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Letter Section

Paleosalinity: confidence limits and future applications

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Abstract

Error propagation is investigated through the only commonly applied technique for reconstruction of paleosalinity, based on oxygen isotope residuals. Although this technique is known to be fairly inaccurate, there remained a need for thorough assessment of confidence limits in a variety of global settings. Here, it is found that a theoretical minimum error bar of between $\pm 0.3\%$ and 0.7% applies to paleosalinity estimates, and that real-life practical limits are rarely better than $\pm 0.6\%$. Best results are expected in the latitudinal ranges $> 50^{\circ}$ N and $> 70^{\circ}$ S, taking care to avoid the sea–ice margin. Confidence intervals at low and mid-latitudes (including marginal seas) are very wide, at least $\pm 1.8\%$ for the Mediterranean and $\pm 2.2\%$ for the equatorial Atlantic. It appears that oxygen isotope distributions are best used in their own right to investigate circulation and advective processes in coupled ocean–atmosphere–cryosphere models, instead of calibrating them to paleosalinity to define restoring boundary conditions. However, isotope residual-based paleosalinity maps from large numbers of (regionally averaged) studies in the above-mentioned latitudinal bands may help in defining initial conditions and first-order validation arguments for models. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Paleosalinity is one of the major unsolved variables in paleoceanographic studies. As yet, it can not be convincingly determined from direct interpretation of any of the available proxy-data. Usually, therefore, paleosalinity is estimated following a rather complex, indirect approach, which uses so-called "oxygen isotope residuals" (among others, Thunell and Williams, 1989; Duplessy et al., 1991; Rostek et al., 1993; Maslin et al., 1995; Hemleben et al., 1996; Labeyrie et al., 1996; Kallel et al., 1997). The present note concerns a critical evaluation of error-propagation through this paleosalinity technique.

2. The relationship between salinity and oxygen isotope ratios

Ignoring subsurface advection (Rohling and Bigg, 1998; Schmidt, 1998), lateral gradients in conservative properties due to mixing of water masses may be assessed using linear mixing relationships between a mean

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freshwater endmember and a mean marine endmember, with salinities S_F and S_w , and oxygen isotope ratios δ_F and δ_w , respectively (e.g., Fairbanks, 1982; Rohling and Bigg, 1998). In fact, oxygen isotope ratios are not fully conservative in the ocean because a correction is needed for the salt-content of the water (Paren and Potter, 1984). However, this correction is normally very small, and therefore often ignored. Using that minor simplification, the combined mixing equations for salinity (*S*) and isotope ratio (δ) give a linear relationship of the form:

$$\delta = \left(\frac{\delta_{\rm w} - \delta_{\rm F}}{S_{\rm w} - S_{\rm F}}\right)S + \delta_{\rm F} \tag{1}$$

where $S_{\rm F}$, the salinity of the freshwater mixing endmember, is virtually equal to 0 and can therefore be omitted.

In paleosalinity reconstructions, isotopic residual signals are obtained from comparison between oxygen isotope values for a time-slice in the past and oxygen isotope values for the present, using carbonate-based oxygen isotope records. These isotopic differences are corrected for the influence of the glacial concentration effect that is caused by preferential ¹⁶O sequestration in ice sheets ($\Delta \delta_g$), and for differences between the calcification-temperatures for the two time-slices. The glacial effect has been related to sea level lowering due to ice sheet accumulation, and amounts to $\Delta \delta_g(\%) = 0.012 \ z_{sl}$, where z_{sl} is the magnitude of sea level drop relative to the present, in meters (Labeyrie et al., 1987; Shackleton, 1987; Fairbanks, 1989). Although Schrag et al. (1996) argue that $\Delta \delta_g(\%) = 0.008 \ z_{sl}$ would be more appropriate, the uncertainty in the isotopic enrichment with sea level lowering is usually estimated around $\pm 0.001\%$ m⁻¹. The temperature effect is constrained by paleo-sea surface temperature (paleo-SST) techniques, and amounts to about 0.25‰ °C⁻¹. SST reconstruction techniques are claimed to achieve an accuracy of order ± 1 to 1.5°C (e.g., Maslin et al., 1995; Pflaumann et al., 1996; Ortiz and Mix, 1997). Hence, paleosalinity reconstructions are interested in the form of Eq. (1) that solves for *S*, which is:

$$S = (\delta_{\rm F} - \delta) \frac{S_{\rm w}}{\delta_{\rm F} - \delta_{\rm w}}$$
(2)

3. Paleosalinity

In paleosalinity calculations, Eq. (2) is considered for both the present-day (indicated with $_0$), and for the past time-slice of interest (indicated with $_1$). Hence, temporal changes are allowed in the endmember properties, so that the S: δ ratio varies in accordance with reasonable changes in the marine and freshwater mixing endmembers. The past δ of sea water at the core site (δ_1) then equals the present-day value plus a sea level related glacial concentration factor ($\Delta \delta_g$) and a factor expressing the temperature-corrected difference between the two time-slices ($\Delta \delta$), or $\delta_1 = \delta_0 + \Delta \delta_g + \Delta \delta$. It is the parameter $\Delta \delta$, the so-called isotopic residual, that is viewed in paleoceanographic studies as a result of change in the evaporation/precipitation regime, and which would therefore provide a measure of salinity difference between the past and present-day time-slices.

The mean marine mixing endmember δ -value is considered to be affected only by the ice volume effect, so that $\delta_{w1} = \delta_{w0} + \Delta \delta_g$. Global ocean salinity also changes with sea level, because of freshwater extraction and 'storage' in the global ice-sheets. The change in salinity due to the ice-volume effect affects the salinity of the mean marine mixing endmember through the simple concentration relationship $S_{w1} = S_{w0}\{1 + z_{s1}/(3900 - z_{s1})\}$ (e.g., Maslin et al., 1995). The confidence interval in past sea level reconstructions is taken as ± 5 m for the last 20,000 years (Fairbanks, 1989, 1990).

Paleosalinity calculation next takes the following steps: (i) the oxygen isotopic composition of sea water at the study site, δ_0 , is calculated using the present-day observed salinity at that site in Eq. (1); (ii) a fossil record

is used to determine the (temperature corrected) isotopic residual, $\Delta \delta$, between the time-slice of interest and the present; (iii) the sea level position for the time-slice of interest is determined, relative to the present, and is used to determine the global ice-volume effects on isotopic composition and salinity; (iv) the past oxygen isotopic composition of sea water at the study site, δ_1 , is calculated using $\delta_1 = \delta_0 + \Delta \delta_g + \Delta \delta$; (v) the value of δ_1 is translated into paleo-salinity, S_1 , using Eq. (2) with the appropriate paleo-values for the mixing endmembers.

Here, I combine these steps into one equation to calculate paleosalinity (Ψ), giving:

$$\Psi = \left(\frac{S_{w1}\delta_{F0} - S_{w1}\delta_{w0}}{S_{w0}(\delta_{F1} - \delta_{w1})}\right)S_0 + \frac{S_{w1}}{(\delta_{F1} - \delta_{w1})}(\delta_{F1} - \delta_{F0} - \Delta\delta - \Delta\delta_g)$$
(3)

The advantage of formulating one single equation for the whole procedure is that it can be differentiated to allow assessment of the propagation of the various errors and uncertainties. The confidence limits to the determination of the present-day and past freshwater endmember values δ_{F0} and δ_{F1} are taken to be $\sigma_{\delta_{F0}} = \pm 10\%$ and $\sigma_{\delta_{F1}} = \pm 20\%$ of the absolute values, respectively. These estimated relative values are chosen so that a present-day high latitude value of -20% is constrained within $\pm 2\%$, a realistic target that in many cases is significantly improved on by multiple analyses in the Atlantic and Pacific watercolumns and of the very high latitude freshwater input (e.g., Craig and Gordon, 1965; Bédard et al., 1981; Fairbanks, 1982; Östlund and Hut, 1984; Brezgunov, 1990; Kipphut, 1990; Létolle et al., 1993; Macdonald et al., 1995), while considerably more freedom is allowed in the accuracy of paleo-values, for which no water-column studies can be undertaken. The confidence limit $\sigma_{\delta_{w1}}$ to the past mean isotopic composition of the marine mixing endmember, δ_{w1} , depends wholly on the accuracy in $\Delta \delta_g$. That accuracy, expressed as $\sigma_{\Delta \delta_g}$, in turn is a function of the confidence limits to sea level reconstructions (± 5 m) and to the ice-volume effect on global oxygen isotope ratios ($\pm 0.001\%$ m⁻¹). Therefore, $\sigma_{\delta_{w1}}$ ranges from 0.06‰ (for present-day sea level) to 0.13‰ (for 120 m sea-level lowering). The confidence interval $\sigma_{\delta_{w1}}$ similarly depends on the accuracy of sea level reconstruction, and can be derived from the concentration relationship as $\sigma_{z_{s1}}$ (3900 S_{w0}) (z_{s1} – 3900)⁻¹ \bigoplus re $\sigma_{z_{s1}}$ is ± 5 m. The final confidence interval that needs to be considered, $\sigma_{\Delta \delta}$, is much more difficult to constrain. Purely on

The final confidence interval that needs to be considered, $\sigma_{\Delta\delta}$, is much more difficult to constrain. Purely on analytical precision, this error would be defined by two separate analyses, one for the past time-slice, and one for the present-day. This would mean a value of $\sigma_{\Delta\delta}$ around 0.2‰. However, the core-top is rarely equivalent to the present-day sediments, and dating inaccuracies for the targeted past time-slice also determine that a range of values from the fossil isotope record needs to be considered. In addition, any isotopic analysis presents a mass-balanced average value for the material that is analysed. Replicate single planktonic foraminifer analyses show 1 σ intervals of 0.2‰, which add to the uncertainty from analytical precision (Tang and Stott, 1993). Two of such confidence intervals are involved in determination of the isotopic residual $\Delta\delta$. Moreover, inaccuracies in paleotemperature reconstruction for the past time-slice of order $\pm 1^{\circ}$ C also cause error in the determination of $\Delta\delta$. Rohling and De Rijk (1999) discuss these issues in more detail, and conclude that resultant values for $\sigma_{\Delta\delta}$ may range up to $\pm 0.6\%$ or more. In the present study, a best and worst case scenario approach is followed, where the former uses $\sigma_{\Delta\delta} = 0.2\%$, and the latter $\sigma_{\Delta\delta} = 0.6\%$. Note that the above discussion concerning $\sigma_{\Delta\delta}$ ignores potential additional sources of inaccuracy rooted in quality of specimen selection, individual species' seasonal and depth ranges, and sediment accumulation rate and mixing by bioturbation. Hence, even the 'worst case' value of $\pm 0.6\%$ used in the present paper may be a low estimate of the real value for $\sigma_{\Delta\delta}$, which would imply that the paleosalinity errors calculated below underestimate the true errors involved.

4. Error propagation

Propagation is considered of $\sigma_{\delta_{wl}}$, $\sigma_{\delta_{Fl}}$, $\sigma_{\delta_{F0}}$, $\sigma_{\Delta\delta}$, $\sigma_{\Delta\delta_g}$, and $\sigma_{S_{wl}}$ through paleosalinity Eq. (3). These evaluations are made for realistic ranges of: salinity at the core-site of $S_{w0} - 5 < S_0 < S_{w0}$; sea level lowering of 0 and 120 m; and isotopic compositions of the present-day freshwater mixing endmember δ_{F0} of 0, -10 and

-20%. The results are expressed in a series of diagrams plotting error in the paleosalinity estimates as a function of the isotopic composition of the past freshwater mixing endmember, $-50 < \delta_{F1} < -5\%$, and of the isotopic residual, $-3 < \Delta \delta < +3\%$.

To consider error propagation, the appropriate derivatives of Eq. (3) are needed:

$$A = \frac{d\Psi}{d\delta_{F1}} = S_{w1} \frac{S_0 \delta_{w0} - S_0 \delta_{F0} + S_{w0} \times \delta_{F0} + S_{w0} \Delta \delta + S_{w0} \Delta \delta_g - S_{w0} \delta_{w1}}{S_{w0} (\delta_{F1} - \delta_{w1})^2}$$
(4)

$$B = \frac{d\Psi}{d\delta_{F0}} = S_0 \frac{S_{w1}}{S_{w0}(\delta_{F1} - \delta_{w1})} - \frac{S_{w1}}{(\delta_{F1} - \delta_{w1})}$$
(5)

$$C = \frac{\mathrm{d}\Psi}{\mathrm{d}\Delta\delta} = \frac{S_{\mathrm{w1}}}{\left(\delta_{\mathrm{w1}} - \delta_{\mathrm{F1}}\right)} \tag{6}$$

$$D = \frac{\mathrm{d}\Psi}{\mathrm{d}\Delta\delta_{\mathrm{g}}} = \frac{S_{\mathrm{w1}}}{\left(\delta_{\mathrm{w1}} - \delta_{\mathrm{F1}}\right)} \tag{7}$$

$$E = \frac{\mathrm{d}\Psi}{\mathrm{d}\delta_{w1}} = -S_{w1} \frac{S_0 \delta_{w0} - S_0 \delta_{F0} - S_{w0} \delta_{F1} + S_{w0} \delta_{F0} + S_{w0} \Delta \delta + S_{w0} \Delta \delta_{g}}{S_{w0} (\delta_{F1} - \delta_{w1})^2}$$
(8)

$$F = \frac{\mathrm{d}\Psi}{\mathrm{d}S_{w1}} = -\frac{S_0 \,\delta_{w0} - S_0 \,\delta_{F0} - S_{w0} \,\delta_{F1} + S_{w0} \,\delta_{F0} + S_{w0} \Delta \delta + S_{w0} \Delta \delta_g}{S_{w0} (\,\delta_{F1} - \delta_{w1})} \tag{9}$$

The error in Ψ is then found using

$$\sigma_{\Psi} = \pm \sqrt{\left(A\sigma_{\delta_{\mathrm{F}1}}\right)^{2} + \left(B\sigma_{\Delta\delta}\right)^{2} + \left(C\sigma_{\delta_{\mathrm{F}0}}\right)^{2} + \left(D\sigma_{\Delta\delta_{\mathrm{g}}}\right)^{2} + \left(E\sigma_{\delta_{\mathrm{w}1}}\right)^{2} + \left(F\sigma_{\delta_{\mathrm{w}1}}\right)^{2}}$$

5. Discussion and conclusions

General results of the error-propagation analysis for various scenarios are plotted in Figs. 1 and 2. These plots show that the greatest variability in σ_{Ψ} is a function of the absolute value of the past isotopic composition of the freshwater mixing endmember, δ_{F1} . The next greatest influences are coming from the magnitude of the isotopic residual ($\Delta \delta$, plotted along vertical axes in Figs. 1 and 2) and its confidence interval $\sigma_{\Delta \delta}$ (contrast between Figs. 1 and 2). A less important, but still appreciable influence comes from the absolute value of the present-day isotopic composition of the freshwater mixing endmember, δ_{F0} . The latter influence disappears when present-day core-site salinity (S_0) equals the present-day marine mixing endmember salinity (S_{w0}) so that $dS_0 = S_0 - S_{w0} = 0$ (Fig. 3). This is logical, since that condition means that the core-site is bathed in 100% marine mixing endmember waters where the freshwater mixing endmember has no importance. In fact, this implies that paleosalinities are best constrained from isotope residuals for sites as remote as possible from freshwater sources.

Fig. 1. Values of the error in paleosalinity calculation (σ_{Ψ}) in ‰, relative to the mean isotopic composition of the past freshwater mixing endmember (δ_{F1}) and to a range of values for the (temperature corrected) oxygen isotopic residual, $-3 < \Delta \delta < +3$ ‰. This figure uses a minimum value for the error in the isotopic residual of $\sigma_{\Delta\delta} = \pm 0.2$ ‰ (Rohling and De Rijk, 1999), and a salinity deviation at the core site of 5 units relative to the marine mixing endmember ($dS_0 = -5$). Plots (a), (b) and (c) represent sea level equal to the present, and plots (d), (e) and (f) are for sea level at 120 m below the present. Plot pairs (a and d), (b and e) and (c and f) are for values of the mean isotopic composition of the present-day freshwater mixing endmember $\delta_{F0} = -20$ ‰, -10‰, and 0‰, respectively.





Fig. 2. The same as Fig. 1, but for the high-end estimate $\sigma_{\Delta\delta} = \pm 0.6\%$ (Rohling and De Rijk, 1999).

The results are most accessible by looking at specific examples, where I use an intermediate value of $\sigma_{\Delta\delta} = \pm 0.4\%$. The first two examples concern the eastern Mediterranean, drawing on a summary of values for the various parameters by Rossinsky and Swart (1993), Rozanski et al. (1993) and Rohling and De Rijk (1999). In that basin, the present-day value δ_{F0} is roughly between -5% and -10%, and estimates for δ_{F1} during the last glacial maximum (LGM, sea level lowered 120 m) are not substantially different. A typical value for the temperature-corrected LGM isotopic residual is around +1%. For $\sigma_{\Delta\delta} = \pm 0.4\%$, the paleosalinity error σ_{Ψ} would be around $\pm 1.8\%$ (Fig. 4b). Similar values for δ_{F0} and δ_{F1} with a residual around $\Delta\delta = -1\%$ for the early-mid Holocene period of sapropel S1 deposition also give $\sigma_{\Psi} \approx \pm 1.8\%$ (Fig. 4a). Such large error-margins imply that paleosalinity reconstructions from oxygen isotope residuals in the Mediterranean (e.g., Thunell and Williams, 1989; Kallel et al., 1997) are untrustworthy. It would seem more sensible to use the isotopic information from that basin in its own right, rather than attempting a calibration to salinity (cf. Rohling and Bigg, 1998; Rohling and De Rijk, 1999).

The third example concerns the equatorial Atlantic, where δ_{F0} is around -2% (I use -5% which, if anything, slightly reduces the observed error-margin) (Rossinsky and Swart, 1993), while also δ_{F1} is unlikely to



Fig. 3. Comparison of the minimum estimates for σ_{Ψ} with $\sigma_{\Delta\delta} = \pm 0.2\%$ (a, b) and $\sigma_{\Delta\delta} = \pm 0.6\%$ (c, d). Minimum error estimates are based on changes at sites bathed in 100% marine mixing endmember waters ($dS_0 = S_0 - S_{w0} = 0$). Plots (a) and (c) for present-day sea level; plots (b) and (d) for sea level lowering of 120 m. Note that if $dS_0 = 0$, then variations in δ_{F0} are insignificant for σ_{Ψ} (see text).



Fig. 4. Values of σ_{Ψ} vs. δ_{F1} and $\Delta\delta$ for the three example settings discussed in the text. These examples use an intermediate value $\sigma_{\Delta\delta} = \pm 0.4\%$. Plots (a) and (b) show eastern Mediterranean conditions ((a) for present-day sea level, (b) for 120 m sea level lowering). Plots (c) and (d) show the equatorial Atlantic ((c) for sea level equal to the present, (d) for 120 m lowering). Plots (e) and (f) represent the N Atlantic ((e) for sea level equal to the present, (f) for 120 m lowering). See text for details on the applied values of δ_{F0} and dS_0 .

have been more depleted than -5% in these areas where precipitation occurs very close to the evaporative source regions. Salinities in equatorial regions commonly are some 2–3 units depleted relative to the marine mixing endmembers, due to a strong excess of precipitation (Fig. 4c,d uses dS = -2.5). For $\sigma_{\Delta\delta} = \pm 0.4\%$, salinities for interglacial periods (Fig. 4c) may at best be reconstructed with an error of $\pm 2.5\%$. For full glacial intervals, the situation is marginally better, with minimum paleosalinity errors around $\pm 2.2\%$ (Fig. 4d).

It becomes obvious that the errors are unacceptably high everywhere, except in regions with a strongly depleted mean past freshwater mixing endmember (δ_{F1}). Such conditions may be expected at the high latitudes, especially in areas that were strongly influenced by calving and melt from continental ice sheets, which normally have isotopic compositions of -35% or less. Because of the strong net freshwater input, high-latitude areas commonly have salinities that are several units lower than that of the marine mixing endmember. Using a representative value of $\delta_{F0} = -20\%$ (Craig and Gordon, 1965; Fairbanks, 1982), a typical estimate for the glacial NW Atlantic of around $\delta_{F1} = -30\%$ (e.g., Rohling and Bigg, 1998), and a sea level lowering of 120 m (Fairbanks, 1989, 1990), a typical average value for σ_{Ψ} is found of about $\pm 0.6\%$ (Fig. 4f). For glacial periods with strongly negative isotopic residual signals in these areas, for example during Heinrich events (e.g., Maslin et al., 1995), these errors increase up to $\pm 0.9\%$ (using $\Delta \delta = -2\%$) (Fig. 4f). Overall, such confidence intervals are not bad, which implies that isotope residual based paleosalinity reconstructions in the high latitudes are a useful tool to investigate lateral salinity trends that might highlight the relative positions of such features as the polar front and major currents like the Gulf Stream.

For most of the world's oceans, with an isotopic composition for the freshwater mixing endmember > -30%, except perhaps in extreme Antarctic conditions, a theoretical minimum error to paleosalinity reconstructions applies of between $\pm 0.3\%$ (Figs. 1c and 3a) and $\pm 0.7\%$ (Figs. 2c and 3c) at sites bathed in 100% marine mixing endmember (i.e., $dS_0 = 0$), depending on the accuracy of determination of the isotopic residual. Reasonably reliable paleosalinity estimates with errors $\leq \pm 1.5\%$ seem possible only in areas where the freshwater mixing endmember has an isotopic value $\leq -20\%$, considering residuals within a normal range of $-1 < \Delta \delta < +1\%$ (Figs. 1–4). Accepting such errors $\leq \pm 1.5\%$, therefore, the latitudinal distribution of isotopic compositions in precipitation (Rozanski et al., 1993) would suggest that the paleosalinity technique using isotopic residuals may be applied to the North of about $50-60^{\circ}$ N latitude, and South of about 70° S latitude. Here, it is emphasized that the above examples rely on $\sigma_{\Delta\delta} = \pm 0.4\%$, whereas it was argued earlier that $\sigma_{\Delta\delta} \geq \pm 0.6\%$ might be more realistic. This would imply that the calculated values for σ_{ψ} represent low estimates of the true errors.

It appears from the present study that oxygen isotope residuals can *not* be reliably used for paleosalinity calculations in lower latitudes, nor in low to mid-latitude marginal seas, where depletions in the isotopic composition of the freshwater mixing endmember are too small.

Temporal variability in isotopic composition of ice sheets during their growth and decay phases (Mix and Ruddiman, 1984) would influence δ_{F1} . Hence, isotope residuals may not be used to reliably estimate temporal (downcore) changes in paleosalinity, even in the above identified latitudinal bands where the technique would appear to be most accurate. Spatial patterns in those regions, however, may be much more successfully reconstructed, since δ_{F1} would be the same at any one time for all sites considered on a regional scale. Moreover, statistical error reduction applies, since the standard error of a mean value is equal to $1/(N)^{1/2}$ times the error margin associated with (independent) individual measurements. Such error reduction proved successful in the identification of main gradients in the LGM and Holocene optimum oxygen isotope distribution in the Mediterranean (Rohling and De Rijk, 1999). It may similarly be applied to paleosalinity reconstructions, using a large number of sites to determine the mean and standard error for a geographically limited watermasses. Trends between these mean values may then be used to define maps of the more salient spatial gradients in high-latitude paleosalinity, with acceptable error bars (around $\pm 0.5\%$ if each watermass at a given location is characterised by at least nine independent observations).

The present assessment of errors in paleosalinity reconstructions does not take into account the effects of sea ice melting and freezing, which seriously complicates the isotopic composition of surface waters (e.g., Strain

and Tan, 1993; Rohling and Bigg, 1998). Consequently, the mapping approach suggested above should be considered with utmost care near the sea-ice margin. In addition, temporal changes in subsurface watermass advection throughout the world ocean may further complicate the issue (Rohling and Bigg, 1998; Schmidt, 1998).

I conclude that the most sensible way forward is to look at oxygen isotope distributions in their own right, using it as a passive tracer in coupled ocean-atmosphere-cryosphere models. Validations may then be performed against conceptual paleosalinity maps for specific high-latitude bands, as discussed above. These maps may be used to determine initial conditions for the models, but should *not* be used to constrain restoring boundary conditions. Instead, deviations between modelled oxygen isotope distributions and the maps should be closely examined in the context of possible changes in subsurface advection relative to the present.

Independently of this work, Schmidt (1999) also investigated error propagation in paleosalinity calculations. Results shown therein are complementary and strongly supportive of the conclusions arrived at here.

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