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Stable isotope mass balance of lakes: a contemporary perspective

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ABSTRACT

The theoretical basis for application of stable isotope mass balance of lakes is described for a range of climatic situations including low latitude, high latitude, high altitude, continental and coastal systems, as well as cases where the atmospheric boundary layer is significantly modified by the lake evaporation process. The effects of seasonality on isotopic offset between precipitation and atmospheric vapour and the slope of the local evaporation line are described. Atmospheric feedback and its role in labelling the isotopic composition of the Laurentian Great Lakes and tropical lakes is discussed. Several important considerations are suggested to improve parameterization of quantitative paleoclimatic reconstructions including use of assumptions that are appropriate for the climatic setting, for the atmospheric feedback situation, for salinity, and headwater setting. Potential for use of dual-isotopes to trace past changes in seasonality and input, and a dual-lake index method that can potentially be used to trace connectivity of lakes are presented. In cases where modern or paleo-evaporation systems may be under-defined there are inherent limitations in the degree of quantification that can be attained.

1. Introduction

The investigation of stable water isotopes (mainly $\delta^{18}O$) records from terrestrial material, as an alternative to marine sediments, was propelled to the forefront of paleoclimate studies in the early 1990s (Swart et al., 1993). The development of water isotope records from lake sediments, in substrates such as carbonates, biogenic silica, kerogen, sedimentary cellulose, and lipids, is typically undertaken with the goal of reconstructing the isotopic history of lake water (Edwards et al., 2004). Analogous to marine studies (Emiliani, 1955; Shackleton and Opdyke, 1973) stratigraphic changes in $\delta^{18}O$ in the lacustrine environment were initially attributed largely to changes in lake or air temperature (Eicher and Siegenthaler, 1976) and interpreted based on the understanding of the temperature dependence of isotopic fraction in the formation of carbonate (Epstein et al., 1953; Friedman and O'Neil, 1977). A number of studies have also utilized modern analogues to develop empirical relationships between temperature and various isotopic proxies (von Grafenstein et al., 1996; Schleser et al., 1999; Wooller et al., 2004). However, an increasing number of studies have pointed out the apparent limitations of this simplified transfer function approach, including the inherent control that water balance and climatic conditions play in determining lake water isotopic composition (Edwards et al., 2004; Jones et al., 2005; Henderson and Shuman, 2009; Steinman et al., 2010a).

More recently, as an emerging trend in the paleoclimate community, multi-disciplinary investigations have sought to gain insight from more holistic contemporary monitoring of spatial and temporal isotope systematics to inform the interpretation of isotope records in the lake sediment record (Benson, 1994; Roberts et al., 2008; Shapeley et al., 2008; Wolfe et al., 2012; Steinman et al., 2013; Zolitschka et al., 2013). Several studies have developed coupled hydrology and isotope mass balance (IMB) models for specific lake systems (Hostetler and Benson, 1994; Benson and Paillet, 2002; Shapley et al., 2008; Jones and Imbers, 2010; Steinman et al., 2010a,b), while others have demonstrated the sensitivity of paleo-archives to hydrological setting (Jones et al., 2007; Shapley et al., 2009; Steinman et al., 2010b, 2012, 2013; Steinman and Abbott, 2013). IMB models were found to be informative for these purposes as they provide a theoretical framework to simulate and quantitatively interpret isotopic signals in lakes (e.g. Dincer, 1968; Gonfiantini, 1986; Gat, 1995). Increasingly, it has been realized that utilization of IMB becomes essential for the

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proper interpretation of lacustrine isotope records as paleoclimate and paleoenvironmental proxies (Cross et al., 2001; Leng and Marshall, 2004; Anderson et al., 2007; Wolfe et al., 2007; St. Amour et al., 2010). Other requirements include specific understanding of local isotope–climate relations and substrate-specific fractionations (e.g. Marshall, 1992; Swart et al., 1993; Kim and O'Neil, 1997; Sauer et al., 2001; Huang et al., 2004).

This review is a process-based summary of important controls on $\delta^{18}O$ or $\delta^{2}H$ in the IMB model. Here we describe IMB as applied in many contemporary studies, discuss the assumptions made to characterize atmospheric moisture and fractionation factors, present calibration approaches such as use of an index lake, describe the influence of headwater conditions, seasonality and atmospheric feedbacks, and configurations of the IMB for specific settings including low latitude, high-latitude, continental and coastal systems, and chain of lakes. Appropriate assumptions for application of IMB to paleo-environmental reconstructions are also described.

2. Theory

2.1. Isotope mass balance

The annual water-mass and isotope-mass balance for a well-mixed lake may be written respectively as

$$dV/dt = I - Q - E \quad \left(\mathrm{m}^3\cdot\mathrm{year}\right) \tag{1}$$

$$V\frac{d\delta_L}{dt} + \delta_L\frac{dV}{dt} = I\delta_I - Q\delta_Q - E\delta_E \quad \left(‰\cdot\mathrm{m}^3\cdot\mathrm{year}\right) \tag{2}$$

where V is the volume of the lake, t is time, dV is the change in volume over time interval dt, I is instantaneous inflow where $I = I_U + I_R + I_G + P_L$; I_U is channelized inflow from upstream lakes, I_R is surface inflow from the catchment area, I_G is groundwater inflow, P_L is precipitation on the lake surface; $Q = Q_Y + Q_Z$ is instantaneous outflow where Q_Y is surface outflow, Q_Z is groundwater outflow; E is evaporation; δ_L is the isotopic composition of the lake; δ_I, δ_U, δ_R, δ_G and δ_P are the isotopic compositions of total inflow and its components, i.e. channelized inflow from upstream lakes, surface inflow, groundwater inflow, and precipitation, respectively; and δ_Q, δ_Y and δ_Z are the isotopic compositions of total outflow and its components, i.e. surface outflow and groundwater outflow, respectively. Here, δ values are defined as isotopic ratios reflecting deviation in per mil (‰) from Vienna-SMOW (Standard Mean Ocean Water), where $\delta_{\mathrm{SAMPLE}} = 1000((R_{\mathrm{SAMPLE}}/R_{\mathrm{SMOW}}) - 1)$, and R is $^{18}O/^{16}O$ or $^{2}H/^{1}H$. Values presented here are normalized on the SMOW-SLAP (Standard Light Arctic Precipitation) scale.

Note that $\delta_I = (\delta_U I_U + \delta_R I_R + \delta_G I_G + P_L\delta_P)/I$ and $\delta_Q = (\delta_Y Q_Y + \delta_Z Q_Z)/Q$, the latter of which, δ_Q and its subcomponents, δ_Y and δ_Z will be identical and approximately equal to δ_L in well mixed lakes to maintain the isotope balance. Three main hydrologic settings can be distinguished including (i) desiccating water bodies ($dV/dt < 0$), where inflow occurs once or periodically, and water bodies at hydrologic steady state ($dV/dt = 0$), including (ii) terminal lakes, where inflow is balanced by evaporation ($I = E$), and (iii) throughflow lakes, where inflow is balanced by evaporation and outflow ($I = E + Q$) (Fig. 1; see also Horita, 1990; Gat, 1981).

Based on the linear resistance model of Craig and Gordon (1965) and using the convention of Gonfiantini (1986) for describing the equilibrium fractionation α^+ as a quantity slightly greater than 1, δ_E can be estimated by:

$$\delta_E = \left(\frac{\delta_L - \varepsilon^+}{\alpha^+} - h\delta_A - \varepsilon_K\right) \Big/ \left(1 - h + 10^{-3}\cdot\varepsilon_K\right) \quad (‰) \tag{3}$$

where h is the relative humidity normalized to water surface temperature (decimal fraction), δ_A is the isotopic composition of atmospheric moisture, ε^+ is the equilibrium isotopic separation (see Horita and Wesolowski, 1994) being related to α^+ by $\varepsilon^+ = (\alpha^+ - 1)\bullet 1000$, and $\varepsilon_K = \theta\cdot C_K\bullet(1-h)$ is the kinetic isotopic separation, where θ is a transport resistance parameter, commonly assumed to be unity when δ_A and h are measured or estimated close to the interface (Gat, 1995). $\theta = 1$ indicates that the evaporation rate is controlled by molecular transport of water through the laminar sublayer (see Horita et al., 2008). C_K is a kinetic constant described later on. Note that air–water isotopic exchange will proceed and the lake water will enrich (or deplete) to an isotopic steady-state reflective of the isotopic and hydrologic characteristics of the system, as described below.

Substitution of eq. (3) into eq. (2) assuming well-mixed conditions yields:

$$V\frac{d\delta_L}{dt} + \delta_L\frac{dV}{dt} = I\delta_I - Q\delta_L - \frac{E}{1 - h + \varepsilon_K/1000} \times \left(\frac{\delta_L - \varepsilon^+}{\alpha^+} - h\delta_A - \varepsilon_K\right) \quad \left(‰\cdot\mathrm{m}^3\cdot\mathrm{year}\right) \tag{4}$$

which under constant atmospheric and hydrologic conditions (i.e. hydrologic steady state, such that $dV/dt = 0$) simplifies to (Gonfiantini, 1986):

$$d\delta_L/dt = -\left[(1 + mx)\delta_L - \delta_I - x\delta^*\right](I/V) \quad (‰) \tag{5}$$

where $x = E/I$ is the fraction of lake water lost by evaporation, $1-x = Q/I$ (being the fraction of water lost to liquid outflows), and

$$m = \left(h - 10^{-3}\cdot\left(\varepsilon_K + \varepsilon^+/\alpha^+\right)\right) \Big/ \left(1 - h + 10^{-3}\cdot\varepsilon_K\right) \quad (\mathrm{dimensionless}) \tag{6}$$

is the temporal enrichment slope, and

$$\delta^* = \left(h\delta_A + \varepsilon_K + \varepsilon^+/\alpha^+\right) \Big/ \left(h - 10^{-3}\cdot\left(\varepsilon_K + \varepsilon^+/\alpha^+\right)\right) \quad (‰) \tag{7}$$

is the limiting isotopic composition. It is significant to note that δ^* is the isotopic composition that a desiccating water body would approach under non-steady-state conditions as it dries up (i.e. $V \to 0$).

Integrating eq. (5) with respect to time, assuming constant values for δ_I, δ_A, ε^+, ε_K, h, I, Q, E yields (Gonfiantini, 1986):

$$\delta_L(t) = \delta_S - (\delta_S - \delta_0)\exp[-(1 + mx)(It/V)] \quad (‰) \tag{8}$$

where $\delta_L(t)$ describes the change in isotopic composition of the lake with time t, δ_0 is the initial isotopic composition of the lake at t_0, and δ_S is the steady-state isotopic composition that the lake approaches as $t \to \infty$. The steady state isotopic composition δ_S is given by Gonfiantini (1986) and Gat (1995) as:

$$\delta_S = (xm\delta^* + \delta_I)/(1 + mx) \quad (‰) \tag{9}$$

which can be rearranged to provide an expression to estimate x (or E/I):

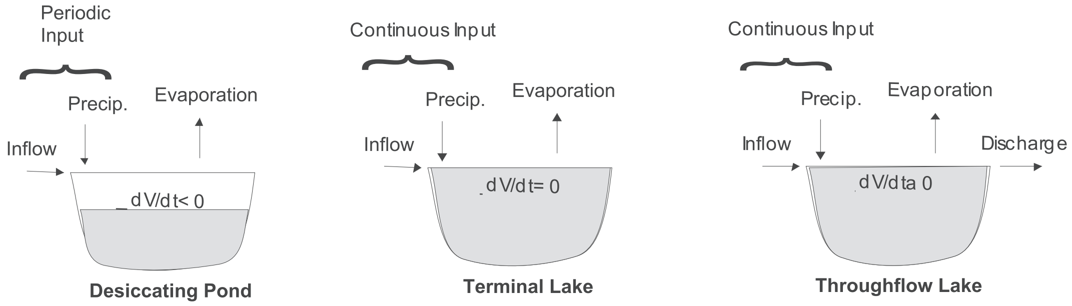

Fig. 1. Schematic showing main hydrologic settings for lakes including (i) desiccating pond, (ii) terminal lake, where inflows are balanced by evaporation, and (iii) throughflow lake or straight-exchange sea (after Horita, 1990).

$$x = (\delta_S - \delta_I) \Big/ \left(m(\delta^* - \delta_S)\right) \quad \text{(dimensionless)} \tag{10}$$

where $x = 1$ corresponds to a terminal lake, and values of x between 0 and approaching 1 reflect varying degrees of throughflow.

The steady state isotopic composition δ_S is commonly used to represent lake water in paleoclimatic scenarios where short-term or seasonal variations are assumed to be minor given the resolution of the records. Perturbations from steady state are commonly observed due to normal variability in atmospheric and hydrologic conditions.

Other hydrological parameters of interest may also be characterized including watershed runoff R

$$R = I_R + I_G = E/x - P - I_U \quad \left(\mathrm{m}^3 \cdot \mathrm{year}\right) \tag{11}$$

For a headwater lake, where $I_U = 0$ we can define annual runoff or water yield WY as

$$WY = R/WA \cdot 1000 \quad (\mathrm{mm} \cdot \mathrm{year}) \tag{12}$$

where WA is land surface area of the watershed. Runoff ratio Z can then be computed as:

$$Z = R/P_{WA} \quad \text{(dimensionless)} \tag{13}$$

where P_{WA} is precipitation on the watershed. Given that the volume of the reservoir can be measured or estimated the residence time of water can estimated using isotopic data as:

$$\tau = xV/E \quad \text{(years)} \tag{14}$$

An IMB schematic for a lake is shown in Fig. 2a, a typical scenario for a small, well-mixed lake that does not significantly influence the humidity or isotopic composition of the atmosphere into which it evaporates. Note that atmospheric fluxes should be evaporation-flux weighted (Gibson, 2002a; Gibson et al., 2008) and liquid water fluxes should be amount-weighted. Also note that lake water, inputs and outputs are normally sampled in the field, or in the case of outputs from a well-mixed lake, are assumed to be representative of lake water values.

While short-term or seasonal variations in lakewater isotopic composition can also be accurately simulated with IMB, factors such as residence time of lake water (Jones et al., 2005) and resolution of archives (Steinman et al., 2013) are inherent limitations in these types of assessments. However, such models may still be very useful for understanding seasonally-biased signals, as for wet–dry seasonal systems (e.g. Kirby et al., 2002; Vonhof et al., 2013).

2.2. Atmospheric moisture

A simple approximation is shown in Fig. 2a whereby atmospheric moisture upwind of the lake is assumed to be in equilibrium with precipitation during the evaporation season (see also Gibson et al., 2008). Other approaches for characterizing atmospheric moisture include direct measurement (Yamanaka and Shimizu, 2007; Iannone et al., 2010; Aemisegger et al., 2012; Good et al., 2012), evaporation pans (Gibson et al., 1999) and use of an index lake.

The index lake approach was proposed for terminal lakes by Dincer (1968) but can essentially be used for any lake with known water and isotope balances. Calibration of the limiting isotopic enrichment, δ^*, in this case is given by:

$$\delta^* = (\delta_S - \delta_I)/xm + \delta_I \quad (‰) \tag{15}$$

where isotope ratios here refer to values in the index lake. A recent example of use of a terminal index lake is presented by Gibson and Reid (2014).

As lake surface area increases, it becomes more common for the evaporation flux from the lake to impact its own boundary layer and modify the overlying humidity and isotopic composition of atmospheric moisture. An IMB schematic for a typical lake with atmospheric feedback is given in Fig. 2b, and is described in Section 2.5.

2.3. Fractionation factors

The equilibrium isotopic fractionation factors α^+ and isotopic separations ε^+ for oxygen and hydrogen are temperature-dependent but these are fairly well-constrained by laboratory experiments in the range of 0–350 °C. Many studies use the values proposed by either Horita and Wesolowski (1994) or Majoube (1971). Horita and Wesolowski (1994) give experimental values of:

$$\alpha^+(^{18}\mathrm{O}) = \exp\Big[-7.685\Big/10^3 + 6.7123/(273.15+T) - 1666.4\Big/(273.15+T)^2 + 350410\Big/(273.15+T)^3\Big] \tag{16a}$$

$$\alpha^+(^2H) = \exp\Big[1158.8\left((273.15+T)^3\Big/10^{12}\right) - 1620.1 \times \left((273.15+T)^2\Big/10^9\right) + 794.84\left((273.15+T)\Big/10^6\right) - 161.04\Big/10^3 + 2999200\Big/(273.15+T)^3\Big] \tag{16b}$$

for oxygen-18 and deuterium, respectively, where T is temperature in °C. The temperature used should correspond to the water surface

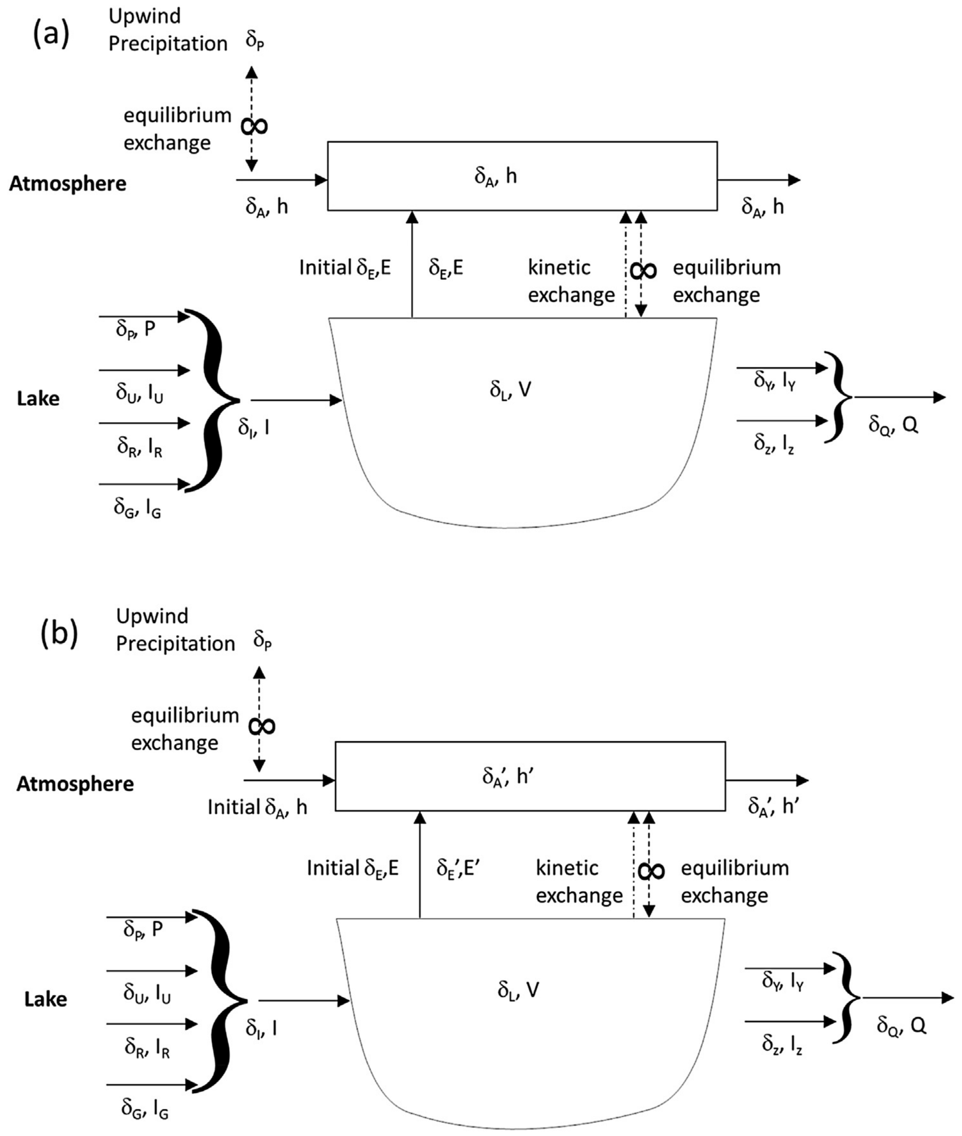

Fig. 2. Schematic showing major water fluxes and isotopic compositions for a well-mixed lake (a) without atmospheric feedback, and (b) with atmospheric feedback. Note that atmospheric parameters are preferably evaporation-flux weighted whereas liquid fluxes to the lake are amount-weighted, and discharge acquires the isotopic signature of the lake water. A simple approximation for atmospheric moisture is also shown that assumes equilibrium with upwind precipitation. Note that atmospheric feedback modifies the isotopic composition and humidity of the overlying air mass. Kinetic and equilibrium exchange between the lake and atmosphere, as shown, are conceptual. These occur in the near-surface boundary layer.

temperature (usually close to the air–water mean temperature). It has been suggested that surficial cooling effects (up to 4 °C) may play a role, particularly for high rates of evaporation (Cappa et al., 2003), although this seems to be less important under natural conditions (Horita et al., 2008). Use of the correct form of the equilibrium fractionation factors has been the primary source of confusion among previous studies. Note that the equilibrium fractionation factors α^+ used above are defined by the convention of Gonfiantini (1986) as the ratio in liquid versus vapour, i.e. $\alpha^+ = R_L/R_V > 1$, where R_L and R_V are the isotope ratios in liquid and vapour, respectively, rather than $\alpha^* = R_V/R_L < 1$ as proposed by Craig and Gordon (1965) and subsequently used by many others (see also Gat, 1996). For clarity, we also include the alternate formulation of eq. (3) for using α^*:

$$\delta_E^{alt} = \left(\alpha^*\delta_L - h\delta_A - \varepsilon^* - \varepsilon_K\right) \Big/ \left(1 - h + 10^{-3}\cdot\varepsilon_K\right) \tag{3a}$$

and in this case eqs. (6) and (7) become

$$m^{alt} = \left(h - 10^{-3}\cdot(\varepsilon_K + \varepsilon^*)\right) \Big/ \left(1 - h + 10^{-3}\cdot\varepsilon_K\right) \quad \text{(dimensionless)} \tag{6a}$$

and

$$\delta^{*alt} = \left(h\delta_A + \varepsilon_K + \varepsilon^*\right) \Big/ \left(h - 10^{-3}\cdot(\varepsilon_K + \varepsilon^*)\right) \quad (‰) \tag{7a}$$

where $\varepsilon^* = (1 - \alpha^*)\cdot 1000$. For lakes, kinetic constants C_K are commonly assumed to be 14.2‰ for oxygen-18 and 12.5 for deuterium (Horita et al., 2008) representing fully turbulent, open-water conditions. For laminar flow conditions, diffusion-controlled settings (i.e. evaporation from soils) or for mixed conditions (i.e. evaporation through leaves), alternate formulations have been proposed based on proportionate weighting of diffusivity ratios and turbulence (see Horita et al., 2008). Note that an alternate kinetic fractionation scheme proposed by Merlivat and

Jouzel (1979) uses separate wind speed-dependent algorithms for smooth and rough surfaces, and is widely applied by the GCM community for simulating evaporation from oceans and continental surface waters (see Schmidt et al., 2005; Lee et al., 2007; Risi et al., 2012). The fundamental influence of using different parameterization schemes in GCMs versus the Craig and Gordon (1965) model has been discussed only recently (Haese et al., 2013), and needs to be kept in mind when GCM outputs are compared to IMB simulations or paleoclimate data.

2.4. Seasonality effects

For non-seasonal climates, where evaporation occurs consistently throughout the year, it is often suitable to assume that atmospheric moisture is in equilibrium with precipitation:

$$\delta_A = \left(\delta_P - \varepsilon^+\right) / \left(1 + 10^{-3} \cdot \varepsilon^+\right) \tag{17}$$

as shown in Fig. 3a, which is an example of an evaporating system with an evaporation line slope close to 3.5. Here, δ_P is mean annual precipitation which is assumed to be the isotopic composition of input to the lake.

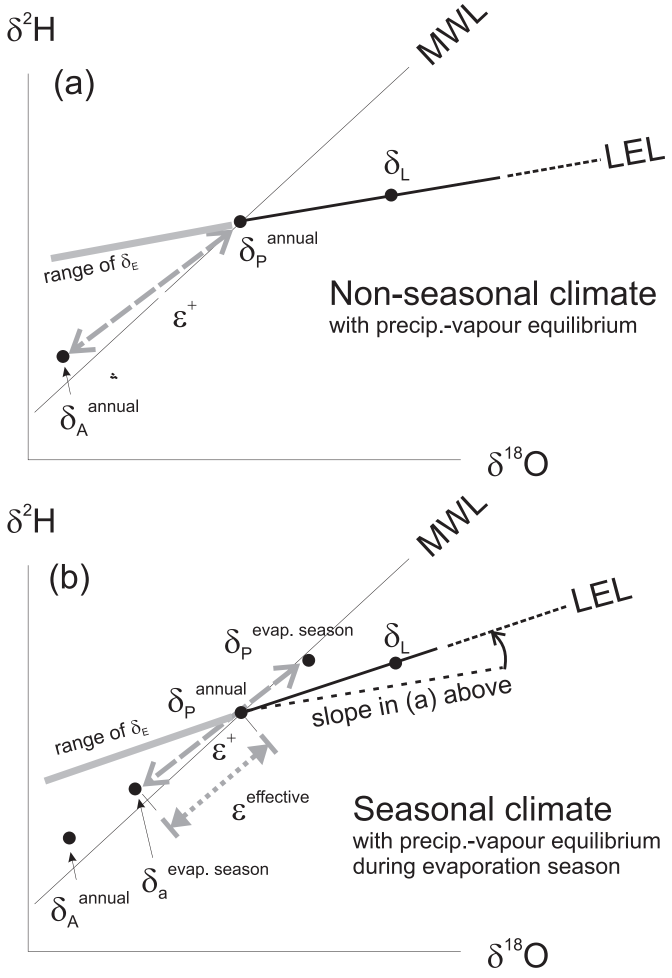

Fig. 3. Schematic $\delta^2H-\delta^{18}O$ plots showing isotopic composition of water and vapour in an ideal lake undergoing evaporation. Two cases are shown including (a) non-seasonal climate where atmospheric moisture is in equilibrium with mean annual precipitation, and (b) seasonal climate, where atmospheric moisture in equilibrium with precipitation falling during the evaporation season. Note that in the latter case, the isotopic separation between mean annual precipitation and the effective atmospheric moisture, termed the effective isotopic separation $\varepsilon^{\text{effective}}$, is less than equilibrium. This situation can be modelled using a selected equilibrium approach (see text for discussion). The MWL is the Global Meteoric Water Line of Craig (1961) (modified from Gibson, 2002a).

In seasonal climates, where evaporation may be highly seasonal, or lakes may even be frozen for a significant part of the year (e.g. Canada or Russia), it is less appropriate to use the equilibrium approximation. For this situation, the atmosphere is better represented by equilibrium with precipitation during the evaporation season, ideally using evaporation flux-weighted values of δ_P to estimate δ_A (Gibson, 2002a; see Fig. 3b). In this case, the typical evaporation line slope is 5 or higher, and the effective isotopic separation between amount-weighted precipitation (falling near the intersection of local evaporation line and meteoric water line) and evaporation-flux weighted moisture, is less than the equilibrium separation. This is termed the effective precipitation-vapour separation ($\varepsilon_{effective}$), as illustrated in Fig. 3b. Gibson et al. (2008) illustrated this concept on a global basis from analysis of the International Atomic Energy Agency's Global Network for Isotopes in Precipitation database, as we present in Fig. 4. Overall, the precipitation – atmospheric moisture separation ($\varepsilon_{effective}$) is slightly compressed at high latitude due to this effect. It is important to note that such maps, while useful for illustrating the global and regional patterns of precipitation and atmospheric moisture, should be interpreted cautiously and are not recommended for interpolating values for individual sites. For seasonal settings where continuous records of δ_A are not available, a 'selected' equilibrium model applied to mean annual precipitation δ_P may be more appropriate using:

$$\delta_A = \left(\delta_P - k\varepsilon^+\right) / \left(1 + 10^{-3} \cdot k\varepsilon^+\right) \quad (‰) \tag{18}$$

where k typically ranges from 0.5 for highly seasonal climates to values approaching 1 for non-seasonal climates. In case studies where both oxygen and hydrogen isotope data are available, the selected equilibrium approach has been used to fit δ_A to match the observed slope of the local evaporation line (Bennett et al., 2008; Gibson and Reid, 2014).

As lower slopes predicted by the equilibrium model (Fig. 3a) do not generally match the observed slopes for seasonal climates, evidently due to improper (or lack of) weighting for the $\delta_A - \delta_P$ separation, it is appropriate to use the selected equilibrium assumption that accounts for the fact that evaporation and isotope exchange does not occur during periods of ice cover or that the process is seasonally variable. An interesting point that is especially relevant for paleoclimate studies is that temporal changes in seasonality likely contributed to a continual shift in the slope of the local evaporation line in the past.

While many paleoclimate studies are based on oxygen-18 only, it is thought-provoking to note that, where possible, use of dual oxygen-18 and deuterium records in lake sediments would provide a method for tracing changes in paleoslope of the evaporation line and therefore potentially offer a basis for examining past seasonality in the lake sediment record. Regression of paleoslopes to the intersection with the meteoric water line could also be used to constrain precipitation input signatures more precisely. Without dual isotopes, paleoclimate studies using oxygen-18 alone might at least consider use of a selected equilibrium assumption to avoid systematic scaling issues in quantification of water balance in seasonal settings. For modern water balance applications, the use of evaporation-flux-weighted δ_A and evaporation-flux-weighted exchange parameters is required to avoid substantial errors in computed long-term values for evaporation to inflow ratios, particularly for strongly seasonal climates where errors may be as high as 50% for low throughflow, high evaporation lakes. One other implication is that slope of local evaporation lines:

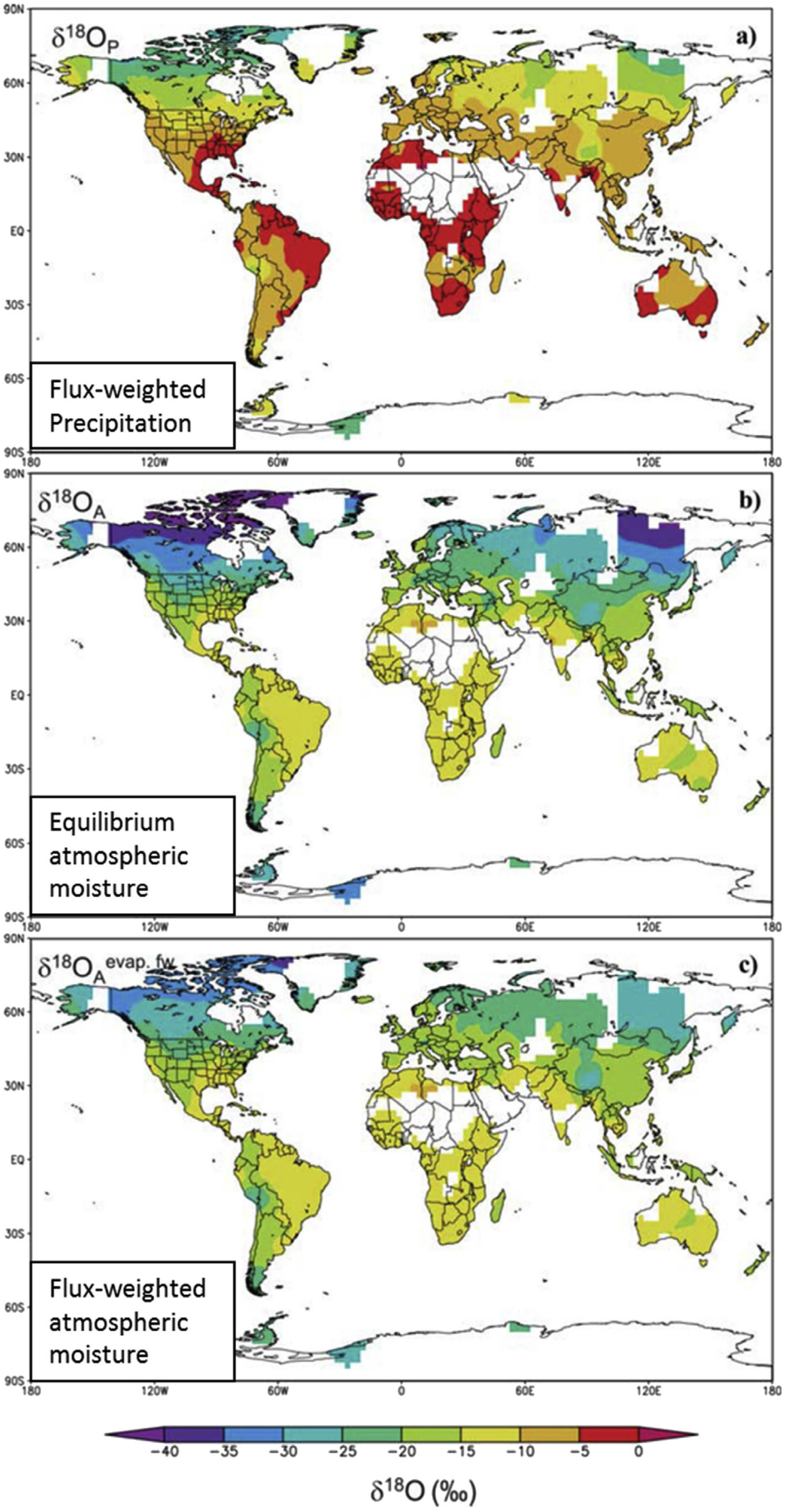

Fig. 4. Maps showing isotopic compositions based on modelling of the Global Network for Isotopes in Precipitation database, (a) Mean annual isotopic composition of precipitation (b) isotopic composition of moisture in equilibrium with mean annual precipitation, (c) evaporation-flux-weighted atmospheric moisture. Note that the separation between (a) and (b) is significantly greater than (a) and (c), especially at high latitudes (modified from Gibson et al., 2008). This map is provided to illustrate global and regional patterns and is not intended to be used for interpolation for individual sites.

$$S_{LEL} = \frac{\left[\dfrac{h(\delta_A - \delta_P) + (1 + \delta_P \cdot 10^{-3})(\varepsilon_K + \varepsilon^+/\alpha^+)}{h \cdot 10^3 - \varepsilon_K - \varepsilon^+/\alpha^+}\right]_2}{\left[\dfrac{h(\delta_A - \delta_P) + (1 + \delta_P \cdot 10^{-3})(\varepsilon_K + \varepsilon^+/\alpha^+)}{h \cdot 10^3 - \varepsilon_K - \varepsilon^+/\alpha^+}\right]_{18}} \quad (19)$$

vary globally, with lower values near the equator and higher values at high latitudes (Fig. 5; see also Gibson et al., 2008). Note that eq. (19) is evaluated based on δ* and the isotopic composition of inflow δ_P assuming lakes fed by precipitation-derived waters. In general, the evaporation slope based on eq. (19), which is atmospherically controlled, can serve as a useful diagnostic variable to determine the appropriate parameterization scheme for both modern and paleoclimate applications. However, it is important to acknowledge that LEL slopes are slightly non-linear and also weakly dependent on water balance when evaluated in the range of δ_P to δ_S as shown in Fig. 6. Caution should also be used when applying slope diagnostics for arid climates where humidity is below 50% as isotopic enrichment becomes unconstrained.

An example of the expected steady-state isotopic enrichment for lakes located in the same climatic zone but under different water balance conditions, as well as differences in evaporate is shown in Fig. 6a, The scenario assumes constant temperature and humidity (T = 10 °C, h = 0.7), constant inflow of precipitation-derived waters with delta values of $\delta_I^{18,2} = (-20\text{‰}; -150\text{‰})$, and constant atmospheric moisture of $\delta_A^{18,2} = (-25.1\text{‰}, -180.9\text{‰})$ which assumes $\delta_A = (\delta_P - 0.75\varepsilon^+)(1 + 10^{-3} \cdot 0.75\varepsilon^+)$. Under changing humidity, temperature and water balance, the slope of the LEL is shown to be strongly dependent on the humidity, moderately dependent on the temperature, and weakly dependent on the water balance (Fig. 6b).

2.5. Atmospheric feedback

For lakes, especially large lakes, where evaporation has a significant influence on the boundary layer, the humidity, atmospheric moisture feedback, and effect on the kinetic fractionation need to be considered. In general, the isotopic composition of the atmosphere above the lake is modified by admixtures of evaporate according to:

$$\delta_A' = (1 - f) \cdot \delta_A + f \cdot \delta_E \quad (\text{‰}) \quad (20)$$

where δ_A' is the modified isotopic composition of the atmospheric admixture and f is the fraction of evaporate added. It is important to note that eq. (20) describes the effect of turbulent mixing between evaporate and the overlying air mass, whereas θ describes the effect on isotopic fractionation in the near-surface boundary layer. Gat (1996) discussed the implications of θ in situations where atmospheric feedback is significant. He noted that the transport parameter $\theta = (1 - h')/(1 - h)$ is appropriate for situations with atmospheric feedback (θ has been shown to have a value close to 0.88 in the vicinity of the Great Lakes and 0.5 for the eastern Mediterranean; Gat (1996), but is expected to be close to 1 for small lakes). The modified isotopic composition of evaporate in a feedback system then becomes:

$$\delta_E' = \left(\left(\delta_L - \varepsilon^+\right)/\alpha^+ - h\delta_A' - \varepsilon_K\right) \Big/ \left(1 - h + 10^{-3} \cdot \varepsilon_K\right) \quad (\text{‰}) \quad (21)$$

noting that $\varepsilon_K = (1 - h')/(1 - h)C_K \bullet (1 - h)$ or $\varepsilon_K = C_K \bullet (1 - h')$ to account for atmospheric feedback. Equations (20) and (21) can be solved iteratively using isotope mass balance by converging on a

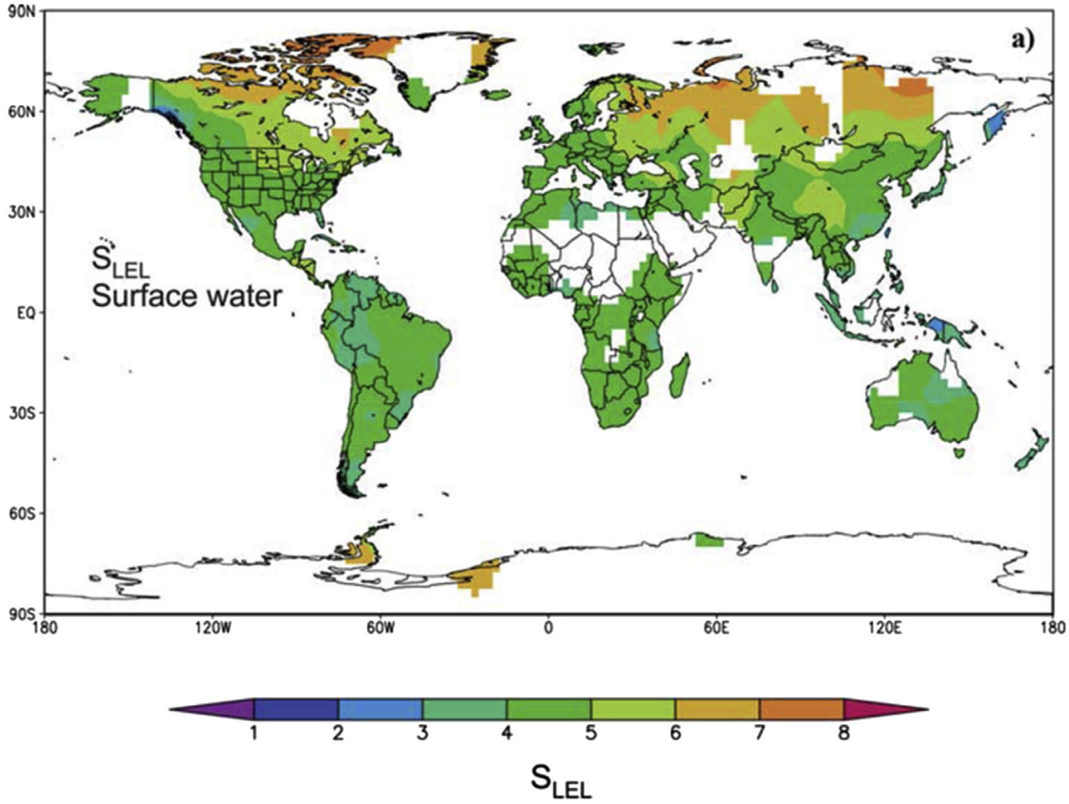

Fig. 5. Simulated slope of local evaporation lines for precipitation-fed lakes showing steepening of slopes, particularly at northern high latitudes (modified from Gibson et al., 2008). This map is provided to illustrate global and regional patterns and is not intended to be used for interpolation for individual sites.

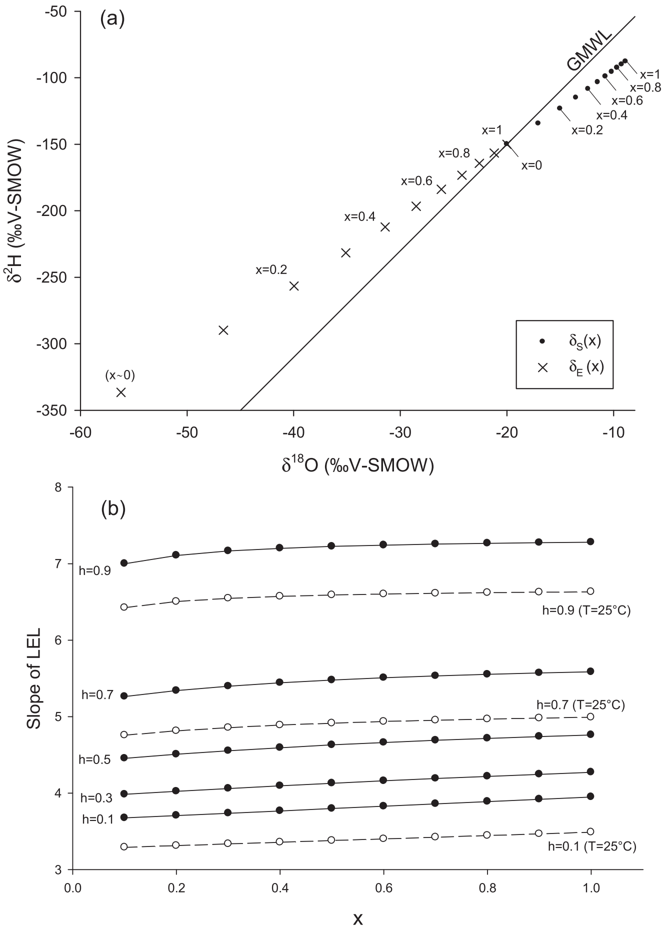

Fig. 6. (a) Deuterium-oxygen-18 plot showing steady-state isotopic composition for lakes under constant temperature (T = 10 °C), humidity (h = 0.7), constant $\delta_I^{18,2}$ (−20‰, −150‰, $\delta_A^{18,2} = (-25.1\,‰, -180.9\,‰)$. The scenario simulates selected equilibrium conditions, i.e ($\delta_A \approx \delta_P - 0.75\varepsilon^+$). (x = 0) denotes the isotopic composition of first evaporate of water with precipitation composition (b) Dependance of slope of LEL on water balance, showing scenarios for T = 10 °C and T = 25 °C. Note that water balance, temperature, and humidity have an increasing importance in determining the slope of LEL. Solid lines depict 10 °C scenarios and dashed lines depict 25 °C scenarios.

matching value for evaporation for both δ^2H and δ^{18}O, as demonstrated by Jasechko et al. (2014).

An IMB schematic for a lake with atmospheric feedback is shown in Fig. 2b.

3. Regional scenarios and examples

There are several informative reviews of lake isotope balance studies (e.g. Dincer, 1968; Gat, 1981; Gonfiantini, 1986) and many other case studies available in the scientific literature (e.g. Zimmerman, 1979; Hostler and Benson, 1994; Sachs, 2002; Tyler et al., 2007; Longinelli et al., 2008; Brooks et al., 2014). Terrestrial water balance at the regional scale derived from lake isotope compositions has also been described (Jasechko et al., 2013). While informative, these studies do not offer significant insight into IMB systematics related to specific climatic regions under study. Variations expected in δ_P,δ_S,δ_A and δ_E are shown for a variety of regional climate scenarios including low latitude, high latitude, temperate regions, large lakes, and coastal lakes (Fig. 7). These examples are included to inform selection of appropriate IMB parameterization schemes for paleoclimatic reconstructions using stable water isotopes. We use constant values of input as a reference case so that direct comparisons can be readily made between scenarios. Example spreadsheet calculations for the scenarios in Fig. 7 are provided as Supplementary material.

3.1. Low latitude lakes

Gat (pers. comm.) described a reference evaporation system in low latitude regions as one that is non-seasonal, characterized by input from precipitation that is in isotopic equilibrium with local vapour, and a lake with throughflow that is well-mixed, in hydrologic steady state, and losing water by surface evaporation. In this case, humidity does not significantly affect the slope of the evaporation line but higher humidity tends to limit the overall offset from the meteoric water line along the local evaporation line (Fig. 6a,b). Ideal examples of the low-latitude (non-seasonal) systems are few, but this model is most suitably applied where slopes of local evaporation lines are approximately 3.5 (see Gibson et al., 2008). However, in almost all cases, subtle seasonal shifts can result in slight departure from precipitation–vapour equilibrium resulting in weak humidity dependence of the local evaporation line. Vallet-Colomb et al. (2008) describe atmospheric moisture conditions over a tropical lake, but find that vapour is not in isotopic equilibrium due to atmospheric feedback effects, and evaporation line slopes are steeper, as discussed later on. The idealized scenarios shown here assume δ_P of −20‰ for δ^{18}O and −150‰ for δ^2H, a mean annual temperature of 20 °C, and $\delta_A - \delta_P$ equilibrium. Two humidity cases are shown, for 55% (Fig. 7a: aridzone) and for 80% (Fig. 7b; humid zone).

3.2. High latitude lakes

High latitude lakes in strongly seasonal climates are considered as another reference scenario whereby evaporation occurs under conditions where the effective isotopic separation ($\varepsilon_{effective}$) is less than the equilibrium separation. This is due to the seasonality effect as described in Fig. 3b. In general, evaporation slopes are steeper than low latitude cases (Fig. 5), with a steeper slope associated with higher humidity and enhanced seasonality (Fig. 7c,d) While temperature is also typically lower than for low latitude lakes, its effect on isotopic enrichment is minor. Many contemporary studies have been conducted at high latitudes in both arctic and subarctic regions (Gibson et al., 1993, 1996, 1998, 2005; Gibson and Edwards, 2002; Ichiyanagi et al., 2003; Leng and Anderson, 2003; Yi et al., 2008; Brock et al., 2009; Jonsson et al., 2009; Gibson and Reid, 2010, 2014; Turner et al., 2010; Anderson et al., 2013; Tondu et al., 2013). A review of IMB highlighting cold regions processes is given by Gibson (2002b). High latitude lakes in continental regions tend to display pronounced evaporative enrichment during the thaw season due to seasonally arid conditions, although this is more limited in coastal areas (Gibson et al., 2005). The scenarios shown here assume a δ_P of −20‰ for δ^{18}O and −150‰ for δ^2H, an evaporation season temperature of 5 °C, and a $\delta_A - \delta_P$ separation ($\varepsilon_{effective}$) equal to 50% of equilibrium. Two humidity cases are shown, for 65% (Fig. 7c; semi-arid zone) and for 80% (Fig. 7d; humid zone).

3.3. High altitude lakes

Similar highly seasonal responses are expected for high-altitude lakes, often with the additional need to consider the effect of glacial meltwater input (This can also occur in some high altitude systems, although not in the reference examples presented above). In general, glacial meltwater is expected to be depleted in isotopic composition relative to precipitation on the lake due to the altitude effect and conceivably due to colder climate when it was deposited.

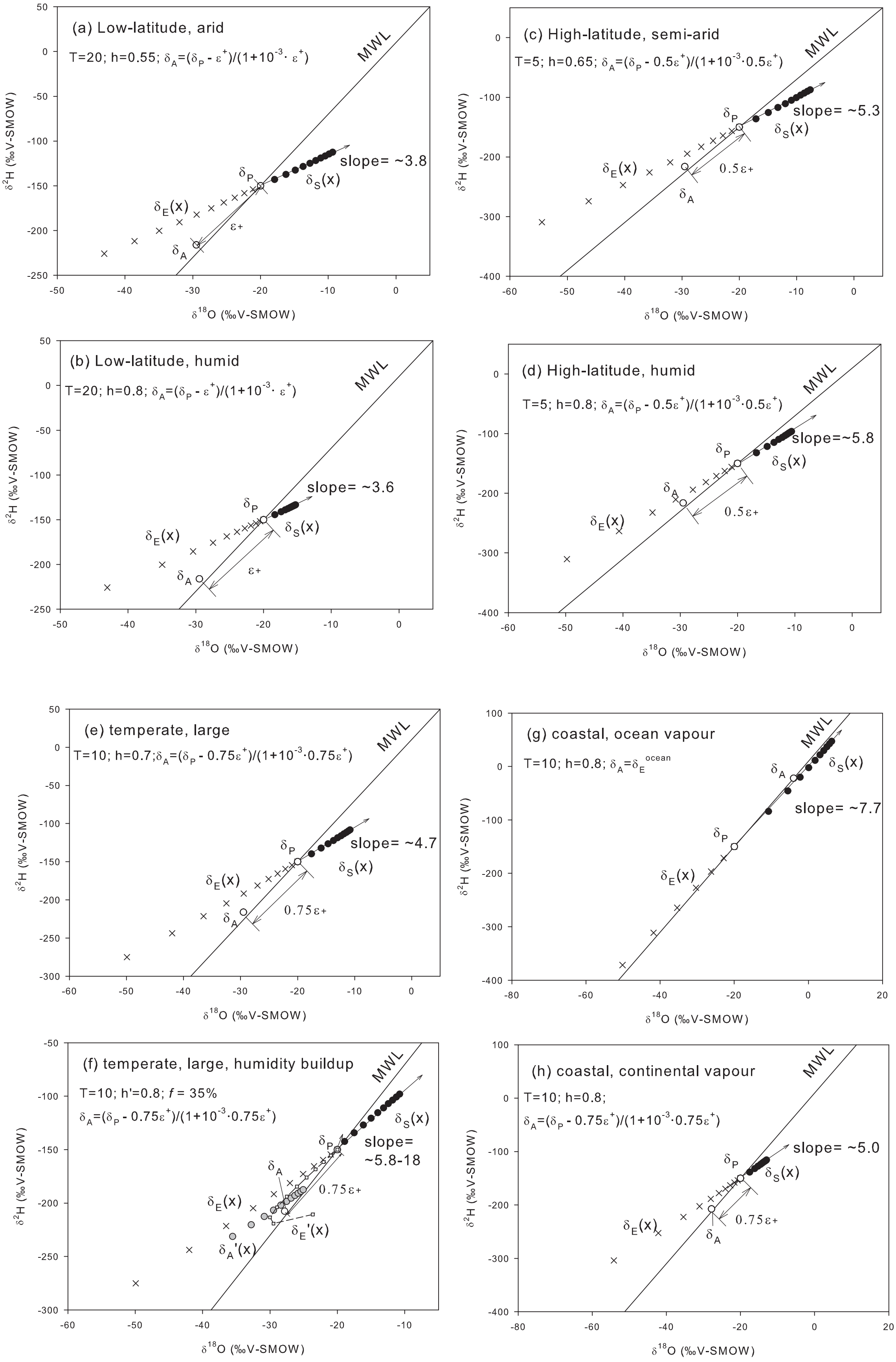

Fig. 7. Schematic δ^2H–δ^{18}O plots showing isotopic composition of water and vapour for various lake water balance scenarios including low latitude, high latitude, temperate, and coastal systems. Note that the MWL is the Global Meteoric Water Line of Craig (1961).

While glacial input may augment or even dominate inflow, it may also produce steepening of local evaporation lines by making net input more isotopically depleted. This is expected to make the effective isotopic separation ($\varepsilon_{effective}$) smaller by making net input more similar to the evaporation-flux-weighted moisture (see Fig. 3b). Studies of contemporary hydrology of high altitude lakes include Guerrieri and Furniss (2004) who traced groundwater exchange in a Colorado Lake using non-steady mass balance methods, Yonge et al. (1989) who examined the altitude effect in lakes and streams in a transect across the Western Cordillera from Calgary to Vancouver, Canada, and Schurch et al. (2003) who describe the rationale for the Swiss national isotope network. In general, evaporative enrichment is more subdued in high alpine areas, with isotopic composition being controlled by groundwater exchange or glacial contributions. Various alpine climate and hydrology reconstructions using δ^{18}O have also been demonstrated, including studies tracing monsoon cycles and atmospheric circulation patterns (Mckenzie and Hollander, 1993; Barker et al., 2001; Jones et al., 2006), paleo-altitude of orogenic belts (Rowley et al., 2001), paleohydrology and paleohumidity (Wolfe et al., 2001) and residence time and evaporation (Fontes et al., 1993).

3.4. Temperate lakes

Temperate regions, located between the tropics and the Polar regions, tend to have an intermediate response compared to low latitude and high latitude systems. As a result evaporation slopes tend to be intermediate (often in the 4–5 range) and are moderately humidity-dependent. There are many examples of isotope balance studies in temperate zones. One recent study presents variation in water balance across the contiguous United States (Brooks et al., 2014). Henderson and Shuman (2009) demonstrate slopes of 4–5 for lakes located at seasonal sites with freezing winters in the United States, which is consistent with weaker seasonality than observed in Canada or Russia.

Other studies presenting long-term datasets also describe parameterizations for temperate lakes (Gat, 1970; Lewis, 1979; Zimmerman, 1979; Hostetler and Benson, 1994; Sachs, 2002; Tyler et al., 2007; Longinelli et al., 2008). Temperate lakes tend to have a range of evaporative enrichment as determined by evaporation loss and throughflow status. Here we summarize two temperate scenarios, for a large lake with and without humidity buildup. These scenarios assume a δ_P of -20‰ for δ^{18}O and -150‰ for δ^2H, an evaporation season temperature of 10 °C, and a $\delta_A - \delta_P$ separation ($\varepsilon_{effective}$) equal to 75% of equilibrium. Two relative humidity cases are shown, for 70% (Fig. 7e; temperate) and for 80% (Fig. 7f; temperate, with humidity buildup). The specific effect of humidity buildup, which may occur more often for large lakes, is described in the following section.

3.5. Large lakes with humidity buildup

Large lakes, such as the Laurentian Great Lakes (Jasechko et al., 2014), have been shown to modify their own boundary layer on an ongoing basis due to admixture of evaporate into the overlying air mass. From an isotopic perspective, this has been addressed using the modified evaporation equations presented in Section 2.5. For the Great Lakes, Jasechko et al. (2014) estimated that between 15% and 40% of water vapour over the lakes is contributed by lake evaporate. Using precipitation records, Gat et al. (1994) estimated that 5–16% of moisture at precipitation stations downwind of the lakes were derived from lake effect moisture (i.e. $\theta = 0.88$ as discussed previously). Together these studies suggest a larger effect over the lakes themselves. This has a significant effect on the isotopic enrichment of the lake, as shown in Fig. 7f for the case of 35% moisture feedback. The evaporation slope is shown to steepen relative to the non-feedback scenario (Fig. 7f) and tends to be steeper at lower values of x (i.e. higher throughflow). The influence of the isotopic composition of evaporate on the overlying atmosphere and humidity are both influential. The steepening of the evaporation slope (see Supplementary material) also contributes to limited overall offset of the lake from the meteoric water line (see Laurentian Great Lakes; Fig. 8) and has created the Great Lakes Water Line, sub-parallel to the GMWL (Fig. 8; see also Jasechko et al., 2014). This steepening and limited offset was also observed by Vallet-Colomb et al. (2008) for a moderately large tropical lake (115 km^2) with significant vapour feedback. It is important to note that failure to account for atmospheric feedbacks over such lakes would have resulted in substantial underestimation of x. For paleoclimate reconstruction, representative humidity for characterizing isotopic changes in large lakes is expected to be up to 30% or so higher than the ambient humidity in near-shore areas. Note that water balance of individual lakes can be strongly influenced by inflows from upstream elements. In the case of the Great Lakes water from upstream lakes is itself enriched relative to the MWL which needs to be considered when solving the isotope mass balance (see Jasechko et al., 2014).

3.6. Coastal lakes

The isotopic response of coastal lakes has not been given much attention in the peer-reviewed literature. While regional surveys of continental lakes often display evaporation lines that lie below the meteoric water line, coastal lakes often plot along the meteoric water line (Fig. 8). This unique response is shown for a spatial survey of small lakes in coastal British Columbia, Canada in comparison with a similar survey in northern Saskatchewan, Canada (Gibson et al., 2010). Overall, Gibson et al. (2010) report that variations in the British Columbia survey are more closely linked to variations in precipitation with altitude along the mountainous coastline, whereas variations in Saskatchewan and neighbouring provinces (Alberta and Manitoba) are driven more by variations in the water balance of lakes. It is also important to appreciate the

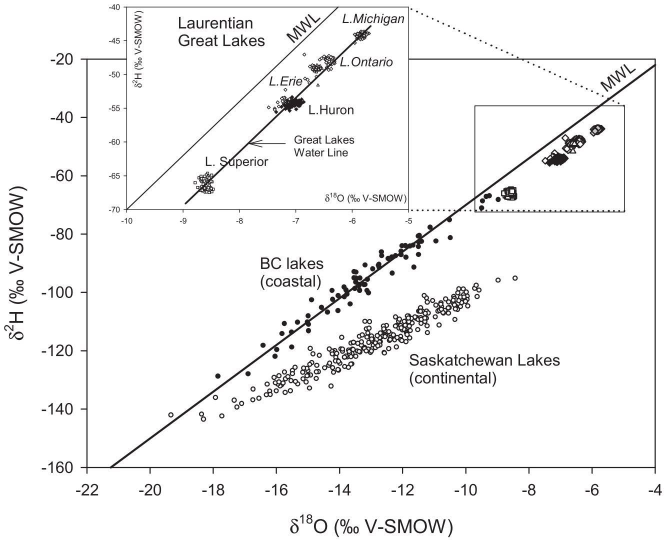

Fig. 8. δ^2H–δ^{18}O plot showing characteristic differences between lakes from coastal environments and continental environments, as well as large lakes with humidity buildup. Note that the BC lakes (Canada) plot along the MWL (Global Meteoric Water Line; Craig, 1961), Saskatchewan lakes (Canada) plot along a well-defined local evaporation line with slope close to 5, and Laurentian Great Lakes (Canada/USA) plot along a trend parallel to but below the MWL.

unique vapour regime associated with coastal areas, especially due to the fact that the atmosphere may oscillate from being ocean-vapour dominated to continental-vapour dominated. Under ocean-dominated conditions, δ_A may become unusually enriched compared to δ_P leading to isotopic exchange and potential for extreme evaporative enrichment along the meteoric water line, although the latter is likely constrained somewhat by high humidity (Fig. 7g). For continental dominated moisture intervals, the enrichment proceeds along a fairly steep slope, with departure from the meteoric water line constrained by high humidity (Fig. 6h). In addition, as humidity increases towards 100% and evaporation stops, the kinetic effects become negligible. In this situation a lake may tend toward an isotopic signature reflecting isotopic equilibrium with the atmosphere, and water balance information is therefore not recorded. Fortunately, humidity intervals close to 100% are usually short-lived. The scenarios shown here assume a δ_P of -20‰ for δ^{18}O and -150‰ for δ^2H, an evaporation season temperature of 10 °C, a $\delta_A - \delta_P$ separation ($\varepsilon_{effective}$) equal to 75% of equilibrium, and a humidity of 80% (Fig. 7g,h). Ocean-dominated moisture is assumed to be close to -4‰ for δ^{18}O and -22‰ for δ^2H, representative of oceanic evaporate (Craig and Gordon, 1965, p. 99), It is important to note that changes in dominance of oceanic versus continental air masses over time, and the overprinting of both precipitation and evaporative enrichment signals along or close to the meteoric water line, makes interpretation of coastal isotopic records potentially more complex.

3.7. *Saline lakes*

The salt effect in saline lakes has been described in detail by Gonfiantini (1986) and Gat (1995) with many informative case studies. While beyond the scope of this article, it is important to be aware that salt decreases the thermodynamic activity of water and its evaporation rate, causes hydration sheaths to form which contain a different isotopic composition to that of free water, and if saturation occurs, salts may precipitate and remove crystallization water that has a different isotopic signature than the remaining liquid (Gonfiantini, 1986). Important modifications to the steady-state balance equations shown here have been applied to account for the thermodynamic activity effects in saline lake case studies (see Gat and Levy, 1978; Horita, 1990). This involves normalization of the humidity (i.e. substitution of h with h/a_W, where a_W is the thermodynamic activity of water).

3.8. *Chain of lakes*

The theoretical case of non-headwater chain lakes has been described in detail by Gat and Bowser (1991) and two recent case studies have also been reported (Gibson and Reid, 2010, 2014). The first case study, reporting IMB results from the continental subarctic near Yellowknife, Northwest Territories, Canada, showed how records from two nearby lakes can be used to reconstruct changes in the degree of connectivity of a string-of-lakes watershed over almost two decades of observation. This approach relies on simultaneous monitoring of a terminal lake and a nearby creek (Baker Creek) draining a watershed comprised of 370 intermittently connected lakes. In general, it was found that as upstream lakes became disconnected, the isotopic composition of Pocket Lake and Baker Creek became more similar (Fig. 9), and this was used quantitatively to estimate the effective drainage area of the Baker Creek watershed, which ranged from about 27% to 88% of the topographically delineated drainage area. Similar strategies could potentially be applied in paleoclimate studies providing a suitable high-closure lake can be identified in the vicinity of a chain of lakes of interest.

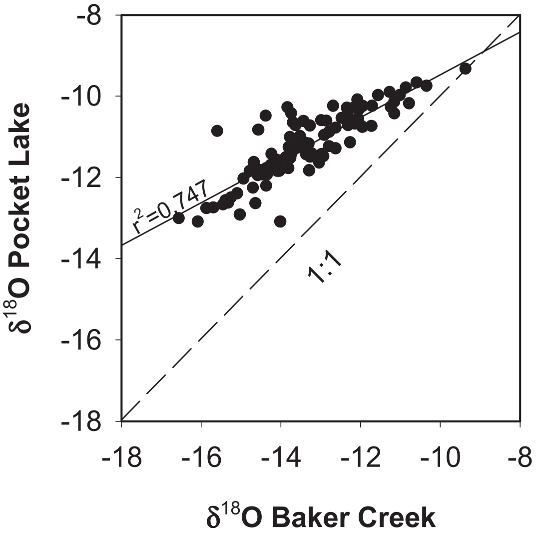

Fig. 9. Crossplot showing isotopic composition (δ^{18}O) of Pocket Lake (a terminal lake) versus Baker Creek (outlet of Martin Lake) sampled during the open water season during 1991–2013. Baker Creek drains a 137 km^2 basin containing 370 intermittently connected lakes. Note that the isotopic composition of the lakes becomes more similar as effective drainage area decreases in the Baker Creek watershed, which was applied by Gibson and Reid (2010) to quantify connected area of the watershed.

The second example is provided by Gibson and Reid (2014) who showed propagation of water down a chain of lakes in a tundra watershed, and illustrated application of the method to track evolution of water yield, runoff ratios and evaporation losses along a chain of several lakes that were continuously connected during the thaw season over a 20-year period. A similar approach to reconstruction of water balance along a chain of paleolakes is also possible as described by Yu et al. (2002). In this case the upstream lake can be used to define δ_U, the middle lake defines δ_S, and the downstream lake defines δ_Q. Both Gibson and Reid (2010, 2014) also estimated evaporation as a percentage of evapotranspiration from the watersheds. Such metrics that capture the balance between the vapour loss mechanisms, and more clearly portray the role of lakes in the regional hydroclimate system, have yet to be applied in the paleohydrologic reconstructions, in many cases due to difficulty in obtaining good control on past changes in some properties such as lake levels and watershed areas. In fact, dating control on lake sediments remains a primary limitation on combined interpretation of co-located lake records. But the potential exists to carry out this kind of study.

4. Summary

Isotope mass balance of contemporary systems can provide considerable insight into expected responses observed in the paleoenvironmental archives, and is an important consideration when using quantitative models to simulate past water balance conditions. An examination of modern systems shows that basic assumptions about atmospheric moisture and humidity can have a large impact on signatures registered in lake sediments. Several important considerations to improve realism of quantitative paleoclimatic reconstructions include use of an isotope mass balance model that is appropriate for the climatic setting, for the atmospheric feedback situation, for salinity, and headwater conditions. We also show potential for use of dual-isotope tracers to trace past changes in seasonality and input, and a dual-lake index method that can be used to trace effective drainage basin areas of lakes. Use of physical water balance information on lakes of interest, tied to modern isotope balance analogues, is a reasonable strategy for paleoclimate studies of lakes to improve realism of the reconstructions. Nevertheless, in cases where modern or paleo systems are under-defined there are inherent limitations in the degree of quantification that can be attained. But as reflected on by Gat (1996), paleoclimatic applications of isotope hydrology have been a greater incentive for the study of stable isotopes in the hydrologic cycle, yielding more useful hydrological information as a byproduct, than hydrological sciences applications directly. We contend that these communities have much to learn from one another.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quascirev.2015.04.013.

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