

34. INFLUENCES ON CALCITE Sr/Ca RECORDS FROM CEARA RISE AND OTHER REGIONS: DISTINGUISHING OCEAN HISTORY AND CALCITE RECRYSTALLIZATION¹

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ABSTRACT

Strontium/calcium ratios in deep-sea carbonate sediments have been used as recorders of paleoceanographic Sr/Ca and as indicators of diagenetic alteration of calcite sediments. We evaluate the relative impacts of ocean history and calcite recrystallization on bulk calcite Sr/Ca records from sediments from the Ceara Rise (CR) and the equatorial Pacific. We present Sr/Ca and Mg/Ca data from bulk calcite analyses of samples from the range of depths drilled at the five sites in the Ocean Drilling Program (ODP) Leg 154 Ceara Rise depth transect. The Sr/Ca and Mg/Ca records appear to vary more consistently with age than with sediment depth, indicating that they more strongly represent records of oceanic Sr/Ca and Mg/Ca ratios, rather than depth-controlled diagenetic alteration. We compare Sr/Ca records from the CR with bulk calcite records from the Ontong Java Plateau (OJP) in the western equatorial Pacific (Leg 130, Sites 803–807) and the eastern equatorial Pacific (EEqP; ODP Leg 138, Sites 844–846, 851, and 853), and with a planktonic foraminifer record. All Sr/Ca records show similar trends, with Sr/Ca values increasing to the present and large fluctuations superimposed on this trend in the Neogene. We use quantitative estimates of celestite (SrSO₄) saturation in pore waters and a Sr-exchange model of calcite diagenesis to evaluate the potential influence of authigenic SrSO₄ precipitation on the bulk calcite Sr/Ca from the CR, OJP, and EEqP. We conclude that celestite does not precipitate in the EEqP sites and probably does precipitate at most or all CR and OJP sites. We further conclude that the precipitation of SrSO₄ at some sites and not others accounts for only a small fraction of the differences in contemporaneous Sr/Ca values in calcite.

INTRODUCTION

Strontium/calcium ratios in deep-sea calcite sediments have been interpreted to reflect paleoceanographic Sr/Ca ratios and therefore changes in the oceanic Sr and Ca budgets (Turekian and Kulp, 1956; Graham et al., 1982; Delaney and Boyle, 1988; Schlanger, 1988). However, in calcite-rich sediments, calcite Sr/Ca and pore-water Sr profiles have also been interpreted to reflect calcite recrystallization. Therefore, these geochemical indicators have been exploited in efforts to understand the timing, nature, extent, and effects of calcite recrystallization on geochemical tracers (e.g., Baker et al., 1982; Elderfield and Gieskes, 1982; Stout, 1985; Delaney, 1989; Apitz, 1991; Richter and Liang, 1993). In fact, it seems clear that calcite Sr/Ca is controlled by the interplay of paleoceanographic variability and the diagenetic effects of calcite recrystallization, with the complexities of each factor hampering initial efforts to tease out either a reliable paleoceanographic history or a solid interpretation of the effects of recrystallization from the existing geochemical records.

Sr and Ca are both conservative elements in the ocean, so their ratio in seawater should be spatially uniform at any one time. Both have long residence times in the modern ocean (on the order of 1 m.y. for Ca and 4 m.y. for Sr), so changes in their ratio in seawater through time should reflect changes in the oceanic budgets of Sr and Ca. Oceanic concentrations of Sr and Ca are controlled by the relative effects of several major geologic processes. Ca is added to the oceans by dissolved river input, a function of continental weathering, and by hydrothermal exchange at mid-ocean ridges, assumed to be in some way related to seafloor-spreading rates. Ca is removed from the oceans in calcium carbonate deposition. Sr is also added to the oceans by dissolved river input and removed in calcium carbonate deposi-

tion. However, because more Sr is preferentially incorporated into aragonite ($D \sim 1.0$) than into calcite ($D \sim 0.1$), the Sr/Ca ratio of seawater is affected by the relative proportion of carbonate deposition on shallow shelves (typically aragonite and high-Mg calcite-dominated) vs. the deep sea (calcite-dominated), a function of sea level (Turekian and Kulp, 1956; Graham et al., 1982; Delaney and Boyle, 1988; Schlanger, 1988). Although the assumption of spatial and water-depth consistency in oceanic Sr/Ca is well justified, Sr uptake into calcite shells is not always simply proportional to the seawater Sr/Ca in the environment of calcification. The partition coefficient (Morse and Bender, 1990) for Sr in biogenic calcite has been observed to vary with the calcification rate (Lorenz, 1981), water depth (McCorkle et al., 1995), and most substantially, between foraminifers and coccolithophorids (Baker et al., 1982; Stout, 1985). However, variability in the uptake of Sr into calcite precipitating from a seawater solution is thought to be smaller than the temporal variability of Sr/Ca over the Cenozoic, which suggests changes in ocean Sr/Ca (Graham et al., 1982).

The partition coefficient for Sr in inorganically precipitated calcite (Baker et al., 1982; Delaney, 1989) is about a factor of 3 lower than that for biogenic calcite (Graham et al., 1982; Delaney et al., 1985). Therefore, calcite diagenesis expels Sr to the surrounding pore waters. The fraction of total Sr in pore waters is small as compared with the fraction of total Sr in calcite sediments, so that even a little calcite recrystallization can cause a significant change in pore-water Sr concentrations. These features of the sedimentary Sr budget make Sr an enticing tool for examining the nature and effects of calcite recrystallization, and a number of studies using geochemical data and numerical models of varying complexity have yielded significant insights into these issues (e.g., Baker et al., 1982; Gieskes, 1983; Apitz, 1991; Stout, 1985; Richter and DePaolo, 1987, 1988; Richter and Liang, 1993; Richter, 1996). Baker and Bloomer (1988) reported the occurrence of celestite nodules in several sites drilled on Lord Howe Rise. These authors calculated that these nodules held a large portion (~20%) of the Sr in the sediment columns where the nodules were found and noted that authigenic celestite is likely to precipitate at other deep-sea, carbonate-dominated sites with the right balance of

¹Shackleton, N.J., Curry, W.B., Richter, C., and Bralower, T.J. (Eds.), 1997. *Proc. ODP, Sci. Results*, 154: College Station, TX (Ocean Drilling Program).

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high pore-water Sr concentrations and intermediate to high pore-water sulfate concentrations. Formation of even a small amount of authigenic celestite can substantially change the Sr distribution at a site. Therefore, it is important to consider the celestite saturation of pore water when evaluating the effects of calcite diagenesis on Sr/Ca. Our own efforts have highlighted site-to-site variations in the evolution of the pore-water environment through time, the sedimentation history of a site, and the precipitation of authigenic celestite (SrSO_4) at some sites as controls on diagenetic Sr/Ca differences (Delaney, 1989; Delaney and Linn, 1993; G. Hampt and M.L. Delaney, unpubl. data).

We present new bulk calcite Sr/Ca and Mg/Ca data from Ocean Drilling Program (ODP) Sites 925–929 in the Leg 154 Ceara Rise (CR) depth transect. We compare these data to bulk calcite Sr/Ca records from ODP sites drilled in the equatorial Pacific (Ontong Java Plateau [OJP], Leg 130, Sites 803–807, Delaney and Linn, 1993; eastern Equatorial Pacific [EEqP], Leg 138, Sites 844–846, 851, and 853, G. Hampt and M.L. Delaney, unpubl. data) and to the planktonic foraminifer Sr/Ca record of Graham et al. (1982). We present equilibrium calculations for celestite solubility at the CR, OJP, and EEqP sites. We use results from a reaction-diffusion model of Sr exchange to evaluate the possible effects of authigenic celestite precipitation on diagenetically altered calcite Sr/Ca. From these comparisons of several Sr/Ca records and model simulations, we consider the relative effects of ocean history and calcite recrystallization on the Sr/Ca record at Ceara Rise.

SITE CHARACTERISTICS

The closely spaced sites in the CR depth transect experience similar surface-water inputs. However, sediments vary from site to site because increasing site water depths result in decreasing carbonate accumulation and decreasing organic matter remineralization within buried sediments (evidence in pore-water SO_4 minima; Table 1). Similar relationships between site water depths and sedimentation characteristics are recognized in the depth transect of sites at OJP. In addition, OJP sites are under a region with similar primary productivity to that at CR, and the total sediment accumulations are comparable in the two depth transects. At the EEqP sites, in contrast to those at CR and OJP, primary productivity is higher and varies among sites,

and carbonate accumulation depends upon the site position relative to overlying equatorial productivity zones, not on site water depth. Overall sediment accumulation is thinner in the EEqP, as the sites are on relatively young oceanic crust, but sedimentation rates are typically higher there.

Sr concentrations at the pore-water Sr maxima (plateau concentrations) are highest at CR (1240–2150 μM), intermediate at OJP (600–1150 μM), and quite low at the EEqP sites (95–290 μM ; Table 1). Sulfate concentrations at the sulfate minima are lowest at CR (5–12 mM), intermediate at OJP (16–25 mM), and highest at the EEqP sites (20–27 mM). The plateau Sr concentrations at OJP decrease with increasing site water depth. At CR, where the deepest pore-water samples are generally only about halfway to the estimated depth to basement, Sr concentrations typically still are increasing in the deepest measured samples, and the order of Sr maxima seems more tied to the depth of the deepest sample at a site. At a given depth or age in the sediments at CR, however, lower Sr concentrations appear to correlate with deeper site water depth, similar to the pattern at OJP. At CR and OJP, SO_4 minima increase with increasing site water depth (with the exception of the short record at Site 927). Higher SO_4 minima in the EEqP indicate less SO_4 reduction in the sediments there, due at least in part to generally deep site water depths.

METHODS

Two distinct approaches exist for determining calcite Sr/Ca: analyzing either isolated sediment fractions (e.g., foraminiferal separates) or bulk calcite. Isolated foraminiferal calcite is considered more likely to have distinguishable controls on biogenic uptake of Sr, which could constrain interpretations of sample variability, and to show visually identifiable effects of recrystallization, which could permit altered samples simply to be excluded from consideration in the paleoceanographic interpretation. However, neither of these “advantages” has been reliably demonstrated. Bulk calcite measurements are more appropriate for evaluating diagenesis because the most sensitive geochemical indicator of recrystallization, pore-water Sr, responds to changes in the bulk calcite. In addition, bulk calcite is dominated by coccolithophorids, which calcify in the photic zone over a relatively small range of water depths. Therefore, the bulk cal-

Table 1. Selected site, sedimentation, and pore water characteristics of ODP sites at Ceara Rise, Ontong Java Plateau, and the eastern equatorial Pacific.

Site characteristics			Sedimentation characteristics					Pore-water chemistry			
Site	Latitude (degrees)	Longitude (degrees)	Water depth (m)	Primary productivity ($\text{gC/m}^2\text{y}$)	Sed. rate (m/m.y.)	Neogene sediment thickness (m)	Basement age (Ma) or depth (mbsf)	Sr max. conc. (μM)	Sr max. depth (mbsf)	SO_4 min. conc. (mM)	Ca gradient (mM/100m)
Ceara Rise, Leg 154											
925	4.2°N	43.5°W	3042	35–60	11–40	496	~1300 mbsf	2152	681	5	3.7
927	5.5°N	44.5°W	3315	35–60	12–46	>305	~1200 mbsf	1170 ^a	307 ^a	17 ^a	5.2
926	3.7°N	42.9°W	3598	35–60	12–35	470	~1150 mbsf	2008	591	10	5.2
928	5.5°N	43.7°W	4018	35–60	7–36	349	~950 mbsf	1240	517	11	5.4
929	6.0°N	43.7°W	4356	35–60	3–41	330	~830 mbsf	1918	782	12	8.5
Ontong Java Plateau, Leg 130											
806	0.3°N	159.4°E	2520	35–60	19–43	738	~1200 mbsf	1150	170	16	2.7
807	3.6°N	156.6°E	2805	35–60	14–41	592	120 Ma	900	175	22	1.1
805	1.2°N	160.5°E	3188	35–60	12–39	528	~1000 mbsf	925	130	22	4.1
803	2.4°N	160.6°E	3410	35–60	8–30	318	90 Ma	900	175	23	6.2
804	1.0°N	161.6°E	3861	35–60	7–24	258	~640 mbsf	600	>200	25	3.7
Eastern Equatorial Pacific, Leg 138											
845	9.6°N	94.6°W	3704	200–500	11–30	290 ^b	17 Ma	138	252	27	-0.3
844	7.9°N	90.5°W	3415	100–200	6–47	290 ^b	18 Ma	154	239	27	0.1
846	3.1°N	90.8°W	3296	100–200	10–61	420 ^b	17 Ma	289	224	20	1.0
853	7.2°N	109.6°W	3715	60–100	4–15	73 ^b	<8.8 Ma	94	26	27	-0.2
851	2.8°N	110.6°W	3760	100–200	16–55	320 ^b	11.4 Ma	184	255	26	0.0

Notes: References: Leg 154, Curry, Shackleton, Richter, et al. (1995); Leg 130, Kroenke, Berger, Janecek, et al. (1991), and Delaney and Shipboard Scientific Party (1991); Leg 138, Mayer, Pisias, Janecek, et al. (1992); primary productivity estimates, Berger and Wefer (1991).

^aDrilling at Site 927 did not penetrate to the depth of pore-water Sr or SO_4 plateaus.

^bDepths to basement. Neogene is incomplete on the young oceanic crust at these sites.

cite should show fewer effects of varying environments of precipitation and thus provide a less noisy input Sr/Ca signal. Both foraminiferal and bulk calcite Sr/Ca records show measurable variation among contemporaneous samples. Therefore, efforts to discern the causes of differences in initial Sr/Ca composition and differences in the effects of recrystallization on Sr/Ca may be aided by attention to both types of records.

We analyzed subsamples of the bulk sediment squeeze cakes (left after shipboard pore-water extraction) for calcite Sr/Ca and Mg/Ca ratios. Typically, the samples we analyzed span the full range of sediment ages recovered at each drill site and have typical sample spacings of 20–40 m, equivalent to 0.5–4.0 m.y. Most samples are composed predominantly of CaCO₃, with samples ranging from 21% to 85% CaCO₃. We excluded two samples from Site 929 from the figures and discussion because those samples were composed of less than 5% CaCO₃, and therefore the bulk sediment extraction could not isolate the calcite component of the sediment. We report sample depths in the standard ODP depth, that is, in meters below sea floor (mbsf). We used shipboard biostratigraphic control points from site sedimentation rates (see table 7 in Shipboard Scientific Party, 1995b, 1995c, 1995f; see table 8 in Shipboard Scientific Party, 1995d, 1995e) to calculate the ages of our Leg 154 samples by linear interpolation between age control points. We calculated the ages of the Leg 138 samples by linear interpolation between age control points from the eastern equatorial Pacific (Mayer, Pisas, Janeczek, et al., 1992; N.J. Shackleton, pers. comm., 1994). We adjusted previously published ages of Leg 130 samples (Delaney and Linn, 1993) to new age control points from the EEQP (N.J. Shackleton, pers. comm., 1994).

We used the method of Apitz (1991) as modified by Delaney and Linn (1993) for bulk calcite geochemical analyses, analyzing all Leg 154 and Leg 138 samples in duplicate. We weighed approximately 20 mg of bulk sediment into acid-cleaned centrifuge tubes and executed a sequence of steps to reduce oxyhydroxides and to remove exchangeable ions from clays in the sediments before dissolving samples in acetic acid for Sr, Mg, and Ca analyses. To each sample, we added 10 mL of reducing solution (25 g NH₂OH · HCl and 200 mL concentrated NH₄OH diluted with 300 mL distilled water), shook at room temperature for 6–12 hr, centrifuged, removed and discarded the solution, and then repeated this sequence. Next, we added 10 mL of ion exchange solution (1M NH₄OH), shook at room temperature for 1 hr, centrifuged, and removed and discarded this solution. Finally, we added 10 mL 0.1-M ammonium acetate-acetic acid buffer, shook at room temperature while samples dissolved for 5 hr, and centrifuged. We then removed aliquots from each sample for Sr, Mg, and Ca analyses and diluted each aliquot to the appropriate concentration range for flame atomic absorption spectrophotometric analysis (FAAS) using 0.023 M lanthanum (acidified to 0.3 M HCl) as an ionization suppressant. We determined dissolved concentrations of Sr, Mg, and Ca in individual sample dilutions by means of FAAS at standard conditions using a Perkin-Elmer Model 2380 spectrophotometer with an air-acetylene flame and a single slot burner head.

Reagent and instrumental blanks were consistently minor compared to solution concentrations of Sr, Mg, and Ca. Within a given run, relative errors of concentration determinations for solution replicates were generally less than ±2% for Sr and Ca and less than ±4.5% for Mg (1s standard deviation/mean). To minimize inter-run variability in results, we adjusted the ratios of samples and consistency standards (a set of four solutions with compositions similar to those of our samples) by sample batch for Leg 154, 138, and 130 data to long-term averages of consistency standards ratios in our lab. The median correction factor applied to the Sr/Ca and Mg/Ca data is 3% (absolute value), and correction factors range from 0% to 15% (absolute value). Reported errors in Sr/Ca and Mg/Ca ratios reflect these corrections. For Sr/Ca and Mg/Ca ratios, replicate analyses over a number of analytical runs of the consistency standards had 1s standard deviations relative to their means equivalent to ±1%–2% for the

Sr/Ca ratios and ±1%–3% for the Mg/Ca ratios. These solutions had known additions of Sr and Mg; the mean measured differences between pairs of these solutions for Sr concentrations ranged from 1.5% to 5% less than the expected differences and for Mg concentrations ranged from 1.5% to 6.5% greater than the expected differences. Relative errors of the means for solid sample replicates for Sr/Ca ratios were typically ±0.1%–3.0%, ranging up to 7.6% within a run. Relative errors of the means for solid replicates for Mg/Ca ratios were typically 0.1%–5.3% within a run, ranging up to 22% within a run. To evaluate the effect of sample inhomogeneity, we analyzed a solid consistency standard in duplicate in each sample batch (Legs 138 and 154 only). The relative error of the mean for this sample was ±4.9% for Sr/Ca and ±12% for Mg/Ca.

The sample pretreatment we applied was optimized to minimize the dissolution of more soluble calcite components and to maximize the removal of noncarbonate cations from terrigenous and authigenic sediment components (Apitz, 1991; Delaney and Linn, 1993). No special attention was paid to the behavior of celestite (SrSO₄) in this procedure. However, we do not think that celestite is soluble under the conditions applied. Celestite is sparingly soluble in water (0.01 g/11 mL) and insoluble in dilute acids (Weast, 1971; Latimer and Hildebrand, 1965).

We determined calcium carbonate content (reported as weight percent CaCO₃) on 5- to 10-mg solid subsamples of the bulk carbonate samples using a UIC, Inc., Coulometrics Model 5012 CO₂ Coulometer. Relative standard deviations on the means were always less than 1% for multiple determinations of a pure calcium carbonate standard, for samples run in duplicate within a given analytical run, and for replicate analyses of the two consistency standards over a number of analytical runs.

We estimated celestite saturation (as the ratio of the ion activity product [IAP] to the conditional solubility product [K_{sp}]) at each depth where pore-water Sr and SO₄ data were available at each site. We used available experimental and theoretical work for these estimates, although the controls on the thermodynamic solubility of celestite in natural solutions are poorly known and understood (indeed, they are poorly known in relatively simple laboratory solutions; for discussions of this issue, see Felmy et al. [1990] and Pitzer [1991]). We used the empirically derived temperature effect on the solubility product determined by Reardon and Armstrong (1987), assuming the bottom-water temperatures at our sites were the same as the temperatures at comparable depths for nearby GEOSECS stations (Broecker et al., 1982) and assuming a typical geothermal gradient of 35°C/km (Skinner and Porter, 1992) at each site. We corrected the temperature-specific solubility products for the effects of pressure using the theoretically derived correction as described in North (1974) and Morel and Hering (1993) and assumed pressure equivalent to hydrostatic pressure at depth in the sediments below sea level. We calculated the IAP by multiplying the measured pore-water concentrations of Sr and SO₄ by their activity coefficients in seawater to correct for the ionic strength and complexation effects on these ions in solution ($\gamma_{Sr} = 0.212$ and $\gamma_{SO_4} = 0.113$, derived using the Pitzer equations to account for the effects of ionic interactions in a seawater solution on the activities of these ions).

Our calculations reflect a number of parameters that are not well constrained and thus may include a significant error. Specifically, we used activity coefficients for Sr and SO₄ that are based on seawater concentrations of major ions. The changing concentrations of Ca, Mg, and SO₄ with depth in the pore waters may significantly reduce the activity coefficient of SO₄ by as much as one half, and proportionally reduce the celestite saturation (R. Hudson, pers. comm., 1996). We assumed the same geothermal gradient at all sites. Increasing or decreasing the geothermal gradient as much as 15°C/km has an increasingly large effect with depth, and can increase or decrease (respectively) the celestite saturation by as much as 5%–10%.

We used Richter's diffusion-reaction model of diagenetic Sr exchange between pore-water and calcite sediments (for a description

of the model, see Richter [1996] and previous papers cited therein). The model has been improved over previous versions in that it now includes (1) a pore-water Ca gradient, which is used to determine Sr incorporation into recrystallized calcite based on Sr/Ca ratios in pore waters, as well as (2) the possibility for authigenic celestite precipitation, with sulfate concentrations in pore water calculated using Berner's equations of organic matter diagenesis (Berner, 1964, 1978).

RESULTS AND DISCUSSION

Records from Ceara Rise

In the Sr/Ca and Mg/Ca records from Ceara Rise, there appears to be more variability in the data reported against depth than against age (Figs. 1, 2; Table 2). We tested this observation statistically by comparing the standard deviations of 3-point running averages of the data from all five sites together, ordered by age and by depth. As expected, these calculations indicate greater variability in the depth-ordered samples than in the age-ordered samples for both Sr/Ca and Mg/Ca data. For Sr/Ca data, the difference we calculated between the age-ordered and depth-ordered samples is more than 99.8% likely to reflect a real, not random, difference between the two (see hypothesis-testing method of Dowdy and Wearden, 1985, p. 207). However, for the Mg/Ca data, the difference we calculated between the age-ordered and depth-ordered samples is only 43.8% likely to reflect a real difference between the two; thus, our statistical test to evaluate the age vs. depth control on Mg/Ca at Ceara Rise is inconclusive. We interpret the smaller variability in the age plots to mean that age has a stronger control than depth on the Sr/Ca, and possibly on the Mg/Ca, signal. Although there are analytically distinguishable differences in the measured Sr/Ca and Mg/Ca values for similar age samples from different sites, similar patterns of Sr/Ca and Mg/Ca with age are evident at all sites.

Measured Sr/Ca values range from 0.78 mmol Sr/mol Ca to 2.30 mmol Sr/mol Ca (with one 23-Ma sample from Site 929 with 2.83 mmol Sr/mol Ca), and our record shows a general increase in Sr/Ca toward the present (Fig. 1A; Table 2). The oldest part of the record to 40 Ma has samples from Site 929 only, and these samples have the lowest Sr/Ca values measured. Superimposed on the general increase in Sr/Ca through time are several fluctuations in the record. Sr/Ca values generally appear to increase until about 25 Ma. Subsequent lows in Sr/Ca are centered at about 18 and 10 Ma. Sr/Ca values increase substantially between 10 and about 3–4 Ma, when samples with some of the highest Sr/Ca values were measured, and then decrease toward the present, with similar Sr/Ca values in the youngest samples from all five sites.

To evaluate the effect of variability in %CaCO₃ on our analytical results, we compared both Sr/Ca and Mg/Ca vs. %CaCO₃ for samples from Site 926 (an intermediate-depth site with less terrigenous input) and Site 929 (the deepest site with more terrigenous input). Linear regression of Sr/Ca vs. %CaCO₃ yields a slope of nearly zero (0.005 mmol Sr/mol Ca/%CaCO₃) and an *R*² value of 0.057, and does not suggest a correlation between Sr/Ca and CaCO₃. Mg/Ca values appear to correlate with %CaCO₃. Linear regression of Mg/Ca vs. %CaCO₃ at the same sites yields a larger slope (−0.14 mmol Mg/mol Ca/%CaCO₃) and an *R*² value of 0.57. However, samples with less than 45% CaCO₃ and Mg/Ca ratios greater than 5.0 mmol Mg/mol Ca appear to be primarily responsible for the strength of these correlations. When we removed data meeting both these criteria from the regressions, the slope was reduced to 0.002, and the *R*² value was reduced to 0.0004. Most of the samples that we removed from the regression were from the shallowest part of the records, where the influence of terrigenous sediment carried to Ceara Rise from the Amazon Fan was greatest (Shipboard Scientific Party, 1995a). Regression of Sr/Ca vs. Mg/Ca for all the CR samples included in this study yielded a slope of 1.5 mmol Mg/mmol Sr and an *R*² value of 0.02, which suggests

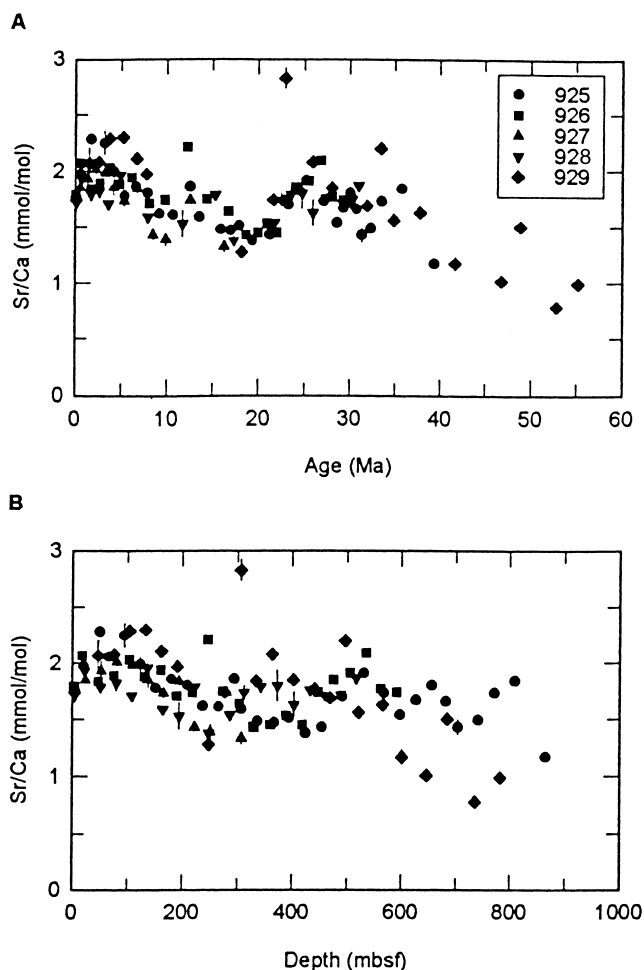


Figure 1. **A.** Bulk calcite Sr/Ca (mean \pm 1s) vs. age for all five sites on Ceara Rise. **B.** Bulk calcite Sr/Ca (mean \pm 1s) vs. depth for all five sites on Ceara Rise.

that the Sr/Ca analyses are not subject to the same influence from terrigenous input as the Mg/Ca analyses. Our interpretations of the significance (and lack thereof) of these correlations are supported by statistical t-tests (as per Dowdy and Wearden, 1985). Regression of all the %CaCO₃ and Mg/Ca data yields the only significant linear association.

There does not appear to be a systematic, site-dependent control on Sr/Ca patterns with age. The Sr/Ca values of the youngest samples at the three shallow sites, with water depths ranging from 3042 to 3598 m, are slightly higher than the Sr/Ca values of the youngest samples from the deep sites, with water depths of 4018 and 4356 m (1.77, 1.79, and 1.78 mmol Sr/mol Ca in samples dated 0.11, 0.09, and 0.10 Ma at the shallow sites, compared to 1.72 and 1.74 mmol Sr/mol Ca with both samples dated 0.12 Ma at the deep sites; Tables 1, 2). However, the difference between the shallow and the deep sites is comparable to the analytical error of our Sr/Ca measurements. If there is any water depth-controlled variability in the input Sr/Ca of bulk calcite at CR, it is obscured by diagenetic alteration.

Comparisons to Other Sr/Ca Records

We compared the bulk calcite Sr/Ca records from Ceara Rise to bulk calcite records from OJP (data from Delaney and Linn, 1993) and from the EEQp (new data) and planktonic foraminifer data from globally distributed samples (from Graham et al., 1982; Fig. 3).

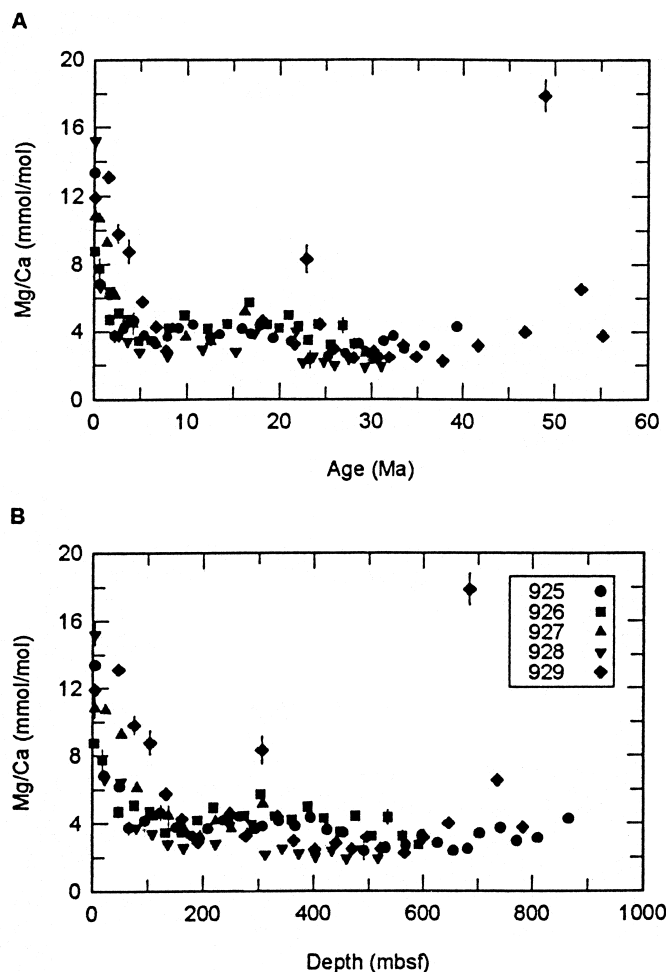


Figure 2. A. Bulk calcite Mg/Ca (mean \pm 1s) vs. age for all five sites on Ceara Rise. B. Bulk calcite Mg/Ca (mean \pm 1s) vs. depth for all five sites on Ceara Rise.

Absolute values of Sr/Ca differ regionally and between bulk and foraminiferal calcite, and the magnitude of changes with age is larger in the bulk than in the foraminiferal record. The bulk calcite Sr/Ca ratios are typically higher than the planktonic foraminifer Sr/Ca ratios, with the exception of samples older than about 40 Ma. The higher Sr/Ca values of the younger bulk calcite samples relative to the planktonic foraminifer samples is consistent with the incorporation of significantly more Sr into coccolithophorid than foraminiferal calcite (Stout, 1985; Apitz, 1991). The lower values of the older bulk calcite samples may be explained by the fact that Graham et al. (1982) excluded from their sample population any samples that appeared physically or chemically to have undergone diagenetic alteration (with anomalously low Sr/Ca relative to contemporaneous samples one criterion for exclusion), whereas all of our lab's bulk sediment data that appeared to reflect calcite Sr/Ca is included.

The Sr/Ca ratios of CR samples are typically higher (by approximately 0.25 mmol Sr/mol Ca) than those of contemporaneous samples from OJP in the part of the record younger than 35 Ma (Figs. 3, 4). In the older part of the record, where samples from fewer sites exist, most Sr/Ca ratios for samples from both regions are among the lowest values measured. In general, the patterns of Sr/Ca with age are very similar for CR and OJP, with a notable exception in the last 2 Ma when CR Sr/Ca values increase and OJP Sr/Ca values decrease.

The Sr/Ca values in the shorter record (maximum age, 18 Ma) from the EEqP range from 1.55 to 2.51 mmol Sr/mol Ca and are higher on average than Sr/Ca values in the other data sets considered here

(Figs. 3, 5). The variability in contemporaneous samples from this region is typically larger than that at either CR or OJP. In addition, the pattern of Sr/Ca with age is significantly different than the patterns at CR and OJP. The samples younger than about 8 Ma do have similar Sr/Ca values to the samples from CR, which are somewhat higher than the Sr/Ca values for contemporaneous samples from OJP. In samples older than about 12 Ma, average Sr/Ca ratios are higher in the EEqP than in the other regions, but many individual data points fall within the range of contemporaneous samples from CR. However, the greatest difference from the other records occurs in the interval centered around 10 Ma, in which samples from CR and OJP have low Sr/Ca values and EEqP samples have some of their highest values.

In broad outline, the bulk calcite record from CR and the combined bulk calcite record from CR, OJP, and the EEqP are similar to each other and to the planktonic foraminifer Sr/Ca record of Graham et al. (1982) (Figs. 3, 6). The Sr/Ca values in both the bulk calcite and foraminiferal records increase through the Cenozoic, although the absolute value of this increase is greater for the bulk calcite records. The difference between the Sr/Ca values in the two records changes through time. The relationship of the combined bulk calcite and the CR records flip-flops between a mode where both records have approximately the same Sr/Ca values and a mode with lower Sr/Ca in the combined record. A difference develops between the absolute values of Sr/Ca in the foraminiferal record and the bulk calcite records during the interval 40–30 Ma and remains throughout the rest of the record; the difference is greatest in approximately the last 7 Ma. The trend of increasing Sr/Ca over the last 2 Ma that we observed in the combined bulk calcite record, but not in the CR record, is similar to the trend in the youngest part of the foraminiferal record. Overall, however, the CR and the combined bulk calcite records are more similar to each other than to the foraminiferal record in the timing of major fluctuations of Sr/Ca. Specifically, the lows noted in the bulk calcite record were centered around 18 and 10 Ma, but in the foraminiferal record, these lows appear to be shifted toward the present by ~2–2.5 Ma. We adjusted the ages of the individual 1-m.y. or 5-m.y. points of the averaged planktonic foraminifer record of Graham et al. (1982) to reflect the ages for these points on the time scale of Cande and Kent (1992). The magnitude of age shift between the records may reflect the intervals chosen for age averaging as much as a true age shift of the records. It is possible that accurate determinations of the ages of the individual samples analyzed by Graham et al. (1982) would reduce some of the differences between the bulk and foraminiferal records.

Influence of Calcite Recrystallization: Authigenic Celestite Precipitation

The similarities among the several bulk calcite records and of the bulk calcite to the foraminiferal record are striking, but significant differences exist, which may be attributable to the differing effects of diagenesis from site to site and from region to region. Conspicuous differences in the pore-water chemistry from region to region provide clues as to the differences in the nature of recrystallization and celestite precipitation at these sites (Table 1). Delaney and Linn (1993) proposed that the pore-water profiles at OJP, with relatively constant depths of the Sr maxima at the different sites, decreasing pore-water Sr plateau concentrations, and increasing pore-water SO_4 minima with increasing site water depths, indicate that authigenic celestite precipitation is taking place at OJP, although celestite has not been identified in the sediments recovered at these sites. We predicted similar relationships among the pore-water profiles at CR, which has a similar range of site water depths, similar primary productivity in the overlying ocean, a similar carbonate-dominated sedimentation history to the sites drilled on OJP, and, based on the pore-water SO_4 minima, a somewhat more reducing pore-water environment (Table 1).

We tested the potential influence of authigenic celestite precipitation on calcite Sr/Ca records using a numerical model of diagenetic

Table 2. Bulk calcite Sr/Ca and Mg/Ca ratios at Ceara Rise, Sites 925–929.

Core, section, interval (cm)	Depth (mbsf)	Age (Ma)	CaCO ₃ (wt%)	Sr/Ca (mmol/mol)	Mg/Ca (mmol/mol)	Core, section, interval (cm)	Depth (mbsf)	Age (Ma)	CaCO ₃ (wt%)	Sr/Ca (mmol/mol)	Mg/Ca (mmol/mol)
154-925E-						3H-3, 145–150	23.45	0.56		1.85 ± 0.00	10.69 ± 0.07
1H-3, 145–150	4.45	0.11		1.77 ± 0.02	13.38 ± 0.02	6H-3, 145–150	51.95	1.38		1.93 ± 0.08	9.26 ± 0.12
3H-3, 145–150	20.95	0.63		1.97 ± 0.06	6.82 ± 0.17	9H-3, 145–150	80.45	2.25		2.01 ± 0.03	6.11 ± 0.02
6H-3, 145–150	49.45	1.73		2.28 ± 0.04	6.18 ± 0.10	12H-3, 145–150	108.95	3.20		1.98 ± 0.00	4.39 ± 0.04
154-925B-						15H-3, 145–150	137.45	4.20		1.85 ± 0.06	4.44 ± 0.62
8H-3, 145–150	65.95	2.22		2.06 ± 0.04	3.74 ± 0.38	18H-3, 145–150	165.95	5.34		1.73 ± 0.04	3.70 ± 0.10
11H-3, 145–150	94.45	3.20		2.25 ± 0.10	4.15 ± 0.28	21H-3, 145–150	194.45	6.78		1.84 ± 0.04	3.29 ± 0.04
14H-3, 145–150	122.95	4.26		1.99 ± 0.07	4.62 ± 0.45	24H-3, 145–150	221.95	8.49		1.43 ± 0.04	4.15 ± 0.03
17H-3, 145–150	151.45	5.40		1.78 ± 0.01	3.76 ± 0.00	27H-3, 145–150	250.45	9.86		1.39 ± 0.06	3.67 ± 0.01
20H-3, 145–150	179.95	6.64		1.86 ± 0.00	3.24 ± 0.15	30H-3, 145–150	278.95	12.55		1.74 ± 0.01	3.40 ± 0.25
23H-3, 145–150	208.45	7.88		1.80 ± 0.01	3.68 ± 0.11	33H-3, 145–150	307.45	16.23		1.33 ± 0.05	5.14 ± 0.08
26H-3, 145–150	236.95	9.12		1.62 ± 0.00	4.17 ± 0.00	154-928A-					
29H-3, 145–150	265.45	10.65		1.61 ± 0.03	4.38 ± 0.16	1H-3, 144–149	4.42	0.12		1.72 ± 0.65	15.25 ± 0.65
32H-3, 145–150	293.90	12.54		1.86 ± 0.04	3.65 ± 0.00	3H-3, 144–149	22.42	0.71		1.93 ± 0.06	6.64 ± 0.06
154-925A-						6H-3, 144–149	50.92	1.69		1.79 ± 0.05	6.48 ± 0.05
3R-2, 140–150	306.60	13.52		1.59 ± 0.01	3.81 ± 0.08	9H-3, 144–149	79.42	2.67		1.82 ± 0.15	3.77 ± 0.15
6R-2, 140–150	336.00	15.92		1.48 ± 0.03	4.11 ± 0.01	12H-3, 144–149	107.92	3.64		1.71 ± 0.11	3.42 ± 0.11
9R-3, 140–150	366.40	16.94		1.47 ± 0.02	3.82 ± 0.07	15H-3, 145–150	136.45	4.94		1.96 ± 0.19	2.81 ± 0.19
12R-2, 140–150	393.70	17.85		1.51 ± 0.04	4.33 ± 0.02	18H-3, 145–150	164.95	7.93		1.59 ± 0.01	2.57 ± 0.01
15R-3, 140–150	424.10	19.31		1.38 ± 0.02	3.61 ± 0.02	21H-3, 145–150	193.45	11.68		1.53 ± 0.07	2.94 ± 0.07
18R-3, 140–150	453.00	21.24		1.43 ± 0.01	3.42 ± 0.01	24X-3, 145–150	222.15	15.27		1.79 ± 0.13	2.81 ± 0.13
22R-3, 140–150	491.50	23.29		1.70 ± 0.00	2.34 ± 0.51	154-928B-					
26R-4, 140–150	530.40	25.23		1.91 ± 0.01	2.54 ± 0.03	27X-3, 140–150	247.60	17.28		1.38 ± 0.00	3.87 ± 0.00
30R-3, 140–150	568.60	27.14		1.73 ± 0.01	2.69 ± 0.03	31X-3, 140–150	285.90	21.77		1.54 ± 0.01	4.01 ± 0.01
33R-3, 140–150	597.50	28.60		1.54 ± 0.01	3.25 ± 0.06	34X-1, 140–150	312.10	22.50		1.74 ± 0.03	2.18 ± 0.03
36R-3, 140–150	626.50	29.33		1.67 ± 0.00	2.82 ± 0.04	37X-2, 140–150	342.60	23.55		1.79 ± 0.06	2.52 ± 0.06
39R-3, 140–150	655.50	30.07		1.80 ± 0.02	2.37 ± 0.01	40X-3, 140–150	372.60	24.73		1.80 ± 0.06	2.23 ± 0.06
42R-1, 140–150	681.50	30.76		1.66 ± 0.00	2.48 ± 0.05	43X-4, 135–150	402.65	25.93		1.63 ± 0.06	2.04 ± 0.06
45R-3, 140–150	703.70	31.34		1.43 ± 0.06	3.40 ± 0.05	46X-5, 135–150	431.89	27.44		1.76 ± 0.12	2.37 ± 0.12
49R-3, 130–150	741.90	32.35		1.49 ± 0.01	3.71 ± 0.08	49X-3, 135–150	458.95	29.26		1.71 ± 0.05	1.92 ± 0.05
53R-3, 130–150	772.14	33.54		1.73 ± 0.01	2.95 ± 0.04	52X-3, 135–150	487.95	30.18		1.72 ± 0.15	2.45 ± 0.15
57R-3, 130–150	809.50	35.80		1.84 ± 0.01	3.13 ± 0.01	55X-3, 135–150	516.95	31.02		1.87 ± 0.07	1.95 ± 0.07
63R-2, 130–150	865.90	39.32		1.17 ± 0.00	4.27 ± 0.08	154-929A-					
154-926A-						1H-3, 136–141	4.36	0.12	28.7	1.74 ± 0.03	11.93 ± 0.07
1H-2, 145–150	2.95	0.09	42.7	1.79 ± 0.00	8.76 ± 0.08	6H-3, 145–150	46.95	1.53	24.7	2.07 ± 0.13	13.12 ± 0.15
3H-3, 145–150	17.95	0.57	38.2	2.07 ± 0.02	7.76 ± 0.59	9H-3, 145–150	75.45	2.59	31.1	2.08 ± 0.04	9.80 ± 0.53
6H-3, 145–150	46.45	1.67	66.2	1.84 ± 0.00	4.70 ± 0.30	12H-3, 145–150	103.95	3.73	30.7	2.29 ± 0.05	8.76 ± 0.69
9H-3, 145–150	74.95	2.67	67.0	1.89 ± 0.01	5.08 ± 0.26	15H-3, 145–150	132.45	5.21	33.2	2.30 ± 0.01	5.76 ± 0.16
12H-3, 145–150	103.45	3.66	71.3	2.03 ± 0.02	4.73 ± 0.07	18X-3, 145–150	161.25	6.70	48.0	2.11 ± 0.01	4.26 ± 0.05
15H-3, 145–150	131.95	4.85	83.0	1.88 ± 0.01	3.46 ± 0.15	21X-3, 145–150	190.15	7.77	75.8	1.97 ± 0.00	2.87 ± 0.01
18H-3, 145–150	160.45	6.16	72.8	1.94 ± 0.00	3.47 ± 0.07	27X-3, 140–150	247.80	18.15	84.5	1.28 ± 0.02	4.62 ± 0.36
21H-3, 145–150	188.95	8.06	72.8	1.71 ± 0.00	4.18 ± 0.08	30X-3, 140–150	276.30	21.63	69.0	1.74 ± 0.01	3.25 ± 0.17
24H-3, 145–150	217.45	9.75	64.1	1.74 ± 0.00	4.93 ± 0.26	33X-3, 140–150	305.40	22.90	36.6	2.83 ± 0.09	8.31 ± 0.80
27H-3, 145–150	245.95	12.23	59.4	2.21 ± 0.03	4.14 ± 0.16	36X-3, 140–150	334.40	24.31	52.0	1.84 ± 0.02	4.41 ± 0.23
30H-3, 145–150	274.45	14.34	70.2	1.75 ± 0.01	4.43 ± 0.28	39X-3, 135–150	363.35	25.92	61.5	2.08 ± 0.04	2.97 ± 0.11
33H-3, 145–150	302.95	16.71	63.9	1.64 ± 0.02	5.71 ± 0.10	43X-3, 135–150	401.75	28.06	69.6	1.85 ± 0.00	2.45 ± 0.00
154-926B-						47X-3, 135–150	440.45	30.21	68.2	1.77 ± 0.05	2.84 ± 0.01
36X-2, 140–150	329.40	18.60	74.1	1.43 ± 0.01	4.39 ± 0.06	50X-3, 135–150	469.35	31.91	59.4	1.69 ± 0.04	2.47 ± 0.17
39X-3, 140–150	359.90	19.93	77.0	1.45 ± 0.01	4.20 ± 0.18	53X-2, 135–150	496.35	33.46	47.0	2.20 ± 0.01	3.17 ± 0.10
42X-3, 140–150	388.50	20.95	66.4	1.53 ± 0.01	4.96 ± 0.08	154-929E-					
45X-3, 140–150	417.50	21.98	81.3	1.45 ± 0.01	4.28 ± 0.00	6R-1, 130–150	521.30	34.86	66.6	1.56 ± 0.03	2.50 ± 0.29
48X-3, 140–150	446.50	23.02	66.7	1.74 ± 0.02	3.49 ± 0.08	10R-5, 130–150	565.60	37.78	60.9	1.63 ± 0.04	2.26 ± 0.01
51X-3, 135–150	475.35	24.13	58.4	1.85 ± 0.02	4.43 ± 0.13	14R-3, 130–150	601.20	41.66	57.2	1.17 ± 0.06	3.17 ± 0.41
54X-4, 135–150	505.75	25.51	60.1	1.91 ± 0.03	3.22 ± 0.10	19R-1, 130–150	646.30	46.78	59.9	1.01 ± 0.01	4.00 ± 0.12
57X-4, 135–150	534.75	26.83	49.1	2.09 ± 0.00	4.35 ± 0.43	23R-1, 130–150	684.50	48.90	20.6	1.50 ± 0.01	17.88 ± 0.92
60X-3, 135–150	562.25	28.08	73.9	1.77 ± 0.01	3.24 ± 0.32	28R-3, 130–150	735.90	52.85	30.9	0.78 ± 0.01	6.55 ± 0.33
63X-3, 135–150	591.25	29.30	73.3	1.74 ± 0.02	2.74 ± 0.09	33R-2, 128–148	782.68	55.21	50.8	0.99 ± 0.01	3.77 ± 0.13
154-927A-											
1H-3, 145–150	4.45	0.10		1.78 ± 0.04	10.82 ± 0.58						

Note: Element/Ca ratios reported as the mean of two replicate samples ± 1s.

Sr exchange. In Figure 7, we compare a pair of results from this reaction-diffusion model of diagenetic Sr exchange between pore waters, biogenic and recrystallized calcite, and, in one case only, authigenic celestite. The model predicts bulk calcite Sr/Ca, pore-water Sr, and pore-water sulfate profiles as a function of their evolution from input values caused by calcite diagenesis, organic matter oxidation of sulfate, and diffusion of ions in the pore waters. In one simulation, authigenic celestite precipitation (or dissolution) removed (or added) Sr to the pore waters when celestite was over(under)-saturated in the pore waters. In the control simulation, celestite precipitation could not occur. The simulations were run with constant input values to the sediments through time of 1.84 mmol/mol bulk calcite Sr/Ca, 90 mM pore-water Sr, and 28 mM pore-water SO₄ (present-day values), and thus the model results in Figure 7 reflect diagenetic changes to initial flat profiles.

The model results show that celestite precipitation can have a powerful influence on pore-water Sr profiles, in this case reducing

the pore-water Sr concentration at the Sr maximum by nearly two-thirds, from ~1830 to 640 μM. The effect of celestite precipitation on pore-water sulfate and on calcite Sr/Ca is less striking, with the bulk calcite Sr/Ca reduced as much as 0.04 mmol Sr/mol Ca and the sulfate minimum reduced 2 mM solely because of the effects of celestite precipitation. It is self-evident that celestite precipitation removes Sr and SO₄ from the pore water and thus lowers their concentrations. Sr concentrations in recrystallized calcite are lower than they would be in the absence of celestite precipitation because celestite precipitation reduces pore-water Sr concentrations. The concentration of Sr in pore water at the time calcite recrystallizes controls the ultimate Sr concentration in calcite sediments. Although our model simulation does not predict a large effect on calcite Sr/Ca relative to the variability observed among contemporaneous bulk and foraminiferal calcite samples, it does generate lower calcite Sr/Ca in sites with celestite precipitation. The precipitation of authigenic celestite at some sites may explain some portion of the site-to-site variability in bulk calcite Sr/

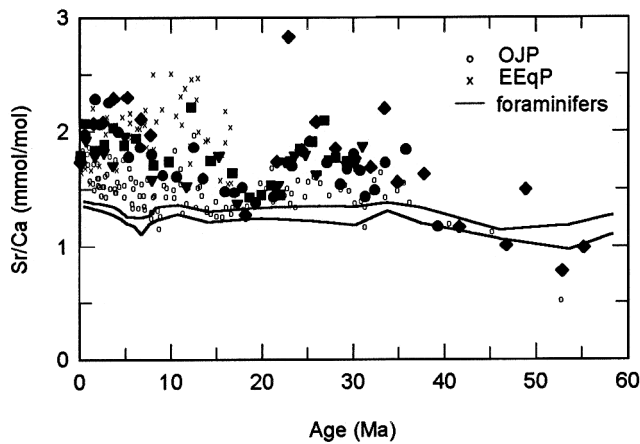


Figure 3. Bulk calcite Sr/Ca from Ceara Rise (CR), Ontong Java Plateau (OJP, Sites 803–807; Delaney and Linn, 1993), and the eastern equatorial Pacific (EEqP; G. Hampt and M.L. Delaney, unpubl. data) and planktonic foraminifer Sr/Ca vs. age (Graham et al., 1982). Symbols for Ceara Rise sites are as in Figures 1 and 2. Planktonic foraminifer Sr/Ca ratios from Graham et al. (1982) are shown as solid lines, which represent 80% confidence intervals about the mean of their data in 1-m.y. increments from 0 to 10 Ma and 5-m.y. increments from 10 to 60 Ma. We replotted the previously published OJP data, with ages corrected to age control points from the EEqP (N.J. Shackleton, pers. comm., 1994) and Sr/Ca values corrected to long-term averages of consistency standards in our lab (see “Methods” section, this chapter). The published ages of the Graham et al. (1982) data reflect the time scales of Berggren (1972) and Berggren and van Couvering (1974). For this plot we adjusted the ages of the individual 1-m.y. or 5-m.y. averages to reflect the ages for these midpoints on the time scale of Cande and Kent (1992). We did not correct the ages of individual data points.

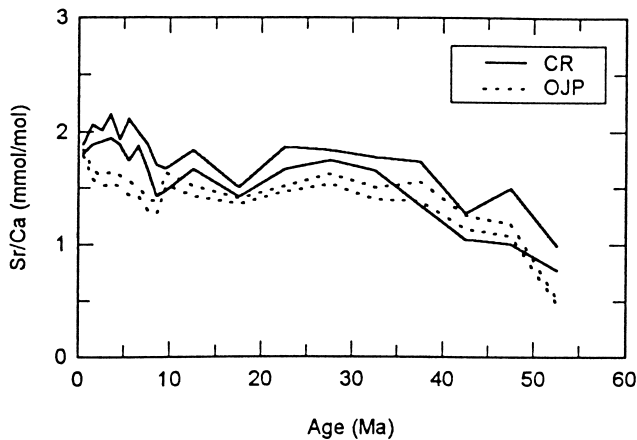


Figure 4. Average bulk calcite Sr/Ca vs. age. We averaged bulk calcite data in 1-m.y. increments from 0 to 10 Ma and in 5-m.y. increments from 10 to 55 Ma, and we plotted the average Sr/Ca in each interval $\pm 2s/\sqrt{N}$.

Ca (if our analytical procedure does indeed capture only the component of sedimentary Sr incorporated in calcite) and, potentially, also in foraminiferal Sr/Ca.

We calculated celestite saturation at the CR, OJP, and EEqP sites to evaluate the possibility of an influence of celestite precipitation on our Sr/Ca records and pore-water geochemical profiles. We do not claim to have determined a perfectly accurate profile of celestite saturation for our sites. Nevertheless, our work does provide a semi-quantitative means to evaluate the possibility of celestite precipita-

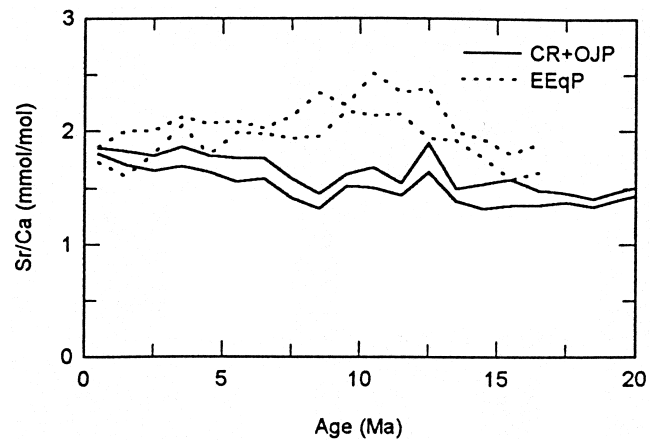


Figure 5. Average bulk calcite Sr/Ca vs. age. We averaged bulk calcite data in 1-m.y. increments from 0 to 20 Ma, and we plotted the average Sr/Ca in each interval $\pm 2s/\sqrt{N}$.

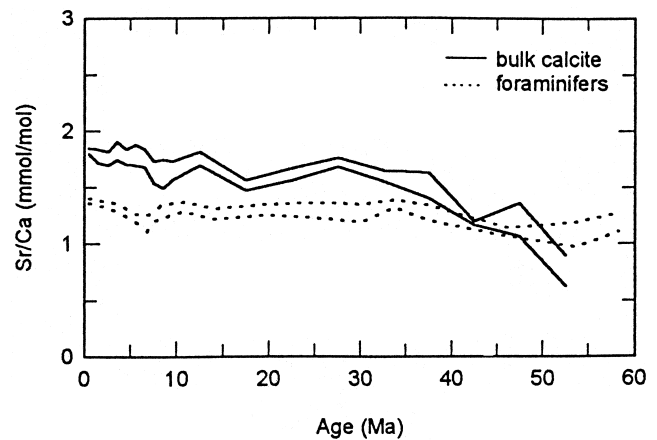


Figure 6. Average bulk calcite Sr/Ca and global planktonic foraminifer Sr/Ca vs. age. We averaged the bulk calcite data from all three regions in 1-m.y. increments from 0 to 10 Ma and in 5-m.y. increments from 10 to 55 Ma, and we plotted the average Sr/Ca $\pm 2s/\sqrt{N}$. Planktonic foraminifer data are plotted as in Figure 3.

tion for the purpose of site-to-site and regional comparisons. According to our calculations, celestite saturation is exceeded at OJP Sites 806 and 807 and pore waters are close to saturation at a number of sites on CR and OJP (Fig. 8). In general, the celestite saturation profiles mimic the pore-water Sr profiles. However, changes in the slope of the celestite saturation profiles also reflect pressure and temperature increases with depth in the sediments.

At the CR (Fig. 8A), celestite saturation profiles fall into two groups. In the shallower sites (925, 926, and 927), pore waters approach celestite saturation in the age interval of ~ 5 –20 Ma. In the deeper sites (928 and 929), the pore waters are increasingly saturated with respect to celestite with increasing sediment age, but never to the degree observed at the shallower sites. At Sites 925, 926, and 928, low SO_4 concentrations at depth seem to drive decreases in saturation at depth (not shown in figure). Regional differences in the celestite saturation profiles are immediately evident (Fig. 8B). Pore waters at the EEqP sites do not approach celestite saturation, a predictable consequence of the low pore-water Sr concentrations in those sites. With the exception of the deepest site at OJP (Site 804), pore waters at those sites are at or near saturation. The higher pore-water SO_4 concentrations at OJP relative to CR appear to generate higher relative

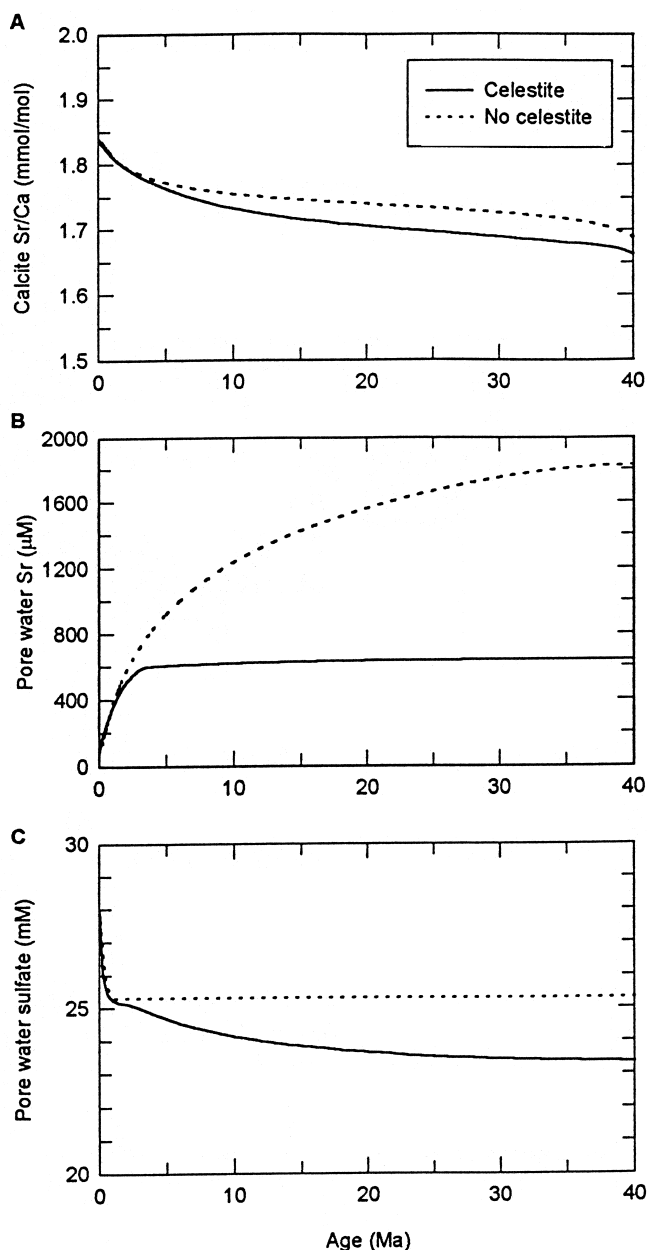


Figure 7. Model results for (A) bulk calcite Sr/Ca vs. age, (B) pore-water Sr vs. age, and (C) pore-water SO_4 vs. age. These are model predictions using a diffusion-reaction model of Sr exchange between calcite sediments and pore waters to predict geochemical profiles after 40 m.y. of sediment accumulation at a sedimentation rate of 40 m/m.y., with constant input values to the sediments through time of 1.84 mmol/mol bulk calcite Sr/Ca, 90 mM pore-water Sr, and 28 mM pore-water SO_4 (present-day values). We used a partition coefficient for inorganic calcite of 0.022, a constant celestite solubility, and a calcite recrystallization rate pattern that is initially rapid, with 20% of biogenic sediments recrystallized after 2 m.y. in the sediments, but tails off by 15 Ma to 0.1%/m.y. (For a discussion of this calcite recrystallization rate, see Richter and Liang, 1993; Richter and DePaolo, 1987, 1988.)

saturation at OJP. However, as at CR, the three OJP sites with shallower water depths (Sites 805–807) have markedly higher celestite saturation than the two deeper sites. OJP Site 803, with intermediate celestite saturation relative to the other sites at OJP, has the saturation profile that is most similar to the profiles of the shallow CR sites. Our celestite saturation calculations suggest that authigenic celestite is

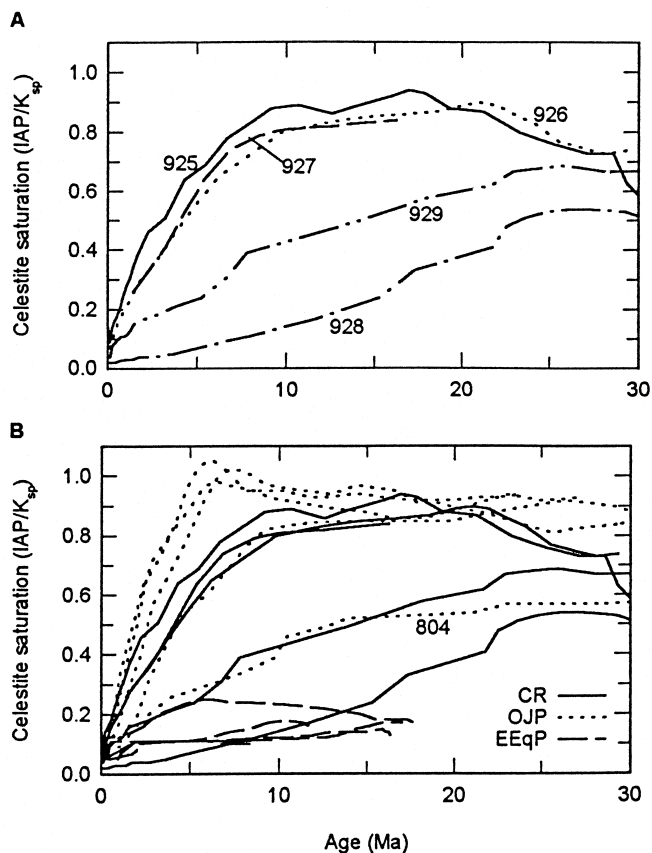


Figure 8. A. Celestite saturation vs. age at five CR sites. B. Celestite saturation vs. age at 15 CR, OJP, and EEQP sites. Lines are 3-point running averages of our calculations.

present at the OJP sites (except the deep Site 804) and at the CR sites (except the deep Sites 928 and 929) and is not present in the EEQP.

SUMMARY AND CONCLUSIONS

Our bulk calcite Sr/Ca records from the five Leg 154 sites at the CR show the same general pattern of age-dependent variations through the Cenozoic. Nevertheless, we found measurable differences in Sr/Ca ratios of contemporaneous samples from different CR sites that do not appear to be consistent through time. Larger differences typically exist in Sr/Ca ratios of contemporaneous samples from different regions and between bulk and foraminiferal calcite. Among the data examined here, OJP samples have the lowest bulk Sr/Ca, CR samples have intermediate values, and EEQP samples have the highest values. Foraminiferal calcite Sr/Ca values (from Graham et al., 1982) are typically lower than bulk calcite values (Delaney and Linn, 1993). In addition, the magnitude of changes through time is larger in the bulk than in the foraminiferal record. However, similar patterns with age among the bulk calcite Sr/Ca records from CR and OJP and the planktonic foraminifer record of Graham et al. (1982), and to a lesser degree, the bulk calcite record from the EEQP, suggest that the ocean history of the seawater Sr/Ca ratios is the dominant influence on these records.

Although the mechanisms that generate differences in biogenic Sr/Ca are still under consideration, bulk calcite seems less likely than foraminiferal calcite to show variations in initial calcite Sr/Ca controlled by calcification depth because it is dominated by calcite precipitated in the photic zone (coccolithophorids). Therefore, local and regional differences in Sr/Ca are likely to be a function of the differ-

ences in the effects of diagenetic recrystallization. Observations and model predictions suggest that authigenic celestite precipitation can substantially affect pore-water Sr profiles and, to some degree, affect pore-water SO_4 profiles and bulk calcite Sr/Ca. Our celestite saturation calculations suggest that authigenic celestite may exist at Sites 925–927 on CR and Sites 803 and 805–807 at OJP. Our model results suggest that Sr/Ca values should be lower at OJP and CR than in the EEQP, as in fact is the case (Fig. 5). However, the differences in bulk calcite Sr/Ca between these regions are much larger (up to 10 times larger in the interval around 10 Ma) than our preliminary model results suggest is possible. Further work could better quantify the occurrence of celestite and the differing effects of different amounts of celestite precipitation on the CR and OJP Sr/Ca records. Because celestite precipitation does not appear to account for the magnitude of the differences in Sr/Ca from site to site, attention to other sedimentary controls on diagenetically altered calcite Sr/Ca may be fruitful.

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