

Isotopic Evolution of Saline Lakes in the Low-Latitude and Polar Regions

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Abstract Isotopic fractionations associated with two primary processes (evaporation and freezing of water) are discussed, which are responsible for the formation and evolution of saline lakes in deserts from both low-latitude and the Polar regions. In an evaporative system, atmospheric parameters (humidity and isotopic composition of water vapor) have strong influence on the isotopic behavior of saline lakes, and in a freezing system, salinity build-up largely controls the extent of freezing and associated isotope fractionation. In both systems, salinity has a direct impact on the isotopic evolution of saline lakes. It is proposed that a steady-state “terminal lake” model with short-term hydrologic and environmental perturbations can serve as a useful framework for investigating both evaporative and freezing processes of perennial saline lakes. Through re-assessment of own work and literature data for saline lakes, it was demonstrated that effective uses of the isotope activity compositions of brines and salinity-chemistry data could reveal dynamic changes and evolution in the isotopic compositions of saline lakes in response to hydrologic and environmental changes. The residence time of isotopic water molecules in lakes determines the nature of responses in the isotopic compositions following perturbations in the water and isotope balances (e.g., dilution by inflow, water deficit by increased evaporation, and/or reduction in inflow). The isotopic profiles of some saline lakes from the Polar regions show that they switched the two contrasting modes of operation between evaporative and freezing systems, in response to climate and hydrological changes in the past.

Keywords Saline lakes · Isotopic compositions · Evaporation · Freezing · Low-latitude · Arctic · Antarctica · Steady-state · Perturbations

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1 Introduction

Saline lakes occur as coastal lagoons and *sabkhas* in restricted marine basins, and as inland terminal saline lakes (ephemeral shallow playas/salinars and deep perennial lakes) in hydrologically closed basins mainly in the high-pressure belts of both subtropical and Polar regions. Local orographic effects (rain shadow) also can create deserts, independently from latitude. In this article for the isotopic compositions of water, saline lakes are defined as lake waters with salinity greater than that of seawater (36 g/l), while a boundary has often been chosen at 5 g/l, based primarily on biological tolerance. Brackish waters are those with salinities between freshwater (<1 g/l) and seawater. Hypersaline brines have salinities above 100 g/l. The terms saline waters and brines are often used interchangeably.

There are two mechanisms of primary importance for the formation of saline waters in lakes: evaporation of water to the atmosphere and freezing of water to ice: see Fig. 1 and Horita (2005) for other mechanisms. Under subaerial conditions, the evaporation of water into the atmosphere from hydrologically restricted water bodies (lakes, marginal seas, etc.) and soil water/groundwater is the primary process for the build-up of salinity in the arid zone. Water molecules evaporating from a surface water body into the atmosphere are invariably depleted in both heavy isotopes, making the remaining water enriched in heavy isotopes. The magnitude of this enrichment depends on many physical (temperature, relative humidity, salinity, etc.) and hydrologic (inflow, outflow, the fraction of remaining

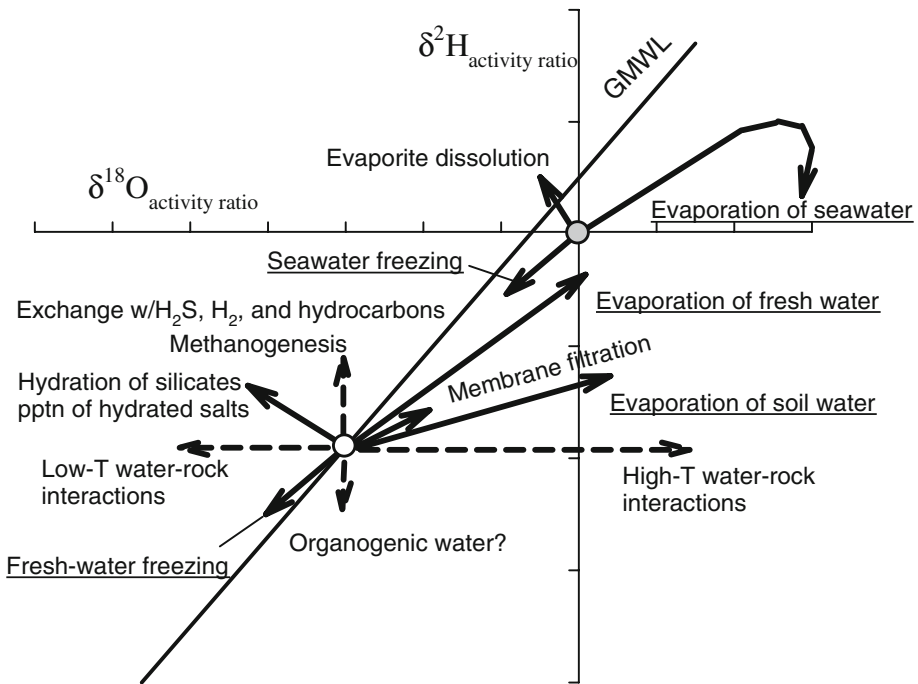


Fig. 1 Schematics for the isotopic evolution of waters in primary, brine-forming processes (solid lines) and secondary, modifying processes (broken lines), after Horita (2005). Evaporation and freezing are the two main processes for the build up of salinity in lakes, which increases and decreases the isotopic compositions of the remaining water, respectively. Note an error in the direction of isotope fractionation by freezing in Horita (2005)

water, etc.) factors. The freezing of water to ice, during which dissolved salts remain largely in the water, is another mechanism for the formation of saline waters. Contrary to the evaporation of water, this process depletes heavy isotopic molecules in the remaining water (Fig. 1). In addition, the magnitude of the isotopic fractionation by freezing is much smaller than those for the liquid–vapour transition of water. The formation of saline waters by freezing in the Polar regions can occur both within ice-covered lakes and fjords, and underground in soils (permafrost).

The sources and behavior of dissolved salts and water in saline lakes often differ significantly. Dissolved salts accumulate within the body of saline lakes over extended periods of time until the water becomes saturated with respect to evaporites and also recycle through dissolution–precipitation within the basins: for evolutionary changes in the chemistry of saline lakes by evaporation, refer to an excellent review (Eugster and Hardie 1978). The residence time of water in saline lakes is, however, usually much shorter than that of dissolved salts, because the water can be readily lost to the atmosphere by evaporation and sublimation of ice. In addition to ephemeral and perennial saline lakes in low-latitude arid zones, the occurrence of both perennially ice-covered and largely ice-free saline lakes in the Arctic and Antarctica have attracted a great interest since their discoveries in the 1940s.

The purpose of this article is threefold: (a) to present principles and models for the isotopic fractionations of water in saline lakes by the two contrasting mechanisms (evaporation and freezing), (b) to discuss the unique characteristics of the isotopic compositions of saline waters (isotope salt effects, namely, the difference between the isotope activity and composition ratios), and (c) to summarize and re-interpret own data and some literature data for the isotopic compositions of saline lakes from subtropical continental and polar deserts within the framework of the steady-state “terminal lake” model and its perturbations. In the end, it is hoped to demonstrate and promote that more rigorous, in-depth modeling and interpretation of high-precision isotopic data can provide much deeper insights into the hydrological and climatic information of saline lakes.

2 Isotope Salt Effects and Analytical Methods for Saline Waters

A fundamental feature of stable oxygen and hydrogen isotopes ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) in saline waters is that the activity ratios of these isotopes differ from their composition ratios, which is known as the “isotope salt effect”. Strong interactions between dissolved electrolyte ions and water molecules (e.g., hydration of ions) change the activity of isotopic water molecules. The isotope salt effect was first discovered in the early 1950s, but it was not until the 1970s that this effect for geochemically important salts was systematically investigated. The isotope salt effects (I^1) can be defined as (Horita et al. 1993b)

$$\Gamma = \frac{R_{\text{activity}}}{R_{\text{composition}}} = \frac{a(^1\text{H}^2\text{HO})/a(\text{H}_2\text{O})}{X(^1\text{H}^2\text{HO})/X(\text{H}_2\text{O})} \text{ or } \frac{a(\text{H}_2^{18}\text{O})/a(\text{H}_2^{16}\text{O})}{X(\text{H}_2^{18}\text{O})/X(\text{H}_2^{16}\text{O})} = \frac{\gamma(^1\text{H}^2\text{HO})}{\gamma(\text{H}_2\text{O})} \text{ or } \frac{\gamma(\text{H}_2^{18}\text{O})}{\gamma(\text{H}_2^{16}\text{O})} \quad (1)$$

where a , X , and γ denote the activity, mole fraction, and activity coefficient of isotopic water molecules, respectively. The R stands for $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$. Using the δ -notation, we obtain:

$$10^3 \ln \Gamma \cong \delta_{\text{activity ratio}} - \delta_{\text{composition ratio}} \quad (2)$$

The hydrogen and oxygen isotope salt effects of several salts near room temperatures are well defined. At a given temperature, the magnitude of the isotope salt effects is practically linear with the molality (mol/kg H₂O), and the oxygen and hydrogen isotope salt effects in chloride-type brines at 20–25°C can be expressed as a sum of the effects of individual electrolyte components (Horita and Gat 1989; Horita et al. 1993b; Sofer and Gat 1972, 1975),

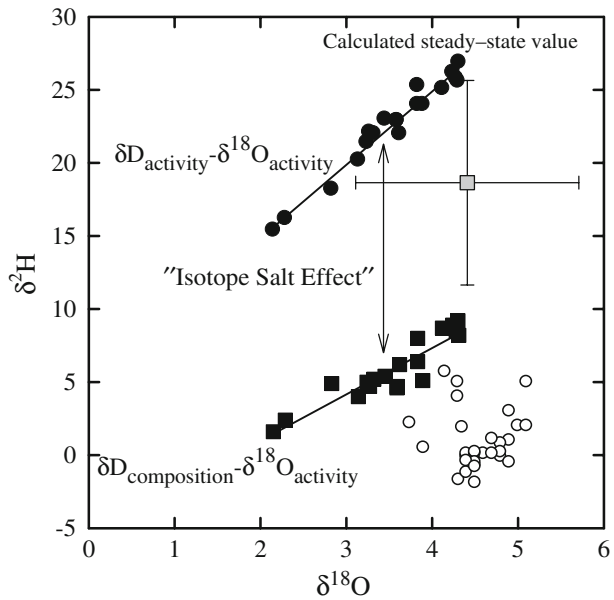
$$\begin{aligned} 10^3 \ln \Gamma(^2\text{H}/^1\text{H}) &= 2.2 \cdot m\text{NaCl} + 2.5 \cdot m\text{KCl} + 5.1 \cdot m\text{MgCl}_2 + 6.1 \cdot m\text{CaCl}_2 \\ 10^3 \ln \Gamma(^{18}\text{O}/^{16}\text{O}) &= 0.16 \cdot m\text{KCl} - 1.11 \cdot m\text{MgCl}_2 - 0.47 \cdot m\text{CaCl}_2 \end{aligned} \quad (3)$$

where m is the molality (mol/kg H₂O). Thus, most salts of geochemical interest increase and decrease the hydrogen and oxygen isotope activities, respectively, compared to their isotope composition ratios (Eq. 3). The linearity with molality and the additive property have been experimentally proven for hypersaline brines with ionic strengths up to nine (Horita et al. 1993a), including natural Dead Sea brines (see below). The magnitude of the isotope salt effects likely increases with decreasing temperature (Horita et al. 1993b, 1995), but the exact values are poorly determined at low temperatures (<10°C) that are usually encountered in the Polar regions.

The two main mechanisms for the formation of saline lakes, evaporation and freezing, involve equilibrium isotope effects at the water–air and water–ice phase transitions. Thus, the isotope activity ratios of water should be used, rather than the isotope composition ratios, by either measuring the isotope activity ratio directly (see below for the analytical methods) or correcting the isotope composition ratios for the isotope salt effects (Eq. 3) (Horita et al. 1993a). In some other geochemical processes, where oxygen and hydrogen isotopes of water behave conservatively such as the mixing of different water bodies, and the dissolution and precipitation of evaporates (e.g., NaCl), the isotope composition ratios of brines are a conservative property. However, because the isotope salt effects are linear with molality (Eq. 3), the isotope activity ratios can also be used. Thus, overall the isotope activity ratios of brines can better serve for modeling and interpreting the isotopic compositions of saline lakes.

In terms of isotopic analysis, high contents of various dissolved salts in saline waters pose serious problems. The isotopic compositions of saline waters have traditionally been determined by the same methods as for fresh waters: metal-(Zn, U, Cr, etc.) reduction and CO₂–water equilibration methods for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, respectively. It should be noted that the former method (metal-reduction) yields the $\delta^2\text{H}$ composition values, but that a gas–liquid reaction in the latter method (CO₂–water equilibration) provides the $\delta^{18}\text{O}$ activity ratio. The measured isotopic ratios should be converted to a consistent isotopic scale, the activity or composition scale, using Eqs. 2 and 3. In addition to this discrepancy in the isotope scales between the two analytical methods, several problems are encountered in the isotopic analysis of brines because of dissolved salts: incomplete reduction of water in brines to H₂ and sluggish isotope equilibration between CO₂ and brines (Horita 1989). The former problem, particularly, resulted in poor $\delta^2\text{H}$ values of hypersaline brines from the Dead Sea (Fig. 2). Using newly developed analytical methods, the H₂–water equilibration method for the $\delta^2\text{H}$ activity ratio (Horita 1988) and the azeotropic distillation method after the removal of alkaline-metal cations for the $\delta^2\text{H}$ composition ratio (Horita and Gat 1988), both the $\delta^2\text{H}$ composition and activity values were determined directly for a suite of Dead Sea brines (Horita and Gat 1989) (Fig. 2). These results show that $\delta^2\text{H}$ composition values of Dead Sea brines from the literature are systematically (up to ca. 10%) lower than the new

Fig. 2 $\delta^2\text{H}-\delta^{18}\text{O}$ relationship for a suite of Dead Sea brines on the different isotope scales. $\delta^2\text{H}$ composition values from the literature (*open circles*, compiled in Gat (1984)) have large systematic errors, after Horita and Gat (1989). A calculated steady-state value for the “terminal lake” is shown for comparison



set of data. The directly measured $^2\text{H}/^1\text{H}$ isotope salt effects ($10^3\ln\Gamma$) for the Dead Sea brines (density 1.2322 kg/l at 25°C, $m\text{NaCl} = 1.95$, $m\text{KCl} = 0.15$, $m\text{MgCl}_2 = 2.00$, and $m\text{CaCl}_2 = 0.49$) is +17.8‰, which is in excellent agreement with that (+17.8) calculated from the experimentally determined equation, Eq. 3. It is very likely that isotope data of many other saline lakes reported in the literature suffered the same analytical problems. In fact, it is not unusual that only $\delta^{18}\text{O}$ values of brines are reported in the literature. A similar problem of isotope fractionation is also encountered for $\delta^{18}\text{O}$ measurements, when water was recovered by vacuum distillation from brines prior to the water- CO_2 equilibration method. Because of these analytical problems, many isotopic studies of brines reported in the literature are not of high quality. In the following discussion of the isotopic data of saline lakes from the literature, both from low-latitude and the Polar regions, their isotopic data were converted to the isotope activity ratios, whenever possible, but this conversion may involve large errors.

3 Isotopic Modeling of Saline Lakes

3.1 Evaporative System

The basic relationships which govern the water, isotope, and salt balances in an evaporative saline lake are given as follows (Gat 1995; Gonfiantini 1986; Horita 1990):

$$dV/dt = F - L - E \text{ (water balance)} \tag{4}$$

$$d(V\delta_V)/dt = F\delta_F - L\delta_V - E\delta_E \text{ (isotope balance)} \tag{5}$$

$$d(VS_V)/dt = FS_F - LS_V \pm Q \text{ (salt balance)} \tag{6}$$

where V is the volume of the water body, which is assumed to be homogeneous chemically and isotopically; F , influx such as precipitation, runoff, groundwater inflow, and seawater

intrusion; L , out flux including leakage; and E , the evaporation flux. The terms δ_V , δ_F , and δ_E are the isotopic compositions of the water body, the inflow, and of the evaporation flux, respectively, all expressed on the isotope activity ratio (see Sect. 2). The terms S_V , S_F , and Q are the salinity of the water body, the inflow, and the sink or source of salinity, respectively. Substituting Eq. 4 into Eq. 5, we obtain:

$$d\delta_V/dt = \frac{F}{V}(\delta_F - \delta_V) - \frac{E}{V}(\delta_E - \delta_V). \quad (7)$$

The isotopic composition of evaporative flux (δ_E) can be described in terms of readily measurable ambient parameters (Craig and Gordon 1965):

$$\delta_E = \frac{\alpha_{V/L} \cdot \delta_V - \bar{h} \cdot \delta_A - (\varepsilon^* + \varepsilon_K)}{(1 - \bar{h}) + 10^{-3}\varepsilon_K} \quad (8)$$

$$\varepsilon = \varepsilon^* + \varepsilon_K \quad (8a)$$

$$\varepsilon^* = (1 - \alpha_{V/L})10^3 > 0 \quad (8b)$$

$$\varepsilon_K = (1 - \alpha_K)10^3 = (1 - h)C_K \cdot 10^3 > 0 \quad (8c)$$

where \bar{h} is the relative humidity of ambient air normalized not only to the saturation vapor pressure at the temperature of the water surface (h), but also to the activity of water in brines ($\bar{h} = h/a_{\text{H}_2\text{O}} > h$). The δ_A is the isotopic composition of atmospheric water vapor, and $\alpha_{V/L}$ (< 1) and α_K (< 1) are the equilibrium vapor–liquid isotope fractionation factor and additional diffusion-controlled isotope effects in the laminar layer, respectively. The term C_K , 0.0125 and 0.0142 (12.5 and 14.2‰) for $^1\text{H}^2\text{H}\text{O}$ and H_2^{18}O , respectively (Gonfiantini 1986), is a kinetic isotope fractionation associated with a turbulent sub-layer above an evaporative water body: refer to Horita et al. (2008) for an updated account of the Craig–Gordon model. Because of this diffusion-controlled isotope effect at the vapor–liquid interface, an evaporative water body becomes progressively enriched in heavy isotopic molecules ($^1\text{H}^2\text{H}\text{O}$ and H_2^{18}O) with typical slopes of 4–6 in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram, compared to a slope of about eight of the Meteoric Water Line, which is controlled largely by equilibrium condensation of liquid water from vapor (Fig. 1). Substituting Eq. 8 to Eq. 7, we obtain:

$$d\delta_V/dt = \frac{F}{V}(\delta_F - \delta_V) - \frac{E}{V} \frac{\{\alpha_{V/L} - (1 - \bar{h})(1 + C_K)\}\delta_V - (\bar{h}\delta_A + \varepsilon)}{(1 - \bar{h})(1 + C_K)}. \quad (9)$$

Thus, if we know or can estimate values of all hydrological and environmental parameters in the above equation, temporal changes in the isotopic composition of an evaporating brine body can be calculated.

In the “evaporation pan” model, which has neither inflow nor outflow, evaporation causes a continuous increase in the normalized relative humidity ($\bar{h} = h/a_{\text{H}_2\text{O}} > h$) due to a salinity buildup. This increasing value of the normalized relative humidity suppresses and eventually reverses the buildup of heavy isotopes, causing a well-documented “loop” or “hook” pattern in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram for experimental salt pans and natural ephemeral saline lakes (Gonfiantini 1965; Lloyd 1966). Sofer and Gat (1975) computed these complex patterns of isotopic evolution in desiccating bodies of 0.5 molal NaCl and MgCl_2 solutions, which depend on several hydrological and environmental parameters (Eq. 9 with $F = 0$). The computed trajectories of the isotopic evolution of the desiccating solutions of NaCl and MgCl_2 differ significantly at late stages of evaporation even under the same

environmental conditions (h and δ_A) (Fig. 3a). However, this is an artifact due to the isotope salt effects in hypersaline brines discussed above, because the data are expressed on the isotope composition ratio for $\delta^2\text{H}$, but on the isotope activity ratio for $\delta^{18}\text{O}$. When these data are expressed on the isotope activity ratios for both isotopes, the trajectories of isotopic evolution of the two solutions under the same environmental conditions start to converge to each other (Fig. 3b). The remaining differences in the trajectories of the NaCl and MgCl_2 solutions are due solely to the differences in the initial isotopic activity compositions (same on the isotope composition scale) and the activity of water between the NaCl and MgCl_2 solutions. Only when an evaporating brine body becomes saturated with respect to evaporite minerals, the activity of water becomes nearly constant, and a steady-state isotopic composition (δ_{SS}) can be reached:

$$\delta_{\text{SS}} = (\bar{h}'\delta_A + \varepsilon)/(\bar{h}' - \varepsilon). \tag{10}$$

A large majority of perennial saline lakes are the “terminal lake,” which has continuous inflow, but no surface and/or subsurface outflow. Then, the general equation for temporal changes in the isotopic compositions of water (Eq. 9) can be reduced under the assumption of water steady state ($dV/dt = F - E = 0$) to:

$$d\delta_V/dt = \frac{F(1 - \bar{h})(1 + C_K)\delta_F - \alpha_{V/L}\delta_V + \bar{h}\delta_A + \varepsilon}{V(1 - \bar{h})(1 + C_K)}. \tag{11}$$

Then, the steady-state composition of δ_V (δ_{SS}) can be obtained as:

$$\delta_{\text{SS}} \cong \alpha_{V/L}^{-1}[(\delta_A - \delta_F - C_k)\bar{h} + \delta_F + \varepsilon^* + C_k]. \tag{12}$$

The steady-state isotopic composition of the “terminal lake” model varies strongly as a function of the normalized relative humidity (Gat 1995; Gonfiantini 1986; Horita 1990). The residence time of isotopic water molecules in a water body, $\tau_{\text{isotope}} \cong (1 - \bar{h})V/F$, is shorter than the residence time of water itself ($\tau_{\text{water}} = V/F$), because both fluxes of evaporation and condensation are taken into account for the isotope budget, while only the net evaporation flux, the difference between evaporation and condensation fluxes, is considered for the water budget. The residence time of salt ($\tau_{\text{salt}} = VS_V/FS_F$) is usually longer by orders of magnitude:

$$\tau_{\text{isotope}} \cong (1 - \bar{h})\frac{V}{F} < \tau_{\text{water}} = \frac{V}{F} \ll \tau_{\text{salt}} = VS_V/FS_F. \tag{13}$$

Surface water bodies that have both inflow and outflow, “flow-trough lake,” or “strait-exchange sea” model, remain largely fresh water. For more details on the isotopic modeling of lakes, refer to several articles (Gat 1995; Gonfiantini 1986; Horita 1990).

It is difficult logistically and analytically to measure or estimate representative values for all hydrological and meteorological parameters in Eq. 9 that are required to accurately calculate temporal changes in the isotopic compositions of saline lakes. Therefore, for the “terminal lake” model the steady–steady approach for the water and isotope balances serves as a useful framework, not only because this assumption reduces the number of necessary parameters, but also the isotopic compositions of terminal lakes in nature could be considered to be perturbations from corresponding steady states. The water steady state, which is a prerequisite for the isotope steady state of a terminal lake, can be attained more easily in saline water bodies than in fresh water bodies due to a feedback mechanism: the evaporation rate increases (decreases) when the inflow increases (decreases), because both surface area and the water activity of brine become greater (smaller). This is particularly

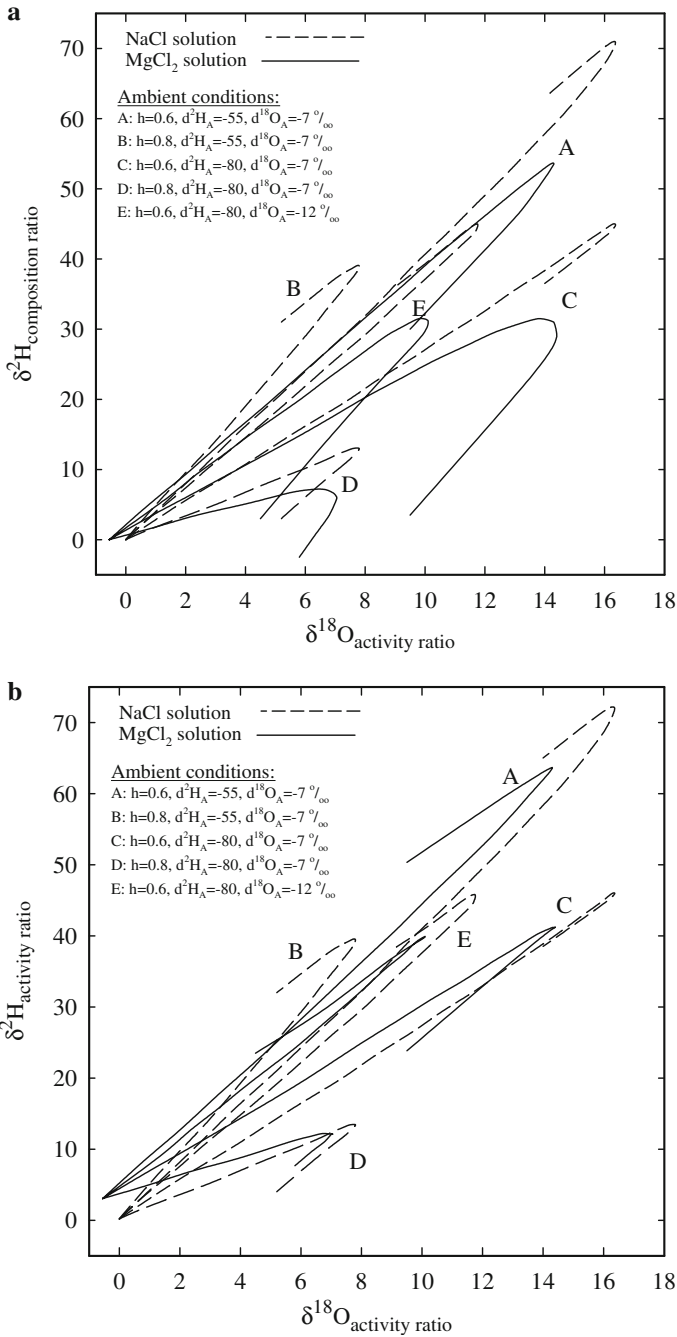


Fig. 3 Computed isotopic evolution during the desiccation of 0.5 molal NaCl and MgCl₂ solutions (“evaporation pan” model) under different atmospheric conditions: **a** original data in the $\delta^2H_{\text{composition ratio}}-\delta^{18}O_{\text{activity ratio}}$ diagram (Sofer and Gat 1975) and **b** after conversion to the $\delta^2H_{\text{activity ratio}}-\delta^{18}O_{\text{activity ratio}}$ diagram. Note that the activity–activity diagrams show similar patterns for NaCl and MgCl₂ solutions under the same conditions and that the differences between the two plots are the isotope salt effects for δ^2H values

true for shallow playa lakes. Several hydrologic events (sudden increases of inflow, water deficits due to reduced inflow or strong evaporation) can perturb the water and isotope balances significantly. The former event is usually characterized by rapid decreases in the salinity and isotopic compositions (Fig. 4), and the latter by gradual increases in the salinity and isotopic compositions. However, once the “terminal lake” returns to a steady-state water balance, the isotopic composition of the lake would also shift to a new steady-state value with a characteristic time of τ_{isotope} , which would vary from months for shallow playa lakes to tens or hundreds of years for deep tectonic lakes. Assuming first-order kinetics for a lake system, the isotopic composition changes from its initial value (δ_{init}) to a steady-state value (δ_{SS}) by the following equation:

$$\delta_t = \delta_{\text{SS}} - (\delta_{\text{SS}} - \delta_{\text{init}})e^{-kt}, \quad k = 1/\tau_{\text{isot}}. \tag{14}$$

Thus, after a period of τ_{isotope} , the isotopic composition shifts more than half way (63%) toward a new steady-state value.

Many variables, especially the atmospheric parameters (temperature, specific humidity, and isotopic composition of water vapor), change significantly over a short time scale, i.e., diurnally, seasonally, and annually. However, it was shown that unless the residence time of isotopes, τ_{isotope} , is much shorter than the cycles of such short-term fluctuations of atmospheric parameters, these short-term periodic variations of the atmospheric parameters are smoothed out and the isotopic composition of a water body would exhibit cyclic changes with much smaller amplitudes and time lags (Fig. 4; Horita 1990).

3.2 Freezing System

Several experimental studies of ice formation show that the isotopic enrichments of ice with respect to water ($\alpha_{\text{ice-water}}$), range from 1.00291 to 1.0048 for $^{18}\text{O}/^{16}\text{O}$ and from

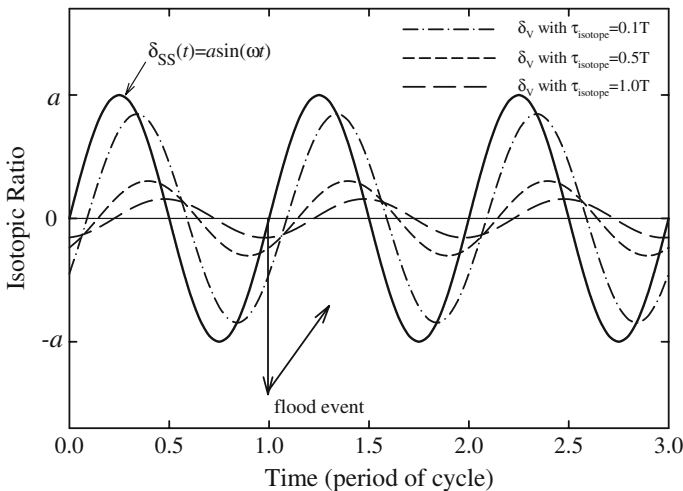


Fig. 4 Diagram showing the effect of the residence time of isotopic water molecules (τ_{isotope} , Eq. 13) on the isotopic variations of lakes. It is assumed that steady-state isotopic compositions of a lake show cyclic variations $\delta_{\text{SS}}(t) = a \cdot \sin(\omega t)$ with amplitude (a), angular frequency (ω), and period ($T = 2\pi/\omega$) due to cyclic variations of the environmental parameters. Unless $\tau_{\text{isotope}} < T$, the isotopic compositions of a lake are not affected by short-term cyclic variations. A typical perturbation by a flood event is also shown (modified after Horita 1990)

1.0171 to 1.0212 for $^2\text{H}/^1\text{H}$ (Horita et al. 2008) with the values of 1.00291 ($^{18}\text{O}/^{16}\text{O}$) and 1.0212 ($^2\text{H}/^1\text{H}$) for the best estimates of the equilibrium fractionation factor (Lehmann and Siegenthaler 1991). Values in the lower end, particularly for $^2\text{H}/^1\text{H}$, have been observed when ice was formed fast, including an apparent fractionation factor of 1.017 that was observed in a freezing experiment of seawater (Wang et al. 2000). Slightly lower values of $\alpha_{\text{ice-water}}(^2\text{H}/^1\text{H})$, 1.013–1.017, have also been observed in ice cover of lakes and rivers (Gibson and Prowse 1999; Michel 1986; Miller and Aiken 1996). Souchez et al. (1987) have measured an apparent fractionation factor for $^1\text{H}^2\text{HO}$ between the ice cover and the lake water, which is roughly half the equilibrium value for water and ice. The transport of water molecules onto the bottom of ice is controlled by a stagnant diffusive layer in the liquid phase, which favors the transport of light water molecules. This partly offsets the equilibrium isotope fractionation occurring at the ice–water interface, which in turn favors heavy water molecules. The degree of this offset is a function of the freezing rate and the degree of mixing of water columns. Ferrick et al. (2002) developed and tested a model to validate that a boundary layer thickness determines an apparent ice–water isotope fractionation factor, where diffusion controls the transport of water molecules.

Figure 5 shows model calculations for the $\delta^{18}\text{O}$ values of seawater during a gradual and fractional freezing to ice with a fractionation factor of 1.003. The data from a deep meromictic basin in Ellis Fjord, Antarctica (Gallagher et al. 1989) follow closely the model trend. Thus, the remaining water would become progressively depleted in heavy isotopic water molecules ($^1\text{H}^2\text{HO}$ and H_2^{18}O) with a slope of about 7 in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram, assuming an equilibrium fractionation factor of 1.021 for $^2\text{H}/^1\text{H}$. As discussed above, the formation of ice in lakes and rivers often accompanies smaller isotope fractionation for $^2\text{H}/^1\text{H}$ (1.013–1.017), resulting in a slope of 5–6 (Gibson and Prowse 1999; Michel 1986; Miller and Aiken 1996) due to a diffusion-controlled kinetic effect at liquid–ice interface. In contrast, a steeper slope of the fractionation (10.8) that was observed during freezing at the stage of mirabilite precipitation at -10°C (Stewart 1974) is due probably to the isotope salt effect on $\delta^2\text{H}$ values in the concentrated (2–2.5 molal) NaCl solutions and seawater: see Sect. 2 for the isotope salt effects. Therefore, natural freezing processes deplete the remaining water in heavy isotopic molecules with typical slopes of 5–6 in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram, which are similar to the slopes by evaporations (4–5), but shallower than that (about 8) of the Meteoric Water Line (Fig. 1). The magnitude of isotopic effects by freezing is, however, much smaller than those by the evaporation of water to vapor, due to the smaller isotope fractionation factors. More importantly, the magnitude of isotopic depletions of seawater by freezing is ultimately determined by the freezing temperature of concentrated seawater. A normal seawater (35 g/kg) has a freezing temperature of about -2°C , and this temperature keeps decreasing with increasing salinity (Fig. 5). Many ice-covered lakes and fjords in the Polar regions, both fresh and saline, are usually stratified because of higher densities of deep waters, and heating by solar radiation through the ice cover and latent heat generated by the freezing of water onto the base of floating ice keep the temperature of lake water much warmer than their surroundings (McKay et al. 1985; Ragotzkie 1978). These relatively warm temperatures of seawater-derived lakes and fjords in the Polar regions would prevent the freezing of seawater much below -15°C , corresponding to the salinity of about less than 200 g/kg (Fig. 5). This salinity and freezing temperature is past the precipitation stage for mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) at -6°C , but is well before the precipitation of hydrohalite ($\text{NaCl}_2 \cdot \text{H}_2\text{O}$) at -23°C (Marion et al. 1999; Thompson and Nelson 1956). Thus, even in the Polar regions, the role of seawater freezing in the formation of hypersaline brines would not be very important. In contrast, soil temperature in the Polar regions can drop below -30°C (Campbell et al. 1998), and the

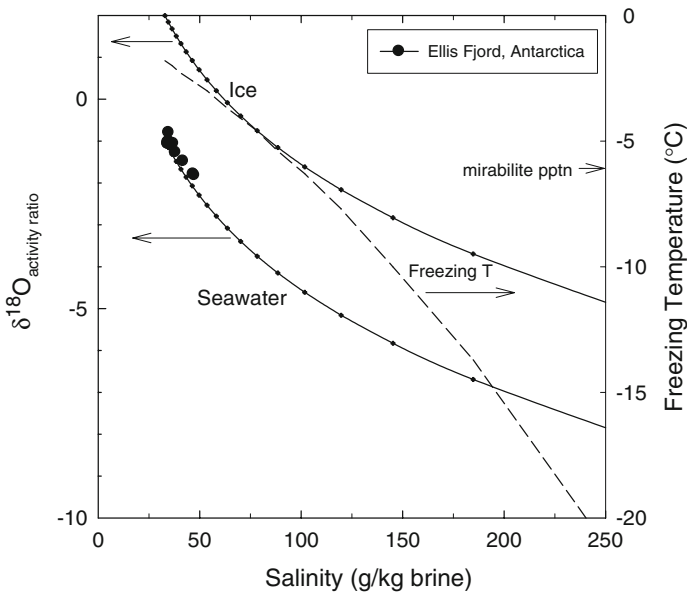


Fig. 5 Oxygen isotopic changes of seawater during Rayleigh-type freezing to ice as a function of salinity and corresponding freezing temperature ($\alpha_{\text{ice-water}} = 1.003$), along with data from the deep meromictic basin in Ellis Fjord, Antarctica (Gallagher et al. 1989)

freezing of soil water can produce hyperhaline brines (>200 g/kg). In terms of the isotopic compositions, the freezing of fresh waters can lower significantly the isotopic ratios of the remaining water, because very large fractions of the water have to be removed before the water becomes hypersaline.

In many ice-covered lakes, the water level and ice thickness appear nearly constant over time, which are controlled by water (inflow vs. surface sublimation) and heat balances. Under the assumption of water steady state ($dV/dt = F - E = 0$), we obtain from Eq. 7:

$$\delta_{SS} = \delta_E (= \delta_F) - \epsilon_{\text{ice-water}} \tag{15}$$

where δ_E is the isotopic composition of the sublimation flux here. This steady-state “terminal lake” model for ice-covered lakes would apply only to the surface waters underneath the ice cover, because their water columns are often stratified and meromictic.

4 Saline Lakes in Low-Latitude Regions

The isotopic compositions of continental saline lakes and marine lagoons in low-latitude (10–30°) regions have been extensively investigated since the mid 1960s. The two most striking features of the isotopic composition of these saline water bodies are: (a) the enrichment of heavy isotopes (^2H and ^{18}O) is greatly suppressed compared to freshwater lakes under similar climate and hydrologic conditions and (b) the behavior of both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of saline waters is complex, first increasing in the early stages, then reaching maxima, and finally decreasing in final desiccation stages (Fontes and Gonfiantini 1967; Gonfiantini 1965; Lloyd 1966). A continuously decreasing activity of water, and thus continuously increasing normalized relative humidity ($\bar{h} = h/a_{\text{H}_2\text{O}} > h$), during the

evaporation of saline lakes is the cause of these phenomena (Fig. 3a, b), because this value strongly affects steady-state values under a given condition (Eq. 10). In the $\delta^2\text{H}-\delta^{18}\text{O}$ diagram, the trajectory of evaporating water bodies has a slope of 4–6, depending on the normalized relative humidity and the isotopic composition of atmospheric water. The commonly accepted notion that the trajectory of evaporative brines in the $\delta^2\text{H}-\delta^{18}\text{O}$ diagram has slopes smaller than those of freshwater bodies is not correct, however. Several investigators (Anati and Gat 1989; Gat 1979, 1995; Gonfiantini 1986; Pierre 1989) provided summaries and reviews on the isotopic composition of continental saline lakes and marine lagoons, mainly of transient and ephemeral nature. Here, our discussion is focused on the Dead Sea, because hydrological and environmental data (Gat 1984), and high-quality isotopic data (Horita and Gat 1989) are available.

4.1 Dead Sea

The Dead Sea is a deep (320 m), hypersaline terminal lake located at 410 m below sea level in the Jordan Rift Valley (31°30'N, 35°30'E). The salinity (Na–Mg–Ca–K–Cl type) steadily keeps increasing from 322 g/l in the 1960s to 340 g/l in the late 1990s with the density of approximately 1.23 g/cm³, due to the diversion of the Jordan River in the 1960s. This chronic water deficit resulted in the complete overturn of the lake in 1978–1979. The isotopic study of the Dead Sea brines have been conducted since the 1950s, and Gat (1984) presented a detailed isotopic study for analysis and modeling of the brines. However, the hydrogen isotope analysis had not been successfully conducted due to the extremely high salinities as discussed above. The new data of $\delta^2\text{H}$ activity and composition ratios (Horita and Gat 1989) vary linearly with $\delta^{18}\text{O}$ activity values, as expected for evaporative water bodies (Fig. 2). It has often been observed that, in the $\delta^2\text{H}-\delta^{18}\text{O}$ diagram, the slope of the trajectory or evaporation line of saline lakes is much smaller (3–4) than that for freshwater lakes (4–6) under similar climatic conditions. This is largely an artefact caused by analytical problems encountered in the $\delta^2\text{H}$ analysis of brines and the isotope salt effects. Horita and Gat (1989) demonstrated that, on the activity scale of both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, the trajectory of the Dead Sea brines has a slope of 5.6, instead of 3.8 as previously reported by Gat (1984). This value is very similar to those observed for fresh-water lakes. In fact, isotopic compositions calculated using the steady-state isotope model for terminal lakes agree reasonably well, within uncertainties of the environmental parameters (Gat 1984), with the measured $\delta^2\text{H}$ and $\delta^{18}\text{O}$ activity values of the Dead Sea (Fig. 2). Several parameters, especially those of the specific humidity and isotopic compositions of the atmospheric water vapor, are often poorly constrained and the causes for large uncertainties in the modeling.

The salinity–isotopic composition relationships (Fig. 6) show that the linear variations of the isotopic compositions of the Dead Sea brine in the $\delta^2\text{H}-\delta^{18}\text{O}$ diagram is largely caused by two major inflow events in the springs of 1980 and 1981, and following evaporative enrichments of heavy isotopes. In a major flooding event of February–March 1980, the isotope–salinity relationships at two sampling stations differ, showing that the surface water was not mixed well. An extrapolation of the isotopic compositions of the two surface waters of March 1980 to zero salinity, using the salinity– σ_{25} [(density at 25°C – 1) × 1000] relationship (Stiller et al. 1984), yielded two distinct isotopic compositions of inflows: $\delta^2\text{H} = -45 \pm 10$ and $\delta^{18}\text{O} = -8.7 \pm 1\text{‰}$ (station 1 at the center of Dead Sea) and $\delta^2\text{H} = -27 \pm 10$ and $\delta^{18}\text{O} = -5.3 \pm 1\text{‰}$ (station 5, unidentified location), respectively. The two inflow waters probably originated from the Jordan River and streams from the Judean Mountains. Flood flows during February–March of 1980 in the western shore of

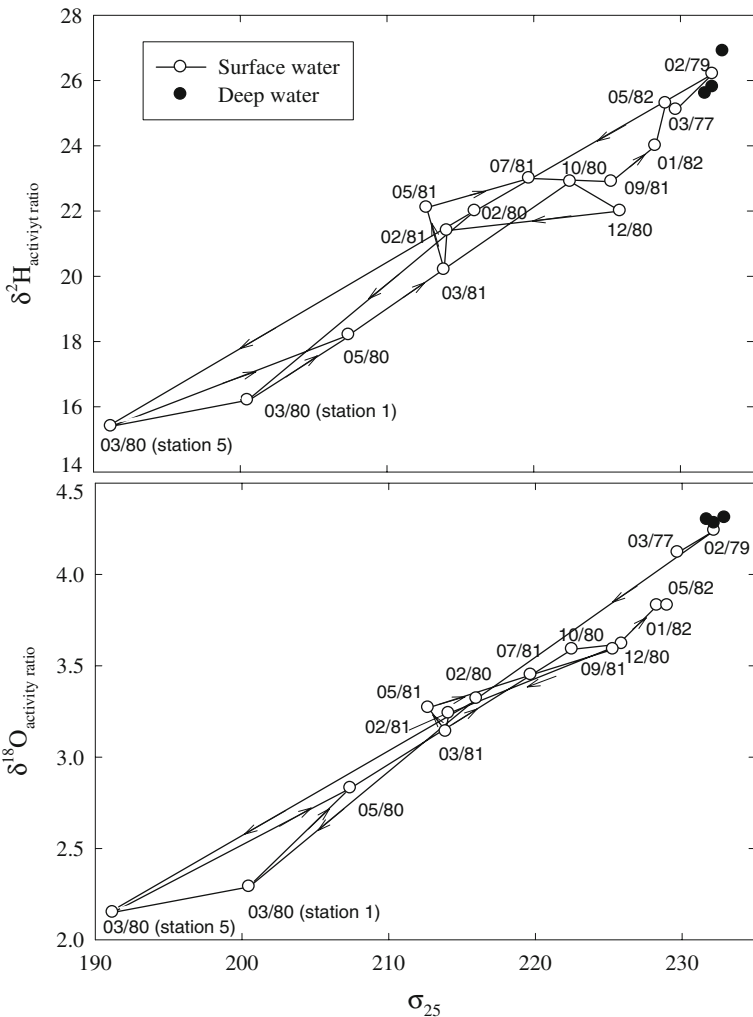


Fig. 6 Isotope–salinity [σ_{25} = (density at 25°C–1) × 1000] relationship for a suite of Dead Sea brines. Two dilution events (February–March 1980 and February–March 1981) and following evaporation events can be seen, along with a possible adjustment to a steady-state from March to May 1981: data from Horita and Gat (1989). Note the σ_{25} unit is not conservative over a wide range

the Dead Sea have $\delta^{18}\text{O}$ values ranging from -4.70 to -7.40‰ (av. -6.1‰) (Gat 1984), which are similar to the estimated values of the two inflow waters above.

During 1979 through 1982, the water balance of the epilimnion of the Dead Sea was clearly out of balance (Anati et al. 1987), and the isotopic compositions were in transient states. However, a short period from March 1981 to May 1981 is characterized by a near-constant water balance (constant value of $\sigma_{25} = 212$) and slight increases in both $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values ($+2$ and $+0.13\text{‰}$, respectively). It is likely that the surface water (ca. 10-m deep) of the Dead Sea during this period was shifting from a transient value to a steady-state composition at this salinity, which should be much greater than the observed transient value. The residence time of isotopic water molecules ($\tau_{\text{isotope}} \cong (1 - \bar{h})V/F$) in the surface

water (10-m deep) could be estimated to be about 2 years. Thus, it is expected from Eq. 14 that the transient isotopic composition of the surface water in March 1981 shifted slightly (ca. 10%), but measurably toward the steady-state value in May 1981.

5 Saline Lakes in the Polar Regions

In several near-coastal regions in the Antarctica and Arctic, where the overall rate of ice sublimation exceeds the annual rate of snowfall, frigid, yet arid and ice-free areas have been discovered. Within these dry regions, which are often referred to as polar deserts or oases, many ice-covered lakes are commonly found. These lakes show unusual physical and chemical properties, including saline and sometimes hypersaline deep waters in the Arctic (Ouellet et al. 1989; Van Hove et al. 2006) and the Antarctica (Burton 1981; Green and Friedmann 1993; Green and Lyons [this issue](#); Lyons et al. 1998b; Torii and Yamagata 1981; Wilson 1979). Ice-covered lakes are also terminal, balanced between the inflows from melt waters of snow and ice, and sublimation flux from the ice-cover.

5.1 Arctic Saline Lakes

Several ice-covered saline lakes have been reported from the Canadian Arctic Archipelago (75°N, 95°W), where the mean annual air-temperature in the region is about -16°C with $+4.3$ and -32°C in summer and winter, respectively. Among those, Lake Garrow and Lake Sophia have been extensively studied, which are stratified meromictic lakes with salinities of deep waters (both about 50-m deep) about 90 and 70 g/kg brine, respectively (Page et al. 1984, 1987). Their major chemistries are very similar to that of seawater and both lakes exhibit a water-column structure that is typical of density-stratified saline meromictic lakes. The $\delta^{18}\text{O}$ values (-20 to -26‰) of their fresh (salinity <5 g/kg) surface waters are similar to that of local precipitations, but the salinity and the isotopic compositions increase rapidly across the chemocline to near constant values of about -10‰ (Fig. 7). The salinity–isotope relationships of the two lakes were interpreted as simple mixing, and the positive deviations in the salinity in the transient zone of Lake Garrow could be due to the diffusional transport of dissolved salts and/or inputs of saline waters at depth. It was interpreted (Ouellet et al. 1989) that the saline waters in the two lakes originated from seawater that were trapped isostatically within the lacustrine basins, including underground, during periods of interglacial high sea-levels. The drops of sea level and post-glacial isostatic rebound isolated the lakes from an open ocean. Seawater trapped in the lakes and underground was concentrated by freezing, and the brines migrated and accumulated in the bottoms of the lakes through taliks of permafrost. In fact, the isotopic composition of the lake waters, both surface and deep waters, are plotted slightly below and nearly parallel to the meteoric water line, showing little sign of evaporative isotope enrichments (Fig. 8).

A close examination of the isotope–salinity relationships of Lake Garrow and Lake Sophia (Fig. 7) suggests that the seawater trapped within the two lacustrine basins were concentrated by freezing to salinities of about 100–120 g/kg brine with $\delta^{18}\text{O}$ values of about -5‰ . The corresponding freezing temperatures are down to about -7°C , near the onset of mirabilite precipitation (Fig. 5). The freezing of seawater could have occurred within either the water columns of the ice-covered lakes or more likely underground permafrost. After the migration of brines to deep waters of the lakes, they are mixed with surface waters from ice-melt waters with very low salinities and isotopic compositions. It

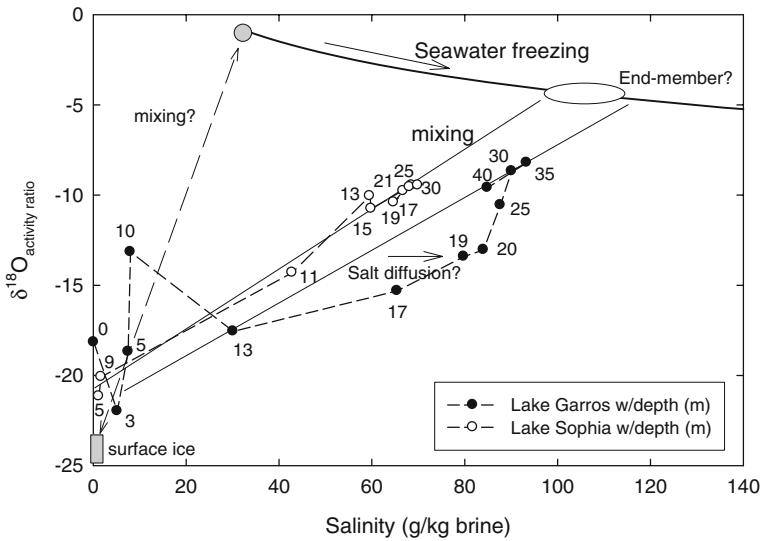


Fig. 7 $\delta^{18}\text{O}_{\text{activity ratio}}$ –salinity relationship of waters from two meromictic, saline lakes (Lake Garros and Lake Sophia) from the Arctic Archipelago (Page et al. 1984). Depth profiles of chemical and isotopic compositions were probably produced by mixing between freeze-concentrated seawater and local precipitation. Note the salinity unit (g/kg brine) is not conservative over a wide range

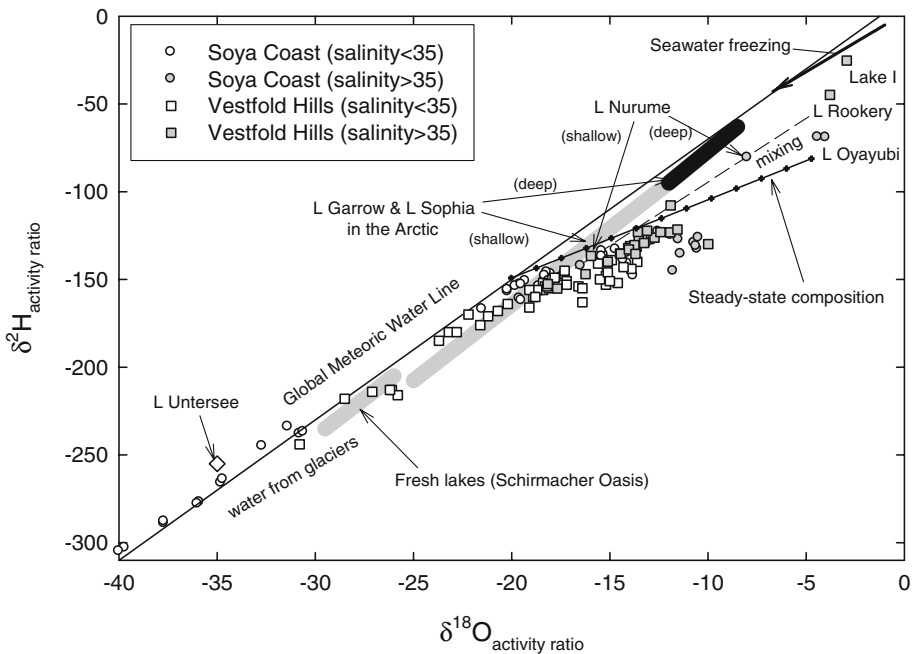


Fig. 8 $\delta^2\text{H}_{\text{activity ratio}}$ – $\delta^{18}\text{O}_{\text{activity ratio}}$ relationship for a suite of fresh and saline lakes on the Eastern Coast of the Antarctica (Bird et al. 1991; Matsubaya et al. 1979; Richter and Strauch 1983), along with the two saline lakes from the Arctic Archipelago (Page et al. 1987). A large ice-covered fresh-water lake (L. Untersee, 71°20'S, 13°30'E) some 150 km inside the Antarctica continent is also shown (Hermichen et al. 1985)

appears that even the most concentrated brines in the lakes have some (20–30%) contributions of surface waters.

5.2 Antarctic Saline Lakes

5.2.1 East Coast

Several ice-free dry areas exist along the east coast of the Antarctica (Gibson 1999; Tominaga and Fukui 1981). Among them, Syowa Oasis in Soya Coast ($69^{\circ}20'S$, $39^{\circ}30'E$) and Vestfold Hills ($68^{\circ}35'S$, $78^{\circ}00'E$) are covered with many lakes (Fig. 9), which receive waters from melt waters of the East Antarctic ice sheet, local snowfall, and possibly seawater. A majority of these lakes are ice-covered fresh lakes, but several saline lakes with the surface below sea level (down to -56 m) are also found with salinity up to above 250 g/kg.

Several investigators (Bird et al. 1991; Hermichen et al. 1985; Matsubaya et al. 1979; Richter and Strauch 1983) have conducted isotopic studies of these fresh and saline lakes from Soya Coast, Vestfold Hills, and other areas (Fig. 8). The isotopic data of saline waters



Fig. 9 Map of the Antarctica, showing three main ice-free regions (McMurdo Dry Valleys, Vestfold Hills, and Syowa Oasis in Soya Coast), where numerous ice-covered lakes and several ice-free lakes, both fresh and saline, are found

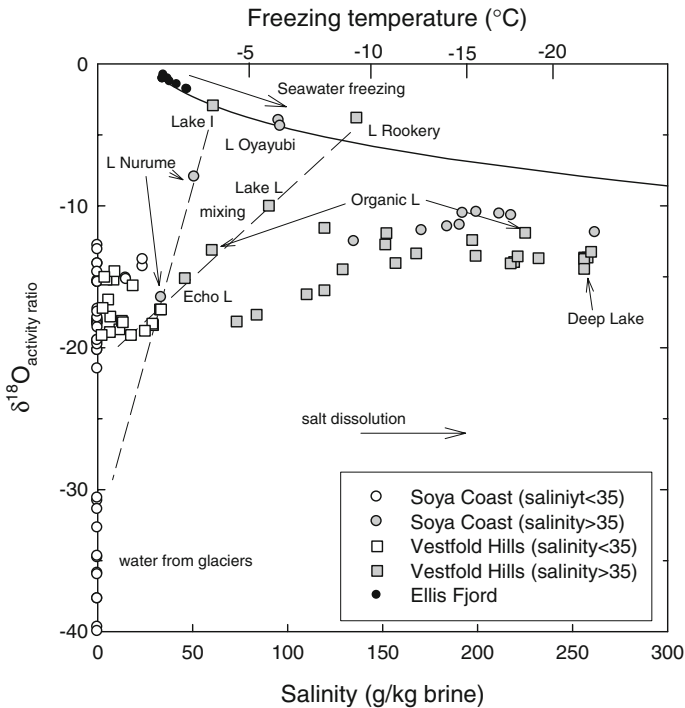


Fig. 10 $\delta^{18}\text{O}_{\text{activity ratio}}$ –salinity relationship of waters from fresh and saline lakes in the Eastern Coast of the Antarctica (Bird et al. 1991; Matsubaya et al. 1979). Several lakes (Lake I, L Rookery, and L Oyayubi) plot along the trend of the freeze-concentration of seawater. A majority of hypersaline lakes show the sign of evaporation (also see Fig. 8). $\delta^2\text{H}_{\text{activity ratio}}$ –salinity diagram of the data show a very similar pattern. Note the salinity unit (g/kg brine) is not conservative over a wide range

in the isotope–salinity diagrams (Fig. 10) show several lakes (Lake I and Lake Rookery in Vestfold Hills, and possibly Lake Oyayubi in Soya Coast) were formed by the freezing of trapped seawater following a gradual drop of sea level (9–10 m) during the past 6,000 years due to an isostatic rebound of the Antarctica (Zwartz et al. 1998), as is the case for Lakes Garrow and Sophia in the Canadian Arctic. Linear trends in the isotope–salinity data of several saline lakes (Echo Lake, Lake L, and upper water of Organic Lake) (dashed lines in Fig. 10) suggest that they could have been formed by the mixing of freeze-concentrated seawater and waters from local precipitation with the isotopic composition of approximately $\delta^2\text{H} = -150$ and $\delta^{18}\text{O} = -20\text{‰}$. The apparent mixing line of the mixolimnion (1.5 m) and monimolimnion (16 m) of Lake Nurume suggest that its surface water was derived from glaciers with very low isotopic compositions ($\delta^2\text{H} = -250$ to -300 and $\delta^{18}\text{O} = -30$ to -40‰). In fact, several fresh-water lakes receive waters from glaciers with very low isotope ratios, rather than local precipitations (Figs. 8, 10). The isotope–salinity relationships also suggest that a number of brackish-water lakes (salinity between 5 and 35 g/kg) could have small contributions (10–20%) from freeze-concentrated seawater. In the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram (Fig. 8), freeze-concentrated seawater and waters resulting from the mixing of this seawater with local precipitations and glaciers would most likely be located slightly below in parallel to the Global Meteoric Water Line. These fresh-water lakes that were derived from the glaciers and ice sheets are slightly displaced to the left

side of the meteoric water line (Fig. 8), because freezing lowers the isotopic composition of the remaining water with a slope of about 5–6 in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram.

A similarity in the major chemistry between several hypersaline lakes from Soya Coast (e.g., Lake Hunazoko, Lake Suribati) and seawater (Tominaga and Fukui 1981) suggest the salts in the lakes originated from trapped seawater. A detailed study on the major chemistry (Stark et al. 2003) revealed that the solutes of lakes from Vestfold Hills were concentrated mainly because of not only the freezing of seawater, but also occasionally because of evaporation. The isotope–salinity and $\delta^2\text{H}$ – $\delta^{18}\text{O}$ relationships of these saline lakes from Soya Coast and Vestfold Hills suggest that a large majority of saline waters with salinity above 100 g/kg have been receiving significant amounts of local meteoric waters, and that their high salinities are produced by the evaporation, rather than by direct freeze concentration of seawater. In fact, many saline lakes with salinity above 150 g/kg are ice free almost year around in these coastal regions of relatively mild climate (Matsubaya et al. 1979). Although accurate information is lacking on the hydrological and environmental parameters in these coastal regions, a locus line for the steady-state isotopic compositions of the “terminal lake” model (Eq. 12) was calculated, using following tentative values: lake temperature of 5°C, normalized relative humidity (h) of 0.4, $\delta^2\text{H} = -150$, and $\delta^{18}\text{O} = -20\text{‰}$ for inflow water, and $\delta^2\text{H} = -240$ and $\delta^{18}\text{O} = -31\text{‰}$ for the atmospheric water vapor (Fig. 8). The $\delta^2\text{H}$ – $\delta^{18}\text{O}$ relationships of fresh- and brackish-water lakes (salinity <35 g/kg) reveal that even many of these lakes show the sign of isotopic enrichments by evaporation. These somewhat contradicting scenarios from the isotope and solute data could be due to the fact that the trajectories of isotopic data between the evaporation and freezing of seawater differ from the beginning (Fig. 1), while the trajectories of solute concentrations between the two processes start to diverge only after the onset of the precipitation of evaporate minerals (gypsum by evaporation and mirabilite by freezing) at about 4–5 times concentrations.

5.2.2 McMurdo Dry Valleys

The McMurdo Dry Valleys, which are located west of the McMurdo Sound of the Ross Sea (77°30'S, 162°00'E), are the largest ice-free region on the Antarctica (Fig. 9). These valleys contain numerous closed-basin, perennially ice-covered lakes and a few ice-free hypersaline lakes (Chinn 1993; Spigel and Priscu 1998). In the last decade, lakes in the Taylor Valley have been extensively studied as part of the U.S. long-term ecological studies (Gooseff et al. 2006; Lyons et al. 1998a). Ice-covered Lake Hoare and Lake Fryxell in the Taylor Valley show vertical salinity profiles that increase with depth to max ca. 0.4 g at 26 m and 7.5 g/kg at 18 m, respectively. Although the vertical profiles of their isotopic compositions that decrease with depth (about 7–13‰ decrease in $\delta^2\text{H}$ and 1–2‰ decrease in $\delta^{18}\text{O}$) are consistent with the freeze-concentration of lake waters, the magnitudes of the observed isotopic profiles are too small to account for the observed salinity gradients. Lyons et al. (1998c) suggested that the lake was a playa with NaCl-saturated brine about 1,000 years ago, and the temperature–salinity profiles of the water column suggest that vertical transport in Lake Fryxell is dominated by molecular diffusion of dissolved salts from the bottom sediments (Spigel and Priscu 1998). However, based on detectable tritium contents in its deep waters, Miller and Aiken (1996) suggested the input of young saline water near the bottom of Lake Fryxell. The water just underneath the ice cover of Lake Fryxell is depleted in $^1\text{H}^2\text{HO}$ by 18‰ and in H_2^{18}O by 2.7‰ relative to the ice cover (Miller and Aiken 1996), and an average isotopic composition of inflows (glaciers and streams) (Gooseff et al. 2006) is close to that of the ice cover (Fig. 11). Thus, the isotopic

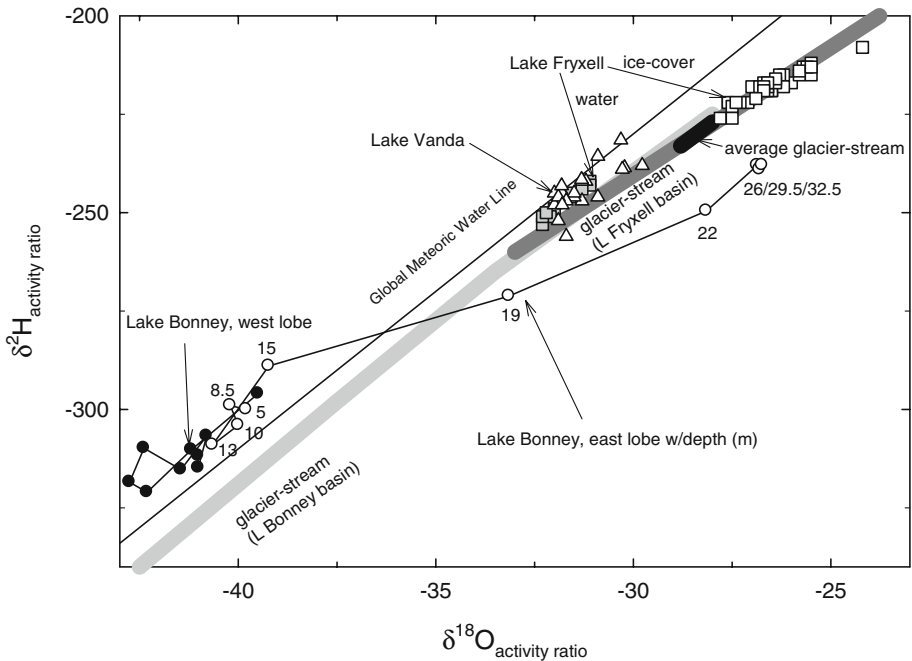


Fig. 11 $\delta^2\text{H}_{\text{activity ratio}}-\delta^{18}\text{O}_{\text{activity ratio}}$ relationship of ice-covered Lake Fryxell and Lake Bonney in Taylor Valley and Lake Vanda in Wright Valley, along with general isotopic composition of glaciers and streams in the Valleys. Only the saline (200 g/kg) deep water of Lake Bonney, east lobe shows the sign of evaporative isotope enrichment. Data sources (Gooseff et al. 2006; Matsubaya et al. 1979; Miller and Aiken 1996)

composition of the upper water in Lake Fryxell appears to be very close to a steady-state value for the ice-covered “terminal Lake” model (Eq. 15) with an annual sublimation flux of about 30 cm.

Lake Bonney in Taylor Valley and Lake Vanda in Wright Valley retain hypersaline deep waters with salinities above 100 g/kg (L Bonney, west lobe and L Vanda) and 200 g/kg (L Bonney, east lobe). Based on the chemical and isotopic profiles of these lakes, several investigators (Hendy et al. 1977; Lyons et al. 1998a; Matsubaya et al. 1979; Nakai et al. 1975; Ragotzkie and Friedman 1965; Torii and Yamagata 1981) interpreted that the saline, deep waters were formed as a result of the evaporation of lakes to small hypersaline ice-free ponds or perhaps to near dryness during a colder and drier climate in the past. Lake Bonney is at least 300-ky old and Lyons et al. (2005) suggested that the hypolimnia of Lake Bonney are remnants of a marine fjord of Miocene time. In fact, the east lobe is underlain by >1-m thick evaporate deposits (Hendy 2000). A recent study on dissolved N_2 and noble gases (Poreda et al. 2004) demonstrated that Lake Bonney east and west lobes have been undergoing contrasting hydrologic history. The east lobe deep brine was formed in an ice-free environment by the evaporation of fresh water. Approximately 1,000–2,000 years ago, it became a stratified lake by the overflow of low salinity water from the west to east lobe in response to a rising water level in the west lobe, and about 200 ± 50 years ago, it became ice covered.

Except for the deep waters of Lake Bonney east lobe, the isotopic data of these saline (Bonney west lobe and Vanda) and other brackish water lakes (Lake Hoare and Lake Fryxell) do not show the sign of the isotopic enrichments by evaporation (Fig. 11). It

should be noted that the original data of Lake Vanda on the isotope composition scale (Matsubaya et al. 1979) indicate that the deep saline waters were concentrated by the evaporation of water, but the same data expressed on the isotope activity scale show no evaporation trend: the calculated isotope salt effects of Lake Vanda brines (Eq. 3) are up to +9 and -1.0‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, respectively. An alternative mechanism for the formation of the deep saline waters of Lake Bonney west lobe and Lake Vanda is the freeze concentration, which deplete the heavy isotopes with a slope of 5–6 in the $\delta^2\text{H}-\delta^{18}\text{O}$ diagram. The displacement of the isotopic data of the saline deep waters from Lake Bonney west lobe and possibly Lake Vanda, relative to those of glaciers and streams in these basins (Fig. 11), is consistent with this scenario. The contribution from saline discharges was also suggested to set the formation of hypersaline deep waters without the isotopic signatures of evaporation (Lyons et al. 1998a). However, stream and moat waters in the frigid environments of the Antarctica show the isotopic enrichments by evaporation in austral summers (Gooseff et al. 2003). Groundwaters also seem enriched in heavy isotopes due to evaporation. For these reasons, the isotopic compositions of inflow waters to lakes are isotopically heavier than those of local snow and near-by glaciers.

5.2.3 Don Juan Pond

Don Juan Pond is a hypersaline brine pond located in a closed basin in the south fork of Wright Valley, Antarctica. The Pond is 300-m long, 100-m wide, and only 10-cm deep with very unique chemistry ($>90\%$ CaCl_2 with salinity ranging from 250 to 400 g/kg brine). Because of this very high salinity, the Pond remains largely unfrozen even in the middle of winter, when air temperatures drop below -40°C . This very shallow, yet perennial pond is sustained in a precarious hydrologic balance between a small influx of water (70% of inflow waters from groundwater and the remaining by intermittent freshwater streams in the austral summer) and year-round evaporation and limited sublimation (Harris and Cartwright 1981). To my knowledge, there exists the only one isotopic study in the literature on this hydrologically and geochemically very unique pond (Matsubaya et al. 1979). Because of the hypersaline nature of CaCl_2 type, they vacuum-distilled water from the brines prior to $\delta^{18}\text{O}$ measurements by means of the CO_2 -water equilibration technique. Their $\delta^2\text{H}$ values were determined following the reduction to H_2 with hot uranium metal. These isotopic data were converted to the isotope activity ratios at 0°C , using the equations for the isotope salt effects (Horita et al. 1995). However, the original isotopic data by Matsubaya et al. (1979) very likely have systematic errors due to the analytical problems discussed above, and the very large isotope salt effects calculated at 0°C (up to +40 and -3.1‰ for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values, respectively) also have large uncertainties.

The hydrological status of Don Juan Pond appears to be in constant change, reflecting in the rapid fluctuations in the lake level and the salinity of pond waters (Harris and Cartwright 1981; Matsubaya et al. 1979). Data on temporal changes of hydrological parameters for the Pond, including those of isotopic compositions, are scarce and poorly constrained. Here, the isotopic data of Don Juan Pond are discussed within the context of the steady-state “terminal lake” model and its perturbations as discussed above. Meteorological data in the Wright and Taylor Valleys show that air temperature varies from about -40°C (winter) to around 0°C (summer) with the average relative humidity of 50–55% year around (Clow et al. 1988; Doran et al. 2002). Evaporation rates of water from Don Juan Pond vary from 0.5 mm/day in winter to 2.0 mm/day in summer (Harris and Cartwright 1981). With a typical water depth of 10 cm, the residence time of water in the Pond ranges from 50 days (summer) to 200 days (winter), and the residence time of isotopic water molecules,

$\tau_{\text{isotope}} \cong (1 - \bar{h})V/F$, is in the range of 20 days (summer) to 70 days (winter). This analysis of residence times suggests that the isotopic composition of the Pond would closely follow that of steady-states nearly in phase in summer, but it would show reduced fluctuations with measurable time lags in winter. The pond appears to be slightly (ca. 5°C) warmer than the ambient air (Matsubaya et al. 1979; Torii and Yamagata 1981), and this effect has to be taken into account for the relative humidity of air. The relative humidity (h) has to be further corrected for the activity of water in brines ($\bar{h} = h/a_{\text{H}_2\text{O}} > h$). The isotopic composition of inflow water to the Pond could be approximated by that of groundwater ($\delta^2\text{H} = -180$ and $\delta^{18}\text{O} = -20\text{‰}$), which are not only saline, but also enriched in heavy isotopes relative to that of fresh snow in the valley, due presumably to the evaporation of water, freeze concentration, and dissolution of salts during groundwater flow and discharge as is the case for Lake Fryxell in Taylor Valley (Gooseff et al. 2003). There are no measurements available on the isotopic composition of atmospheric water vapor, and Matsubaya et al. (1979) assumed the values of $\delta^2\text{H} = -350$ and $\delta^{18}\text{O} = -45\text{‰}$. If they are close to be in isotopic equilibrium with snow, the values would be $\delta^2\text{H} = -325$ and $\delta^{18}\text{O} = -42\text{‰}$.

Using the steady-state “terminal lake” model (Eq. 12), the isotopic compositions of Don Juan Pond are calculated as a function of the normalized relative humidity ($\bar{h} = h/a_{\text{H}_2\text{O}} > h$) at 0°C in summer (January) and at -35°C in winter (July). The steady-state isotopic compositions for winter are much heavier than those in summer, because the assumed temperature of Pond (-35°C). Very large vapor–liquid isotope fractionation factors used at brine temperature of -35°C (1.194 and 1.018 for $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$, respectively) are only estimates based on the ice–vapor fractionation factor. The measured isotopic compositions and the salinity of Don Juan Pond from December 1963 to January 1975 (Figs. 12, 13) show very large variations, compared to those of the Dead Sea (Figs. 2, 6), because of the former’s very shallow nature (10 cm). Several factors (large liquid–vapor isotope fractionation factors at low water temperature and relatively heavy isotopes of the groundwater inflow) increase the isotopic compositions of Don Juan Pond, compared to those of the other ice-covered lakes in the McMurdo Dry valleys (Fig. 11). On the other hand, the extremely low water activities in the brines (down to about 0.42) increase the normalized relative humidity (\bar{h}), which in turn suppresses the enrichment of heavy isotopes. Several other small lakes in the Wright Valley (Torii et al. 1989), which are much less saline, also show isotope enrichments along the locus line of steady-state terminal lakes (Fig. 12). A linear trend of the isotopic compositions of Don Juan Pond in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram suggest relatively simple cycles of surface evaporation and dilutions by surface and subsurface waters. The locus line of the calculated steady-state isotopic compositions for austral summer is also positioned close to the data, suggesting the isotopic compositions of Don Juan Pond may follow steady-state values of the “terminal lake” model (Fig. 12). However, an examination of the isotope–salinity diagram (Fig. 13) reveals more complex and dynamic behaviors of the Pond. If the isotopic compositions of the Pond are largely controlled by evaporation–dilution cycles, a simple linear trend would be observed in the isotope–salinity diagram (see Fig. 6 for the Dead Sea). If the isotopic compositions were always close to steady-state values, then their trends would generally follow the calculated locus lines for the steady-state “terminal lake” model, which predicts decreasing isotopic compositions with increasing salinity (Fig. 13).

The isotopic data reported by Matsubaya et al. (1979), which were collected over a period of 11 years, indicate that both evaporation–dilution process and following shifts to new steady-state conditions control the salinity and the isotopic composition of Don Juan Pond. For example, decreases in the both isotopic compositions and salinity during the period from December 1968 to November 1969 and from December 1973 to July 1974 are

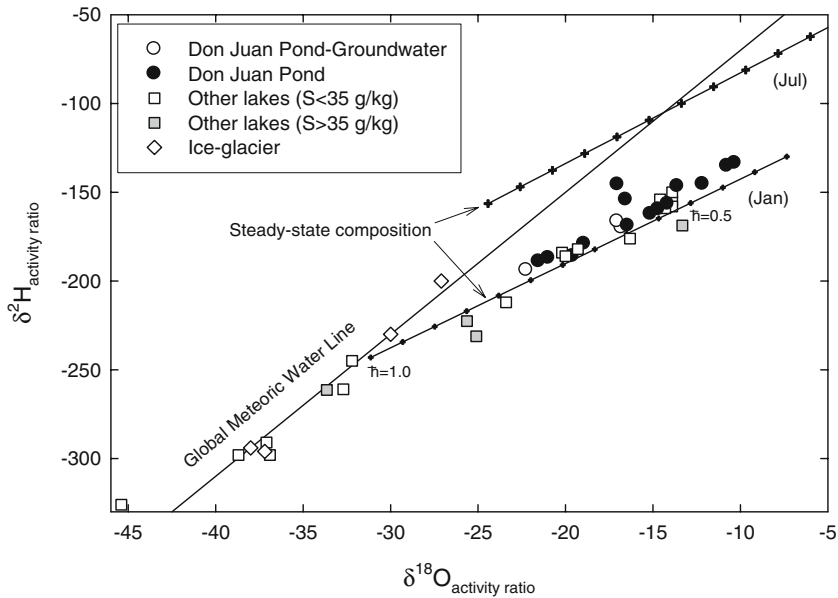


Fig. 12 $\delta^2\text{H}_{\text{activity ratio}}-\delta^{18}\text{O}_{\text{activity ratio}}$ relationship for ice-free, hypersaline Don Juan Pond, along with other fresh and saline lakes in the labyrinth area of the Wright Valley. Two locus lines (summer and winter) for steady-state values of the “terminal lake” model are shown according to Eq. 12. Data modified for the isotope salt effects after (Matsubaya et al. 1979; Torii et al. 1989)

due almost certainly to the inflow of groundwaters and/or surface waters. The former event is characterized by a low isotopic composition ($\delta^2\text{H} = -300$ and $\delta^{18}\text{O} = -40\text{‰}$ from Upper Wright Glacier? (Torii et al. 1989)) and the latter by a heavy isotope (ca. $\delta^2\text{H} = -220$ and $\delta^{18}\text{O} = -27\text{‰}$). Increases in the isotopic compositions and salinity during the period from November 1973 to December 1973 and from July 1974 to January 1975 were likely caused by strong evaporation in austral summers. The period from January 1971 to November 1973 shows an increase in the salinity, but a decrease in both the isotopic compositions. This trend is similar to that predicted by the calculated locus line for the steady-state “terminal lake” model, suggesting that the isotopic compositions of the Pond adjusted to new steady-state isotopic values following the evaporation event from November 1969 to January 1971. A trend from January 1965 to December 1968 could also be explained in a similar fashion. An increase in the isotopic composition, but almost no change in salinity from November 1969 to January 1971 may reflect a large change in the steady-state isotopic composition. Due to the relatively short residence time of isotopic waters in Don Juan Pond ($\tau_{\text{isotope}} = 20$ and 70 days in summer and winter, respectively), the isotopic composition of the Pond can respond to new steady-state isotopic compositions in short periods of time, following changes in their hydrological and environmental parameters, and perturbations in the isotopic compositions.

6 Conclusion

Isotopic studies of saline lakes made significant headway in the early 1960s. By the mid-1970s, the oxygen isotopic evolution of saline lakes in low-latitude zones was very well

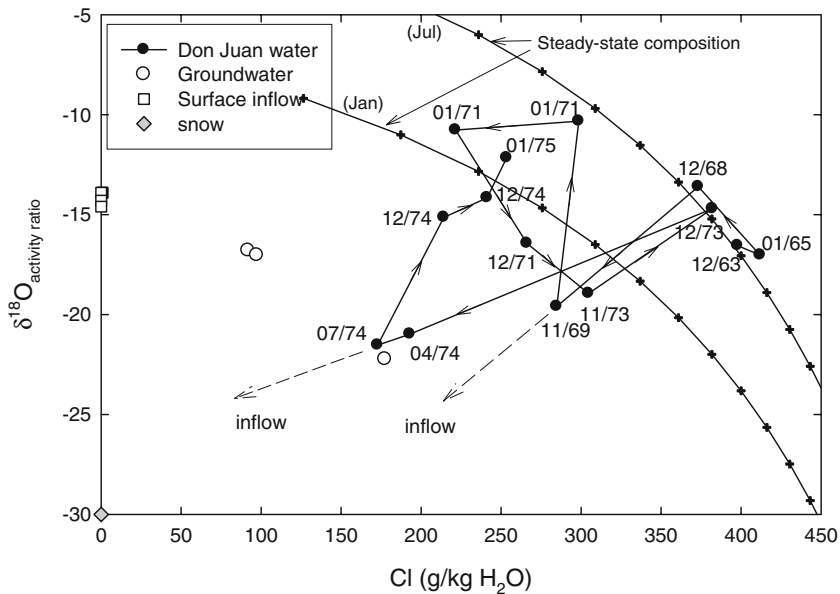


Fig. 13 $\delta^{18}\text{O}_{\text{activity ratio}}$ –salinity relationship of Don Juan Pond waters during the period of over 11 years. Two locus lines (summer and winter) are for steady-state values of the “terminal lake” model (also see Fig. 12). In addition to dilution–evaporation cycles, several adjustments to new steady-state isotopic compositions can be seen, due to short residence times (ca. 20–70 days) of isotopic water molecules in the Ponds. Data modified for the isotope salt effects after Matsubaya et al. (1979). $\delta^2\text{H}_{\text{activity ratio}}$ –salinity diagram of the data show a very similar pattern. The salinity unit (g/kg water) is conservative in mixing

understood and modeled. However, it was not until the late 1980s that the hydrogen isotope behavior of saline lakes came to be properly understood, because of our lack of the understanding of the isotope salt effects and of proper analytical techniques for the hydrogen isotope ratios in brines until then. These two issues (the isotope salt effects and analytical difficulties), which are unique to the isotopic studies of saline waters, have not properly been dealt with in many isotopic studies in the literature. Also, it should be emphasized that the activity–activity diagram of isotopic compositions is of primary utility for many physical and chemical processes that are operative in saline lake systems, including evaporation and freezing.

In addition to the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram, the salinity–isotope diagram serves a very useful purpose—for identifying different physical and chemical processes of lake waters (evaporation–dilution cycles, freezing, mixing, shifts to steady-state isotopic compositions)—because the isotopic trends of these processes tend to overlap with each other in the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram. For perennial, evaporative saline lakes, their isotopic compositions can be modeled and interpreted within the framework of the steady-state “terminal lake” model. Any deviations from the steady-state model can then be treated as perturbations (dilution by inflows and water loss by evaporation) from and following re-adjustments to the steady states of water and isotope balances. The response time to the steady states depends strongly on the residence time of water and isotopic water molecules in lakes. The contrasting behaviors of the Dead Sea and Don Juan Pond in the salinity–isotope diagrams illustrate the role of the residence time on the dynamic nature of their isotopic compositions. In ice-covered lakes, waters underneath the ice covers could also be close to an

isotopic steady state, balanced precariously between the input of melt waters and the sublimation of surface ice.

The occurrence of fresh and saline lakes in the Arctic and Antarctica provide a unique opportunity for investigating their origins and isotopic evolution. The freezing of seawater, along with the dissolution of salt deposits, appears a main physical and chemical process for the formation of several saline lakes in coastal Polar regions. However, the freezing alone may have a rather limited role in producing hypersaline brines, because the freezing temperature of brines keeps decreasing with increasing salinity, and because many ice-covered lakes are much warmer than the surroundings due to solar heating. Freezing in permafrost and subsequent transport to lakes' deep waters would be a more viable process for the formation of hypersaline brines. With increasing salinity of lake water, the lakes becomes ice-free at least in summers, and the evaporation of water starts to play an important role in controlling their isotopic compositions, both at the present and in the past. These chemical and physical processes in lakes from polar deserts proceed at rates much slower than those for their counterparts in low-latitude deserts. It is very interesting to investigate by means of stable isotope techniques when and how saline lakes in the Polar regions switch from evaporative to freezing systems, and vice versa. A synergistic approach, using both high-quality chemical and isotopic data, should prove very powerful to decipher the evolutionary history of saline lakes of different types, including paleoclimate studies of saline lakes and their deposits in the Polar regions.

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