

Lake Tyrrell, Australia, and its Potential for Strategic Resources

A review was undertaken of the favourability of Australian salt lake systems from arid areas for potash, lithium, boron, and calcrete-hosted uranium deposits (Mernagh et al., 2013). The same approach has now been applied to Lake Tyrrell, Victoria.

Lake Tyrrell is a hypersaline, ephemeral playa lake in the Mallee region of the Murray–Darling Basin. It is typically dry for approximately three-quarters of the year, but may be covered with up to one metre of water for the remainder of the year (Figure 1). It is the main inland production site for halite in Victoria. Lake Tyrrell also has potash in the form of alunite and jarosite being precipitated in the near-surface sediments (Fegan et al., 1992). Additionally, discharging brines contain rare earth elements (REEs) that may have been sourced from heavy minerals in the Loxton–Parilla Sands, which is the regional aquifer that feeds Lake Tyrrell (Macumber, 1983).

This report evaluates the potential prospectivity of Lake Tyrrell for potash, lithium and boron, based on published and newly collected data.

Geology

The lake deposits are up to five metres thick and consist of clay, silt and sand and are covered by an ephemeral halite-gypsum crust (30–60 centimetres thick). The sediments show a cyclic pattern that reflects alternating periods of wet and dry conditions. Radiocarbon analyses (Bray et al., 2012) indicate that the sediments are about 7500 years old. Decaying algal mats occur locally on the lake floor causing reducing conditions and creating a build-up of sulfide minerals (Long et al., 2009).

Hydrology

Lake Tyrrell is a groundwater-fed lake with minor surface-water inflow from Tyrrell Creek. There are three main groundwater bodies in the Tyrrell Basin: regional groundwater, and intermediate and dense playa reflux brines (Macumber, 1992) (Figure 2).

Highly complex interactions occur in both the basinal and lake groundwater system leading to the formation of acidic conditions. These include oxidation of oxygen-deficient regional groundwaters in discharge zones at springs within and surrounding the lake (Macumber, 1992), reflux of evaporated and concentrated brines (Long et al., 1992), fluid mixing (Hines et al., 1992) and biogeochemical processes (Hines et al., 1992; Welch et al., 2004). 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 ranges between 260 000 milligrams per litre (mg/L) and 360 000 mg/L (Macumber, 1991; Macumber, 1992).



Figure 1: ASTER False Colour mosaic of Lake Tyrrell in Victoria. Areas of high albedo (white) show seasonal distribution of a dry salt crust cover. The image is extracted from Cudahy et al. (2012).

The biochemical oxidation of iron and sulfides in groundwater initiates the acidification process which progresses along the hydrologic flow path until it reaches the spring zone area, or the groundwater discharge zone, where ferrolysis (Mann, 1983; Giblin, 1987) becomes the dominant process. During acidification, HCO₃⁻ is removed and the water becomes relatively enriched in magnesium as well as in aluminium and iron.

When the groundwater is discharged into Lake Tyrrell at springs, calcium is removed during evaporation and precipitation of gypsum. The resulting brine is a Na(Mg)–Cl⁻ (SO₄²⁻) solution with low pH and high concentrations of aluminium and iron. The Fe–Al–SO₄²⁻–K assemblage precipitates alunite, jarosite and iron oxyhydroxides on evaporation. The evolution of Lake Tyrrell brine is summarised in Figure 3.

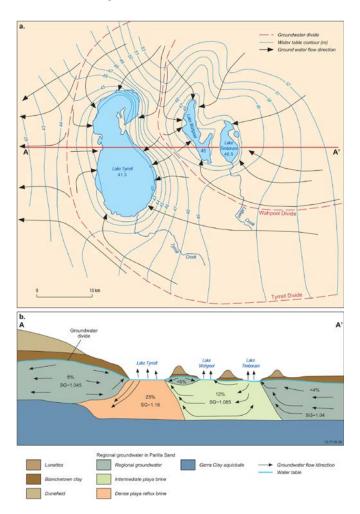


Figure 2: (A) Potentiometric surface and groundwater flow lines for the Pliocene Loxton-Parilla Sand aquifer in Victoria's Tyrrell Basin. The water table contours are strongly affected by the three discharge lakes, Tyrrell, Wahpool and Timboram. The floor of each lake intersects the regional water table. The closed contours around Lake Tyrrell and Lake Wahpool indicate groundwater inflow from all directions, while Lake Timboram (without similar contour closure) only receives inflow from the east. The groundwater flowlines demonstrate that regional groundwater flow enters Lake Tyrrell only 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 (weight %) and specific gravity (SG, in g/cm³) variations of the regional Parilla Sand aquifer (3-5%), the Lakes Timboram-Wahpool reflux brine pool (9-12.5%), and the Lake Tyrrell reflux brine pool (20-29%). Groundwater underflow from the Lakes Wahpool-Timboram system to Lake Tyrrell is also indicated. Figure is modified from Magee (2009) after Macumber (1991).

New chemical analyses of waters

Results of comprehensive chemical analyses of newly acquired Lake Tyrrell waters are provided in Tables 1 and 2.

New isotopic analyses of waters

The stable isotopes of three new shallow groundwater samples collected along the western shore of Lake Tyrrell ($\delta^{18}O = -3$ to -0.5 and $\delta D = -26$ to -15%; Table 3) are consistent with a surface origin for the water modified by evaporation, as proposed earlier by Herczeg et al. (1992) and Petrides et al. (2006). The most evaporated groundwater obtained from an approximately 60 metre deep pumping bore at the Cheetham salt works ($\delta^{18}O = 1.9\%$ and $\delta D = -9\%$) represents the dense reflux brine. The sulfur isotopic composition ($\delta^{34}S$) of the sampled waters ranges from 16.2% to 19.2% (Table 3) and broadly correlates positively with sulfate concentrations (4400 to 22800 mg/L).

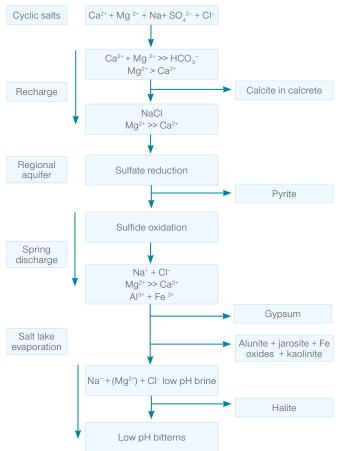


Figure 3: Evolution of Lake Tyrrell-style acid brines (modified from Long et al., 1992a).

These values suggest that the groundwaters are in equilibrium with gypsum (three gypsum samples collected locally have δ^{34} S from 19.2% to 21.2%; Table 3).

A marine sea salt origin for the sulfur is similar to that of other surficial sulfates (δ^{34} S = 19.9 to 20.5‰) in the region (Chivas et al., 1991).

New sediment analyses

A one metre-long sediment core was collected from the south western side of Lake Tyrrell by hand-driving an auger into the lake bed. Three samples were taken from this core and analysed using X-ray Diffraction (XRD) Spectrometry. The results of the analysis are presented in Figure 4.

In addition, nine surface samples were collected from the salt lake and analysed using a Portable Infrared Mineral Analyser (PIMA) and XRD. Using PIMA, most of the sediment samples collected from the lake surface were identified as a combination of gypsum and anhydrite, while quartz, muscovite, halite and magnetite were identified by XRD analysis.

	Log	Unit	XRD Analysis				
			Mineral	Wt%			
		Tyrrell Beds black clay	Quartz White mica Feldspar Halite Goethite Gypsum Magnetite	64.6 10.6 8.0 7.0 5.4 3.9 0.5			
1 metre		red Loxton- Parilla Sand	Quartz Kaolinite Goethite Halite Maghemite	70.7 14.1 10.7 2.7 1.8			
¥.		yellow Loxton- Parilla Sand	Quartz Feldspar White mica Halite Gypsum Goethite	66.0 8.8 7.9 6.5 6.9 3.9			

Figure 4: Sediment core from Lake Tyrrell.

Mineral systems

Salt lakes in closed drainage basins typically have potential for the extraction of multiple resources. Previous mineral systems analyses of salt lakes (Mernagh et al., 2013) has shown that the two most important factors are source rocks with readily leachable elements of interest and hydrological connectivity between the source rocks and the salt lake. Halite is already being harvested from Lake Tyrrell and, as a consequence, this study considers only the potential for potash, lithium, and boron (Figure 5).

Potash

Potash is the common name for various salts containing potassium in water-soluble form and it is an important component of many fertilisers. Figure 5a shows plots of potassium/chloride ratios for lake and ground waters in the region. Only a few samples show potassium enrichment above that of seawater with most waters in the area depleted in potassium relative to seawater.

This may be explained by the precipitation of alunite and jarosite from these waters prior to sampling of residual waters (Figure 3). Fegan et al. (1992) and long et al. (1992b) reported that alunite and jarosite occur in the top 20 centimetres of the Lake Tyrrell sediments. Further investigation is needed to determine the amount of potassium in the lake sediments.

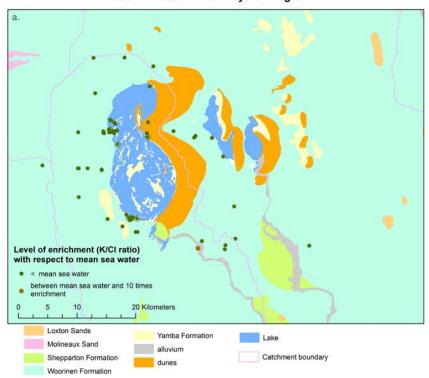
Lithium

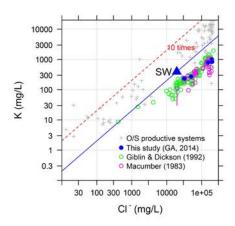
Lithium is mined from salt lakes in South America, China, and Tibet (Mernagh et al., 2013). Figure 5b shows plots of lithium/chloride ratios for lake and ground waters in the Lake Tyrrell region. Many of the sample sites contain lithium concentrations greater than that of seawater with samples from Tyrrell Creek showing greater than 50 times enrichment. Despite this, the enrichment values are below those reported for productive salt lakes in other countries. As a result, the potential for economically extracting lithium from Lake Tyrrell is considered to be low.

Boron

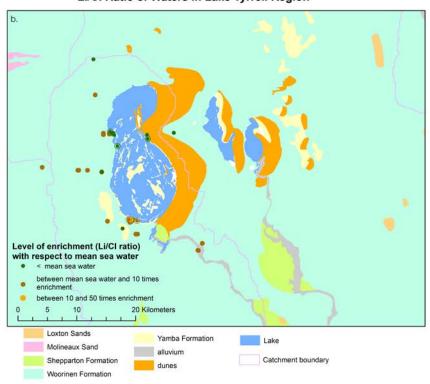
Boron is commonly associated with potassium- and lithium-rich brines in overseas salt lakes (Mernagh et al., 2013) which resulted in consideration of the potential of Lake Tyrrell for borate deposits. Figure 5c shows plots of boron/chloride ratios for lake and ground waters in the Lake Tyrrell region. Some groundwaters distant from Lake Tyrrell show slight (up to 10 times) enrichment in boron. However, the enrichment values are still below those reported for productive salt lakes elsewhere.

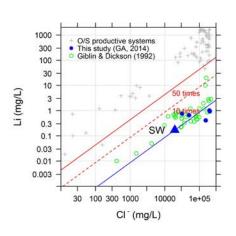
K/CI Ratio of Waters in Lake Tyrrell Region





Li/CI Ratio of Waters in Lake Tyrrell Region





B/CI Ratio of Waters in Lake Tyrrell Region

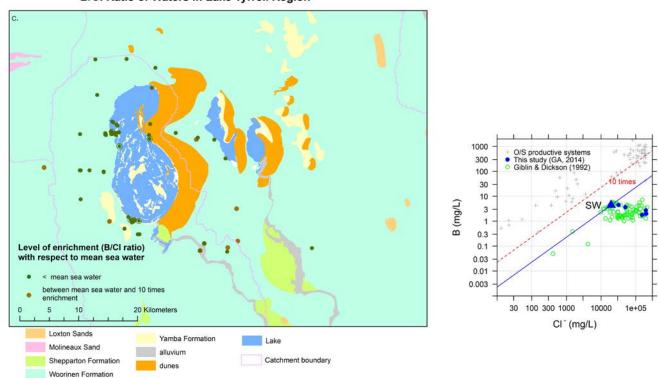


Figure 5: Element/chloride ratios of groundwaters and lake waters corresponding to different enrichment threshold values compared to average seawater for K, Li, and B respectively (SW; Drever, 1997). On these plots '+' represents data from salt lake systems (inflow and lake waters) with economic-grade concentrations of appropriate commodities overseas (O/S). The blue line shows the evaporation trend of average seawater. Dashed and solid red lines show evaporation trends for waters with different levels of enrichment in element/chloride (enrichment level labelled) compared to an evolved seawater of the same chloride concentration. Data points from Macumber (1983) are not shown on the map because of their imprecise location.

Table 1: Hydrochemistry data for major components (in mg/L; Electrical Conductivity (EC) in µS/cm; Alkalinity (Alk) in mg/L of CaCO₃).

ID	EC	рН	Alk	F-	Cl⁻	Br	NO ₃ -	SO ₄ ²⁻	Ca	K	Mg	Na
2013 057 004	114,000	3.94	<5	3.5	50,300	135	<8	6,890	441	271	2,470	27,900
2013 057 011	204,000	5.82	32	<4	195,000	585	<32	20,800	337	1010	12,130	98,500
2013 057 016	87,600	3.47	<5	6.68	31,800	101	<3	4,410	398	232	1,820	17,500
2013 057 017	200,000	5.03	38	<2	152,000	408	<19	18,200	442	786	7,930	78,900
2013 057 018	207,000	6.75	38	<2	199,000	515	<19	22,800	576	836	11280	108,000

ID	S _{tot}	P _{tot}	Si	Al	В	Ва	Cu	Fe _{tot}	Li	Mn	Sr	Zn
2013 057 004	2,160	<0.5	22.6	7.52	3.70	0.21	0.03	13.00	0.66	0.19	9.5	0.14
2013 057 011	6,580	<2	5.4	2.08	2.74	0.14	<0.08	0.88	1.02	1.44	5.7	0.28
2013 057 016	1,420	<0.5	37.1	78.9	4.48	0.02	0.04	2.94	0.76	0.13	14.0	0.08
2013 057 017	5,700	<1	5.5	0.11	1.77	0.02	<0.06	19.15	0.41	0.24	5.8	0.05
2013 057 018	7,320	<1	1.2	0.09	1.99	0.02	< 0.05	< 0.04	0.95	0.02	8.3	< 0.04

Table 2: Selected trace elements (Pb, Th, U, REEs) (in mg/L; Pb, Th, and U in µg/L).

ID	Pb	Th	U	Dy	Eu	Gd	Но	La	Lu	Nd	Pr	Sm	Tm	Yb	Се
2013 057 004	42.3	0.4	0.8	0.033	<0.01	0.036	<0.01	0.052	<0.01	0.140	0.032	0.030	<0.01	0.014	0.239
2013 057 011	<3.5	<1.8	<1.8	<0.035	<0.04	<0.04	<0.04	<0.035	<0.035	<0.035	<0.035	<0.035	<0.035	<0.035	0.049
2013 057 016	46.6	0.2	18.8	0.039	0.011	0.046	<0.01	0.081	<0.01	0.206	0.045	0.051	<0.01	0.018	0.291
2013 057 017	<2.3	<1.1	<1.1	<0.023	<0.02	<0.02	<0.02	<0.023	<0.023	<0.023	<0.023	<0.023	<0.023	<0.023	<0.023
2013 057 018	<4.4	<2.2	<2.2	<0.022	<0.02	<0.02	<0.02	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022	<0.022

Table 3: Stable isotope data for waters and gypsum samples for Lake Tyrrell.

ID	$\delta^{\text{18}} O_{H2O}$	δD _{H2O}	δ^{34} S	Comment on δ³4S	ID	δ ³⁴ S	Comment on δ³⁴S
2013 057 004	-1.9	-25	16.2	BaSO ₄ precipitate	2013 057 008	19.2	Gypsum
2013 057 011	-0.5	-15	19.2	BaSO ₄ precipitate	2013 057 009	21.2	Gypsum
2013 057 016	-3.0	-26	18.1	BaSO ₄ precipitate	2013 057 015	20.1	Gypsum
2013 057 017	1.9	-9	19.0	BaSO ₄ precipitate			
2013 057 018			18.9	BaSO ₄ precipitate			

Summary

Compared to many Australian salt lakes with known potential for potash deposits (Mernagh et al., 2013), brines of the Lake Tyrrell system are considered less favourable for the formation of economic concentrations of potash. However, it may be possible to extract potash from alunite and jarosite concentrates in the top 20 centimetres of the lake sediments. The lack of enrichment in lithium and boron in the brines may be associated with the absence of suitable source rocks within the catchment and underlying basement, or to precipitation reactions. Iron-oxyhydroxides and sulfidic sediments may act as sinks for these and other metals, but the economic significance of this process remains to be evaluated.

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