.2.2.1 Giblin groundwater hydrochemistry dataset

The only national-scale compilation of hydrogeochemistry of groundwaters was produced by Giblin (CSIRO data base; Dickson and Giblin, 2006). Geochemical data in this dataset are of variable quality and provenance and distribution of samples are not uniform. Apart from the concentration of major cations, the data on the concentration of minor elements such as Li, B, U, and V is unavailable or is available only for a limited number of samples (e.g. only 22% samples have values for V; 54% for Li). The situation with regard to U and B is better (82% for B and 95% for U). For this project we have developed a smaller set of data restricted to the major elements of interest to us which are Li, B, K, Cl, U and V.

A.2.2.2 Hydrogeochemical data for the north-east Yilgarn Craton

More information about this groundwater dataset can be found in Gray, D.R. *et al.* (2009), Hydrogeochemical mapping of north-east Yilgarn groundwater. CSIRO Report P2009/1612. Perth, Commonwealth Scientific and Industrial Research Organisation, 72p. In this project we have only considered conductivity, total dissolved solids (TDS), B, K, Li, Cl, U, Li/Cl, B/Cl, and K/Cl.

A.2.2.3 Hydrogeochemical data for Lake Frome from Draper and Jensen

Additional hydrogeochemistry for Lake Frome was also obtained from Draper and Jensen (1976). At the time of the survey about 10% of the lake was covered with water. Both surface and subsurface waters were hypersaline (26% to 34%) and characterised by high concentrations of sodium and chloride ions. No enrichment of minor elements was detected In the brines, but Pb appears to be leached from the sediments as soluble chloride complexes. In this project we have only considered TDS, K, CI, B, Li, Li/CI, B/CI and K/CI.

A.2.2.4 Curnamona hydrochemistry dataset

The Curnamona dataset was derived from a geochemical assessment of groundwater in the Broken Hill area, south of Lake Frome (Caritat *et al.*, 2005). For this project we have used a subset of the original data restricted TDS and Li, B, Cl, K, Li/Cl, B/Cl and K/Cl.

Appendix B Maps showing the results of the favourability (prospectivity) analysis of Australian salt lakes

Four maps have been produced showing the areas most favourable for economic concentrations of lithium, boron, potash and calcrete-hosted uranium as described in detail in Chapter 5. These maps are too large to be included in this report but they may be downloaded from the Geoscience Australia internet site at: http://www.ga.gov.au/. A brief description of the maps is as follows:

- Map 1 A map of Australian salt lakes systems prospective for lithium deposits [Geocat No. 75878]
- Map 2 A map of Australian salt lakes systems prospective for boron deposits [Geocat No. 75877]
- Map 3 A map of Australian salt lakes systems prospective for potash deposits [Geocat No. 75875]

These three maps show salt lake regions favourable for lithium, boron, and potash (potassium). For a more detailed description of the selection method see Chapter 5.

Lithium, boron, and potassium concentrations assigned to salt lakes were estimated from three datasets: Geoscience Australia's Ozchem (for whole-rock analysis); NGSA samples in the catchments (catchment outlet sediments); and Groundwaters (dataset described by Dickson and Giblin, 2006). Lithium and boron concentration in the NGSA samples were determined in aqua regia extract and thereby represent a minimum estimate of total lithium and boron concentration in the sample. The mean values of concentration were derived by averaging of values in samples (separately for each of the three datasets) located in the catchment. These mean values were assigned to salt lakes located in the catchment. In those cases when values from three datasets overlapped, the highest value was assigned to the overlapping part of the salt lake. Thus, these values do not represent elemental concentration in the salt lakes but the concentration of these elements in the catchment in which salt lakes are located.

NGSA catchment boundaries are sourced from Caritat and Cooper (2011).

Australian salt lakes were derived from the Australian 1:250 000 digital topographic dataset (https://www.ga.gov.au/products/servlet/controller?event=GEOCAT_DETAILS&catno=64058). The topographic dataset comprises over 128,000 water bodies including perennial and non perennial lakes. Only non perennial lakes were selected which limited the analysis to lakes in arid and semi-arid regions of Australia. A size threshold was applied, with lakes less than 4.9 km² removed from the analysis, leaving 1200 non-perennial lakes shown on the map.

The spatial distribution of palaeovalleys, which are regarded as significant in influencing groundwater system flow to salt lakes, was sourced from the WASANT Palaeovalley Map (Bell *et al.*, 2012).

The outline of arid and semi-arid zones is based on Köppen-Geiger classification (Stern et al., 2013).

The groundwater flow direction in the palaeovalley is assumed to dominantly follow palaeovalley gradients which are deduced from palaeovalley drainage networks constructed during the production of WASANT Palaeovalley Map (Bell *et al.*, 2012; English *et al.*, 2012).

Groundwater data shown on inset maps and on evaporation-trend plots have been extracted from the following sources:

Northern Territory: Water Resources Branch, Department of Land Resource Management, Northern Territory (http://www.lrm.nt.gov.au/nrmapsnt)

South Australia: Water Connect, Department of Environment, Water and Natural Resources, Government of South Australia (https://www.waterconnect.sa.gov.au); Geological Survey of South Australia, Department for Manufacturing, Innovation, Trade, Resources and Energy, Government of South Australia; Draper and Jensen (1976); Caritat *et al.* (2005).

Western Australia: Gray *et al.* (2009); Water Information Management, Department of Water, Government of Western Australia (http://www.water.wa.gov.au/).

The inset maps show Li/Cl, B/Cl and K/Cl ratios of groundwaters corresponding to different enrichment threshold values compared to average sea water (Drever, 1997). The Li-Cl, B-Cl and K-Cl plots accompanying each inset map show concentrations of lithium, boron, potassium and chlorine in groundwaters. On these plots red dots represent data from salt lakes (inflow and lake waters) with economic-grade concentrations of lithium, boron, and potassium outside Australia. The blue line shows the evaporation trend of average sea water. The large blue dot represents the composition of average sea water. Other dashed and solid sloping lines show evaporation trends for waters with different levels of enrichment in Li-Cl, B-Cl or K-Cl (enrichment level labelled) compared to an evolved sea water of the same chloride concentration. The green vertical line represents the line of saturation with respect to halite (NaCl).

Map 4 – A map of Australian salt lakes systems prospective for calcrete-hosted uranium deposits [Geocat No. 75876]

This map shows regions favourable for calcrete-hosted uranium mineral systems. For a more detailed description of selection method see Chapter 5.

Uranium (only in felsic rocks) and vanadium concentrations are sourced from Geoscience Australia's Ozchem database. The map shows mean values of uranium and vanadium concentrations in the source rocks in the NGSA catchments. The mean values were derived by averaging of values in Ozchem samples located in the catchment.

NGSA catchment boundaries are sourced from Caritat and Cooper (2011).

The spatial distribution of calcrete is extracted from the 1:1 million Surface Geology of Australia (Raymond, 2012).

The spatial distribution of palaeovalleys, which are regarded as significant in influencing groundwater system flow to salt lakes as well as the formation of valley calcrete and calcrete aureoles around salt lakes, was sourced from the WASANT Palaeovalley Map (Bell *et al.*, 2012).

The groundwater flow direction in the palaeovalley is assumed to dominantly follow palaeovalley gradients which are deduced from palaeovalley drainage networks constructed during the production of WASANT Palaeovalley Map (Bell *et al.*, 2012; English *et al.*, 2012).

U²/Th values are derived from measurement of U and Th by gamma-ray spectrometry as recorded in the Airborne Radiometric dataset (Minty *et al.*, 2009).

Uranium concentration in groundwater data are sourced from a database described in Dickson and Giblin (2006).