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# Paleosalinity and $\delta^{18}O$: A critical assessment

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**Abstract.** In paleoceanography, a traditional application of oxygen isotope ratios in fossil carbonate from deep-sea cores concerns the reconstruction of paleotemperatures. Recently, isotopic data have been increasingly employed in the reconstruction of paleosalinities as well. This application involves a number of basic assumptions, a critical review of which is presented here. As the calculation of paleosalinity from $\delta^{18}O$ residuals assumes constant and linear surface water salinity ($S$):$\delta^{18}O$ relationships, we investigate this basic assumption for areas with important and variable freshwater budget and/or sea-ice influences. We show that it is particularly unwarranted to assume such temporally invariant linearity in temperate and subpolar seas because of the effects of freezing and melting. More critically, we argue that the determinant of many regions' $S$:$\delta^{18}O$ is advection, not the local water balance, so that the basic $\delta^{18}O$ of seawater in many regions of the world ocean would likely have changed in a manner somewhat different from that expected from the ice volume record. Although the differences may not be significant for the gross reconstruction of such features as past sea level, we believe they do potentially bias paleosalinity reconstructions, mostly toward high salinities. To fully exploit the potential of oxygen isotope records as quantitative paleosalinity indicators, both the spatial and temporal variabilities need to be constrained. Hence we recommend that (1) for any time slice of specific interest to paleoceanographic and paleoclimatological studies, a coupled ocean-atmosphere-isotope model, or at least an ocean-isotope model driven by a paleoclimate-isotope model, should be used to define the distribution of the base, mixing end-member, $\delta^{18}O$ of sea water; (2) much further regional-scale research is needed on flux rates and isotopic compositions of the various terms in the freshwater budget, as well as on the variability in the various advective terms. The latter variability may be assessed from reconstructions of past sea-ice distributions and of volume fluxes/isotopic compositions of outflow from marginal seas and through sea straits/passages.

## 1. Introduction

### 1.1. Stable Oxygen Isotopes in (Paleo)Oceanography

Stable oxygen isotope analyses on fossil carbonate have played a pivotal role in paleoceanographic/ paleoclimatological science during the last 4 decades. A wide variety of purposes has been served, including (1) the development of high-resolution time-stratigraphic frameworks for sediment cores worldwide; (2) description of sea level history; (3) paleotemperature and paleosalinity determination; and (4) important contributions to process-oriented studies depicting paleohydrography, water masses, mixing, and circulation patterns. This paper concentrates on the latter two applications.

In general terms, the use of $\delta^{18}O$ in studies of paleotemperature and paleosalinity is based on the change with temperature in isotopic fractionation between water and carbonate and the changes in the isotopic composition of sea water through evaporation and freshwater input (the freshwater budget). Here we concentrate on isotopic composition of seawater and not the water to carbonate fractionation processes (the so-called "temperature effect"). The freshwater budget not only influences the isotopic composition of seawater, but also its salinity. As a result, variations in $\delta^{18}O$ due to evaporation and freshwater input have gained the popular name "salinity effect," but would be more aptly termed "freshwater budget effect." A further process to be taken into account in paleoceanographic studies is the long-term isotopic enrichment of the oceans during glacial periods, caused by "fixation" of the lighter isotope ($^{16}O$) in ice sheets. This "glacial effect," the basis of $\delta^{18}O$-supported sea level studies, is essentially a long-term variant of the freshwater budget effect, since it originates in preferential uptake of $^{16}O$ during evaporation.

Paleosalinity studies using $\delta^{18}O$ records from fossil carbonate commonly involve a correction for the glacial effect according to an enrichment by $0.012 \pm 0.001$‰ per meter sea level lowering [*Labeyrie et al.*, 1987; *Shackleton*, 1987; *Fairbanks*, 1989]. Next, there is a correction for the temperature of calcification using seawater temperature estimates obtained by, for instance, assumptions, transfer functions, modern analog functions, or organic biomarkers ($U^{k}_{37}$). Finally, the remaining $\delta^{18}O$ deviation relative to present-day values (the $\delta^{18}O$ residual) is related to



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salinity, usually on the basis of linear regressions between modern salinity ($S$) and $\delta^{18}O$ measurements (i.e., linear $S$:$\delta^{18}O$ relationships). Uncertainties, errors and assumptions concerning input parameters propagate through this method of paleosalinity calculation from $\delta^{18}O$ residuals, and together define a practical error margin of at least $\pm 1$‰ in the resultant paleosalinity values.

For process-oriented studies of (paleo)hydrography, water masses, mixing, and circulation patterns, $\delta^{18}O$ data are employed (1) directly, represented in profiles or maps of the $\delta^{18}O$ distribution for a given period; or (2) after conversion into temperature and salinity information as outlined above. Both applications of: (1) $\delta^{18}O$-values directly to portray water masses and mixing; and (2) $\delta^{18}O$-derived salinity values using a $S$:$\delta^{18}O$ relationship are based on an underlying assumption that $\delta^{18}O$ in seawater may be treated as a more or less conservative property. However, these two applications use rather different interpretations of conservation. The first application assumes that $\delta^{18}O$ is representative of a water mass, just as salinity and potential temperature have traditionally been so treated, and that changes in $\delta^{18}O$ with position indicate degrees of mixing between different water masses. This technique has been extensively used in contemporary oceanography [e.g., *Weiss et al.*, 1979; *Fairbanks*, 1982; *Kipphut*, 1990; *Frew et al.*, 1995], particularly for tracing the influence of $^{18}O$-depleted terrestrial run-off in coastal waters. *Paren and Potter* [1984] showed that, theoretically, $S$:$\delta^{18}O$ mixing is slightly nonlinear, and that $(1\text{-}S)\delta^{18}O$ is the actual quantity that exhibits linear mixing with salinity. In practice, however, the difference is slight for noncoastal situations. This use of $\delta^{18}O$ to assess water mass mixing assumes no sources or sinks and so is not applicable in surface waters, where precipitation, evaporation, run-off, melting, or freezing [*Strain and Tan*, 1993] are significant terms in the freshwater budget, except where run-off is very important and can be regarded as a separate water mass of zero salinity.

The second application assumes, in contrast, that mixing of waters is unimportant and that the $S$:$\delta^{18}O$ relationship of seawater is due to the precipitation-evaporation cycle alone. This will only be true of surface waters of unchanging origin, away from significant riverine or glacial input, and in regions without permanent or seasonal sea ice. In addition, for paleosalinity studies, it is assumed that the $S$:$\delta^{18}O$ relationship of surface waters over a particular region is unchanging in time. This ratio is generally less than the theoretical value of 1:0.24 [*Dansgaard*, 1964] but varies significantly over the world ocean: 1:0.50 in the Atlantic and Pacific [*Broecker*, 1989]; between 1:0.41 [*Thunell et al.*, 1987], 1:0.35 [*Pierre et al.*, 1986], and 1:0.27 [*Pierre et al.*, 1986] in the Mediterranean (excluding four high salinity outliers; see Figure 1 and Table 1); and 1:0.28 in the Bay of Bengal [*Rostek et al.*, 1993]. Hence the assumption that the $S$:$\delta^{18}O$ relationship of surface waters over a particular region is constant through time relies on an underlying assumption that there is no variability in the evaporation-precipitation-reevaporation cycle that causes deviation from the theoretical value [*Epstein and Mayeda*, 1953; *Craig and Gordon*, 1965].

Although both applications of the $S$:$\delta^{18}O$ ratio are fundamentally different, they both rely on a linear relationship whereas examination of local $S$:$\delta^{18}O$ relationships in as near synoptic a fashion as possible might reveal nonlinearities (see, e.g., Figure 1 with analysis of significance of the quadratic fit in the caption [*Pierre et al.*, 1986]). Nonlinearity would imply nonconservative behaviour for $\delta^{18}O$. If, however, the nonlinearity can be reason ably assumed, or demonstrated, to be constant through time, then it may be easily corrected for. In that case, we use the term quasi-conservative for the behaviour of $\delta^{18}O$.

## 1.2. This Paper

Below we evaluate whether or not $\delta^{18}O$ may be safely used as a (quasi-)conservative property for the above-mentioned applications in marginal basins (section 2) and the ocean at large (section 3). For marginal basins this amounts to determining the relative importance of external sources and sinks for $\delta^{18}O$ compared with the advective terms. The eastern Mediterranean is chosen as a test area since it is a large marginal basin with a relatively well-studied salinity and $\delta^{18}O$ structure [e.g., *Pierre et al.*, 1986]. We present a simple mass-balanced box model for the surface to intermediate water circulation in the eastern Mediterranean Sea in which salinity and $\delta^{18}O$ budgets are calculated to determine what proportion of inflow through the Strait of Sicily is affected by the freshwater budget of the basin. Comparison of the results for salinity and $\delta^{18}O$ illustrates whether $\delta^{18}O$ shows the sufficiently conservative behaviour required to warrant its use as a (quasi-)conservative tracer on both the short (monthly to seasonal) timescales involved in contemporary oceanographic studies and the long (greater than several centuries) timescales involved in paleoceanographic reconstructions. Some restrictions are placed, however, with the long timescale applications. The Red Sea and Black Sea are discussed to investigate whether these restrictions are typical for the eastern Mediterranean only or whether they apply more generally to marginal basins.

In section 3 we consider the use of $\delta^{18}O$ for paleosalinity/hydrography work in the global ocean. We assess the assumptions underlying the most careful analyses to date [e.g., *Duplessy et al.*, 1993; *Wang et al.*, 1995] using simple analytical ideas and the results of an atmospheric general circulation model of the modern and last glacial maximum (LGM) [*Joussaume*, 1993]. We test two basic assumptions: first, that the $S$:$\delta^{18}O$ ratio is linear and has not changed over the last glacial cycle; and second, that the $\delta^{18}O$ of a parcel of seawater advected past a given location has not been significantly altered over the last glacial cycle by temporal changes in its trajectory. In examining the latter assumption we can ignore the integrated effect of evaporation/precipitation along the parcel's path because this is implicitly contained within the $S$:$\delta^{18}O$ ratio.

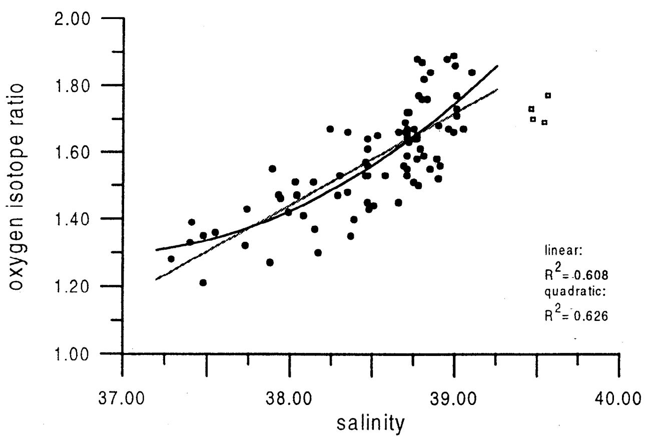


**Figure 1.** Modified after *Pierre et al.* [1986]. Plot of salinity (‰) versus $\delta^{18}O$ (SMOW, ‰) based on the Mediterranean measurements of *Pierre et al.* [1986]. Regression lines shown are for the data excluding the four very high salinity outliers (open squares). The grey line represents a linear fit ($\delta^{18}O$ = 0.276814 $S$ - 9.07815), and the black line represents a second-order polynomial fit ($\delta^{18}O$ = 0.098715 $S^2$ - 7.27788 $S$ + 135.438). The polynomial fit presents a better representation of the data at the 95% significance level, as demonstrated by the analysis of variance (ANOVA) in Table 1.

**Table 1.** Analysis of Variation

| Source of Variation | Sum of Squares | Degrees of Freedom | Mean Square | F test[a] |
|---|---|---|---|---|
| Linear Regression | 1.253 | 1 | 1.253 | A = 0.645/9.071 × $10^{-3}$ |
| Quadratic Regression | 1.290 | 2 | 0.645 | A = 71.08 |
| Addition by Quadratic | 0.036 | 1 | 0.036 | B = 0.036/9.071 × $10^{-3}$ |
| Quadratic Deviation | 0.771 | N-3 = 85 | 9.071 × $10^{-3}$ | B = 4.00 |
| Total Variation | 2.061 | N-1 = 87 | | |

[a] Following *Davis* [1986].
Ratio *A* tests the significance of the quadratic fit; ratio *B* tests the significance of improvement of the quadratic over the linear fit. F test tables show that both values are significant at the 95% level.

## 2. Marginal Basins

### 2.1. Eastern Mediterranean

All salinity and $\delta^{18}O$ measurements used here were obtained from sites in the eastern Mediterranean Sea within a short period of time (September-October 1986; *Pierre et al.* [1986]). This provides a "snapshot" view of the distribution of both properties, unaffected by interseasonal, annual, or decadal changes in the basin that might be in progress [cf. *Béthoux et al.*, 1990; *Leaman and Schott*, 1991; *Rohling and Bryden*, 1992].

Excess of evaporation over freshwater input determines an antiestuarine circulation in the Mediterranean with surface inflow of Atlantic water and subsurface outflow of Mediterranean waters through the Strait of Gibraltar. Exchange between the western and eastern basins through the Strait of Sicily is similar. Two layers are recognized in the inflow into the eastern Mediterranean: a more saline and warmer layer at the very surface and a less saline, cooler subsurface layer of waters that can be traced back to the original (Atlantic) inflow through the Strait of Gibraltar called modified Atlantic water (MAW) [e.g., *Manzella et al.*, 1988]. This subdivision results from the effects of evaporation and insolation at the very surface, while the water mass below is "shielded" from such interaction with the atmosphere. In the area between Cyprus and Rhodes, intensive evaporation sets up very high salinities at the very surface, and further buoyancy loss due to outbreaks of cold, dry air leads to convective overturn to depths between 100 and 600 m. The resultant water mass is called Levantine intermediate water (LIW) and spreads throughout the eastern Mediterranean between about 150 and 600 m water depth. LIW forms the main component of subsurface outflow from the eastern Mediterranean through the Strait of Sicily [*Wüst*, 1961].

We follow a simple mass-balanced box model approach to describe the distribution of conservative properties in the eastern Mediterranean surface to intermediate water system outlined above (Figure 2). The model allows for calculation of the concentration of a conservative property (*PR*) in the LIW box according to

$$PR_{LIW} = \frac{(\alpha V_{in} - X)\, PR_{surcyp} + (1 - \alpha)\, V_{in}\, PR_{in}}{V_{in} - X} \qquad (1)$$

Subscripts in and surcyp indicate a property associated with the inflow through the Strait of Sicily and at the surface in the Cyprus-Rhodes area, respectively. *V* is volume, and *X* is the excess of evaporation over freshwater input in the eastern basin of the Mediterranean (i.e., E-(P+R)). Coefficient $\alpha$ determines the proportion of inflow in the very surface layer which is influenced by excess evaporation (Figure 2). Coefficient 1-$\alpha$ determines the proportion of inflow that remains subsurface and unaffected by excess evaporation, thus providing a simplified representation of MAW [cf. *Manzella et al.*, 1988] (Figure 2).

The relative contributions of very surface waters and MAW to the formation of LIW can then be simply calculated by rearranging (1) to solve for $\alpha$, giving

$$\alpha = \frac{V_{in}\,(PR_{LIW} - PR_{in}) + X\,(PR_{surcyp} - PR_{LIW})}{V_{in}\,(PR_{surcyp} - PR_{in})} \qquad (2)$$

In (1) and (2), values for $V_{in}$ and $X$ are needed, which are related to one another via conservation of mass and salt according to $V_{in} = X\, S_{out} / (S_{out} - S_{in})$. Here $S_{in}$ stands for mean salinity of inflow, i.e., 37.81‰, and $S_{out}$ stands for mean salinity of outflow, i.e., 38.73‰, both measured at the Strait of Sicily (Table 2). The mean value $X = 9.15 \times 10^{11}$ m$^3$ yr$^{-1}$ is derived from *Sarmiento et al.* [1988]. Combined, these values determine a mean value of $V_{in} = 3.85 \times 10^{13}$ m$^3$ yr$^{-1}$. *Manzella et al.* [1988] found about double that value from current meter measurements, which might indicate that the value for *X* above underestimates the actual value. However, since $V_{in}$ and *X* are essentially related according to a constant (the much easier to determine ratio of salinities) and therefore change strictly proportionally to one another, the magnitudes per se do not influence the calculations in this paper.

There are inaccuracies, uncertainties, errors, etc. involved in every input parameter (listed as $\Delta$ values in Table 2), and their combined influence on the accuracy of $\alpha$ should be determined. The first step in the error analysis concerns the error in the calculated value of $V_{in}$, which is expressed as $\Delta V_{in}$ and depends on propagation of the errors $\Delta S_{in}$, $\Delta S_{out}$, and $\Delta X$ through the equation $V_{in} = X\, S_{out} / (S_{out} - S_{in})$. It is calculated [*Squires*, 1988] according to

$$(\Delta V_{in})^2 = \left(\frac{\partial V_{in}}{\partial S_{in}}\,\Delta S_{in}\right)^2 + \left(\frac{\partial V_{in}}{\partial S_{out}}\,\Delta S_{out}\right)^2 + \left(\frac{\partial V_{in}}{\partial X}\,\Delta X\right)^2 \qquad (3)$$

This gives an error in $\Delta V_{in}$ equivalent to $\pm 23\%$ of the calculated value of $V_{in}$. This may seem very large, but the error propagation through (2) is such that neither $\Delta V_{in}$ nor $\Delta X$ is of any importance to the accuracy of the calculated value for $\alpha$. The error in $\alpha$ (i.e., $\Delta\alpha$) depends on propagation of the errors $\Delta PR_{in}$, $\Delta PR_{surcyp}$, $\Delta PR_{LIW}$, $\Delta V_{in}$ and $\Delta X$ through equation (2) and is calculated following the same method as that shown in (3).

Appropriate values for *S* or $\delta^{18}O$ (Table 2) can be used in (2), to find $\alpha$. In the case of salinity, $\alpha = 0.77$ and $\Delta\alpha = \pm 0.15$, implying that $77 \pm 15\%$ of the water contributing to LIW formation was affected by the freshwater budget.

If $\delta^{18}O$ is taken to be a conserved quantity, then using the values in Table 2, $\alpha = 0.94 \pm 0.52$. If *Paren and Potter* [1984] are followed, taking $(1\text{-}S)\delta^{18}O$ as the conserved quantity, then $\alpha$ is identical to two significant figures. Given the error bars and that the simple model does not allow mixing or diffusion between the surface and subsurface waters between the Strait of Sicily and Cyprus, this $\delta^{18}$O-based estimate is more or less compatible with the salinity-based estimate for $\alpha$. Roughly 80% of LIW has come from water that was affected by the atmosphere in the eastern Mediterranean, while some 20% can be thought to derive from unaltered subsurface MAW. This result also shows that advection and the local freshwater budget are both important in determining the properties of water in marginal basins.

It is worth considering the origin of the error bars in these two computations of $\alpha$. Figure 2c shows that more than 95% of $(\Delta\alpha)^2$ in the salinity determination is due to the wide ranges of values reported for salinity of surface water in the Cyprus area ($S_{surcyp}$) and of LIW ($S_{LIW}$). Similarly, Figure 2d for the computation using $\delta^{18}$O shows that some 99% of $(\Delta\alpha)^2$ derives from the scatter in $\delta^{18}$O values observed in LIW and at the surface in the Cyprus area.

The results for the eastern Mediterranean suggest that $\delta^{18}$O may be used with some confidence as a tracer in marginal basins in spite of the presence of significant external sink and source terms for $\delta^{18}$O related to the freshwater budget. In other words, $\delta^{18}$O seems to show a sufficiently quasi-conservative behaviour on the short (monthly to seasonal) timescales involved in contemporary oceanographic surveys to warrant its use as a quasi-conservative tracer.

On longer geological timescales (greater than several centuries), there are complications. Changing climatic conditions would cause variability in the flux rates for the various terms in the freshwater budget, and in their individual isotopic compositions (see examples in Table 3). Then, substantial temporal variability in the $S$:$\delta^{18}$O nonlinearity should be expected. Consequently, $\delta^{18}$O may only be considered a quasi-conservative property on these longer timescales if supported by a comprehensive understanding of the fluxes and $\delta^{18}$O compositions of the main freshwater terms. This prerequisite severely complicates the use of $\delta^{18}$O for paleosalinity and paleocirculation reconstructions, as suggested by *Bigg* [1995].

### 2.2. Red Sea

The above discussion implies that the $S$:$\delta^{18}$O relationship shown by contemporary oceanographic data should show a near-linear trend in basins with a very simple (one term) freshwater budget. The modern Red Sea is such a basin, characterized by very high evaporation (about 2 m yr$^{-1}$) and negligible freshwater input from run-off and precipitation (no more than 5% of the amount evaporated each year) [*Pedgley*, 1974; *Grasshoff*, 1975].

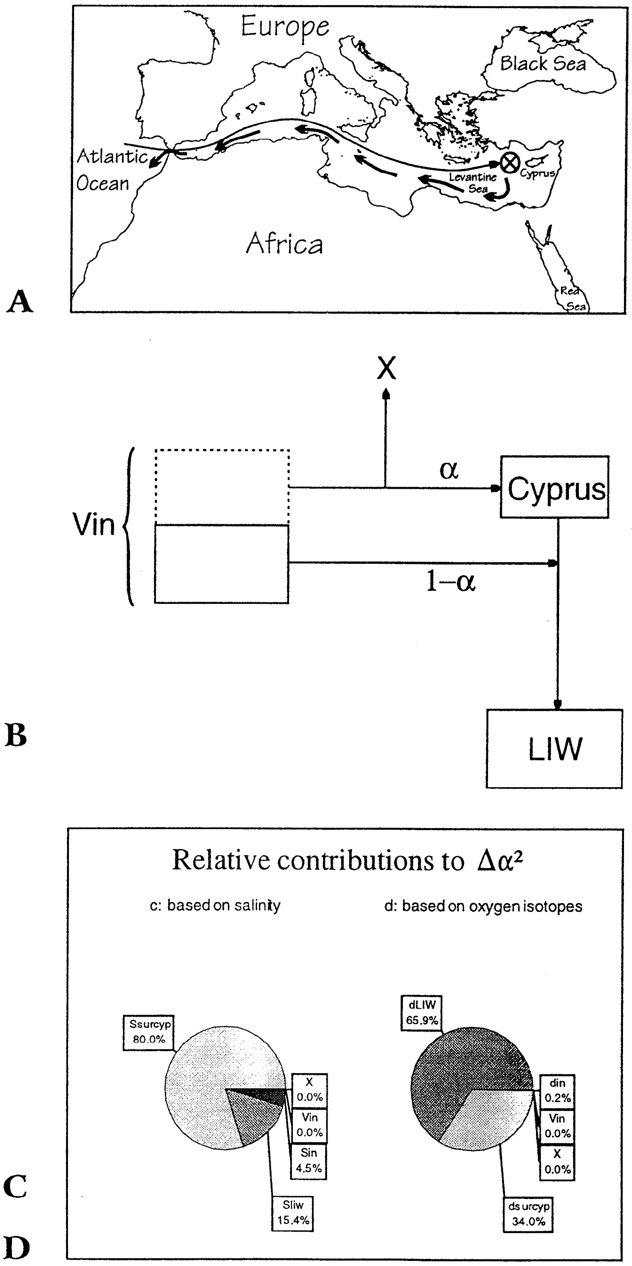


**Figure 2.** (opposite) (a) Schematic presentation of the trajectory of surface waters of Atlantic origin toward the NE Levantine basin where it is transformed into Levantine intermediate water (LIW), which subsequently forms the main component of subsurface outflow through the Straits of Sicily and Gibraltar. (b) Mass-balanced box-model for the description of conservative property distribution in the eastern Mediterranean surface to intermediate water system. Surface water originates from inflow through the Strait of Sicily and is represented by two boxes describing (1) waters transported at the very surface and directly subjected to the freshwater budget (evaporation E, run-off R, and precipitation P), and (2) waters transported in a subsurface layer and not influenced by the freshwater budget. Contrary to reality, the model allows no mixing between these two water masses until the final mixing occurs that produces Levantine intermediate water (LIW). Although such strict "separation" may not be fully realistic, it does provide an adequate method for estimating the relative contributions of the surface and subsurface inflowing water masses to the formation of LIW. The subsurface inflow through the Strait of Sicily portrayed in the model may be viewed as a simplified representation of the subsurface inflow of so-called modified Atlantic water (MAW) [cf. *Manzella et al.*, 1988], which can be recognized as far eastward as the Levantine basin [e.g., *Malanotte-Rizzoli and Bergamasco*, 1989]. Therefore we use the name MAW for it in the text. (c) Pie chart showing the relative contributions of errors in the various parameters to make up the error $(\Delta\alpha)^2$ for the calculations based on salinity values. It is obvious that the contributions of errors in $X$ and $V_{in}$ are negligible, that the error in $S_{in}$ contributes only very little, and that the errors in $S_{LIW}$ and in particular $S_{surcyp}$ constitute the bulk of $(\Delta\alpha)^2$. Abbreviations in the labels: Ssurcyp = $\Delta S_{surcyp}$; Sliw = $\Delta S_{LIW}$; Sin = $\Delta S_{in}$; Vin = $\Delta V_{in}$; and X = $\Delta X$. (d) Pie chart showing the relative contributions of errors in the various parameters to make up the error $(\Delta\alpha)^2$ for the calculations based on $\delta^{18}$O values. It is obvious that the contributions of errors in $X$, $V_{in}$, and $\delta^{18}O_{in}$ are negligible, and that the errors in $\delta^{18}O_{surcyp}$ and in particular $\delta^{18}O_{LIW}$ constitute the bulk of $(\Delta\alpha)^2$. Abbreviations in the labels: dsurcyp = $\Delta\delta^{18}O_{surcyp}$; dliw = $\Delta\delta^{18}O_{LIW}$; din = $\Delta\delta^{18}O_{in}$; Vin = $\Delta V_{in}$; and X = $\Delta X$.

**Table 2.** Means and Error Margins for Salinity and $\delta^{18}O$ Values Used in the Box Model

| | Salinity, ‰ | Error, ± ‰ | $\delta^{18}O$, ‰ | Error, ± ‰ |
|---|---|---|---|---|
| Inflow[a] | $S_{in} = 37.81$ | $\Delta S_{in} = 0.18$ | $\delta^{18}O_{in} = 1.41$ | $\Delta\delta^{18}O_{in} = 0.10$ |
| Outflow[b] | $S_{out} = 38.73$ | $\Delta S_{out} = 0.05$ | $\delta^{18}O_{out} = 1.63$ | $\Delta\delta^{18}O_{out} = 0.14$ |
| Surface Near Cyprus[c] | $S_{surcyp} = 39.18$ | $\Delta S_{surcyp} = 0.24$ | $\delta^{18}O_{surcyp} = 1.71$ | $\Delta\delta^{18}O_{surcyp} = 0.10$ |
| LIW[d] | $S_{LIW} = 38.85$ | $\Delta S_{LIW} = 0.08$ | $\delta^{18}O_{LIW} = 1.69$ | $\Delta\delta^{18}O_{LIW} = 0.13$ |

All salinity and isotope values are from *Pierre et al.* [1986]. The volume of excess evaporation $X$ is $9.15\times10^{11}$ m$^3$ yr$^{-1}$ [from *Sarmiento et al.*, 1988]; the error $\Delta X$ is $\pm9.15\times10^{10}$ m$^3$ yr$^{-1}$ and is based on an assumed ±10% range.
[a] 0-105 m in Strait of Sicily
[b] 150-500 m in Strait of Sicily.
[c] 0-100 m at Rhodian and Anatolian stations.
[d] 150-500 m in Ionian, Rhodian, and Anatolian stations.

In the absence of temporally variable $\delta^{18}O$ sources from freshwater input the present-day S:$\delta^{18}O$ data are indeed found to be distributed in a very linear fashion, with a slope of 1:0.29 [*Craig*, 1966; 1969].

*Rohling* [1994] argued that no substantial change occurred between LGM and modern rates of net evaporation from the Red Sea, so that the $S$:$\delta^{18}O$ relationship should have been similar. However, a budget of oxygen isotope input, output and reservoir values for the Red Sea [from *Locke*, 1986; *Locke and Thunell*, 1988; *Thunell et al.*, 1988; *Andrié and Merlivat*, 1989] does suggest change in the $S$:$\delta^{18}O$ relationship, apparently due to variation in the $\delta^{18}O$ of evaporated water from about -10‰ today to a glacial value of about -5‰ [*Rohling*, 1994]. This was explained in terms of increased mean wind speed over the basin (> 7 m s$^{-1}$ during the LGM *versus* about 5 m s$^{-1}$ today [*Cember*, 1989]) related to increased vigor of the LGM winter (NE) monsoon since an increase to > 7 m s$^{-1}$ would cause a rapid "step wise" decrease in the kinematic fractionation factor for $^{18}O$ with evaporation [*Merlivat and Jouzel*, 1979]. New isotopic data for the glacial Red Sea [*Hemleben et al.*, 1996], however, show a much higher mean isotopic value for the LGM Red Sea than the previous data sets [*Locke*, 1986; *Locke and Thunell*, 1988; *Thunell et al.*, 1988]. Fed through *Rohling*'s [1994] calculations, this new value would refute the perceived change in the $\delta^{18}O$ of evaporated water between the LGM and the present. Obviously, more study is needed to investigate this discrepancy as it funda mentally influences conclusions on the applicability of the modern $S$:$\delta^{18}O$ relationship for paleoceanographic purposes in the Red Sea.

### 2.3. Black Sea

The Black Sea is a "dilution basin" where the positive freshwater budget (E<P+R) causes an estuarine exchange at the connection (Bosporus Strait) between the Black Sea and the Aegean Sea. Subsurface Aegean water with ($S$, $\delta^{18}O$) characteristics of about (38.5, 1.8) flow into the Black Sea. Dilution of this inflow by the net freshwater influx results in Black Sea surface waters averaged over the upper 100 m with ($S$, $\delta^{18}O$) characteristics of about (19, -2.5) [*Swart*, 1991a; 1991b]. The volume fluxes and isotopic

**Table 3.** Examples of Recorded Changes in Freshwater Fluxes, $\delta^{18}O$ Compositions of Freshwater Terms, and Geographic Shifts of Sea-Ice Related Processes (Freezing/Melting)

| Where | When | Flux or $\delta^{18}O$ Variation | References |
|---|---|---|---|
| Nile River | Holocene climatic optimum | Discharge volume increased by factor of 2 compared to modern pre-Aswan dam values | *Rossignol-Strick et al.* [1982] and *Béthoux* [1984] |
| Eastern Mediterranean | last glacial maximum | precipitation 4 to 2‰ less depleted in $\delta^{18}O$ than today | *Sonntag et al.* [1978], *Joussaume and Jouzel* [1993], and overview by *Bigg* [1995] |
| North Atlantic | last glacial maximum | sea-ice influences extended further south than today | [*CLIMAP*, 1981] (see Figure 4) |
| Northern North Atlantic | last glacial maximum | freshwater from surrounding land mass depleted in excess of 30‰ in $\delta^{18}O$ because of the presence of glacial ice | *Craig and Gordon* [1965], *Yapp and Epstein* [1977], and *Joussaume and Jouzel* [1993] (see section 3.1.3) |
| Red Sea | last glacial maximum | isotopic fractionation during evaporation halved relative to present. Possibly because of variation in mean wind speed | [*Rohling*, 1994] |
| Paleo-Nile catchment area | ~ 120,000 years B.P. | Lacustrine carbonates reflect mean $\delta^{18}O$ around -9.5‰ compared with modern -2‰ | *McKenzie* [1993] *Rossignol Strick et al.* [1982] |

compositions of precipitation and evaporation into the basin are similar to one another and therefore virtually cancel each other out. Consequently, the freshwater end-member for the mixing line is more or less determined by the river input, with ($S$, $\delta^{18}O$) characteristics of (0, -10) [*Swart*, 1991a,b]. The Black Sea surface water $S$:$\delta^{18}O$ relationship could thus be approximated by $\delta^{18}O = (1.8+10)/38.5\ S - 10$ or $\delta^{18}O = 0.30S - 10$. With the modern average salinity of about 19‰ in the upper 100 m this linear equation predicts an isotopic ratio of about -4.3‰. However, the observed value is only -2.5‰, which would correspond to a salinity of 25‰. This illustrates that in reality, mixing in the Black Sea does not occur in a linear fashion between net freshwater input with ($S$, $\delta^{18}O$) of (0, -10) and marine Aegean input of (38.5, 1.8), but instead shows a distinctly convex pathway through Black Sea surface water (19, -2.5), and Black Sea deep water (22.3, -1.7) [*Swart*, 1991a,b]. From *Swart*'s [1991a,b] box model it may be inferred that this nonlinearity results from a "recirculation process": (1) about 4.5 units of ambient Black Sea waters are entrained with every 1 unit of subsurface inflow from the Aegean Sea; (2) together these form Black Sea deep water, which (3) owing to the estuarine circulation in the basin, subsequently rises to interact with the freshwater budget, thus producing Black Sea surface water, and so completing one cycle of the recirculation. The resultant nonlinear mixing line suggests the addition of a "third component" to the mixing relationship of the Black Sea somewhere during the recirculation process, which is hard to speculate on without further detailed investigations.

If the above inference is correct, that marine inflow and entrainment of ambient waters importantly modifies the pathway of mixing lines in the Black Sea $S$:$\delta^{18}O$ plot, then it is interesting to conceptualize changes in the basin's $S$:$\delta^{18}O$ relationship during the last deglaciation (Figure 3). Exchange between the Black Sea and Aegean Sea is limited by the only 40 m deep Bosporus strait. The sea level rise from -120 m at the last glacial maximum reached sill depth around 10,000 calendar years ago [*Fairbanks*, 1989], but the critical sill depth required for two-layered exchange was only reached around 1000 years later [*Lane-Serff et al.*, 1997]. Before critical sill depth was reached the Black Sea essentially was "Black Lake", with outflow over the sill compensating for the net freshwater gain. In the absence of subsurface Aegean inflow, only the freshwater budget would have influenced salinity and $\delta^{18}O$ in Black Lake. The only variations to be expected therefore would consist of a background signal of $\delta^{18}O$ variability during the course of deglaciation, as atmospheric temperature rose and modified the $\delta^{18}O$ of precipitation while glacial drainage patterns into the basin evolved. When, around 9000 years ago, critical sill depth was established, Aegean waters began to trickle into Black Lake. Initially, all ambient waters entrained with this Aegean inflow were of the fresh Black Lake type, and mixing would have followed simple near linear path ways connecting the net freshwater and marine components entering the basin. With rising sea level, Aegean inflow increased, causing Black Lake waters to be expelled from the basin over a period of about 3500 years [*Lane-Serff et al.*, 1997]. As Aegean inflow increased, the volume of entrained ambient waters likely increased as well. At the same time the longer-term effect of marine inflow from the Aegean caused a change in the character of the entrained waters from the initial, fresh, preconnection Black Lake waters to increasingly marine influenced (brackish) waters. Resultant changes in the $S$:$\delta^{18}O$ relationship are conceptualized in Figure 3. The conclusion here must be that oxygen isotope ratios from fossils might only be used to reliably estimate paleosalinities in the Black Sea when supported by sufficient understanding of the histories of the volume fluxes and isotopic compositions of the water mass exchange through the Bosporus Strait, of the general Black Sea circulation and possible internal recirculation, and of the fluxes and compositions of the various terms in the freshwater budget.

## 3. Open Ocean

Two basic assumptions are made in paleosalinity reconstructions. First, the surface $S$:$\delta^{18}O$ ratio of the region is considered to be invariant with time. Second, the relative geographical distribution of surface $\delta^{18}O$, neglecting the impact of the local freshwater budget and ice volume effects, is also considered to be invariant with time. Both assumptions are inextricably linked with both the atmosphere and the ocean; we examine each in turn.

### 3.1. Permanence of the S:$\delta^{18}O$ Ratio in Time

**3.1.1. Local freshwater budget influences.** Like salinity the $\delta^{18}O$ of surface water changes in response to the local freshwater budget (i.e., evaporation, precipitation, and run-off), as well as to advection. Unlike salinity, however, $\delta^{18}O$ values are not constant and equal to 0‰ for all terms in the freshwater budget.

Isotopic compositions of river run-off cover a wide range of different values and essentially reflect an integration of the range observed in precipitation over the total catchment area and possible melt-water contributions (Table 4). The $\delta^{18}O$ values of precipitation over the global oceans show a rough zonality, from values > -2‰ around the equator to strongly depleted values of -10‰ in polar seas [*Rossinsky and Swart*, 1993] to as low as -30‰ over the ice sheets [*Joussaume and Jouzel*, 1993]. The zonality is disturbed by meridional components in the atmospheric circulation, most notably in the NW Pacific and North Atlantic.

As a result of the variety of $\delta^{18}O$ values observed in freshwater terms, significant variability in the $S$:$\delta^{18}O$ relationship should be expected in any place where the freshwater terms are significant relative to advection. Consequently, influences of the local freshwater budget will be most notable in marginal basins and coastal regions (cf. section 2), and of lesser importance to the open ocean. The major supplies of freshwater to the global ocean may, however, have a much wider impact on the base $\delta^{18}O$ of water masses that make up a large portion of the global ocean. Before considering this wider influence of the freshwater budget we discuss two examples of how known changes to the freshwater budget in the Quaternary affected the local $S$:$\delta^{18}O$ ratio: (1) the Atlantic coastal waters of the United States, where *Fairbanks* [1982] provides a good knowledge of present day conditions, and (2) the Bay of Bengal, where *Rostek et al.* [1993] provide data. Both regions experienced radically different climates during the last glacial maximum (LGM) compared to the present; glacial meltwater would have been a major input to U.S. coastal waters, while over the Indian subcontinent the monsoon was significantly weaker [*Bigg and Jiang*, 1993].

The $S$:$\delta^{18}O$ ratio of the modern near-surface waters of the New York Bight shows strong seasonal modulation [see *Fairbanks*, 1982, Figure 11] because of the $\delta^{18}O$ signature of the run-off. The best fit line for New York Bight data on *Fairbanks*' [1982] Figure 10, representing data from spring to midsummer, shows a modern $S$:$\delta^{18}O$ ratio of 1:0.26. The zero-salinity intercept of -9.5‰ of this line of best fit is consistent with a freshwater source from the Hudson River [*Fairbanks*, 1982]. Note that the slope of this line of best fit is midway between the local extremes found in March and off the shelf. March is characterised by a large melting sea-ice contribution and effectively no variation of $\delta^{18}O$ with salinity (despite the fact that the coastal run-off is approaching its annual maximum [*UNESCO*, 1971]). Off the

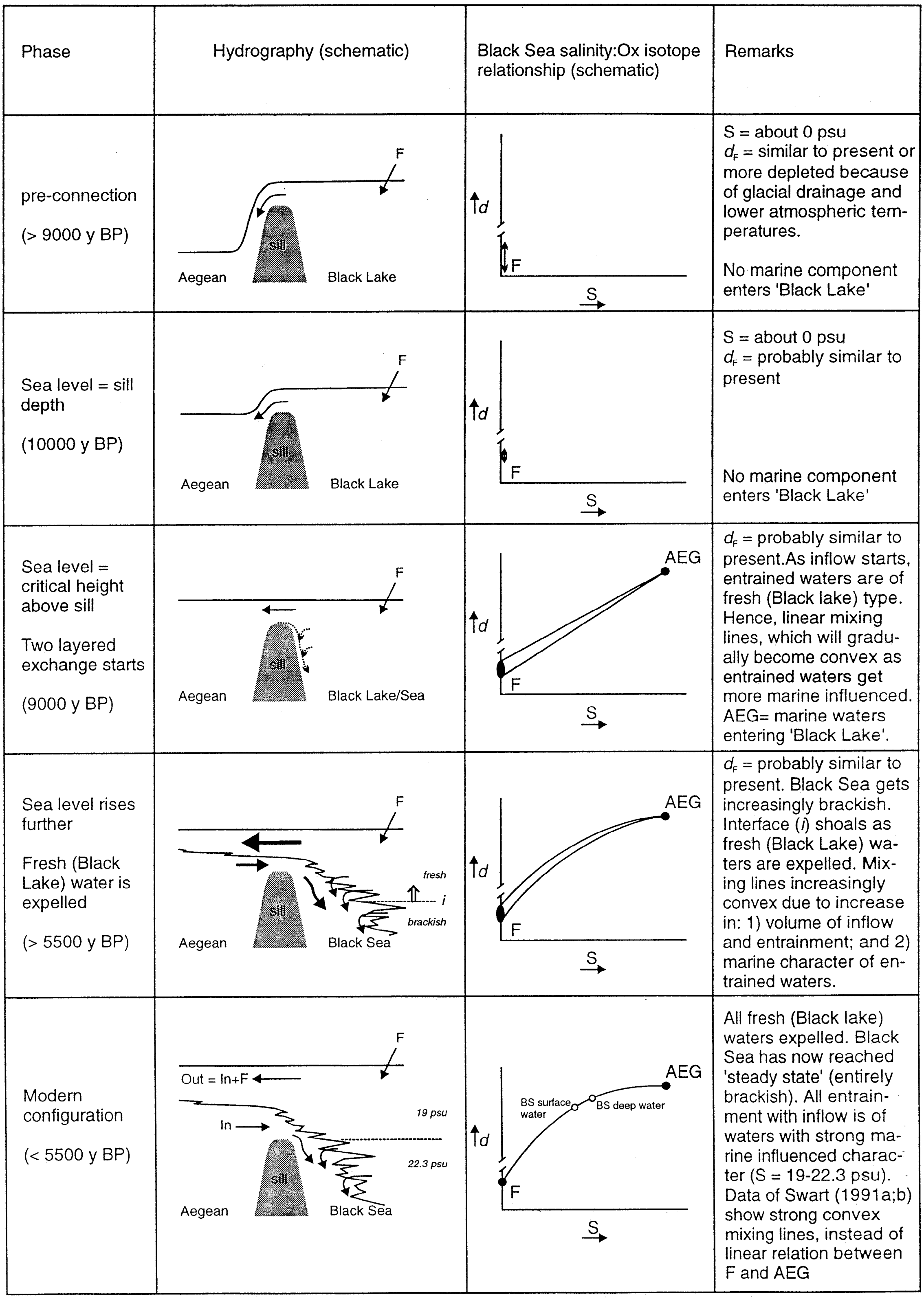


**Figure 3.** Schematic representation of the Black Sea - Aegean Sea connection due to postglacial sea level rise [after *Lane-Serff et al.*, 1997] and the conceptualized effects on the $S$:$\delta^{18}O$ relationship in the Black Sea drawing on interpretation of the box model results of *Swart* [1991a,b]. $F$ stands for the net freshwater input, *AEG* stands for Aegean inflow, $S$ stands for salinity, and $d$ stands for $\delta^{18}O$. Ages are in calendar years, after *Lane-Serff et al.* [1997].

**Table 4.** Examples of isotopic compositions in modern rivers

| River/Catchment basin | Average Isotopic | References |
|---|---|---|
| Nile River | $\delta^{18}O \approx -2‰$ | *Rossignol-Strick et al.* [1982] |
| Basins from which Eurasian rivers discharge into Mediterranean | $-10‰ \leq \delta^{18}O < -5‰$ | *Rozanski et al.* [1993] |
| Eastern Amazon basin | $-5.0‰ < \delta^{18}O < -3.4‰$ | *Bird et al.* [1993] |
| Orinoco (Venezuela) | $-9‰ < \delta^{18}O < -4‰$ | *Mook* [1982] |
| Parana (Argentina) | $-4.5‰ < \delta^{18}O < -3.5‰$ | *Mook* [1982] |
| Indus (Pakistan) | $-11.5‰ < \delta^{18}O < -9‰$ | *Mook* [1982] |
| MacKenzie (Canada) | $-21‰ < \delta^{18}O < -18‰$ | *Mook* [1982] |

shelf, the $S$:$\delta^{18}O$ ratio shows little seasonal variation around 1:0.63 [*Fairbanks*, 1982]

To estimate the impact of changing climate on this 1:0.26 ratio, we use the -17‰ oxygen isotope hindcast of LGM precipitation (and hence run-off) for the northeast coast of the United States [*Joussaume and Jouzel*, 1993]. We assume, as is done in paleosalinity determinations, that the only change to the present offshore water ($S$, $\delta^{18}O$) of (36.0, 1.0) [see *Fairbanks*, 1982, Figure 7] results from the global concentrating effects related to 120 m glacial sea level lowering [*Fairbanks*, 1989] in today's mean ocean depth of 3800 m [*Pickard and Emery*, 1982], and the sequestration of $^{18}O$-poor water in the ice sheets (e.g., *Shackleton* [1987] and section 1 above). These glacial enrichments lead to LGM offshore ($S$, $\delta^{18}O$) values of (37.1, 2.4). The said run-off and offshore values lead to an LGM mixing line of $\delta^{18}O = 0.52S - 17$, demonstrating that even a change in only glacial run-off, but not in the local evaporation-precipitation balance, would be likely to have caused a change in the $S$:$\delta^{18}O$ ratio by a factor of two, relative to the present. Thus, for example, using today's $S$:$\delta^{18}O$ ratio in interpreting a LGM increase in $\delta^{18}O$ of 0.5 to 1‰, after accounting for the above concentrating effects, would lead to over-estimates of 0.9 to 1.8‰ in salinity, respectively. It is worth noting that these estimates assume a local origin for the LGM meltwater when it might, in fact, have derived from regions of the Laurentide ice sheet with considerably lower $\delta^{18}O$ levels, resulting in an even steeper $S$:$\delta^{18}O$ slope. Furthermore, the above estimates also ignore any effect of the LGM circulation patterns of the North Atlantic which could potentially have altered the offshore limit.

The second example concerns the distinctly different environment of the Bay of Bengal, which was shielded from direct glacial ice sheet influences. The LGM intensity of its characteristic monsoonal circulation, however, was significantly reduced relative to the present, causing reductions in precipitation over the Himalayas and run-off into the Bay of Bengal (overview in *Bigg and Jiang* [1993]).

Today, surface water in the Bay of Bengal is significantly diluted by river run-off. A typical surface salinity in the center of the Bay at approximately 15°N and 90°E is 32.5‰. The salinity of the main Indian Ocean south of India is roughly 34.5‰ [*Gorshkov*, 1978]. The surface waters of the Bay, therefore, appear to be diluted by roughly 5% fresh waters from the Ganges, Brahmaputra and Irrawaddy Rivers. Simulation of LGM climate indicates little change in the oxygen isotopic ratio of precipitation (-10‰) over the Himalayas from today, in spite of a substantial decrease in rainfall by as much as 90% [*Joussaume and Jouzel*, 1993]. This would imply that the reduction of surface salinity in the Bay due to riverine dilution likely was of order 0.2‰ compared to 2‰ today, a difference of 1.8‰ caused by remote, rather than local, freshwater effects. *Rostek et al.* [1993] demonstrate a modern Bay of Bengal $S$:$\delta^{18}O$ ratio of 1:0.28, giving $\delta^{18}O = 0.28S - 10$. Altering the modern ($S$, $\delta^{18}O$) endpoints of the line, (0, -10) and (34.5, -0.3), to (0, -10) (i.e., no landward change) and (35.6, 1.1) (taking into account glacial enrichment processes as above), respectively, gives a slope of the mixing line of 11.1/35.6 = 0.31, so that the LGM mixing relation would be $\delta^{18}O = 0.31S - 10$. The $S$:$\delta^{18}O$ ratio seems therefore not to have changed substantially, but the bias in base $\delta^{18}O$ of the glacial seawater (due to altered dilution) could be misinterpreted as a spurious temperature change.

**3.1.2. Open ocean freshwater budget influences.** The examples in section 3.1.1 illustrate the sensitivity of coastally dominated waters to climatically driven changes in the base $\delta^{18}O$ of seawater. However, the influence of changes in the freshwater budget is not restricted to local or regional scales. The modern North Atlantic $\delta^{18}O$ shows a strong underlying signal of an Arctic freshwater source with $\delta^{18}O = -21.7‰$ [*Craig and Gordon*, 1965; *Fairbanks*, 1982; R.D. Frew et al., The oxygen isotope composition of water masses in the northeastern North Atlantic, submitted to *Journal of Geophysical Research*, 1996 (hereinafter referred to as Frew et al, 1996)]. This is the freshwater end-member for $\delta^{18}O$ mixing lines over the entire subpolar North Atlantic. A similar freshwater end-member is found in the northeast Pacific [*Kipphut*, 1990].

The low $\delta^{18}O$ of this end-member is due to significant contributions from marine precipitation (average Arctic value of -21±0.7‰ [*Östlund and Hut*, 1984]) and glacial meltwater from calving ice originating from the high ice cap of central Greenland (west Greenland observation of -21.7‰ [*Bédard et al.*, 1981]). Arctic riverine and other glacial meltwater inputs generally do not contain such $^{18}O$-depleted water (for example, Mackenzie River in Canadian Arctic: -18.9‰ [*Macdonald et al.*, 1995]; western Russian Arctic including major rivers: down to -18.9‰ but becoming much less depleted to the west [*Brezgunov*, 1990; *Létolle et al.*, 1993]). Only in the very eastern Siberian Arctic is the $\delta^{18}O$ of river water more depleted (down to -24‰ in the Kolyma River [*Létolle et al.*, 1993]), but those rivers have only a tenth of the flow of the significantly less depleted western Russian Arctic rivers [*UNESCO*, 1971].

During the LGM the general Arctic source was likely to be significantly more depleted in $^{18}O$ because of the much more extensive area of high glaciation and the colder conditions in the Arctic that would have resulted in more $^{18}O$-depleted LGM marine precipitation [cf. *Joussaume and Jouzel*, 1993]. As argued in section 3.1.1, a significant change to the freshwater end-member would influence the slope of the $S$:$\delta^{18}O$ relationship. The possible LGM change in this slope can be assessed on the basis of the LGM simulation of *Joussaume and Jouzel* [1993], which indicates that over the Arctic and northern Eurasia, $\delta^{18}O$ of LGM precipitation was further depleted by an average 6‰, compared to the present, with a depletion of some 8‰ over the high icefields (compared to modern day central Greenland). Given the greater proportion of high-altitude glacial meltwater that would have contributed to the LGM Arctic freshwater budget, depletion in the LGM Arctic freshwater end-member by 7‰ relative to the present -21.7‰ (to -28.7‰) does not seem unreasonable. Today the subpolar $S$:$\delta^{18}O$ mixing line has a salty, subtropical, end-member with ($S$, $\delta^{18}O$) of (36.0, 1.0) (see section 3.1.1). Again, assuming that the only alteration to glacial $S$ and $\delta^{18}O$ at this point on the mixing line is due to the global enrichments discussed earlier, the salty marine end of the mixing line was (37.1, 2.4) (see section 3.1.1). Consequently, the present day mixing line of $\delta^{18}O = 0.63S - 21.7$ would have been very different at glacial times, namely, $\delta^{18}O = 0.84S - 28.7$.

These simple arguments demonstrate that realistic adjustment of the freshwater end-member of subpolar waters in the LGM North Atlantic would steepen the $S$:$\delta^{18}O$ ratio by about a third. Therefore ascribing a change in foraminiferal $\delta^{18}O$ of 0.5 or 1‰ purely to the salinity effect using the present-day $S$:$\delta^{18}O$ ratio would cause an error of 0.2‰ or 0.4‰ in the inferred LGM salinity. Moreover, this calculation likely predicts only a minimum error. More meltwater potentially entered the North Atlantic from the glaciers south of the Arctic, presenting yet another source of $\delta^{18}O$-depleted freshwater to be considered in mixing reconstructions. Also, the glacial polar front was positioned further south than at present. Today the $S$:$\delta^{18}O$ ratio of subtropical Atlantic water equals 1:0.5 [*Broecker*, 1989]. If this ratio were used to hindcast LGM salinity in the midlatitudes, where subtropical water today was replaced by subpolar water, then an even bigger error in hindcast salinity would result.

There are further implications. It is usually assumed in paleosalinity reconstructions that the local $S$:$\delta^{18}O$ ratio is caused uniquely by the local evaporation-precipitation balance (see section 1.1, application 2). *Bigg* [1995] has already shown this to be unlikely for the semi-enclosed waters of the Mediterranean. Similarly, the discussions in section 3.1.1 and section 3.1.2 suggest that mixing, and thus advection, is the predominant factor determining the $S$:$\delta^{18}O$ ratio in North Atlantic subpolar waters. This would imply that most of the regional or basin-scale $S$:$\delta^{18}O$ ratios exceeding the theoretical evaporation-precipitation balance ratio of 1:0.24 [*Dansgaard*, 1964] are not due to atmospheric recycling [*Epstein and Mayeda*, 1953; *Craig and Gordon*, 1965] but to advection and mixing processes.

**3.1.3. Sea ice influences.** *Strain and Tan* [1993] demonstrated that the melting-freezing cycle introduces nonlinearities to the $S$:$\delta^{18}O$ relationship through the contrast between small $^{18}O/^{16}O$ fractionation and large rejection of salt during freezing. Indeed, enrichment of ice in $^{18}O$ at the expense of the water from which it is formed (by $2.57 \pm 0.10$‰ [*Macdonald et al.*, 1995]) adds to this nonlinearity. These nonlinearities cannot be removed by use of $(1\text{-}S)\delta^{18}O$ instead of $\delta^{18}O$. Melting flattens the $S$:$\delta^{18}O$ curve for lower salinities (Figure 4) and freezing steepens it, although less dramatically. Consequently, significant changes in the near-surface $S$:$\delta^{18}O$ relationship can occur during spring and summer before the upper ocean water column is fully mixed in autumn. The changes are not necessarily reversible; increased surface salinity during freezing can lead to convection and transport of existing surface waters into the ocean interior. Frew et al. (1996) illustrated this process in the modern North Atlantic during the formation of Labrador Sea water. As a result, even in the absence of coastal and open ocean freshwater budget influences (section 3.1.1 and section 3.1.2), the existing slope, and indeed the linearity, of the paleo-$S$:$\delta^{18}O$ relationship cannot be guaranteed in regions of temperate and polar seas with varying sea ice conditions over the period of salinity reconstruction.

For example, consider the change in the near-surface $S$:$\delta^{18}O$ ratio a month after the melting of both 1 and 3 m thick layers of seaice using realistic melt rates and vertical exchange velocities [*Strain and Tan*, 1993]. This lag roughly represents the time by which a spring bloom peak in foraminiferal production would occur, providing the fossil carbonate remains employed by paleoceanographers for $\delta^{18}O$ analysis to reconstruct paleoenvironmental conditions. Open ocean seasonal sea ice in the northern Atlantic and Greenland Sea typically only attains a thickness of 1 m, but thicknesses of up to 3 m may be reached in more enclosed seas like Baffin Bay or the eastern Russian Arctic [*Bourke and Garrett*, 1987].

Figure 4 shows the impact of *Strain and Tan*'s [1993] melting model on the $S$:$\delta^{18}O$ ratio of the upper ocean for these two ice

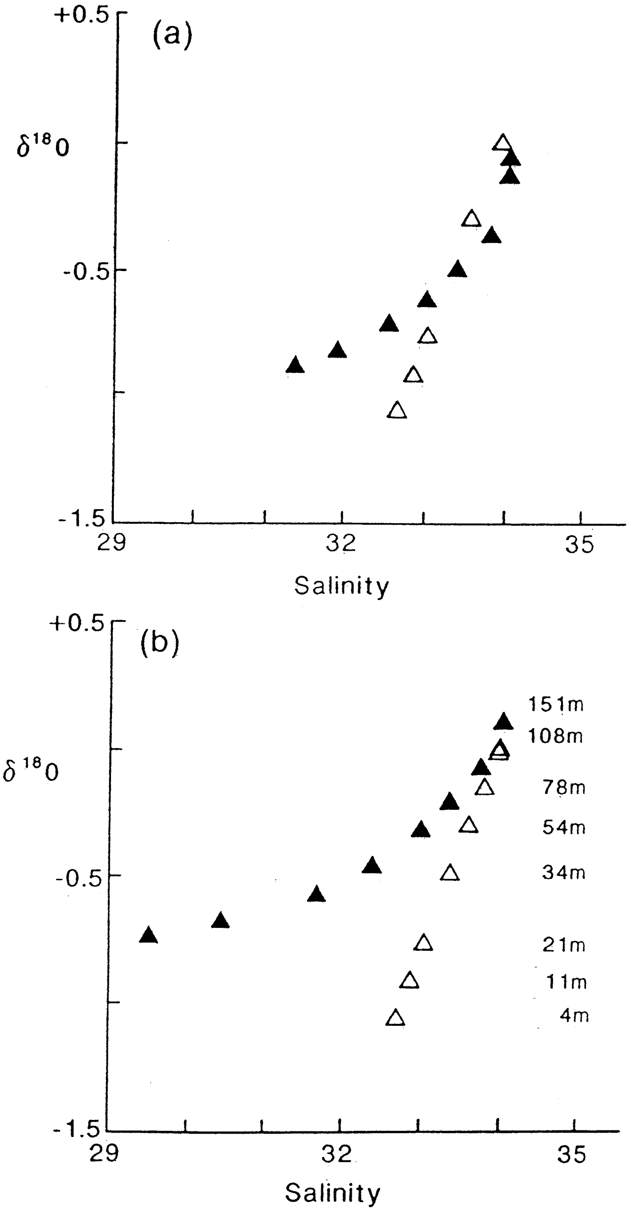


**Figure 4.** Modeled changes in the $S$:$\delta^{18}O$ relationship during melting, according to *Strain and Tan* [1993]. (a) A 1 m thick layer of sea-ice is allowed to melt at a rate of 0.1 m d$^{-1}$ with a vertical velocity of $3 \times 10^{-6}$ m s$^{-1}$. The initial $S$:$\delta^{18}O$ curve for the top 151 m of Davis Strait sea-water is shown by open triangles; the final curve, after 42 days, is shown by solid triangles. (b) Using the same conditions but starting with a 3 m thick ice layer. The final curve, after 63 days, is shown by solid triangles.

thicknesses and a typical profile from the Labrador Sea. The initial surface ($S$, $\delta^{18}O$) in each case was (32.7, -1.0). A month after the 1m and 3m layers of ice had melted the new surface ($S$, $\delta^{18}O$) had become (31.2, -0.75) and (28.9, -0.65), respectively. The initial $S$:$\delta^{18}O$ ratio was 1:0.62 (Figure 4, also section 3.1.2). Using this robust ratio to forecast the salinity associated with the post-melting $\delta^{18}O$, the impact of melting the 1 m and 3 m thick ice layers would cause overestimates of 32.7 + (-0.75 - -1.0)/0.62 - 31.2 = 1.9‰ and 32.7 + (-0.65 - -1.0)/0.62 - 28.9 = 4.4‰, respectively. These large mismatches between mean and seasonal $S$:$\delta^{18}O$ relationships may persist for several months according to the results of *Strain and Tan* [1993].

Regarding the last glacial maximum (LGM), the potential for significant over-estimation of surface salinity because of summertime sea ice melting could affect a large part of the global ocean, as illustrated by the *Climate: Long-Range Investigation, Mapping, and Prediction (CLIMAP)* [1981] reconstruction of the seasonal and permanent sea ice extent in the North Atlantic (Figure 5). While the CLIMAP reconstructions probably overestimated the glacial southward extent of sea ice [*Rind and Peteet*, 1985; *Hebbeln et al.*, 1994], much of the glacial North Atlantic between 40°N and 60°N would have had seasonal sea ice and, consequently, a much more temporally variable $S$:$\delta^{18}O$ relationship than today. Trying to extrapolate from present-day $S$:$\delta^{18}O$ ratios to near-surface paleosalinities in this region potentially involves errors of as much as 1-4‰ because of sea ice melting effects, which add to the potential errors due to coastal and open ocean freshwater budget influences (section 3.1.1 and section 3.1.2).

### 3.2. Water Masses and $\delta^{18}O$

Section 3.1 demonstrates that changes to the distribution and size of freshwater input and the more extensive presence of seasonal sea ice at the LGM, relative to the present, would likely have significantly altered local (section 3.1.1) or basin-wide (section 3.1.2) $S$:$\delta^{18}O$ ratios, the base $\delta^{18}O$ of sea water on regional scales (section 3.1.1), and the near-surface $\delta^{18}O$ over large areas (section 3.1.3).

Such modifications of regional and basin-wide LGM sea water oxygen isotope signatures have ramifications for the global ocean. Water masses moving subsurface show conservative behaviour in the oxygen isotope/salinity ratio (Frew et al., 1996), and when water masses from different sources mix, the resulting mixture's (1-$S$)$\delta^{18}O$ is a linear combination of that property in the original water masses [*Paren and Potter*, 1984]. Thus changes to the oxygen isotope characteristics of oceanic source waters (e.g., from the Labrador Sea, the NE Atlantic or the Mediterranean) will influence the base sea water $\delta^{18}O$ at places and depths far removed from the regions where those initial $\delta^{18}O$ modifications were experienced.

This is also true for waters which experience periods of atmospheric influence, such as the near-surface waters of the North Atlantic subtropical gyre. These waters, with a standard North Atlantic $S$:$\delta^{18}O$ ratio of 1:0.5, are an end product formed by relatively seasonally invariant advection and mixing of distinct water masses, as well as any evaporation-precipitation forcing. However, should the basic combination of water masses be subjected to substantial $\delta^{18}O$ modifications, then the extrapolation of local salinity from the local $\delta^{18}O$ in the "end product" will be in error.

## 4. Discussion and Conclusions

We have demonstrated that the fundamental assumption in calculations of paleosalinities from oxygen isotope residuals, i.e., that the residuals may be transformed into salinities on the basis of present-day $S$:$\delta^{18}O$ relationships, introduces potential error margins in the paleosalinity results ranging from region to region between 0.2‰ and >4‰. These errors were quantified using conservative magnitudes for possible glacial $\delta^{18}O$ anomalies. The

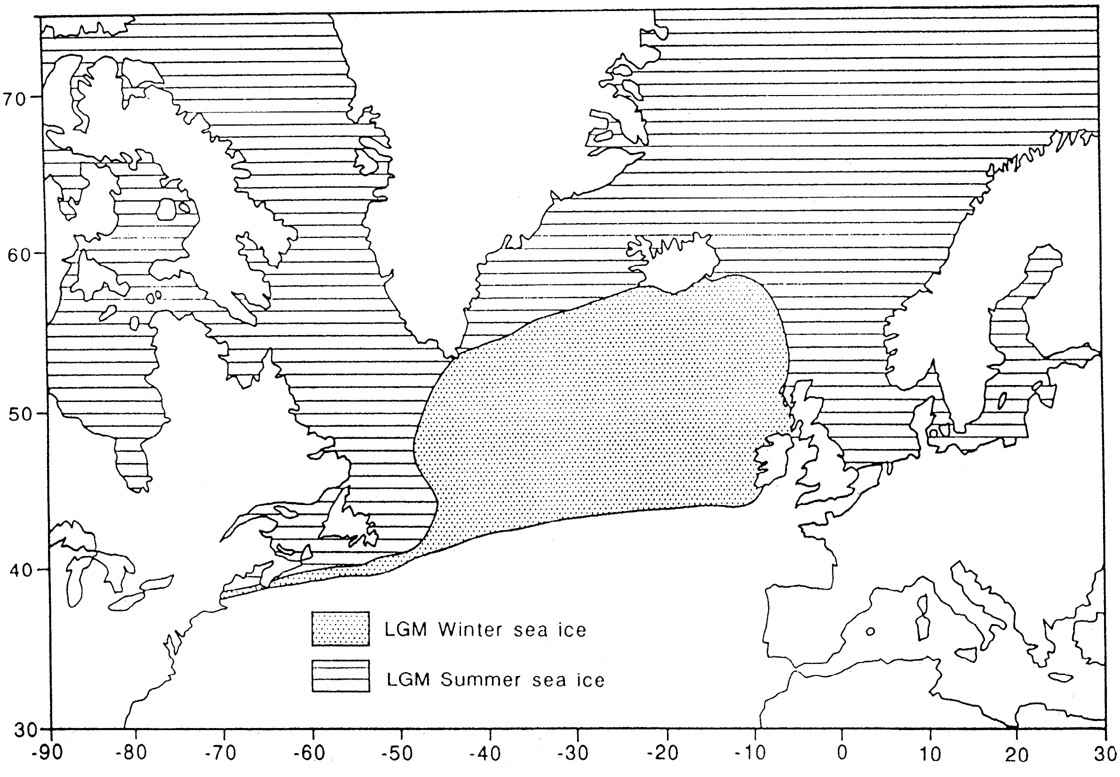


**Figure 5.** Map of summer and winter sea-ice extent at the last glacial maximum (LGM) over the North Atlantic, reconstructed from *CLIMAP* [1981].

errors originate from a combination of temporal nonlinearities in the $S$:$\delta^{18}O$ relationship and changes to the properties of the basic water masses making up the global ocean, and they add to further sources of error in paleosalinity estimates related to assumptions, uncertainties and inaccuracies in input parameters that propagate through the paleosalinity calculations and that amount to $\pm 1‰$ or more.

Potential nonlinearities in the $S$:$\delta^{18}O$ relationship in any specific area arise from the distinct presence of external sources and sinks for $\delta^{18}O$ from the freshwater budget and the impact of sea ice, causing nonconservative behaviour in $\delta^{18}O$, whereas the absence of external sources and sinks for salt define a conservative property. The degree of nonlinearity depends on (1) the volumetric importance of the freshwater budget and/or sea ice formation relative to the marine advective terms; and (2) the individual isotopic compositions of the various terms in the freshwater budget. Relative or absolute changes in the flux rate or isotopic composition of any source/sink (examples in Table 3) would, therefore, result in variability of the degree of nonlinearity through time. Because such variations through time cause complex temporal variability in the degree of nonlinearity in the $S$:$\delta^{18}O$ ratio, it would not suffice to simply account for possible modern (measurable) nonlinearity in a local $S$:$\delta^{18}O$ relationship to calibrate paleosalinity calculations based on fossil $\delta^{18}O$ records.

To further complicate matters, this temporal variability combines with distinct spatial variability of freshwater budget and sea ice influences to determine complex, regionally dependent, temporal variations in $S$:$\delta^{18}O$ relationships. In other words, in a certain area with substantial variations in fluxes and/or isotopic composition of freshwater budget terms (sections 2.1, 2.2, 3.1.1, and 3.1.2), internal recirculation processes (section 2.3), or seasonal or permanent sea-ice coverage (section 3.1.3), it may not be assumed (1) that the $S$:$\delta^{18}O$ relationship should, per definition, be linear, or (2) that the $S$:$\delta^{18}O$ relationship, be it linear or nonlinear, would have been temporally invariant. Furthermore, it appears unreasonable to expect (3) that magnitudes of temporal variations in the $S$:$\delta^{18}O$ relationship would be identical for different regions. Instead, some show distinct, up to factor 2, glacial steepening of the $S$:$\delta^{18}O$ ratio, while others show little variation if any (see sections 3.1.1 and 3.1.2). Finally it needs to be taken into account (4) that advection and mixing of waters from basins with temporal changes in $S$:$\delta^{18}O$ characteristics affect the entire ocean and could thus influence the $S$:$\delta^{18}O$ ratios in areas perceived to be "stable" (sufficiently remote from the discussed freshwater budget and sea-ice influences). Indeed, we suspect that advection is the dominant process in determining the $S$:$\delta^{18}O$ ratio for many areas of the global ocean. To stress this point, we emphasize that the "problem areas," the marginal basins and the high latitudes, provide most of the source waters advecting into the ocean interior, so that the potential for upsetting the $S$:$\delta^{18}O$ relationships in the perceived stable areas may not be dismissed but merits further study.

To warrant a meaningful quantitative interpretation, paleosalinity determinations from $\delta^{18}O$ residuals must account for the demonstrated probability of variations in the $S$:$\delta^{18}O$ relationship through time, with these not being geographically homogeneous. In view of these complications we propose the following recommendations to improve the method: (1) Development of coupled ocean-atmosphere-isotope models, or at least ocean-isotope models driven by a paleoclimate-isotope model, to provide base seawater $\delta^{18}O$ distributions per time slice, and (2) Continued research to characterize variations in the volume fluxes and $\delta^{18}O$ of the various terms in the freshwater budget; the past distributions of seasonal and permanent sea ice; and the volume fluxes and $\delta^{18}O$ from marginal basins and through sea straits and passages in general, to determine variations in marine advective terms. Such parameters need to be accurately determined for any study area in any time slice of interest before the $\delta^{18}O$ composition of seawater in the oceans can be understood in relation to water mass and conservative property distribution, mixing, and circulation.

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