



# Empirical partition coefficients for Sr and Ca in marine barite: Implications for reconstructing seawater Sr and Ca concentrations

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[1] A robust record of fluctuations in seawater Sr and Ca concentrations is critical for understanding the long-term global carbon cycle as it is influenced by the history and location of carbonate precipitation, chemical weathering, and hydrothermal activity. Such a record is also necessary for interpretation of paleoceanographic records (temperature, productivity) derived from carbonate sources (e.g. Sr/Ca, Mg/Ca, Li/Ca). Marine barite, an inorganic phase preserved in oxic, deep-sea sediments, may record seawater Sr and Ca concentrations. Using core top barite samples we have derived the partition coefficients for Sr ( $D_{Sr} = 2.9 \times 10^{-5}$ ), Ca ( $D_{Ca} = 1.9 \times 10^{-8}$ ), and Sr/Ca ( $D_{Sr/Ca} = 1.6 \times 10^3$ ) in barite. The natural variability of core top marine barite Sr/Ca, Sr/Ba, and Ca/Ba ratios, selected from different ocean basins, is 10.1%, 15.0%, and 16.3%, respectively. Since estimates of Cenozoic fluctuations in seawater Sr/Ca ratios are large (possibly greater than 80%) relative to the variability recorded in core tops, marine barite may be used to reconstruct seawater Sr/Ca ratios, and Sr and Ca concentrations, using empirically derived partition coefficients.

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## 1. Introduction

[2] Evidence suggests that the dramatic changes in atmospheric CO<sub>2</sub> through Earth's history may have been driven by variables in carbonate deposition, chemical weathering, and hydrothermal activity [Holland, 1978; Walker *et al.*, 1981; Raymo *et al.*, 1988; Caldeira, 1995; Stoll and Schrag, 2001]. Quantitatively determining how fluctuations in these processes influence the carbon cycle is necessary in order to interpret mechanisms of

climate change. Precise and continuous records of seawater Sr and Ca concentrations ( $[Sr]_{sw}$  and  $[Ca]_{sw}$ ), Sr/Ca ratios ( $[Sr/Ca]_{sw}$ ), and Sr isotopic composition ( $[^{87}Sr/^{86}Sr]_{sw}$ ), may be able to constrain relative changes in the above processes. The  $[Sr]_{sw}$ ,  $[Ca]_{sw}$ , and  $[^{87}Sr/^{86}Sr]_{sw}$  change in response to the relative rates of input and removal, as well as the chemical signature of Sr and Ca sources and sinks (weathering of carbonate and silicate rocks, hydrothermal activity, sedimentation of carbonates and sulfates) [Richter *et al.*, 1992;



*Elderfield et al.*, 2000; *Graham et al.*, 1982; *Palmer and Elderfield*, 1985; *Stoll and Schrag*, 1998, 2001]. Accordingly, a reliable record of seawater Sr and Ca concentrations, along with Sr isotopic composition, and other paleoceanographic data (sea level, spreading rates), may be able to constrain the relative influence of these various processes on atmospheric CO<sub>2</sub> and better define the geochemical cycling of these elements.

[3] Although robust records of Cenozoic [<sup>87</sup>Sr/<sup>86</sup>Sr]<sub>SW</sub> exist [*Burke et al.*, 1982; *Palmer and Elderfield*, 1985; *Hess et al.*, 1986; *McArthur et al.*, 2001], and attempts have been made to reconstruct [Sr/Ca]<sub>SW</sub> using marine carbonates [*Graham et al.*, 1982; *Delaney et al.*, 1985; *Stoll and Schrag*, 2001; *Lear et al.*, 2003], no reliable record of [Sr]<sub>SW</sub> and [Ca]<sub>SW</sub> has been developed, in part due to the complex effects of other variables (e.g., temperature, growth rate, diagenesis) on the Sr/Ca ratio in carbonates.

[4] Marine barite, shown in Figure 1a, is not subject to the same complications as carbonate proxies, because it precipitates inorganically in microenvironments in which saturation with respect to barite is achieved by release of Ba associated with the decay of organic matter (R. Ganeshram et al., An experimental investigation of barite formation in seawater, manuscript submitted to *Geochimica et Cosmochimica Acta*, 2003, hereinafter referred to as Ganeshram et al., submitted manuscript, 2003). Approximately 30% of barite flux is preserved in marine sediments [*Dymond et al.*, 1992; *Paytan and Kastner*, 1996], and since barite crystals behave as a closed system, barite is not prone to diagenetic alteration after burial in oxic conditions [*Paytan et al.*, 1993, 1996a, 1996b, 1998]. The fact that barite precipitates in the water column, combined with its ubiquity and preservation in deep-sea sediments (0.2–2% wt, CaCO<sub>3</sub> free) [*Bostrom et al.*, 1973], suggests that barite may be a reliable monitor of seawater chemistry.

[5] Indeed, experimental data indicate that complete solid-solution exists between BaSO<sub>4</sub> and SrSO<sub>4</sub> [*Bostrom et al.*, 1967; *Hanor*, 1968, 1969; *Palmer and Elderfield*, 1985]. Raman spectral data

also suggest that both Sr and Ca substitute for Ba in the marine barite structure [*Averyt et al.*, 2001]. If the environmental conditions and mechanism of barite precipitation have not changed significantly through time, the Sr and Ca content of barite separated from deep-sea sediments may be used to reconstruct [Sr]<sub>SW</sub> and [Ca]<sub>SW</sub>. Here we use a core top calibration to derive empirical partition coefficients for Sr and Ca in marine barite, and show that [Sr]<sub>SW</sub>, [Ca]<sub>SW</sub>, and seawater Sr/Ca ratio curves may be developed using marine barite.

## 2. Methodology

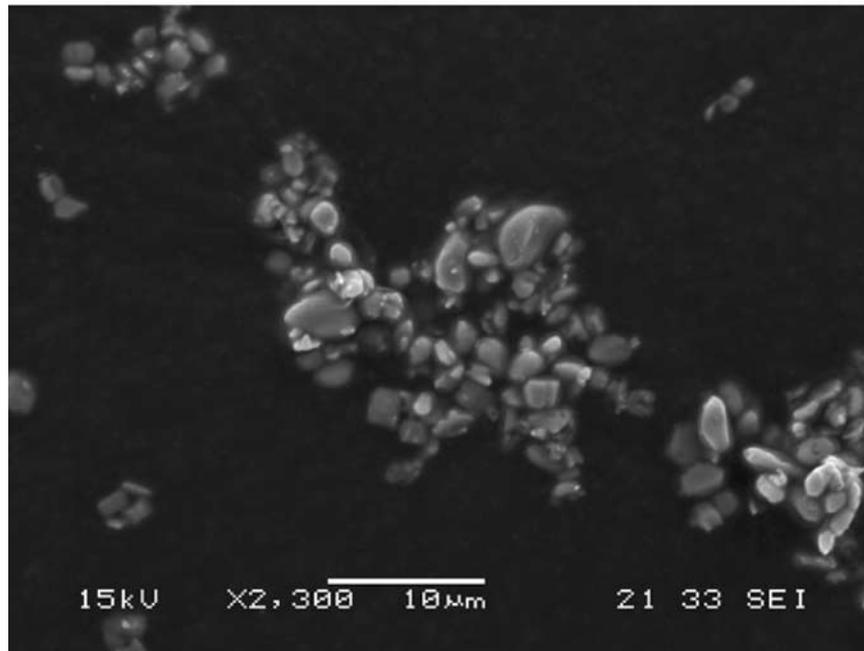
[6] Analyses of the Sr/Ba, Ca/Ba, and Sr/Ca content of marine barite separated from modern sediments from a wide range of depositional environments will establish the natural variability in these elemental ratios among samples. Since the residence times of Sr and Ca in the ocean are greater than the mixing time of the ocean, the Sr and Ca concentrations of seawater (87 μM and 10 mM, respectively) should be practically homogenous. Provided that Sr and Ca are incorporated into marine barite in proportion to their respective concentrations in seawater, the Sr and Ca content of marine barite should not vary significantly among ocean basins or among samples within each basin. Based on the Sr/Ba, Ca/Ba, and Sr/Ca ratios in barite from core top sediments, empirical partition coefficients for Sr and Ca in natural marine barite may be derived. Assuming that the mechanisms controlling the partitioning of Sr and Ca into marine barite have not varied through time, empirical partition coefficients will allow for calculation of ancient seawater Sr and Ca concentrations from down core [Sr/Ba]<sub>barite</sub> and [Ca/Ba]<sub>barite</sub> data.

### 2.1. Sample Selection

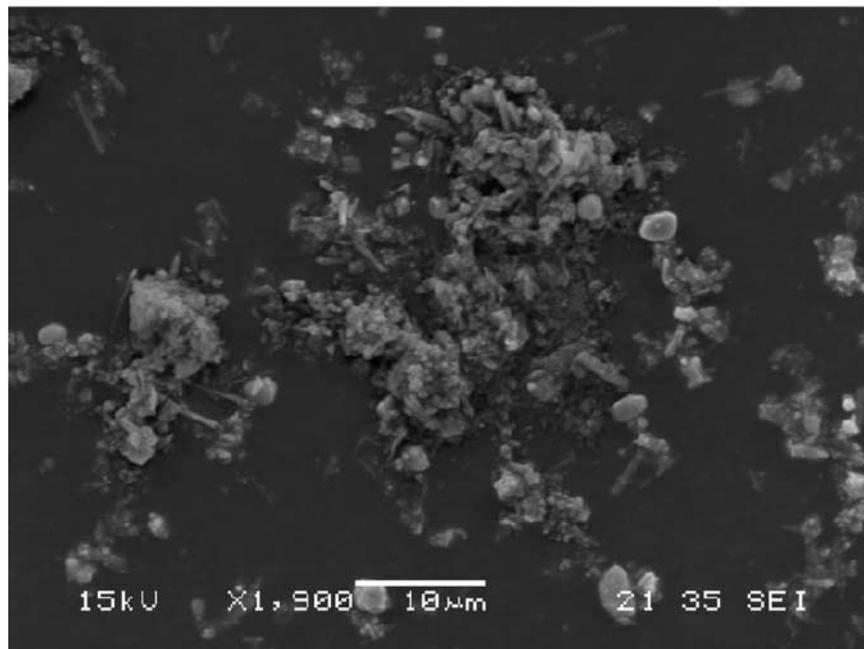
[7] Careful site selection is important in studies using marine barite. Marine barite is not preserved in sulfate reducing sediments, where barite remobilization occurs [*Bolze et al.*, 1973; *Dean and Schreiber*, 1978; *Brumsack and Gieskes*, 1983; *Breit et al.*, 1990; *Torres et al.*, 1996; *Breheret and Brumsack*, 2000; *McManus et al.*, 1998]; therefore sediment samples were only selected



a



b



**Figure 1.** SEM micrographs of marine barite separates from deep-sea sediment. Figure 1a shows a barite sample that is >80% barite (PLDS). Figure 1b is a sample that is approximately 50% barite (ERDC). Other refractory minerals are evident in the ERDC sample.

from cores in which pore water  $\text{SO}_4^{2-}$  concentrations > 19 mM. Attempts were made to include samples from all major ocean basins; however, since the marine barite accumulation rate is a

function of export production [Eagle *et al.*, 2003; Paytan *et al.*, 1996a, 1996b], sedimentary barite concentrations are greatest in high productivity waters, and measurable quantities of barite are

**Table 1a.** Core Top Barite Sample Analytical Data From the Pacific Ocean<sup>a</sup>

Sample Name	Latitude	Longitude	Depth (m)	Sr/Ca (mol/mol)	Sr/Ba (mmol/mol)	Ca/Ba (mmol/mol)	Raman Spectra Evaluation
PLDS-66BX 0–3 cm	0.943	–104.102	3496	<b>14.44</b>	–	–	No Data <sup>c</sup>
PLDS-66BX 5–10 cm	0.943	–104.102	3496	<b>15.16</b>	–	–	No Data <sup>c</sup>
PLDS-68BX 0–5 cm	1.028	–105.498	3650	<b>12.85</b>	–	–	No Data <sup>c</sup>
PLDS-68BX 5–10 cm	1.028	–105.498	3650	15.42	–	–	No Data <sup>c</sup>
PLDS-68BX 5–10 cm	1.028	–105.498	3650	<b>11.64<sup>b</sup></b>	<b>32.94</b>	<b>2.83</b>	Borderline
PLDS-70BX 0–5 cm	1.058	–107.215	3694	<b>15.60</b>	–	–	No Data <sup>c</sup>
PLDS-70BX 5–10cm	1.058	–107.215	3694	15.72	–	–	No Data <sup>c</sup>
PLDS-70BX 5–10 cm	1.058	–107.215	3694	<b>14.34<sup>b</sup></b>	<b>40.13</b>	<b>2.80</b>	Borderline
PLDS-72BX 0–5 cm	1.013	–109.260	3626	<b>14.82</b>	–	–	No Data <sup>c</sup>
PLDS-77BX 5–10 cm	1.060	–119.930	4366	<b>13.45</b>	<b>37.23</b>	<b>2.77</b>	Good Spectra
PLDS-77BX 10–15 cm	1.060	–119.930	4366	<b>13.71</b>	<b>36.26</b>	<b>2.65</b>	Good Spectra
PLDS-77BX 30–35 cm	1.060	–119.930	4366	<b>14.91</b>	<b>23.97</b>	<b>1.61</b>	Good Spectra
TT013-143MC 0–5 cm	8.920	–139.850	4992	0.65	<b>33.63</b>	51.77	Poor Spectra, CaF <sub>2</sub> <sup>f</sup>
TT013-104MC 5–6 cm	5.780	–140.130	4413	1.15	<b>25.34</b>	22.03	Poor Spectra, CaF <sub>2</sub> <sup>f</sup>
TT013-104MC 12–14 cm	5.780	–140.130	4413	0.75	<b>24.05</b>	32.04	Poor Spectra, CaF <sub>2</sub> <sup>f</sup>
TT013-82MC 0–5 cm	2.500	–140.920	4412	<b>14.12</b>	<b>26.41</b>	<b>1.87</b>	Good Spectra
TT013-82MC 8–9 cm	2.500	–140.920	4412	<b>14.06</b>	<b>35.13</b>	<b>2.50</b>	Good Spectra
TT013-82MC 10–12 cm	2.500	–140.920	4412	<b>15.57</b>	<b>35.73</b>	<b>2.29</b>	Good Spectra
TT013-82MC 8–12 cm	2.500	–140.920	4412	<b>15.23<sup>d</sup></b>	<b>33.84<sup>d</sup></b>	<b>2.22<sup>d</sup></b>	Good Spectra
TT013-82MC 8–12 cm	2.500	–140.920	4412	<b>14.89<sup>d</sup></b>	<b>28.91<sup>d</sup></b>	<b>1.94<sup>d</sup></b>	Good Spectra
TT013-82MC 14–16 cm	2.500	–140.920	4412	<b>13.94</b>	<b>33.61</b>	<b>2.41</b>	Good Spectra
TT013-88MC 0–5 cm	1.000	–139.750	4315	<b>12.93</b>	<b>26.14</b>	<b>2.02</b>	Borderline
TT013-88MC 3–6 cm	1.000	–139.750	4315	<b>15.79</b>	<b>32.32</b>	<b>2.05</b>	Good Spectra
TT013-88MC 3–4 cm	1.000	–139.750	4315	<b>12.83</b>	<b>24.57</b>	<b>1.91</b>	Good Spectra
TT013-88MC 16–18 cm	1.000	–139.750	4315	2.73	<b>30.91</b>	11.30	Poor Spectra, CaF <sub>2</sub> <sup>f</sup>
TT013-69MC 18–20 cm	0.100	–139.720	4301	<b>14.39<sup>c</sup></b>	<b>36.55<sup>c</sup></b>	<b>2.54<sup>c</sup></b>	Good Spectra
TT013-69MC 18–20 cm	0.100	–139.720	4301	<b>14.42<sup>c</sup></b>	<b>39.26<sup>c</sup></b>	<b>2.72<sup>c</sup></b>	Good Spectra
TT013-69MC 20–24 cm	0.100	–139.720	4301	<b>14.26<sup>d</sup></b>	<b>31.84<sup>d</sup></b>	<b>2.23<sup>d</sup></b>	Good Spectra
TT013-69MC 20–24 cm	0.100	–139.720	4301	<b>14.25<sup>d</sup></b>	<b>38.41<sup>d</sup></b>	<b>2.69<sup>d</sup></b>	Good Spectra
TT013-20MC 5–7 cm	–1.870	–139.700	4376	4.27	<b>29.27</b>	6.86	Fluorescence
TT013-20MC 16–18 cm	–1.870	–139.700	4376	<b>13.17</b>	<b>37.35</b>	<b>2.84</b>	Good Spectra

<sup>a</sup> Core Top Barite Sample Analytical Data from the Pacific Ocean and Southern Oceans (Table 1b) (name, latitude, longitude, water depth). PLDS and TT013 samples are from the equatorial Pacific, and TN057 samples are from the Southern Ocean. Sr/Ca, Sr/Ba, and Ca/Ba data in bold type are reliable data points as described in the text (adjusted according to appropriate footnotes); those in regular type contained contamination based on SEM screening or Raman spectra. All samples contained >80% barite. For some individual samples, Ca/Ba results were eliminated but Sr/Ba were not. Samples were not used if SEM screening showed significant quantities of non-barite minerals and Raman spectra were borderline or ambiguous. See *Berger and Killingsley* [1982], *DeMaster and Pope* [1994], *Eagle et al.* [2003], and references therein for age model details.

<sup>b</sup> Data from the second analysis were used because samples were treated with additional reagents (HNO<sub>3</sub>, HCl) after the first analysis.

<sup>c</sup> Data represent analysis of the same barite sample in the same ICP run. The average value was used in determining empirical partition coefficients.

<sup>d</sup> Data represent analysis of the same barite sample in different ICP runs. The average value was used in determining empirical partition coefficients.

<sup>e</sup> Samples for which no Raman data are available were completely consumed during early analyses. Ba concentrations were not determined in early stages of the work, therefore no Sr/Ba or Ca/Ba data are available.

<sup>f</sup> CaF<sub>2</sub> is suspected as the Ca contaminating phase based on fluorescing patterns in the Raman spectra (which are often indicative of *F* species), and high Ca concentrations in the analyte solution.

not easily attained from all deep-sea sediments. Further, sediments deposited along ocean margins often include high quantities of terrigenous material; this results in dilution of the relative barite signal with refractory minerals left as insoluble residue in barite separates [*Martin et al.*, 1995]. For these reasons, ideal cores for marine barite work were selected from open-ocean sites in high productivity regions where the input of terrigenous

minerals is low and the sediments remain oxic. Details of the core locations from which barite was separated are described in Tables 1 and 2.

## 2.2. Sample Analysis

[8] Marine barite was separated from deep-sea sediments using a sequential leaching procedure [*Paytan et al.*, 1996a, 1996b; *Eagle et al.*, 2003].



**Table 1b.** Core Top Barite Sample Analytical Data From Southern Ocean

Sample Name	Latitude	Longitude	Depth (m)	Sr/Ca (mol/mol)	Sr/Ba (mmol/mol)	Ca/Ba (mmol/mol)	Raman Spectra Evaluation
TN057-13MC 0–5 cm	–53.175	5.127	2851	<b>11.88</b>	<b>33.13</b>	<b>2.79</b>	Good Spectra
TN057-13MC 1–5 cm	–53.175	5.127	2851	2.42	27.69	11.45	no BaSO <sub>4</sub> peak
TN057-10MC 0–6 cm	–47.087	5.920	4398	<b>13.17</b>	<b>29.85</b>	<b>2.27</b>	Good Spectra
TN057-10MC 10–11 cm	–47.087	5.920	4398	<b>11.90</b>	<b>27.34</b>	<b>2.30</b>	Good Spectra
TN057-10MC 11–15	–47.087	5.920	4398	<b>10.89</b>	<b>30.45</b>	<b>2.80</b>	Good Spectra

The residual barite samples were screened for purity using Scanning Electron Microscopy with EDAX. Subsequently, the integrity of the sample was evaluated using a Raman spectral procedure [Averyt *et al.*, 2001]. Relative Sr and Ca concentrations were determined using Inductively Coupled Argon Plasma Spectroscopy (ICP-OES); the precision of this method is <0.7% (Sr/Ca), <0.6% (Sr/Ba), and <1.0% (Ca/Ba) [Averyt *et al.*, 2003].

### 3. Results

#### 3.1. Core Top Sample Screening

[9] For all samples analyzed, the  $[Sr/Ba]_{\text{barite}} > [Ca/Ba]_{\text{barite}}$ , despite greater seawater Ca concentrations (10 mM Ca as compared with 87  $\mu\text{M}$  Sr). Such significant concentrations of Sr in barite are not unusual and have been shown in previous studies [Hanor, 1969; Church, 1970; Dehairs *et al.*, 1980; Rushdi *et al.*, 2000]. Preferential Sr substitution, as opposed to Ca, is enhanced by the similarity in ionic size between the Sr and Ba cations and accompanying steric limitations, as

well as the isomorphic crystal structure of barite and celestite [Church, 1979].

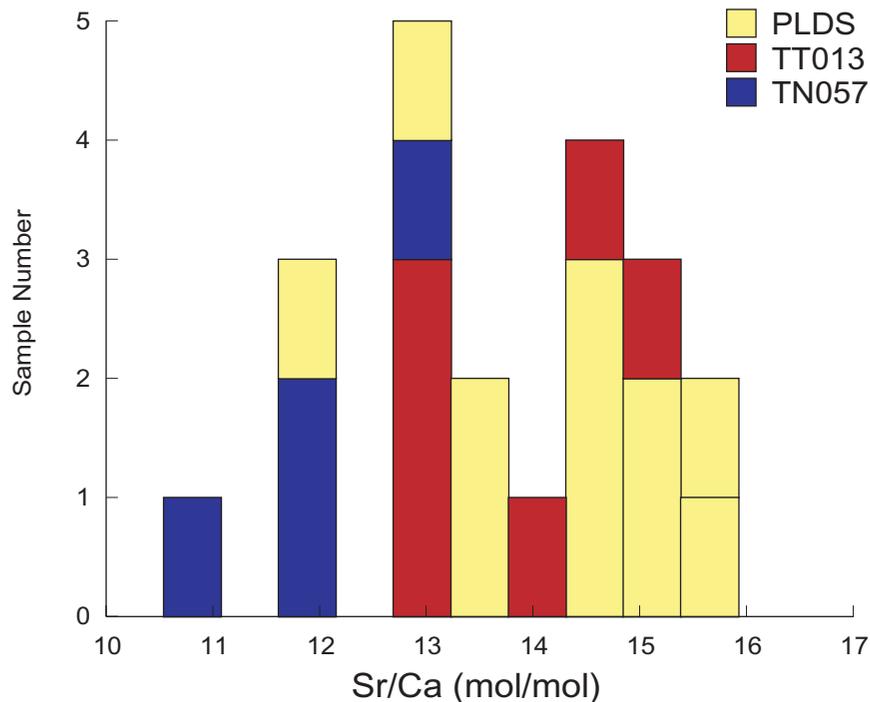
[10] To accurately determine empirical partition coefficients in natural marine barite, we must be confident that barite is the only source for Sr and Ca in the analyzed samples. However, barite sample residues obtained from deep-sea sediments typically contain rutile, zircon, monesite, and other refractory phases (Figure 1b); significant quantities of such impurities may compromise data. Accordingly, individual natural samples had to be extensively screened for the existence of other potential Sr or Ca bearing phases before including the appropriate Sr and Ca concentration data in our calculations.

[11] Marine barite separates from central equatorial Pacific Ocean (PLDS, TT013) and Southern Ocean sediments (TN057) all contain more than 80% barite (Figure 1a), thus, the Sr and Ca for these samples is predominantly from the barite phase. These samples showed consistent and reproducible results (Table 1a1b). In contrast, samples from the

**Table 2.** Core Top Barite Sample From the Indian (DODO), Atlantic (INMD), and Western Pacific Oceans (ERDC)<sup>a</sup>

Sample Name	Latitude	Longitude	Depth (m)	Sr/Ca (mol/mol)	Sr/Ba (mmol/mol)	Ca/Ba (mmol/mol)	Raman Spectra Evaluation
ERDC-125BX 5–10 cm	–0.003	160.998	3368	0.03	44.61	1281.47	No BaSO <sub>4</sub> peak
ERDC-77BX 0–15 cm	4.850	156.058	3585	0.05	38.41	713.57	No BaSO <sub>4</sub> peak
INMD-101BX 0–2 cm	6.947	–26.445	4093	41.46	0.01	0.39	Clogged ICP, Bad Data
INMD-100BX 1–10 cm	10.993	–34.173	5386	37.44	0.01	0.32	Clogged ICP, Bad Data
DODO-177G 5–10 cm	–7.167	68.783	2816	6.83	39.06	5.72	Borderline
DODO-59P 1–10 cm	–16.183	108.350	5347	1.93	38.75	20.06	Poor Spectra, CaF <sub>2</sub>
DODO-126P 6–10 cm	–8.933	55.500	3485	12.82	38.95	3.04	Borderline

<sup>a</sup> The DODO and ERDC samples included in the table are the only samples from these locations that gave Sr/Ba data; other samples from these locations clogged the ICP due to significant quantities of insoluble, non-barite minerals in the sample analyte. A few representative INMD results are included to illustrate the poor analytical results caused by clogging of the ICP. All INMD results are similarly compromised. These samples all contained <80% barite.

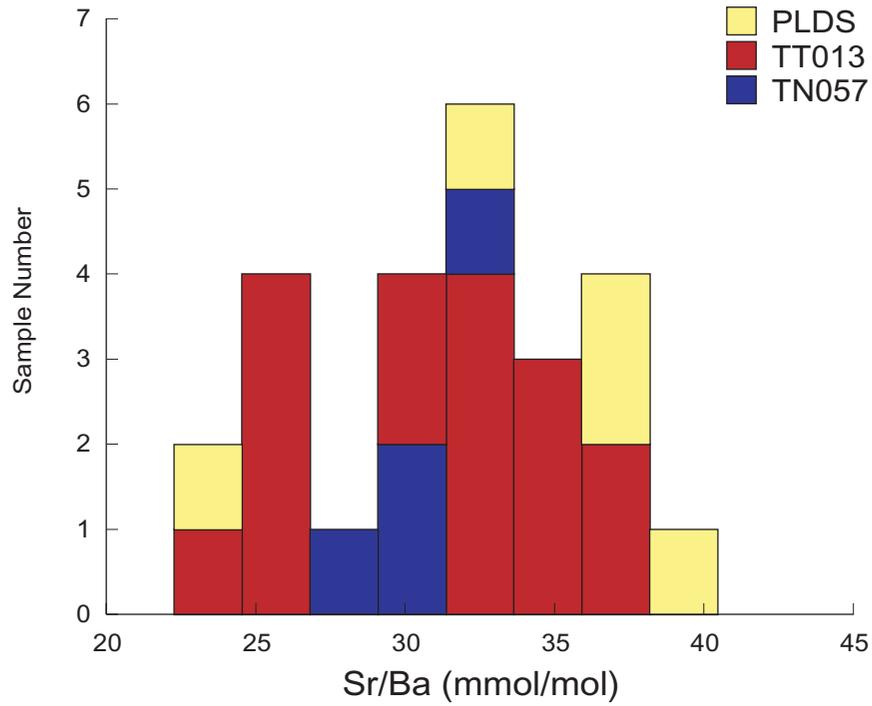


**Figure 2.** Histogram representing the variability of core top Sr/Ca ratios. The mean of the data is  $13.7 \pm 1.4$  mol/mol ( $N = 21$ ).

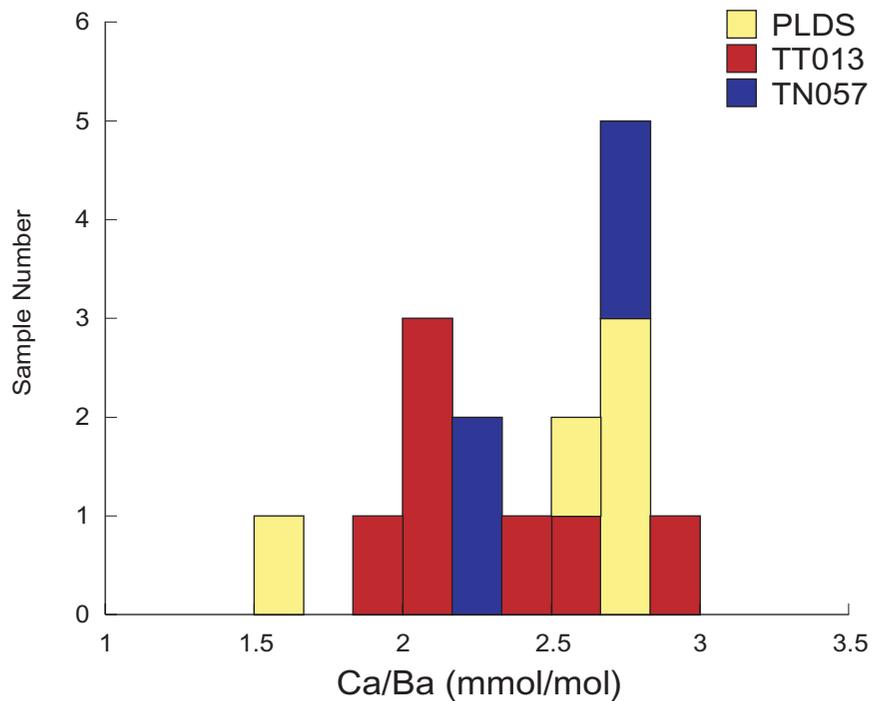
Atlantic Ocean (INMD), the Indian Ocean (DODO), and the western Pacific (ERDC) resulted in unusual or irreproducible data. SEM screening of barite separates from the INMD, DODO, and ERDC cores show significant quantities of insoluble minerals other than barite (Figure 1b). For the INMD samples, the presence of refractory material caused clogging of the ICP introduction system and nebulizer, thereby compromising all analytical data. Raman spectral evidence showed no visible barite peak in any ERDC separates, which is consistent with the low quantities of barite seen using SEM, and the anomalous concentration data. The DODO samples from the Indian Ocean also contained significant amounts of rutile and other terrigenous material. The low barite content of samples separated from INMD, ERDC, and DODO sediments is implied by the ambiguous Raman Spectra that were collected for these residues (Table 2). Further, statistical permutation analyses show the ERDC and DODO  $[\text{Sr}/\text{Ba}]_{\text{barite}}$  data are significantly higher than the TT013, TN057, and PLDS data (99% confidence level). Since all barite separates from the central equatorial Pacific and the Southern Ocean are >80% barite (based on SEM screening),

it is likely that the additional Sr in the western Pacific and Indian Ocean barite separates is attributed to the non-barite component of ERDC and DODO samples. Consequently, the insufficient purity of samples from these sediments (where barite is less than 80% of insoluble residue) precludes their use for core top calibration.

[12] Raman spectral evidence implies that Ca bearing phases (possibly  $\text{CaF}_2$ ) may also be responsible for impurities in a few samples from the central equatorial Pacific and Southern Ocean sites [Averyt *et al.*, 2001, Tables 1a and 1b]. Since Ca contamination does not affect  $[\text{Sr}/\text{Ba}]_{\text{barite}}$ , Sr data were not disregarded based on the presence of Ca impurities detected by Raman spectra. However, Ca concentration data for samples that show impurities attributable to calcium fluoride were eliminated. All the separates containing high barite concentrations (e.g., equatorial Pacific and Southern Ocean) that were not contaminated with  $\text{CaF}_2$  (based on Raman data), were used to calculate partition coefficients. The range of the reliable data used to calculate partition coefficients are shown in Figures 2, 3, and 4.



**Figure 3.** Histogram representing the variability of core top Sr/Ba ratios. The mean of the data is  $31.6 \pm 4.8$  mol/mol ( $N = 25$ ).



**Figure 4.** Histogram representing the variability of core top Ca/Ba ratios. The mean of the data is  $2.4 \pm 0.4$  mol/mol ( $N = 16$ ).



### 3.2. Empirical Partition Coefficients for Sr and Ca in Marine Barite

[13] Partition coefficients define the substitution of an element (Sr, Ca) into a precipitate (BaSO<sub>4</sub>). Trace element substitution in a solid varies as a function of the elemental concentration in the solution from which the precipitate forms, and may be affected by thermodynamic (temperature, pressure) and kinetic factors (precipitation rate). To determine the empirical partition coefficients for Sr, Ca, and Sr/Ca ratios in marine barite ( $D_{Sr}$ ,  $D_{Ca}$ ,  $D_{Sr/Ca}$ ), the mean Sr/Ba, Ca/Ba and Sr/Ca ratios determined from core top barite separates are compared to appropriate seawater Sr and Ca concentrations. Seawater Ba concentrations are not important because seawater is generally undersaturated with respect to barite [Monnin *et al.*, 1999; Rushdi *et al.*, 2000], and barite will only precipitate in microenvironments where supersaturation is achieved. For this reason, fluctuations in seawater Ba concentrations do not affect  $[Sr/Ba]_{barite}$  and  $[Ca/Ba]_{barite}$ . Therefore, the empirical partition coefficients for Sr/Ba and Ca/Ba are best represented by using the  $[Sr]_{sw}$  and  $[Ca]_{sw}$ , relative to the saturation concentration of [Ba] at the depth of barite formation, rather than  $[Ba]_{sw}$ . Assuming that the [Ba] necessary for supersaturation has not changed through time, then only fluctuations in  $[Sr]_{sw}$  and  $[Ca]_{sw}$  will affect  $[Sr/Ba]_{barite}$  and  $[Ca/Ba]_{barite}$ .

[14] The partition coefficients ( $D_{Sr}$ ,  $D_{Ca}$ , and  $D_{Sr/Ca}$ ) are calculated as follows:

$$D_{Sr} = \frac{[Sr]_{Ba, barite}}{[Sr]_{sw}} \frac{[Ba]_{ss}}{[Ba]_{ss}} \quad D_{Sr} = 2.9 \times 10^{-5} \pm 6.4 \times 10^{-6} \quad (1)$$

$$D_{Ca} = \frac{[Ca]_{Ba, barite}}{[Ca]_{sw}} \frac{[Ba]_{ss}}{[Ba]_{ss}} \quad D_{Ca} = 1.9 \times 10^{-8} \pm 4.8 \times 10^{-9} \quad (2)$$

$$D_{\frac{Sr}{Ca}} = \frac{[Sr/Ca]_{barite}}{[Sr/Ca]_{sw}} \quad D_{\frac{Sr}{Ca}} = 1.6 \times 10^3 \pm 1.9 \times 10^2 \quad (3)$$

The mean values of  $[Sr/Ba]_{barite}$ ,  $[Ca/Ba]_{barite}$ , and  $[Sr/Ca]_{barite}$  are from the reliable core top data (sites TT013, PLDS, and TN057) in Table 1a.  $[Ba]_{ss}$  is the concentration of Ba at saturation in

seawater at the approximate depth of barite formation (200 to 300 m) corrected for temperature, pressure, and salinity (80 nM, Monnin *et al.*, 1999). Concentrations of  $[Sr]_{sw}$  ( $87.4 \pm 0.5 \mu\text{M}$ ), and  $[Sr/Ca]_{sw}$  ( $8.5 \times 10^{-3} (\pm 3.8 \times 10^{-5})$ ) are based on global seawater averages [De Villiers, 1999], and  $[Ca]_{sw}$  ( $10.2 \pm (1.6 \times 10^{-2}) \text{ mM}$ ) is calculated from these values.

## 4. Discussion

### 4.1. Natural Variability

[15] The natural variability in Sr/Ba, Ca/Ba, and Sr/Ca (15.0%, 16.3%, and 10.1%) from the non-contaminated, high barite content, core top samples (Table 3, equatorial Pacific and Southern Ocean core top data; TT013, PLDS, TN057) is significantly greater than expected from the range of modern  $[Sr]_{sw}$ ,  $[Ca]_{sw}$ , and  $[Sr/Ca]_{sw}$  (2–3%) [De Villiers, 1999]. This suggests that the [Sr] and [Ca] within microenvironments (where barite precipitates) are more variable than in the open ocean, or that the conditions of barite precipitation (e.g., temperature, pressure, precipitation rate) are variable and affect the partition coefficients. Since the mechanism of barite formation has only recently been experimentally validated (Ganeshram *et al.*, submitted manuscript, 2003), the processes affecting [Sr] and [Ca] within these microenvironments, or the partitioning of these elements into marine barite in the natural environment of formation, are unknown. Therefore, based on these empirical data, we must discuss the processes that may be contributing to the observed natural variability, and determine whether these variations will affect future down core interpretations. It must be kept in mind, however, that as long as the conditions and mechanisms of barite formation represented by our core top samples are representative of past oceanic environments, the empirical partition coefficients calculated here may be used for paleoceanographic reconstructions.

#### 4.1.1. Thermodynamic and Kinetic Regulation

[16] Laboratory studies show that the partition coefficients of Sr and Ca in barite are influenced



**Table 3.** Natural Variability and Calculated Empirical Partition Coefficients<sup>a</sup>

	[Sr/Ca] <sub>barite</sub> D <sub>Sr/Ca</sub>	[Sr/Ba] <sub>barite</sub> D <sub>Sr</sub>	[Ca/Ba] <sub>barite</sub> D <sub>Ca</sub>
All data (TT013, TN057, PLDS)	13.7 ± 1.4 mol/mol 1.6 × 10 <sup>3</sup> ± 1.9 × 10 <sup>2</sup>	31.6 ± 4.8 mmol/mol 2.9 × 10 <sup>-5</sup> ± 6.4 × 10 <sup>-6</sup>	2.4 ± 0.4 mmol/mol 1.9 × 10 <sup>-8</sup> ± 4.8 × 10 <sup>-9</sup>
Equatorial Pacific (TT013, PLDS)	14.1 ± 1.1 mol/mol 1.7 × 10 <sup>3</sup> ± 1.9 × 10 <sup>2</sup>	31.9 ± 5.1 mmol/mol 2.9 × 10 <sup>-6</sup> ± 3.3 × 10 <sup>-6</sup>	2.4 ± 0.4 mmol/mol 1.9 × 10 <sup>-8</sup> ± 5.1 × 10 <sup>-9</sup>
Southern Ocean (TN057)	12.0 ± 0.9 mol/mol 1.4 × 10 <sup>3</sup> ± 1.9 × 10 <sup>2</sup>	30.2 ± 2.4 mmol/mol 2.8 × 10 <sup>-5</sup> ± 3.3 × 10 <sup>-6</sup>	2.5 ± 0.3 mmol/mol 2.0 × 10 <sup>-8</sup> ± 3.7 × 10 <sup>-9</sup>

<sup>a</sup>The top values in each box are the mean core top barite concentration ratios (equatorial Pacific data, Southern Ocean, both basins). Errors represent the standard deviation of the data. Partition coefficients were calculated as described in the text. Partition coefficient errors represent the absolute extreme scenario, and were calculated using the maximum and minimum of the range from core top concentration data, compared with the respective minimum and maximum range of appropriate seawater concentrations. Statistical analyses show that the [Sr/Ca]<sub>barite</sub> and [Sr/Ba]<sub>barite</sub> are significantly lower (99% and 77% confidence) in samples from the Southern Ocean compared with those from the equatorial Pacific.

by temperature and pressure and that Sr and Ca substitution increases as a function of increasing temperature, and decreasing pressure [e.g., Church, 1979]. The distribution of dissolved Ba in seawater, sediment trap data, and radium isotope trends suggest that barite precipitates in the upper water column at approximately the same depth globally [Dymond and Collier, 1996; Legeleux and Reyss, 1996]. The temperature range in the present-day upper water column where much of the barite forms is between 5 and 20°C in the equatorial Pacific and 1 to 3°C in the Southern Ocean. Accordingly, we might expect lower [Ca/Ba]<sub>barite</sub> and [Sr/Ba]<sub>barite</sub> in the Southern Ocean (TN057) relative to the Equatorial Pacific (TT013, PLDS); since the temperature effect is greater for Ca than it is for Sr, the [Sr/Ca]<sub>barite</sub> will also be lower. Indeed, [Sr/Ca]<sub>barite</sub> and [Sr/Ba]<sub>barite</sub> from the Southern Ocean samples are lower than at other locations (Table 3). This is qualitatively consistent with the temperature effect on partition coefficients [Church, 1979]. However, [Ca/Ba]<sub>barite</sub> does not follow this trend, suggesting that temperature changes do not constitute the major control on the distribution partition. In addition, assuming that the temperature difference between the equatorial Pacific and Southern Ocean at the depth of barite formation is in the range of 10°C, the expected percent change in the [Sr/Ba]<sub>barite</sub> and [Ca/Ba]<sub>barite</sub> based on theoretical partitioning calculations [Church, 1979] would be approximately 10 and 34%, respectively. Variations in Sr and Ca content of barite precipitated in controlled laboratory experiments at different temperatures exhibit fluctuations of approximately 15% in Sr and Ca

content over 20°C intervals [Church, 1979]. This range is similar to the natural variability captured in our core top samples for [Sr/Ba]<sub>barite</sub> and [Ca/Ba]<sub>barite</sub>. Therefore, although temperature variations may affect partitioning of Sr and Ca in natural barite, given the range of temperatures (1 to 20°C) at which the marine barite in our core top calibration likely precipitated, variations in temperature as they affect saturation state and Sr and Ca partitioning, are represented in the variability within our calculated partition coefficients. Thus, temperature changes within this range (1 to 20°C) at present and in the past should not have a significant influence on the empirical partition coefficients, based on the average composition of the core tops analyzed here.

[17] Our calculations of the empirical partition coefficients (section 3.2) assume that barite forms in the upper water column. Indeed, ample evidence supports this assertion, including the distribution of dissolved Ba in seawater, the abundance of particulate barium and barite in the water column, observations that much of the organic matter is regenerated at such depths, and the Ra isotope activities in barite [Bishop, 1988; Dehairs et al., 1980; Dymond and Collier, 1996; Legeleux and Reyss, 1996]. However, we cannot rule out the possibility that barite forms at other depths in the water column. To test the effect of barite precipitation at depth we have calculated D<sub>Sr</sub> and D<sub>Ca</sub> (equations (1) and (2)) using the Ba saturation at 2°C and 5000 m depth [Monnin et al., 1999]. These values are 7.23 × 10<sup>-5</sup> and 4.76 × 10<sup>-8</sup>, respectively both of which are 2.5 times greater



than the average partition coefficients in Table 3. Accordingly, we looked for a correlation among  $[\text{Sr}/\text{Ba}]_{\text{barite}}$ ,  $[\text{Ca}/\text{Ba}]_{\text{barite}}$ , and  $[\text{Sr}/\text{Ca}]_{\text{barite}}$  for core tops and water depths. It is expected that these ratios will decrease with depth due to the effect of pressure on the partition coefficients. No significant correlation with depth is observed (see Table 1). This implies that pressure does not appreciably affect the partitioning of Sr and Ca into the barite structure in natural environments, or that the majority of barite formation is confined at a particular depth interval in the water column, and is therefore not subject to precipitation in different pressure regimes.

[18] With respect to kinetic effects, the relative homogeneity in crystal shape and size among our samples (Figure 5a) indicates that precipitation rates are not dramatically variable. Laboratory experiments in which barite was precipitated at different rates resulted in a wide range of barite crystal shapes and sizes (Figure 5b). We are aware that this argument is only qualitative; however, changes in Sr and Ca in the microenvironments and precipitation rates cannot be decoupled using natural samples. In fact, these processes may be related. Our major point is that the overall conditions in the microenvironments control the partition coefficients. Therefore, as long as our samples, which come from very different oceanic settings, are representative of the potential variability of both past and present natural environments where barite forms, our empirical partition coefficients may be used. It must be stressed, as in section 4.2, that to capture the variability in past oceans, it is required that several cores of the same age from different settings be used to represent the potential variability in the oceans and microenvironments at any given time.

#### 4.1.2. Microenvironments

[19] Since plankton decomposition is the source of Ba that leads to barite formation (Ganeshram et al., submitted manuscript, 2003), it is also possible that differences in the bulk Sr or Ca composition of sinking particulate aggregates may cause variability within microenvironments where barite precipitates. In fact, the relatively lower  $[\text{Sr}/\text{Ca}]_{\text{barite}}$  and

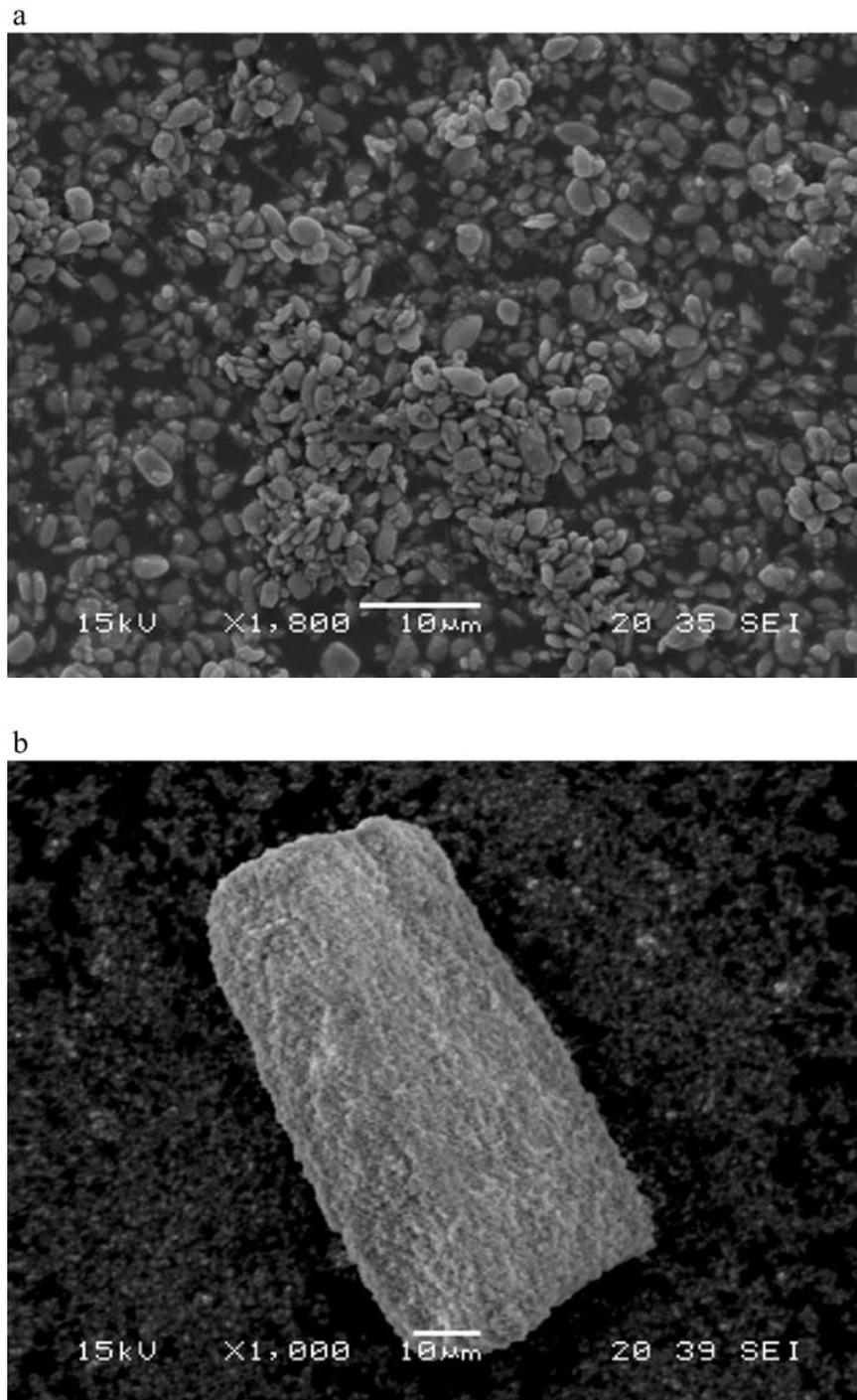
$[\text{Sr}/\text{Ba}]_{\text{barite}}$  core top results from the Southern Ocean may reflect the lower abundance of acantharia in polar waters. Acantharia actively precipitate biogenic celestite ( $\text{SrSO}_4$ ) and contribute significant quantities of Sr to pools of decaying particulate matter [Bernstein et al., 1987, 1991]; acantharia are hypothesized to dominate the cycling of Sr in the oceans and account for the “semi-nutrient” nature of the dissolved Sr depth profile [De Villiers, 1999; Bernstein et al., 1987, 1991]. Since acantharia are more abundant in tropical and sub-tropical waters, the lack of this planktonic group in the water column of the Southern Ocean may decrease Sr concentrations in the environment where barite forms, resulting in lower  $[\text{Sr}/\text{Ca}]_{\text{barite}}$  and  $[\text{Sr}/\text{Ba}]_{\text{barite}}$  ratios. This process should not influence the  $[\text{Ca}/\text{Ba}]_{\text{barite}}$  significantly.

[20] It is also reasonable to expect that  $[\text{Ca}/\text{Ba}]_{\text{barite}}$  may be influenced by the relative abundance of various organisms in the water column, due to significant variations in tissue and hard part Ca content (i.e., coccolithophore abundance). However, more subtle regional or temporal trends in species composition are unlikely to be resolved in our core top barite, since we have limited regional coverage, and because bioturbation and sampling resolution result in an integrated age signal. More systematic work with sediment trap barite is needed to resolve specific changes related to phytoplankton assemblage.

[21] For these reasons, we believe that the most important parameter influencing the natural variability observed in core top barite samples (Figures 2, 3, and 4) is the natural variability in the Sr and Ca composition in microenvironments where barite precipitates. Any effect of temperature or pressure on the degree of substitution of these elements is implicit in the empirical partition coefficients calculated here as long as the variability in environmental conditions (e.g., temperature and depth) for barite formation is represented in the range of our core top samples.

#### 4.2. Limitations and Implications

[22] The relatively large range of  $[\text{Ca}/\text{Ba}]_{\text{barite}}$ ,  $[\text{Sr}/\text{Ba}]_{\text{barite}}$ , and  $[\text{Sr}/\text{Ca}]_{\text{barite}}$  observed in core top



**Figure 5.** SEM images of (a) natural marine barite separates and (b) those precipitated in the laboratory. Note the scale bars; the size difference between the two crystal types represents the contrast in precipitation rates.

marine barite samples compared to what is expected from seawater Sr and Ca concentrations may result from differences in the temperature and depth at the location of barite formation (thermo-

dynamic effects on partition coefficients), precipitation rates (kinetic effects), the Sr/Ca ratio within the microenvironment in which barite precipitates, or all of the above.



[23] However, if barite precipitates throughout the water column, representing the whole range of oceanic temperature and pressure conditions, a much larger, and depth dependent, variability in  $[Ca/Ba]_{\text{barite}}$ ,  $[Sr/Ba]_{\text{barite}}$ , and  $[Sr/Ca]_{\text{barite}}$  would be expected. For these reasons, we consider it likely that the bulk part of marine barite precipitation is confined to a particular region within the water column (as suggested by other independent observations, e.g., Bishop [1988], Dehairs *et al.* [1980], Dymond and Collier [1996] and Legeleux and Reyss [1996]). The empirical partition coefficients calculated here represent significantly different oceanic regimes and therefore, regardless of the mechanism and external influences on formation, the variability caused by these processes is implicit in the calculated empirical partition coefficients (Table 3). Assuming that the most significant Sr and Ca contribution to the microenvironment is from seawater, and that natural variability accounted for in core tops is representative of the variability over geological time,  $D_{Sr}$ ,  $D_{Ca}$ , and  $D_{Sr/Ca}$  as determined in (1), (2), and (3) are functions of  $[Sr]_{SW}$  and  $[Ca]_{SW}$ . These empirical partition coefficients can thus be used to calculate  $[Sr/Ca]_{SW}$ ,  $[Sr]_{SW}$ , and  $[Ca]_{SW}$  from precise measurements of  $[Sr/Ca]_{\text{barite}}$ ,  $[Sr/Ba]_{\text{barite}}$ , and  $[Ca/Ba]_{\text{barite}}$  of marine barite separates, as long as the fluctuation in these ratios over time is larger than the variability in core tops. Also, it is assumed here that the mechanism of Sr and Ca incorporation has not changed through time, and that the extent of natural variability has not changed appreciably. These are reasonable assumptions since our calibration includes data from significantly different oceanographic regimes (Pacific and Southern Oceans). However, at any given time interval it is important to use samples from several distinct oceanic regimes to verify that indeed the variability among sites has not changed and is comparable to the range represented by core tops.

[24] Since global carbon cycle models predict that  $[Sr/Ca]_{SW}$  has fluctuated considerably over the past 65 million years [Graham *et al.*, 1982; Delaney *et al.*, 1985; Stoll and Schrag, 2001; Wallman, 2001; Lear *et al.*, 2003], any uncertainties introduced by calibrating Sr and Ca empirical partition coeffi-

cients using core top data are insignificant in comparison to long-term  $[Sr/Ca]_{SW}$  fluctuations.

## 5. Conclusions

[25] The natural variability among core top  $[Sr/Ca]_{\text{barite}}$ ,  $[Sr/Ba]_{\text{barite}}$ , and  $[Ca/Ba]_{\text{barite}}$  (10.1%, 15.0%, and 16.3%, respectively) reflects complex and unspecified processes occurring within pools of particulate organic matter that affect local trace metal concentrations. Although Sr and Ca substitute into marine barite environmental factors, such as phytoplankton assemblage, may influence the recorded Sr/Ba and Ca/Ba ratios. This is demonstrated by the small depletion in Sr concentrations in marine barite separates from Southern Ocean sites. However, since our empirical core top calibration includes samples from oceanographically diverse areas (equatorial Pacific and Southern Ocean); environmental factors including both temperature and elemental composition in the microenvironments are not only implicit in the natural variability among our data, but also in the calculated partition coefficients. Estimates of Cenozoic fluctuations in seawater Sr/Ca ratios ( $\sim 80\%$ ) are significantly greater than the natural variability of our core top data, and we consider it unlikely that the partitioning of Sr and Ca into marine barite would be influenced by environmental factors to this extent. To develop paleoseawater Sr and Ca concentration curves, deep-sea cores should be carefully selected from sites that are likely to yield adequate barite residues ( $>80\%$ ). Assuming barite formation and preservation mechanisms in the past were similar to present, the empirical partition coefficients calculated here for Sr ( $D_{Sr} = 2.9 \times 10^{-5}$ ), Ca ( $D_{Ca} = 1.9 \times 10^{-8}$ ), and Sr/Ca ( $D_{Sr/Ca} = 1.6 \times 10^3$ ) can be used to define long-term records of seawater Sr and Ca concentrations, based on the  $[Sr/Ba]_{\text{barite}}$  and  $[Ca/Ba]_{\text{barite}}$  measurements of barite samples.

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