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Are seawater Sr/Ca variations preserved in Quaternary foraminifera?

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Abstract—High precision measurements of Sr/Ca in planktonic foraminifera for the last 150 ka reveal Sr/Ca variations of up to 12% on glacial/interglacial time scales. Although records showing the largest variations appear to be strongly influenced by selective dissolution, other records show Sr/Ca variations of 3–5% that do not covary with indicators of dissolution intensity and that are reproduced in sites of contrasting Quaternary dissolution histories. These systematic variations are characterized by high Sr/Ca ratios during glacial maxima, followed by steep decreases during deglaciation and gradual increases through interstadial periods, closely following $\delta^{18}\text{O}$ curves. Foraminiferal Sr/Ca variations may reflect changes in the Sr/Ca ratio of seawater, or they may be due to kinetically or biologically induced changes in Sr partitioning. Coupled numerical models of the Sr and Ca budgets of the ocean reveal that sea level changes, together with large changes in river fluxes and carbonate accumulation rates, can produce seawater Sr/Ca variations that approximate both the shape and amplitude of foraminiferal Sr/Ca variations. However, such extreme changes in river and carbonate fluxes conflict with existing data on carbonate accumulation rates and Sr isotopic constraints on the magnitude of variations in the river flux. Smaller variations (1–3%) in the Sr/Ca ratio of seawater likely characterize Quaternary glacial cycles. Changes in Sr partitioning due to glacial-interglacial changes in the carbonate ion concentration and other environmental factors likely produce additional variation in the Sr/Ca record of planktonic foraminifera. Copyright © 1999 Elsevier Science Ltd

1. INTRODUCTION

The long residence time of Sr in the ocean frequently leads to inferences that its concentration in the ocean does not vary over short time scales in the Quaternary. In fact, the modern Sr budget is far from steady-state (Schlanger, 1988), and models of the Sr and Ca budgets of the ocean show that variations in seawater Sr concentrations and Sr/Ca ratios can result from the large perturbations in Sr fluxes produced by Quaternary sea level variations (Stoll and Schrag, 1998). Most of the Sr/Ca variation results from release of large amounts of Sr to the ocean during recrystallization of shelf aragonites exposed by sea level falls. Previous models predict a range of likely variation in seawater Sr/Ca of 1–3% over glacial cycles, with 0.5% to 1.1% decreases occurring since the last glacial maximum (Stoll and Schrag, 1998). Although this predicted range of variation is small, it has important consequences for high precision paleoceanographic studies, particularly coral Sr/Ca paleotemperature estimates.

One way to reconstruct past variations in the Sr/Ca ratio of seawater is to measure the downcore Sr/Ca variation in foraminiferal tests. Culture experiments show that the Sr/Ca ratio of foraminifera depends on the Sr/Ca ratio in the culture solution (Delaney et al., 1985). However, reconstructing 1% to 3% variations in seawater Sr/Ca is likely to be difficult because secondary effects on the incorporation and preservation of Sr in foraminiferal calcite may partially obscure this signal in some records. Consequently, it is unlikely that we will find an ubiquitous pattern of variation in the Sr/Ca ratio of all foraminifera.

A foraminiferal record of variation in the mean Sr/Ca ratio of seawater, if it exists, must be extracted by seeking evidence for a pattern of Sr/Ca variation that is reproduced in multiple sites and that cannot be readily explained by known secondary effects.

Culture studies of several species suggest that the influence of temperature and salinity on Sr partitioning is minimal (Delaney et al., 1985; Martin et al., 1997), although Sr/Ca ratios of different species in sediment traps and core tops roughly correlate with calculated calcification temperatures (Delaney et al., 1985; Opdyke et al., 1993). However, other factors also may cause the Sr/Ca ratio to vary among different species, such as different calcification rates and crystal growth mechanisms that influence Sr partitioning in inorganic calcites (Paquette and Reeder, 1995; Lorens, 1981). Measuring Sr/Ca ratios in mono-specific foraminiferal assemblages is likely to minimize these latter effects.

Selective dissolution may also exert a significant influence on Sr/Ca ratios of foraminifera in sediments. During different life stages, foraminifera have been shown to precipitate calcite with different isotopic and minor element characteristics, possibly due to different calcification rates (Nurnburg et al., 1996; Rosenthal and Boyle, 1993; Lohman, 1995). Because these chemically distinct portions of the test have different solubilities, foraminifera are subject to effects of selective dissolution, as modeled by Lohman (1995) and measured by Brown and Elderfield (1996). Consequently, changes in the dissolution intensity at a single site over time may lead to changes in the bulk composition of foraminifera preserved in the sediment record. Covariation of Sr/Ca variations with changes in dissolution intensity for a particular site would suggest strong selective dissolution control over the Sr/Ca record. Conversely,

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Table 1. Location and depth of sites in this study.

Site	Latitude	Longitude	Water depth, m	Strat. ref.	Diss'n. ref.	Species	Size frac, μm	Tests, #	Cleaning proced.	Record length, ky
ODP 758	5°23'N	90°21'E	2925	1	7	<i>Globigerinoides sacculifer</i>	355–425	30	WASH	50
						<i>Globigerinoides sacculifer</i>	355–425	30	SON	50
						<i>Globorotalia menardii</i>	425–600	20	SON	60
DSDP 572A/C	1°26'N	113°51'W	3903	2	7	<i>Globorotalia tumida</i>	425–600	10–12	WASH	150
						<i>Globorotalia tumida</i>	425–600	15	PDIS (9 ml)	150
						<i>Orbulina universa</i>	425–600	20	SON	150
CHN82–24	41°43'N	32°51'W	3427	3	8	<i>Orbulina universa</i>	425–600	20	WASH	150
						<i>Orbulina universa</i>	425–600	20	SON	150
						<i>Globorotalia tumida</i>	425–600	10	SON	150
TT013-PC72	0°06'N	139°24'W	4298	4	9	<i>Globorotalia tumida</i>	425–600	10	PDIS (6 ml)	150
						<i>Globorotalia tumida</i>	425–600	10	SON	150
						<i>Orbulina universa</i>	425–600	30	WASH	150
DSDP 502B	11°29'N	79°04'W	3052	5	5	<i>Orbulina universa</i>	425–600	30	SON	80
						<i>Orbulina universa</i>	425–600	30	SON	80
						<i>Globigerina bulloides</i>	425–600	20	WASH	80
E49-21	42°11'S	94°53'E	3288	6	10	<i>Globigerina bulloides</i>	425–600	20	SON	80
						<i>Globigerina bulloides</i>	425–600	20	SON	80

Location and depth of sites in this study, along with details on foraminiferal Sr/Ca records produced for each site and sources of stratigraphy and dissolution records for each site. Cleaning procedures are described in detail in text. Data sources are: (1) Clemens et al., 1993, (2) Farrell, 1991, (3) Boyle and Keigwin, 1986, (4) Murray et al., 1995, (5) Prell, 1982, (6) Howard and Prell, 1992, (7) Chen, 1989, (8) Crowley, 1981, (9) LaMontagne et al., 1996, (10) Howard and Prell, 1994.

reproducibility of Sr/Ca variations from sites of contrasting dissolution histories would indicate that selective dissolution was not the dominant control over those Sr/Ca records.

A final complication may arise from small local variations in the Sr/Ca ratio of seawater in the photic zone where planktonic foraminifera calcify. Because the residence times of Sr and Ca in seawater are much longer than the timescale of ocean mixing, Sr/Ca ratios of seawater are generally spatially uniform. However, removal of SrSO₄ from the surface ocean by acantharia can depress the Sr/Ca ratio of the surface ocean by up to 2% relative to the deep ocean (de Villiers, 1994). Changes in the mean Sr/Ca ratio of seawater should still be reproduced in foraminiferal records from multiple sites; however, changes in acantharia production may superimpose additional variability.

To seek evidence for variation in the mean Sr/Ca ratio of seawater over glacial cycles, we measured Sr/Ca ratios of monospecific assemblages of foraminifera for multiple sites from different ocean basins for the last 150 ky. Unfortunately, it is not possible to use the same species for every site because foraminiferal populations change geographically. However, interspecific differences should affect only the absolute Sr/Ca ratios and not the record of past variations in seawater Sr/Ca. To assess the influence of selective dissolution on our records, we selected sites from different ocean basins with different dissolution histories and compared foraminiferal Sr/Ca variations in each site with changes in indices of dissolution intensity for that site. In several sites, we documented Sr/Ca variations that appear to be controlled by selective dissolution. However, in other sites we identified reproducible foraminiferal Sr/Ca variations that are unrelated to changes in dissolution intensity and cannot be explained by temperature-dependence of Sr partitioning in foraminifera or by local Sr/Ca variations due to acantharia productivity. Nonetheless, these reproducible Sr/Ca variations are considerably larger than our previous model predictions for changes in the mean Sr/Ca ratio of seawater. By using numerical simulations of the Sr and Ca budgets of the ocean, we investigated the changes in carbonate budgets and sea level history that are required to produce comparable variations in seawater Sr/Ca and assessed whether

these changes are permitted by available data on past carbonate accumulation, river fluxes, and sea levels. If it is not possible to simulate such large variations in the Sr/Ca ratio of seawater with geologically reasonable fluxes, then the pattern of foraminiferal Sr/Ca variation must be due to other, undocumented secondary effects on the incorporation or preservation of Sr in foraminiferal calcite.

2. MATERIALS AND METHODS

2.1. Site Selection and Analytical Methods

We examined samples from the Equatorial and Southern Indian Ocean (ODP site 758 and E49-21), from the Equatorial Pacific (DSDP site 572A/C and TT013-PC72, hereafter PC72), and from the North Atlantic (CHN82-24 and DSDP site 502B). We have tried to minimize the potential for selective dissolution by selecting cores with a water depth greater than ≈ 3000 m, significantly deeper than the depth at which dissolution of gametogenic calcite is complete (Brown and Elderfield, 1996; Opdyke et al., 1993; unpublished data). The exact locations and depths of each site are given in Table 1.

Single species of foraminifera were picked individually from restricted size fractions, as summarized in Table 1. Several cleaning procedures were used, with the objective of removing foreign material adhered to tests (mainly carbonate fine fraction) and minimizing within-sample heterogeneities in Sr/Ca ratios by partially dissolving the tests. In the simplest cleaning procedure, samples were crushed to break open the chambers and were washed with ethanol and distilled water (WASH), analogous to the procedure of Brown and Elderfield (1996) but without the ion exchange step which we found unnecessary for Sr. This procedure did not significantly dissolve foraminiferal carbonate but did remove nearly all fine fraction adhered to tests. For the partial dissolution procedures (PDIS), whole tests were shaken for 0.5 h in ethanol to remove fine material. The ethanol was aspirated off and several milliliters (amounts in Table 1) of 0.001 N HNO₃ were added to whole foraminifera and samples were shaken for 0.5 h. After the 0.001 N HNO₃ was removed, samples were crushed and washed in ethanol and distilled water as in the first cleaning procedure. The most rigorous cleaning procedure (SON) sonicates crushed samples for more efficient removal of adhered material; however, this procedure also leads to more extensive dissolution of the foraminiferal carbonate than either of the aforementioned techniques. Samples were twice sonicated for 2 min in 1.5 ml of distilled water, followed by sonication in 1.5 ml of ethanol, followed by sonication in 1.5 ml of distilled water, and finally rinsed with 1 M NH₄Cl and distilled water. In Results and Discussion, where duplicate records for the same site were prepared by

using different cleaning techniques, the technique abbreviation is given in parentheses after the site and species of the record.

All cleaned samples were dissolved in 2% HNO₃ for determination of Sr/Ca ratios via inductively coupled plasma emission spectroscopy on a Jobin–Yvon simultaneous instrument, model 46-P. Samples were run at concentrations of 20 ppm to 90 ppm Ca. Analytical precision for replicate samples run on multiple days averaged 0.1% (1 s). However, the measured ratio varies with the Ca concentration as a second order polynomial so that dilutions of the same sample yield Sr/Ca ratios that vary by 5% over concentrations of 20 ppm to 100 ppm Ca. In each analytical run, we included five dilutions each of two or more gravimetric standards of known Sr/Ca ratios and calculated the coefficients of the concentration dependence to correct the samples for this concentration effect. This correction reduces the precision slightly, to 0.2% to 0.4% (1s), based on replicate analyses of different dilutions of the same sample solution. All data shown in the figures have been corrected for the concentration effect.

2.2. Age Models and Dissolution Records

Age models for all sites are based on $\delta^{18}\text{O}$ stratigraphy correlated with the SPECMAP stack (Imbrie et al., 1984). Oxygen isotopic records and age assignments were produced by the sources given in Table 1, with the exception of site 502B, to which we assigned ages based on the $\delta^{18}\text{O}$ data of Prell (1982) using the chronostratigraphy of Martinson et al. (1987).

Sources of records of dissolution intensity are given in Table 1. No single index of dissolution intensity was available for all sites. The most robust index is probably the Composite Dissolution Index (Howard and Prell, 1994), which combines numerous indicators of dissolution intensity. The percentage of whole planktic foraminifera also has been shown to be a reliable dissolution index (e.g., Thunell, 1976; Thunell et al., 1982; Peterson and Prell, 1985; Howard and Prell, 1994). The percentage coarse fraction, used for 502B, may be less reliable because dissolution-induced fragmentation is not the only control on percentage coarse fraction: changing foraminifera/coccolith production rates also can change the percentage coarse fraction independently of dissolution variations (Peterson and Prell, 1985).

3. RESULTS

Time series for different sites show Sr/Ca variations ranging from 2% to 12% (Fig. 1). Many of the variations appear to be largely independent of different cleaning techniques, including partial dissolution, although several records show differences including the *Orbulina universa* records for site CHN82-24 and *Globigerina bulloides* records for site E49-21. In sites PC72 and 572, the patterns of Sr/Ca variations in *Globorotalia tumida* crushed and washed were the same as those that were partially dissolved, except during the 100- to 110-ky interval in PC72 (Fig. 1a and b). Although the absolute values differ, the patterns of Sr/Ca variations in *O. universa* from site 502B were also similar in the crushed and washed samples and those subjected to more rigorous cleaning and sonication (Fig. 1c). In contrast, *O. universa* samples from site CHN82-24 yielded opposing patterns of Sr/Ca variations with different cleaning techniques. The Sr/Ca ratios were much higher and there were variations of greater amplitude in the crushed and washed samples than in the sonicated, more rigorously cleaned samples (Fig. 1d). However, this difference may not be entirely due to the cleaning procedure because white or translucent, thin-shelled specimens were picked to produce the former record, and opaque, thicker-shelled specimens were picked for the latter. Sr/Ca variations in *Globigerinoides sacculifer* from site 758 and *G. bulloides* in site E49-21 also showed different trends for the crushed and washed samples and the sonicated, more rigorously cleaned samples (Fig. 1e and f). However, the

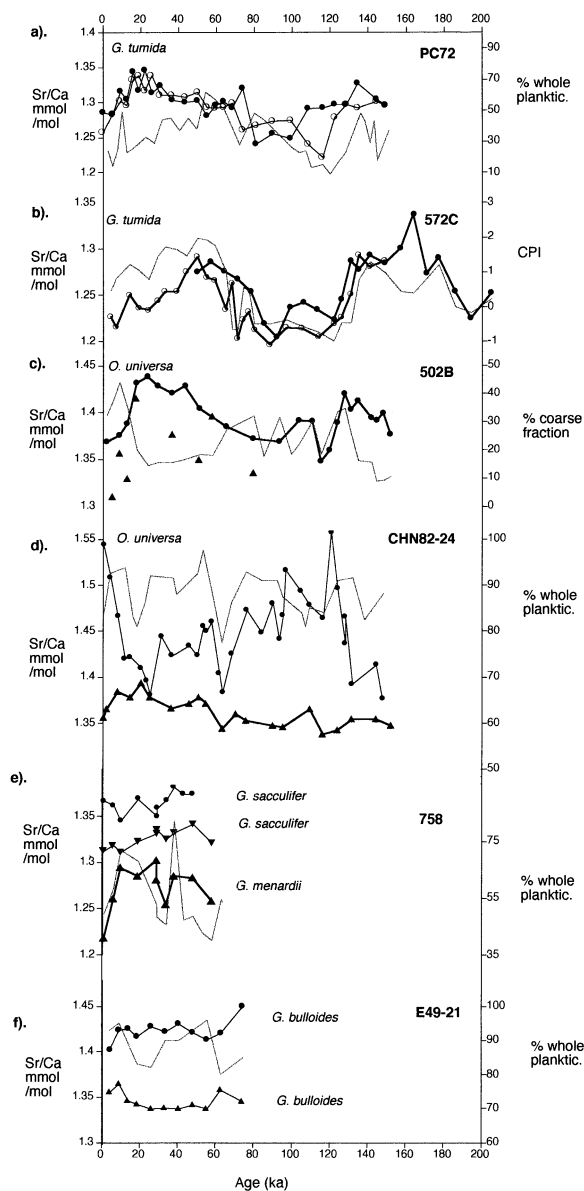


Fig. 1. Sr/Ca time series records for all sites shown with record of dissolution intensity for each site. Symbols indicate different cleaning procedures described in text. Closed circles, ethanol crushed and washed (WASH); open circles, partial dissolution (PDIS); triangles, full sonication cleaning (SON). Dissolution intensity is indicated by the thin gray line, with decreased dissolution upward. References for dissolution histories and stratigraphy for each site are given in Table 1.

amplitudes of Sr/Ca variations in these sites are only $\approx 2\%$, and discrepancies on this level may not be significant for these species because Sr/Ca ratios of two populations of *G. bulloides* from a single depth in the CHN82-24 core differed by 2%. Much lower variance (0.3–0.4%) was observed between replicate picks of *G. tumida* and *O. universa* from this and other cores.

In several sites, Sr/Ca variations follow records of variations in dissolution intensity, as Figure 1 illustrates. In the records of *G. tumida* from site 572, Sr/Ca variations of 7% to 9% closely

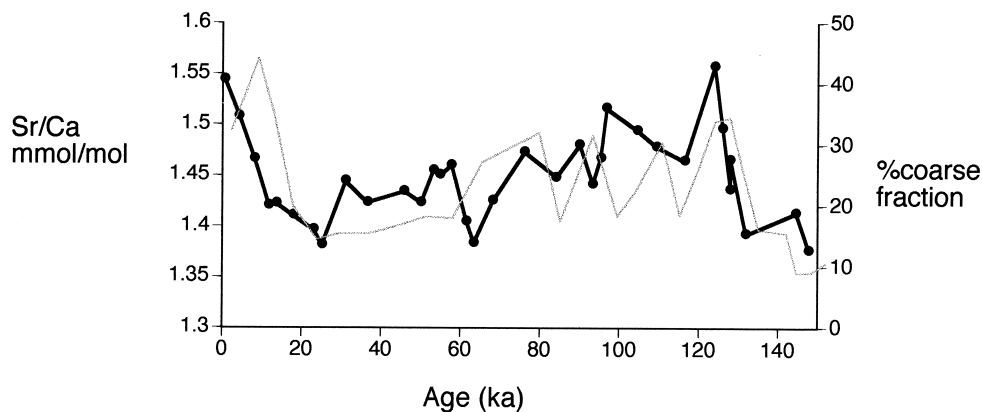


Fig. 2. Record of Sr/Ca from *O. universa* (WASH) in CHN82-24 (filled circles) compared with dissolution history at 502B (gray line).

follow variations in the composite preservation index (Fig. 1b). The 7% variation in Sr/Ca of *Globorotalia menardii* in site 758 shows a strong similarity with the percentage whole planktic foraminifera record for that site (Fig. 1e). Sr/Ca variation of 12% in the *O. universa* in CHN82-24 (WASH) also resembles the dissolution history of the other Atlantic record, 502B (Fig. 2).

Sites 502B, PC72, and the *O. universa* (SON) record of site CHN82-24 showed a common pattern of Sr/Ca variation characterized by gradual increases in Sr/Ca ratios leading up to glacial maxima, followed by rapid decreases in Sr/Ca ratios after glacial maxima. The amplitude of this variation was $\approx 5\%$ in PC72 and 502B and $\approx 3\%$ in CHN82-24 (Fig. 3). The penultimate glacial in CHN82-24 (SON) is not characterized by a Sr/Ca maximum, but this may be an artifact of the 15-ky sampling gap over the penultimate glacial interval in this core. Although times of particularly intense dissolution may influence the details of the record, dissolution does not appear to be the major control over the pattern of Sr/Ca variations in these records. Although Atlantic and Pacific sites show contrasting

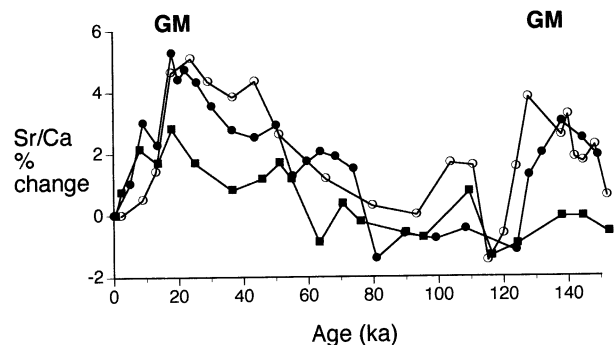


Fig. 3. Reproducible Sr/Ca variations plotted as percentage difference from present Sr/Ca ratio. Filled circles, average of Sr/Ca data from *G. tumida* (WASH) and *G. tumida* (PDIS) in site PC72; open circle, *O. universa* from site 502B; square, *O. universa* (SON) from CHN 82-24. The age models for these records have been slightly refined to bring oxygen isotopic stages 1.1, 2.2, 5.5, and 6.2 into agreement with each other. GM labels indicate timing of glacial maxima as defined by oxygen isotopes.

variations in dissolution intensity, they have coherent variations in Sr/Ca. The pattern of glacial/interglacial variation appears to be superimposed on a long term increase in Sr/Ca ratios by $\approx 1\%$ over the last 120 ky.

The *G. sacculifer* and *G. bulloides* records of site 758 and E49-21 showed Sr/Ca variations that were much lower in amplitude, $\approx 2\%$, and that did not follow the trend of high glacial Sr/Ca ratios nor variations in the dissolution intensity.

4. DISCUSSION

4.1. Sr/Ca Variations in Quaternary Foraminifera

The numerous secondary effects that influence the Sr/Ca of foraminifera are likely responsible for the diversity of variations in the measured Sr/Ca records. The smallest Sr/Ca variations of 2% in *G. bulloides* (E49-21) and *G. sacculifer* (758) records are not reproduced in any other sites nor in the same site with different cleaning procedures and show no relation with changes in dissolution intensity. Sr/Ca of replicates of *G. bulloides* from the same depth interval vary by as much as 2%. Sr/Ca ratios of *G. sacculifer* from core tops on the Ontong Java Plateau range from 1.45 to 1.25 mmol/mol (Brown and Elderfield, 1996) and are not correlated with site depth. Because of the large degree of intraspecimen or interspecimen heterogeneity, we conclude that the small Sr/Ca variations in the *G. sacculifer* record of 758 and the *G. bulloides* record of E49-21 are not likely to have paleoceanographic significance.

Selective dissolution is likely the predominant control over the largest amplitude Sr/Ca variations of 7% to 9% observed in records from *G. tumida* in site 572 and in *G. menardii* from site 758. Both *G. tumida* and *G. menardii* secrete an outer crust or keel of more dissolution-resistant low Sr/Ca and Mg/Ca in addition to juvenile calcite of higher Sr/Ca and Mg/Ca (Lohmann, 1995; Brown and Elderfield, 1996), resulting in lower Sr/Ca with progressive dissolution of the test. In core tops on the Ontong Java Plateau, Sr/Ca ratios of *G. tumida* decrease from a mean of 1.4 to 1.2 mmol/mol from 1500 m to 3500 m (Brown and Elderfield, 1996), interpreted as the progressive dissolution of juvenile calcite with depth. The loss of juvenile calcite appears to be complete by ≈ 3700 m (Brown and Elderfield, 1996). *G. tumida* at 572 are thus likely to be sensitive

to the effects of selective dissolution during glacial times of depressed lysoclines in the Pacific, when juvenile calcite is preserved to greater depths. The Sr/Ca record of *G. tumida* in deeper site PC72 is probably less sensitive to changes in dissolution intensity because even during times of high preservation, dissolution of juvenile calcite is complete by the site depth of 4300 m.

Dissolution may also influence the Sr/Ca variations in *O. universa* CHN82-24 (WASH). The Sr/Ca variations in this record correlate with other Atlantic dissolution records from 502B and the Cape Basin (Howard and Prell, 1994). Although *O. universa* is not a keeled species, in cold waters it may produce a thick calcite crust (Hemleben, 1989), which as in *G. tumida* and *G. menardii* may have lower Sr/Ca and Mg/Ca and therefore may be more resistant to dissolution. If the Sr/Ca variation in CHN82-24 (WASH) is due to selective dissolution, then the high Sr component must have been removed entirely during the rigorous cleaning procedure in the second CHN82-24 (SON) record. The selection of thin shelled, translucent *O. universa* for the first record may have biased this record toward the juvenile calcite, as the crust was likely absent or thin, accentuating the influence of selective dissolution. Opaque, thick-shelled specimens selected for the second record likely had more calcite crust, and the rigorous cleaning procedure may have preserved the calcite crust and dissolved the higher Sr and higher Mg juvenile calcite. If the Sr/Ca variations are not due to selective dissolution, they may reflect a large temperature dependence on Sr partitioning, although this has not been observed in culture studies with *O. universa* (Martin et al., 1997). It is also possible that some contaminating phase was removed by the more rigorous cleaning procedures, although it is difficult to envision how this contribution would have been so systematic.

Despite the array of variations induced by selective dissolution effects and interspecimen heterogeneity, there is a reproducible pattern of moderate amplitude Sr/Ca variations of 3% to 5% that do not covary with dissolution intensity (e.g., Fig. 3, *G. tumida* in site PC72, *O. universa* in site 502B, and the *O. universa* (SON) from CHN82-24). Very similar variations of 4–5% have been observed in both planktonic and benthic foraminifera from several sites by Martin et al. (1997). The persistence of these variations in both the Atlantic and Pacific, which have contrasting dissolution histories over glacial cycles, further suggests that the overall pattern is not the result of selective dissolution. Slight differences in the timing of increases in the Sr/Ca ratio among different sites may be caused by uncertainties in chronology. The reproducibility of this pattern of variation suggests that there may be a global component of variation in foraminiferal Sr/Ca, which is obscured to varying degrees by secondary effects in other records.

In the context of most of the measured records (including those of Martin et al., 1997), the 3% amplitude of variations in the CHN82-24 (SON) record is slightly anomalous, and it is possible that the amplitude of this variation has been damped by secondary effects. For example, the CHN82-24 (SON) record may still contain a small component of the phase containing or causing the opposite-phased Sr/Ca variation observed in the less rigorously cleaned *O. universa* (WASH) from this site, which damps the signal. It is also possible that the global component of variation is only 3% and that it has been

enhanced in all the other records, but we consider this less likely.

The Sr/Ca variations observed in *G. tumida* record from 572, although influenced by selective dissolution, also showed Sr/Ca variations similar to those of PC72 (Fig. 4a). The trends diverged primarily during episodes of enhanced preservation in 572 between 30 ka and 60 ka and 130 ka and 150 ka. It is possible that when preservation was worse or equivalent to modern conditions, dissolution of inner chamber calcite was complete by the site depth of 3900 m, and the Sr/Ca ratio was thus much less sensitive to changing preservation. However, during times of enhanced preservation between 30 ka and 60 ka and 130 ka and 150 ka, some inner calcite may have survived to this depth and contributed to higher Sr/Ca ratios. When we subtract the Sr/Ca variation of site PC72 from the Sr/Ca records of 572, the residual Sr/Ca variations still covary with indices of dissolution intensity (Fig. 4b). In the *O. universa* (WASH) from CHN82-24, perhaps more strongly affected by selective dissolution, residual Sr/Ca variations also covary with indices of dissolution intensity. The covariance of residuals with dissolution history in both sites leaves open the possibility that a global component of 5% Sr/Ca variation is present in these records but obscured by other effects.

The reproducibility of this pattern of Sr/Ca variations and its potential persistence in other records suggests that there may be a global pattern of variation in the Sr/Ca ratio of foraminifera. As we have discussed, this pattern of variation cannot be explained by selective dissolution. Temperature effects on Sr partitioning are small, and the Sr partitioning coefficient increases with increasing temperatures (Martin et al., 1997), so high Sr/Ca ratios during glacial maxima cannot be explained by temperature effects. It is also unlikely that changes in surface Sr/Ca ratios due to acantharia productivity account for the entirety of the signal because variable acantharian productivity in the modern ocean produces gradients of <2% (de Villers et al., 1994). In addition, upwelling eliminates the effect of acantharian SrSO₄ production on sea surface Sr/Ca ratios, but the reproducible pattern of Sr/Ca variations (as opposed to patterns clearly attributable to other effects) is observed in the Equatorial Pacific Upwelling region in site PC72. Finally, Sr/Ca ratios are uniform at depth due to the rapid dissolution of acantharian SrSO₄, yet the same pattern of Sr/Ca variations is observed in benthic Sr/Ca records of Martin et al. (1997).

Because we are unable to ascribe the reproducible change in foraminiferal Sr/Ca to known secondary effects, we conclude that it must reflect either changes in the mean Sr/Ca ratio of seawater or reproducible secondary effects that have not yet been documented. If foraminiferal Sr/Ca variations reflect 5% changes in the Sr/Ca ratio of seawater, they imply large biases in paleotemperature determinations from the Sr/Ca ratio of scleractinian corals (e.g., Guilderson et al., 1994). However, 5% changes in the Sr/Ca ratio of seawater are unlikely. Previous models that used a range of published estimates for carbonate budgets and other parameters predicted variations of only 1–3% in the Sr/Ca ratio of seawater. Furthermore, the modeled decrease in Sr/Ca since the last glacial maximum was only 0.5–1.1%, much lower than 5% decreases in foraminiferal Sr/Ca since the last glacial maximum. In the following section, we investigate whether it is possible for the Sr/Ca ratio of seawater to have decreased by 5% since the last glacial max-

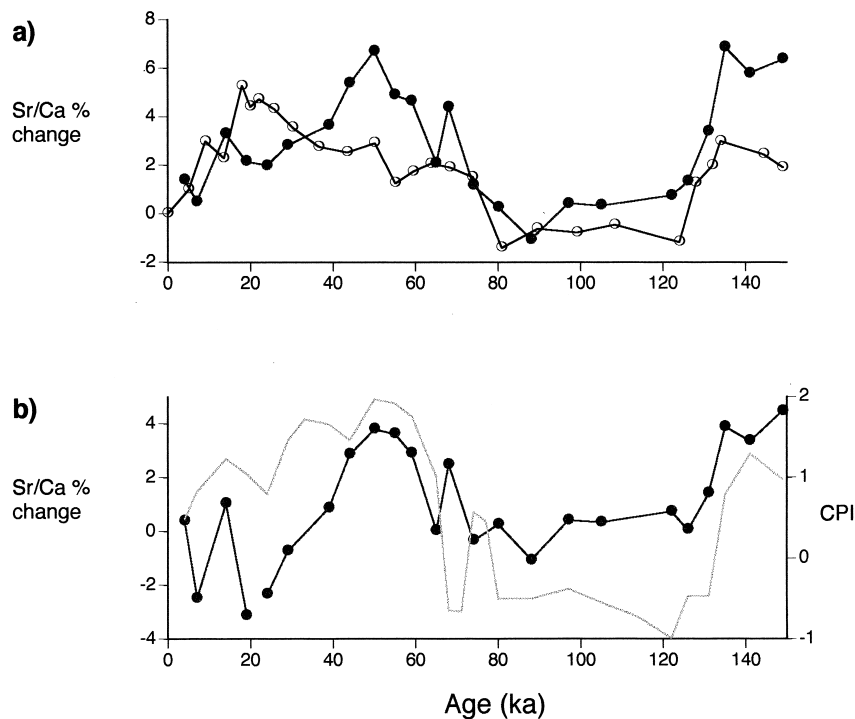


Fig. 4. (a) Sr/Ca variations in site PC72 (open circles, average as in Fig. 3) and 572 (filled circles) plotted as percentage difference from present Sr/Ca ratio. (b) Residual variation in 572 (filled circles) after subtraction of PC72 record of (a) as described in text. Thin gray line, dissolution history of 572 (refs. in Table 1).

ima, as required if the reproducible foraminiferal Sr/Ca variations are to be entirely attributed to changes in seawater Sr/Ca ratios. We used the numerical model presented by Stoll and Schrag (1998) to see what changes in the carbonate budget and sea level history are necessary to reproduce both the shape and the amplitude of the foraminiferal Sr/Ca variations and assessed whether these parameter choices are feasible.

4.1. Modeling Changes in Seawater Sr/Ca in the Quaternary

The structure of the model is identical to that presented in Stoll and Schrag (1998), in which a simple box model is used to simulate the Sr and Ca budgets of the ocean and track the concentration of Sr and Ca in the ocean over time. Sr and Ca are supplied to the ocean by rivers and hydrothermal exchange and are removed from the ocean in shelf and deep sea carbonates with mean Sr/Ca distribution coefficients of 0.9 and 0.176, respectively (Roselle, 1985; Schlanger, 1988; Hess et al., 1986). Shelf carbonate accumulates in discrete 1-m thick boxes; the Sr and Ca content of each box is inventoried through time. Deposition of shelf carbonate is restricted to 0 m to 50 m below sea level, following observations of modern reef systems (Boggs, 1987). Boxes exposed above sea level recycle Sr and Ca to the ocean via recrystallization and dissolution. As in the previous study, model simulations are run for 6 my to achieve steady state, and the combined river and hydrothermal influxes are adjusted to balance the Sr and Ca budgets so that long-term drift is $<0.20\%$ for Sr and Ca concentrations. Unlike the previous model simulations, here variations in shelf and deep

sea carbonate accumulation rates are no longer controlled strictly by sea level changes but are altered to optimize agreement with the foraminifera Sr/Ca record. Likewise, variations in the river flux are timed to optimize agreement with the foraminiferal record.

Reproducing the steep 5% Sr/Ca decrease of the foraminiferal record since the last glacial maxima is the biggest challenge for the model simulation, as our previous model results yielded no more than a 1.1% decrease. Because Sr and Ca both have long residence times in the ocean, this rapid decrease cannot represent the return to steady-state concentrations following addition of Sr from shelf carbonate recrystallization but instead requires accentuated removal of Sr from the ocean and increased addition of Ca from sources with low Sr/Ca ratio such as rivers, hydrothermal sources, or calcite dissolution. In the 20 ky following glacial maxima, we increased the combined river and hydrothermal influx by 100%, specified net deep sea carbonate dissolution of 1.44×10^{13} mol/yr, and elevated shelf carbonate accumulation to 3.3×10^{13} mol/yr. Because we assumed that the hydrothermal flux remains constant over glacial timescales, increases in the river flux relative to the hydrothermal flux imply lower Sr/Ca ratios of this flux because the mean Sr/Ca ratio of the hydrothermal influx (4–5 mmol/mol; Palmer and Edmond, 1989) is much higher than that of the river flux (1–2 mmol/mol; Holland, 1984). Accordingly, during the increased river/hydrothermal fluxes, we lowered the Sr/Ca ratio of this flux by 25%. These changes are summarized along with other parameter choices in Table 2, and the resulting fluxes and Sr and Ca concentrations are illustrated in Figure 5.

Table 2. Parameters and fluxes in the model simulation of seawater Sr and Ca budgets.

Parameter	Description	Values
Sr_o	Initial Sr concentration	87 $\mu\text{mol/L}$
Ca_o	Initial Ca concentration	10.2 mmol/L
$D_{Sr\text{deep}}$	Sr partitioning in deep sea carbonate	0.176
$D_{Sr\text{shelf}}$	Sr partitioning in shelf carbonate	0.9
$J_{Sr\text{riv}}$	River/hydrothermal Sr influx to ocean	To balance budget
$J_{Ca\text{riv}}$	River/hydrothermal Ca influx to ocean	To balance budget
$A_{riv\text{Sr}}$	Amplitude of variation in Sr influx to ocean	0.75*
$A_{riv\text{Ca}}$	Amplitude of variation in Ca influx to ocean	1.0*
$J_{carb\text{avg}}$	Mean carbonate accumulation rate	2.4 E13 mol/yr*
$X_{shell\text{avg}}$	Mean fraction of carbonate accumulation in shelf	0.4
Deep diss	Net deep sea carbonate dissolution (138–118, 18–0 ka)	1.44 E13 mol/yr*
$J_{dis\text{max}}$	Maximum glacial shelf carbonate dissolution flux	0.48 E13 mol/yr*
τ_{rxlln}	Half decay time of shelf recrystallization	10 ky
X_{rxlln}	Extent of shelf recrystallization	0.9
H_{shelf}	Thickness of shelf accumulation zone (meters below sea level)	50 m
Max shelf ₁	Maximum carbonate accumulation rate in shelf (138–118, 18–0 ka)	3.3 E13 mol/yr
Max shelf ₂	Maximum carbonate accumulation rate in shelf (118–80)	1.8 E13 mol/yr
Max shelf ₃	Maximum carbonate accumulation rate in shelf (80–18)	1.2 E13 mol/yr
Min shelf	Minimum carbonate accumulation rate in shelf (all interla)	0

Rapid decreases in Sr/Ca during deglaciation also are accentuated by increasing the rate of shelf carbonate recrystallization and by adjusting the sea level curve so that minimum sea levels are attained several thousand years prior to the glacial maximum (Fig. 5a). Both of these adjustments help flush more Sr out of shelf carbonates before the glacial maximum (Fig. 5d), which is important because continued Sr release from shelf carbonates during the postglacial sea level rise maintains high Sr/Ca ratios.

Minor adjustments in shelf carbonate accumulation rates and sea level history are used to simulate the shape of the foraminiferal Sr/Ca record from 120 ky to 18 ky. Maintaining low Sr/Ca ratios from 120 ky to 80 ky requires a reasonably active sink of Sr in shelf carbonates and little release of Sr from recrystallization of exposed reefs. Shelf accumulation rates peak at 1.8×10^{13} mol/yr during sea level rise or stasis (Fig. 5e). Sr loss from shelf carbonates is minimized by maintaining relatively high sea levels through this interval (Fig. 5a and e) and keeping accumulation of shelf carbonates relatively deep, from 0 m to 50 m, so that they are not exposed during early sea level falls. Times of most rapid increase in foraminiferal Sr/Ca ratios are simulated by concentrating the interstadial sea level falls in two steps, at ≈ 75 ka and ≈ 35 ka. To increase overall Sr concentrations during this time, we also reduced the shelf carbonate sink of Sr during the 80- to 20-ka interval by reducing maximum shelf carbonate accumulation rates to 1.2×10^{13} mol/yr (Fig. 5e), while retaining the dependence on the rate of sea level change. Finally, we increased the average Quaternary carbonate accumulation rate to 2.4×10^{13} mol/yr, which increased the overall amplitude of Sr/Ca variations.

The seawater Sr/Ca variations that resulted from this model parameterization had an amplitude of 5.1%, and their phasing was in excellent agreement with the Sr/Ca variations in the foraminiferal record (Fig. 6). In the following section, we assess whether this parameterization is reasonable or whether agreement with estimated budgets requires lower amplitudes of seawater Sr/Ca variations.

4.2. Evaluation of Model Parameterization: River and Hydrothermal Flux and Sr/Ca Ratio of the Flux

To reproduce the amplitude of foraminiferal Sr/Ca variations, the model requires that the combined river and hydrothermal flux increase by 100% in the 20 ky following glacial maxima. Simultaneous reduction of the Sr/Ca ratio of this influx by 25% yields a net increase in the Sr influx of 75%. However, any combination of fluxes used to produce seawater Sr/Ca changes also must satisfy the constraints imposed by Sr isotopic data. We included conservation equations for ^{87}Sr and ^{86}Sr in model simulations and compared the effect of increased fluxes on the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater and with $^{87}\text{Sr}/^{86}\text{Sr}$ data obtained by Henderson et al. (1994). Isotopic ratios of rivers and hydrothermal fluxes were taken from Palmer and Edmond (1989) and Capo and DePaolo (1990). We assumed that the hydrothermal flux remains constant over the Quaternary and that all changes in the combined flux result from changes in the riverine flux of dissolved Sr and Ca. Consequently, Sr influxes that vary by 75% actually represent increases of 109% in the river flux with a constant hydrothermal flux, assuming that the hydrothermal flux accounts for $\approx 32\%$ of the combined river and hydrothermal Sr input as suggested by Hodell et al. (1990). Glacial/interglacial $\Delta^{87}\text{Sr}$ variations of 11 ppm result from 75% variations in riverine/hydrothermal Sr fluxes, which are compared with $^{87}\text{Sr}/^{86}\text{Sr}$ data obtained by Henderson et al. (1994) in Figure 7. Although in nearly all cases the isotopic variation induced by this flux change lies within 2 SD of the data points, the modeled $^{87}\text{Sr}/^{86}\text{Sr}$ variation has a mean square weighted deviation (MSWD = $\{\sum \Delta y^2 / \sigma y^2\} / (n - 2)$) of 1.8, which is not a statistically good fit to this data set (statistically good fit for $n = 48$ requires a MSWD < 1.4 ; Wendt and Carl, 1991). Reducing variations in the combined hydrothermal and river influx to 50%, coupled again with a 25% reduction in the Sr/Ca ratio of this flux, reduces the amplitude of Sr/Ca variations by 0.5%. Despite the lower amplitude of the resulting variations in seawater $^{87}\text{Sr}/^{86}\text{Sr}$, the modeled variations are still a poor fit to the data (MSWD of 1.8) because they are out of phase with the data from 0 ka to 50 ka.

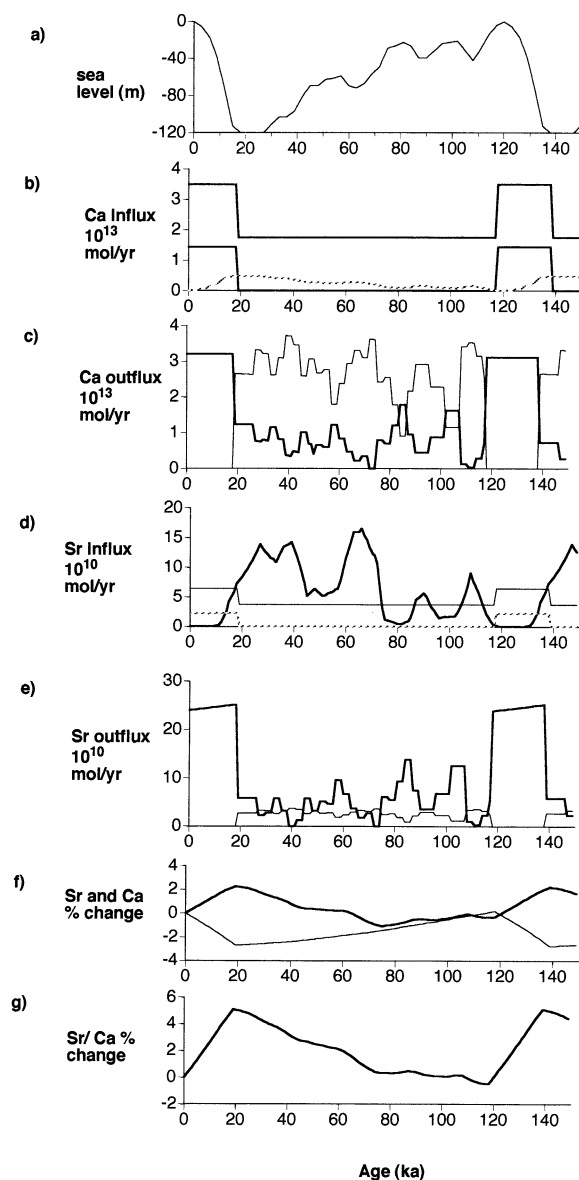


Fig. 5. Model sea level history, Sr and Ca fluxes, and resulting variation in seawater Sr and Ca concentrations and Sr/Ca ratio for the last 150 ka. (a) Sea level history used in model. (b) Fluxes of Ca into the ocean. Thick line, combine riverine and hydrothermal influx; thin line, dissolution of deep sea carbonates; dashed line, dissolution of shelf carbonates. (c) Fluxes of Sr out of the ocean. Thick line, removal in shelf carbonates; thin line, removal in deep sea carbonates. (d) Fluxes of Sr into the ocean. Thick line, influx from recrystallization of shelf carbonates; thin line, influx from combine riverine and hydrothermal sources; dashed line, influx from dissolution of deep sea carbonates. (e) Fluxes of Sr out of the ocean. Thick line, removal in shelf carbonates; thin line, removal in deep sea carbonates. (f) Variations in the concentrations of Sr (thick line) and Ca (thin line) in seawater, expressed as percentage difference from modern concentrations. (g) Variations in the seawater Sr/Ca, expressed as percent difference from modern concentrations.

Recent work by Hart et al. (1994) on low temperature hydrothermal exchange suggests that the discrepancy between the model-required fluxes and $^{87}\text{Sr}/^{86}\text{Sr}$ data may be much worse. Low temperature hydrothermal exchange yields fluids of much

lower Sr/Ca ratios (0.05 to 1.8 mmol/mol) and higher $^{87}\text{Sr}/^{86}\text{Sr}$ than the high temperature vent fluids measured by Palmer and Edmond (1989), which are the basis for the aforementioned budget. It is unclear what fraction of the hydrothermal flux is derived from low and high temperature environments, but because of the low Sr contents of the low temperature hydrothermal fluids, the low temperature fluids have little effect on the mean $^{87}\text{Sr}/^{86}\text{Sr}$ of hydrothermal fluids even if low temperature alteration is the source of 90% of the hydrothermal Ca flux. However, if the low temperature alteration is a significant source of Ca to the ocean, then we have overestimated the Sr/Ca ratio of the hydrothermal flux and have reduced unduly the Sr/Ca ratio of the combined hydrothermal and riverine flux during elevated river influxes. If the mean ratio of the hydrothermal flux were lower, of order 1–2 mmol/mol (assuming high T, high Sr/Ca vents contribute only 1/3–1/5 of the hydrothermal Ca flux), then the Sr/Ca ratio of the combined riverine/hydrothermal input would not change when the riverine component increased. Consequently, the amplitude of model-predicted Sr/Ca variations would decrease by 0.35%. In addition, the larger variation in the riverine Sr flux (100% instead of 75%) also would produce greater amplitude variations in the Sr isotopic composition of seawater, of 18 ppm instead of 11 ppm. This would lead to an even worse fit to the $^{87}\text{Sr}/^{86}\text{Sr}$ data of Henderson et al. (1994), with a MSWD of 2.6.

Taken as a whole, the available Sr isotopic constraints suggest that the modeled variation in the river flux exceeds reasonable limits. To obtain statistically good agreement with $^{87}\text{Sr}/^{86}\text{Sr}$ data, variations in river fluxes must either be much lower (<50% increase in total Ca flux) or of different phasing, both of which would drastically lower the variation in seawater Sr/Ca ratios.

4.3. Deep Sea Calcite Dissolution

The model solution requires that deep sea carbonate dissolution rates exceed preservation rates by 1.44×10^{13} mol/yr in the 20 ky following glacial maxima. Although there is evidence for net dissolution of calcite at 4000 m to 5000 m in the Pacific during the Holocene, estimated dissolution fluxes are much lower than net preservation fluxes elsewhere in the ocean. Sediment-mixed layer models of Oxburgh (1998) require dissolution fluxes of up to 0.24×10^{13} mol/yr in the deep Pacific during the Holocene. This flux is much smaller than net preservation fluxes at shallower depths in the Pacific or in the Atlantic (Francois et al., 1990) and therefore precludes a large excess of dissolution over preservation in deep sea carbonates. A large excess of dissolution over preservation is invoked for the Holocene by the carbonate/alkalinity models of Walker and Opdyke (1995), who suggest that net deep sea dissolution of 1.8×10^{13} mol/yr results from alkalinity drawdown during episodes of enhanced shelf carbonate accumulation during sea level rises. These rates are much larger than estimated by Oxburgh (1998) and imply lysocline shifts of >1 km, larger than those observed in the sedimentary record, although chemical erosion may reduce the preservation of such shifts in the sedimentary record (Walker and Opdyke, 1995). However, even if the Walker and Opdyke (1995) model can be reconciled with sediment data, their calculated dissolution flux assumed constant addition of alkalinity and dissolved carbon from riv-

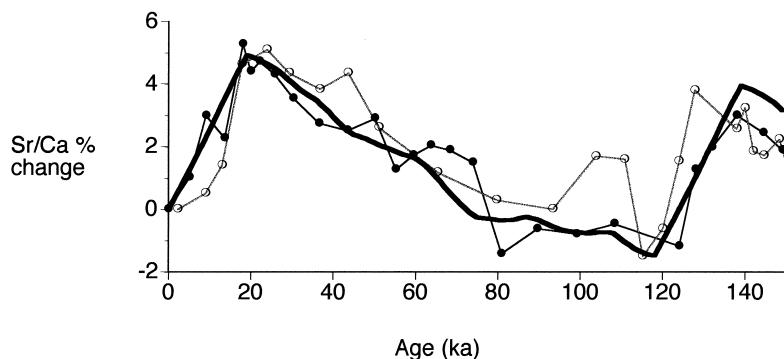


Fig. 6. Comparison of model-predicted variations in seawater Sr/Ca (thick line) with foraminiferal Sr/Ca variations observed in sites 502B (open circle) and PC72 (filled circle). A long term increase in Sr/Ca ratios of 1%/120 ka has been added to the model curve to facilitate comparisons with the amplitude of Sr/Ca changes at both the last glacial maximum and penultimate glacial maximum, as described in the text.

ers, whereas in our simulation, the additional alkalinity from 20 ky of increased postglacial river fluxes must significantly decrease the amount of deep sea carbonate dissolution. Without a detailed model of ocean alkalinity and deep sea carbonate saturation, we cannot assess what magnitudes of dissolution fluxes might persist despite increased river fluxes. However, the 1.4×10^{13} mol/yr net deep sea dissolution flux that we have used is much higher than estimated from sediment data, and alkalinity considerations suggest that it is also much too high to accompany increased river fluxes. Removal of the dissolution flux from our model decreases the amplitude of Sr/Ca variations by 1.2%.

4.4. Carbonate Accumulation Rates

The model solution requires shelf carbonate accumulation rates of 3.3×10^{13} mol/yr in the 20 ky following glacial

maxima, which appear to be higher than estimated shelf accumulation rates during the Holocene. The highest estimate for present day accumulation rates in the shelf environment is 2.3×10^{13} mol/yr (Opdyke and Walker, 1992); a comparable production rate is estimated by Milliman and Droxler (1996), although they suggest that only 1.5×10^{13} mol/yr accumulates in that environment. Milliman and Droxler (1996) emphasize that this estimate is probably accurate "within a factor of 1" (meaning a factor of 2?), leaving open the possibility for significantly higher accumulation rates. Another caveat is that maximum shelf accumulation rates in the modern ocean may not be representative of rates for the past 18 ka. Nonetheless, maximum shelf carbonate accumulation rates of 3.3×10^{13} mol/yr used in our model may be too high. A more reasonable choice may be 2.4×10^{13} mol/yr, which reduces the amplitude of Sr/Ca variations only slightly, by 0.09%. On average, shelf

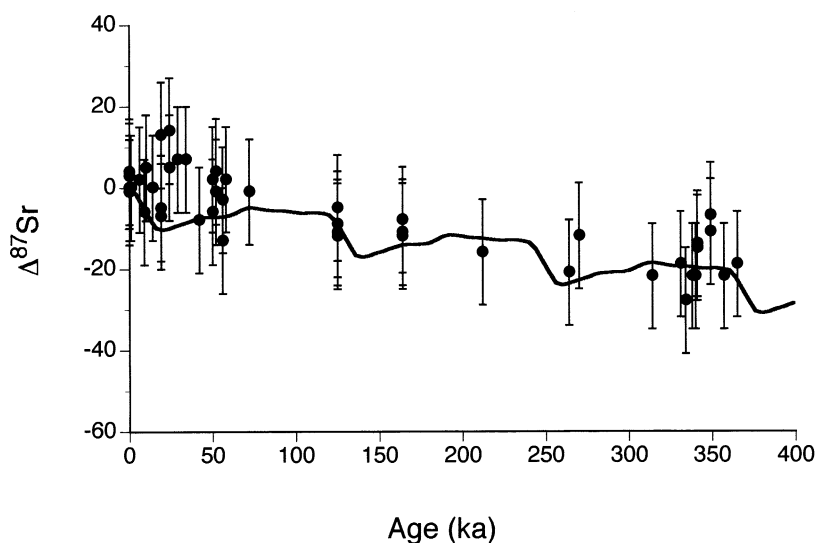


Fig. 7. Comparison of model-predicted variation in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ for increased river fluxes with $^{87}\text{Sr}/^{86}\text{Sr}$ data on foraminifera for the last 350 ky. Thick line, model-predicted isotopic variation for 75% increase in river and hydrothermal influx in the 20 ky following glacial maxima. Closed circles, data of Henderson et al., (1994); errors are 2 SD external repeatability of the analysis reported as 13 ppm. $\Delta^{87}\text{Sr}(\text{ppm}) = \{(^{87}\text{Sr}/^{86}\text{Sr} \text{ in sample}/0.709158) - 1\} \times 10^6$.

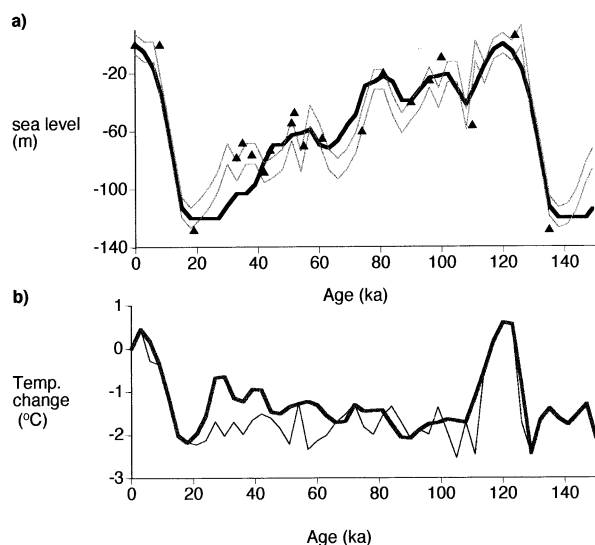


Fig. 8. (a) Comparison of sea level curve used to force our model (thick line) with sea levels estimated from reef altimetry (triangles; from Chappell et al., (1996) and sea level changes based on benthic and planktonic $\delta^{18}\text{O}$ records (thin gray lines showing ± 7 m uncertainties in sea level estimates of Shackleton, 1987). (b) Deep ocean temperature changes calculated from the $\delta^{18}\text{O}$ record of V19-30. Thick line, temperatures implied by the by sea level curve used to force our model. Thin line, temperature changes implied by assuming negligible temperature change in tropical sea surface temperatures (from Shackleton, 1987).

carbonate comprises 60% of carbonate accumulation, in agreement with estimates of Opdyke and Wilkinson (1988). The maximum shelf dissolution flux of 0.48×10^{13} mol/yr is similar to Schlanger's (1988) estimate of 0.3×10^{13} mol/yr.

Average total carbonate accumulation rates of 2.4×10^{13} mol/yr are required by the model simulation. Estimates of average carbonate accumulation rates range from 2.0×10^{13} mol/yr (Opdyke and Walker, 1992; Berner and Berner, 1996) to 2.5×10^{13} mol/yr (Milliman and Droxler, 1996). Milliman and Droxler (1996) estimate an uncertainty of 25% to 50% in this figure. Our choice of average carbonate accumulation rates of 2.4×10^{13} mol/yr is not unreasonable. Lower average accumulation rates of 2.0×10^{13} mol/yr decrease the amplitude of Sr/Ca variations by 0.6%. Higher average accumulation rates of 2.6×10^{13} mol/yr would increase the amplitude of Sr/Ca variations but also would increase all carbonate fluxes, including the already high maximum shelf carbonate accumulation rates.

4.5. Sea Level History

The model simulation requires a sea level history in which the lowest sea levels are attained several thousand years before glacial maxima and in which the final sea level falls before the last glacial maximum is initiated ≈ 40 ka. Reef altimetry provides low resolution data on the height of sea level through the last 140 ky (e.g., Chappell et al., 1996), which compares well with the sea level curve used in our model simulation but which does not allow us to evaluate the timing of our sea level falls after 40 ky nor the time when maximum lowstands are

achieved (Fig. 8a). A more detailed, but more ambiguous, sea level curve was produced by Shackleton's (1987) attempt to separate the sea level and temperature component of a benthic $\delta^{18}\text{O}$ record by assuming negligible temperature changes in equatorial sea surface temperatures over the last 140 ka. Chappell et al. (1996) estimate that the error in the isotopic sea level curve is ± 7 m in sea level and ± 5 ky in chronology. The uncertainty in chronology for our sea level curve may be worse because it has been adjusted to optimize agreement for our foraminiferal records, whose chronology is far less precise than that of Shackleton's $\delta^{18}\text{O}$ records. In general, the isotopically derived sea level estimates agree well with the curve we have used to drive our model, although the model curve is more smoothed (Fig. 8a). The primary divergences between the curves occur after 40 ky, where our curve drops more abruptly and reaches minimum sealevels sooner. Differences in the sea level curves imply different temperature contributions to the benthic $\delta^{18}\text{O}$ record and hence different histories of deep ocean temperature changes. We use the benthic $\delta^{18}\text{O}$ record of V19-30 to calculate changes in deep ocean temperature implied by our sea level curve following the approach of Chappell et al. (1996) and compare these temperatures with those calculated by Shackleton (1987) in Figure 8b. Aside from differences due to further smoothing of our sea level record, the calculated temperatures diverge only between 40 ka and 25 ka, where our sea level curve implies a slight (1°) warming rather than the constant temperatures calculated by Shackleton (1987). The small differences in the two sea level curves and the ambiguities in the isotopic sea level curve suggest that the curve used in our model may be reasonable. If the isotopically derived sea level curve is substituted in the model, the amplitude of Sr/Ca variations decreases by 0.6%.

4.6. Summary of Model Feasibility

The extremely dynamic behavior of the carbonate budget over glacial cycles leads to large uncertainties in estimates of nearly all carbonate parameters. However, existing sediment data and alkalinity considerations indicate that the model's large excess of deep sea carbonate dissolution over preservation for the last 20 ka is unreasonable. Elimination of the deep sea dissolution excess decreases Sr/Ca variations to 3.9%. The large variations in the river flux are also not in accordance with data on variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ of seawater over the last 400 ky. River fluxes in closer agreement with $^{87}\text{Sr}/^{86}\text{Sr}$ data (25% change in combined river/hydrothermal Sr and Ca fluxes) reduce the amplitude of Sr/Ca variations by 1.6%. Other aspects of our parameterization cannot be ruled out on the basis of comparisons with data on carbonate budgets or estimates of sea level history, although the parameter choices do not yield the best agreement with existing data and are the most extreme ones that can be made without violating the constraints of existing data. No alternative combination of more reasonable parameters could simulate comparable variation in seawater Sr/Ca ratios. If we eliminate the unreasonable deep sea dissolution excess and reduce the combined river and hydrothermal variation to 25%, the maximum variation in mean seawater Sr/Ca since the last glacial maximum is 2.3%, which cannot account for all of the reproducible Sr/Ca variation in foraminifera.

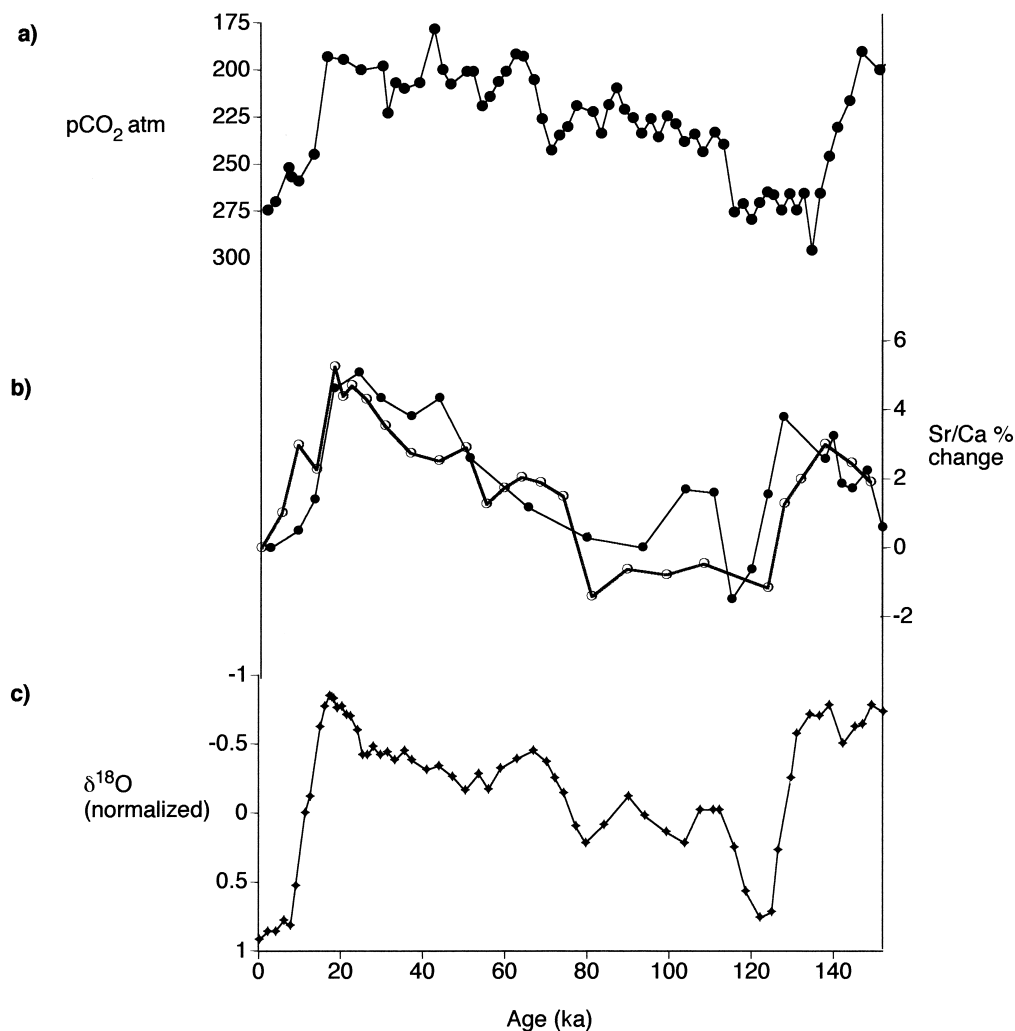


Fig. 9. Comparison of (a) atmospheric pCO₂ record from Vostok ice core (from Barnola et al., 1987); (b) foraminiferal Sr/Ca variations in sites 502B (open circles) and sites PC72 (filled circles); and (c) stacked benthic δ¹⁸O record (heavy black line; from Pisias et al., 1984).

4.7. Other Potential Kinetic or Biological Effects on Foraminiferal Sr/Ca

Although known kinetic or biological effects on Sr partitioning in foraminifera (e.g., temperature and salinity) cannot satisfactorily explain the observed reproducible variations in foraminiferal Sr/Ca, it is possible that other kinetic or biological effects influence Sr partitioning to a greater extent. In addition to temperature and salinity, numerous other environmental parameters change over glacial cycles and could result in changes in Sr partitioning. The carbonate ion concentration of seawater is one such factor that may control calcification rates and hence Sr partitioning, which is strongly dependent on calcification rate and growth mechanism (Paquette and Reeder, 1995; Lorens, 1981). In seawater, the [Ca²⁺] concentration substantially exceeds [CO₃²⁻] so the precipitation rate of CaCO₃ is effectively controlled by [CO₃²⁻]. Over glacial cycles, the surface water carbonate ion concentration must have varied in response to changes in atmospheric pCO₂ because the

pCO₂ of the atmosphere and the sea surface must be in approximate equilibrium. Decreased atmospheric pCO₂ during glacial (Barnola et al., 1987) would have resulted in higher surface water [CO₃²⁻]. If the behavior observed for inorganic calcites is also true for calcification in foraminifera, then lower glacial pCO₂ and higher [CO₃²⁻] would cause higher Sr/Ca in foraminiferal calcites. The reproducible foraminiferal Sr/Ca variations are inversely correlated with the Vostok pCO₂ record as would be expected if variations in [CO₃²⁻] caused the foraminiferal variation through changes in Sr partitioning (Fig. 9a and b). However, temperature, salinity, and other environmental parameters follow a similar pattern of variation over glacial cycles as evidenced by the similarity between the composite δ¹⁸O curve and the foraminiferal Sr/Ca record (Fig. 9a and c), suggesting that other environmental influences also may affect Sr partitioning. Ironically, we would not expect correlation between δ¹⁸O and Sr/Ca if Sr/Ca variations were merely the result of reef weathering during sea level lowstands, as our

modeling indicated. Additional core-top and culture studies are needed to document the potential for carbonate ion and other effects on Sr partitioning in foraminifera. Further work also is needed to consider how changes in acantharian productivity over glacial cycles may contribute to variation in the seawater Sr/Ca ratio.

5. CONCLUSIONS

Although Sr/Ca ratios of some species of planktonic foraminifera seem to be predominantly controlled by selective dissolution, systematic variations in the Sr/Ca ratios of other species do not covary with indicators in dissolution intensity and are reproduced in both Atlantic and Pacific sites that have contrasting Quaternary dissolution histories. These systematic variations of 3% to 5% are characterized by high Sr/Ca ratios during glacial maxima, followed by a steep decrease during deglaciation and gradual increases through interstadial periods, closely tracking the $\delta^{18}\text{O}$ curve. Using coupled numerical models of the Sr and Ca budgets of the ocean, we have shown that sea level changes, together with large changes in river fluxes and carbonate accumulation rates, can result in similar variations in the Sr/Ca ratio of seawater of 4%. However, the large changes in river fluxes required to reach this amplitude imply changes in seawater $^{87}\text{Sr}/^{86}\text{Sr}$, which are not a statistically good fit to data on seawater $^{87}\text{Sr}/^{86}\text{Sr}$ over the last 400 ky. In addition, although the other flux changes cannot be ruled out based on comparisons with estimates of carbonate budgets and sea level data, they are the most extreme ones that can be made without violating the constraints of existing data. Consequently, we consider it highly unlikely that the entire amplitude of reproducible foraminiferal Sr/Ca variations represents changes in seawater Sr/Ca ratios. Variation in the Sr/Ca ratio of seawater is likely at the 1% to 3% level with changes of <2.3% since the last glacial maximum. Changes in Sr partitioning due to changes in the carbonate ion concentration and other environmental factors likely produce additional variation in the Sr/Ca record of planktonic foraminifera.

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