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Potash in Australian Acid Salt Lakes

Potash is the common name for various salts that contain potassium (K) in water-soluble form and is an important component of many fertilisers. Because of its importance, a review was carried out into the potential of Australian salt lake systems from arid areas for potash, lithium, boron, and calcrete-hosted uranium deposits (Mernagh et al., 2013). Following this study, Geoscience Australia investigated the depositional environments, studied various examples and considered exploration histories of Australian acid salt lakes.

Background

Continental salt lakes in most places round the world generally tend towards higher pH with increasing levels of salinity (Hardie and Eugster, 1970). Many Australian salt lakes (Figure 1) diverge from this pattern, being near neutral with respect to pH (De Deckker, 1983). In addition, many salt lakes in southern Australia are acidic including those in the Eyre Peninsula (Lock, 1988), southwest Western Australia (Mann et al., 1983; McArthur et al., 1991) and parts of the Mallee region of Victoria and South Australia, most notably Lake Tyrell (Long et al., 2009; Macumber, 1992).

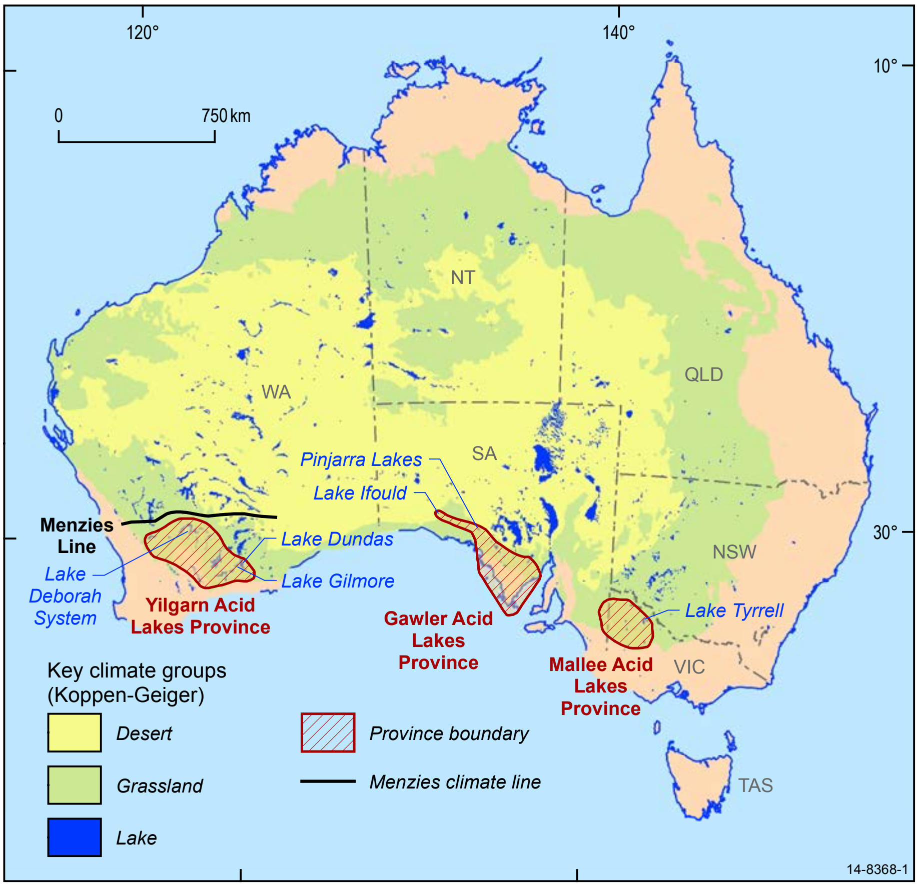

Figure 1: Map of Australia showing distribution of salt lakes and areas containing lakes with low pH.

A consequence of these saline, acidic conditions is the occurrence of distinctive sulfate minerals, specifically alunite [$KAl_3(SO_4)_2(OH)_6$] and jarosite [$KFe_3(SO_4)_2(OH)_6$] which are much more abundant relative to global and other less acidic Australian salt lakes (McArthur et al., 1991). Alunite and jarosite both contain significant potassium (9.4% and 7.8% respectively), which is precipitated at lower brine concentrations than potassium chloride species such as sylvite (KCl) and carnallite ($KMgCl_3 \bullet 6(H_2O)$). The most detailed studies of acid lakes in Australia have been those on 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; Worrall and Clarke, 2004).

Formation of low pH brines

A common feature of all Australian acid salt lakes is that they occur in the southern part of the Australian arid zone, south of the Menzies Line in Western Australia, where winter rains dominate (Figure 1; Butt et al., 1977). The winter rainfall pattern is conducive to the development of hypersaline brines in the arid zone (Gray, 2001). 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:

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

This reaction was proposed to occur at the weathering front involving both bedrock sulfides and ferrous iron-bearing silicates. However, a study by McArthur et al. (1991) showed that weathering of basement had a comparatively minor contribution to the brine chemistry with the key processes being 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.

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 (Long et al., 2009; Macumber, 1992). Although the source of ferrous iron is different, the reaction is essentially the same equation as shown above. 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 (McArthur et al., 1991).

More recently, an alternative hypothesis for acid lakes to those of Mann et al. (1983) and McArthur et al. (1991) has been suggested (Worrall and Clarke, 2004). It proposes the oxidation of pyrite in Eocene sediments that occur in palaeovalley sequences overlying basement in both southern Western Australia and on Eyre Peninsula. This hypothesis has not been tested in detail, but 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.

Case studies and examples

Lake Tyrrell

Figure 2: Acid seeps precipitating iron along the western shore of Lake Tyrrell. (Photo: Helen Dulfer).

Lake Tyrrell (Figure 2) is a groundwater-fed lake with minor surface-water contributions from Tyrrell Creek. The lake has been the site of halite production for many decades (McHaffie and Buckley, 1995). 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 Total Dissolved Solids (TDS) (Macumber, 1992). Highly complex interactions occur 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 concentrated brines (Long et al., 2009), fluid mixing (Hines et al., 1992) and biogeochemical processes (Hines et al., 1992).

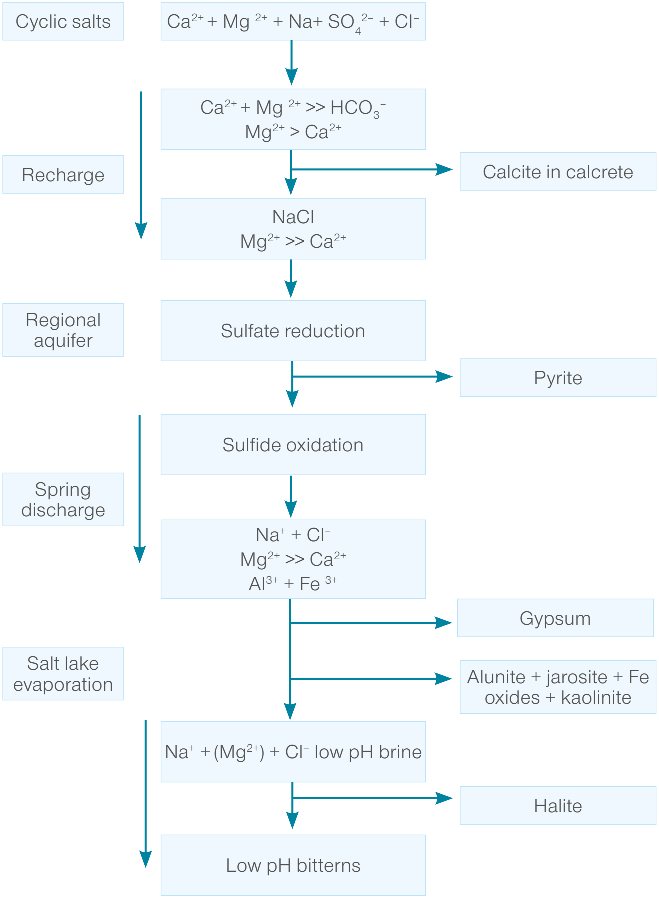

Figure 3: Evolution of Lake Tyrrell-style acid brines from a cyclic marine salt source (modified from Long et al., 2009).

A proposed model (Figure 3; Long et al., 2009) for the evolution of the acid brines of Lake Tyrrell showed that the brines are not easily classified according to the classic (Hardie and Eugster, 1970) model, which described the evolution of continental rather than marine waters.

Lake Tyrrell, in common with most Australian continental lakes, has a marine-like chemical signature. Starting with the deposition of salts of marine composition in rainfall, Ca and HCO_3^- are removed in the near surface through precipitation of calcite in calcretes prior to entering the regional aquifer. Ferrolysis and sulfide oxidation in groundwater initiates the acidification process which 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, HCO_3^- 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 by precipitation of gypsum during the evaporation process. The resulting brine is a $Na(Mg){-}Cl^-(SO4_2^-)$ solution with low pH and high concentrations of Al, and Fe^{3+}. The $Fe - Al - SO_4^{2-} - K$ assemblage precipitates alunite, jarosite and iron oxides during evaporation.

Gawler Craton

Alunite and subordinate jarosite have also been identified in 22 ephemeral lakes on Eyre Peninsula in South Australia (Lock, 1988), and are associated with highly acidic groundwaters and lakewaters in a granite province of the Gawler Craton. (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 (1986).

A study of Pinjarra Lakes (Figure 4), the most remote of those in the Narlaby Palaeovalley, showed that these lakes had surface water pH values as low as 3.6 and estimated surface salinities of up to 92 000 mg/L TDS at the time of measurement (Kimber, 2002). The geomorphology of the Pinjarra Lakes is complex, with numerous small lakes and sub-basins set within larger lakes. Each sub-basin has a distinctive pattern of evaporitic crusts. Groundwater discharge into the lakes occurs through point sources (springs and seeps) and by diffuse flow through lakebed sediments.

Figure 4: Pinjarra Lakes, Eyre Peninsula. (Google Earth image). The irregular geometry and absence of inflow shows that this is a groundwater-fed system.

Yilgarn Craton

Studies of lakes and groundwater across the Yilgarn Craton (Mann, 1983; McArthur et al., 1991) reveal that most have pH values between 7.0 and 3.8 and that salinities almost invariably are more than 35 000 mg/L TDS. Based on a study of 59 ephemeral lakes in southern Western Australia, Bowen and Benison (2009) reported that approximately 40% of the lakes and 84% of the measured groundwaters were extremely acidic with pH of less than 4 and the lowest measured pH being 1.7 (Figures 5 and 6).

Figure 5: Small Acid Lake (Gneiss Lake) south of Lake Dundas, WA, showing yellow alunite deposits on lake bed. (Photo: K. Benison).

The salinity of these lake waters and groundwaters ranged from fresh (rare) to brines with more than 280 000 mg/L TDS. Chemical and isotopic compositions of lake water and shallow groundwater from 21 of these lakes led Benison et al. (2007) and Bowen and Benison (2009) to conclude that they 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. The sediments deposited in these lakes 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.

Figure 6: Trench showing a cross-section of sandflat of small lake south of Lake Dundas, WA (Trifecta Lake). There is abundant alunite and jarosite, as well as some haematite here. (Photo: K. Benison).

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.

Figure 7: Lake Chandler excavation (Historic photo: Martin Jacobsen, ActivEX Ltd.).

Consequences and economic implications of acid lakes

Deposition of the potassium, aluminum and iron sulfates, alunite and jarosite, may be a significant reaction for sequestering of potassium found in brines, with Alpers et al. (1992) reporting that the alunite in Lake Tyrrell was the potassium-rich end member and that little or no sodium was present. In Western Australia alunite is particularly widespread and abundant in the Lake Brown system of playas, part of the Deborah Lakes System (Figure 1). In Lake Chandler, part of the Deborah Palaeovalley, alunite constitutes 60% of the sediments to a depth of six metres (Hall, 1978). McArthur et al. (1991) measured alunite as comprising 13% to 29% of samples from Lakes Gilmore and Swann, south and southeast of Norseman, Western Australia.

In South Australia, Lock (1988) reported a number of small lakes from 2 to 10 hectares in the Minnipa-Kyancutta area which contained more than 50% combined alunite and jarosite to depths of up to 2.3 metres below lake surface. Radiocarbon dating of the lake sediments indicates that these have accumulated during approximately the past 5000 years.

Acid brines are highly effective in the mobilisation of rare earth elements (REEs; Johannesson et al., 1994). REEs appear to be carried into lakes by discharging groundwater and are rapidly bound in the lake sediments. REE grades of less than 0.1% are below what is generally considered economic, although the possibility of new technologies to access and extract REEs cannot be excluded.

Exploration for alunite and jarosite

To date, exploration programs for potash in alunite and jarosite have been carried out at Lake Chandler and Lake Campion in Western Australia and at Lake Ifould in South Australia (Figure 1). Exploration 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 could be considerable.

Lake Chandler (Figure 7), previously produced potash in the form of glaserite ($K_3Na(SO_4)_2$) which is derived from alunite (Bayliss, 1980). It has been the site of an exploration program by ActivEX Ltd. The present inferred resource is almost 5.78 million tonnes at 5.73% K_2O in alunite (ActivEX, 2009).

At Lake Chandler the alunite-bearing clay is six metres 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 identified the potential for additional mineralisation peripheral to the current resource but within the confines of Lake Chandler. No drilling has been carried out on the nearby Reward Lake but records show potash contents at the surface similar in grade to Lake Chandler (ActivEX, 2013).

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 (Lake Pidinga in older literature) is a palaeovalley saline lake along the margin of the Eucla Basin in South Australia (Figure 8) underlain by lignitic sediments of Eocene age. Potash deposits have been known to occur in the area since at least 1948. 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 was carried out through Southern Potash Pty. Ltd., a wholly owned subsidiary of WPG Resources Ltd (WPG Resources, 2012). Land access issues led to the relinquishment of the licence in 2013 (M Jacobsen, pers. comm.).

Figure 8: Lake Ifould on the margins of the Eucla Basin in South Australia. The lake is inset into Cenozoic sediments exposed in marginal breakways and floored by Eocene palaeovalley-filling sediments inset into crystalline basement. (Photo: Martin Jacobsen, WPG Resources).

Further potential

The location of almost all acid salt lakes either in, or close to potential markets in the wheat belt regions of Western Australia, South Australia and Victoria may make these small deposits profitable. To further validate the potential of these lakes, more information is needed on the distribution of their potassium-bearing sediments. Additional drilling would determine their thickness and links to the distribution of sulfide-bearing Cenozoic sediments.

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