Geology

Cretaceous strontium isotope stratigraphy using marine barite

Sarah Mearon, Adina Paytan and Timothy J. Bralower

Geology 2003;31:15-18

Notes

Geological Society of America
**ABSTRACT**

The strontium isotope ratios ($^{87}$Sr/$^{86}$Sr) of marine barite microcrystals separated from Cretaceous sedimentary deposits from Ocean Drilling Program and Deep Sea Drilling Project sites from the Pacific and Indian Oceans have been compared to the composite Sr isotope curve of McArthur et al. The barite in these cores accurately recorded the seawater $^{87}$Sr/$^{86}$Sr ratio, thereby reaffirming the composite Cretaceous strontium curve. Moreover, marine barite is a more reliable recorder of $^{87}$Sr/$^{86}$Sr than is carbonate in sedimentary deposits with high clay content, thereby providing an opportunity for Sr isotope stratigraphy and dating in carbonate-poor or diagenetically altered sediments. We have used the barite-derived Sr isotope record to refine the biostratigraphic age models of the sites investigated.

**Keywords:** barite, strontium isotopes, stratigraphy, Cretaceous.

**INTRODUCTION**

The Sr isotope composition ($^{87}$Sr/$^{86}$Sr) of seawater has changed over the course of the Phanerozoic as a result of variations in the input of strontium from continental crust and mantle sources (e.g., Burke et al., 1982; Jones et al., 1994). These variations are caused by changes in climate, tectonic activity, weathering, and hydrothermal activity (e.g., Veizer et al., 1999). Because the oceanic residence time of strontium is about three orders of magnitude greater than the mixing time of the oceans, the $^{87}$Sr/$^{86}$Sr in the oceans at any point in time is uniform (Elderfield, 1986). As such, Sr isotope stratigraphy in the open ocean is independent of latitude and facies (DePaolo and Ingram, 1985). Accordingly, the Sr isotope record can be used for interpreting paleoceanographic changes through geologic time, as well as for stratigraphic correlation and age dating.

In many intervals of time, Sr isotope stratigraphy can provide finer temporal resolution than can be obtained with biostratigraphy or magnetostratigraphy (e.g., Hess et al., 1986; McArthur et al., 1993, 1994). This ability is especially important for Cretaceous marine sedimentary deposits, in which long time intervals have no magnetic reversals and biostratigraphic zones may range to several million years (e.g., Bralower et al., 1995). Moreover, Sr isotopes may be used in nonfossiliferous or poorly fossiliferous sedimentary deposits and in correlation of shallow-marine sequences (Ludwig et al., 1988; McKenzie et al., 1988; Jenkyns et al., 1995; Lehmann et al., 1999).

In order for marine minerals to serve as accurate recorders of the seawater $^{87}$Sr/$^{86}$Sr ratio over time, diagenetic alteration must be excluded (e.g., Burke et al., 1982; Elderfield and Gieskes, 1982; Gieskes et al., 1986; Denison et al., 1994; Veizer et al., 1997). Exchange with Sr from other minerals and from interstitial waters during burial typically results in higher $^{87}$Sr/$^{86}$Sr ratios compared to the original values, although lower ratios have been observed under certain circumstances (Richter and Liang, 1993).

The most common marine minerals used for reconstructing the seawater Sr isotope curve over time and for Sr isotope stratigraphy are carbonates. Carbonates are susceptible to diagenetic alteration that may compromise original Sr isotope signatures, especially in older sedimentary rocks (Gieskes et al., 1986) and those rich in clay (e.g., Bralower et al., 1997). Accordingly, rigorous tests and screenings for diagenetic alteration must be employed. Investigations of Cretaceous sections have typically demonstrated that >50% of carbonate samples are altered (Veizer and Compston, 1974; Jones et al., 1994; Bralower et al., 1997; McArthur et al., 2001). Moreover, a large part of the ocean floor is covered by noncalcareous sedimentary deposits. Ichthyoliths have been previously used for determining Cretaceous Sr isotope stratigraphy in carbonate-poor sediments (Ingram et al., 1994). However, this application is only viable in sections that had very low sedimentation rates, and where fish debris are plentiful, and thus cannot provide very high resolution stratigraphy; moreover, such records may be affected by postdepositional Sr incorporation from surrounding shales (Bralower et al., 1997). An alternative phase is required that records the seawater Sr isotope composition and can be applied in cases where the record based on carbonates is compromised or where carbonates are unavailable. We show here that marine barite can fill these requirements, and therefore can be used for seawater Sr isotope ratio reconstructions and for Sr isotope stratigraphy.

Marine barite precipitates in the water column (Dehairs et al., 1980; Bishop, 1988), incorporating strontium from seawater into the crystal structure. Barite contains 7000–10,000 ppm strontium and is a ubiquitous mineral in oxic deep-sea sedimentary deposits. Barite is less susceptible to diagenetic alteration than carbonate minerals during burial under oxygenated conditions (Dymond et al., 1992). Paytan et al. (1993) showed that barite reliably records variations in seawater $^{87}$Sr/$^{86}$Sr over the past 35 m.y. Therefore, this phase may provide an alternative means for Sr isotope stratigraphy and correlation in older marine sedimentary rocks and in sites and time intervals where carbonates are rare or where the Sr isotope signature recorded by the carbonates is affected by postdepositional alteration, thereby rendering the carbonates unsuitable for Sr isotope analysis.

**SITE CHARACTERISTICS**

Two sites drilled in the Pacific and Indian Oceans were selected for this study: Deep Sea Drilling Project (DSDP) Site 305 (32°00.13'N, 157°51.00'E, 2903 m depth), spanning the interval 135–78 Ma, and Ocean Drilling Program (ODP) Site 766 (19°55.925'S, 110°27.243'E, 3998 m depth), spanning the interval 122–78 Ma. These sites have reasonably complete Cretaceous sections, but the published biostratigraphy is of poor resolution, which limits stratigraphic correlation. An Sr isotope record from an unaltered phase such as barite could help set limits on the age models and sedimentation rates for these cores and help correlate them with sections of similar age.

The Cretaceous sedimentary deposits at Site 305 are primarily composed of foraminiferal-nanofossil ooze, chalk, and chert in the upper part of the section and radiolarian-bearing limestone and chert in the lowermost part of the section (Larson and Moberly, 1975). Core recovery was low in most of the section and typically restricted to small core-catcher samples of firm chalk and chert. Most microfossils are poorly preserved and provide only broad age assignments (Bakry, 1975; Cannon, 1975; Sliter, 1992). Coccoclines were abundant, but poorly to moderately preserved; radiolarians were rare and poorly preserved; and foraminiferal biostratigraphic control was...
poor below the Albian because of scarce recovery of carbonates.

The Cretaceous sedimentary deposits at Site 766 (Hole 766A) are composed primarily of nanofossil ooze and nanofossil chalk from the Maastrichtian down to the lower Aptian. The Valanginian to Barremian consists of claystone, sandstone, and siltstone (Gradstein and Ludden, 1990). In contrast with Site 305, calcareous nanofossils are abundant in sedimentary deposits from Hole 766A, particularly in the upper part of the section. However, foraminiferal preservation is moderate to poor, and abundance is fairly low, especially near the base of the hole. Radiolarians are relatively rare and are poorly to moderately preserved. At Site 766, deposition was continuous from the late Valanginian to Maastrichtian. A few Cretaceous samples from Site 765 (Hole 765C) from lithologies similar to those of Site 766 were also analyzed.

METHODS

Barite was separated from sediment samples by using a sequential leaching procedure described in Eagle et al. (2002). Following this procedure, the samples were examined with a scanning electron microscope (SEM). Acceptable samples contained few contaminants and were characterized by subhedral to euhedral, spherical to elliptical, primary barite microcrystals ranging in size from 1 to 5 μm (Fig. 1A). Samples dominated by large (>10 μm) diagenetic barite crystals (Fig. 1B) were discarded, as were those that contained a significant amount (>5%) of silicate material, because the silicate contributes different strontium ratios than those recorded for seawater.

Pure barite (~1–4 mg) was dissolved by chelation in a cation exchange resin at 90°C (Church, 1970). The cations were stripped from the resin, and strontium was separated by using conventional ion chromatographic procedures. Samples were loaded on Ta filaments and analyzed by thermal ionization mass spectrometry (Finnigan 261). Values have been normalized to 86Sr/88Sr = 0.1194. We measured the SRM987 standard along with each batch of samples and adjusted the 87Sr/86Sr of the samples to SRM987 = 0.71024, which is the average value measured in the laboratory along with the samples.

RESULTS

Strontium isotope data for Site 305 and Site 766 barite and carbonate samples are given in Table 1 and plotted in Figure 2, along with the McArthur et al. (2001) LOWESS composite Sr isotope curve for the Cretaceous. The LOWESS curve was compiled by using Sr isotope data from 11 literature sources for the Cretaceous section after correction for interlaboratory bias. The LOWESS curve is the best available data set for seawater Sr isotopic composition in the Cretaceous.

The Sr isotope ratio for each barite sample analyzed was plotted at its corresponding Sr isotope value of the LOWESS curve. Accordingly, the assigned age of the barite samples (column 5) corresponds to the appropriate 87Sr/86Sr age from the compiled curve of McArthur et al. (2001). The 87Sr/86Sr values of the carbonates for the same samples were plotted by using the age derived from the barite samples. For comparison we report the published biostratigraphic zonal ranges and the estimated biostratigraphic age for each sample (Bukry, 1975; Mutterlose, 1992; Moran, 1992). Age calibration of biostratigraphic datums is after Berggren et al. (1995) for the Paleocene, Erba et al. (1995) for the Maastrichtian to early Turonian, Bralower et al. (1997) for the early Turonian to late Barremian, and Bralower et al. (2002) for the late Barremian to Valanginian.

DISCUSSION

The Sr isotope data for barite samples plotted with respect to the curve of McArthur et al.
theless are within analytical error (±0.00002), as defined by the thin solid lines above and below the McArthur et al. (2001) curve. In addition, Sr isotope ratios for samples in the late Albian (105–100 Ma) plot slightly above the curve. The data used to produce the LOWESS curve show more scatter in the late Albian than elsewhere in the Cretaceous (J.M. McArthur, 2001, personal commun.). It is possible that the barite ratios are more reliable than the LOWESS curve. The barite data presented here suggest that refinement of the LOWESS curve through this interval is needed. Bulk carbonate Sr isotope data from Site 305 compare well with the barite data for the same intervals (within analytical error). As with the barite data, there is some scatter in the carbonate data between ca. 65 and 75 Ma that can be attributed to analytical error, and ratios in the late Albian plot slightly above the LOWESS curve.

There is fairly good agreement between the ages derived from barite strontium stratigraphy and the biostratigraphic zones for both sites (Fig. 2). However, at Site 305, the ages derived from Sr isotope ratios for samples between 77 and 73.5 Ma are generally younger than the ages estimated by assuming linear sedimentation between zonal datums, and are not within the published biostratigraphic zones. We think that the Sr isotope ages are more reliable than the microfossil biostratigraphic ages, because it is highly unlikely that diagenetic processes would alter the Sr isotope ratios in barite samples in a relatively small depth range in the core while retaining the trend expected for the seawater Sr isotope curve. Diagenetic effects should increase scatter in the Sr isotope ratios (see results for carbonate samples from Site 766) or flatten stratigraphic trends to a limited range of values (those of the pore fluids). Similarly, it is unlikely that both the barite and carbonates in the core will retain a similar Sr isotope ratio after alteration. The Sr isotope data obtained for barite in Site 766, where the biostratigraphy provides higher resolution, agree well with the bizonal assignments and are within ±2 m.y. of the ages estimated by using nanofossils. Moreover, sulfur isotope data from the same barite samples in both sites accurately record the seawater value, further supporting the lack of alteration. In contrast, several barite samples from Site 765 yield Sr isotope values that are more radiogenic than expected from their appropriate age, as well as significantly higher sulfur isotope ratios than contemporaneous seawater values (Paytan et al., 2002). These samples have been altered by diagenesis, as indicated by their large crystal size compared to barite crystals that precipitate in the water column (see Fig. 1B). Although the barite Sr isotope data from both sites are consistent with the stratigraphic position in the cores, the agreement between the carbonate and barite Sr isotope ratios in Site 766 is not evident. The carbonate isotope ratios in this core are all significantly more radiogenic than expected for Cretaceous samples of corresponding age (and from the respective barite data for the same samples). The data are scattered, and no obvious trend is observed with age. These results suggest diagenetic alteration of the carbonate Sr isotope record. Upon examination of carbonate samples from Site 766, it is clear that they have been subjected to more significant diagenetic alteration (Fig. 3A) than samples from Site 305 (Fig. 3B). The proximity of Site 766 to Australia during the Cretaceous suggests that contributions of detrital silicates rich in radiogenic Sr are likely the cause of the elevated 87Sr/86Sr in the carbonate samples produced during diagenetic reactions. The high clay content in the core supports this conclusion; similar Sr isotope offsets have been observed in clay-rich Cretaceous sedimentary deposits from nearby Site 763 on Exmouth Plateau (Bralower et al., 1997). In contrast, Site 305 was far from continental margins during the Cretaceous and accumulated less terrigenous material (lower clay content), which may explain why the Sr isotope ratios from the carbonate at this site were unaltered. These observations necessitate a rigorous screening process and evaluation of clay content when using marine sediment samples for Sr isotope work.

Biostratigraphic resolution for the Cretaceous based on single microfossil groups is typically on the order of a few million years and can be as large as 14 m.y. (e.g., Bralower et al., 1995). In contrast, Sr isotope data shown here can provide much higher stratigraphic resolution and can define the actual age of the sample to within <0.5 m.y. for much of the record. In addition, the seawater Sr isotope curve represents a global time reference that is not dependent on locally variable sedimentation rates, reducing some of the errors associated with age extrapolations using an assumption of linear sedimentation rate. The age model based on Sr isotopes can be used to estimate sedimentation rates, calculate barite accumulation rates, and interpret the data in terms of biological productivity (Paytan and Mearon, 2001; Paytan, 2002). The age model could also be used to delimit other paleoceanographic and geochemical data obtained from these cores, such as the sulfur isotopes or Sr/Ca ratios. The relatively large gaps in the 87Sr/86Sr curve produced here by using marine barite (Fig. 2) result from very low core recovery at Site 305 below about the upper Santonian (80 Ma), which accounts for the lower density of data in the Lower Cretaceous to the lower part of the Upper Cretaceous. Similarly, core recovery for Site 766 was very low between ca.125 and 100 Ma, which accounts for the paucity of data during this interval.

CONCLUSIONS

Marine barite is an accurate recorder of Cretaceous seawater 87Sr/86Sr and provides a much higher age resolution than published biostratigraphic zonations. The ratios follow the trend of the previously established seawater Sr isotope curve and are generally compatible with the ranges of biostratigraphic ages provided for the corresponding samples. This result has important implications, given that the Sr isotope ratios of a large fraction of Cretaceous clay-rich carbonate sedimentary deposits have been altered diagenetically and thus cannot be used for stratigraphy and correlation. The results of this study have extended the geologic time range that could be accurately dated by using 87Sr/86Sr from marine barite to almost 140 Ma and refined the stratigraphy for two previously poorly dated cores.

ACKNOWLEDGMENTS

We thank the Ocean Drilling Program (ODP) core repositories for providing sediment samples. S. Mearon thanks the Natural Science and Engineering
REFERENCES CITED


Manuscript received April 10, 2002
Revised manuscript received September 6, 2002
Manuscript accepted September 13, 2002

Printed in USA