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## Strontium and neodymium isotopic analyses of marine barite separates

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**Abstract**—Strontium and neodymium isotopic data are reported for barite samples chemically separated from Late Miocene to Pliocene sediments from the eastern equatorial Pacific. At a site within a region of very high productivity close to the equator, <sup>87</sup>Sr/<sup>86</sup>Sr ratios in the barite separates are indistinguishable from those of foraminifera and fish teeth from the same samples. However, at two sites north of the productivity maximum barite separates have slightly, but consistently lower (averaging  $62 \times 10^{-6}$ ) ratios than the coexisting phases, although values still fall within the total range of published values for the contemporaneous seawater strontium isotope curve. We examine possible causes for this offset including recrystallization of the foraminifera, fish teeth or barite, the presence of non-barite contaminants, or incorporation of older, reworked deep-sea barite; the inclusion of a small amount of hydrothermal barite in the sediments seems most consistent with our data, although there are difficulties associated with adequate production and transportation of this phase. Barite is unlikely to replace calcite as a preferred tracer of seawater strontium isotopes in carbonate-rich sediments, but may prove a useful substitute in cases where calcite is rare or strongly affected by diagenesis. In contrast to the case for strontium, neodymium isotopic ratios in the barite separates are far from expected values for contemporary seawater, and appear to be dominated by an (unobserved) eolian component with high neodymium concentration and low <sup>143</sup>Nd/<sup>144</sup>Nd. These results suggest that the true potential of barite as an indicator of paleocean neodymium isotopic ratios and REE patterns will be realized only when a more selective separation procedure is developed.

### INTRODUCTION

An ideal paleoceanographic indicator would be an authigenic phase that accurately incorporates seawater chemical characteristics and then remains inert to chemical change during burial and lithification. In addition, it should be relatively abundant in deep-sea sediments. Barite microcrystals (2–3 μm) appear to fit these criteria. They are believed to precipitate directly from seawater, they are highly insoluble in oxic sediments, suggesting they may be less affected by alteration than such commonly studied phases as calcite or apatite, and they are relatively common in deep-sea sediments (Arrhenius and Bonatti, 1965). In addition, marine barite has very high strontium concentrations, typically >1% (Church, 1979), permitting the use of very small samples for strontium isotope studies. Goldberg et al. (1969) found that barite crystals from surface sediment have strontium isotopic compositions similar to present-day seawater, and we recently reported results illustrating a general correspondence between seawater strontium isotope ratios determined from marine barite and those obtained from carbonates for the past 30 Ma (Paytan et al., 1993). Guichard et al. (1979) also reported relatively high neodymium concentrations (5–100 ppm) for marine barite which could make it useful for neodymium isotope studies. Finally, barite may also provide a record of ancient seawater sulfur (Goldberg et al., 1969) and oxygen (Cecile et al., 1983) isotope compositions.

The mechanism of barite microcrystal formation in the open ocean is poorly understood. Seawater is undersaturated with respect to barite, and an increasing body of evidence suggests that the crystals precipitate in the upper portion of the water column within microenvironments of decaying or-

ganic matter (Chow and Goldberg, 1960; Dehairs et al., 1980, 1990; Bishop, 1988). This is consistent with the observation that the abundance of barite crystals in the sediments appears to correlate roughly with surface productivity (Church, 1979; Bishop, 1988). Some crystals may also precipitate within the sediment, because pore fluids have been shown to be saturated with respect to barite (Church and Wolgemuth, 1972; Von Breymann et al., 1992). Ocean surface waters have neodymium isotope values distinct from bottomwaters (Piepgras et al., 1979; Piepgras and Wasserburg, 1980), therefore, accurate measurements of the neodymium isotopic composition of sedimentary barite may resolve the site of its formation.

In order to further evaluate the paleoceanographic potential of deep-sea barite, we compared the strontium isotopic compositions of separated barite crystals with those of coexisting foraminifera, as well as some fish teeth and pore fluids from sections of several Deep Sea Drilling Project (DSDP) cores spanning the age range 2.5 to 9 million years. The reason for concentrating on this particular age is that Hodell et al. (1989) have reported an abrupt change in seawater <sup>87</sup>Sr/<sup>86</sup>Sr over this interval based on measurements made on foraminifera from DSDP sites distributed around the globe. They found relatively constant <sup>87</sup>Sr/<sup>86</sup>Sr values from 8 to 5.5 Ma, a rapid increase of 0.0001 between 5.5 and 4.5 Ma, and approximately constant values again from 4.5 to 2.5 Ma. Because data from different laboratories for foraminifera from several different cores agree closely over this age span, the measured values must be an accurate representation of seawater <sup>87</sup>Sr/<sup>86</sup>Sr. The strontium isotopic composition of marine barite should mimic that of the other sedimentary components through this interval if it is indeed a reliable monitor of seawater isotopic composition. We also measured neodymium

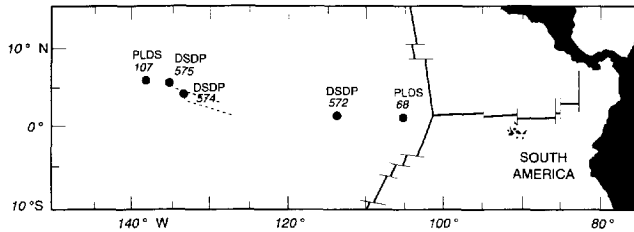


FIG. 1. Map of the eastern equatorial Pacific illustrating the locations of DSDP and PLDS sites referred to in the text. Dashed lines show back-tracking for the past 9 Ma for Sites 574 and 575 from Weinreich and Theyer (1985).

concentrations and isotopic compositions for several of the barite and fish teeth samples. If barites record deep water chemistry, their isotopic ratios should agree with values from fish teeth as well as published data for nearby manganese nodules.

Miocene/Pliocene samples were analyzed from DSDP Sites 572, 574, and 575 (Fig. 1, Table 1) in the eastern equatorial Pacific. These sites were chosen because they are located within a region of high barite concentration previously identified by Church (1979). Also, none has experienced significant sulfate reduction (Table 1), a process that may affect barite stability. In addition, these sites span a range of latitudes, from the modern equatorial productivity maximum to slightly lower productivity conditions at 5°N (Table 1, also see Fig. 1 for backtracked locations of DSDP sites), and thus, probably also experienced a range of biogenic barite supply rates. Samples were dated using excellent biochronologic control for all three sites (Barron et al., 1985), magnetostratigraphic control for Sites 574 and 575 (Weinreich and Theyer, 1985), and the Berggren et al. (1985) timescale. Although we compare our data with the record from Hodell et al. (1989), an important aspect of this paper is that we mea-

sured different phases from the same sediment sample, thereby minimizing potential errors introduced by absolute age estimates. Additional isotopic measurements were made on barite and fish teeth separated from two box cores collected in the same region during the Scripps Institution of Oceanography Pleiades (PLDS) Expedition in 1976 (Fig. 1, Table 1), as well as a barite sample collected from a hydrothermal chimney in the Marianas Trough and an Archean stratiform barite from Karnataka, India (Hoering, 1988) (Table 1).

Our earlier paper (Paytan et al., 1993) demonstrated that barite strontium isotope ratios generally fall within the range of published values for biogenic calcite over the past 30 Ma. In the present study we discovered that there are small but consistent and systematic differences in strontium isotopic compositions between barite and other coexisting sedimentary phases. In addition, we found that the barite separation techniques we employ, which are similar to those described by others (e.g., Church, 1979; Guichard et al., 1979), apparently do not adequately separate barite from detrital phases that can dominate the neodymium isotopic composition of the resulting sample. We will discuss the evidence for, and the possible causes of, these apparent problems and evaluate their effect on the potential use of marine barite as a paleoceanographic monitor.

## METHODS

Samples with dry weights ranging from ~4 to as much as 200 g (for box core samples) were disaggregated in water using ultrasonic agitation. The sediment was then sieved into three size fractions: <38  $\mu\text{m}$ , 38–150  $\mu\text{m}$ , and >150  $\mu\text{m}$ . Foraminifera and fish teeth were handpicked from the largest size fraction and examined for signs of recrystallization using Scanning Electron Microscopy (SEM). One or two clean specimens were then dissolved in 1.8N HCl and strontium was separated for mass spectrometry using standard cation exchange procedures.

Barite crystals were isolated from the smallest size fraction using a series of chemical leaches modified from Church (1979). First,

Table 1. - Site information for DSDP Leg 85 and PLDS.

Site	Modern Location	Water Depth (m)	Depth in Core (m)	Sedimentation Rate (m/Ma)	[SO <sub>4</sub> ] <sup>3</sup> (mM)	Lithology	Modern Productivity <sup>4</sup> (gC/m <sup>2</sup> /y)
<b>Miocene/Pliocene Sediments from DSDP Leg 85</b>							
572	1.26°N 113.50°W <sup>1</sup>	3893 <sup>1</sup>	50 - 210 <sup>1</sup>	15 - 50 ave. = 28 <sup>1</sup>	24 - 28.2	nanno-diatom ooze <sup>1</sup>	90 - 125
574	4.12°N 133.19°W <sup>1</sup>	4561 <sup>1</sup>	10 - 75 <sup>1</sup>	5 - 16 ave. = 8 <sup>1</sup>	26 - 28.7	siliceous nanno-ooze <sup>1</sup>	40 - 60
575	5.1°N 135.02°W <sup>1</sup>	4536 <sup>1</sup>	5 - 12 <sup>1</sup>	2.2 - 4.4 ave. = 2.6 <sup>1</sup>	28 - 28.2	clayey siliceous calc. ooze <sup>1</sup>	30 - 40
<b>Recent Sediments from PLDS box cores</b>							
68	1.01°N 105.29°W <sup>2</sup>	3650 <sup>2</sup>	0 - 0.04 <sup>2</sup>	24 <sup>2</sup>	NA	72% CaCO <sub>3</sub> <sup>2</sup>	125 - 180
107	6.09°N 138.16°W <sup>2</sup>	4849 <sup>2</sup>	0.04 - 0.1 <sup>2</sup>	7 <sup>2</sup>	NA	35% CaCO <sub>3</sub> <sup>2</sup>	30 - 40

<sup>1</sup> From Mayer and Theyer et al. (1985).

<sup>2</sup> From Berger and Killingsley (1982).

<sup>3</sup> From Stout (1985).

<sup>4</sup> Modern synthetic primary production for each site from Berger et al. (1988).

carbonate was dissolved in 1.6 N HNO<sub>3</sub>. Organic components were partially removed using warm Chlorox. Fe-Mn oxides were leached in 0.02 M hydroxylamine with 25% (by volume) acetic acid. Silicates were dissolved in a series of 5 N then 9 N HF leaches, followed by heating in 0.1 N HNO<sub>3</sub> saturated with aluminum chloride to remove fluorides. Finally, each sample was filtered through a 0.45 μm filter and ashed at 600°C for 1 h to remove remaining organic material. This varies slightly from the procedure employed by Paytan et al. (1993) in the use of nitric rather than acetic acid to dissolve the carbonate, the normality of the HF leaches and a 600°C rather than 700°C ashing temperature. The processing method described by Paytan et al. (1993) is being used for ongoing work. Residue from processing was analyzed by X-ray Diffraction (XRD) and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS). The SEM surveys were not systematic, but involved scanning several thousand crystals from each sample at a range of magnifications. The primary contaminants observed were fine needles of anatase and rutile (typically a few microns in size), which, like barite, are resistant to the chemical leaching process employed. They also have similar physical properties to barite and are therefore very difficult to separate. Guichard et al. (1979) reported similar contaminants in the marine barite separates they used for rare earth analyses. Total barite yields in our work ranged from approximately 0.01 to 1.8 wt% of the unprocessed samples, varying with location and dilution by carbonate.

Three different techniques were employed to dissolve the barite for isotopic analysis. Initially, the samples were placed in a pressure bomb with 1.8 N HCl and heated to 95°C. However, dissolution was often incomplete and barite crystals appeared to reprecipitate when the pressure bombs were opened. Several neodymium analyses are reported for samples dissolved in this manner (Table 3). Samples analyzed for <sup>87</sup>Sr/<sup>86</sup>Sr, as well as several analyzed for <sup>143</sup>Nd/<sup>144</sup>Nd, were dissolved using cation exchange resin following Church (1979). Samples were heated to 95°C for several days in a mixture of cation resin and double-distilled water. The cations were then leached from the resin with 4.5 N HCl and separated on a cation exchange column using standard procedures. Procedural blanks for this processing technique were approximately 15 pg strontium and 13 pg neodymium. This method is not uniquely selective for barite and probably dissolves or partially dissolves any other phases in the residue as well. Eventually we employed a more barite-selective dissolution technique using Na<sub>2</sub>CO<sub>3</sub>, as described by Breit et al. (1985). Barite was converted to a barium (strontium) carbonate by heating a 1:10 mixture of barite and sodium carbonate in 2 mL double-distilled water at 95°C overnight. Samples were then centrifuged, decanted, and the solids rinsed several times with double-distilled water. The BaCO<sub>3</sub> was then dissolved in 1.8 N HCl, followed by cation exchange to separate the elements of interest. Although even ultrapure Na<sub>2</sub>CO<sub>3</sub> has relatively high strontium concentrations (400 ppb for the batch used in this work), strontium introduced during dissolution is minor compared to that from the barite and contributes <1 ppm on <sup>87</sup>Sr/<sup>86</sup>Sr (see Breit et al., 1985, for discussion). In contrast, neodymium from Na<sub>2</sub>CO<sub>3</sub> can be significant relative to that from the barite. Two different batches analyzed in this study contained 164 (ultrapure) and 2.5 ppb neodymium (reagent grade). For the latter concentration, the maximum neodymium blank contributed only 0.6% of the total neodymium. The small amounts of undissolved residue sometimes remaining after dissolution by these methods were very difficult to recover and thus were not weighed. Therefore, all concentration data in Table 3 are maximum values.

Separation of barite from the PLDS 107 box core surface samples for neodymium analyses followed the general procedure described above, but varied in the details of the HF treatment and dissolution method employed (Table 3). Aliquots 1 and 2 were leached in 5 N HF followed by 9 N HF and dissolved in a pressure bomb. Aliquots 3 and 4a were also leached in 5 N and 9 N HF, but the separated barite was dissolved using cation resin. Aliquots 4b, 5, 6a, and 6b received multiple HF treatments and were then dissolved using cation resin (4b, 5, 6a) or reagent grade sodium carbonate (6b). In order to determine if neodymium was incorporated into the barite crystals during processing, an isotopically enriched neodymium spike was added to two samples (3 and 4a) at various stages of the leaching treatment. No neodymium uptake

was detected. No concentration data are available for these two samples because of this procedure.

For comparison with barites that did not require chemical separation, two additional samples were analyzed: barite from a hydrothermal chimney in the Mariana Trough and an Archean stratiform barite from Karnataka, India (Hoering, 1988). In both cases the samples separated for analysis were large, pure crystals or crystal fragments.

Original pore fluid samples from DSDP Leg 85 are no longer available, therefore, strontium pore fluid data reported in Table 2 represent samples that were squeezed from the cores following six years of cold storage at the DSDP repository. Because strontium concentrations and isotopes were the only properties measured, no corrections could be made for evaporation or crystallization. However, the fact that measured strontium concentrations plot on the strontium concentration profiles of Stout (1985) argues against significant alteration of the pore fluid during storage.

All analyses were performed on a VG-54 mass spectrometer with a six sample turret. Most turrets included only two to three samples from this study, and standards were analyzed every 10–15 samples. There was no specific order to the analyses, although in general, barite, foraminifera, and fish teeth from one sample were analyzed in sequence, and most of Site 574 analyses were run first, followed by Site 572 and finally Site 575. The fact that low barite <sup>87</sup>Sr/<sup>86</sup>Sr values were measured throughout the entire data collection period (1991–1993) argues against machine drift as a source of the anomalous low ratios. Strontium samples were loaded on single W filaments and 300 ratios were collected at 1.5 V. Neodymium samples were loaded on single rhenium filaments and analyzed as NdO<sup>+</sup> at 0.7 V for 300 ratios. Reproducibility of nine replicate strontium analyses ranged from 9–43 × 10<sup>-6</sup>, and averaged 18 × 10<sup>-6</sup>. This agrees well with a total variability of ±22 × 10<sup>-6</sup> for all NBS-987 standards analyzed at Scripps which we state as our minimum uncertainty.

## RESULTS

Strontium concentrations and isotopic data are given in Table 2, and the isotopic compositions are plotted vs. age for the three DSDP sites in Figure 2. Neodymium concentrations and isotopic ratios are given in Table 3.

Figure 2 shows that at Site 572, the measured <sup>87</sup>Sr/<sup>86</sup>Sr values for coexisting barite, foraminifera and fish teeth all agree within the analytical uncertainty at each depth in the core and together closely follow the line segments approximating the three-point running mean data of Hodell et al. (1989). However, the situation is quite different at the other two DSDP sites. For these, <sup>87</sup>Sr/<sup>86</sup>Sr values for barite fall significantly and consistently below the values for coexisting phases and pore fluids. As at Site 572, the results for foraminifera and fish teeth closely track the average values from Hodell et al. (1989). Note that in view of these data it may be significant that at Site 572 <sup>87</sup>Sr/<sup>86</sup>Sr values in barite are consistently lower than those for foraminifera and fish teeth, albeit within analytical uncertainty. It should be pointed out that the discrepancies at Sites 574 and 575 are not large—the largest difference between a barite and coexisting foraminifera sample is 1 × 10<sup>-4</sup>—and that the total range of the data used to construct the Hodell et al. (1989) running mean would encompass most of our data, including the barite. However, the differences are systematic and well outside our analytical uncertainty, and must, therefore, be a real effect. The error in age estimates generated by this difference will, of course, vary with the steepness of the strontium isotope curve; for the interval investigated it could be as much as 2.5 Ma.

**Table 2.** - Sr isotope data for barite separates and pore waters, and isotope and concentration data for foraminifera and fish teeth.

Site (hole- core- section, interval)	Age <sup>1</sup> (Ma)	Barite		Foraminifera		Fish Teeth		Pore fluid <sup>5</sup> $^{87}\text{Sr}/^{86}\text{Sr}(2\sigma)^2$
		$^{87}\text{Sr}/^{86}\text{Sr}(2\sigma)^2$		$^{87}\text{Sr}/^{86}\text{Sr}(2\sigma)^2$	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}(2\sigma)^2$	Sr (ppm)	
<b>Leg 85 Site 572</b>								
C-6-4, 30-32 cm	2.5	0.709057 (22)		0.709072 (22)	1097	0.709064 (22)		
A-7-2, 30-132 cm	3.6	0.709043 (22)		0.709067 (22)	1179	0.709058 (22)	1502	
A-7-2, 30-132 cm	3.6	0.709046 (22) <sup>3</sup>						
A-10-2, 18-20 cm	4.3	0.709045 (22)		0.709066 (22)	971	0.709061 (22)	1733	
C-13-3,140-142 cm	4.9	0.709005 (22)		0.709010 (22)	998	0.709031 (22)	2570	
A-14-4, 46-48 cm	5.1	0.708995 (22)		0.709013 (22)	1128	0.709026 (22)	2116	
C-16-3, 18-20 cm	5.4	0.708978 (22) <sup>3</sup>		0.708987 (22)	914			
D-5-5, 68-70 cm	6.3	0.708945 (22)		0.708949 (22)	1039			
D-7-5, 92-94 cm	7.0	0.708942 (22)		0.708945 (22)	1180			
<b>Leg 85 Site 574</b>								
2-5, 110-112 cm	2.5	0.708996 (22)		0.709086 (22)		0.709084 (22)	1216	
2-5, 110-112 cm	2.5	0.709006 (24)						0.709059 (22)
2-5, 112-118 cm	2.5	0.709096 (22)						
2-5, 112-118 cm	2.5	0.709082 (22) <sup>3</sup>						
3-1, 84-86 cm	3.1	0.709030 (22)		0.709062 (22)				
4-1, 48-50 cm	3.8	0.708973 (22)		0.709040 (24)		0.709061 (22)	1932	
4-1, 48-50 cm	3.8	0.708959 (22)						
4-1, 48-50 cm	3.8	0.708956 (28) <sup>3</sup>						
4-1, 132-138 cm	3.8							0.709037 (22)
4-1, 60-62 cm	3.8	0.708952 (25) <sup>4</sup>						
4-5, 70-72 cm	4.4	0.708968 (22)		0.709069 (30)				
4-5, 24-26 cm	4.4	0.708985 (22) <sup>4</sup>						
5-1, 38-40 cm	4.8	0.708971 (22)		0.709043 (22)				
5-5, 120-122 cm	5.4	0.708931 (22)		0.708977 (22)				
6-3, 10-12 cm	6.0	0.708873 (25)		0.708970 (22)				
6-3, 10-12 cm	6.0	0.708917 (22)						
6-3, 34-36 cm	6.0	0.708916 (22) <sup>4</sup>						
7-3, 30-32 cm	7.6	0.708928 (24)		0.708959 (38)		0.708956 (22)	1490	
7-3, 30-36 cm	7.6	0.708919 (22)						0.708947 (22)
9-5, 80-82 cm	9.0	0.708913 (22)		0.708900 (24)		0.708958 (26)		
9-5, 80-82 cm	9.0			0.708917 (32)				
<b>Leg 85 Site 575</b>								
1-4, 84-86 cm	2.5	0.709003 (22) <sup>3</sup>		0.709047 (22)	939			
2-1, 142-144 cm	5.1	0.708906 (26) <sup>3</sup>		0.709014 (23)	924			
2-4, 130-132 cm	6.0	0.708905 (22) <sup>3</sup>		0.708974 (22)	788			
<b>Marianas backarc</b>								
Hydrotherm. Chimney	Recent	0.704746 (22)						
<b>PLDS 107</b>								
4-10 cm	.017	0.709122 (22)						
4-10 cm	.017	0.709135 (22)						
4-10 cm	.017	0.709121 (22)						
4-10 cm	.017	0.709080 (26)						
4-10 cm	.017	0.709134 (22)						
4-10 cm	.017	0.709129 (24) <sup>3</sup>						
Average		0.709120						

<sup>1</sup> From Weinreich and Theyer (1985).<sup>2</sup> Standard  $^{87}\text{Sr}/^{86}\text{Sr}$  values are 0.710260 for NBS 987 and 0.709175 for seawater. All samples have been assigned a minimum uncertainty of  $\pm 0.000022$ , equivalent to the total variability of repeat standard analyses. All ratios are fractionation corrected to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ .<sup>3</sup> Barite samples dissolved using the  $\text{Na}_2\text{CO}_3$  technique.<sup>4</sup> Barite samples processed from the carbonate-rich unit nearest the original sample to determine whether  $\text{CaCO}_3$  content affected the  $^{87}\text{Sr}/^{86}\text{Sr}$  values. As the data illustrate, there was no detectable difference.<sup>5</sup> Sr concentration data are not reported for pore fluids because no evaporation correction was made. See Methods for discussion.

The neodymium data in Table 3 are for barite and fish teeth separated from selected samples at Sites 572 and 574, and two box core surface samples from PLDS 107 and 68, as well as the two pure barite samples from a modern hydrothermal chimney and an Archean stratiform deposit. For all of the DSDP and box core samples it is clear that there are large differences in isotopic composition between barite separates and coexisting fish teeth, with barite exhibiting a wide range of concentrations, but similar and consistently lower  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. Both hydrothermal and stratiform pure barite samples yielded very low neodymium concentrations.

## DISCUSSION

### Strontium Isotopes

There are several possible causes for the lower  $^{87}\text{Sr}/^{86}\text{Sr}$  values in barite separates from Sites 574 and 575 compared to foraminifera and fish teeth: (1) recrystallization or precipitation of barite within the sediment in the presence of porewater with lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios; (2) the presence in the barite separates of undissolved "contaminant" phases with lower strontium isotopic ratios; (3) the presence of a small amount of barite with lower isotopic ratios; and (4) the possibility that the barite indeed re-

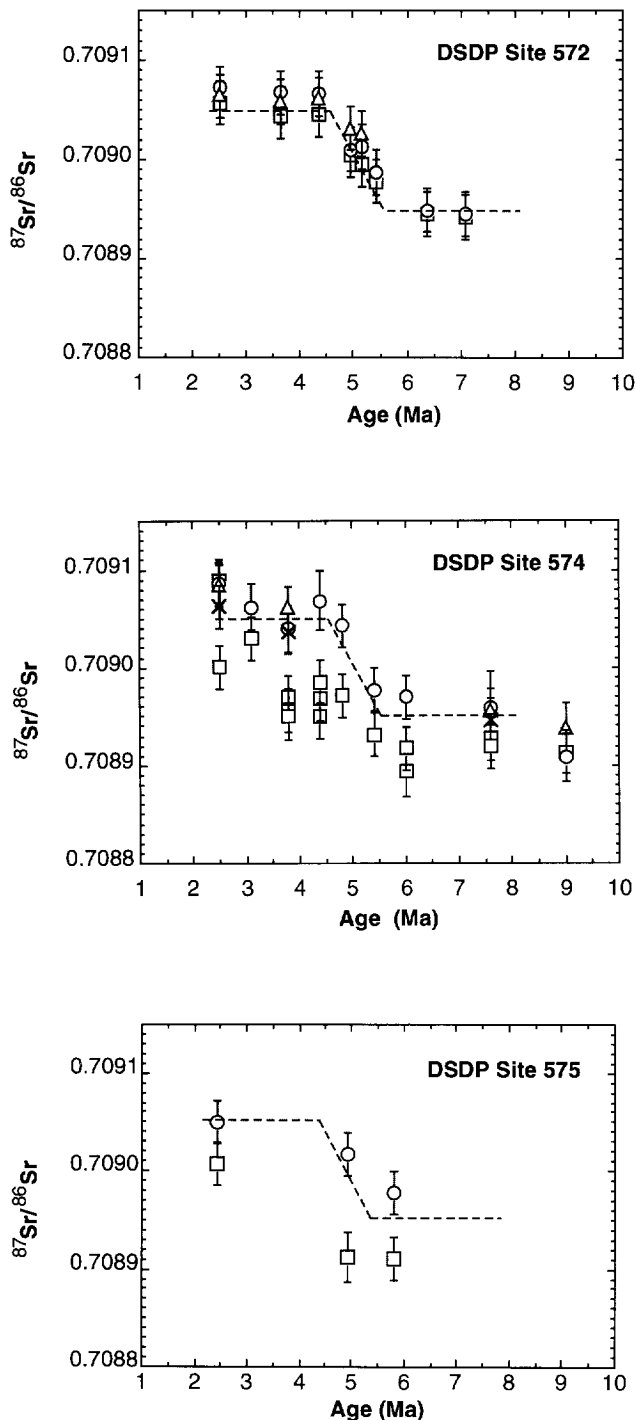


FIG. 2. Age vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  values for barite ( $\square$ ), foraminifera ( $\circ$ ), fish teeth ( $\triangle$ ), and pore-waters ( $\times$ ) from DSDP Sites 572, 574 and 575. Replicate samples of barite and foraminifera listed individually in Table 2 have been averaged and plotted as single points. Barite separates from the same sample interval that were processed differently during chemical separation or dissolution (Table 2) are not true replicates and have been plotted individually. The dashed line is an approximation of a three point running mean of globally distributed carbonate data that was taken from Hodell et al. (1989) and corrected for interlaboratory bias. The shaded region outlines the total range of carbonate data and their associated errors for samples plotted in Hodell et al. (1989, 1991). Excellent agreement is observed for all three phases analyzed at Site 572. In contrast, strontium isotopic ratios for barite separates from Sites 574 and 575 tend to be low relative to other phases, and also plot below the line approximating the three point running mean.

fects the true contemporary seawater value, while the fish teeth and foraminifera are discrepant. We consider the latter possibility to be unlikely given that our data from foraminifera and fish teeth are consistent at all three sites examined, and in addition they agree with a large body of data from the literature that includes analyses of foraminifera from localities distributed throughout the world's oceans. We consider the other possibilities in some detail in the following sections.

#### Recrystallization

During dissolution and recrystallization of biogenic carbonate, strontium is partitioned into the pore fluid, typically creating a concentration gradient between a strontium maximum at depth and lower, seawater values at the sediment/water interface. At Site 574, the strontium maximum occurs at 200–300 m in Early Miocene sediments (Stout, 1985). This is deeper than our samples and within carbonate with lower  $^{87}\text{Sr}/^{86}\text{Sr}$ . The resulting strontium concentration gradient is, thus, a potential source of strontium with an isotopic ratio lower than the ambient seawater from which the barite originally precipitated. However, three pore fluid samples from the same interval sampled for barite yield  $^{87}\text{Sr}/^{86}\text{Sr}$  values essentially identical to those preserved in foraminifera and fish teeth (Table 2, Fig. 2). As discussed previously, although these pore fluids were squeezed from stored portions of DSDP cores, the strontium concentration data suggest that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios have not been altered during storage. Because the pore fluids and barite have distinct isotopic ratios, precipitation, recrystallization, or partial recrystallization of barite in the presence of this fluid does not appear to be a likely explanation for the measured values.

#### Non-Barite contaminant

Any mineral phase that survives the extensive chemical processing of the barite separates must be highly insoluble in acids. Most minerals in deep-sea sediments meeting this criterion have an authigenic or eolian origin; examples are rutile, anatase, zircon, and sphene. Of these we have positively identified only rutile and anatase in the barite separates. Strontium concentrations for all of these minerals are quite low, ranging from ~5–150 ppm (DeWitt et al., 1984; Becker and Dietze, 1986) and their  $^{87}\text{Sr}/^{86}\text{Sr}$  values should be equal to, or greater than, seawater values.

Nakai et al. (1993) recently identified the South American arc system as the source of eolian material in the east Pacific south of the Intertropical Convergence Zone (ITCZ), where all of our sites would have been located during the time interval of interest (Fig. 1; Hovan, 1995). Strontium concentrations of the arc-derived eolian component range from 120–280 ppm, with  $^{87}\text{Sr}/^{86}\text{Sr} \sim .707$ . Thus at a minimum, bulk material with these characteristics would have to constitute over half of the sample to produce the average offset observed at Sites 574 and 575. Based on SEM observations this is clearly not the case. Furthermore, we find essentially the same results for barite dissolved using all three dissolution techniques (Table 2), despite the fact that dissolution of silicates and oxides should be minimized using the sodium carbonate method (Breit et al., 1985). Thus, although it is conceivable

**Table 3.** - Nd isotope and concentration data for barite separates and fish teeth .

Sample	Age	Barite			Fish Teeth		
		$^{143}\text{Nd}/^{144}\text{Nd}$ ( $2\sigma$ ) <sup>1</sup>	$\epsilon_{\text{Nd}}$ ( $2\sigma$ ) <sup>2</sup>	Nd (ppm)	$^{143}\text{Nd}/^{144}\text{Nd}$ ( $2\sigma$ ) <sup>1</sup>	$\epsilon_{\text{Nd}}$ ( $2\sigma$ ) <sup>2</sup>	Nd (ppm)
<b>PLDS 107</b>							
4-10 cm (1a)	Recent	0.512062 (14)*	-11.2 (.27)	361	0.512428 (14)	-4.1 (.27)	436
4-10 cm (1b)	Recent	0.512036 (14)*	-11.7 (.27)	286			
4-10 cm (1c)	Recent	0.512051 (14)*	-11.4 (.27)	303			
4-10 cm (2)	Recent	0.512050 (14)*	-11.5 (.27)	377			
4-10 cm (3)	Recent	0.512062 (14)*	-11.2 (.27)	NA			
4-10 cm (4a)	Recent	0.512063 (14)*	-11.2 (.27)	NA			
4-10 cm (4b)	Recent	0.512064 (14)*	-11.2 (.27)	100			
4-10 cm (5)	Recent	0.512047 (14)*	-11.5 (.27)	35			
4-10 cm (6a)	Recent	0.512036 (16)*	-11.8 (.31)	4			
4-10 cm (6b)	Recent	0.512101 (17) <sup>§</sup>	-10.5 (.33)	6			
<b>PLDS 68</b>							
0-4 cm	Recent	0.512294 (14)*	-6.7 (.27)	4	0.512468 (14)	-3.3 (.27)	691
<b>Leg 85, Site 572</b>							
A-7-2,130-132 cm	3.6 Ma <sup>3</sup>	0.512173 (14) <sup>§</sup>	-9.1 (.27)	7	0.512496 (14)	-2.8 (.27)	2103
<b>Leg 85, Site 574</b>							
2-5, 110-112 cm	2.5 Ma <sup>3</sup>	0.512055 (14)*	-11.4 (.27)	24	0.512466 (14)	-3.3 (.27)	946
4-1, 48-50 cm	3.8 Ma <sup>3</sup>				0.512460 (14)	-3.5 (.27)	1649
4-5, 70-72 cm	4.4 Ma <sup>3</sup>	0.512123 (18) <sup>#</sup>	-10.0 (.35)	10			
<b>Marianas Backarc</b>							
Hydrotherm. Chim.	Recent	0.513052 (16) <sup>#</sup>	+8.1 (.31)	1.5			
Hydrotherm. Chim.	Recent	0.513045 (23) <sup>#</sup>	+7.9 (.45)	2			
<b>S. India</b>							
Stratiform	Archean	0.509900 (14) <sup>#</sup>	-53.4 (.27)	0.2			

<sup>1</sup>  $^{143}\text{Nd}/^{144}\text{Nd}$  value for the La Jolla standard is 0.511859. All samples have been assigned a minimum uncertainty of  $\pm 0.000014$ , (0.27  $\epsilon_{\text{Nd}}$  units) equivalent to the total variability of repeat standard analyses. All ratios are fractionation corrected to  $^{148}\text{NdO}/^{144}\text{NdO} = 0.242436$ .

<sup>2</sup>  $\epsilon_{\text{Nd}} = [^{143}\text{Nd}/^{144}\text{Nd}_{\text{(sa)}} / ^{143}\text{Nd}/^{144}\text{Nd}_{\text{(CHUR)}} - 1] \times 10^4$ ;  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{(CHUR)}} = 0.512638$ .

<sup>3</sup> From Weinreich and Theyer (1985).

<sup>#</sup> Barite samples dissolved in a pressure bomb.

\* Barite samples dissolved using the cation resin technique.

<sup>§</sup> Barite samples dissolved using sodium carbonate.

that some unobserved trace phase is present in our barite separates and accounts for the slightly lower strontium isotopic ratios, there is no obvious candidate.

#### Reworked barite

It is possible that the separates contain barite from more than one source. Either reworked older deep-sea barite or hydrothermal barite could have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios less than the Miocene/Pliocene seawater values. The aluminum content and  $^{226}\text{Ra}/\text{Ba}$  ratios of particulate matter recovered from sediment traps in the region of our samples have been presented as evidence that barite (together with other material) is advected from the shelf to the deep ocean (Moore and Dymond; 1991). However, according to this scenario, the reworked material is only hundreds to thousands of years old. Thus, there would be no measurable difference in strontium isotopic composition between the recycled barite and that accumulating in the surface sediments. If a similar transport process occurred over the time interval represented by our samples, the reworked barite would have to be at least ten million years older than the contemporary sediments and constitute half the sample or more in order to explain our data. It is unlikely that an advected contaminant would make up such a large portion of the

sample, and difficult to pinpoint a source of abundant 10 million year old reworked barite. In addition, neither the fish teeth or foraminifera exhibit evidence of reworking.

#### Hydrothermal barite

Hydrothermal vent fluids have  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of approximately 0.703, thus, hydrothermal barite may have  $^{87}\text{Sr}/^{86}\text{Sr}$  values much lower than barite precipitated directly from seawater. Although few samples have been measured, barite recovered from hydrothermal vent chimneys in the Mariana Trough has  $^{87}\text{Sr}/^{86}\text{Sr}$  near 0.7047 (Table 2). Less than 2% of such material could account for the average offset in strontium isotopic ratios between barite and foraminifera in our samples, and even the maximum difference observed would require only 2.5%. If dispersed barite precipitating from vent fluids has higher  $^{87}\text{Sr}/^{86}\text{Sr}$  than the Mariana Trough vent-chimney barite, a larger fraction of the hydrothermal component would be required to produce the observed offset.

Hydrothermal barite would behave similarly to the water-column barite during the chemical separation process. Barite crystals have been reported from white smoker chimneys on the EPR (Haymon and Kastner, 1981; Styr et al., 1981; Haymon, 1989) and in the particulate material separated from hydrothermal plume samples collected by submersible at 11

and 21°N (McConachy and Mottl, 1988; Mottl and McConachy, 1990). However, it is a minor component of the chimneys (Haymon and Kastner, 1981) and occurs only as a trace constituent of plume particulates (McConachy and Mottl, 1988; Mottl and McConachy, 1990). Thus, current production may not be adequate to generate even the small quantities of hydrothermal barite necessary to account for the data at Sites 574 and 575.

Transport of hydrothermal barite from the East Pacific Rise (EPR) is also somewhat problematic, first, because the distance is large even for micron-sized particles, and second, because barite can dissolve in the water column (Church and Wolgemuth, 1972; Feeley et al., 1987). Unless protected by an organic coating or some other exterior protection, barite crystals would be unlikely to survive the approximately 4000 km journey from the EPR to Sites 574 and 575. Furthermore, we have observed no physical evidence (from SEM surveys) that our separates contain hydrothermal barite. Based on data from sediment traps and ALVIN samples collected in and near hydrothermal plumes along the Juan de Fuca Ridge (Feely et al., 1987, 1990; Dymond and Roth, 1988), the hydrothermal barites range in size from 2 to 200  $\mu\text{m}$ , and in general are more euhedral with a tabular morphology, in contrast to the rounded, lozenge-shaped crystals common in our barite separates (see Paytan et al., 1993, for SEM photos).

Despite these difficulties, there are some present-day details which are consistent with the presence of hydrothermal barite. In particular, the distribution of sites showing discrepancies in strontium isotope ratios between barite and foraminifera may reflect known deep ocean current flow. Craig (1990a,b) reported helium isotopes as well as temperature and salinity data defining a westward-flowing "jet" in the Eastern Pacific centered at 7.5°N. The helium data in particular confirm a hydrothermal component in this abyssal current. Based on temperature and salinity data, Talley and Johnson (1994) have recently defined this westward-flowing plume in more detail, extending to 155°W. If this feature is long-lived, it could conceivably have transported hydrothermal barite from the EPR to the vicinity of DSDP Sites 574 and 575 which were located between 2 and 5°N during the time interval of interest. Site 572 does not show the discrepancy between barite and foraminifera observed at the other two sites, and was within 2° of the equator during this period (Weinreich and Theyer, 1985). In this region there is likely to be eastward flow at the depth of the more northerly westward-flowing jet (Craig, 1990a,b). There is also a substantial decrease in primary productivity with distance from the equator and to the west along the equator identified by Berger et al. (1988; see especially Figs. 4 and 8). Synthetic primary productivity values from Berger et al. (1988) are reported for each site in Table 1. Given these variations in surface productivity, a small flux of hydrothermal barite might be overwhelmed by biologically mediated barite at Site 572, but comprise a more significant fraction of the total at Sites 574 and 575.

The general relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of barite separates and distance from the equator appears to exist for a present-day sediment sample as well. Paytan et al. (1993) showed that barite from core-top samples located within a few degrees of the equator in the eastern Pacific record modern seawater strontium isotope values (0.709175). Although this

was true for the 0–4 cm interval of PLDS 107 from 6°N, six separate individually-processed samples from the 4–10 cm interval of this same core ( $^{14}\text{C}$  dated at 17,390 y; Berger and Killingley, 1982) yield consistently lower values, averaging  $0.709120 \pm 24$  (Table 2). Similar small-scale variability occurs at Site 574, where different 2.5 Ma samples separated by only 2 cm in the core repeatedly yielded two sets of values: one equivalent to the contemporaneous foraminifera and fish teeth, and another set lower by  $88 \times 10^{-6}$  (Table 2, Fig. 2). The origin of this variability is not understood, but could be due to either temporal variations in the jets transporting hydrothermal barite, or changes in the quantity and/or strontium isotopic composition of the barite produced by hydrothermal systems at the ridge. Large, short timescale changes in the total particulate flux have been observed for an active vent system near the Juan de Fuca Ridge (Dymond and Roth, 1988) and are likely to be common at other locations along the ridge.

Like transported hydrothermal barite, any eolian contaminant that survives the barite separation procedure would be expected to have an influence on measured strontium isotopic ratios that is inversely proportional to sedimentation rate and biologically-mediated barite production. It might also be expected to show temporal variations in concentration. However, as mentioned earlier, we can identify no such phase with appropriately high Sr concentration and low  $^{87}\text{Sr}/^{86}\text{Sr}$ .

In summary, if the offset in  $^{87}\text{Sr}/^{86}\text{Sr}$  between barite separates on the one hand and foraminifera and fish teeth on the other is due to the presence of a "contaminant" phase, only hydrothermal barite appears to meet the requirements of resistance to acid dissolution, high strontium concentration and low  $^{87}\text{Sr}/^{86}\text{Sr}$ . On the other hand, transport of such material from the EPR to the site of deposition without dissolution would be difficult unless the crystals are somehow "protected." The existence of a deep westward jet at the appropriate latitude, and the correlation between the presence of the offset in strontium isotopic ratios and latitude make hydrothermal barite a plausible explanation. However, more detailed studies, particularly in modern sediments as a function of latitude and position relative to hydrothermal vents, will be required to solve this problem.

### Neodymium Isotopes

Data for the box core surface sample PLDS 107 (Table 3) are particularly instructive for understanding our neodymium results. Barite was separated from six different aliquots of homogenized sediment from this sample, and ten separate analyses were made following slightly different acid leaching and dissolution treatments as discussed in the Methods section. While neodymium isotopic compositions are very similar for all samples, concentrations vary widely from 4 ppm to 377 ppm. The highest neodymium concentration values were measured in barite separates given only one 5N–9N HF treatment, and subsequently dissolved in a pressure bomb. For samples given additional HF treatments and dissolved using cation resin, measured concentrations are substantially lower. But neodymium isotopic ratios are essentially the same ( $\epsilon_{\text{Nd}} = -11.3 \pm 0.8$ ) and much lower than the value measured for a fish tooth from the same sample ( $\epsilon_{\text{Nd}} = -4.1$ ). The fish

tooth value agrees well with a measurement reported by Elderfield et al. (1981) for a manganese nodule from a nearby locality ( $\epsilon_{Nd} = -4.2$ , corrected for interlaboratory bias). There appears to be little difference in the measured data for samples dissolved using the cation exchange or sodium carbonate techniques. These data suggest that there is a contaminating phase or phases in our barite separates with a high neodymium concentration and  $\epsilon_{Nd} \sim -11.3$ . If this is true, the actual neodymium content of the pure barite is much less than 4 ppm.

As discussed earlier, the only contaminants we have observed in the barite separates are rutile and anatase. Although few data are available, neodymium concentrations are likely to be in the range of several hundred ppm for rutile (Becker and Dietze; 1986) and are probably similar for anatase. This is much too low to account for the high values measured in PLDS 107-1 and 107-2 (Table 3). Concentrations of at least several thousand ppm would be required, based on the small amounts of rutile and anatase actually observed. The neodymium concentrations measured by Nakai et al. (1993) for the total eolian fraction throughout the north and central Pacific are, of course, much lower, ranging from 10–30 ppm. However, individual accessory minerals commonly associated with rutile in eolian sediments do have very high neodymium concentrations, e.g., sphene (thousands of ppm up to 2%, Lyakhovich, 1962; Fleischer and Altschuler, 1969) and zircon (up to at least 5000 ppm, Lyakhovich, 1962). In terms of chemical resistance during the barite separation process and appropriate neodymium content, no other common minerals are consistent with the observations.

The eolian particulate concentration in PLDS 107 sediments should be quite high because there is a maximum in the eolian flux at approximately 5°N (Hovan, 1992, 1995), and also because surface productivity is moderate at this latitude. Rutile is readily apparent on the XRD trace of separated barite from this site, suggesting it constitutes at least 5% of the analyzed sample. However, neither zircon or sphene XRD peaks were observed, nor were individual crystals of these minerals found during SEM surveys, indicating that, if present, they constitute a small fraction of the sample.

Nakai et al. (1993) reported neodymium isotopic compositions of Pacific eolian dust, but did not analyze any samples from the immediate vicinity of our sites. At locations further north, where the dust is derived from the Asian continent, they measured  $\epsilon_{Nd}$  values of approximately  $-10$ , slightly more radiogenic than our proposed contaminant in PLDS 107, Site 572 and Site 574 samples. However, the location of these sites relative to the ITCZ suggests that the primary eolian source should be from the Americas to the east. This material should have  $\epsilon_{Nd} = -5$  (Nakai et al., 1993), similar to the value we measured at PLDS 68, but again slightly more radiogenic. Therefore, the  $\epsilon_{Nd}$  values of our barite separates are consistent with those of some potential eolian contaminants in the Pacific, although not necessarily with those of the expected source material of specific locations.

These data suggest that the relatively high REE concentrations reported for deep-sea barite by Guichard et al. (1979) may also be due to a continental contaminant. These authors analyzed chemically separated barite by neutron activation.

They noted up to 10% rutile and anatase in their barite separates; however, they did not mention zircon or sphene.

The nonsedimentary barites analyzed in this work have low neodymium concentrations (Table 3). The hydrothermal barite from the Mariana Trough contains 1–2 ppm neodymium with  $\epsilon_{Nd}$  values similar to mid ocean ridge basalts, while the Archean stratiform barite contains only 0.2 ppm neodymium. Although these barites have very different origins from those separated from pelagic sediments, their low neodymium concentrations support the conclusion that the sedimentary barites also have low neodymium contents, and that the high values observed in the separates are due to a contaminating phase.

## CONCLUSIONS

The data suggest that while deep-sea barite is potentially useful as a recorder of paleo-seawater isotopic compositions, its utility may be hampered by the presence of various contaminants not easily removed using standard chemical separation techniques. Because pelagic barites have high strontium and low neodymium concentrations, the isotopic compositions of these two elements are affected differently by the presence of these contaminants. Several potential contaminating phases in continentally derived eolian material have high neodymium concentrations and low neodymium isotopic ratios relative to seawater, giving the chemically separated barite samples a “continental”  $\epsilon_{Nd}$  signature. In contrast, these phases have no effect on strontium isotopic ratios because of their low strontium contents relative to the barite itself. However, the presence of hydrothermal barite could lower observed strontium isotopic ratios, relative to seawater, with little or no effect on neodymium isotopic ratios.

Therefore, the central problem in such work is to obtain pristine marine barite separates. Chemical separation, which basically involves dissolving other phases and leaving barite as a residue, is the presently favored technique but is not selective to deep-sea barite. Because of its small crystal size and low abundance in most sediments, it is difficult to isolate barite by physical means. In regions of high productivity with high barite production, the effect of contaminants on the measured strontium isotopic ratio may be insignificant, but in regions of lower productivity the influence can be substantial.

This study only evaluated Neogene and Quaternary aged sediments. For these samples it is not clear that barite offers a significant advantage over calcite or phosphate for seawater strontium isotopic measurements where these phases are available. An important step will be to investigate considerably older sediments in which calcite has clearly undergone diagenesis. If barite resists recrystallization under these conditions, it may be a better guide to seawater compositions. However, the problem of foreign contaminants remains, regardless of age. This is especially true for neodymium; if barite is to fulfill its promise as a recorder of seawater REE patterns and neodymium isotopic compositions, a more selective procedure for obtaining pure barite separates must be devised.

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