



## Geochemical characteristics of naturally acid and alkaline saline lakes in southern Western Australia

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### ABSTRACT

Abundant shallow saline lakes on the Archean Yilgarn Craton in southern Western Australia exhibit a rare spectrum of geochemical conditions. Here the field geochemistry over three seasons (pH, salinity, and temperature), as well as major ions, trace elements, and H, O, and S stable isotopes of surface waters and shallow groundwaters from 59 ephemeral lakes in southern Western Australia (WA) are reported. Approximately 40% of the lakes and 84% of the measured groundwaters in WA are extremely acidic (pH < 4) and pHs are observed as low as 1.7. The salinity of lake waters and groundwaters ranges from rare freshwaters to common saline waters and brines with total dissolved solids >28%. The fluids are typically Na–Cl to Na–Mg–Cl–SO<sub>4</sub> brines with variable yet locally high amounts of Ca, K, Al, Fe, Si, and Br. The acid brine fluid compositions are unusual. For example, in some fluids the amount of Al ≫ Ca, the amount of Br > K, and comparison of total S to SO<sub>4</sub><sup>2-</sup> values suggest the presence of other uncommon S-bearing species. Trends in δ<sup>18</sup>O and δ<sup>2</sup>H illustrate the separation between surface lake water and shallow groundwaters, and indicate the contribution of meteoric waters to the lakes. The chemical and isotopic compositions of these fluids indicate a spatially and temporally dynamic, yet regionally consistent, history of brine evolution that is fundamentally different from most other terrestrial closed basin brines. The WA lake brines do not evolve from surface evaporation of dilute inflow waters, but rather are fed by highly evolved regionally acid saline groundwaters. The lake waters then diversify with locally varying surface and near-surface processes such as meteoric dilution by flooding, evapoconcentration, mineral precipitation and dissolution, and fluid mixing. The WA lake waters and groundwaters are somewhat similar to those in an entirely different geologic setting in northeastern Victoria, illustrating the potential for different geochemical pathways to lead to the formation of similar lacustrine acid brines. Although these types of environments are rare in modern settings, ancient ephemeral acid saline lake deposits have been recognized in the geologic record on Earth and on Mars, indicating that natural evolution of acid saline waters may be more ubiquitous than previously recognized.

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### 1. Introduction

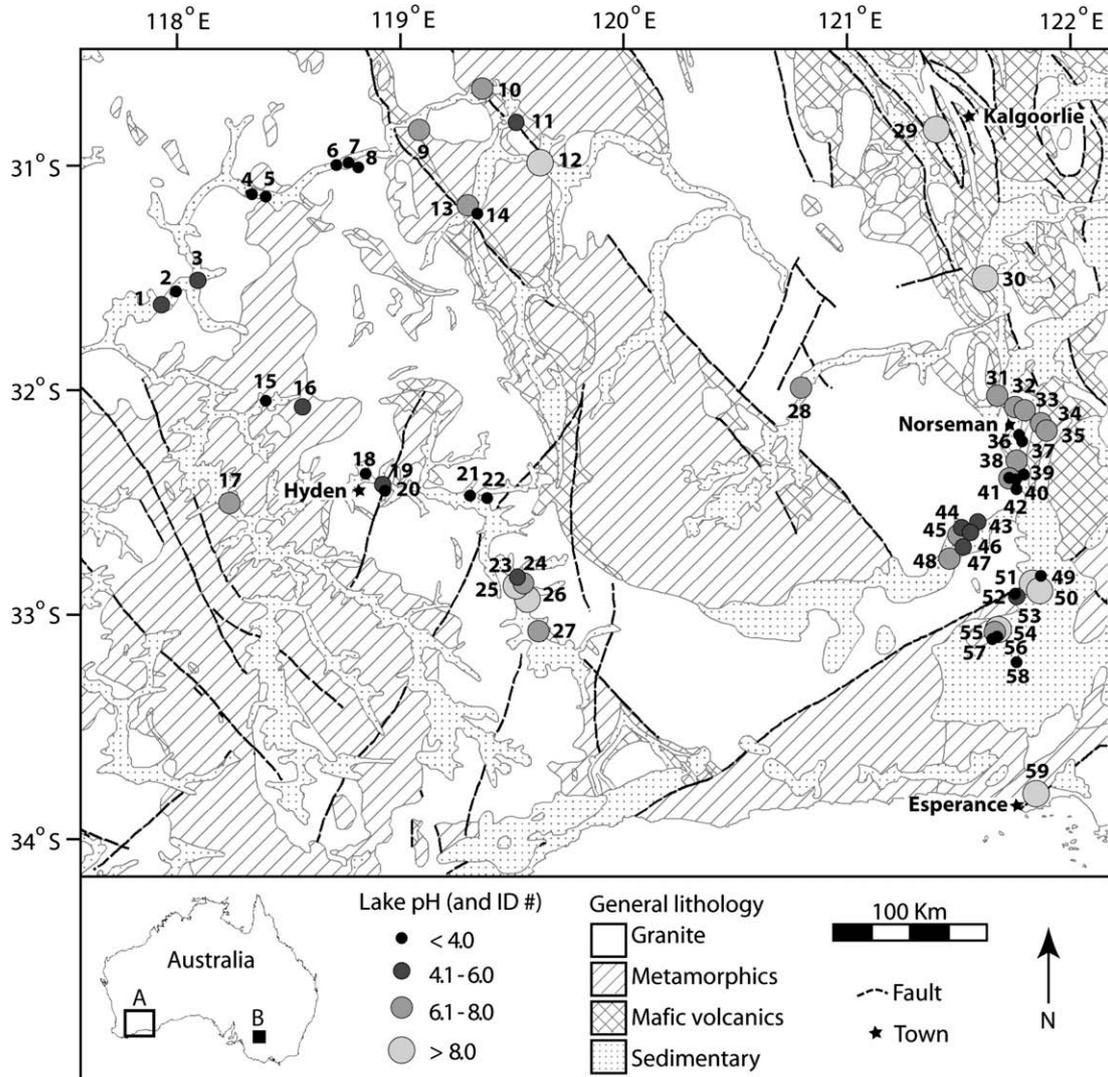
Ephemeral saline lakes are common features of the arid landscape in southern Western Australia (WA) (Fig. 1). The lakes range in surface area from <1 to 100's km<sup>2</sup> and have an extreme and rare range of natural hydrogeochemical conditions. Many WA lake waters and groundwaters are hypersaline and acidic (Mann, 1983; McArthur et al., 1989, 1991; Gray, 2001; Benison and Goldstein, 2002). Somewhat similar acid saline lake waters and groundwaters occur in a very different geologic setting in the Murray River Basin in Victoria (Bowler and Teller, 1986; Lyons et al., 1990, 1992; Fegan et al., 1992; Giblin and Dickson, 1992; Hines et al., 1992; Long et al., 1992; Macumber, 1992). Unlike other

known natural acid lakes elsewhere in the world, these lakes are not fed by volcanic or hydrothermal waters (e.g., Risacher et al., 2002), or waters in direct contact with massive sulfide deposits; and, unlike typical saline systems, which are commonly neutral to alkaline, the WA lake brines have a pH as low as 1.5. The processes and conditions that allow the development of acid saline lake systems are not well understood.

Natural acid saline lake systems are rare in modern settings, but may have been significant in the geologic past. Mid-Permian redbed and evaporite units from the mid-USA are now recognized as having been acid saline lacustrine depositional and diagenetic environments (Benison et al., 1998; Benison and Goldstein, 2002). In addition, sedimentary rocks in the Meridiani Planum region on Mars were also likely deposited and modified by acid saline fluids (Squyres et al., 2004, 2006). These rocks on Mars have mineralogical, sedimentological, and geochemical similarities to both the USA Permian and the modern WA acid systems (Benison and LaClair, 2003; Benison, 2006; Benison and Bowen, 2006; Bowen et al., 2008).

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**Fig. 1.** General locality map of Western Australia (WA) field area. Lake localities showing pH range and highly generalized bedrock geology. Numbers at field sites correspond to field data in Table 1. On outline of Australia, box A outlines WA field area, and box B indicates location of Victoria field area.

The existence of acid saline waters in the geologic past suggest that the system in southern WA may represent more than just a geochemical anomaly, but rather may be an important indicator of larger-scale continental evolution processes. Long and Lyons (1990) theorized that acid saline waters may be the natural late stage product of continental evolution. The combination of acidity and extreme salinity requires an unusual set of conditions including a source of acidity, a lack of natural buffers, and an arid climate. Naturally occurring acid waters do occur in other highly weathered Archean cratons such as the Canadian Shield (Kwong and Lawrence, 1998), but limited evaporation in this area keeps them from also being saline. Recognition of ancient acid saline systems, and interpretation of how specific tectonic and climatic settings affect sedimentary geochemistry in these settings, first requires knowledge of the factors controlling the geochemical variability of acid saline systems in modern environments.

The purposes of this paper are to: (1) characterize the geochemical range of the lake waters and shallow groundwaters in WA; (2) evaluate the differences between the surface lake waters and the shallow groundwaters; and (3) investigate potential processes affecting the observed geochemical variability. This research is a part of ongoing interdisciplinary research on the sedimentology, hydrogeochemistry, palynology, microbiology and environmental

evolution of these extreme systems (e.g., Jagniecki et al., 2005; Hong et al., 2006; Story et al., 2006; Benison et al., 2007; Bowen et al., 2008).

## 2. Background

### 2.1. WA geologic setting

The abundant lakes in southern WA occupy shallow closed depressions in buried fluvial paleodrainage inset-valleys that are remnants of Jurassic to Middle Eocene (Clarke et al., 1996; deBroekert and Sandiford, 2005) incision into the Archean Yilgarn Craton. The basement rocks on the Yilgarn are composed of granite-gneiss complexes and greenstone belts, have undergone extensive deformation, and host major economic deposits of Au and Ni, and minor deposits of other metals (e.g., Cu, Zn, W, etc.) (Fig. 1). The inset-valleys that host the modern lake basins tend to follow lithologic and structural contacts resulting in complex outcrop patterns and a variety of exposed rock types in the lake basins including porphyritic granites, basic granulite, gneiss, amphibolite, anorthosite, schist, quartzite and ironstone. The Archean shield in WA is tectonically stable and much of this area has remained above sea level exposed to weathering since the Mesozoic (Bettenay and

Butt, 1979; Mann, 1983). As a result, the basement rocks are covered with thick zones of highly-weathered and chemically-altered regolith in many areas. Siliceous, ferruginous, and calcareous duricrusts are common, although highly localized, throughout the Yilgarn (Anand and Paine, 2002).

The Archean basement is sparsely overlain by limited zones of Mesozoic and younger inset-valley-filling sedimentary rocks including: Eocene lignites, siltstones, sandstones, and marine limestones (Clarke et al., 1996). At least two marine transgressions occurred during the Tertiary, filling some of the paleovalleys with seawater and marine sediments (Clarke et al., 1996). River flow in these paleodrainages ended in the late Eocene (Clarke, 1994) with uplift of the Darling Range to the west of the Yilgarn. The uplift of these mountains dammed westward flow of the paleodrainages, ponding the surface waters and allowing for the formation of individual closed lake basins (Salama, 1994). The modern lake basins may contain up to 100 m of lacustrine sediments that in places include at least 9 m of evaporites and date back to the Pliocene, suggesting a long-lived history (~2 Ma) for some of these lake systems (Salama, 1994; Salama et al., 1992; Clarke, 1993, 1994). However, for most of the lakes in this area, the history of the deposits and evolution of hydrogeochemistry has not been well documented.

The modern sedimentology of the WA lake basins is characterized by a combination of ephemeral lake, sandflat, mudflat, ephemeral channel and dune facies (Benison et al., 2007). The modern dune deposits surrounding the lakes are up to 12 m thick (Lawrance, 2001), and are composed of gypsum-, quartz-, and hematite-rich eolian sands that form when desiccation of lakes allows for reworking of lake-bottom evaporites (Bowen et al., 2008). Average annual evaporation in WA (~180–280 cm/a) outpaces rainfall (~26–34 cm/a), leaving many of the lakes dry for some of the year. We have observed lake waters actively precipitating gypsum, halite, Fe oxides, and kaolinite during evapoconcentration stages. During flooding and extremely wet periods, the lake waters reach their maximum observed depths of ~0.5 m. Flooding transports dilute waters, siliciclastic sand and silt grains, and plant remains into lakes. Meteoric water input during storms partially or totally dissolves halite and gypsum. Early diagenetic precipitates from the shallow acid saline groundwater include gypsum, halite, hematite, jarosite, alunite, and kaolinite (Benison et al., 2007).

Land use within the WA field area includes a combination of agriculture (part of the “wheatbelt” region) and localized salt and metal mining, but most of the area remains remote and unused with a mallee-type vegetation (eucalyptus, wattle and saltbush forests).

The acid saline waters in northwestern Victoria (Lake Tyrrell) occupy a different geologic setting. The semi-arid climate is similar with ~30 cm/a of rain and ~200 cm/a of evaporation (Macumber, 1992). A major difference between the two field areas is that WA is underlain by diverse Archean bedrock and the Lake Tyrrell area is underlain by up to 600 m of Tertiary sediments with active groundwater recharge and discharge through the river basin (Macumber, 1992). Shoreline terraces at Lake Tyrrell suggest that this was 13 m deep 50–30 ka ago, although the lake is currently only ~0.5 m deep (Macumber, 1992).

## 2.2. Past hydrogeochemical studies

Previous workers have noted the extreme and variable lake and groundwater geochemistry in southern WA. Mann (1983) deduced an apparent north–south trend in pH and elemental concentrations that he attributed to spatial changes in climate that affected the geochemical basement weathering patterns and the complexity of the related groundwaters. McArthur et al. (1989, 1991) evaluated several playas and shallow groundwaters in the southeastern

part of the Yilgarn during two field seasons (July 1987 and November 1989), focusing on possible sources of salts (McArthur et al., 1989) and the unique conditions that have allowed for massive formation of diagenetic alunite in this region (McArthur et al., 1991). These results challenged Mann’s interpretation of pH gradients and the tie to regional climate variability (McArthur et al., 1991).

Many of the past hydrogeochemical studies have focused on the “problem” of salinity related to agriculture and management of limited fresh water resources in WA (Salama et al., 1993a,b; Fitzpatrick, 2003), and what the chemistry of specific fluids might suggest in terms of mineral resource formation and distribution (Johannesson et al., 1994, 1996; Gray, 2001). In specific catchments, groundwater salinity was found to be highest in localized pockets upstream from compartmentalizing basement structures (Salama et al., 1993a). However, even the most saline waters identified by Salama et al. (1993a) (<5700 mg/L Cl) are comparable to the lowest salinity lakes in this study (e.g., Lake Lefroy, Ted’s Lake).

The hydrogeology and geochemistry of the Lake Tyrrell acid brine system in Victoria has been studied in great detail (Alpers et al., 1992; Bowler and Teller, 1986; Lyons et al., 1990, 1992; Fegan et al., 1992; Giblin and Dickson, 1992; Hines et al., 1992; Long et al., 1992; Macumber, 1992). Low pH (pH ~ 4.2) groundwaters evolve in specific zones of the extensive sandy subsurface aquifer system and enter Lake Tyrrell in localized springs (Giblin and Dickson, 1992). Specific brine populations with traceable geochemical evolution have been identified. Abiotic S and Fe oxidation in the aquifer can account for the moderate acidity in the Tyrrell system. These waters are similar to the WA waters in that they are saline and somewhat acidic, but have extreme differences in geologic setting, spatial extent, hydrology and history of brine evolution.

## 3. Methods

### 3.1. Field analyses

Waters from 59 lakes in southern WA were investigated over three field seasons including July–August 2001, June–July 2005, and January 2006 (Table 1; Fig. 1). These visits covered seasonal extremes as well as a variety of weather conditions. In addition, seven lake systems were investigated in northeastern Victoria in August 2001 and July 2005. Lake water and groundwater pH, salinity and temperature were measured in the field at the time of sampling (Table 1; Figs. 2–5). The sedimentological setting was evaluated in detail (Benison et al., 2007), and samples were collected for mineralogical, palynological, and microbiological analyses. However, the focus of this paper is the water. Field geochemical measurements, water and sediment samples were collected along detailed transects at Lakes Brown, Aerodrome, Prado and Twin West. In addition, Hyden and Norseman rain water and ocean waters from the Indian Ocean in Perth, WA, the Southern Ocean in Esperance, WA, the Pacific Ocean near Brisbane, Queensland (Surfer’s Paradise), were collected and analyzed alongside the lake and shallow groundwater samples. The consistent results for rain and seawater samples provided an additional external check (in addition to the standard reference materials analyzed) for the analytical methods utilized.

While in the field, four Oakton Double Junction pHTestr 2 portable pH meters designed for harsh conditions and equipped with automatic temperature compensation were used. These pH meters have a range of –1.0 to 15.0 pH and accuracy to 0.1 pH unit. During the 2001 field trip, an Orion 230A portable pH meter accurate to 0.01 pH units was also used and it was found that it always matched field measurements taken by portable Oakton meters. The pH meters were calibrated at the start of each field day with Oakton or Orion pH 10, 7, and 4 buffer solutions. The pH of select

**Table 1**

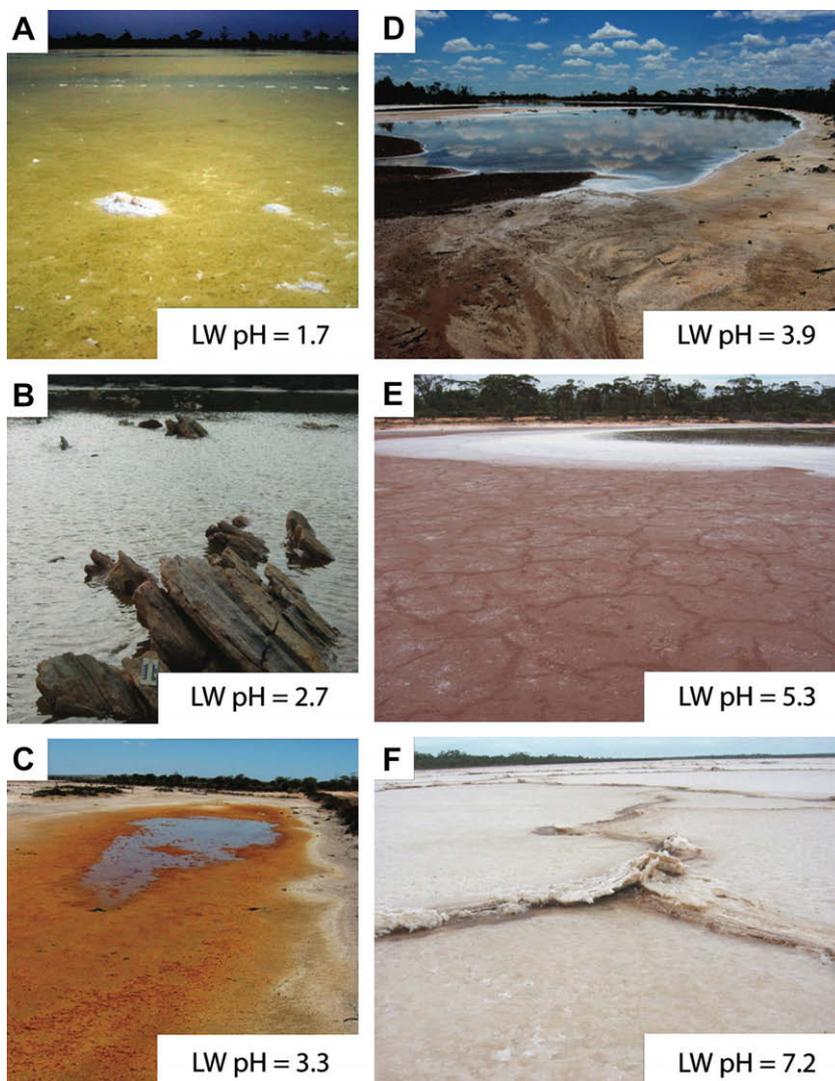
Field data. WA and Victoria field sites. GPS location, year of field season when site was visited, and ranges of all observed pH, salinity (total dissolved solids (TDS) measured in g/L), and temperature (°C) values for lake water (LW) and groundwater (GW). A dash means that no GW was observed.

Site #	Lake	S Lat.	E Long.	2001	2005	2006	LW pH	LW TDS	LW temp	GW pH	GW TDS	GW temp
<i>WA field sites</i>												
1	Doodlakine <sup>a</sup>	31.632	117.910		X		5.1	45	21	–	–	–
2	Dead Kangaroo	31.583	117.966		X	X	3.3–4.3	40–130	17–35	–	–	–
3	Hines Hill <sup>a</sup>	31.541	118.068		X		4.5–5	–	–	–	–	–
4	Brown <sup>a</sup>	31.128	118.307		X	X	3.9–4.5	130–230	12–47	3.1–3.7	150–160	–
5	Campion <sup>a</sup>	31.129	118.309		X	X	3.7	250	40	–	–	–
6	Bullfinch	31.008	118.745			X	3.5	70	30	–	–	–
7	Bottle	31.009	118.761			X	2.9	200	39	3.0	120	36
8	Warrachuppin	31.006	118.694			X	2.8	135	38	–	–	–
9	Deborah West <sup>a</sup>	30.843	119.051			X	7.2	170	30	–	–	–
10	Deborah East <sup>a</sup>	30.828	119.452			X	7.0	260	32	–	–	–
11	Koolyanobbing	30.816	119.506			X	5.3	270	30	3.1	230	32
12	Seabrook <sup>b</sup>	31.014	119.634			X	8.1	60	32	–	–	–
13	Polaris <sup>a</sup>	31.181	119.312			X	7.3	280	27	5.8	280	30
14	Pete's Piggery	31.215	119.339				3.8	150	34	–	–	–
15	Walker <sup>a</sup>	32.062	118.389		X	X	3.5–4.1	10–30	12–21	3.1	50–60	10–17
16	Ski <sup>a</sup>	32.093	118.517			X	4.7	12	18	3.7	60	25
17	Kondinin <sup>a</sup>	32.510	118.221		X		7.8	80	–	–	0	–
18	Gounter <sup>a</sup>	32.406	118.839			X	2.5	280	25	4.1	115	26
19	Wave Rock 1	32.434	118.906		X	X	5.5–6.1	65	4–23	–	–	–
20	Wave Rock 2	32.433	118.906		X	X	1.7–2.5	240–280	4–24	3.2–3.3	70–150	9–23
21	Crusty	32.483	119.305			X	3.0	270	26	–	–	–
22	Yellow	32.497	119.367			X	2.6	280	26	2.8	230	27
23	Fox	32.883	119.521		X		5.5	120	–	–	–	–
24	Fox Road	32.886	119.528		X		7.0	220	–	7.3	185	–
25	Sand Dune	32.887	119.522		X		8.1	52	–	–	–	–
26	Stella	32.965	119.603		X		8.2	182	16	–	–	–
27	King <sup>a</sup>	33.090	119.618		X		7.8	110	15	–	–	–
28	Johnston <sup>a</sup>	32.005	120.789			X	7.6	90	26	5.8	190	25
29	Douglas <sup>a</sup>	30.845	121.391			X	8.2	0	28	–	–	–
30	Lefroy <sup>a</sup>	31.496	121.597	X		X	8.2	5	38	–	–	–
31	Cowan NW <sup>a</sup>	32.061	121.681	X		X	6.9	26	38	–	–	–
32	Cowan W <sup>a</sup>	32.193	121.748			X	6.1–8.4	80–100	28–32	6.0	200	25
33	North Royal Mine <sup>a</sup>	32.119	121.808			X	7.1	150	16	–	–	–
34	Daisy Mine <sup>a</sup>	32.181	121.861			X	6.6	200	24	–	–	–
35	Dundas NE <sup>a</sup>	32.176	121.841			X	7.6	100	18	–	–	–
36	Aerodrome	32.211	121.759	X	X	X	2.7–4.5	80–130	17–35	2.5–3.7	65–240	13–29
37	Cumulate Raceway	32.214	121.758	X	X	X	3.1–4.1	80–90	25	3.0–4.1	190–240	20–26
38	Emu Track	32.353	121.760	X		X	6.9–7.6	120	23	–	–	–
39	Roo	32.395	121.762			X	3.9	120	22	–	–	–
40	Picnic	32.395	121.770			X	3.6	55	18	–	–	–
41	Salty	32.428	121.718	X	X	X	6.8–8.5	50–72	3–20	–	–	–
42	Prado	32.433	121.718	X	X	X	2.5–4.1	145–240	17–23	3.2–3.7	65–225	12–23
43	Gilmore <sup>a</sup>	32.610	121.561	X		X	5.8	45	20	2.6–3.0	80–190	20
44	Channel	32.642	121.514			X	4.2	38	24	3.0	140	23
45	Island	32.762	121.462			X	6.6	30	24	3.5	100	23
46	White Sands	32.640	121.508			X	4.9	29	25	3.6	80	20
47	Quickest Ever	32.848	121.856			X	4.5	75	23	–	–	–
48	Ted's	32.852	121.858			X	7.7	38	26	3.4	70	26
49	Hobby	32.924	121.746			X	3.9	140	28	5.9	150	23
50	Weird Veg	32.907	121.830			X	8.5	38	28	6.9	85	27
51	Sunrise Hill	32.905	121.793			X	8.6	60	25	–	–	–
52	Dead Tree	33.050	121.675	X		X	2.9–3.5	12	26	–	–	–
53	Cyclone	33.075	121.685			X	4.2	30	29	3.2	70	17
54	Gastropod East	33.083	121.684		X	X	8.0	30–60	23	3.7–5.3	83–165	12
55	Gastropod West	33.082	121.684		X	X	6.6–6.8	90–175	17	3.5–3.7	130–180	16
56	Twin East	33.056	121.676	X	X	X	2.7–3.9	110–215	13–21	2.9–5.1	60–200	10–14
57	Twin West	33.054	121.675	X	X	X	2.7–3.8	115–210	15–22	2.4–5.4	50–240	11–18
58	Gneiss	33.220	121.755	X	X		2.7–3.3	80	14	3.3–3.7	75–90	11
59	Pink <sup>a</sup>	33.844	121.845	X	X		7.9–8.2	80	16	7.2	100	–
<i>Victoria field sites</i>												
	Tyrrell <sup>a</sup>	35.445	142.849	X	X		5.0–7.0	100–150	12	3.5–5.5	68–250	12
	Crosbie <sup>a</sup>	35.045	141.720	X	X		6.9–7.2	150	9–11	6.1	218	–
	Last Drop	34.642	141.962		X		8.0	100	19	–	–	–
	Mad Max	34.594	142.185		X		6.7	215	16	–	–	–
	Hardie <sup>a</sup>			X			6.9	100	–	–	–	–
	Day Trap <sup>a</sup>			X			5.3	140	–	–	–	–
	Road Bend			X			5.0	100	–	5.0	70	–

<sup>a</sup> indicates official lake names from maps. All other lake names were given.

water samples were also checked in the laboratory with a Corning 130 desktop pH meter accurate to 0.001 pH units (and calibrated with pH 10, 7, 4, and 1.38 buffer solutions); these values matched

the field measurements. In addition, the portable pH meters were tested against each other for precision several times each day and recalibrated, if needed. High resolution pH strips, accurate down to



**Fig. 2.** Field photos of lakes. Lakes shown here represent the observed spectrum of size, character, and geochemistry. Lake water pH at the time of photo is indicated on image. All photos are from Jan. 2006, except for B, which was June 2005. (A) Wave Rock 2; (B) Twin East; (C) Dead Kangaroo; (D) Brown; (E) Koolyanobbing, and (F) Deborah West.

0.0 pH and within 0.5 pH units, were used for supplemental pH measurements.

Three Hauke optical salinity refractometers with automatic temperature compensation, models HRS-10 and HRS-28, were used to measure total dissolved solids in the field. One refractometer measured up to 280 g/L the other two refractometers measured up to 100 g/L TDS. Any measurements at this upper limit are reported as >100 g/L or >280 g/L TDS depending on the device used. Water temperatures were measured with plastic-encased glass and alcohol thermometers.

Field geochemical measurements were taken for each water sample collected. Measurements were also recorded along detailed transects (Fig. 6) where only representative samples were collected to document lateral spatial geochemical variations within lakes and across other depositional facies, such as sandflats and mudflats. Any salinity, temperature or pH stratification in lake water was tested by sampling waters at various water levels with an eye dropper and measuring temperature, salinity and pH. No evidence of stratification was found in any of these shallow lake waters.

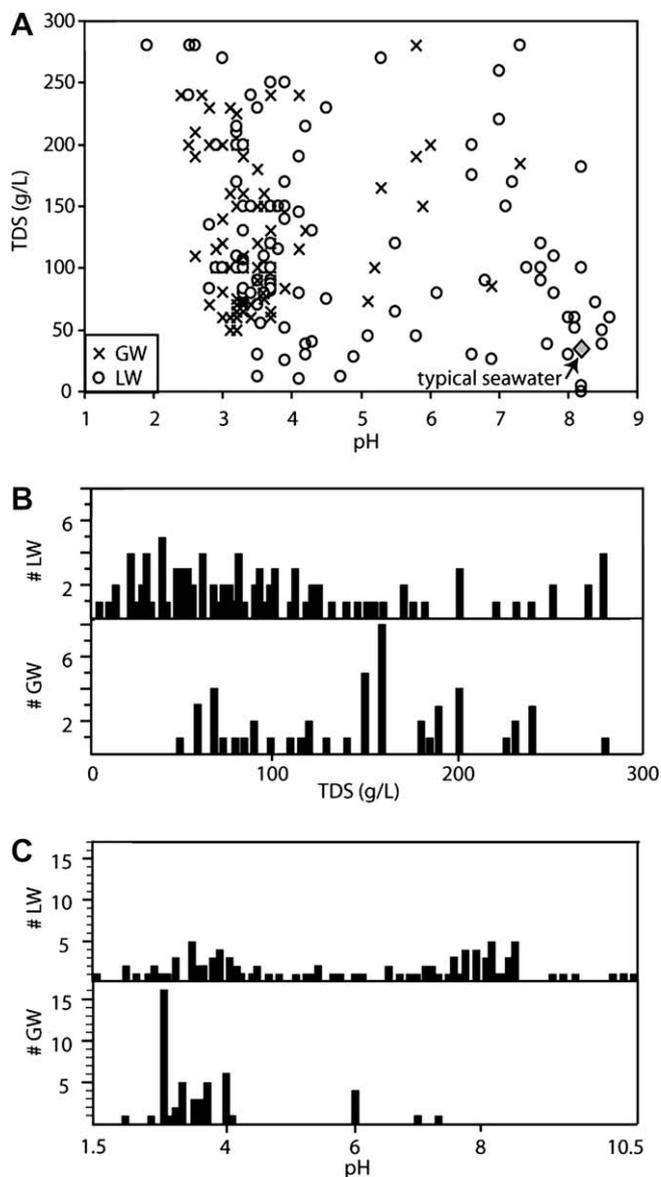
Lake waters were collected by dipping sterile HDPE bottles into the lakes and allowing them to fill to the top and then capping

them and labeling the bottles. Shallow groundwaters, were accessed by digging into sandflats and mudflats adjacent to the lakes with shovels or trowels. Groundwaters were generally encountered at depths shallower than ~1 m or not at all. Sterile HDPE bottles were immediately placed into the hole and allowed to fill with groundwater, then capped and labeled.

Waters were stored in an insulated cooler at room temperature while in the field and while in transit from the field to the lab to keep the water samples at similar temperatures at which they were when sampled. Once returned to the laboratory, water samples were vacuum-filtered with 0.45  $\mu\text{m}$  Millipore filters into sterile HDPE bottles and stored at room temperature. Waters were analyzed within 1–6 months.

### 3.2. Laboratory analyses

Major ion concentrations in the fluids were analyzed with a variety of techniques. Conductivity-suppressed ion chromatography was used (IC; Dionex DX-320 in the Geology Department at Central Michigan University) to determine the concentrations of major inorganic ionic species (Supplementary Tables 1 and 2; Figs. 7 and 8). These analyses required that the samples be diluted



**Fig. 3.** Field pH and salinity (total dissolved solids (TDS) in g/L) data for all WA lake and groundwaters. (A) Range of all pH and salinity. Value of typical seawater included. (B) and (C) histograms showing number of all measured lake waters and groundwaters with various salinity and pH values, respectively.

1:1000. Sample splits were analyzed in two separate runs, for cations and anions, respectively. The Li, Na, K, Mg, and Ca concentrations were determined using Dionex CS12A separation and CG12A guard columns coupled with a CRS–ULTRA membrane suppressor. The Cl, Br, F, PO<sub>4</sub>, NO<sub>2</sub>, NO<sub>3</sub>, and SO<sub>4</sub> concentrations were determined using AS9–HC and AG9–HC guard columns, and an ASRS–ULTRA membrane suppressor. Calibration of the instrument was performed during each set of analyses using sets of seven solutions of known concentration prepared from certified standards purchased from Dionex and Spex CertiPrep. To correct for shifts of instrument sensitivity, calibration was performed twice, at the beginning and at the end of each run, and check standards were placed in the middle of the run. For sample and standard dilution, as well as for preparation of eluents double distilled water de-ionized to resistivity of >17.8 MΩ cm produced using a Barnstead NANOpure water system was used. Standard deviation for all species analyzed was ≤5% of the measured concentrations based on two replicates, and averaged only 1–2% for most species.

X-ray fluorescence was also employed on non-diluted solutions (XRF; Bruker S4 Explorer in the Geology Department at Central Michigan University) for measurement of selected elements (Supplementary Table 3; Figs. 9 and 10). Runs were done under He gas. All elements in the periodic table from O to U can be detected down to ~20 mg/L with the three crystals used (PET, LiF(200), and OVO-55). Raw counts from XRF analyses were converted to concentration via calibrations based on multiple standards with known concentrations for Al, Fe, and S over similar ranges as the observed sample values. The root mean squares for these calibrations are 75 mg/L for Al, 63 mg/L for Fe, and 151 mg/L for S. Other data (e.g., Si) are modeled (i.e. semi-quantitative) but agree within ±10 weight% for liquids with known concentrations (including seawaters and multi-element standard solutions). Field measured salinities have a linear correlation to the percent of solids detected by XRF with an  $R^2$  of 0.97. In addition, several trace elements were analyzed by Activation Laboratories (Sr, Mn, Cu, Sb, etc.) using inductively coupled plasma–optical emission spectroscopy (ICP–OES) (Supplementary Table 3).

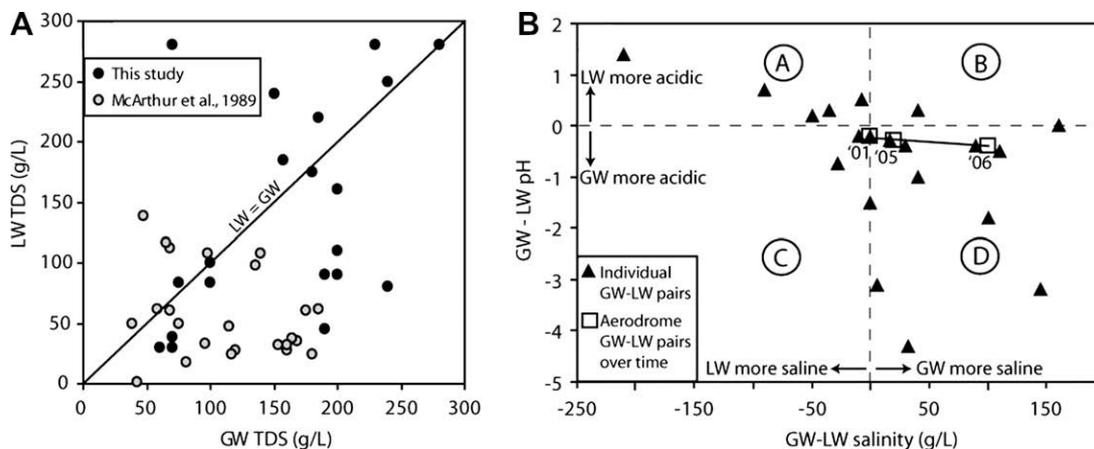
Bicarbonate concentrations were measured by Brighton Analytical using an alkalinity titration method with a Mettler DL12 titrator. A methods standard containing 50 mg/L bicarbonate and independent check EPA-provided standards were used. Accuracy of both the method standard and the independent check standards are within 5% (Supplementary Table 4; Fig. 9).

Water samples were prepared and analyzed for δ<sup>2</sup>H and δ<sup>18</sup>O at the SIRFER (Stable Isotope Ratio Facility for Environmental Research) facility at the University of Utah (Supplementary Table 5; Figs. 11 and 12). Water from the samples was purified through vacuum distillation and cryogenic trapping. A single small (10 μL) aliquot of water was injected onto a column of glassy C held at 1400 °C to produce H<sub>2</sub> and CO gases. These were separated chromatographically in a He carrier gas stream and introduced sequentially into the ion source of an IRMS (Delta + XL, ThermoFinnigan) for isotope ratio determination. Samples were analyzed in duplicate, with average precision of 1.5‰ for δ<sup>2</sup>H and 0.2‰ for δ<sup>18</sup>O (1σ) for replicate analyses. δ<sup>18</sup>O and δ<sup>2</sup>H and values are reported relative to standard mean ocean water (SMOW).

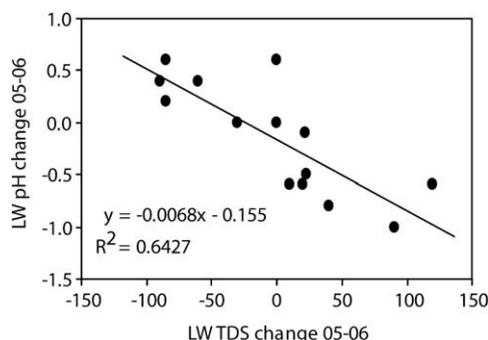
Representative WA water and chemical precipitates (gypsum and alunite) were analyzed for <sup>34</sup>S (VG 602 isotope ratio mass spectrometer) by Activation Laboratories (Table 2). Seawater BaSO<sub>4</sub> and Fisher BaSO<sub>4</sub> were run as internal laboratory standards at the beginning and end of each set of samples and were used to normalize the data as well as correct for any instrument drift. All results are reported in the per mil notation relative to the international CDT standard. Precision and reproducibility was reported as better than 0.2‰ (n = 10 internal laboratory standards).

### 3.3. Analytical challenges with acid brines

Methods for evaluating hypersaline acid waters are not well documented in the geologic literature. The combination of high acidity, high salinity, and complex composition causes challenges in terms of the use of some analytical instrumentation and the production of comparable standards. For example, dissolved oxygen meters do not yield accurate results for brines, so no dissolved oxygen meters were used in the field or laboratory. However, all of the waters were presumed to be oxidized because they were somewhat exposed to surface atmospheric condition in the field and Fe oxides were actively forming. Some important and abundant ions and compounds in the WA brines such as S, Fe, and Si, are notoriously difficult to measure by traditional chemical analyses. For example, many instruments use silica glassware, thus excluding Si as an analytical target. Many instruments, such as ICs and mass spectrometers, produce inaccurate results or are damaged by fluids of high ionic strengths. But dilution of the brines enough



**Fig. 4.** Differences between lake water (LW) and associated shallow groundwaters (GW). (A) Salinity comparison between LW and GW from this study and McArthur et al. (1989). (B) The difference in pH and salinity for sites where both lake water (LW) and groundwater (GW) were present. Open boxes indicate temporally changing (2001, 2005, 2006) typical values from Lake Aerodrome. Field A = TDS LW > GW, pH LW < GW ( $n = 5$ ), field B = TDS LW < GW, pH LW < GW ( $n = 1$ ), field C = TDS LW > GW, pH LW > GW ( $n = 4$ ), field D = TDS LW < GW, pH LW > GW ( $n = 9$ ).



**Fig. 5.** Temporal field geochemical lake water data. Difference in salinity (TDS g/L) and pH for individual lake waters that were measured in June–July 2005 and January 2006. pH was observed to decrease as salinity increased, illustrating how surface evapoconcentration (and dilution) effects lake water pH in a predictable way.

to yield appropriate salinity fluids for analyses may decrease the amounts of minor and trace elements so that they are not measurable. No stripping columns exist that could extract the high levels of Na or Cl in these brines without removing other important components.

The dissolved solids were extracted via standard distillation methods for the H and O isotope analyses, and any acids were likely extracted along with the waters. However, any H in the acids is likely in equilibrium with the H in the water, and the volume of potential acids is likely negligible in relation to the volume of the water in effecting the  $\delta^2\text{H}$ . Some of the measured ions may have been present in acids such as HCl or HBr, but are believed to fully dissociate for measurements with ion chromatography. Traditional wet chemical methods for analyses of specific compounds and ions, such as adding BaCl to precipitate BaSO<sub>4</sub>, thereby producing measurable S, may give total S for most natural fluids. However, the WA acid brines have other S-species besides SO<sub>4</sub><sup>2-</sup> (such as HSO<sub>4</sub><sup>-</sup>) and may already contain Ba, so this method would not give total S.

Based on the IC data, some of the samples have electrical imbalances up to 30%, in excess of positive over negative ions, but ~80% of the waters have only a 10% imbalance, and ~95% of the waters have imbalances <15% (Fig. 8B). The largest imbalances are in complex, highly acidic and extremely saline lake waters. In addition to the observed complexity of these fluids that may account for the

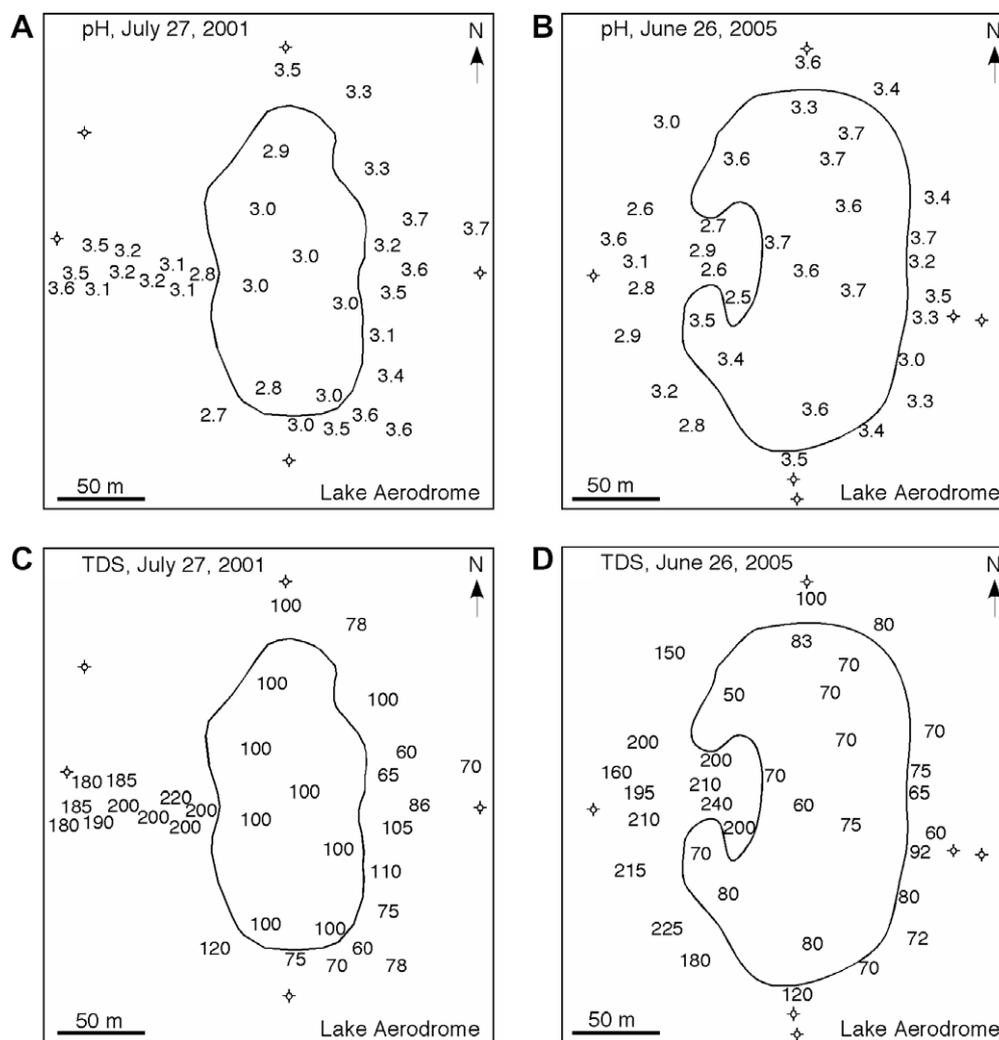
electrical imbalance (e.g., extremely high Al values), this discrepancy may suggest the presence of additional fluid constituents that have not been fully characterized. For example, there may be incomplete dissociation of H<sub>2</sub>SO<sub>4</sub> in some acid waters, causing variations in concentrations of various S species such as H<sub>2</sub>SO<sub>4</sub>, SO<sub>4</sub><sup>2-</sup>, and HSO<sub>4</sub><sup>-</sup>. The state of understanding of H<sub>2</sub>SO<sub>4</sub> disassociation does not allow knowing exactly how much H<sub>2</sub>SO<sub>4</sub>, HSO<sub>4</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and other possible S species such as thiosulfate and thiosulfite may be present in these fluids.

## 4. Results

### 4.1. Field data

The WA field area covers two separate regional hydrologic catchments and multiple drainage basins, yet shows similar variations in water chemistry range. The lakes evaluated range in surface area from <1 to >800 km<sup>2</sup> and have water depths that range from ~0 to 48 cm. All of the lakes listed in Table 1 had some standing surface water during at least one of the visits. Several other lake basins were visited where no surface water existed, and were therefore not included as a part of this study. As these lakes are very shallow, the aerial extent of the surface water varies considerably. Many of the larger lakes have irregular shapes, while the smaller lakes tend to be ellipsoidal or circular in shape. All of the saline lakes in WA are ephemeral, and at least partially fed by rainwater and surface runoff. There is no apparent surface connection between any of the individual lakes, and each lake occupies a topographically closed basin. There is likely, however, mixing of fluids in the shallow subsurface, as well as some transfer of evaporated solutes by winds.

The sedimentology of the lake systems is described in detail in Benison et al. (2007) and is only described briefly here. All of the lakes had some form of evaporite minerals, including halite and/or gypsum, actively precipitating from the lake water and/or the shallow groundwater. At Wave Rock Lake 2, 45 cm of halite precipitated in the six months between the 2005 and 2006 field season. In addition to these more common evaporites, the acidic lakes commonly precipitate minerals including hematite, alunite, jarosite and possibly other chemical precipitates as evaporites. The siliclastic sediments in the lake basins included quartz sourced from the surrounding basement rocks and gypsum that had been reworked into grains from wind erosion of past lake evaporite crusts.



**Fig. 6.** Maps of Lake Aerodrome showing spatial and temporal pH and salinity variability. (A and B) show pH values measured on July 27, 2001 at the end of a 3 year drought (map A; lake water maximum depth = 7 cm) and during a flooding stage on June 26, 2005 (map B; lake water maximum depth = 9 cm). (C and D) show the TDS in g/L measured at the same time as pH. Lake shorelines are marked; numbers in shape are lake water measurements; numbers outside of lakes are shallow groundwater measurements. Cross symbols indicate location of dry holes (places where ~1 m deep pits were dug but now groundwater was encountered). Note spatial variations and how at any one point lake water pH and salinity fluctuate more than do groundwaters over time.

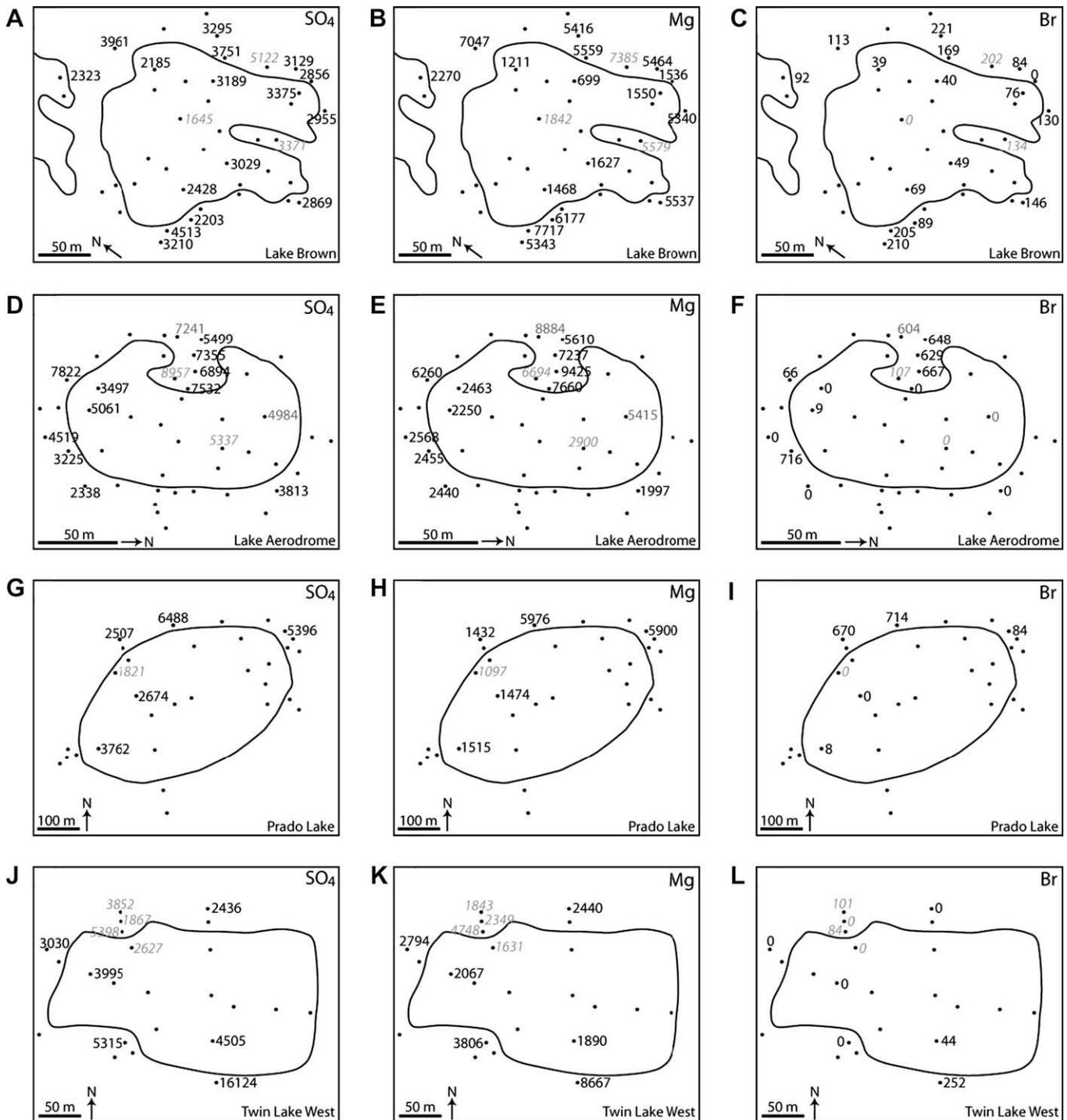
#### 4.1.1. pH, salinity, and temperature

**4.1.1.1. pH.** The WA field data show an extreme range in geochemical conditions from waters within apparently similar hydrologic settings and with fairly consistent surrounding geologic conditions. The spatial distribution and range of both acidity and salinity shows considerable variability both locally and regionally (Table 1, Figs. 1, 3–6). During July–August (winter) of 2001, 14 lakes in WA were studied in the field and had shallow groundwater pHs ranging from 2.5 to 7.9 (median = 3.6) and lake water pHs ranging from 2.5 to 7.6 (median = 3.3). During June–July (winter) 2005, 24 lakes were observed (including 8 of the same lakes that were studied in 2001) and pHs of the groundwater ranged from 2.4 to 7.3 (median = 3.5) and lake water ranged from 2.5 to 8.4 (median = 3.7). Six months later, during January (summer) of 2006, 47 lakes were observed (including eight of the same lakes observed in 2001 and 14 of the same lakes that were studied in 2005) and pHs of the groundwaters ranged from 2.5 to 6.9 (median = 3.2) and lake water ranged from 1.7 to 8.6 (median = 4.4). Six lakes were visited during all three field seasons and 16 were visited in two field seasons. Overall, approximately 40% of the lakes, and 84% of the measured groundwaters, were extremely acidic (pH < 4) at some time. In contrast, ~35% of the lake waters were moderately alkaline, with

pHs > 7. The minimum pH of 1.7 observed in this study is considerably lower than the minimum of 2.8 noted in past studies (e.g., McArthur et al., 1991). In addition, the range and variability observed in this study exceeds those of past studies in this area.

In Victoria, the observed pHs were overall much less acidic than those observed in WA. Groundwaters in the region ranged from 3.5 to 6.1 and lake waters were consistently moderately acid to moderately alkaline (~5–8). Of the seven Victoria lakes surveyed during two field seasons, the only waters with pH < 4 were shallow groundwaters encountered under the sandflats along the shoreline of Lake Tyrrell. Previous studies have reported groundwater pH values as low as 2.8 in the aquifer that feeds Lake Tyrrell (Macumber, 1992), but the acidity in northwestern Victoria is much more highly localized than in WA. The mineral suite precipitating at the salt lakes in Victoria reflects this geochemistry, with abundant halite, and localized zones of the acid minerals hematite and jarosite found as early diagenetic cements at Lake Tyrrell's sandflats.

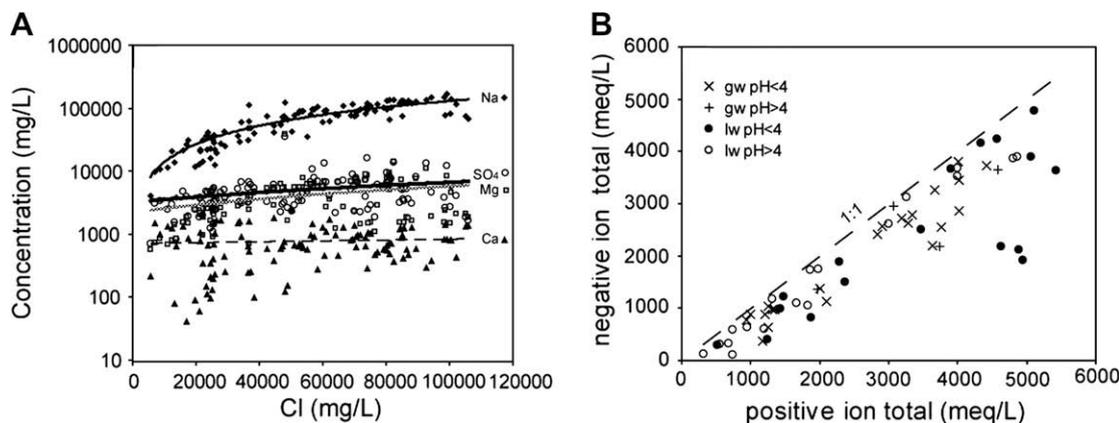
**4.1.1.2. Salinity.** The waters observed in WA ranged from fresh to hypersaline with total dissolved solids >28‰ (eight times the salinity of seawater). In the winter of 2001, salinity (measured as total dissolved solids g/L) in WA ranged from 40 g/L to 150 g/L



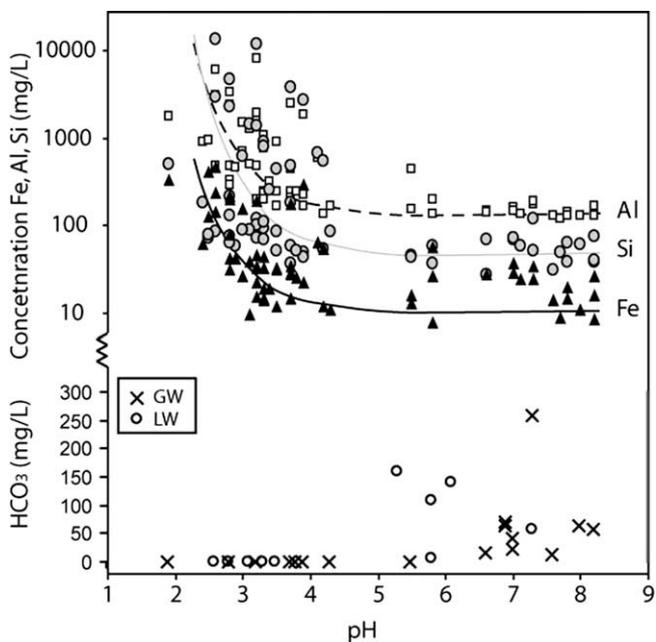
**Fig. 7.** Spatial variability in concentration of  $\text{SO}_4$ , Mg, and Br in lake water and groundwaters at sites that were studied in detail (IC data). (A–C) Lake Brown, (D–F) Lake Aerodrome, (G–I) Prado Lake, and (J–L) Twin Lake West. Numbers in grey roman text = 2001; black roman text = 2005; grey italic text = 2006. Numbers within lake outlines indicate lake water data, while numbers outside the outline indicate groundwater values. Lake outlines from 2005.

(avg = 98 g/L) for groundwater and 75–200 g/L for lake waters (avg = 181 g/L). In the winter of 2005, salinity ranged from 50 ppt to 240 g/L (avg = 118 g/L) for groundwater and 30–240 g/L for lake waters (avg = 127 g/L). In the following summer of 2006 salinities ranged from 50 g/L to >280 g/L (avg = 145 g/L) for groundwater and 0 g/L to >280 g/L (avg = 112 g/L) for lake water. In Victoria, the range of salinities was between 100 g/L and 215 g/L for lake water and 68 g/L and 250 g/L for groundwater over the course of two winter field seasons.

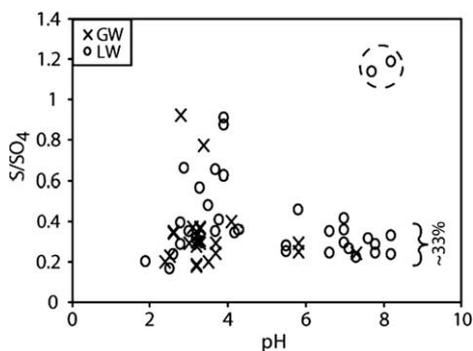
**4.1.1.3. Temperature.** Lake water temperature measurements in WA ranged from 12 to 27 °C (avg = 19.3 °C) during the winter of 2001, 3–24 °C (avg = 15.8 °C) during the winter of 2005, and from 17 to 47 °C (avg = 26.8 °C) during the summer of 2006. These shallow lake water temperatures were quite similar to air temperatures, typically differing by less than 2 °C. Shallow groundwater temperatures varied less, ranging from 12 to 21 °C (avg = 14 °C) during the summer of 2001, 9–23 °C (avg = 12.9 °C) during the winter of 2005, and 16 to 39 °C (avg = 24.7 °C) during the summer



**Fig. 8.** Major ion chemistry of WA lake and groundwater brines. (A) Total concentration of Na, SO<sub>4</sub>, Mg, and Ca (note log scale) with increase in Cl (IC data). (B) Comparison of total meq/L of positive and negative charge ions in WA lake and groundwaters (combination of IC and XRF data). Waters with the greatest difference (“lack” of charge balance) are some of the most acidic and unusual lake waters with extremely high values of typically uncommon metals and elements (i.e., Wave Rock Lake 2).



**Fig. 9.** Relative concentrations of Fe, Al, and Si in WA lake waters and groundwaters versus pH (XRF data). Lower portion of graph shows HCO<sub>3</sub><sup>-</sup> concentrations (via alkalinity titration) in LW and GW.



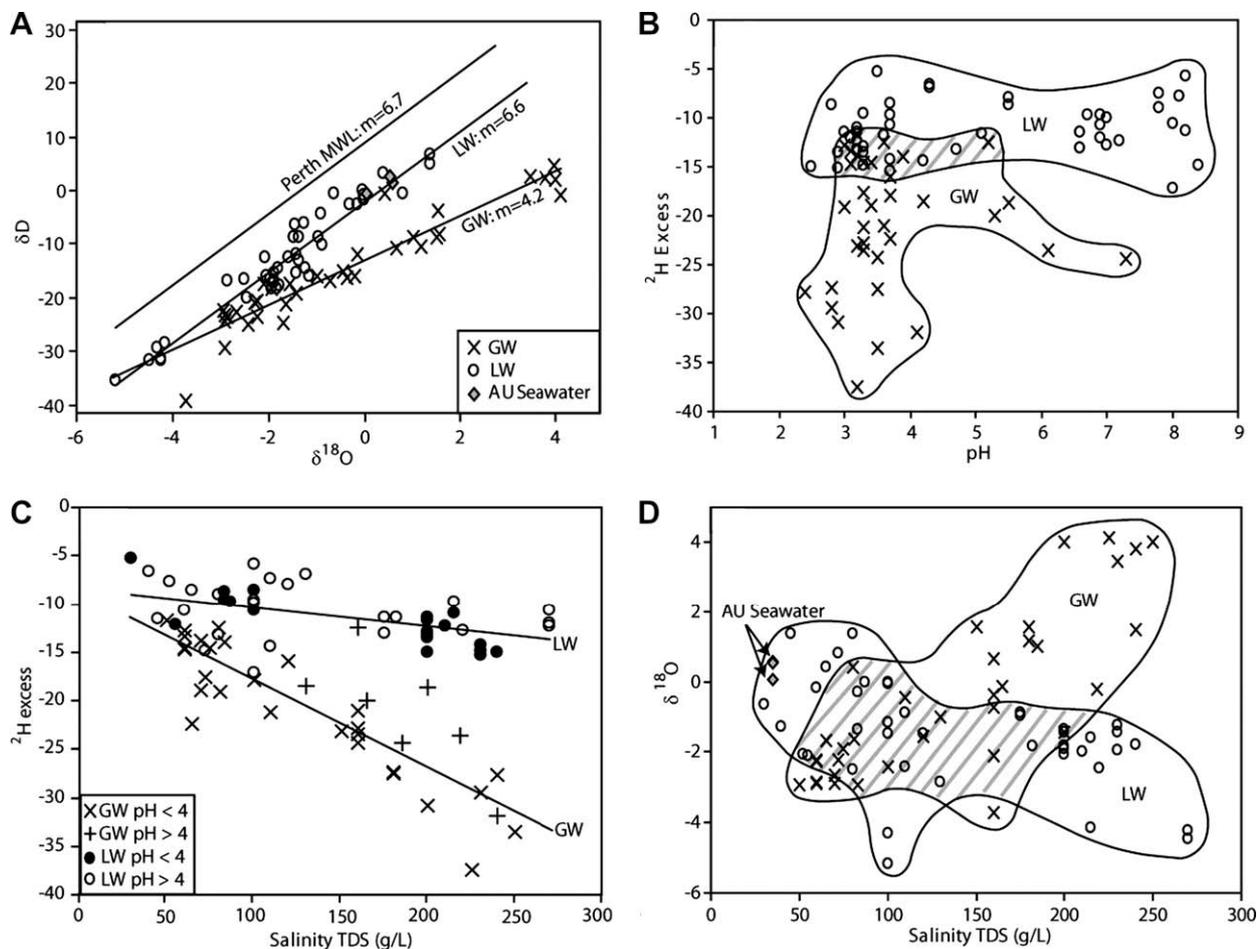
**Fig. 10.** pH versus S/SO<sub>4</sub>. For fluids where SO<sub>4</sub> is the only S species, this ratio should be ~0.33 (approximate range noted on graph). For many of the more extremely acid fluids, there is excess S, indicating the presence of other S-bearing species in addition to SO<sub>4</sub>. The two lakes in the dashed circle that do not follow this trend are localities with very low SO<sub>4</sub> values relative to the other sites (Lefroy and Ted’s) which skews this relationship.

of 2006. Temperatures reflect mostly day time temperatures, but some midnight readings and several early morning (~6 am) readings were taken as well to record daily temperature range. Temperatures measured at Victoria lakes during two winter field trips ranged from 7 to 18 °C for lake water and from 8.5 to 13 °C for groundwaters.

**4.1.1.4. Groundwater versus lake water.** For 19 of the lake systems in WA, pairs of both lake water and shallow groundwater were present. Comparisons between these two water types show that there is not a consistent trend of one being more saline or acidic than the other (Figs. 3 and 4). Detailed transects at some lakes (Supplementary Table 3) included analyses of multiple lake waters and groundwaters that showed significant localized spatial variability in pH, salinity and ion concentrations (Figs. 6 and 7). As these data show, characterizing a “typical” groundwater from a specific lake is difficult. In spite of this potential spatial variability, however, there are 4 different possible scenarios with respect to the groundwater–lake water salinity and pH relationship (Fig. 4B). Most commonly, the salinity of the lake water is lower than the groundwater and the pH in the lake water is higher than the groundwater. Individual lakes may fluctuate from one situation to another, as lakes transition from flooding to evapoconcentration stages and back. For example, typical conditions at Lake Aerodrome from 2001, 2005, and 2006 are plotted on Fig. 4B. The lake was more flooded with each progressive visit, and the difference between the pH and salinity of the lake water and groundwater increased. While the lake water pH changed over time by nearly 1 pH unit, and salinity fluctuated by up to 50 ppt, the groundwater pH and salinity remained fairly constant (Fig. 6).

**4.2. Major ion and elemental geochemistry**

In general, the WA lake waters and groundwaters are Na–Cl (or Na–Mg–Cl–SO<sub>4</sub>) brines with variable yet locally high amounts of Ca, K, Al, Fe, Si, and Br (Figs. 8A and 9) Supplementary Tables 1–4). On average, Na and Cl account for 88% of the ions, but range from 66% to 97%, with the more extremely acid fluids having more of the ions besides Na and Cl (e.g., the most acid water observed, Wave Rock 2 lake water, has the lowest percentage of Na and Cl). Major ions commonly have a separate evaporation trend between the lake and groundwaters (Fig. 13). Four of the WA lakes were studied in great detail and have local scale spatial variations in the concentration of SO<sub>4</sub>, Mg, and Br, as well as other components (Fig. 7; Supplementary Table 2).

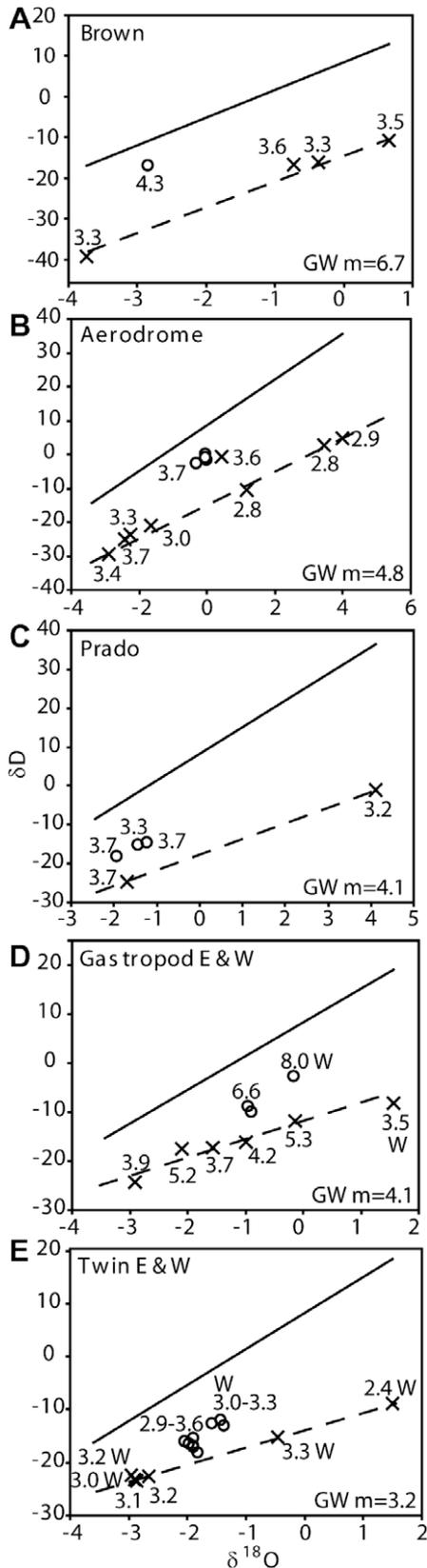


**Fig. 11.** (A) Range of stable isotopes of H and O in WA and Victoria lake water, groundwater, and representative seawaters. Solid upper line is the meteoric water line ( $\delta^2\text{H} = 6.67 * \delta^{18}\text{O} + 9.02$ ) calculated from the isotopic composition of rain water in Perth from 1962 to 2000 (data from the Global Network for Isotopes in Precipitation (GNIP) by IAEA and WMO). (B) pH versus  $^2\text{H}$  excess lake waters and groundwaters. (C) Salinity (total dissolved solids in g/L) versus  $^2\text{H}$  excess. Extremely acid (pH < 4) versus more alkaline fluids indicated. (D) Salinity versus  $\delta^{18}\text{O}$  versus (total dissolved solids in g/L). Dashed grey zones indicate groundwater–lake water mixing zones.

Several elements that are typically trace constituents in natural waters, are quite abundant in the WA lake and groundwaters, especially in the more acidic fluids. Elemental concentrations of Fe, Al, and Si increase in the more acidic fluids (Fig. 9; Supplementary Table 3). In contrast, all fluids with a pH < 4 are virtually  $\text{HCO}_3^-$  free, and the amount of  $\text{HCO}_3^-$  present in more alkaline fluids varies considerably (Fig. 9). The concentration of Fe also has a positive correlation with salinity with the more saline waters having the higher Fe values. This relationship is not seen however with Al and Si, which increase together with a positive linear correlation ( $R^2 = .88$ ). Some of the relative amounts of specific constituents for these waters are quite unusual compared to typical marine-sourced or continental brines. For example, in some fluids, the amount of Al  $\gg$  Ca (Supplementary Tables 2 and 3). Aluminium concentrations at the most extreme lake (Wave Rock 2) are as high as 8000 mg/L, which is an order of magnitude higher than Al-rich fluids described from acid mine waters (Nordstrom and Ball, 1986) and several orders of magnitude higher than seawater (0.002 mg/L, Drever, 1988). In addition, comparison of the total S to  $\text{SO}_4^{2-}$  values suggest the presence of other uncommon S-bearing species in many of the acidic waters (Fig. 10).

Trace amounts of Li (<5 mg/L), and  $\text{NH}_4^+$  (<9 mg/L) are detected (by IC) in ~25% of the measured WA waters respectively. Only 13 fluids (of 69 measured) have detectable concentrations of F (up to 31 mg/L F). Nitrite,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  are undetectable by IC in >93% of the WA samples. Several of the waters show significant enrichment

of Br relative to expected seawater evaporation trends. Acidic groundwaters (pHs = 3.0–4.2) from Gastropod, Aerodrome, and Prado Lakes have Br values that exceed the K values (Supplementary Tables 1 and 2). ICP-OES data show that Sr values are up to 65 mg/L and tend to increase with salinity, but also show a relationship with pH, with the more acidic waters (pH < 4) having the highest amounts (>20 mg/L). 59% of the fluids have detectable Mn (<46 mg/L), showing a slight positive correlation with both salinity and acidity. Forty-nine percent of the fluids have detectable Cu (<9.5 mg/L) which increases in the more acidic waters. Some of the most acidic waters have elevated levels of trace metals including Zn (<5.2 mg/L), Ni (<3.4 mg/L), Mo (<4.1 mg/L), and Co (<1.9 mg/L). However, these elevated metal levels exist in only ~20–50% of the very acidic fluids (pH < ~3.2) and are not present in the other very acidic fluids. These metals are not seen in any of the less acidic fluids. Several of the fluids had randomly elevated levels of Ce, Pb, Sb, Te, and W although none of these have any correlation with pH or salinity. Isolated individual samples from specific lakes (Aerodrome, Wave Rock) have elevated levels of Ba, Cd, Cr, Se, Ag, Bi, and Tl. Some of these elements are potentially toxic, such as Sb, a metalloid that is more commonly associated with hydrothermal waters. Sb typically has concentrations of <0.001 mg/L in non-polluted surface waters. The WA lakes and groundwaters contain up to 3 mg/L Sb, which is 500 times the US EPA toxic limit. Sb is thought to react with Cl in acid saline solutions, although due to the uncommon nature of this type of fluid,

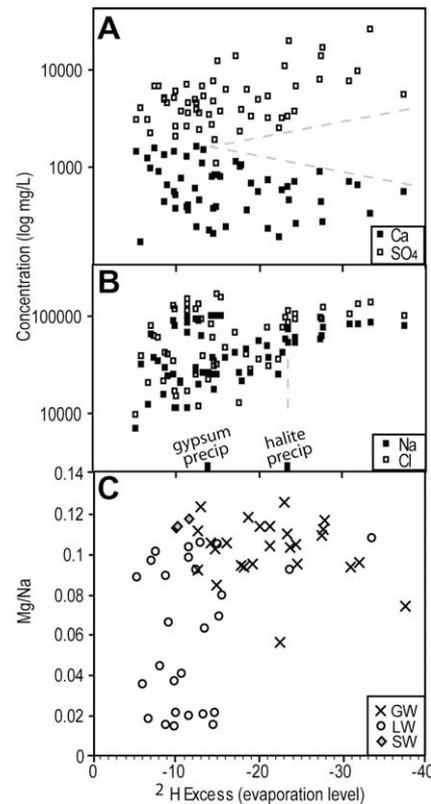


**Fig. 12.** Range of H and O stable isotopes in WA lake waters and groundwaters at specific lakes. (A) Brown, (B) Aerodrome, (C) Prado, (D) Gastropod East and West, and (E) Twin Lake East and West. pH of individual water samples indicated next to data point. X = groundwater, O = lake water. Solid line = Perth meteoric water line. Dashed line = regression for groundwaters at that lake; specific slopes indicated in lower right corner. Slopes range from 3.2 to 6.7 for various lakes, indicating a range of evaporative conditions at individual lakes.

**Table 2**

Sulfur-34 isotope values (‰),  $^{34}\text{S}$  from WA lake water, groundwater, and chemical precipitates.

Site #	Lake	Sample type	pH	TDS	$\delta^{34}\text{S}$
<i>WA field sites</i>					
36	Aerodrome	LW	3.7	67	19.1
36	Aerodrome	GW	2.8	180	18.4
36	Aerodrome	Gypsum			20.4
57	Twin West	LW	3.2	200	17.0
57	Twin West	GW	2.8	70	17.0
57	Twin West	Alunite			18.9
20	Wave Rock 2	LW	1.9	280	18.3
20	Wave Rock 2	GW	3.3	70	18.6
20	Wave Rock 2	Gypsum			20.2
13	Polaris	LW	7.3	280	17.8
13	Polaris	GW	5.8	280	17.6



**Fig. 13.** Possible evaporite precipitation evidence versus  $^2\text{H}$  excess. (A)  $^2\text{H}$  excess versus concentration of Ca and  $\text{SO}_4$  showing a chemical divide at a  $^2\text{H}$  excess value of about  $-14$ . (B)  $^2\text{H}$  excess versus concentration of Na and Cl. A possible break in slope at a  $^2\text{H}$  excess value of about  $-23$  may indicate the initiation of halite precipitation. (C)  $^2\text{H}$  excess versus Mg/Na values. Excess Mg commonly accumulates in brine relative to Na with uptake of Na into precipitating halite. The groundwaters are enriched in Mg compared to the lake waters.

is not well understood and has been described as having “little relevance for natural environments” (Pokrovski et al., 2006).

4.3. Stable isotopes:  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{34}\text{S}$

The  $\delta^{18}\text{O}$  of the lake waters ranges from  $-5.18\text{‰}$  to  $+1.37\text{‰}$  and the groundwaters range from  $-3.74\text{‰}$  to  $+4.11\text{‰}$  (Fig. 11; Supplementary Table 5). The lake water  $\delta^2\text{H}$  values range from  $-35.49\text{‰}$  to  $+6.63\text{‰}$  and the groundwaters range from  $-39.38\text{‰}$  to  $+4.66\text{‰}$ . The lake water data lie parallel to, but offset from, the Perth meteoric water line (MWL) (Figs. 11 and 12). The lake waters and groundwaters form two distinct populations (Fig. 11A). Groundwa-

ters from individual lake systems show locally variable changes in slope when their  $\delta^2\text{H}$  is plotted against their  $\delta^{18}\text{O}$ . In contrast, lake waters from specific systems tend to cluster (Fig. 12). The waters from Victoria have isotopic compositions similar to lake waters and groundwaters from WA.

Sulfur-34 isotopic analysis was conducted on 11 samples from three acid saline lakes and one neutral saline lake in WA. Samples included four lake waters, four shallow ground waters, two bottom-growth gypsum crystals, and one early diagenetic alunite. Results are shown in Table 2. Sulfur-34 values ranged from  $+17.0\text{‰}$  to  $19.1 \pm 0.2\text{‰}$  (CDT) in the water samples and from  $+18.9\text{‰}$  to  $20.4 \pm 0.2\text{‰}$  (CDT) in the solid samples. No geographic trends in the  $\delta^{34}\text{S}$  data were noted and no distinct differences between the results from acid and neutral lakes.

## 5. Discussion

### 5.1. Evolution of lacustrine acid brines

The formation and evolution of natural acid saline brines are not well understood. While these lakes do have much in common with other typical neutral to alkaline ephemeral saline lakes (i.e. Eugster and Hardie, 1978; Lowenstein et al., 1989), there are also some significant differences. Brines in non-marine closed basin lakes typically evolve from relatively dilute rivers and groundwaters and the composition of the resulting brine largely depends on the lithology of the surrounding drainage basin. In contrast, solutes from influx of surface waters play a minimal role in the creation of the WA brines. The lakes are fed by (1) diffuse seepage of concentrated groundwater brines and (2) meteoric water. The regionally acidic groundwater brines in the Yilgarn area are likely quite ancient and have evolved by evaporation past the carbonate divide (consuming alkalinity) and have acquired low pHs and unusual compositions through extreme bedrock weathering, sulfide oxidation and ferrollysis (e.g., Mann, 1983; Ollier, 1988; McArthur et al., 1991; Anand and Paine, 2002).

The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values show that the WA lake waters are largely composed of meteoric water, but  $\delta^{34}\text{S}$  values and major ion ratios suggest that many of the solutes have a marine origin. An original marine source for some of the major constituents has been suggested by ion/Cl ratios (Mann, 1983),  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope values (McArthur et al., 1989), and  $^{34}\text{S}$  isotopes in sulfate precipitates (Chivas et al., 1991). Marine-sourced solutes may have been transported to the inland waters as seaspray aerosols (e.g., Hingston and Gailitis, 1976), or from dissolution of marine evaporites that could have been deposited in the paleo-valleys during Eocene sealevel regressions. Influx of meteoric water into dry lake beds commonly causes evaporite dissolution which can result in high surface water salinity, without a corresponding increase in evaporation (Fig. 11).

### 5.2. Spatial and temporal variability

The acid saline waters only represent a portion of what occurs in this area; many of the waters are neutral to alkaline brines, as well as brackish acids (Fig. 3). There is no apparent spatial gradient in overall pH (Fig. 1), contrary to the postulation of Mann (1983). The salinity and acidity of the groundwater at a single lake system can vary significantly (Fig. 6). The initial hypothesis was that mining and agriculture may have contributed to the observed unique chemistry; however, the data reported here do not support that assertion. Observed patterns in acidity do not follow the patterns of crop cultivation or mining. For example, all waste mine waters measured were neutral (see North Royal Mine and Daisy Mine in Table 1), as were the lake and groundwaters nearest the major

mining centers of Kalgoorlie and north and east of Norseman. In addition, no evidence of fertilizers in the forms of  $\text{NO}_3$  or  $\text{PO}_4$  was detected in the waters. As was also observed by Mann (1983), acid waters occur in both cleared and uncleared areas, and neutral waters are observed in some of the heavily cultivated areas. Clearing of native vegetation has, however, caused a regional rise in the water table, bringing acid saline fluids from the deeper subsurface to surface environments.

Spatial differences in groundwater salinity in WA have been attributed to latitudinal variations in climate and aridity (Mann, 1983; McArthur et al., 1989, 1991), and differences in elevation (Gray, 2001). Previous workers have noted the highest salinities in regional groundwater along the major paleo-drainages (Gray, 2001), which coincides overall with the location of the ephemeral salt lakes. Salama et al. (1993a) noted that in some drainages, groundwater salinities were highest upstream of basement highs caused by changes in lithology or geologic structure. The spatial patterns of geochemical diversity presented here suggest that regional climate gradients and catchment partitioning alone cannot account for the varying compositions of these brines.

Comparing waters from the same locations at different times reveals the complexity and site-specific variability of this system. Many of the lakes became more saline and shallower between July 2005 and January 2006. Temporal changes in lake water pH and salinity show that as the lakes evaporated during this time, the salinity increased and the pH went down (Fig. 5). A salinity increase of 150 g/L correlated with increase in acidity of  $\sim 1$  pH unit. For  $\sim 1/3$  of the lakes, this time saw a decrease in salinity (dilution), that corresponded with an increase in pH. Evapoconcentration of surface lake waters appears to be a process that can locally decrease pH, while dilution with meteoric input raises pH. Laboratory experiments confirm that evaporation of waters with  $\text{pH} < 7$  causes concentration of acids and results in lowering of pH (Foster and Benison, 2006). A similar relationship between pH and salinity was not observed in the shallow groundwaters.

#### 5.2.1. Acid versus neutral lakes in Western Australia

The distribution of lake pH is random on the Yilgarn Craton (Fig. 1), but the groundwaters are generally acidic on a regional scale, regardless of the lake pH (e.g., Fig. 3B and C). Three reasons are suggested for why some lakes are neutral or moderately alkaline despite the regional acid groundwater system: (1) higher ratio of meteoric water to acid groundwater; (2) perched aquifer lakes; and (3) localized buffering by subsurface limestones. Some lakes with larger surface areas and catchments and slower groundwater seepage, may have a greater input of meteoric water from rainfall and runoff than contribution from acid groundwaters. Other lakes with neutral to moderately alkaline lake waters are physically separated from acid groundwaters by clay layers. For example, the Gastropod Lakes are moderately alkaline, yet their shallow groundwaters are extremely acid. At some lakes, the pH may be neutralized by varying amounts of buffers in subsurface host rocks, including isolated Eocene limestones (Clarke et al., 1996). Focused zones of neutral surface and shallow ground water have been observed in the central and northern parts of the Lake Cowan basin that are directly above cores containing localized limestone. However, other parts of the Lake Cowan basin have extremely acid lake and ground waters. Extreme and varied waters can co-exist within meters of each other. For example, a lake with a pH of 8 may have shallow groundwater with a pH of 3 in adjacent sandflats, suggesting very little mixing between these separate water bodies. While lakes with varying geochemistry within the same geographic location are not uncommon (e.g. Last, 1994), the range in salinities and pHs in WA and the resulting variations in elemental concentrations are.

### 5.2.2. WA versus Victoria

Fluids that are somewhat similar in composition to the WA fluids have evolved independently and in a different geologic setting in Victoria, southeastern Australia. Although the geochemical reactions such as S oxidation and ferrollysis that are likely responsible for creating the acidity are similar in WA and Victoria, the geology and hydrogeochemistry in WA appears to be quite different. The WA acid brines are more acidic, diverse and geographically extensive than comparable acid saline brines in Victoria. The Victoria acid brines are fed into the lakes at point-specific springs and seeps where groundwaters discharge from specific localities where aquifer conditions favor the formation of acid. The WA system lacks any specific springs and the low pH groundwater seems to have formed regionally in association with the Archean bedrock. The WA waters are more highly concentrated to create even lower pHs than those observed in Victoria. These low pHs then invoke further reactions with surrounding rocks and promote further modifications to the fluids. The similarities between the two acid brine systems illustrate how different evolutionary pathways can lead to the development of similar acid and saline lake water, which points to some of the possible complications in interpreting acid saline systems in the geologic record.

### 5.3. Evaporation trends and seawater comparisons

Salinity in closed lake basins is generally governed by the amount of precipitation versus evaporation ( $P/E \sim$  aridity) and the preservation of evaporite minerals in the geologic record is commonly considered the best evidence of high paleosalinities (Gierlowski-Kordesch and Rust, 1994).  $P/E$  ratios on the Yilgarn Craton are very low ( $P/E = 0.026\text{--}0.22$ ), and salinity in the WA lakes may be expected to reflect spatial changes in climatic conditions. However, recycling of lake bed evaporites and spatial variability of the groundwater cause extreme salinity variations between lakes at any one time. Despite identical  $P/E$  conditions, the salinities can range from nearly fresh in one lake to over eight times the salinity of seawater at a nearby lake. Data from any one WA lake would not reflect regional climate or allow for characterization of the region's "typical" water chemistry. The diversity of water salinities in WA illustrates how salinity cannot be used as a simple proxy for aridity.

Stable isotope analyses of lake waters and groundwaters show a distinct separation between these waters and provide evidence of different evolutionary pathways (Fig. 11). Saline lake waters elsewhere are typically enriched in heavy isotopes relative to related groundwaters (Gat, 1996), but in this system, the groundwaters are more evaporated and enriched in heavy isotopes than the lake waters. The consistent offset between the meteoric water line and the lake waters suggests that these fluids have a significant meteoric source. If an increase in salinity was caused by evaporation, the resulting fluids would be enriched in  $\delta^{18}\text{O}$ , however, the WA lake waters are depleted in  $\delta^{18}\text{O}$  with increasing salinity (Fig. 11D). In addition, the lake waters increase in salinity, without an appreciable change in the  $^2\text{H}$  excess (Fig. 11C). In contrast, the groundwaters show a more predictable evaporation-controlled relationship between  $^2\text{H}$  excess,  $\delta^{18}\text{O}$ , and salinity. Increase in lake water salinity without a corresponding enrichment in  $\delta^{18}\text{O}$  or  $^2\text{H}$  excess, illustrates the importance of evaporite dissolution, rather than surface water evaporation, in creating variations in lake water salinity.

In most aqueous geochemical studies, Cl is considered a conservative ion that is not adsorbed, precipitated or exchanged at low temperatures and can therefore be used as a proxy for overall evaporation. If Cl enters the WA system via rainfall (as is hypothesized by McArthur et al. (1989) and Alpers et al. (1992), and others) along with other solute components, any change in the ion/Cl ratio

must reflect interaction with surrounding rocks and/or recycling of halite during flooding–evapoconcentration–desiccation events. Halite was actively precipitating and dissolving at various times at most of the lakes, indicating that Cl may not be a good proxy for evaporation in this system. Lake waters can have very high Cl due to dissolved halite in recently flooded lakes, or because they are highly evaporated. Because of the mobility of Cl in these lake systems, deuterium ( $^2\text{H}$ ) excess provides a more robust proxy for evaporation (Fig. 13).

Mann (1983) interprets ion/Cl ratios to be similar to seawater in this region, suggesting that the groundwater samples fall along a simple seawater evaporation–dilution curve and were therefore sourced from seawater that has entered the catchment as rainfall, and have not been modified via water–rock interactions. The observed spatial and temporal complexity, however, cannot be explained by a simple evaporation model. Several of the WA fluids show depletion of major elements relative to seawater values and many of the fluids are abundant in ions that are of very low abundance in seawater. For example, seawater has 0.002 mg/L Al, while many of the WA waters have more than 1000 mg/L, and as much as 8000 mg/L Al (Fig. 9; Supplementary Table 3). Seawater contains 1.3 mg/L F, but WA waters ranges from 0 to 31 mg/L F. Seawater has 0.18 mg/L Li, while WA waters have 0–1 mg/L Li. Magnesium is a major component of seawater (1290 mg/L) (Drever, 1988), but some of the WA waters have only half as much Mg, while many others have twice to 30 times as much Mg. Magnesium/Cl shows markedly different trends for lake water versus groundwater (Fig. 13C). The WA groundwater follow an evaporation trend comparable to that of evaporating seawater, however the lake waters cover a broad range and are depleted in Mg relative to Na, possibly reflecting the variable stages of halite precipitation and dissolution in these systems. Alternatively, the higher Mg values in the groundwater could be evidence of partial or complete dissolution of possible marine evaporites in the subsurface. Or, Mg-rich minerals may be precipitating in the surface environment from the lake waters, resulting in this relative decrease in lake water Mg (although Mg-bearing chemical precipitates have not yet been identified).

Bromide has traditionally been used by evaporite geochemists as an indicator of marine versus nonmarine deposition (Hardie, 1984; Holser, 1966). Because seawater has 67 mg/L (Drever, 1988) Br and Br is a geochemically conservative element, evaporated seawaters and their precipitated halite have Br values higher than 67 mg/L (often reported up to  $\sim 200$  mg/L Br). Halites with Br concentrations lower than 67 mg/L have been interpreted as either nonmarine in origin or recrystallized (i.e., Hardie, 1984; Holser, 1966). The WA waters have an extremely wide range of Br values, from 0 to 941 mg/L, suggesting that Br here is not simply controlled by evaporation of seawater. Most of the extremely high Br values are from site-specific acid lake groundwaters (Fig. 7). These high values could possibly be related to dissolution of isolated local evaporite deposits with varying compositions, or to water–rock interaction with other Br-bearing rocks.

### 5.4. Acidity and fluid–rock interactions

Highly elevated concentration of Al, Fe, Si, S, and trace metals and elements in the most acidic fluids reflect the important contribution of water–rock interactions and acid leaching of host rocks as an influence on the character of these waters. Previous authors (Mann, 1983; McArthur et al., 1989) have attributed the regional acidity to sulfide and Fe oxidation. Oxidation of massive Ni-sulfide deposits in the region near Kalgoorlie has likely contributed locally to acidity. However, the regional prevalence of acid groundwaters in areas  $>300$  km away in a system with very slow to stagnant groundwater flow suggests that it is not the presence of these

deposits alone that are responsible for the acidity. Diffuse sulfide veins observed in some of the Archean basement rocks, and Tertiary coal deposits in southernmost WA (Holdgate and Clarke, 2000) could also provide organic and sulfidic materials that could oxidize to form acidity.

The sustainability of the acidity is a significant characteristic of the WA system. Field observations of lake pH during storm events illustrated that fluids that have been freshened due to meteoric input are able to regain acidity rapidly. Part of the acidity may be locally sustained by ongoing Fe cycling and redox reactions that generate  $H^+$  ions. The amount of Fe increases significantly in the more acid waters (Fig. 9), and authigenic Fe mineralization (oxides and sulfates, e.g., hematite and jarosite) is abundant throughout the acid lake sediments.

These processes of proposed acid formation are geochemically similar to those active in acid mine drainage systems (Singh et al., 1997), although the amount of metals such as Al in the WA waters can far exceed values reported for acid mine drainage waters. The anomalously high Al and Si concentrations in some waters are likely due acid-related mobilization of clays that formed in association with the highly weathered Archean granites (Anand and Paine, 2002). Some of the fluids are supersaturated with respect to Si and Al, and small opal crystals have been petrographically observed as solid inclusions within halite. The spatial variability in Si concentrations is extreme, and only small, localized zones of fluids are supersaturated, therefore, large zones of silcrete mineralization are not expected and are not observed in the lake sediments.

The variable amounts of elements in the more acid waters reflect spatial variations in host rock mineralogy, weathering, available buffers, microbial elemental cycling, and precipitation/dissolution of authigenic acid minerals such as hematite, alunite and jarosite. Buffering related to the dissolution of kaolinite at a pH of 3 should make an absolute groundwater lower pH limit of 3 (Gray, 2001). However, 15% of the waters sampled, including both lake and groundwaters, have values of  $pH \leq 3$ . This suggests that abnormal weathering conditions or the effects of evapoconcentration are a stronger influence than buffering by Al. In acid conditions where aluminosilicates have dissolved, alunite precipitates, which would theoretically be reflected by K and  $SO_4$  depletion (McArthur et al., 1989). Potassium and/or  $SO_4$  depletion have not been observed in the more acid waters, although there is abundant authigenic alunite throughout the field area (Alpers et al., 1992; Benison et al., 2007) suggesting that the fluids have continued to evolve since precipitation of the alunite.

Comparing the  $^2H$  excess with the pH of the fluid (Fig. 11B) shows that the low pH fluids tend to be the most evaporated, but not necessarily the most saline. The more acidic waters are commonly also the most evaporated waters, but not all acidic waters are similarly evaporated. The two fluid populations overlap in the 2.5–5.5 pH range ( $^2H$  excess –10 to –15 range) indicating that these are the “mixing conditions” between the lake waters and groundwaters.

### 5.5. Lake waters versus groundwaters

The shallow groundwaters in WA are acid on a regional scale, despite some local modifications, and seem to stay relatively consistent in their chemical composition through time. In contrast, the lakes are fed by a combination of both acid saline groundwaters and dilute meteoric waters and undergo constant fluctuations due to surface processes including flooding, evaporation and mineral precipitation and dissolution.

Salinity increases in groundwaters, relative to adjacent lake waters, are typically the result of brine reflux. However, stable isotopic analyses show that the shallow groundwaters from WA are

more evaporated than the lake waters (Figs. 11 and 12), indicating that they are not locally refluxed lake waters. Furthermore, the variability in the lake water pH compared to groundwater (Fig. 3), suggests that the groundwater is fluxing into the lakes. This diffuse upward seepage of the subsurface brines could be driven by the pressure of dense fluids, as well as abundant subsurface chemical precipitation in the limited volume of pore space (e.g. Salama et al., 1992). Local temporal changes in this discharge rate may be responsible for some of the observed spatial difference in lake water compositions.

For individual lake systems, the range of  $\delta^2H$  and  $\delta^{18}O$  in the groundwater compared to the lake water values suggest that groundwaters are locally modified by different processes. In general (especially for Aerodrome, Twin W, and Twin E) there is a trend of the more evaporated waters (i.e., enriched in  $\delta^{18}O$ ) being the most acidic, which supports the hypothesis that increased evaporation concentrates  $H^+$  and increases the acidity. In addition, regression lines for the groundwater isotopes have varying slopes for various lakes, illustrating the range of evaporative (and perhaps humidity) conditions at individual lakes (Fig. 12).

### 5.6. Sulfur

The data show that the more acid waters are significantly enriched in total S, and that some of this is likely present as uncommon S-bearing species and  $H_2SO_4$  (Fig. 10). If  $SO_4$  is the only S species, the S concentrations should be ~33% by mass of the  $SO_4$  concentrations. If there are other S species, such as  $HSO_4^-$  or dissolved S, the S measurements should be higher than 33% of the  $SO_4$  measurements. This is approximately true for many of the lakes, but for some of the more acidic lakes (pH 2–4) S/ $SO_4$  ratios are much higher, suggesting the presence of other S species. The coincidence of high S values with high acidity suggests that in some areas, water–rock interactions that result in acidity also result in high S. Dissolution and chemical weathering of subsurface sulfate sediments, and fluid interactions with sulfide-rich basement rocks have also likely contributed an important S component to the fluids. Below pHs of ~2–3, the dissociation of  $H_2SO_4$  is not well understood, however,  $HSO_4^-$  is a likely candidate for a second S species.

The  $^{34}S$  isotope work by Chivas et al. (1991) suggested that 87% of the S in this area was derived from cyclic  $SO_4$  sources that originated from marine biogenic S. This theory was additionally supported by regional gradients suggesting that S had been transported as aerosols in wind northward into the interior of the Yilgarn from the Southern Ocean. The Chivas et al. (1991) study focused on Lake Lefroy, a neutral lake south of Kalgoorlie that is likely isolated from acidic groundwater brines by lake bottom clay beds. These data suggest that the majority of the S originated from a marine source, however, there is still a significant component (13%) that was derived elsewhere (Chivas et al., 1991).

The present  $\delta^{34}S$  results of +17.0 to 20.4‰ (CDT) for lake waters, shallow groundwaters, gypsum and alunite from four lakes in southern WA are consistent with previous  $\delta^{34}S$  data. Twelve samples of gypsum, alunite, and jarosite from three other lakes in WA had  $\delta^{34}S$  values ranging from +17.8‰ to +20.1‰ (CDT; Alpers et al., 1992; Chivas et al., 1991; McArthur et al., 1989). The solid samples were slightly enriched in  $^{34}S$  compared to their aqueous counterparts, suggesting a small positive fractionation of  $^{34}S$  into the solid phase. Thode and Monster (1965) showed a fractionation factor of +1.65‰ for gypsum, indicating that the gypsum and alunite analyzed here are close to equilibrium (with respect to S isotopes) with the lake and groundwater with which they are in contact. In addition, lake and groundwaters had very close  $\delta^{34}S$  values for individual lakes, with differences of 0–0.7‰, regardless of the acidity of the lake.

The relatively high positive values of  $\delta^{34}\text{S}$  in these saline lake systems do not point to one single S source because the values overlap with  $\delta^{34}\text{S}$  signatures from several different geologic systems (e.g., Seal et al., 2000). However, the high  $\delta^{34}\text{S}$  values indicate that neither bacterial S reduction nor sulfide oxidation is the main source of the S. The results are closer to modern marine dissolved  $\text{SO}_4^{2-}$  values of  $+21.0\text{‰} \pm 0.2\text{‰}$  (Rees et al., 1978), supporting the hypothesis that the S in WA originated from: (1) sulfates carried inland as sea spray aerosols (McArthur et al., 1989; Chivas et al., 1991; Alpers et al., 1992); (2) eolian transport of marine and marginal marine sulfate minerals inland and subsequent dissolution of those sulfate minerals in closed basins; and/or (3) the recycling of possible older marine evaporites formed during local marine regressions. No such geographic trend of decreasing  $\delta^{34}\text{S}$  values is seen in the inland, downwind directions, and the lake sampled closest to the current shoreline (~92 km distance, Twin Lake West) has the lowest values measured for both lake water and shallow groundwater ( $\delta^{34}\text{S}$  of +17.0). In addition to original transport either as aerosols or as solids by winds, sulfates have also been extensively recycled and redistributed between lake systems (Benison et al., 2007). The  $\delta^{34}\text{S}$  values observed in WA are slightly lower than marine  $\delta^{34}\text{S}$  values. This implies that other processes must have lowered  $\delta^{34}\text{S}$ . Sulfide oxidation, bacterial sulfide oxidation, and meteoric inflow are all processes that have been inferred or directly observed based upon field work (Benison et al., 2007). These processes would all deplete the system in  $^{34}\text{S}$ . Another process documented by field observations is evapoconcentration, which would enrich the waters (and resulting chemical precipitates) in  $^{34}\text{S}$  (Alpers et al., 1992; Seal et al., 2000). It is proposed that a combination of factors are responsible for the  $\delta^{34}\text{S}$  values detected in southern WA lakes.

Lake Polaris, the only neutral saline lake for which S isotopes were measured, had  $\delta^{34}\text{S}$  values that fell within the same range as the acid saline lakes. This suggests that the acidity is not currently being made at individual lakes by processes involving S. Instead, these data seem to confirm that the acidity is a regional phenomenon that is currently being modified by local processes that may not rely too heavily upon S reactions (such as local buffering by thin, laterally-discontinuous subsurface carbonate rocks).

### 5.7. Implications and future work

Detailed characterization of the WA fluids reveals the need for expansion of existing models for brine evolution to include acid and saline waters. The classic model for brine evolution (Eugster and Hardie, 1978) assumes that brines evolve from undersaturated inflow, which is not the case in WA. In addition, most evaporative trends are assumed to begin with precipitation of carbonate, a constituent not present in these highly weathered acid systems. A new branch for acid saline continental brines is needed to account for the evolution of systems with high salinity and low pH shallow groundwater with no apparent deep source of the salinity.

The low pH fluids of southern WA are actively creating modern redbed and evaporite sediments and rocks. Acidic and oxidizing conditions may have played an important role in the formation of other continental redbeds (Walker, 1967; Mann, 1983), and may be a natural late-stage characteristic of continental evolution (e.g., Long and Lyons, 1990). A better understanding of the factors controlling the development and evolution of natural acid saline system will help expand models for both terrestrial and extraterrestrial acid saline depositional sedimentary environments. In addition, these types of metal-rich acid saline fluids may be important as modern analogs for sedimentary ore forming brines.

The dynamic and complex nature of these waters, as illustrated by this study, require a long-term and spatially detailed study to fully characterize their geochemistry; as well as: (1) speciation calculations, (2) comparisons of the calculations and observed chemical

precipitates, and (3) more detailed studies of the thermodynamic properties of highly acid brines, which are needed to effectively model the chemical evolution of these waters.

## 6. Conclusions

Unusual ranges and variability in pH, salinity, major ions, elements, and stable isotopes in lake waters and groundwaters from southern Western Australia reflect a complex history and a variety of processes influencing the fluid chemistry. While solutes may have originally been supplied by seaspray aerosols or Tertiary marine incursions, groundwaters have been modified by fluid–rock interactions to create regionally prevalent acidity in the brines. This acidity has resulted in significant mobilization of elements such as Fe, Al, Si, and S from subsurface sediments and Archean host rocks. These acid groundwaters diffuse into the abundant lake basins in the region, mixing with meteoric surface waters. The resulting lake waters contain solutes from the groundwaters as well as from pre-existing evaporites that are dissolved when meteoric water enters the lakes. Small-scale spatial variability in sediment–water interactions contribute to geochemical differences in groundwaters around the lakes. Despite the wide range of geochemical characteristics in these fluids, there are overall regional trends in the fluid geochemistry that reflect the importance of evaporative processes in the evolution of both the lake waters and the groundwaters. The complexity of natural continental acid brine evolution should be considered when interpreting past evaporite acid environments.

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## Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2008.11.013.

## References

- Alpers, C.N., Rye, R.O., Nordstrom, D.K., White, L.D., King, L., 1992. Chemical, crystallographic and stable isotopic properties of alunite and jarosite from acid-hypersaline Australian lakes. *Chem. Geol.* 96, 203–226.
- Anand, R., Paine, M., 2002. Regolith geology of the Yilgarn Craton. *Aust. J. Earth Sci.* 49, 3–162.
- Benison, K.C., 2006. A Martian Analog in Kansas: comparing Martian Strata with hypersaline saline lake deposits. *Geology* 34, 385–388.
- Benison, K.C., Bowen, B.B., 2006. Acid saline lake systems give clues about past environments and the search for life on Mars. *Icarus* 183, 225–229.
- Benison, K.C., Goldstein, R.H., 2002. Recognizing acid lakes and groundwaters in the rock record. *Sed. Geol.* 151, 177–185.
- Benison, K.C., LaClair, D.A., 2003. Modern and ancient extremely acid saline deposits: terrestrial analogs for martian environments? *Astrobiol.* 3, 609–618.
- Benison, K.C., Bowen, B.B., Oboh-Ikuenobe, F.E., Jagniecki, E.A., LaClair, D.A., Story, S.L., Mormile, M.R., Hong, B., 2007. Sedimentary processes and products of ephemeral acid saline lakes in southern Western Australia. *J. Sed. Res.* 77, 366–388.
- Benison, K.C., Goldstein, R.H., Wopenka, B., Burruss, R.C., Pasteris, J.D., 1998. Extremely acid Permian lakes and ground waters in North America. *Nature* 392, 911–914.

- Bettenay, E. Smith R.E., Butt, C.R.M., 1979. Physical features of the Yilgarn Block. In: 25th International Geological Congress, Excursion Guide No. 41C, pp. 5–10.
- Bowen, B.B., Benison, K.C., Oboh-Ikuenobe, F., Story, S., Mormile, M.R., 2008. Active hematite concretion formation in modern acid saline lake sediments, Lake Brown, Western Australia. *Earth Planet Sci. Lett.* 268, 52–64.
- Bowler, J.M., Teller, J.T., 1986. Quaternary evaporites and hydrological changes, Lake Tyrrell, north-west Victoria. *Aust. J. Earth Sci.* 33, 43–63.
- Chivas, A.R., Andrew, A.S., Lyons, W.B., Bird, M.J., Donnelly, T.H., 1991. Isotopic constraints on the origin of salts in Australian playas. 1. Sulphur. *Paleogeog. Paleoclimatol. Paleoecol.* 84, 309–332.
- Clarke, J.D.A., 1993. Stratigraphy of the Lafroy and Cowan paleodrainages, Western Australia. *J. Roy. Soc. Western Australia* 76, 13–23.
- Clarke, J.D.A., 1994. Lake Lefroy, a palaeodrainage playa in Western Australia. *Aust. J. Earth Sci.* 41, 417–427.
- Clarke, J.D.A., Bone, Y., James, N.P., 1996. Cool-water carbonates in an Eocene paleoestuary, Norseman Formation, Western Australia. *Sed. Geol.* 101, 213–226.
- deBroekert, P., Sandiford, M., 2005. Buried inset-valleys in the Eastern Yilgarn Craton, Western Australia: geomorphology, age, and allogenic control. *J. Geol.* 113, 471–493.
- Drever, J.I., 1988. *The Geochemistry of Natural Water*, second ed. Prentice Hall, Englewood Cliffs, NJ.
- Eugster, H.P., Hardie, L.A., 1978. Saline Lakes. In: Lerman, A. (Ed.), *Lakes: Chemistry, Geology, Physics*. Springer-Verlag, New York, pp. 237–293.
- Fegan, N.W., Long, D.T., Lyons, W.B., Hines, M.E., Macumber, P.G., 1992. Metal partitioning in acid hypersaline sediments: Lake Tyrrell, Victoria, Australia. *Chem. Geol.* 96, 167–181.
- Fitzpatrick, R.W., 2003. Overview of acid sulfate soil properties, environmental hazards, risk mapping and policy development in Australia. In: Roach, E.C. (Ed.), *Adv. Regolith*, pp. 122–125.
- Foster, R.M., Benison, K.C., 2006. Acid saline weathering experiments using acid lake host rocks from Western Australia: preliminary results. *Geol. Soc. Am. Abstracts with Programs* 8 (7), 502.
- Gat, J.R., 1996. Oxygen and hydrogen isotopes in the hydrologic cycle. *Ann. Rev. Earth Planet Sci.* 24, 225–262.
- Gierlowski-Kordesch, E., Rust, B.R., 1994. The Jurassic East Berlin Formation, Hartford Basin, Newark Supergroup: A saline lake-playa-alluvial plain system. In: *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes*, SEPM Special Publication No. 50, pp. 249–265.
- Giblin, A.M., Dickson, B.L., 1992. Source, distribution and economic significance of trace elements in groundwaters from Lake Tyrrell, Victoria, Australia. *Chem. Geol.* 96, 133–149.
- Gray, D.J., 2001. Hydrogeochemistry in the Yilgarn Craton. *Geochem. Explor. Environ. Anal.* 1, 253–264.
- Hardie, L.A., 1984. Evaporites: marine or nonmarine? *Am. J. Sci.* 284, 193–240.
- Hines, M.E., Lyons, W.B., Lent, R.M., Long, D.T., 1992. Sedimentary biogeochemistry of an acidic, saline groundwater discharge zone in Lake Tyrrell, Victoria, Australia. *Chem. Geol.* 96, 53–65.
- Hingston, F.J., Gailitis, V., 1976. The geographic variation of salt precipitated over Western Australia. *Aust. J. Soil Resour.* 14, 319–335.
- Holser, W.T., 1966. Bromide geochemistry of salt rocks. In: Rau, J.L. (Ed.), *Second Symp. on Salt*. Northern Ohio Geological Society, pp. 248–275.
- Holdgate, G.R., Clarke, J.D.A., 2000. A review of Tertiary Brown coal deposits in Australia – their depositional factors and eustatic correlations. *Am. Assoc. Petrol. Geol. Bull.* 84, 1129–1151.
- Hong, B.-y., Christiansen, J.M., Oboh-Ikuenobe, F.E., Bowen, B.B., Benison, K.C., Mormile, M.R., 2006. Microbial diversity found in the acid saline lakes of Australia. In: *Am. Soc. Microbiol. 106th General Meeting*, May 2006, Orlando, FL.
- Jagniecki, E.A., Benison, K.C., Mormile, M.R., 2005. “Hairy blobs”: microbial suspects in halite and gypsum from acid saline lakes. *Geol. Soc. Am. Abstracts Programs* 37, 7, 322.
- Johannesson, K.H., Lyons, W.B., Fee, J.H., Gaudette, H.E., McArthur, J.M., 1994. Geochemical processes affecting the acidic groundwaters of Lake Gilmore, Yilgarn Block, Western Australia: a preliminary study using neodymium, samarium, and dysprosium. *J. Hydrol.* 154, 271–289.
- Johannesson, K.H., Lyons, W.B., Yelken, M.A., Gaudette, H.E., Stetzenbach, K.J., 1996. Geochemistry of the rare-earth elements in hypersaline and dilute acidic natural terrestrial waters: complexation behavior and middle rare-earth element enrichments. *Chem. Geol.* 133, 125–144.
- Kwong, Y.T.J., Lawrence, J.R., 1998. Acid generation and metal immobilization in the vicinity of a naturally acidic lake in central Yukon Territory, Canada. In: Geller, W., Klapper, H., Salomons, W. (Eds.), *Acidic Mining Lakes*. Springer, Berlin, pp. 5–86.
- Last, W.M., 1994. Paleohydrology of playas in the northern Great Plains: Perspectives from Pallister’s Triangle. In: Rosen, M.R. (Ed.), *Paleoclimate and Basin Evolution of Playa Systems*. Geological Society of America Special Paper 289, pp. 69–80.
- Lawrance, L.M., 2001. Multi-element dispersion within salt-lake environments: case study of the buried Hannan South gold deposit, Western Australia. *Geochem. Explor. Environ. Anal.* 1, 323–339.
- Long, D.T., Lyons, W.B., 1990. Aridity, continental weathering, and groundwater chemistry. *Geol. Soc. Am. Abstracts Programs* 23169, 295.
- Long, D.T., Fegan, N.E., McKee, J.D., Lyons, W.B., Hines, M.E., Macumber, P.G., 1992. Formation of alunite, jarosite and hydrous iron oxides in a hypersaline system: Lake Tyrrell, Victoria, Australia. *Chem. Geol.* 96, 183–202.
- Lowenstein, T.K., Spencer, R.J., Pengxi, Z., 1989. Origin of ancient potash evaporates: clues from the modern nonmarine Qaidam Basin of Western China. *Science* 245, 1090–1092.
- Lyons, W.B., Chivas, A.R., Lent, R.M., Welch, S., Kiss, E., Mayewski, P.A., Long, D.T., Carey, A.E., 1990. Metal concentrations in surficial sediments from hypersaline lakes, Australia. *Hydrobiologia* 197, 13–22.
- Lyons, W.B., Welch, S., Long, D.T., Hines, M.E., Giblin, A.M., Carey, A.E., Macumber, P.G., Lent, R.M., Herczeg, A.L., 1992. The trace-metal geochemistry of the Lake Tyrrell system brines (Victoria, Australia). *Chem. Geol.* 96, 115–132.
- Macumber, P.G., 1992. Hydrological processes in the Tyrrell Basin, southeastern Australia. *Chem. Geol.* 96, 1–18.
- Mann, A.W., 1983. Hydrogeochemistry and weathering on the Yilgarn Block, Western Australia – ferrollysis and heavy metals in continental brines. *Geochim. Cosmochim. Acta* 47, 181–190.
- McArthur, J.M., Turner, J., Lyons, W.B., Osborn, A.O., Thirlwall, M.F., 1991. Hydrochemistry on the Yilgarn Block, Western Australia: ferrollysis and mineralization in acidic brines. *Geochim. Cosmochim. Acta* 55, 1273–1288.
- McArthur, J.M., Turner, J., Lyons, W.B., Thirlwall, M.F., 1989. Salt sources and water-rock interaction on the Yilgarn Block, Australia: isotopic and major element tracers. *Appl. Geochem.* 4, 79–92.
- Nordstrom, D.K., Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters. *Science* 232, 54–56.
- Ollier, C.D., 1988. The regolith in Australia. *Earth Sci. Rev.* 25, 355–361.
- Pokrovski, G.S., Borisova, A.Y., Roux, J., Hazemann, J.-L., Petdang, A., Tella, M., Testemale, D., 2006. Antimony speciation in saline hydrothermal fluids: a combined X-ray absorption fine structure spectroscopy and solubility study. *Geochim. Cosmochim. Acta* 70, 4196–4214.
- Rees, C.E., Jenkins, W.J., Monster, J., 1978. The sulphur isotope geochemistry of ocean water sulphate. *Geochim. Cosmochim. Acta* 42, 377–382.
- Risacher, F., Alonso, H., Salazar, C., 2002. Hydrochemistry of two adjacent acid saline lakes in the Andes of northern Chile. *Chem. Geol.* 187, 39–57.
- Salama, R.B., 1994. The evolution of saline lakes in the relict drainage of the Yilgarn River, Western Australia. *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes*, SEPM Special Publication 50, 189–199.
- Salama, R.B., Barber, C., Hosking, J., Briegel, D., 1992. Geochemical evolution of Lake Deborah East, prototype salt lake in the relict drainage of the Yilgarn River of Western Australia. *Aust. J. Earth Sci.* 39, 577–590.
- Salama, R.B., Farrington, P., Bartle, G.A., Watson, G.D., 1993a. The role of geological structures and relict channels in the development of dryland salinity in the wheatbelt of Western Australia. *Austral. J. Earth Sci.* 40, 45–56.
- Salama, R.B., Farrington, P., Bartle, G.A., Watson, G.D., 1993b. Salinity trends in the wheatbelt of Western Australia: results of water and salt balance studies from Cuballing catchment. *J. Hydrol.* 145, 41–63.
- Seal, R.R. II, Alpers, C.N., Rye, R.O., 2000. Stable isotope systematics of sulfate minerals. In: Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (Eds.), *Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance*. Reviews in Mineralogy and Geochemistry, vol. 40, Mineralogical Society of America, Washington, DC, pp. 541–602.
- Singh, B., Harris, P.J., Wilson, M.J., 1997. Geochemistry of acid mine waters and the role of micro-organisms in such environments: a review. *Adv. Geoecol.* 30, 159–192.
- Story, S., Oboh-Ikuenobe, F.E., Benison, K.C., Bowen, B.B., Mormile, M., 2006. Acid Hypersaline Lakes in Southern Western Australia: preliminary palynological interpretations. *Geol. Soc. Am. Abstracts Programs*, 105–106.
- Squyres, S.W., Grotzinger, J.P., Arvidson, R.E., Bell, J.F., Calvin, W., Christensen, P.R., Clark, B.C., Crisp, J.A., Farrand, W.H., Herkenhoff, K.E., Johnson, J.R., Klingelhofer, G., Knoll, A.H., McLennan, S.M., McSween, H.Y., Morris, R.V., Rice, J.W., Rieder, R., Soderblom, L.A., 2004. In situ evidence for an ancient aqueous environment at Meridiani Planum, Mars. *Science* 306, 1709–1714.
- Squyres, S.W., Knoll, A.H., Arvidson, R.E., Clark, B.C., Grotzinger, J.P., Jolliff, B.L., McLennan, S.M., Tosca, N., Bell III, J.F., Calvin, W.M., Farrand, W.H., Glotch, T.D., Golombek, M.P., Herkenhoff, K.E., Johnson, J.R., Klingelhofer, G., McSween, H.Y., Yen, A.S., 2006. Two years at Meridiani planum: results from the opportunity rover. *Science* 313, 1403–1407.
- Thode, H.G., Monster, J., 1965. Sulfur-isotope geochemistry of petroleum, evaporites, and ancient seas. *Am. Assoc. Petrol. Geol. Mem.* 4, 367–377.
- Walker, T.R., 1967. Formation of red beds in modern and ancient deserts. *Geol. Soc. Am. Bull.* 78, 353–368.