Chemical diversity in south-eastern Australian saline lakes II: biotic implications

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Abstract. This study explores how differences in ionic composition of south-eastern Australian saline lake waters, caused by path differentiation according to the Eugster–Jones–Hardie models of solute evolution and halite recycling, influence species composition of ostracod faunas. Ostracod occurrences are reported as physiologically important ionic ratios set in a marine–meteoric framework, with chemical boundaries determined by mixing and evaporation models. The occurrence of halophilous ostracods coincides with changes in the ionic structure of lake waters. Chemical diversity is found to be biologically important, with most ostracods preferring a specific pathway of the Eugster–Jones–Hardie models. Path preference predominantly reflects the different tolerance ranges of species to a combination of Na^+/H^+, Na^+/Ca^{2+} and alkalinity/Cl^- activity ratios, which probably govern acid–base balance and Na^+ and Ca^{2+} regulation. An alkalinity/Cl^- activity ratio of $\sim$–2.3 corresponds to the main division in the ostracod data and reflects the abrupt change in alkalinity/Cl^- ratios that occurs when a seawater-like solute matrix is diluted with a large amount of meteoric water (95%). Most halobiont ostracods occur in waters enriched with Na–Cl as a result of halite recycling. Evidence is presented that the same geochemical processes are relevant to other aquatic organisms (e.g. zooplankton, diatoms, insects) found in salt lakes.

Extra keywords: athalassic, cyclic salts, ion regulation, pCO_2, salinity ranges, sulfate reduction.

Introduction

Background

Most salt lakes in south-eastern Australia are dominated by Na^+ and Cl^- ions because cyclic salts of marine origin have been the main source of solute (Herczeg *et al*. 2001). Also, the abundance of major ions in Australian lakes usually follows the sequence: $Na^+ > Mg^{2+} > K^+ < or > Ca^{2+} >$ and $Cl^- > SO_4^{2-} < or > HCO_3^-$, as in seawater (Bayly and Williams 1966). As a consequence of this apparent chemical uniformity, solute composition has not been considered a likely determinant of Australian lake biota, except under unusual circumstances (see Bayly 1969). However, the first paper in this series (Radke *et al*. 2002), showed that a range of processes modify cyclic salt assemblages and give rise to chemical diversity within the Na–Cl framework (Table 1). Most of this diversity can be described by subtle differences in the relative amounts of Ca^{2+}, Mg^{2+}, SO_4^{2-} and $HCO_3^- + CO_3^{2-}$ (alkalinity = Alk) in solution (Radke *et al*. 2002). These ions drive the Eugster–Jones–Hardie (EJH) models of solute evolution, in which different chemical pathways evolve in distinct and predictable ways when minerals dissolve or precipitate. Lakes that become enriched in soluble Na^+ and Cl^- ions when salt crusts dissolve are also common features of the south-eastern Australian landscape and contribute additional chemical diversity (Radke *et al*. 2002).

This study explores the extent to which the differences in ionic composition of south-eastern Australian salt lake waters identified by Radke *et al*. (2002) influence ostracod distribution. Ostracods are micro-crustaceans that are enclosed within two calcium carbonate valves; they are ideally suited to studying the effect of ionic composition on the distribution of aquatic invertebrate species because they are the most diverse and abundant metazoan group found in the lakes (De Deckker 1981). In addition, it has been shown in North America that some ostracod species are found only in waters of a specific EJH chemical type, as defined by the Ca^{2+}/Alk ratio (Forester 1983; Smith 1993). The work by Forester and others provided an important conceptual

advancement to studies initiated by Delorme (1969), which demonstrated that ostracod shells preserved in the sediments of lakes were a valuable source of palaeochemical and other palaeoenvironmental information. Nowadays, ostracod-based reconstructions of chemistry often utilise the EJH models (Currey 1997).

Abiotic factors challenge the physiological efficiency of organisms and the range of habitats that they can potentially occupy. The challenge of ionic-regulation by organisms when water chemistry is not compatible is met at a metabolic cost (Hochachka and Somero 1984) and this should have implications for the outcome of inter-specific competition and anti-predator behaviour (see Dunson and Travis 1991). Despite this, knowledge of the processes by which major ion composition influences aquatic organisms are not well known and have developed little beyond the identification of an apparent control imposed by the Ca^{2+}/Alk ratio. Moreover, the physiological basis of EJH path preference has not been investigated, despite evidence by Mezquita *et al.* (1999*a*) that a trade-off between calcification and ion-regulation explains some ecological patterns in non-marine ostracods.

After first defining the 'preferred salinity ranges' of ostracods in south-eastern Australian lakes, this paper expands on previous work in two important ways. First, chemical modelling was undertaken to define the hydro-chemical framework for south-eastern Australian lakes in terms of a mixing system for marine water and meteoric water. Second, within this framework, ostracod occurrences were related to the ionic composition of the host waters, including ratios corresponding to ion-exchange mechanisms that influence the passage of ions between crustacean haemolymph and their environment.

The hydrochemical framework of lakes in south-eastern Australia

Cyclic salts of oceanic origin are the main source of solute for lakes in south-eastern Australia (Herczeg *et al.* 2001). Consequently, the lake chemistries are seawater-like in terms of the relative abundance of major ion species (Bayly and Williams 1966) and insofar as Na^+ and Cl^- ions dominate ionic assemblages (Herczeg and Lyons 1991). However, a range of processes modify Ca^{2+} and Alk concentrations and give rise to subtle chemical differentiation that corresponds to paths 1B, 2A and 2B of the EJH models (Table 1; Radke *et al.* 2002). Importantly, the processes that alter the relative amounts of Ca^{2+} and Alk (Table 1) imprint on the chemical composition of south-eastern lakes in much the same way that mixing between seawater (Ca^{2+} > Alk) and meteoric water (Alk > Ca^{2+}) in near-shore marine areas does, because the lake chemistries are seawater-like overall. Consequently, the complex system can be modelled, in general terms, by theoretical mixing of seawater and meteoric water.

Ion regulation

Epithelial cells of the antennal glands, gut, integument and gills in crustaceans regulate the passage of anions and cations between the environment and the haemolymph to maintain ionic activities at tissue-specific concentrations (Ahearn *et al.* 1999). Transport occurs by diffusion and via exchangers, pumps and ion specific channels. The pumps and exchangers transport pairs of ions in opposite directions across cell membranes. Passive exchange is replaced by ATP-driven exchange (pumps) when thermodynamic limits are exceeded. The energy (E) to drive the exchange increases with the trans-membrane activity gradients of the ions involved e.g.:

$$E = 2.3 \ RT \ \ln (Ca_i/Ca_o)^a/(H_i/H_o)^b \tag{1}$$

where T is the Kelvin temperature, R is the gas constant, a and b are the numbers of Ca^{2+} and H^+ ions (in this example) transported per cycle and the subscripts 'i' and 'o' refer to the concentrations of Ca^{2+} and H^+ (in this example) inside and outside a cell, respectively (McConnaughey and Whelan 1997). Because the functional role of ion regulation is to maintain internal ion concentrations within specific ranges, Ca_i and H_i should vary only within a small range and the ratios of relevant ions in the external environment (e.g. $Ca_o:H_o$) are potential drivers of system energetics.

Na^+/Ca^{2+}, Alk/Cl^- and Na^+/H^+ activity ratios are considered in this study because exchange mechanisms involving these pairs of ions contribute to the regulation of pH, calcium and monovalent ionic activities and cell volumes in crustaceans (Ahearn *et al.* 1999). SO_4^{2-}/Cl^- and Na^+/Mg^{2+} activity ratios governing Mg^{2+} (see Cornell 1979) and SO_4^{2-} regulation (Ahearn *et al.* 1999) were also considered because these divalent ions are the most strongly regulated of all ions (Mantel and Farmer 1983). This is perhaps because sulfate is a heavy ion and can influence buoyancy (Sanders and Childress 1988) and because high extracellular concentrations of Mg^{2+} can block neuro-muscular transmission (Robertson 1953).

Materials and methods

Study area

The locations of the four study areas are shown in Fig. 1. The Riverine Plain (A), the Wimmera (D) and the Coastal Plain (C) occur in the southern part of the Murray Basin, which extends across the states of Victoria, South Australia and New South Wales. The Western Plains ('Basalt Plains') study area (B) is situated roughly 100 km west of Melbourne, in Victoria. Detailed lake locations and descriptions of the geology and hydrology in the regions are provided in Radke *et al.* (2002).

Sample collection and analysis

Lake water and ostracods were seasonally sampled from 73 lakes between August 1993 and December 1994.

Ostracod samples

Ostracod samples were collected using a hand-held 150 μm net fitted with a pomade jar at its extremity. In the absence of limitations
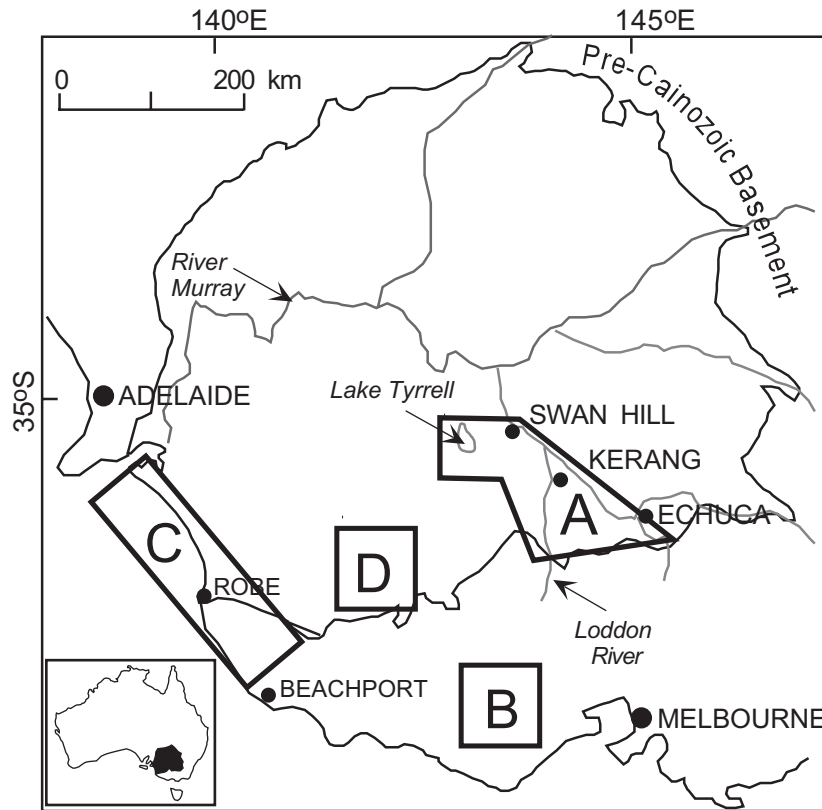
Fig. 1. Map showing the locations of the study areas: A, the Riverine Plain; B, the Western Plains; C, coastal South Australia and the Wimmera (C).

imposed by turbidity, all visible microhabitats at a given location were sampled (e.g. plant communities or sediment textural differences). The biological samples were immersed in 100% ethanol immediately after collection. In the laboratory, the samples were washed through nested sieves of 2.83 mm (to remove large material such as twigs and leaves) and 178 μm (to remove some fine inorganic material). The samples were then divided into four replicate samples using a sediment splitter fitted with two Perspex containers. The divided sample contents were captured on detachable plates, which had small holes to permit the drainage of alcohol. Ostracods were handpicked from these plates under a binocular microscope, using a fine paintbrush. All ostracods in the first replicate sample were counted. Further replicates were counted only if fewer than 100 ostracods had been found. The tallies of each species in the sample were extrapolated to take account of uncounted replicates.

Physical and chemical variables

Major ions, conductivity, pH and temperature were measured according to methods described in Radke *et al*. (2002). Dissolved oxygen and % oxygen saturation (DO and %DO) and turbidity (nephelometric units) were measured *in situ* using a YSI model 55 dissolved oxygen meter (www.YSI.com/environmental; accessed November 2003) and a Horiba U-10 water quality checker (www.horiba.com; accessed November 2003) respectively. Samples for total nitrogen (TN) were collected in new 60 mL HDPE bottles that were rinsed four times in distilled water, followed by four times in Milli-Q water. Samples for total phosphorus (TP) determination were collected in 50 mL amber glass bottles that were prepared by rinsing once in 1:1 nitric acid, followed by four times in distilled water and then

four times in Milli-Q water. The bottles were then capped with aluminum foil and then heated at 400°C for 1 h. Sterilised teflon sheeting was placed between the caps and bottles at the time of sampling because the caps supplied with the bottles could not be sterilised. All bottles and sampling equipment were well rinsed with the lake water before sample collection. The samples were discharged from the same 1 L container as the anion and cation samples. Nutrient samples were stored on ice until analysis at ACT Electricity and Water (Canberra, Australia) following standard procedures (APHA 1985).

Other data

Additional ostracod and jointly collected chemical data (mainly salinity) were acquired from several published (Bayly and Williams 1964; Bayly and Williams 1966; Bayly 1970; Timms 1974, Timms 1981, Timms 1983, Timms 1998; De Deckker 1975; Buckney and Tyler 1976; Williams and Buckney 1976; Geddes *et al*. 1981; Halse 1981; De Deckker and Williams 1982; Martens *et al*. 1985; Chivas *et al*. 1986; Gell *et al*. 1994; Halse *et al*. 2000a, 2000b; Pinder *et al*. 2002) and unpublished sources (e.g. datasets of S. A. Halse and P. De Deckker). These additional presence/absence data, which included sources in Western Australia, greatly expanded the size of the datasets for some uses (e.g. cluster analysis and calculating preferred salinity ranges).

Chemical modelling

Theoretical mixtures containing seawater (SW; data from Plummer, *et al*. 1988) and meteoric water (e.g. coastal bulk precipitation (CBP)) were first generated and then evaporated in PHRQPITZ (Plummer *et al*. 1988). The mixtures consisted of: 50% SW:50% CBP; 25% SW7:5% CBP; 10% SW:90% CBP; 5% SW:95% CBP; 1% SW:99% CBP and

0.01% SW:99.9% CBP. The mixtures were then equilibrated with atmospheric partial pressures of CO_2 and calcite ($\Omega_{calcite} = 1.0$) at 25°C, before their simulated evaporation. The imposition of subsequent phase boundaries was mixture specific. Where thermodynamically appropriate (e.g. Path 1; Ca > Alk), gypsum was allowed to precipitate while still maintaining equilibrium with calcite. All evaporations were terminated at the halite (NaCl) phase boundary. The evaporation of Baringhup 10003 groundwater was also simulated (see Radke *et al.* 2002). This sample is Path 2 end-member, but has a higher alkalinity than CBP owing to the weathering of tholeiitic basaltic rock (see Radke *et al.* 2002).

Chemical preference

Canonical correspondence analysis

Canonical correspondence analysis (CCA) was performed on the ostracod and geochemical data (73 lake; this study only) using CANOCO 4 (ter Braak and Smilauer 1998; available from Microcomputer Power, Ithaca, NY, USA). The geochemical data used in the analysis were nutrient concentrations (TN and TP), DO, %DO, turbidity, major ion concentrations (milliequivalents per litre; meq L^{-1}), partial pressures of carbon dioxide (pCO_2), Ca^{2+}/Alk ratios and the relative percentages of the different major ions. Two measures of ion concentration were also used: salinity and ionic strength. Ionic strength and pCO_2 were calculated in PHRQPITZ. With the exception of ion percentage data, physical and chemical data were tested for normality and were log_{10} transformed, where appropriate, to achieve an approximately normal distribution. Ostracod species (collected during this study only) were expressed as relative percentages of the total ostracod count in a sample; species present in only one sample or having a maximum relative abundance of less than 1% were excluded. Canonical correspondence analysis is well suited to the use of percentage data (ter Braak and Smilauer 1998). The option for down weighting rare species was implemented in all cases.

The forward selection procedure in CANOCO 4 is analogous to step-wise multiple regression. This option was used to select a subset of environmental variables that explained variation within the species data almost as well as the full dataset but without the problem of multicollinearity, which can render analyses unstable (ter Braak and Smilauer 1998). Variables determined to be redundant by forward selection played no role in the analysis but were subsequently integrated into the CCA biplot as 'passive' variables to show their relationship with respect to ostracod species and the other environmental variables. The significance of the forwards-selected environment variables and the CCA axes were assessed using Monte Carlo permutation tests (999 permutations; $P < 0.001$), with Bonferroni-adjusted probability levels (Manly 1991).

Graphical analysis

Ostracod presence/absence data were plotted on Ca–Mg–Alk ternary diagrams that differentiate water according to Paths 1B, 2A and 2B of the EJH models (Radke *et al.* 2002). Medians and 25th and 75th percentiles were also calculated to define the 'optima' and 'preferred ranges' of species for salinity, seawater-normalised $Na^+ + Cl^-$ concentrations (nNaCl), Ca^{2+}/Alk ratios and the following physiologically important ratios: aSO_4^{2-}/aCl^-; aNa^+/aMg^{2+}; Alk/aCl^-; aNa^+/aCa^{2+} and aNa^+/aH^+ (where 'a' indicates ion activity). Ion activities were used in preference to concentrations in the physiologically important ratios because uncharged ion-pairs can form in solution (e.g. $MgSO_4^o$, $Na_2SO_4^o$, $CaCl_2^o$, $MgCl_2^o$, $NaCl^o$, $NaHCO_3^o$, KCl^o, HCl^o and others) and these reduce the 'effective' concentrations and physiological impact of the constituent ions. Ion activities were calculated using NETPATH (for samples with an ionic strength of < 0.05; Plummer *et al.* 1991) and PHRQPITZ (for samples with an ionic strength > 0.05; Plummer *et al.* 1988).

Cluster analysis

Cluster analysis was performed on the presence/absence ostracod dataset ($n = 608$) using STATISTICA (StatSoft 1984–1995). Most cluster analyses follow two steps: (*i*) measures of similarity or distance are computed between pairs of objects; and (*ii*) the objects are amalgamated into larger groups on the basis of increasing dissimilarity. Ward's amalgamation method was applied to a Euclidean distance matrix consisting of ostracod presence and absences. Ward's method uses an analysis of variance to minimise the sum of the squares of any two clusters that can form at each step (StatSoft 1984–1995).

Results

Chemical modelling

Measured ionic concentrations minus effective concentrations (activities) of ions are shown in Fig. 2. The amount of ion-pair formation increases with salinity and causes significant divergence between measured and effective concentrations at ~1000 mg L^{-1} ($10^{3.0}$ mg L^{-1}; Alk), ~3200 mg L^{-1} ($10^{3.5}$ mg L^{-1}; Na^+) and ~10 000 mg L^{-1} ($10^{4.0}$; Cl^-, SO_4^2, Mg^{2+} and Ca^{2+}, as well as K^+ (not shown)).

Results from mixing and evaporation models are shown in Figs 3 and 4. Processes other than mixing and evaporation that can influence the magnitudes of the ratios are also shown. Meteoric additions to a seawater matrix lowers log Ca^{2+}/Alk ratios in the initial solutions (Fig. 3*a*). At the onset of $CaCO_3$ precipitation, Ca^{2+}/Alk ratios increase in the case of Path 1 waters and decrease in the case of Path 2 waters. The onset of calcium carbonate precipitation is delayed in Path 1 water compared to Path 2 waters. The 0.01% seawater mixture has a Ca^{2+}/Alk ratio of ~1 and is used as a dividing line to separate Path 1 from Path 2 waters. The slope of the increase in pH with salinity starts to diminish at the onset of calcium carbonate precipitation (Fig. 3*b*). Solutions with more of the meteoric end-member have higher pH values at a given ionic concentration than solutions with relatively more of the seawater end-member. The photosynthetic consumption of CO_2 would cause pH to increase relative to the model results.

Meteoric additions to a seawater matrix cause an initial lowering of aNa^+/aCa^{2+} ratios (Fig. 4*a*). The ratio then increases, commensurate with evaporation, in Path 2 waters. The aNa^+/aCa^{2+} ratio changes little with evaporation in Path 1 waters. Gypsum dissolution and the 'reverse exchange' (Table 1) can increase Ca relative to Na^+ and thus lower aNa^+/aCa^{2+} ratios compared to the models. The aNa^+/aH^+ ratio increases with evaporation in all series, although highest values are observed in waters with Path 2 hydrochemical compositions (Fig. 4*b*). The photosynthetic consumption of CO_2 would increase aNa^+/aH^+ ratios relative to the models. Meteoric additions to a seawater matrix cause $aAlk/aCl^-$ ratios to increase, particularly in mixtures with less than 5% seawater (Fig. 4*c*). The ratio decreases with the onset of $CaCO_3$ precipitation in all series. Particularly high $aAlk/aCl^-$ are found in the Baringhup evaporation model owing to the weathering of basalt rocks (see Table 1). Sulfate
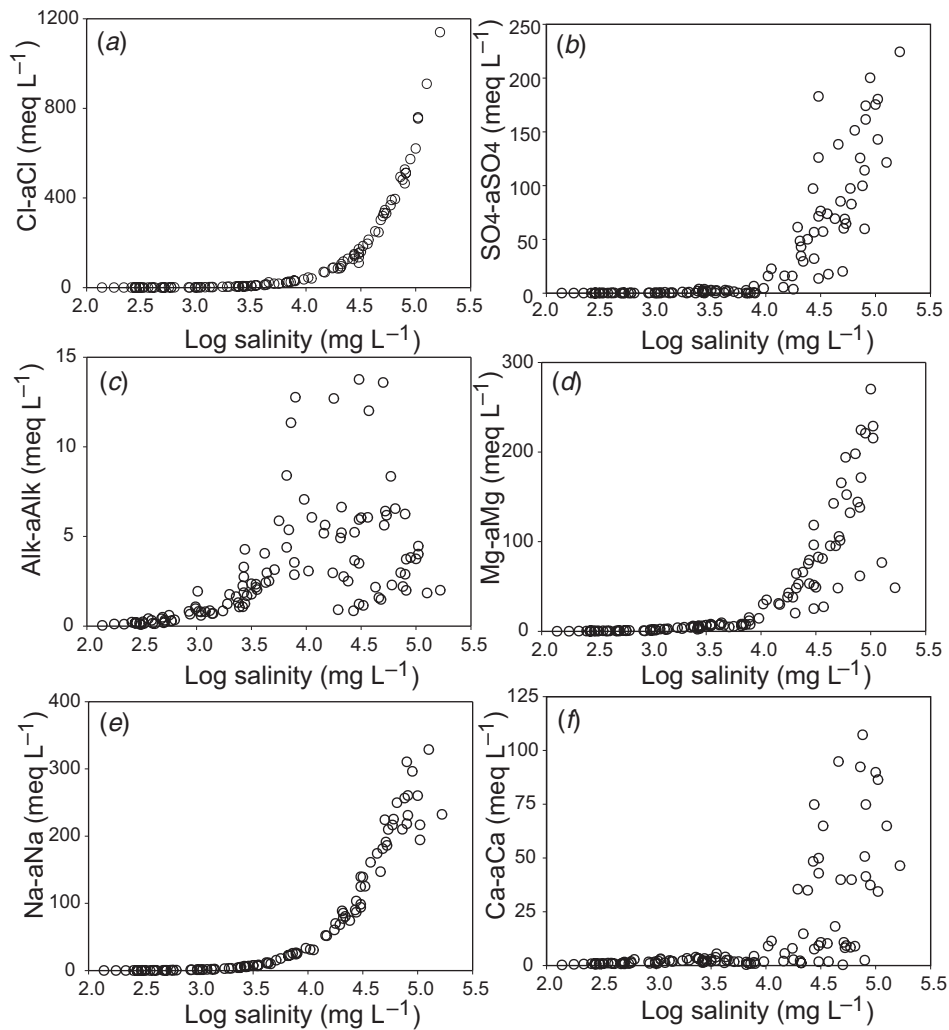
Fig. 2. Measured concentrations of major ions in milliequivalents per litre (meq L^{-1}) minus effective concentrations (or activities) of the same ions.

reduction should be expected to increase aAlk/aCl$^-$ ratios relative to the models; the recycling of salt crusts composed predominantly of Na–Cl may cause the ratios to diminish relative to the models (Table 1).

Chemical preference of ostracods

Salinity preference

Fifty-five species of ostracods were found in the study. Abbreviated names and sample sizes used to define the preferred salinity ranges and medians for mostly known species are shown in Table 2. The absolute salinity ranges and preferred salinity ranges for the ostracods are shown in order of increasing median salinity in Fig. 5. Only absolute salinity ranges have been published previously (De Deckker 1981, 1983).

Canonical correspondence analysis

The results of the CCA are shown in Fig. 6. To reduce complexity, environmental variables and species scores are shown on separate diagrams. Forward selection identified four variables that could explain the variance in the species data about as well as the full dataset. These variables were ionic strength, pH, SO_4^{2-} and pCO_2. Axis 1 explained 5.2% of the variance in the species data and is a gradient of increasing ionic concentration (e.g. ionic strength, salinity and the conservative ions Na$^+$, Cl$^-$, Mg^{2+} and K$^+$). This value is typical of noisy, heterogeneous ecological data with many zero values in the species matrix. Axis 2 explained 3.2% of the variance of the data. This axis differentiates samples with comparatively high pH values from waters with relatively lower pH values. Partial pressures of carbon dioxide and Ca^{2+} and Mg^{2+} concentrations also varied on axis 2 and in an inverse relationship with pH. Both axes were highly significant on the basis of Monte Carlo permutation tests ($P < 0.001$; 999 permutations).

Ostracods that occur most often at salinities less than ~3200 mg L^{-1} (log $10^{3.5}$ mg L^{-1}) form a group on the left in
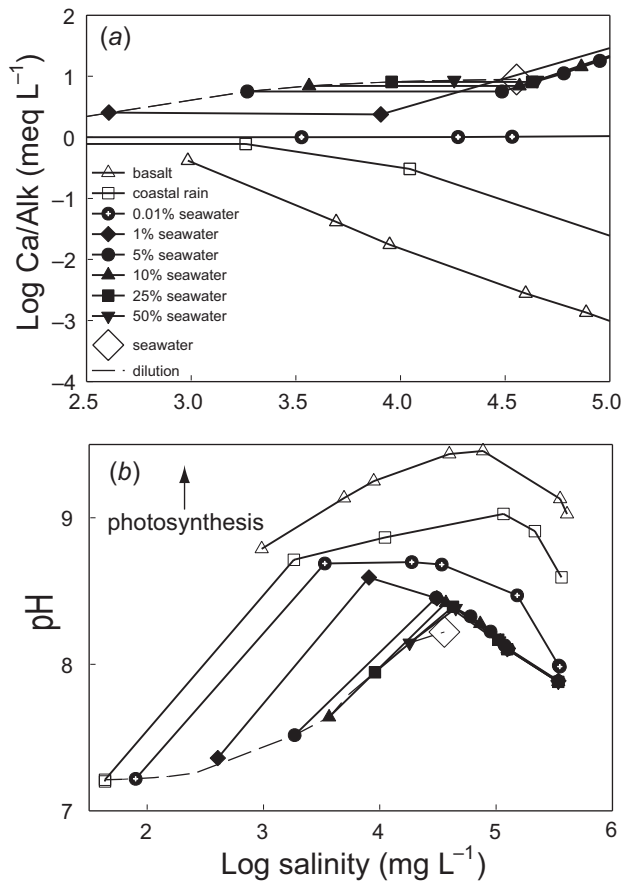
Fig. 3. Modelled evaporation paths of Baringhup 10003 (Bar) groundwater, coastal rainwater, and different mixtures of coastal rainwater and seawater (as % seawater) for log Ca^{2+}/Alk ratios and pH. Closed symbols are indicative of Path 1 chemistries, and open symbols are indicative of Path 2 chemistries. The major inflections in the diagram mark the onset of calcite precipitation. The positions of seawater and the seawater-dilution line are also shown.

Fig. 6*b*. The ostracods in the low-salinity group also vary on axis 2 in terms of increasing weighted averages for pH (and conversely pCO_2) with salinity. A different saline suite of genera (*Australocypris*, *Cyprideis*, *Diacypris, Leptocythere*, *Mytilocypris*, *Platycypris* and *Reticypris*) is found in the high salinity end of the diagram. Species belonging to these halophilous and halobiont genera are found most frequently at salinities greater than 3200 mg L^{-1} ($10^{3.5}$ on a log scale; Fig. 5) and their weighted averages for pH (and conversely pCO_2) remains relatively constant or decreases as salinity increases (on axis 1). *Cyprinotus edwardi* (CYNedw), *Mytilocypris henricae* (MYThen) and *Candonocypris incosta* (CACin) stand out on axis 2 on the basis of much elevated weighted averages for pH (and conversely low pCO_2) with respect to the other species.

Cluster analysis

The results of the cluster analysis are shown in Fig. 7. Cluster analysis found four groups of species within the
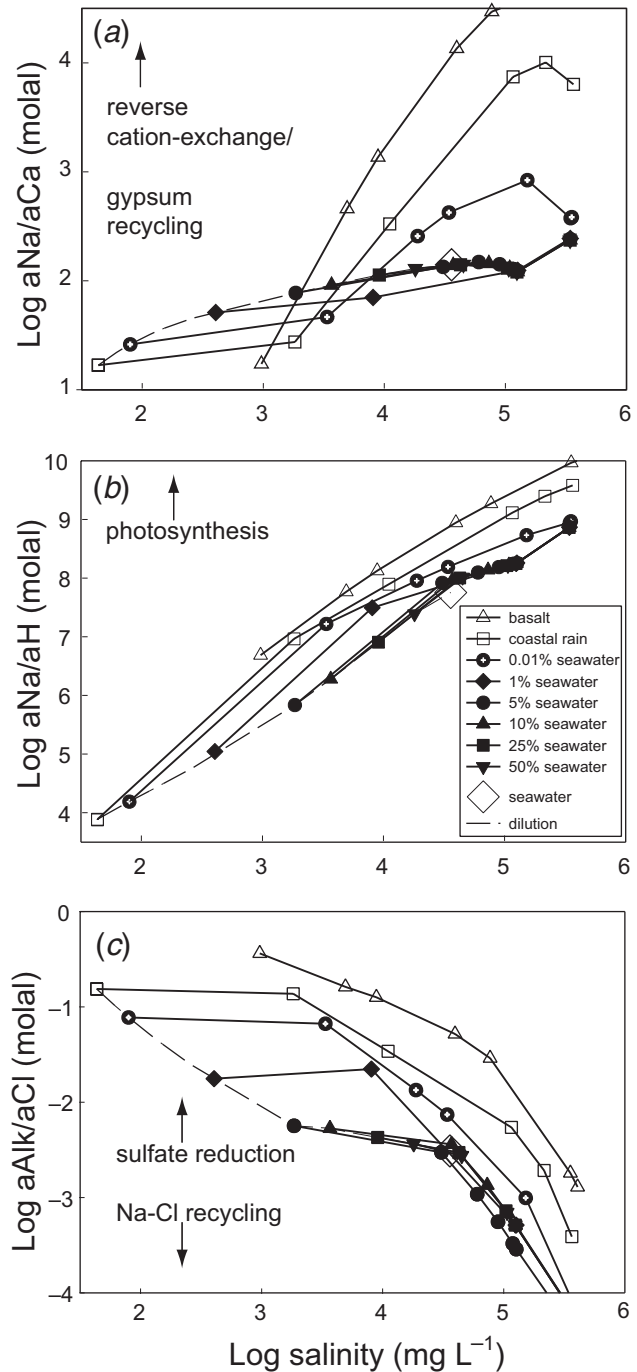

Fig. 4. Modelled evaporation paths of Baringhup 10003 (Bar) groundwater, coastal rainwater, and different mixtures of coastal rainwater and seawater (as % seawater) for log Na^+/Ca^{2+}, Na^+/H^+ and Alk/Cl^- activity ratios. Closed symbols are indicative of Path 1 chemistries, and open symbols are indicative of Path 2 chemistries. The major inflections in the diagram mark the onset of calcite precipitation. The positions of seawater and the seawater-dilution line are also shown.

halophilous and halobiont genera. These groups are designated: Ya (*Leptocythere lacustris*, *Mytilocypris ambiguosa*, *Mytilocypris mytiloides* and *Cyprideis australis*);

Table 1. Geochemical processes that alter Ca²⁺/Alk ratios of lakes and groundwater in south-eastern Australia

Processes that increase alkalinity equivalents relative to Ca²⁺	Processes that increase Ca²⁺ equivalents relative to alkalinity
Rock weathering primary silicate + H_2O + CO_2 = clay + cations + HCO_3^- + SiO_2 (Thomas 1995; Radke *et al.* 2002)	*dolomitisation* $(2-x)CaCO_3 + Mg^{2+} + xCO_3^{2-} = CaMg(CO_3)_2 + (1-x)Ca^{2+}$ (Thomas 1995)
sulfate reduction $8SO_4^{2-} + 2Fe_2O_3 + 15C + 7H_2O \Leftrightarrow 4FeS_2 + 14HCO_3^- + CO_3^{2-}$ (Thomas 1995; Radke *et al.* 2002)	*pyrite oxidation* $FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + SO_4^{2-} + 2H^+$ (Macumber 1991)
cation exchange Ca^{2+} (solution) + $2Na^+$ (clay) $\Leftrightarrow$ $2Na^+$ (solution) + Ca^{2+} (clay)	*reverse cation exchange* $2Na^+$ (solution) + Ca^{2+} (clay) $\Leftrightarrow$ Ca^{2+} (solution) + $2Na^+$ (clay) (Herczeg *et al.* 2001)
add meteoric water (i.e. river water or rainwater)	*add seawater*
artificial weathering? colloid-M^+ + H_2O = colloid-H^+ + M^+ + OH^- (Radke *et al.* 2002).	*dissolve gypsum* ($CaSO_4.2H_2O$) (Radke *et al.* 2002)

Table 2. List of ostracod species and their abbreviated names (abbrev.) and samples sizes (*n*) used for defining salinity ranges

Species	Abbrev.	*n*	Species	Abbrev.	*n*
Alboa worooa De Deckker, 1981	ALBwor	61	*Diacypris whitei* (Herbst, 1958)	DIAwhi	52
Australocypris insularis (Chapman, 1966)	AUSin	195	*Eucypris virens* (Jurine, 1820)	EUCvir	9
Australocypris rectangularis De Deckker,1978	AUSrec	30	*Gomphodella maia* De Deckker, 1981	GOMmai	20
Australocypris robusta De Deckker, 1974	AUSrob	43	*Heterocypris vatia* De Deckker, 1981	HETvat	23
Bennelongia australis (Brady, 1886)	BENaus	19	*Ilyocypris australiensis* Sars, 1889	ILYaus	80
Bennelongia barangaroo De Deckker, 1981	BENbar	59	*Ilyocypris perigundi* De Deckker, 1981	ILYper	49
Candona sp. nov. 1	CANnd1	14	*Ilyodromus viridulus* (Brady, 1886)	ILYvir	7
Candonocypris incosta De Deckker, 1981	CACin	3	*Leptocythere lacustris* De Deckker, 1981	LEPlac	10
Candonocypris novaezelandiae (Baird, 1843)	CACnov	57	*Limnocythere dorsosicula* De Deckker, 1981	LIMdor	48
Cypricercus salinus	CYCsal	58	*Limnocythere milta* De Deckker, 1981	LIMmil	3
Cyprinotus dahli Sars, 1896	CYNdah	9	*Limnocythere mowbrayensis* Chapman, 1914	LIMmow	30
Cyprinotus dentato-marginalis (Baird 1859)	CYNd-m	2	*Limnocythere porphyretica* De Deckker, 1981	LIMpor	33
Cyprinotus edwardi McKenzie, 1978	CYNedw	57	*Mytilocypris ambiguosa* De Deckker, 1978	MYTamb	51
Cyprinotus kimberliensis McKenzie, 1966	CYNkim	24	*Mytilocypris henricae* (Chapman, 1966)	MYThen	37
Cypretta minna (King 1855)	CYTmin	6	*Mytilocypris mytiloides* (Brady, 1886)	MYTmyt	127
Cypretta viridis (Thomson 1878)	CYTvir	3	*Mytilocypris praenuncia* (Chapman, 1936)	MYTpra	36
Cyprideis australiensis Hartmann, 1978	CYDaus	8	*Mytilocypris splendida* (Chapman, 1966)	MYTspl	83
Cypridopsis funebris Brady, 1886	CYNfun	21	*Newnhamia fenestrata* King 1855	NEWNf	48
Darwinula sp. nov. 1	DARnd1	8	*Plesiocypridopsis newtoni* Brady & Robertson, 1870	PLEISn	36
Diacypris compacta (Herbst, 1958)	DIAcom	170	*Platycypris baueri* Herbst, 1957	PLATb	203
Diacypris dictyote De Deckker, 1981	DIAdic	78	*Reticypris clava* De Deckker, 1981	RETcla	117
Diacypris dietzi (Herbst, 1958)	DIAdzt	110	*Reticypris herbsti* McKenzie, 1978	RETher	39
Diacypris fodiens (Herbst, 1958)	DIAfod	37	*Sarscypridopsis aculeata* Costa, 1847	SARSa	171
Diacypris spinosa (De Deckker, 1981)	DIAspi	81			

Yb (*Mytilocypris henricae, Mytilocypris splendida, Mytilocypris praenuncia* and *Diacypris spinosa*); Za (*Diacypris whitei, Diacypris fodiens, Reticypris herbsti* and *Australocypris rectangularis*); and Zb (*A. insularis, Diacypris dictyote, Platycypris baueri, Diacypris compacta, Diacypris dietzi* and *Reticypris clava*). The greatest dissimilarity was between the Y and Z groups.

Eugster–Jones–Hardie path preference

The preferred ranges of halophilous and halobiont ostracods for log Ca²⁺/Alk ratios are shown in Fig. 8. With the exception of the Yb ostracods, which are found mainly in Path 2 waters, most ostracods have a general preference for Path 1 waters (Fig. 8*a*). *Mytilocypris henricae* and *M. splendida* were the only ostracod species found in Path 2B waters (Fig. 8*b*). Although there is no evidence for path preference in the case of *D. spinosa, P. baueri* and *D. dietzi*, these ostracods are found at higher salinity levels in Path 1 waters than in Path 2 waters (Table 3). There is no evidence for path preference, or of an influence of EJH path on salinity tolerance, in the data for *D. compacta* (Table 3).

Combined reaction paths and chemical preferences

The preferred ranges of halophilous and halobiont ostracods for log aNa^+/aCa^{2+}, aAlk/aCl^-, aNa^+/aH^+, aSO_4^{2-}/aCl^- and aNa^+/aMg^{2+} ratios are shown in Table 4.
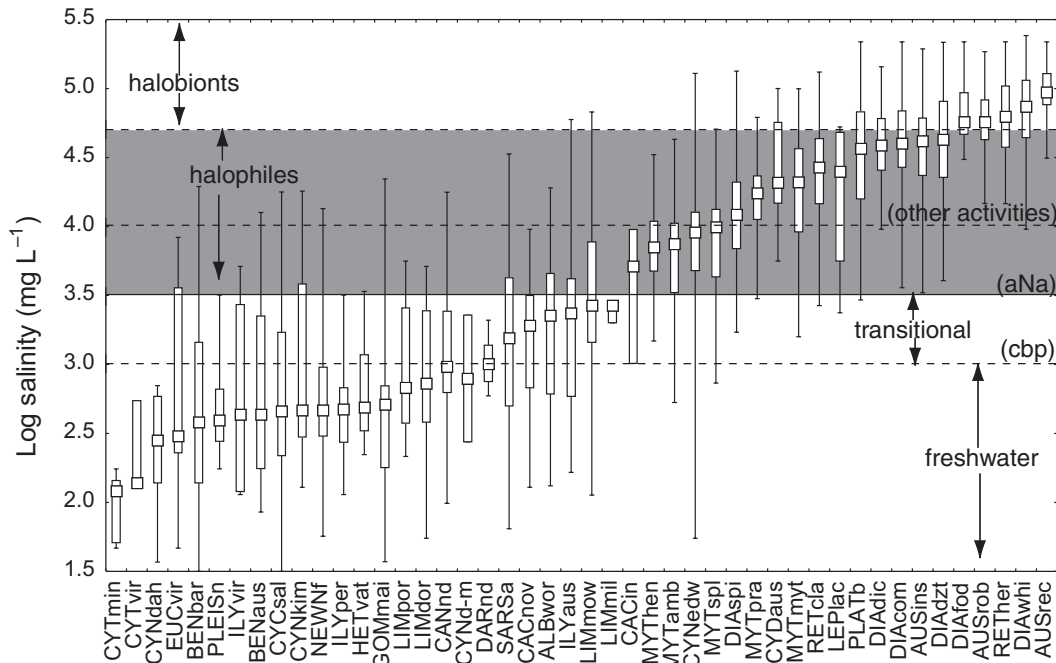
Fig. 5. Medians, ranges and preferred salinity ranges (i.e. 25th and 75th percentiles) of ostracods. Lines in the diagram indicate the salinity levels at which calcite starts to precipitate ('cbp'), and when Na^+ ('aNa') and other ions ('other activities') begin to form ion-pairs. The transition from freshwater and brackish species to halophilous and halobiont species is centered at about $10^{3.5}$ log salinity units (or at ~3200 mg L^{-1}).

Figure 9 shows the medians of ostracods in log aNa^+/aCa^{2+} v. log $aAlk/aCl^-$ space and log aNa^+/aH^+ v. log $aAlk/aCl^-$ space. Both diagrams provide a good separation of Path 1 and 2 water chemistries and the species that prefer them (Fig. 9*a,b*). We highlight that the Z-group ostracods can be differentiated from Y-group ostracods at an $aAlk/aCl^-$ ratio of ~–2.3. Figure 10*a* shows the medians of ostracods in log aSO_4^{2-}/aCl^- v. log aNa^+/aMg^{2+} space. Interestingly, the medians of the Zb ostracods (and *P. baueri*, *A. robusta*, *M. henricae* and *D. compacta*) follow the expected trend for seawater evaporated though the gypsum branchpoint (based on the model in Plummer *et al.* 1988), despite the fact that virtually all water samples were under-saturated with gypsum.

Seawater-normalised Na$^+$ and Cl$^-$ concentrations (nNaCl)

The medians and absolute and preferred ranges of ostracods for seawater-normalised Na^+ and Cl^- concentrations (nNaCl) are shown in box-and-whisker diagrams in Fig. 11. The Za ostracods stand out among species found mainly in Path 1 waters for their occurrence in waters with nNaCl concentrations similar to, or greater than, seawater evaporated to the point of halite saturation (based on the model of Plummer *et al.* 1988). Of the species found mainly in Path 2 lakes, at least 25% of the occurrences of *P. baueri*, *A. robusta* and *D. compacta* were in waters in which nNaCl exceed 1150. The halite saturated playa lakes of the Western Plains (Path 2) can be differentiated from the high-salinity

but halite under-saturated maar lakes (Path 2), also of the Western Plains, at about this value.

Discussion

The chemical transition to halophilous and halobiont ostracods

This study lends support to the suggestion of Buckney and Tyler (1976) that geochemical criteria play a role in the biological demarcation of fresh and saline waters. The CCA identified two groups of ostracods: a lower-salinity group in which species are differentiated on the basis of increasing weighted averages for both pH and salinity; and a higher-salinity group in which the weighted averages of species for pH remained relatively constant, or decreased as salinity increased (Fig. 6). These patterns of pH change with salinity are expected before, and following, the calcite branchpoint: pH should increase with salinity until calcium carbonate begins to precipitate, carbonate alkalinity then decreases in waters that are actively precipitating calcium carbonate, causing pH levels to stabilise or diminish (Fig. 3*b*). The pH plateau, and a 'stoichiometric constriction on divalent ion proportions' caused by Ca^{2+} precipitation in carbonates, both of which have a sound geochemical basis, were also used by Buckney and Tyler (1976) to differentiate fresh from saline waters.

Calcium carbonate often begins to precipitate when salinity levels exceed 1000 ($10^{3.0}$) mg L^{-1} in south-eastern
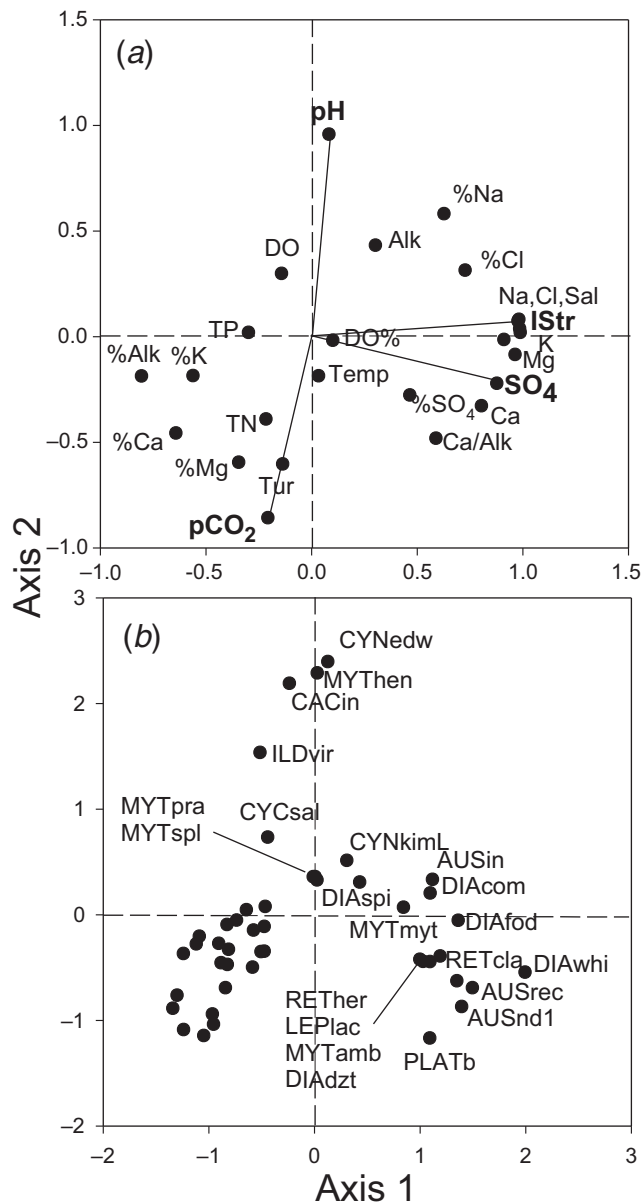
Fig. 6. Canonical correspondence analysis environmental (*a*) and species (*b*) plots showing axis 1 and axis 2. Abbreviations in the diagram include: IStr (ionic strength), Sal (salinity), Temp (temperature), Tur (turbidity), TN (total nitrogen), TP (total phosphorus), DO (dissolved oxygen), %DO (dissolved oxygen saturation) and pCO_2 (partial pressure of carbon dioxide).

coincides with important physiological and ecological transitions in ostracods because a different suite of genera begin to occur (*e.g. Australocypris, Cyprideis, Diacypris, Leptocythere, Mytilocypris* and *Reticypris*) (Figs 5, 6). Moreover, freshwater species with medians for salinity < 1000 mg L^{-1} are found in lower numbers over this range and even more infrequently at salinity levels > 3200 mg L^{-1} (Fig. 5). The transition to a predominantly halophilous and halobiont fauna (see Bayly 1972) is centred at 3200 mg L^{-1}. A small number of transitional species have salinity medians in the range from 1000–3200 mg L^{-1} (Fig. 5).

Pair formation involving ions other than CO_3^{2-} and Na^+ becomes significant at a salinity of ~10000 mg L^{-1} (10^4 on a log scale) (Fig. 2*a,b,d,f*) and may provide the basis for another ecological transition. The 25th percentiles for salinity of all the Z-group ostracods are higher than this value (Fig. 5), which is the upper salinity tolerance of several types of freshwater crustaceans (Bayly 1967). Within the Z-group, the Za ostracods (and *A. robusta*) have medians for log salinity in the range 63000 to 100000 mg L^{-1} (e.g. $10^{4.8}$–10^5 mg L^{-1}; Fig. 5) and are classified here as halobionts.

Differentiation of ostracods based on water chemistry

A dividing line at a log aAlk/aCl$^-$ ratio of ~$10^{-2.3}$ mg L^{-1} separates the medians of the Y-group ostracods from those of the Z-group ostracods and corresponds to the main division in the ostracod data (Fig. 9). The HCO_3^-/Cl$^-$ ratio is also an important discriminator of copepods in Australian lakes (Bayly 1969) and ostracods in rivers in Spain (Mezquita *et al.* 1999*b*). The latter observation was explained by a trade-off between osmoregulation and calcification, whereby ostracods must pump HCO_3^- ions outward to maintain internal Cl$^-$ concentrations, but HCO_3^- is also required for the formation of the ostracod carapace (Mezquita *et al.* 1999*a*).

Acid–base balance and ion-regulation (e.g. Na^+ and Cl$^-$) in aquatic crustaceans are also known to be linked, in this case via transepithelial fluxes of endogeneous HCO_3^- and H^+ (or NH_4^+) ions against external Cl$^-$ and Na^+ respectively (Wheatley and Henrey 1992). When the salinity to which an animal has been acclimated increases, extra-cellular acidosis can develop, when it decreases, alkalosis can occur (Truchot 1987) and even slight changes in cellular pH levels can have profound effects on the stability of proteins and on rates of metabolic processes (Hochachka and Somero 1984). Consequently, a compromise between opposing transports for ion-regulation and acid–base balance may contribute to the split in the ostracod data with respect to the log aAlk/aCl$^-$ ratio and to species replacements throughout the salinity spectrum. Calcium exchange for Na^+ also has a role in Na–Cl (and Ca^{2+}) regulation in crustaceans. As with aAlk/aCl$^-$ ratios, log aNa$^+$/aCa^{2+} ratios start to deviate

Australian lakes (Radke *et al.* 2002) and this causes major inflections in log aNa$^+$/aCa^{2+}, aNa$^+$/aH$^+$ and aAlk/aCl$^-$ ratios (Fig. 4). Furthermore, significant pair formation involving CO_3^{2-} and Na^+ ions occurs at salinity levels of ~1000 and ~3200 mg L^{-1} respectively ($10^{3.0}$ and $10^{3.5}$ on a log scale) (Fig. 2*c,e*). Thus, major changes in the ionic structure of south-eastern Australian lake waters occur in the salinity range from ~1000 to ~3200 mg L^{-1}. This salinity range also
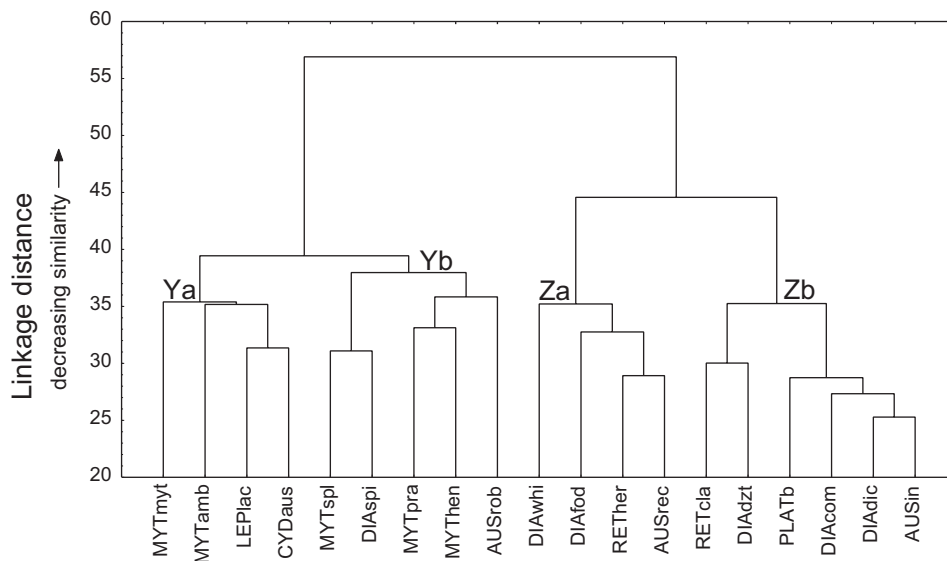
Fig. 7. Cluster analysis dendrogram differentiating the ostracods into four main groups.

markedly from seawater values in mixtures containing less than 5% seawater (Fig. 4*a,c*).

Zb ostracods

The Zb ostracods occur mainly in Path 1 waters with log aAlk/aCl$^-$ ratios < –2.3 and log Na$^+$/aH$^+$ ratios > 7.9 (Figs 8, 9*b*). The medians of the Zb ostracods for salinity, aAlk/aCl$^-$, aNa$^+$/aCa^{2+}, aNa$^+$/aH$^+$ and aNa$^+$/aMg^{2+} ratios also tend to cluster around seawater values (Figs 5, 9*a,b*, 10*a*), suggesting that these species may have origins in marginal marine habitats. Such habitats were extensive in the Murray Basin during the early Miocene (Brown 1989). The Zb ostracods are often found today in coastal settings, in lakes that are intersected by seawater through the groundwater system (e.g. the lakes in the Coorong region of South Australia; De Deckker and Geddes 1980). They can also be found in lakes in inland regions (e.g. the Murray Basin), where groundwater chemical evolution returns infiltrating Path 2 waters to a composition closer to that of seawater (see for example Herczeg *et al*. 2001).

The Zb ostracods can tolerate modest fluctuations of salinity that occur with seasonal wetting and drying cycles. However, extensive dilution of seawater-like chemistries by freshwater seems to present a physiological barrier to Zb ostracods because they are seldom found at log aAlk/aCl$^-$ ratios <–1.8 (Table 3). The medians of Zb ostracods for aNa$^+$/aMg^{2+} ratios are also close to that of seawater and aSO$_4^{2-}$/aCl$^-$ ratios are generally higher than seawater (Fig. 10*a*, Table 4). Correspondingly, the Zb ostracods may not be able to regulate internal Mg^{2+} and SO$_4^{2-}$ concentrations when a seawater-like salt matrix is extensively diluted. However, medians of Zb ostracods for Na$^+$/aH$^+$ ratios are similar to those of most of Yb species (Fig. 9*b*) and this

might account for the occurrence of some Zb species in Path 2 waters (*P. baueri*, *D. compacta* and *D. dietzi*; Fig. 8). Of these species, *P. baueri* and *D. dietzi* are found at higher salinity levels in Path 1 lakes than in Path 2 lakes (Table 3). This may be because aNa$^+$/aH$^+$ ratios are optimal in the lower salinity (and aAlk/aCl) range in Path 2 waters. Anionic proportions have been shown to play a major role in the salinity tolerance of aquatic invertebrates (including ostracods; Forester 1986) in other studies (Bayly 1969), perhaps for similar reasons.

Za ostracods

The Za species dominate the ostracod faunas of the most concentrated Path 1 lakes. The medians of these halobiont ostracods for nNaCl are greater than, or near equal to that of seawater evaporated to the point of halite saturation (Fig. 11). This is despite the fact that halite saturation occurs at a salinity of ~350 000 mg L^{-1} in seawater ($10^{5.5}$ on a log scale), which is well outside the salinity ranges of all the halobiont ostracods (Fig. 5). Even the known occurrences of ostracods living in gypsum-saturated waters (~122 000–345 000 mg L^{-1}, depending on the Ca^{2+}/Alk ratio) are limited to a diminishing population of *R. clava* in a lake on the Riverine Plain and to the single occurrence of *D. whitei* in a lake in Western Australia. These results suggest that the normal pattern of salinity increase with evaporation is not conducive to the occurrence of Za ostracods. We suggest rather, that Za ostracods (and potentially other halobiont organisms) are adapted to salt recycling phenomenon.

Halobiont organisms are mainly found in evaporative groundwater-dominated lakes (playas) in which outflow is restricted. These conditions promote salt accumulation and the development of salt crusts that dissolve and precipitate
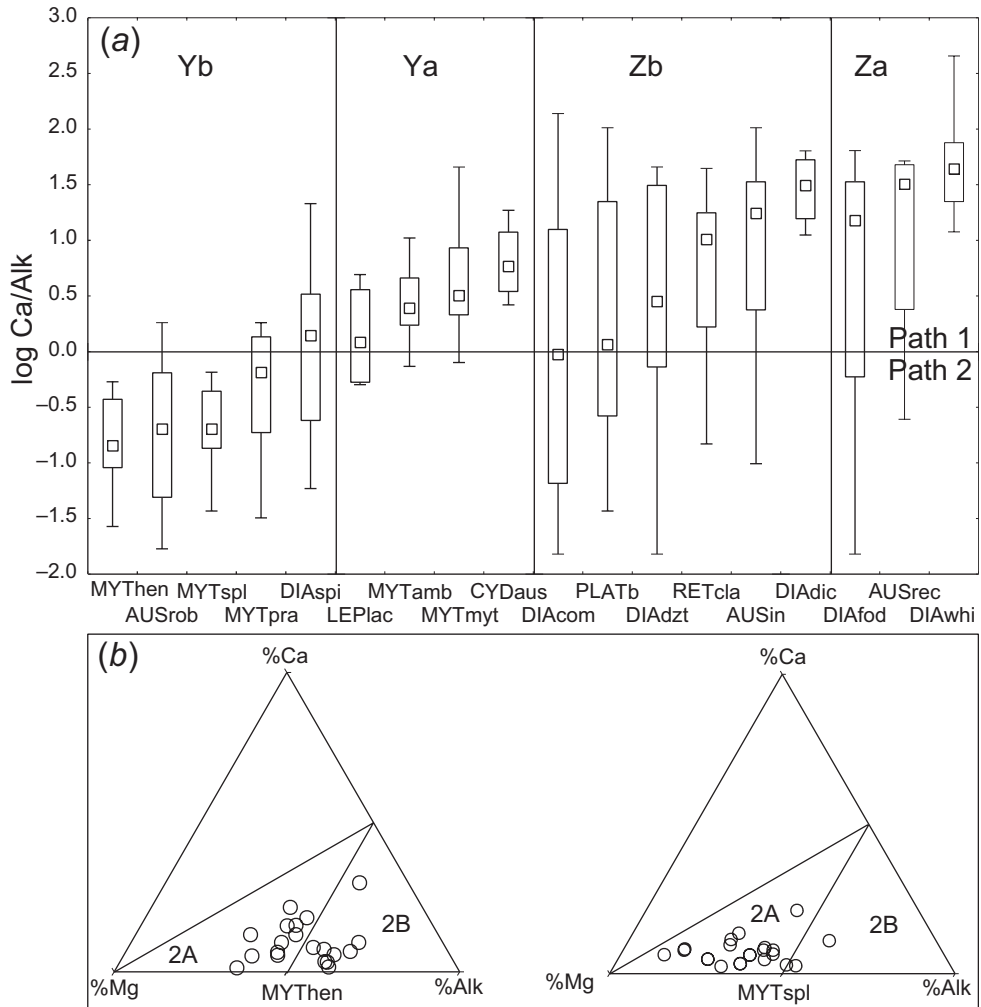
Fig. 8. (*a*) Box-and-whisker diagrams showing the medians, ranges and preferred ranges (i.e. 25th to 75th percentile range) of the four main groups of halophilous and halobiont ostracods for log Ca^{2+}/Alk ratios. The dividing line at zero separates Path 1 water chemistries ($Ca^{2+} >$ Alk) from Path 2 water chemistries ($Ca^{2+} <$ Alk). (*b*) The positions of *Mytilocypris henricae* and *Mytilocypris splendida* in a Ca–Mg–Alk triplot.

Table 3. A comparison of the preferred ranges of ostracods for log salinity in Path 1 and Path 2 waters

Preferred ranges are calculated both on the basis of the range between the 25th and 75th percentiles and the range between the mean plus the standard error (s.e.) and the mean minus the standard error

Species	n	25th–75th percentile Path 1	± s.e. Path 1	n	25th–75th percentile Path 2	± s.e. Path 2
DIAcom	16	4.6–4.9	4.5–4.8	22	4.6–4.9	4.6–4.7
DIAdzt	14	4.6–5.0	4.7–4.9	11	4.5–4.7	4.5–4.7
PLATb	17	4.6–4.9	4.6–4.8	12	4.0–4.8	4.3–4.5
DIAspi	15	4.0–4.4	4.1–4.3	15	3.6–4.2	3.8–4.0

during wetting and drying. The dissolution of crusts composed predominantly of halite (i.e. halite recycling) modifies solute matrices because the most soluble salts come to dominate water chemistries (e.g. NaCl rather than $CaCO_3$). Moreover, the dense fluids that remain post halite

saturation can down-well (reflux) into underlying aquifers, taking with them very soluble ionic constituents such as Mg^{2+} and SO_4^{2-} (Macumber 1991). Consequently, brine reflux and halite recycling cause playa lake waters to become enriched in Na^+ and Cl^- ions and deficient in HCO_3^-, Mg^{2+}

Table 4.   Preferred ranges (i.e. 25th–75th) of halophilous and halobiont ostracods for log aNa⁺/aCa²⁺, aAlk/aCl⁻, aNa⁺/aH⁺, aSO₄²⁻/aCl⁻ and aNa⁺/aMg²⁺ ratios

The overall medians of the same ratios for scoria lake dataset (Western Plains) used by Radke *et al.* (2002), and in seawater, are shown for comparison

Species	n	Group	Log aAlk/aCl	Log aNa/aCa	Log aNa/aH	Log aNa/aMg	Log aSO₄/aCl	Log aNa/aH
MYTspl	20	Yb	−1.3 to −0.8	2.0 to 2.5	7.3 to 8.1	1.2 to 1.5	−2.6 to −2.1	7.3 to 8.1
MYThen	15	Yb	−1.3 to −0.7	1.9 to 2.7	7.7 to 9.0	1.4 to 1.8	−3.9 to −2.1	7.7 to 9.0
DIAspi	25	Yb	−2.2 to −1.4	1.9 to 2.6	7.7 to 8.5	1.2 to 1.5	−2.4 to −1.9	7.7 to 8.5
AUSrob	20	Yb	−2.6 to −1.9	2.7 to 3.9	8.1 to 8.7	1.3 to 1.7	−3.1 to −2.5	8.1 to 8.7
MYTpra	13	Yb	−2.0 to −1.4	2.1 to 3.0	8 to 8.6	1.2 to 1.5	−2.7 to −2.1	8 to 8.6
MYTamb	8	Ya	−2.0 to −1.3	1.5 to 1.8	6.8 to 7.8	1.2 to 1.3	−2.3 to −1.6	6.8 to 7.8
LEPlac	4	Ya	−2.2 to −0.8	1.6 to 2.2	6.8 to 7.8	1.1 to 1.4	−2.1 to −1.7	6.8 to 7.8
MYTmyt	36	Ya	−2.5 to −1.7	1.6 to 2.1	7.1 to 8.3	1.2 to 1.4	−2.3 to −1.7	7.1 to 8.3
CYDaus	4	Ya	−2.6 to −2.0	1.9 to 2.1	7.5 to 7.7	1.3 to 1.3	−2.6 to −2.0	7.5 to 7.7
DIAdzt	22	Zb	−2.7 to −1.8	1.9 to 2.7	8.0 to 8.5	1.2 to 1.6	−2.5 to −2.0	8.0 to 8.5
DIAcom	27	Zb	−2.7 to −2.1	2.1 to 3.8	8.0 to 8.8	1.4 to 1.8	−2.8 to −2.1	8.0 to 8.8
PLATb	30	Zb	−2.8 to −1.9	1.9 to 2.9	7.6 to 8.6	1.3 to 1.7	−2.8 to −2.2	7.6 to 8.6
RETcla	21	Zb	−2.6 to −2.2	1.9 to 2.5	8.0 to 8.5	1.2 to 1.5	−2.5 to 2.2	8.0 to 8.5
AUSin	38	Zb	−3.2 to −2.5	1.9 to 2.3	7.8 to 8.7	1.3 to 1.6	−2.7 to −2.2	7.8 to 8.7
DIAdic	4	Zb	−3.9 to −3.1	1.9 to 2.0	7.2 to 9.7	0.9 to 1.4	−2.7 to −1.8	7.2 to 9.7
DIAfod	13	Za	−3.2 to −2.2	1.9 to 2.5	7.5 to 8.7	1.4 to 1.5	−2.8 to −2.5	7.5 to 8.7
AUSrec	4	Za	−3.3 to −2.6	1.8 to 2.7	8.0 to 8.5	1.3 to 1.6	−2.8 to −2.3	8.0 to 8.5
DIAwhi	29	Za	−3.7 to −3.1	1.9 to 2.1	7.6 to 8.3	1.3 to 1.5	−2.8 to −2.3	7.6 to 8.3
Median scoria			−0.4	4	9	3	−2.8	9
seawater			−2.5	2.2	7.8	1.4	−2.1	7.8

and SO_4^{2-} ions (Dutkiewicz *et al.* 2000; Macumber 1991). Therefore, organisms living in hypersaline waters not only have to offset potential water loss and salt gain, but probably also require adaptations that enable them to excrete Na^+ and Cl^- ions against steep gradients that are directed inwards (see for *Paratemia* example in Geddes 1975). Halobiont ostracods must also regulate pH and construct carbonate shells in waters with very low aAlk/aCl⁻ ratios.

Seawater-normalised Na^+ and Cl^- concentrations in the range of seawater at halite saturation occur quite early on in the chemical evolution of Path 2 lakes because Mg-mineral precipitation and sulfate reduction are more extensive than in Path 1 lakes (see Radke *et al.* 2002). Consequently higher nNaCl values must be used to define halite recycling in Path 2 waters. A nNaCl value of 1150 separates the seasonally halite-saturated playa lakes of the Western Plains, from the high-salinity but halite under-saturated maar lakes, also of the Western Plains and appears to be an appropriate value to define Path 2 lakes affected by halite recycling. *Diacypris compacta*, *A. robusta* and *P. baueri* are tolerant of such Na–Cl enriched conditions (Fig. 11), but are not restricted to them.

Ya Ostracods

The Ya ostracods can be differentiated from the Z-group ostracods on the basis of their higher medians for log aAlk/aCl⁻ and aSO_4^{2-}/aCl^- and their lower medians for aNa^+/aMg^{2+} and aNa^+/aH^+ ratios (Figs 9, 10). They occur mainly in Path 1 lakes, at salinity levels < ~25 100 ($10^{4.4}$) mg

L^{-1}. The chemical conditions where these species are found are indicative of seawater dilution by meteoric water. Note for example, that most Ya ostracods plot close to the seawater dilution line in Figs 9*a*, 10*a*. Correspondingly, Ya ostracods are commonly found in lakes of the Coastal Plain, where intruded seawater is diluted by meteoric waters flowing from coastal dunes (see for example De Deckker and Geddes 1980). While *L. lacustris* and *C. australis* are restricted to coastal lakes because they require permanent water to reproduce (De Deckker 1983), *M. ambiguosa* and *M. mytiloides* are commonly found inland where Path 1 groundwaters mix with typically more dilute Path 2 waters of surface or groundwater origin. Such lakes are common features of the Riverine Plain (e.g. the mixed lakes of Radke *et al.* 2002). They also form the 'Centre Lake Series' (*sensu* Bayly and Williams 1966) and Mount Arapiles Lake Complex of the Wimmera region. Ya ostracods are also found in lakes situated in silicious sandy soils in Western Australia. This may be because the sands have only a limited capacity to impart alkalinity to infiltrating rainwater such that Ca^{2+} equivalents are maintained in excess of Alk equivalents in the groundwaters that feed the lakes.

Although the medians of Ya ostracods for log aAlk/aCl⁻ ratios are similar to some Yb ostracods (Fig. 9), they seldom occur in Path 2 waters (Fig. 8). This may be because the Ya ostracods are intolerant of rising aNa^+/aH^+ and aNa^+/aCa^{2+} ratios that accompany evaporative evolution of Path 2 waters (note rainwater series in Fig. 9*a,b*). Ya ostracods may also have a lower level of fitness in Path 2
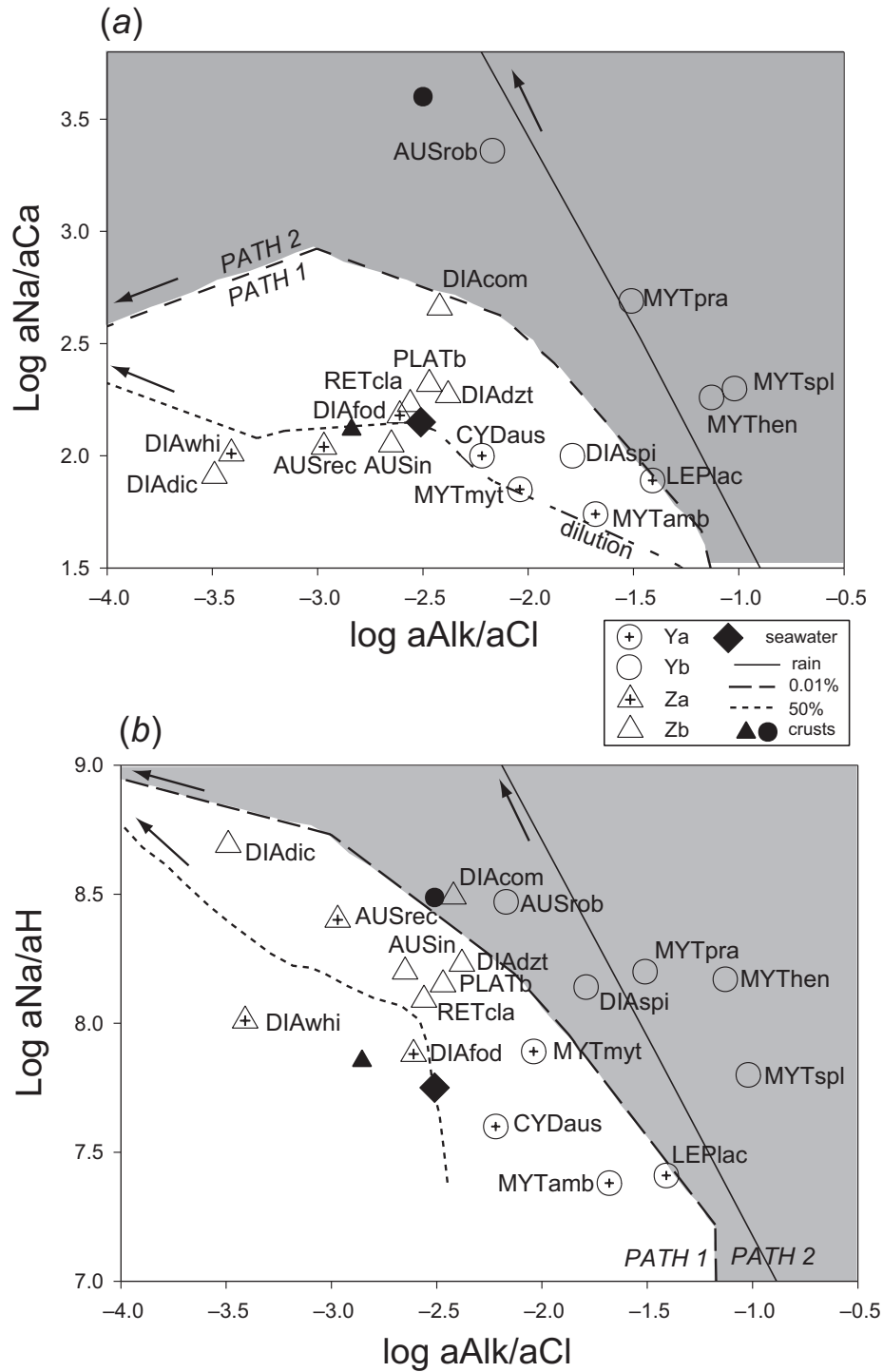
Fig. 9. The medians of halophilous and halobiont ostracods in log aAlk/aCl⁻ v. log aNa⁺/aCa²⁺ space (*a*) and log aNa⁺/aH⁺ space (*b*). The positions of seawater, of dissolved Path 1 and 2 salt crusts, and pathways taken by evaporating coastal rain, and mixtures containing 0.01% and 50% of seawater are also shown. The 0.01% seawater mixture is the approximate dividing line between Path 1 and Path 2 chemistries.

waters because sulfate reduction and Mg-mineral precipitation occur often and tend to lower aSO_4^{2-}/aCl^- ratios and increase aNa^+/aMg^{2+} ratios.

Yb ostracods

The Yb ostracods can be differentiated from Ya ostracods on the basis of their preferences for waters with higher
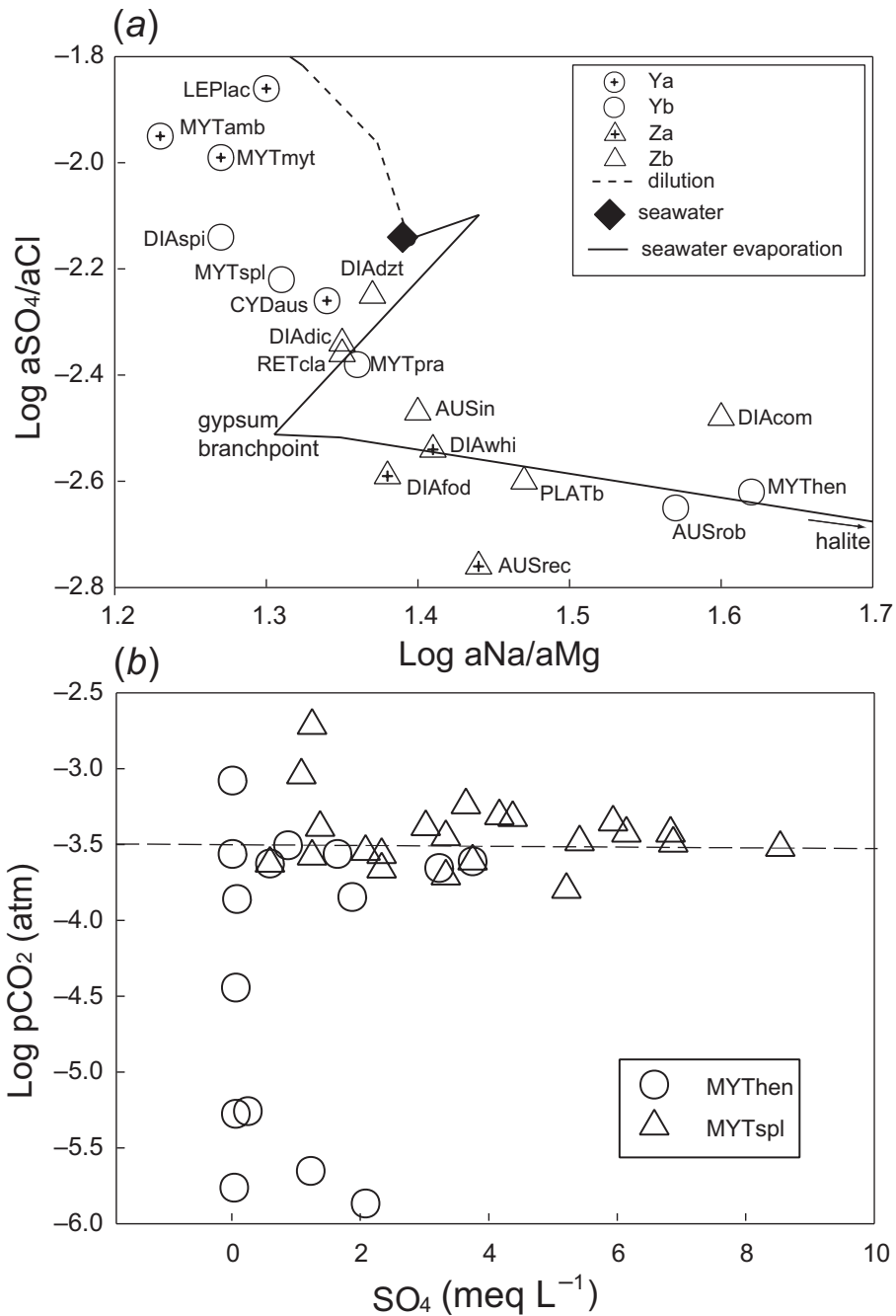
Fig. 10. (*a*) The medians of halophilous and halobiont ostracods for log SO_4^{2-}/Cl^- *v.* log Na^+/Mg^{2+} activity ratios. Seawater, the path taken by evaporating seawater and the seawater dilution line are also shown. The distribution *of M. henricae* and *M. splendida* in log pCO_2 and SO_4^{2-} space are shown in (b).

aNa^+/aCa^{2+} and aNa^+/aH^+ ratios, at a given $aAlk/aCl^-$ ratio (Fig. 9*a,b*). In fact, this is a defining characteristic of Path 2 water chemistries and the effects of these ionic ratios on acid–base balance as well as Na^+ and Ca^{2+} regulation may control EJH path preference by aquatic organisms. With the exception of *D. spinosa*, Yb ostracods are found mainly in Path 2A waters (Fig. 8) and appear to be absent from Western

Australia, where this chemical pathway is uncommon (see for example Geddes *et al.* 1981; Halse *et al.* 2000a; Pinder *et al.* 2002). While *D. spinosa* has been observed mainly in association with Ya species, it is also found frequently in Path 1 waters (Fig. 8). However, *D. spinosa* has a similar preferred range for log aNa^+/aH^+ ratios in waters of both chemical types (e.g. Path 1 = 7.7 to 8.6; Path 2 = 7.6 – 8.5).
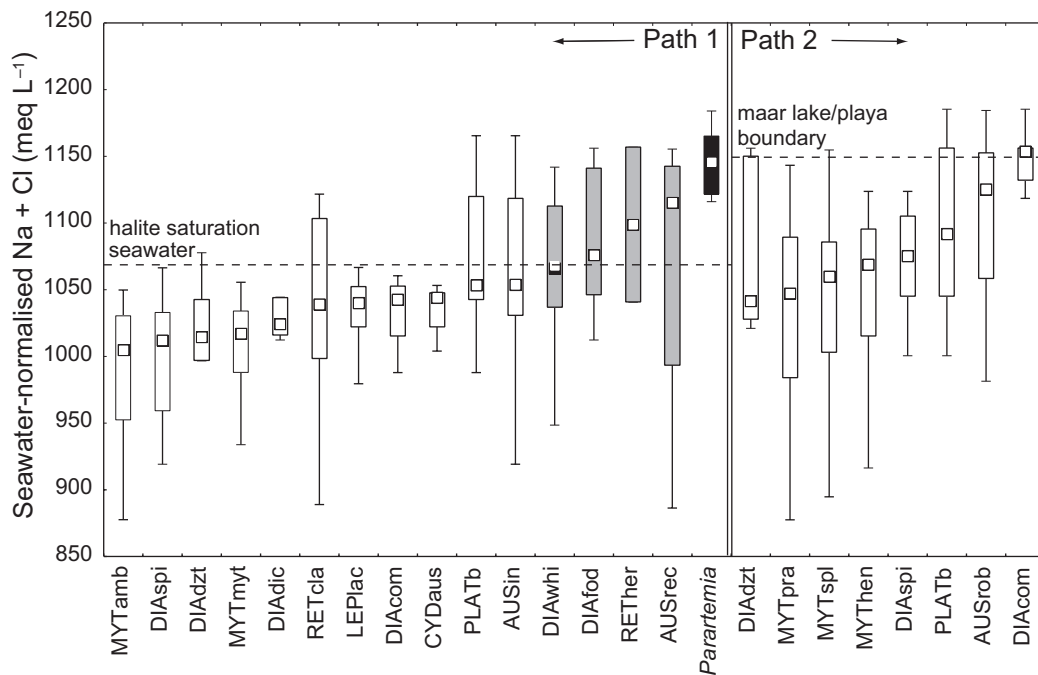
Fig. 11. Medians, ranges and preferred ranges (i.e. 25th and 75th percentiles) of halophilous (no shade) and halobiont (grey shade) ostracods (and *Paratemia*) for seawater-nomalised Na^+ and Cl^- concentrations (nNaCl) in milliequivalents per litre. Species found mainly in Path 1 and Path 2 chemistries are shown in separate windows; species having no apparent path preference are shown twice. Horizontal Lines in the diagram indicate seawater at halite saturation (Path 1) and the approximate nNaCl concentration that separates the halite saturated playa lakes of the Western Plains (Path 2) from the high salinity but halite under-saturated maar lakes (Path 2), also of the Western Plains.

This range of values occurs over a lower salinity range in Path 2 waters (Fig. 4*b*) and may explain why *D. spinosa* is also found over a lower salinity range in Path 2 waters (Table 3).

Mytilocypris henricae and *M. splendida* are found exclusively in Path 2 waters (Fig. 8*a*) and have similar preferred ranges for salinity (Fig. 5) and log aAlk/aCl⁻ ratios (Table 4). Both species were sometimes found in association with Path 2B water chemistries, although only *M. henricae* did so commonly (Fig. 8*b*). Most of the Path 2B lakes from which *M. henricae* was collected were situated in the Wimmera region. Alkalinity was increased over $Ca^{2+}+Mg^{2+}$ in these and other lakes where *M. henricae* is found, through a combination of sulfate reduction and magnesium mineral precipitation. Consequently, *M. henricae* is found at lower SO_4^{2-} and Mg^{2+} concentrations than *M. splendida* (i.e. median of 42.7 *v.* 158 mg L^{-1} for SO_4^{2-} and 120 *v.* 178 mg L^{-1} for Mg^{2+}) and at lower log aSO_4^{2-}/aCl^- ratios and higher log aNa^+/aMg^{2+} ratios (Fig. 10*a*).

Mytilocypris henricae and *M. splendida* can also be differentiated in terms of pCO_2 and aNa^+/aH^+ ratios of the waters in which they occur (Figs 9*b*, 10*b*). *Mytilocypris henricae* was often found in lake waters in which carbon dioxide had been substantially reduced through its photosynthetic consumption by submerged aquatic vege-tation (mainly *Ruppia*) (Figs 6, 10*b*) and this also accounts for its higher median with respect to aNa^+/aH^+ ratios (Fig. 9*b*). In comparison, *M. splendida* was often found in more turbid waters (i.e. median of 29.0 NTU's compared to 7 for *M. henricae*), in which the carbon dioxide content was close to equilibrium with air (Fig. 10*b*). Interestingly, there has only been a single documented occurrence of either of these species (*M. splendida*) in the Path 2B scoria lakes of the Western Plains, when a lake was at low salinity (Timms 1983). Weathering of the scoria elevates the Na^+ and alkalinity contents of groundwater feeding the lakes (Radke *et al.* 2002), causing aAlk/aCl⁻, aNa^+/aCa^{2+} and aNa^+/aH^+ ratios to increase with evaporation to beyond the preferred ranges of these species and all other ostracods in the dataset (Table 4).

Influence of Eugster–Jones–Hardie pathways on other organisms?

There is circumstantial evidence that EJH pathway influences distributions of aquatic organisms other than ostracods. For example, Blinn (1971) reviewed earlier evidence that seasonal shifts in major cations influenced vegetative algal growth in aquatic habitats and suggested that the cation shifts may result from selective salt precipitation. Moreover, in a quick perusal of the literature, we found

several CCA diagrams of salt lake organisms with diagnostic EJH signatures, usually on the second ordination axis (i.e. Ca^{2+} antipathetic to CO_3^{2-}, HCO_3^{-} or pH and/or %Mg and %SO_4 antipathetic to %Na). The taxa included a range of zooplankton collected from lakes in Western Canada (Bos *et al*. 1996), as well as diatoms from lakes in North America (Fritz *et al*. 1993), Africa (Gasse *et al*. 1995) and Australia (Gell 1997). In addition, Gell (1997) showed by way of ordination that the diatom flora of the scoria lakes (Path 2B) was distinctly different than other lakes (mostly Path 2A) in the Western Plains region. Insects are also abundant in the Path 2A lakes of Western Plains and in alkaline lakes in North America and even dominate benthic standing crops in the Path 2B scoria lakes (Timms 1983). However, insects comprised less than 50% of total invertebrate count in a detailed survey of 230 Path 1 lakes in south-western Australia (see Pinder *et al.* 2002). They are also poorly represented in the sea and this has perplexed scientists for years, given their unparalleled success in terrestrial environments.

In conclusion, chemical diversity in Australian lakes is biologically important. Changes in the ionic structure of water caused by $CaCO_3$ precipitation and Na^+ involvement in ion-pairs begin in the salinity range 1000 to 3200 mg L^{-1} and coincide with emergence of a halophilous suite of ostracod genera. Despite the strong dominance of lake waters by Na^+ and Cl^- ions, most of the halophilous ostracods have preferences for either Path 1 or Path 2A of the EJH models of solute evolution. Our preliminary evidence shows that path preference is seldom absolute, but reflects different tolerance ranges of ostracods to a combination of aNa^+/aH^+, aNa^+/aCa^{2+} and $aAlk/aCl^-$ ratios. These ratios may play a role in acid–base balance, Na^+ and Ca^{2+} regulation and salinity tolerance of organisms and are subject to variation in the marine–meteoric system. However, the main division in the halophilous/halobiont ostracod data did not correspond to EJH pathway or to salinity, but occurred at an $aAlk/aCl^-$ ratio of ~–2.3 (see also Radke 2002). This value corresponds to an abrupt change in $aAlk/aCl^-$ ratios that occur when seawater (or a seawater-like solute matrix) is mixed with a sufficient amount of meteoric water (e.g. with more than 95% meteoric water; Fig. 4*c*). Consequently, ostracod faunas are sensitively poised to changes in local hydrology that alter the relative amounts of Path 1 and Path 2 waters intersecting a lake basin (e.g. by seawater intrusion, river regulation and rising water tables). We also present evidence that most halobiont ostracods are adapted to enrichment of waters by Na^+ and Cl^- ions resulting from halite recycling. Of utmost importance is the fact that the chemical and biological principles identified in this study may apply more generally to explain changing patterns of other aquatic biota across the landscape. We hope this study stimulates the re-exploration of ionic influences on other aquatic biota from a more rigorous geochemical perspective than has been attempted previously.

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