

Frigidly Concentrated Seawater and the Evolution of Antarctic Saline Lakes

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Introduction

The frigid concentration or freezing of seawater is an important natural phenomenon in the polar regions and results in the precipitation of a different sequence of salts—and thus produces brines of different composition—to that formed during isothermal evaporation under temperate conditions (ca. 20–25°C).^[1–5] Seawater freezing, however, has been studied less extensively than evaporation and somewhat greater uncertainty exists over the exact nature of the compositional pathway followed. Most investigators have shown that the precipitation of mirabilite (Na₂SO₄·10 H₂O) or gypsum (CaSO₄·2 H₂O), which both occur at the same seawater concentration factor (SWCF), is the critical difference between frigid and evaporative concentration, respectively, a consequence of the very different temperature dependence of the solubilities of these salts, as well as the effect of sodium chloride on these properties.^[5] This difference can be considered to represent a temperature-dependent *chemical divide* in the closed-basin concentration of seawater because it determines significantly the major ion composition of the brine and the salt mineral assemblage precipitated on further evolution of the system.^[6,7] Recently new insights into seawater freezing have been achieved through improvements in existing chemical equilibrium models.^[8,9] Along with the results of some associated experimental work,^[9] this has provided evidence for the formation of gypsum during freezing, contradicting the accepted Ringer–Nelson–Thompson model of frigid concentration firmly established in the 1950s and through subsequent studies,^[1–3,10–12] but validating an alternative model proposed by Gitterman two decades earlier.^[11,13]

Antarctica is mostly a frozen desert but there are a small number of regions on the continent, called oases, where glacial retreat has left behind a largely ice-free landscape and liquid water is present within lakes and ponds. One of the larger Antarctic oases is the Vestfold Hills in Princess Elizabeth Land, East Antarctica. This region consists of three low-lying peninsulas of total area ca. 400 km², separated by fjords, and is the site of Australia's Davis station.^[14] Like the

majority of Antarctic oases, the Vestfold Hills is located on the coast and is of recent geomorphic origin, dating back to only ca. 8000–10 000 years before present to the beginning of the Holocene. This period is characterized by the gradual retreat of the Antarctic ice sheet following the Last Glacial Maximum and subsequent uplift of the coastal margins of the continent. Over time this process, known as isostatic rebound, has isolated shallow marine basins and fjords to form lakes,^[14–16] (Fig. 1). Under the cold, arid climate of Antarctica, the trapped seawater has been frigidly and evaporatively concentrated into hypersaline brines, some with an absolute salinity (total dissolved salt concentration) greater than 200 g kg⁻¹.^[17–20]

The Vestfold Hills currently contains several hundred saline as well as fresh and brackish water bodies, ranging in size from small tarns to large lakes and stratified marine basins.^[15,18,21] These exhibit great variety in their physicochemical properties (e.g. absolute salinity, temperature, dissolved gases, water column stratification),^[18–23] sedimentology^[15] and the characteristics (e.g. productivity, species diversity and distribution) of the mainly microbial ecosystems that flourish within them.^[24,25] Irrespective of their salinity, all of the lakes retain a major ion composition signature similar to that of the seawater from which they originated but with significant and variable differences owing to the precipitation of salts and possibly other solute removal or exchange processes active during their evolution.^[17–20] The presence of salt in the Vestfold Hills is widespread: within lake sediments, in surface deposits around lake shorelines, and as terrestrial salt efflorescence.^[15,17,18,26]

As part of a multidisciplinary research program investigating the lakes of the Vestfold Hills, we examined the major ion chemistry of some of the most saline lakes of the region. The complementary aims of and motivation for this work^[27] were:

- to quantify accurately the concentration of the major ions of the saline lakes (i.e. the solutes that contribute significantly to the absolute salinity)—this knowledge is

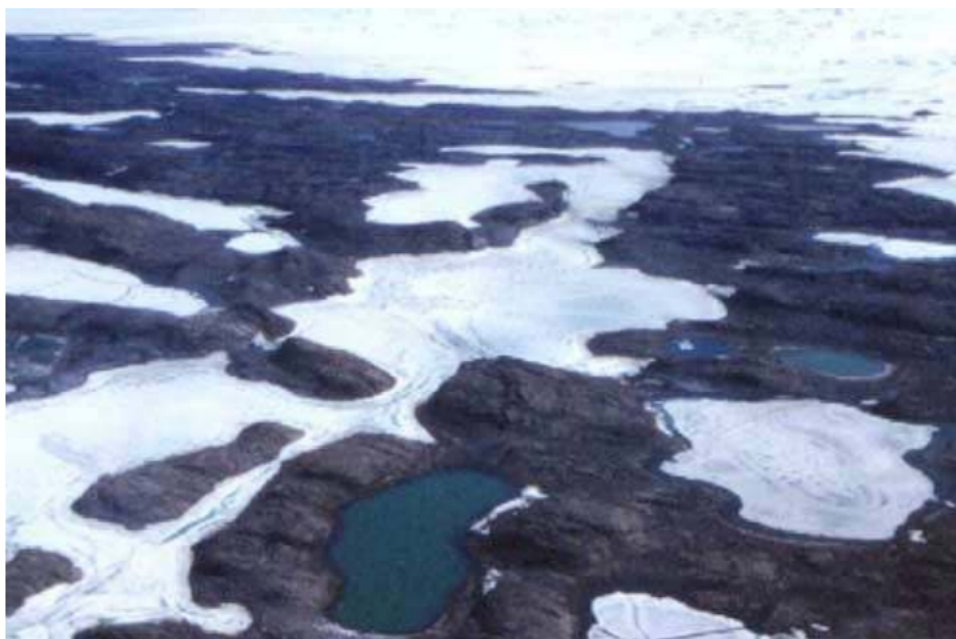


Fig. 1. An aerial view of the northern Vestfold Hills in summer showing several lakes (with or without an ice-cover) and a convoluted marine inlet which contains stratified basins. The distance from the lakes in the foreground to the coast is approximately 4 km.

important when considering the thermodynamics or kinetics of reactions involving major or trace components in solution.^[28–30]

- to determine the current state of salt mineral equilibria in the brines, and the factors that affect this, and clarify the process of geochemical evolution from seawater to saline lake—understanding the closed-basin concentrative evolution of saline lakes provides a basis for the interpretation of lake sediment and water chemistry data in the context of recent and ancient environments.^[7,31,32]

Analysis of Major Ions in Marine-Type Brines

Determining the major ion composition of a natural water usually involves at least six different analyses (e.g. Na, K, Mg, Ca, Cl, SO₄). In the modern, well-equipped environmental chemistry laboratory this task is carried out routinely using two instrumental techniques, atomic optical spectrometry and ion chromatography, which have a precision ca. ± 0.5 –1% under optimum conditions.^[33,34] A measure of the gross or overall accuracy of such an analytical procedure is given by the ion balance error (the ratio of the difference of the equivalents of anions and cations to their sum). For waters with a total ionic concentration of 6–1600 meq L⁻¹ an ion balance error of ± 2 –5% is generally considered acceptable,^[34] and this is readily achievable using these instrumental methods as long as there are no uncorrected interferences in the analyses. For water samples with a high salt matrix, however, physical and chemical interference by the dominant solutes can make a complete analysis of major ions by instrumental methods difficult. Although simple dilution or matrix suppression procedures may be employed to counter these problems, accuracy and precision is often reduced when

analyzing concentrated, multicomponent brines, especially for the less abundant ions.^[33,34] In our investigation we required a very accurate and precise analysis of the major ions—ideally with an ion balance error <1%, and a precision in the range of 0.5–0.1% or better for each ion. To satisfy these criteria it was necessary to employ analytical methods of proven reliability in the analysis of seawater and related brines.

For well over a century, considerable effort has been devoted by analytical chemists to characterizing the chemical composition of seawater, the most abundant and complex natural water on Earth. One of the great achievements of chemical oceanographers is the development of the salinity concept and demonstration of constant major ionic composition for the world's oceans and seas. In general, the relative proportions of all the major ions of seawater are independent of changes in the absolute salinity, S_A . A direct measurement of this parameter can only be made by summing the results of separate determinations of the major ionic species because of the problems caused by volatile salts in a gravimetric determination, but it can be calculated very accurately, via the *practical salinity*, from precise measurement of a single physicochemical property: typically the conductivity, density or chlorinity, Cl (total halide concentration).^[29,30,35] Critical to this work has been the development and use of very accurate and precise analytical methods for the major ions. For practical as well as historical reasons, most of these have involved classical wet-chemistry techniques like gravimetry or titrimetry, because only these relatively simple methods are capable of the high precision ($\leq 0.1\%$) required to verify constant ionic composition.^[36,37]

To analyze major ions in Vestfold Hills saline lake waters, we chose to employ a combination of wet-chemical methods

Table 1. Analytical methodology for the analysis of major ions in Vestfold Hills saline lakes

Determination	Method	Reference	Mean replicates	Mean precision (% rsd)
Total halides	Potentiometric titration (incl. 1st deriv., Gran, titration curve fitting)	[41,42]	6	0.04 (± 0.02) (1st deriv. method)
Br	Kolthoff–Yutzy titration	[37]	4	0.25 (± 0.11)
SO ₄	Gravimetry	[37]	1	0.2 (estimate)
Total alkalinity	Potentiometric titration (1st deriv.)	[43]	2	0.09 (± 0.09)
Na	Flame atomic emission spectrometry (bracket stds)	[34]	3	0.22 (± 0.11)
K	Flame atomic emission spectrometry (bracket stds)	[34]	3	0.37 (± 0.22)
Ca	Photometric titration (Gran-type linearization)	[44,45]	4	0.11 (± 0.06)
Mg (+Sr)	Photometric titration (Gran-type linearization)	[44,45]	4	0.08 (± 0.05)
Total alkaline earths	Photometric titration (by summation)	[44,45]	4	0.07 (± 0.05)
Total alkaline earths	Potentiometric titration (1st deriv.)	[46,47]	3	0.06 (± 0.07)
Mg	Potentiometric titration (by difference)	[46,47]	3	0.07 (± 0.07)
Sr	Flame atomic absorption spectrometry (std addn)	[34]	1	≥ 1 (estimate)

(mainly potentiometric and photometric titrations developed for the analysis of seawater) and instrumental methods (atomic spectrometry). Emphasis was placed on the use of automated titration methods because this increases the versatility of the technique by readily allowing collection of a large number of data to define the titration curve. A variety of simple to complex procedures can then be employed, with the help of a computer if necessary, to provide an accurate and precise calculation of the equivalence point.^[38–40] A summary of these analytical methods, along with the average precision obtained for each of the determinations, is presented in Table 1.

The results obtained in the analysis of representative samples from ten of the most saline lakes of the Vestfold Hills demonstrated that the methods can be used with confidence to obtain a reliable major ion profile for marine-type brines.^[27] The gross accuracy and precision of the set of methods was high with a mean (absolute) ion balance error of ca. 0.1% obtained (0.09 (± 0.07)% for 36 samples). The accuracy of the individual methods was confirmed by the satisfactory analysis of a local seawater sample standardized against International Association for the Physical Sciences of the Ocean (U.K.) Standard Seawater and by analyte recovery tests.

Absolute salinity of the brines was calculated as the sum of the results for the different ionic components and ranged from 35–240 g kg⁻¹ with an average uncertainty of 0.05 (± 0.02)%. Data for S_A , Cl , and the major ions were combined with very precise measurements of brine density at 20°C (d_{20}), made using a vibrating tube densimeter, to derive empirical composition equations (S_A-d_{20} , $Cl-d_{20}$, and $[ion]-Cl$)^[48]. These can be combined with conductivity–temperature–density equations for Vestfold Hills saline lakes^[49] to enable the reliable calculation of S_A and a reasonable estimation of major ion composition from an in situ conductivity or density measurement over a wide range of temperatures.

Salt Equilibria and Brine Evolution in the Vestfold Hills

To examine the major ion geochemistry of Vestfold Hills saline lakes, we compared our major ion data set to

two different models for the closed-basin concentration of seawater: evaporation at ca. 20–25°C^[4,5,50–52] and freezing.^[1–3,11–13] These natural processes can serve as constraining models for the geochemical evolution of marine-derived brines in coastal Antarctica. A comparison was also made with major ion data determined for four of the saline lakes in some earlier studies^[17,18,53,54]—in general, the historical data were consistent with our data set.

Analysis of the various data sets was carried out by considering the nature of correlations between ion concentration ratios for brines (e.g. Na/Cl, SO₄/Cl, Mg/Cl, Mg/Ca, Mg/Br) and theoretical brine compositions calculated from SWCFs based on the presumed conservative concentration of Mg, Br, and K into the latter stages of evaporation and freezing. These methods provide information on the relative behaviour of each major ionic species in the brines: i.e. depletion, conservation, or enrichment.^[27]

The most accurate indicator of brine concentration was found to be Mg—only with SWCFs calculated from the concentration of Mg (range 2.6–9.8) was it possible to account quantitatively, with the same low uncertainty associated with the original analytical data, for solutes depleted from the brines using a simple sequence of salts. This was the salt assemblage predicted to precipitate during the freezing of seawater as defined by the Ringer–Nelson–Thompson pathway but with the inclusion of gypsum, as in the Gitterman model. It was concluded that Mg has been conserved during brine evolution, which is consistent with the absence of Mg salts in lake sediments.

All of the other major ions were either conserved or depleted to some extent relative to Mg. Essentially all of the lake brines were markedly depleted in Na and especially SO₄ owing to the precipitation of mirabilite during the early stages of brine evolution (over the SWCF range 3.5–9.0) and current conditions of saturation with this salt. Mirabilite and thenardite (Na₂SO₄) deposits are common around and within lakes in the Vestfold Hills.^[17,18,26]

All of the brines exhibited at least minor depletion in Cl, but only the two most saline and Cl-depleted lakes were concentrated enough to be saturated with hydrohalite (NaCl·2 H₂O) at the time of sampling; the SWCF values for

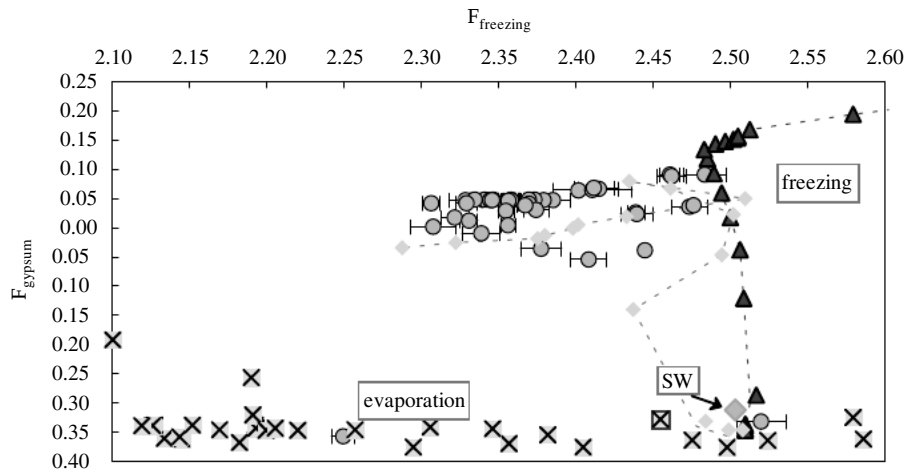


Fig. 2. Correlation between the 'freezing' and 'gypsum' composition functions for Vestfold Hills saline lakes and brines produced by freezing and evaporation of seawater at 25°C. ●: Vestfold Hills brines; ◆: seawater; ▲: freezing-R (from ref. [11]); ✕: evaporation-M (from ref. [4]); ◆: freezing-G (from ref. [13]).

these lakes (9.0–9.8) indicated that with minor dilution, saturation conditions would no longer prevail. However, minor depletion of Cl as well as K and Br in all of the brines suggests that in the past, under more frigid and arid conditions, the lakes were considerably more saline than at present and probably saturated with hydrohalite, sylvite (KCl), and possibly also the very soluble magnesium chloride dodecahydrate ($\text{MgCl}_2 \cdot 12 \text{H}_2\text{O}$)—all of these salts coprecipitate Br. The retention of a compositional signature indicative of saturation with these salts in the past could then be a consequence of the loss of a small proportion of salts from lacustrine systems through diagenetic processes (e.g. simple burial and compaction in the sediment) or erosion (e.g. dispersal from the shoreline and subsequent removal from the catchment by wind). This has prevented a complete dissolution of salt deposits on dilution and warming of the lake waters. Other mechanisms may also have contributed to the removal of K and Br from the brines, including adsorption by solid phases (e.g. ion-exchange of K onto basaltic material) and biological assimilation (e.g. formation of volatile bromocarbons by micro-organisms).^[7,31,32,51]

All of the brines were depleted in calcium, attributed to the precipitation of calcite (accounting for depletion of bicarbonate) and also gypsum (balancing the excess of sulfate depletion not attributable to mirabilite deposition). The precipitation of gypsum is of particular interest and may result from several different mechanisms. In the Ringer–Nelson–Thompson model for seawater freezing, Ca is conserved in solution until the eutectic is reached at -54°C and antarcticite ($\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$) precipitates.^[1–3,9–12] In the alternative Gitterman model for seawater freezing, however, the precipitation of hydrohalite (beginning at -22.9°C) causes a partial dissolution of mirabilite, in turn leading to gypsum precipitation. This gradually removes Ca from the brine as concentration proceeds, with $\text{MgCl}_2 \cdot 12 \text{H}_2\text{O}$ the last salt to precipitate at the eutectic (-36.2°C).^[9,13] Thus evolution along the Gitterman pathway will ultimately produce

brines that are closer in composition to those produced during temperate evaporation in which gypsum is the first salt to precipitate (see Fig. 2, discussed below).

Recently Marion and coworkers successfully simulated the alternative pathway for seawater freezing by improving parameterization of the sulfate equilibria in a thermochemical model for frigid, concentrated brines, and also provided experimental evidence for the precipitation of gypsum during freezing. Arguing that this represents the thermodynamically more stable freezing pathway, the differences in the models were attributed to slow kinetics of gypsum precipitation and fractional crystallization—sufficient mirabilite must be in contact with the brine during hydrohalite precipitation for gypsum to form.^[8,9] These factors have almost certainly influenced the outcomes of past experimental investigations, and in real world systems like saline lakes, they would undoubtedly also play an important role in determining the precise path followed during the frigid concentration of seawater.

Another possible mechanism for the precipitation of gypsum in the saline lakes is associated with dilution and warming of lake waters sometime after the frigid concentration of seawater. At the very bottom of the most saline lake that we examined there is evidence that localized dissolution of mirabilite and hydrohalite deposits is correlated with the removal of Ca from the brine, presumably as gypsum, and possibly also Sr and K. Therefore the primary mechanism for Ca depletion in Vestfold Hills saline lakes might be dependent on changes in lake hydrology (i.e. dilution) and local climate (i.e. warmer temperatures). If this process can be quantified and modelled it may provide another limnological tool for assessing recent environmental change in Antarctica, like the use of fossil diatom assemblages as a proxy for the past salinity of lakes.^[55]

A useful method for comparing different brine evolution pathways is to examine correlations between composition functions that are either dependent or independent of key

salt precipitation/dissolution equilibria and normalized to the concentration of a conservative ion, in this case Mg.^[56,57] A 'freezing function' which is invariant to the precipitation or dissolution of mirabilite and hydrohalite/halite but dependent on gypsum precipitation/dissolution is given by Equation (1).

$$F_{\text{freezing}} = \frac{[\text{Cl}] - [\text{Na}] + 2[\text{SO}_4]}{[\text{Mg}]} \quad (1)$$

A simpler 'gypsum function' which is independent of the precipitation or dissolution of gypsum but not of other sulfate salts is defined by Equation (2).

$$F_{\text{gypsum}} = \frac{[\text{Ca}] - [\text{SO}_4]}{[\text{Mg}]} \quad (2)$$

Figure 2 illustrates the correlation between F_{freezing} and F_{gypsum} for Vestfold Hills saline lakes and brines produced by freezing and evaporation of seawater at 25°C. The pathway followed during temperate evaporation^[4] is directed left from the seawater origin with decreasing and constant F_{freezing} and F_{gypsum} values, respectively. In the case of freezing via the Ringer–Nelson–Thompson pathway, here characterized by the data of Richardson,^[11] F_{freezing} maintains the initial seawater value (the slight decrease apparent in F_{freezing} is due to a small quantity of gypsum included in Richardson's phase calculations) until the precipitation of sylvite and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, but F_{gypsum} increases steadily as the brine is depleted in SO_4 and enriched in Ca. Contrasting this, the Gitterman pathway^[13] is at first identical to the Ringer–Nelson–Thompson pathway (allowing for experimental error), but then diverges with the onset of mirabilite dissolution coupled with gypsum precipitation, which causes both F_{freezing} and F_{gypsum} to decrease. The Vestfold Hills brine data plot to the left of the Ringer–Nelson–Thompson pathway, close to the Gitterman pathway for freezing. Either of the two mechanisms discussed above for the precipitation of gypsum in the brines could produce this correlation pattern. Indeed one shallow and, during the summer months, relatively warm Vestfold Hills lake plots well within the seawater evaporation field, suggesting that the conversion of mirabilite to gypsum has been very significant in this brine.

Conclusion

Our geochemical analysis of Vestfold Hills saline lakes demonstrates that their major ion composition can be modelled accurately using a relatively simple closed-basin brine evolution model based on seawater freezing. The deviations from this model are generally minor and can be reconciled by considering various mechanisms operating during different stages of brine concentration in the past. Depletion of Ca from the brines may be a consequence of evolution along the thermodynamically more stable Gitterman pathway during seawater freezing, but mirabilite and hydrohalite dissolution on dilution and warming could also account for the precipitation of gypsum and possibly other compositional changes occurring in brines where, owing to kinetic limitations, Ca was originally concentrated conservatively according to the

Ringer–Nelson–Thompson model. A comprehensive discussion of this investigation of Vestfold Hills saline lake geochemistry, including the analytical methodology employed, will be presented in forthcoming publications.

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