



Progress in paleosalinity: Overview and presentation of a new approach

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[1] This paper concerns the use of stable oxygen isotope ratios ($\delta^{18}\text{O}$) and stable hydrogen isotope ratios ($\delta^2\text{H}$ or δD) to derive paleosalinity. First, I evaluate the potential and limitations of existing methods based on $\delta^{18}\text{O}$ and δD separately. Next, I propose a new theoretical framework for the combined use of $\delta^{18}\text{O}$ and δD to constrain the impact of the hydrological cycle on the surface waters and to thus characterize changes in surface water salinity. This new method is accompanied by an error propagation exercise to demonstrate its limitations and areas of potential improvement. A feasible strategy is outlined for achieving reconstructions of paleosalinity change with an uncertainty of 1 practical salinity unit or less with the newly proposed method (especially in regions with high deuterium excess values).

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1. Introduction

[2] To characterize ocean circulation patterns, a sound understanding of density gradients is essential. At any given pressure, density is determined by seawater temperature and salinity through the equation of state. Both these properties can be measured very accurately in modern oceanographic surveys. When studying past ocean circulation, however, we need to rely on so-called “proxy” measurements for these properties, which achieve nothing like that sort of accuracy (notably for salinity).

[3] For temperature, quite a few different proxies exist. The main ones are (1) transfer functions, modern analogue techniques, and artificial neural network approaches, which use faunal or floral microfossil abundance data and a calibration of such data from the modern ocean to temperature; (2) organic geochemical indices, such as $\text{Uk}'37$ and Tex86 ; and (3) Mg/Ca ratios in microfossil calcite. Inter-comparisons may reveal a remarkable degree of disagreement between temperature estimates from the different proxies. A lot of this disagreement can be ascribed to the fact that the techniques rely on different aspects of biogenic temperature recording, where bias can arise because of different water depth habitats; temporal and spatial variability in the season or depth at which the different biota live (and used to live); anomalous behavior due to stress near the environmental/ecological tolerance limits of the various biota; impacts of geochemical changes through time (e.g., ocean alkalinity); etc. Although complex, however, there is a general consensus that this richness of paleotemperature information from the diverse suite of differently affected proxies does have the potential to deliver considerable

insight into past temperature variations (with spatial and temporal structure) with reasonable confidence.

[4] For salinity, the situation is markedly different. Although new concepts are arising, such as the use of foraminiferal Ba/Ca ratios in settings near river mouths [Woldeab *et al.*, 2007], only a few techniques have yet found some more regular use, such as (1) dinoflagellate- and diatom-based transfer function approaches and (2) a variety of calibrations of stable oxygen isotope ratios ($\delta^{18}\text{O}$) measured on carbonate microfossils. The latter have been fashionable for a while, but have since been found to carry unreasonably large uncertainties in the reconstructed values [Rohling and Bigg, 1998; Schmidt, 1999a; Rohling, 2000]. The search is on therefore for new, complementary paleosalinity methods, to allow combination with paleotemperature estimates for a better understanding of past ocean density structures and circulation. This requirement for new paleosalinity techniques is especially pressing now that paleoceanographic records are increasingly being used in comparisons with climate modeling approaches to address the problem of abrupt and large-scale climate change. The paleostudies offer test beds that help determine how well models can simulate real-world abrupt and large-scale changes, which informs us about their suitability for projections of climate change outside the instrumentally recorded range of variability (into our greenhouse future). Clearly, such work requires robust proxy records with well-understood and clearly stated confidence margins.

[5] The present paper focuses on stable isotope-based methods to derive paleosalinity. I consider stable isotope ratios of the two main elements in H_2O : stable oxygen isotope ratios ($\delta^{18}\text{O}$) and stable hydrogen isotope ratios ($\delta^2\text{H}$ or δD). Of these, $\delta^{18}\text{O}$ is the most established measurement to have been applied in previous paleosalinity studies, but the use of δD is gaining increasing attention.

[6] I first look in detail at the potential and limitations of existing methods for paleosalinity characterization based on $\delta^{18}\text{O}$ and δD measurements separately. Next, I propose a

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new theoretical framework for the combined use of $\delta^{18}\text{O}$ and δD to constrain the impact of the hydrological cycle on surface waters, and to thus characterize changes in surface water salinity. This new method is accompanied by an error propagation exercise to demonstrate its limitations and areas of potential improvement.

2. Paleosalinity Estimates Based on Paired $\delta^{18}\text{O}$ and Mg/Ca Analyses of Carbonate

[7] The latest developments in $\delta^{18}\text{O}$ applications to paleosalinity concern paired stable oxygen isotope ratio and Mg/Ca analyses of a single aliquot of sample carbonate. This offers an improved capacity for “removal” of the temperature-dependent water to carbonate fractionation component in the stable oxygen isotope ratio of carbonate ($\delta^{18}\text{O}_c$, hereinafter δ_{Oc}), and thus a better characterization of the past $\delta^{18}\text{O}$ of the water itself ($\delta^{18}\text{O}_w$, hereinafter δ_{Ow}).

[8] Simple propagation of entirely random, nonsystematic uncertainties through the method allows an objective determination of the potentials and limitations of reconstructed changes in δ_{Ow} . I start with three optimistic assumptions: (1) The paired δ_{Oc} and Mg/Ca analyses are performed on perfectly homogenized splits of exactly the same material; (2) Mg/Ca ratios can somehow be determined without any analytical uncertainty (which is seriously optimistic given the differences that can arise from different cleaning protocols); and (3) the calcites analyzed are perfectly clean and 100% free of any diagenetic alteration or contamination.

[9] I focus on the errors that propagate through a reconstructed change between two individual values, which are measured in exactly the same way, on exactly the same foraminiferal species, in exactly the same size fraction. This is actually the best constrained approach, since it renders absolute values irrelevant; it concerns a purely relative change. Consequently, we can ignore such inconvenient complications as species-specific paleotemperature relationships, vital effect offsets, and calibrations of values measured relative to the VPDB standard to values on the VSMOW scale (for an overview, see *Rohling and Cooke* [1999]). This simplifies the argument to the point that any measured change in δ_{Oc} (i.e., $\Delta_{\delta_{\text{Oc}}}$) is directly related to a component of change in δ_{Ow} (i.e., $\Delta_{\delta_{\text{Ow}}}$) and a component of change in δ_{Oc} due to T changes (i.e., $\Delta_{\delta_{\text{Oc}}(\text{T})}$), so that $\Delta_{\delta_{\text{Oc}}} = \Delta_{\delta_{\text{Ow}}} + \Delta_{\delta_{\text{Oc}}(\text{T})}$. This means that the change in δ_{Ow} can be reconstructed according to $\Delta_{\delta_{\text{Ow}}} = \Delta_{\delta_{\text{Oc}}} - \Delta_{\delta_{\text{Oc}}(\text{T})}$.

[10] Any $\Delta_{\delta_{\text{Ow}}}$ thus depends on the difference between two δ_{Oc} values, both with their individual uncertainties ($\sigma_{\delta_{\text{Oc}1}}$ and $\sigma_{\delta_{\text{Oc}2}}$), which define an uncertainty in $\Delta_{\delta_{\text{Oc}}}$ according to $\sigma_{\Delta_{\delta_{\text{Oc}}}} = \sqrt{(\sigma_{\delta_{\text{Oc}1}}^2 + \sigma_{\delta_{\text{Oc}2}}^2)}$. The random measurement uncertainty (external precision) for a good δ_{Oc} analysis typically equals $\sigma_{\delta_{\text{Oc}}} = 0.06\text{‰}$. Consequently, $\sigma_{\Delta_{\delta_{\text{Oc}}}} = \sqrt{(2 \times 0.06^2)} = 0.09\text{‰}$.

[11] Similarly, any $\Delta_{\delta_{\text{Ow}}}$ involves the use of two Mg/Ca temperature values, both with their uncertainties ($\sigma_{\text{T}1}$ and $\sigma_{\text{T}2}$), giving an uncertainty in ΔT according to $\sigma_{\Delta\text{T}} = \sqrt{(\sigma_{\text{T}1}^2 + \sigma_{\text{T}2}^2)}$. Under the idealized assumption (see above) that a Mg/Ca ratio can be determined without analytical uncertainty, the random error in a Mg/Ca-based temperature determination derives entirely from the calibration between

the measured Mg/Ca ratio and temperature. Published calibrations typically seem to have 1σ uncertainties of roughly 0.5° to 1.0°C (e.g., the works of *Elderfield and Ganssen* [2000], *Anand et al.* [2003], *McConnell and Thunell* [2005], *Skinner and Elderfield* [2005, 2007], *Benway et al.* [2006], *Rosenthal et al.* [2006], and *Marchitto et al.* [2007] and their references). Note, however, that such calibrations can of course be determined only for extant organisms, whereas the framework for extinct organisms has to rely on generalized assumptions and is therefore much more uncertain. I proceed initially with an optimistic smallest 1σ value of 0.5°C , and later consider the implications of a more realistic value of 1.0°C . In terms of impact on the equilibrium fractionation of O isotopes between water and calcite, a temperature 1σ of 0.5°C would determine that $\sigma_{\Delta\text{T}} = 0.13\text{‰}$ [*O'Neil et al.*, 1969; *Kim and O'Neil*, 1997]. Consequently, $\sigma_{\Delta\text{T}} = \sqrt{(2 \times 0.13^2)} = 0.18\text{‰}$.

[12] Propagation of the above uncertainties offers an uncertainty in the reconstructed $\Delta_{\delta_{\text{Ow}}}$ that amounts to $\sigma_{\Delta_{\delta_{\text{Ow}}}} = \sqrt{(\sigma_{\Delta_{\delta_{\text{Oc}}}}^2 + \sigma_{\Delta\text{T}}^2)}\text{‰} = 0.20\text{‰}$. In other words, any thus reconstructed change in δ_w is subject to a random, nonsystematic margin of uncertainty of $\pm 0.20\text{‰}$ at the 1σ level (68% probability), or $\pm 0.40\text{‰}$ at the 2σ level (95% probability). These uncertainty margins derive from propagation of (1) a statistically expressed external precision of measurement equipment and (2) a calibration based on a statistical best fit through empirical data. Hence the uncertainties are truly random, and can in no way be assumed to be systematic (and hence “canceling out”) between temporally closely spaced samples. Because these are random uncertainties, however, statistical error reduction does apply when multiple replicate analyses are undertaken on the same material. Thus the standard error of the mean (SE) reduces according to $\text{SE} = \sigma/\sqrt{N}$, where N is the number of replicate analyses. Consequently, the routine analysis of 9 replicate pairs would reduce the uncertainty interval that applies to our reconstructed $\Delta_{\delta_{\text{Ow}}}$ to only $0.20/3 = 0.07\text{‰}$.

[13] Realistically, however, the problems do not end there. The $1\sigma = 0.5^\circ\text{C}$ assumed for Mg/Ca-based temperatures may be generously small, especially in a deep-time context where extinct organisms are being analyzed. Moreover, the Mg/Ca to temperature calibrations in the present-day ocean use mean values for the approximate living habitat of the specimens involved. This may oversimplify the true variability, especially for planktonic foraminifera, which live and calcify over a considerable depth range in a both spatially and temporally variable pelagic environment. Finally, one might argue that the three idealized assumptions specified in the beginning of this section are unlikely to be fully realized in real life, so that there are further sources of random uncertainties that would need to be propagated. Consequently, the $\sigma_{\Delta_{\delta_{\text{Ow}}}}$ values determined above are lower limit estimates. Use of a more realistic, wider margin of $1\sigma = 1.0^\circ\text{C}$ would increase $\sigma_{\Delta_{\delta_{\text{Ow}}}}$ from 0.20 to 0.37‰ . To achieve the same $\text{SE}_{\Delta_{\delta_{\text{Ow}}}}$ of about 0.07‰ , we then require the routine analysis of about 25 replicate pairs.

[14] Although there is considerable work involved, it is evident that the uncertainty limits in $\Delta_{\delta_{\text{Ow}}}$ can be brought down to acceptable levels (below 0.1‰). Unfortunately,

even such tight uncertainty limits do not translate into paleosalinity estimates with similarly tight uncertainty margins. This is because the translation of δ_{Ow} into paleosalinity suffers from large uncertainties in the temporal behavior of the S: δ_{Ow} relationship [Rohling and Bigg, 1998; Schmidt, 1999a; Rohling, 2000]. For a variety of reasons, for a large part but not exclusively because of large uncertainties in (changes through time in) the slope and zero-salinity $\delta^{18}\text{O}$ intercept of the S: δ_{Ow} relationship, paleosalinity calculations cannot be satisfactorily closed on the basis of δ_{w} alone. It is essential that another method is found that does not critically depend on the poorly constrained and temporally variable paleo-S: δ_{Ow} relationship. Only such an independence will do justice to the narrow uncertainly limits in $\Delta_{\delta_{\text{Ow}}}$ that now are technically achievable by performing multiple replicates of paired $\delta^{18}\text{O}_{\text{c}}$ and Mg/Ca analyses.

3. Paleosalinity Estimates Based on Organic Compound-Specific δD Analyses

[15] Although the δD of modern water samples (δ_{Dw}) is easy to measure, paleostudies require a proxy for that value, which has to be obtained from fossil material. Recent studies have built up a better understanding of the measurement protocols and interpretation of organic compound-specific (alkenone) δ_{Da} analyses of marine algal matter [Schouten *et al.*, 2006, and references therein]. Tank experiments demonstrate that δ_{Da} changes more rapidly than δ_{Dw} , by a factor of 2.65 ± 0.30 (4 to 5 over 1.7) [Schouten *et al.*, 2006]. By a process of elimination of changes in their tank experiments, those authors infer that this may reflect a salinity-dependent control on the hydrogen isotope fractionation between the water and the alkenones synthesized therein. The study then infers that this might be used as a paleosalinity proxy, where the fundamental equations are

$$\alpha_{\text{a-w}} = (1000 + \delta_{\text{Da}})/(1000 + \delta_{\text{Dw}}) \quad (1)$$

$$\alpha_{\text{a-w}} = aS + b \quad (2)$$

[16] Here $\alpha_{\text{a-w}}$ is the isotopic fractionation factor between alkenones (subscript a) and water (subscript w). Equation (2) represents the linear regression found between $\alpha_{\text{a-w}}$ and salinity (S), with slope a and intercept b . According to the data of Schouten *et al.* [2006], $a = 0.003 \pm 0.001$ and $b = 0.676 \pm 0.03$ for *Geophyrocapsa oceanica*. These seem to be rather conservative estimates of the uncertainties around the regression, and the actual uncertainties may turn out to be smaller when more data would be added.

[17] Equations (1) and (2) can be rearranged to give

$$S = \frac{(1000 + \delta_{\text{Da}})/(1000 + \delta_{\text{Dw}}) - b}{a} \quad (3)$$

[18] This allows calculation of S for any given measurement of δ_{Da} , but only if there is information on the hydrogen

isotope ratio of the past water (δ_{Dw}). It was inferred that δ_{Dw} might be constrained by using the so-called meteoric water line (MWL), which determines a proportional relationship between δ_{D} and δ_{O} (but it may not fully apply to surface waters, see below and Figure 1). Schouten *et al.* [2006] did not elaborate this, but instead diagnosed the potential by observing the $\delta_{\text{Dw}}:S$ relationship from their tank experiments.

[19] In the real ocean-atmosphere environment, the MWL is the relationship between δD and $\delta^{18}\text{O}$ along which meteoric (= fresh) waters develop relative to one another in the hydrological cycle, and it is close to $\delta_{\text{D}} = 8\delta_{\text{O}} + 10$ (the so-called global MWL [Craig, 1961; Craig and Gordon, 1965]). Under the assumption that the MWL may be applied to represent the surface water relationship therefore δ_{Dw} in equation (3) would be resolved by the substitution $\delta_{\text{Dw}} = 8\delta_{\text{Ow}} + d$, where d stands for the appropriate value of the deuterium excess, and where an appropriate past δ_{Ow} could be evaluated from temperature-corrected δ_{Oc} . In landlocked marginal seas, the slope of the meteoric water line remains close to 8, but the intercept (the “deuterium excess”) may reach much higher values; for example, the eastern Mediterranean value is close to 22 [Gat, 1996; Matthews *et al.*, 2000; McGarry *et al.*, 2004]. It is important to note, however, that the relationship that seems to be called for to solve equation (3) is not the MWL, but the corresponding relationship for surface seawater. The latter differs significantly from a MWL, in that the zero δ_{O} intercept (= d) for the surface water relationship is much smaller (near -0.7‰) over most of the world ocean, and may only rise to higher values (around $+6\text{‰}$) in highly evaporative regions, where also the slope of the mixing line becomes much less than 8 (see Figure 1).

[20] The deviation of the mixing line from a slope of about 8 in surface waters of evaporative regions (see also Gat [1996] and Figure 1) was explained by Craig and Gordon [1965], using both data and theory. Key to the problem are the different proportions of the vapor pressure enrichments (ε) for oxygen and hydrogen isotopes upon evaporation from water to vapor. This ε consists of the sum of the equilibrium enrichment (ε^*) and the kinetic enrichment ($\Delta\varepsilon$). At 25°C , ε^* is about 9 for oxygen-18, and 69 for deuterium [Craig and Gordon, 1965, p. 82]. The ε^* values are proportioned close to the value of 8 that is seen in the slope of the meteoric water line, but the kinetic enrichments are not – their difference is much smaller. Craig and Gordon [1965] report theoretical values for $\Delta\varepsilon$ of about 14 and 3 for oxygen-18 and deuterium, respectively (Craig *et al.* [1963] give experimental values of about 20 and 5, respectively). Gat [1996, pp. 234–235] presents the relevant details to derive $\Delta\varepsilon$ specifically for the eastern Mediterranean, and the apparent values are 2.1 and 1.9 for oxygen-18 and deuterium, respectively. The ratio of changes in δ_{Dw} and δ_{Ow} during evaporation (i.e., $\Delta_{\delta_{\text{Dw}}}/\Delta_{\delta_{\text{Ow}}}$) is then approximated by the ratio of the terms $\varepsilon^* + \Delta\varepsilon/(1 + h)$ for each of the isotopes, where h is relative humidity [Craig and Gordon, 1965, p. 99]. Consequently, the ratio $\Delta_{\delta_{\text{Dw}}}/\Delta_{\delta_{\text{Ow}}}$ is smaller than 8, because $\Delta\varepsilon$ is smaller relative to ε^* for deuterium than is the case for oxygen-18. Craig and Gordon [1965] thus illustrate why surface waters in evaporative regions are typically char-

acterized by $\Delta_{\delta_{Dw}}/\Delta_{\delta_{Ow}}$ ratios of about 6 or less (see also Figure 1 and *Gat et al.* [1996]), rather than the value of about 8 in MWLs. Although the assumption that the common slope of about 8 of MWLs might be applied to surface waters may work in regions of low E/P ratios, this assumption would introduce considerable error when there is a significant evaporation term. This adds to great uncertainty about the applicable value of d for the sea surface water (Figure 1).

[21] The above indicates that a paleosalinity method from δ_{Da} measurements as advocated by *Schouten et al.* [2006] would suffer from inevitably large uncertainties in the absolute paleo- δ_{Dw} value that would need needed in the calculations. These uncertainties derive from the following key issues: (1) Parameters a and b in equation (3) are not yet sufficiently tightly constrained; (2) there is great uncertainty about both the past slope and the past intercept of the relationship that might be used to calculate surface water

paleo- δ_{Dw} from paleo- δ_{Ow} ; and (3) the employed paleo- δ_{Ow} would need to be an absolute value obtained from a temperature-corrected δ_{Oc} , and so is subject to many pitfalls that introduce large uncertainty (see previous section).

[22] In short, it appears that a uniquely δ_{Da} -based paleosalinity method would likely suffer from problems that are quite similar to those in uniquely δ_{Ow} -based paleosalinity reconstructions. Although measurements may be very carefully performed with many replicates, so that only small uncertainties apply, the final calibration to salinity requires the bold application of some highly uncertain relationships and/or derived absolute values for the water, which seem to be almost impossible to constrain through time.

[23] Clearly, there is a need for a paleosalinity method that does justice to the high-quality measurements. This may be achieved by developing a method that does not require a final uncertain calibration step. Another key aspect of the new method should be that it emphasizes differences or gradients, rather than absolute values, since differences between identically performed measurements are much better understood and much less uncertain than calibrations to absolute (water) values.

4. A New Paleosalinity Method

[24] Here I present the theoretical framework for a new approach. It uses the fact that both O and H isotopes in surface water are primarily affected by the freshwater budget, and that fractionation for oxygen-18 and deuterium is not entirely the same. Thus the two isotope systems can be used to converge on a solution for the magnitude of the freshwater flux relative to the marine water supply. This

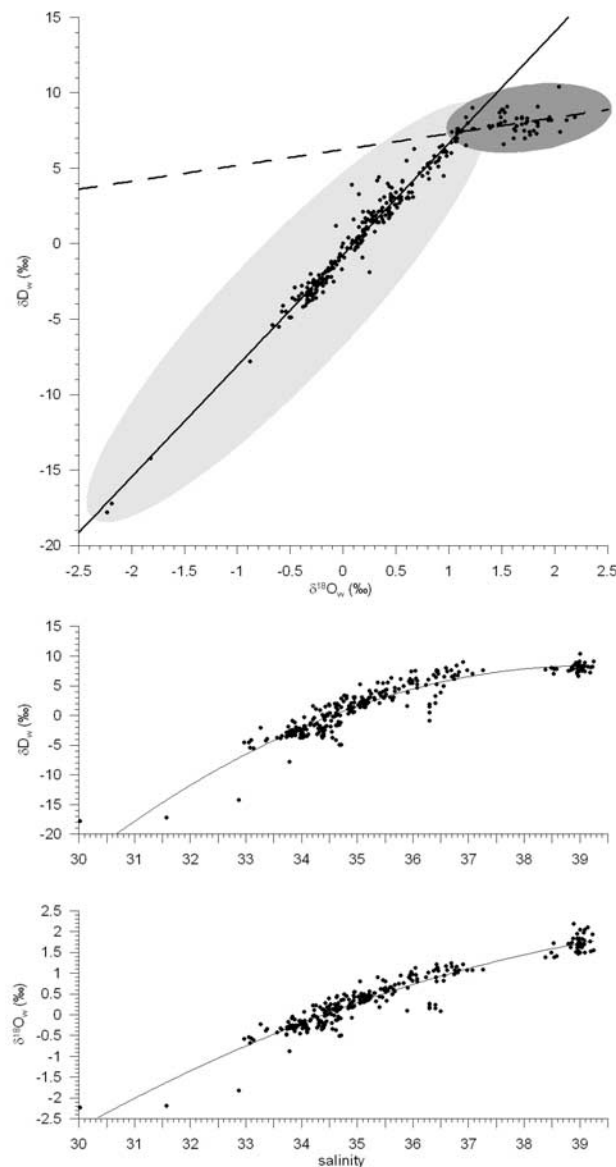


Figure 1. Modern surface ocean (top 250 m) relationships between salinity, δ_{Ow} , and δ_{Dw} . (top) General relationship between $\delta^{18}O$ and δD of the sample waters (δ_{Ow} and δ_{Dw}). There is a well-defined relationship (solid line, light grey area) for all points with δ_{Ow} lower than 1.3 permil according to $\delta_{Dw} = 7.37 \delta_{Ow} - 0.72$ ($N = 244$; $R^2 = 0.97$). In the points of higher values, there is no well-defined relationship. The dashed line illustrates the (nonsignificant) relationship $\delta_{Dw} = 1.05 \delta_{Ow} + 6.24$ ($N = 62$; $R^2 = 0.21$) for all points with δ_{Ow} above 1.0 permil (dark grey area). (middle) Relationship between salinity and δ_{Dw} for the same water samples, with a second-order polynomial fit to illustrate the overall nonlinear nature of the distribution and (bottom) same for salinity and δ_{Ow} . These plots illustrate that the generally applicable surface water δ_{Dw} and δ_{Ow} relationship “breaks down” for samples from areas of high net evaporation (high salinity), corroborating the observations and theoretical arguments of *Craig and Gordon* [1965]. Data are obtained from G. A. Schmidt et al. (*Global Seawater Oxygen-18 Database*, 1999, available at <http://data.giss.nasa.gov/o18data/>) as compiled by *Schmidt* [1999b] and *Bigg and Rohling* [2000], and originally reported by *Duplessy* [1970], *Weiss et al.* [1979], *Aharon and Chappell* [1986], *Ostlund et al.* [1987], *Yobbi* [1992], *Gat et al.* [1996], and *Delaygue et al.* [2001].

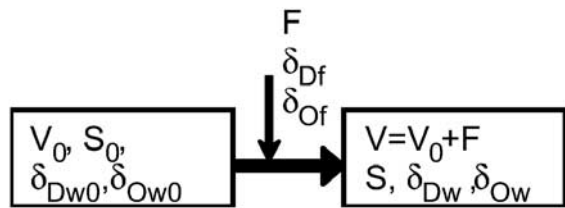


Figure 2. Simple system considered in the present paper for calculation of paleosalinity change based on paired information on hydrogen isotopes measured on alkenones and oxygen isotopes of seawater derived from analysis of carbonates in combination with Mg/Ca-based temperature corrections. The freshwater terms represent the net effects of evaporation, precipitation, and runoff.

relative freshwater flux influence then determines the change in salinity.

[25] I develop the relationships governing the impacts of the net hydrological flux on a flux of seawater (Figure 2), avoiding any complications due to mass balanced mixing between different seawater masses. The key relationships to be considered are expressed in their simplest form for salinity: $S = S_0 V_0 / (V_0 + F)$. Here S is the salinity of the final water, as determined by the initial salinity (S_0), the marine water flux (V_0) and the net freshwater flux (F). Throughout this paper, values marked with subscript “0” (e.g., δ_{Dw0} , δ_{Ow0} , V_0 and S_0) represent the initial values. The above equation simply represents conservation of salt for any given net change in water volume, and if we determine a relative flux ratio $x = F/V_0$, then

$$S = \frac{S_0}{(1 + x)} \quad (4)$$

[26] The corresponding O-isotope mass balance (for water) is $\delta_{Ow} = (\delta_{Ow0} + x\delta_{Of}) / (1 + x)$. Here the subscript f indicates the mass balanced mean isotopic composition of the net freshwater flux. If we reorganize the equations for S and δ_{Ow} so that they solve for $(1 + x)$, then we can equate them, giving $(1 + x) = S_0/S = (\delta_{Ow0} + x\delta_{Of})/\delta_{Ow}$ so that

$$S = S_0 \frac{\delta_{Ow}}{\delta_{Ow0} + x\delta_{Of}} \quad (5)$$

[27] Similarly, the H-isotope mass balance (for water) is $\delta_{Dw} = (\delta_{Dw0} + x\delta_{Df}) / (1 + x)$, and the same reorganization and equation procedure then gives a further solution for S as

$$S = S_0 \frac{\delta_{Dw}}{\delta_{Dw0} + x\delta_{Df}} \quad (6)$$

[28] For the hydrogen isotopes, the proxy that can be measured is not the δ_{Dw} that we would ideally want, but the δD of alkenones (δ_{Da}), which changes more rapidly than δ_{Dw} by a factor $C = 2.65 \pm 0.30$, where the uncertainty represents the total range [Schouten *et al.*, 2006]. In other

words, $\delta_{Da} - \delta_{Da0} = C(\delta_{Dw} - \delta_{Dw0})$. This can be rearranged to give $\delta_{Dw} = (\delta_{Da} - \delta_{Da0} + C\delta_{Dw0})/C$. Substituted into (6) this gives

$$S = S_0 \frac{\delta_{Da} - \delta_{Da0} + C\delta_{Dw0}}{C(\delta_{Dw0} + x\delta_{Df})} \quad (7)$$

[29] Note that, by keeping the constant C rather than putting its fixed value, the developed equations can more easily accommodate any new insights into the (range of) values of C . Also, if/when a method would be developed that allows direct determination of paleo- δ_{Dw} , then the equations can be used in the same form, but simply with $C = 1$.

[30] We can now seek the convergence of the various solutions of S for any given value of the relative freshwater flux condition x . At each value of x , these calculated salinities in a real basin must be identical (i.e., the actual salinity in the basin). Equation (7) is a more useful version of (6), because it needs a basic assumption only for the initial δ_{Dw0} and resolves the rest on the basis of measurable parameters. Hence the equations to be used are (4), (5), and (7). Note, however, that there are no sound means to obtain paleoestimates for either δ_{Of} or δ_{Df} in equations (5) and (7). These uncertain terms will therefore first be eliminated from the equation.

[31] Although the individual values of δ_{Df} and δ_{Of} are not known, the relationship between these two terms can be reasonably constrained. In a given system without outside influences, the evaporation-derived vapor values and precipitation values develop relative to one another along the $\delta_O:\delta_D$ trajectory of a so-called meteoric water line (MWL), with a slope value close to 8 [e.g., Craig and Gordon, 1965; Gat, 1996] (Figure 3). Hence the relationship between δ_{Df} and δ_{Of} can be represented by approximation as $\delta_{Df} = \lambda\delta_{Of} + d$, where the slope (λ) is close to 8. The “deuterium excess” value (d) depends on the specific study region’s characteristics. Note that, in contrast to the surface water relationship that was sought in the δ_D -only section above, we are here concerned with the true MWL development.

[32] In a given enclosed basin with a simple hydrological cycle (without outside freshwater influences), the appropriate d value from the regional MWL can be used (i.e., about 22 for Mediterranean-sourced meteoric water). If there also are external meteoric water influences, however, then the applicable “net” value for d will need to be resolved/estimated. The easiest way would be to estimate a range between realistic upper and lower bounds for the “net d .” In the equations, a mean value would then be used, while the substantial uncertainty range is considered in the subsequent error propagation analysis. In the final section, I elaborate an example for the Mediterranean. Making the $\delta_{Df} = \lambda\delta_{Of} + d$ substitution, and using $\Delta_{\delta Da} = \delta_{Da} - \delta_{Da0}$ in (7), gives

$$S = S_0 \frac{\Delta_{\delta Da} + C\delta_{Dw0}}{C(\delta_{Dw0} + x(\lambda\delta_{Of} + d))} \quad (8)$$

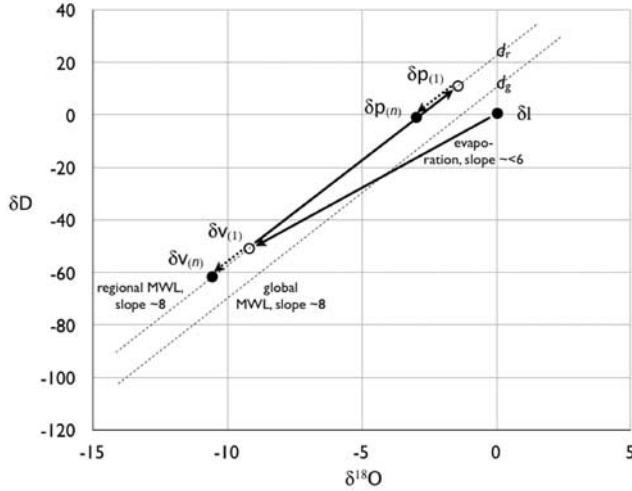


Figure 3. Simplified schematic representing the directions of development in $\delta_{\text{O}}:\delta_{\text{D}}$ space of the main components in the hydrological cycle of an enclosed region with an important evaporative flux relative to one another. Here δl is the initial composition of the surface water, δv is the composition of the vapor derived from that surface water by evaporation, and δp is the composition of precipitation formed by condensation of the vapor. Subscript “(1)” indicates the initial composition; subscript “(n)” indicates the subsequent development. Zero δ_{O} intercepts d_r and d_g represent the deuterium excess values that apply to the portrayed regional MWL and global MWL. Note that no attempt was made to work to exact values (scales) but that the scales are simply there to gauge the approximate amplitude of the various changes, and most importantly, to indicate how the various parameters relate to the MWLs.

[33] The remaining uncertain parameter δ_{Of} can then be eliminated by solving (5) for the term $x\delta_{\text{Of}}$ which gives $x\delta_{\text{Of}} = (S/S_0)\delta_{\text{Ow}} - \delta_{\text{Ow0}}$, and substituting this into (8). After that substitution, (8) needs to be solved again for S , which yields

$$S = \frac{S_0}{C} \frac{\Delta_{\delta\text{Da}} + C(\delta_{\text{Dw0}} - \lambda\delta_{\text{Ow}})}{C(\delta_{\text{Dw0}} + xd - \lambda\delta_{\text{Ow0}})} \quad (9)$$

[34] Regarding the hydrogen isotopes, the solution for S is now determined by the difference between the initial value and the final value (or, in more practical terms: the difference between the value of alkenones in inflow into a basin/region, and final value of the same alkenone compound inside that basin/region). Thus the solution is no longer dependent on absolute water values, except for the initial (inflow) value δ_{Dw0} , which will be dealt with later.

[35] Two major variables now remain to be resolved: S and x . Variable x can be resolved first, by equating the two solutions for S given in (4) and (9) and solving for x . This gives

$$x = \frac{\Delta_{\delta\text{Da}} - \lambda C \Delta_{\delta\text{Ow}}}{C(d + \lambda\delta_{\text{Ow}} - \delta_{\text{Dw0}}) - \Delta_{\delta\text{Da}}} \quad (10)$$

[36] Substitution of x from (10) into equation (9) then yields

$$S = S_0 \frac{(\delta_{\text{Dw0}} - \lambda\delta_{\text{Ow}} - d) + \frac{\Delta_{\delta\text{Da}}}{C}}{\delta_{\text{Dw0}} - \lambda\delta_{\text{Ow0}} - d} \quad (11)$$

[37] Equation (11) still requires individual absolute water O-isotope values for both the initial water (inflow) and the final product water. This again raises the issue that (temperature corrected) gradients between identically measured proxy values are much more reliable than conversions to absolute water values, which are subject to vital effect offsets, poorly understood regional species-specific paleotemperature equations, etc. Hence the term δ_{Ow} needs to be removed from (11). This is easily done using $\Delta_{\delta\text{Ow}} = \delta_{\text{Ow}} - \delta_{\text{Ow0}}$, which following some reorganization, results in

$$S = S_0 \left(1 + \frac{\frac{\Delta_{\delta\text{Da}}}{C} - \lambda\Delta_{\delta\text{Ow}}}{\delta_{\text{Dw0}} - \lambda\delta_{\text{Ow0}} - d} \right) \quad (12)$$

[38] Since $S = S_0 + \Delta_S$, this shows

$$\Delta_S = S_0 \left(\frac{\frac{\Delta_{\delta\text{Da}}}{C} - \lambda\Delta_{\delta\text{Ow}}}{\delta_{\text{Dw0}} - \lambda\delta_{\text{Ow0}} - d} \right) \quad (13)$$

[39] Note that (10), which allows calculation of the net freshwater flux relative to the marine influx ($x = F/V_0$), simplifies to

$$x = \frac{1}{\left(\frac{d + \lambda\delta_{\text{Ow0}} - \delta_{\text{Dw0}}}{\frac{\Delta_{\delta\text{Da}}}{C} - \lambda\Delta_{\delta\text{Ow}}} \right) - 1} \quad (14)$$

[40] With (12), we finally have a solution that depends on a limited number of rather well constrainable parameters: $\Delta_{\delta\text{Ow}}$, which is a difference between identically measured values from paired δ_{Oc} and Mg/Ca analyses, and $\Delta_{\delta\text{Da}}$, which is a difference between identically measured values from compound-specific alkenone analyses. These differences are measured between the final value in the basin/region of study, and the “unaffected” inflow into that region. The uncertainties in these difference terms can be reduced by the application of multiple replicate analyses for the values at both ends of the gradient. Note that, if a future technique arises that allows direct measurement of past δ_{Dw} , then it is simple to adapt equations (12)–(14) by substituting the term $\Delta_{\delta\text{Dw}}$ (the gradient in directly measured δ_{Dw} values) instead of the term $\Delta_{\delta\text{Da}}/C$.

[41] The equations also require an estimated value for the “net” deuterium excess (d). For open ocean studies, d will be very close to 10 (giving the global MWL). For highly

evaporative regions with evaporation into continually undersaturated air masses, d will be considerably higher, such as a value of about 22 in the modern eastern Mediterranean [Craig and Gordon, 1965; Gat, 1996; Matthews et al., 2000; McGarry et al., 2004]. Below, it will be shown that generous uncertainties can be allowed to the estimated value of d , as it has relatively little impact on the overall error propagation. The slope of the applied MWL (λ) is always close to 8. Finally, the factor C is needed, which can be obtained from experimental results, and which equals about 2.65 for two different coccolithophore species [Schouten et al., 2006].

5. Constraining Salinity Change Through Time

[42] For many settings, but in particular marginal basins, (12) can be used to derive a specific solution for the temporal change in salinity (Φ_S) between two time slices t_1 (older) and t_2 (younger) so that $\Phi_S = \Delta_{S(t_2)} - \Delta_{S(t_1)}$. If the difference in time between two states is small, an assumption can be made that the properties of inflow into the basin remained (almost) constant from one state to the next. In other words, the isotopic changes measured within the marginal basin would result entirely from changes in the climatological forcing over that basin. An example would be the abrupt onset of sapropel (anoxic sediment) deposition in the eastern Mediterranean, because of enhanced freshwater flooding into the basin [e.g., Rohling and Gieskes, 1989; Rohling, 1994; Cramp and O'Sullivan, 1999; Emeis et al., 2000; Rohling et al., 2002, 2004].

[43] The temporal change in salinity (Φ_S) is the difference in the basin's salinity before and after the onset of sapropel deposition, and both may be calculated using (12). We assume that no changes occurred in the inflow properties δ_{Dw0} , δ_{Da0} , δ_{Ow0} , S_0 . Also, C is constant in time (the same compounds are analyzed throughout). The slope (λ) of the applicable "net" MWL (a function of both the regional Mediterranean MWL, and the global MWL that applies to externally sourced meteoric water) is near to 8 (Figure 3). In the absence of detailed insight into temporal changes in the "net d ," we have to assume it is roughly constant for the basin, and allow a generous band of uncertainty. These assumptions result in simplifications that yield

$$\Phi_S = S_0 \left(\frac{\frac{\Phi_{\delta Da} - \lambda \Phi_{\delta Ow}}{C}}{\delta_{Dw0} - \lambda \delta_{Ow0} - d} \right) \quad (15)$$

[44] Here $\Phi_{\delta Da}$ represents the temporal change in the alkenone hydrogen isotope composition in the basin (e.g., eastern Mediterranean), from t_1 (e.g., before the sapropel onset) to t_2 (e.g., after the onset). Similarly, $\Phi_{\delta Ow}$ is the change in the reconstructed water oxygen isotope composition in the basin from t_1 to t_2 .

6. A Simple Application With Full Propagation of Errors

[45] Individual compound-specific hydrogen isotope analyses have a precision of $\sigma_{\delta Da} = 3\%$ to 5% [Schouten et al.,

2006]. Using 5% , and if no replicate analyses are performed, the terms $\Delta_{\delta Da}$ and $\Phi_{\delta Da}$ are determined with error margins of $\sigma_{\Delta_{\delta Da}} = \sigma_{\Phi_{\delta Da}} = \sqrt{(2 \times 5^2)} = 7\%$. The total range of C is illustrated by experimental results for two different coccolithophore species, giving $C = 2.65 \pm 0.30$ [Schouten et al., 2006]. Since this is the total range, it is reasonable to estimate that $\sigma_C = 0.1$. For S_0 some assumption is needed, and the importance of its uncertainty should be investigated by means of sensitivity tests.

[46] As a first approximation, it is reasonable to consider that the initial values δ_{Dw0} and δ_{Ow0} are related according to something close to their modern multidecadal average open ocean surface water relationship, which is $\delta_{Dw} = 7.4\delta_{Ow} - 0.7$ (Figure 1). Consequently, the term $(\delta_{Dw0} - \lambda\delta_{Ow0})$ in (12) (13) (14) and (15) would normally be very close to zero, and certainly will be negligible in comparison to the range of values of the "net" deuterium excess value (d), which will be between the global value of 10 and the regional Mediterranean value of 22 (values from Craig and Gordon [1965], Gat [1996], Matthews et al. [2000], and McGarry et al. [2004]). The entire term $(\delta_{Dw0} - 8\delta_{Ow0} - d)$ can therefore be closely approximated by $-d$ alone.

[47] Equations (12), (13) and (15) can thus be simplified to

$$S \cong S_0 \left(1 + \frac{\frac{\Delta_{\delta Da} - \lambda \Delta_{\delta Ow}}{C}}{-d} \right) \quad (16)$$

$$\Delta_S \cong S_0 \left(\frac{\frac{\Delta_{\delta Da} - \lambda \Delta_{\delta Ow}}{C}}{-d} \right) \quad (17)$$

$$\Phi_S \cong S_0 \left(\frac{\frac{\Phi_{\delta Da} - \lambda \Phi_{\delta Ow}}{C}}{-d} \right) \quad (18)$$

[48] For the Mediterranean, the range of apparent "net" values for d can be roughly approximated as a result of the regional hydrological cycle and remotely sourced freshwater. Today, the balance between evaporation and locally sourced precipitation and runoff in the basin is of the order of $E:P = 1:0.4$ [Rohling, 1999, and references therein]. Hence there is a net evaporative flux $\psi = 0.6E$ that fuels locally sourced precipitation, developing along the regional Mediterranean MWL ($\delta_D = 8\delta_O + 22$). Added to this is a remotely sourced freshwater component (R), which has developed along the global MWL ($\delta_D = 8\delta_O + 10$) (e.g., Figure 3). Through the Quaternary, R has been larger than 0 but smaller than ψ (the basin remained net evaporative overall [e.g., Rohling, 1999; Rohling et al., 2004]). We can thus establish a rough range for the "net" value of d

between 22 ($R = 0$) and 16 ($R = \psi$), or $d = 19 \pm 3$. More precise estimation would require an array of time series of direct measurements throughout the Mediterranean catchment area, for example from speleothem fluid inclusions.

[49] Using f to identify the functions (i.e., S , Δ_S , or Φ_S), error propagation is calculated using

$$\sigma_f = \sqrt{\left(\frac{\partial f}{\partial \Delta_{\delta_{\text{Da}}}} \sigma_{\Delta_{\delta_{\text{Da}}}}\right)^2 + \left(\frac{\partial f}{\partial \Delta_{\delta_{\text{Ow}}}} \sigma_{\Delta_{\delta_{\text{Ow}}}}\right)^2 + \left(\frac{\partial f}{\partial d} \sigma_d\right)^2 + \left(\frac{\partial f}{\partial C} \sigma_C\right)^2 + \left(\frac{\partial f}{\partial S_0} \sigma_{S_0}\right)^2} \quad (19)$$

[50] Because they have identical forms, error propagation for (18) is identical to that for (17), although it would in (19) require replacement of $\Delta_{\delta_{\text{Da}}}$ and $\Delta_{\delta_{\text{Ow}}}$ by $\Phi_{\delta_{\text{Da}}}$ and $\Phi_{\delta_{\text{Ow}}}$, respectively.

[51] To calculate an example of error propagation, some realistic values are needed. A first illustration can be given using oxygen isotope and alkenone SST data through the onset of last interglacial sapropel S5 in the Aegean Sea [Marino *et al.*, 2007]. That data set suggests an approximate value of $\Phi_{\delta_{\text{Ow}}} = -1.5\text{‰}$. Unpublished alkenone-based hydrogen isotope data on the same samples (courtesy of M. van der Meer and S. Schouten, Royal Netherlands Institute for Sea Research (NIOZ), Texel, Netherlands, 2006) suggest an amplitude of $\Phi_{\delta_{\text{Da}}} = -25\text{‰}$. Using these values in equation (19) together with $C = 2.65$ [Schouten *et al.*, 2006], a deuterium excess value of $d = 19$ (see above), and (similar to the present inflow into the Mediterranean) $S_0 = 36.2$, offers a value of $\Phi_S = -4.9$ practical salinity units (psu) for the salinity change associated with the onset of sapropel S5 deposition in the SE Aegean Sea. Using errors of $\sigma_{\Phi_{\delta_{\text{Da}}}} = 7\text{‰}$, $\sigma_{\Phi_{\delta_{\text{Ow}}}} = 0.3\text{‰}$, $\sigma_C = 0.1$, $\sigma_{S_0} = 1.8$ (i.e., 5%), $\sigma_d = 3$, the calculated $\sigma_{\Phi_S} = 6.9$ psu (note that this is a factor 2 better than the uncertainty based on the δ_{Da} -only method if calculated with similar assumptions and values). The size of σ_d has only negligible impact on the overall uncertainty.

[52] In the example above, without extensive replicate analyses, the salinity change associated with the onset of S5 in the SE Aegean Sea is calculated as -4.9 ± 6.9 psu, where it should be noted that the size of the error margin is to a large extent due to $\sigma_{\Phi_{\delta_{\text{Da}}}}$ and $\sigma_{\Phi_{\delta_{\text{Ow}}}}$. These are the uncertainties associated with the measured changes in δ_{Da} and δ_{Ow} across the onset of S5, and these uncertainties can be reduced by running multiple replicates, calculating the mean value and its standard error (SE). Statistical error reduction then works to give $\text{SE}_{\Phi_{\delta_{\text{Da}}}} = \sigma_{\Phi_{\delta_{\text{Da}}}}/\sqrt{N}$ and similarly for $\text{SE}_{\Phi_{\delta_{\text{Ow}}}}$. If both δ_{Da} and δ_{Ow} were to be constrained by 25 analyses before and after the onset of S5, then the uncertainty in the calculated Φ_S values is ± 1.7 psu (or ± 2.0 based on 16 sets of replicates rather than 25). This would constrain the salinity change associated with the onset of S5 to a much more convincing -4.9 ± 1.7 psu. Clearly, multiple replicate analyses are an essential component of this new method to approach paleosalinity (but note that the same is true for the conventional approaches).

[53] There are two caveats. First, the presented example may give a rather favorable account of the method's poten-

tial, since the high deuterium excess values in the Mediterranean region may promote the development of amplified signal responses relative to those expected in areas with lower values of d . Secondly, work is needed to establish to which water mass the inferred salinity change applies. Does it characterize changes in only a very thin freshwater-

affected layer (or lenses) at the very surface, or does it apply to the entire summer or winter mixed layer? Note that this problem is again not unique to the method presented here; it applies to all existing paleosalinity techniques, and indeed also to the vast majority of paleotemperature proxies. Insight into this aspect may be obtained by detailed quantitative considerations of signal differences between multiple pelagic species from the same samples [cf. Rohling *et al.*, 2004].

7. Scope for Further Improvement

[54] Note that the values calculated for σ_{Φ_S} are representative also for σ_{Δ_S} as their equations have the same form, and that for σ_S a first estimate can be obtained by determining $\sqrt{(\sigma_{S_0}^2 + \sigma_{\Delta_S}^2)}$. It is interesting to consider on this theoretical basis what needs to be done to achieve uncertainties in paleosalinity change estimates from this method that are smaller than, or equal to ± 1.5 psu. Here we need to take into account that the assumption as used already, that $\sigma_{\Phi_{\delta_{\text{Ow}}}} = 0.3\text{‰}$, requires that individual δ_{Ow} is constrained to about $\pm 0.2\text{‰}$, which likely is near the very limit of the possibilities. Improvement should therefore be sought primarily in the δ_{Da} analyses, which are currently constrained within $\pm 5\text{‰}$. To achieve an uncertainty in calculated Φ_S (or Δ_S) values of about ± 1.5 psu, $\sigma_{\Phi_{\delta_{\text{Da}}}}$ (or $\Delta_{\delta_{\text{Da}}}$) needs to be about 2‰ , which implies that individual δ_{Da} analyses would need to be constrained within about $\pm 1.4\text{‰}$. As I can see it, this may be the most feasible technological route toward further improved paleosalinity estimates. Secondary ways to reduce the overall uncertainties in the calculated Φ_S (or Δ_S) values concern further reductions of the uncertainties in C and the “net” value of d (e.g., by a geographically widespread network of measurements on fluid inclusions in speleothems). On theoretical grounds it should be possible to achieve uncertainties in Φ_S (or Δ_S) of ± 1 psu or slightly smaller with the present method in regions with relatively high deuterium excess values.

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