Click Here for Full Article

Reply to comment by D. Wang et al. on "Empirical partition coefficients for Sr and Ca in marine barite: Implications for reconstructing seawater Sr and Ca concentrations"

Kristen B. Averyt

IPCC Working Group I Support Unit, Boulder, Colorado 80305, USA (averyt@ucar.edu)

Adina Paytan

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305, USA (apaytan@stanford.edu)

[1] *Wang et al.* [2007] argue that the empirical distribution coefficient for Sr in marine barite obtained from the Sr/Ba composition of Holocene core top marine barite could not be used to reconstruct past seawater Sr concentrations. The premise for this argument is that Sr substitution into barite is not primarily a function of ambient Sr concentrations at the time barite precipitated. *Wang et al.* [2007] base their argument on the relatively large range of Sr/Ba ratios measured by *Averyt and Paytan* [2003] in the core top barite. They suggest that variable spatial and temporal ocean temperatures are responsible for the variations and without knowledge of the seawater temperature at the time and location of barite precipitation, the empirical distribution coefficient may not be used. However, we believe that we arrived at the best possible partition coefficient for Sr in marine barite based on the data available in 2003 and that despite ignoring the temperature effects this coefficient is useful if applied correctly.

[2] While there is no question that our data are accurate (this is not disputed by *Wang et al.* [2007]), our assumptions in calculating the distribution coefficient [see *Averyt and Paytan*, 2003] may or may not be valid. Indeed, we fully agree (and have not argued otherwise) that the partition coefficient for any given system will be affected by the temperature at which the reaction occurs. It should be noted that in our paper [*Averyt and Paytan*, 2003] we report an error for our empirically derived D_{Sr} ($2.9 \times 10^{-5} \pm 6.4 \times 10^{-6}$). This error estimate is based on the range of Sr/Ba ratios of the barite in the core top sediments analyzed, and therefore captures the temperature variation that *Wang et al.* [2007] suggest that we neglect. Our paper goes into detail about what controls D_{Sr} in barite and why core tops cover a range of values.
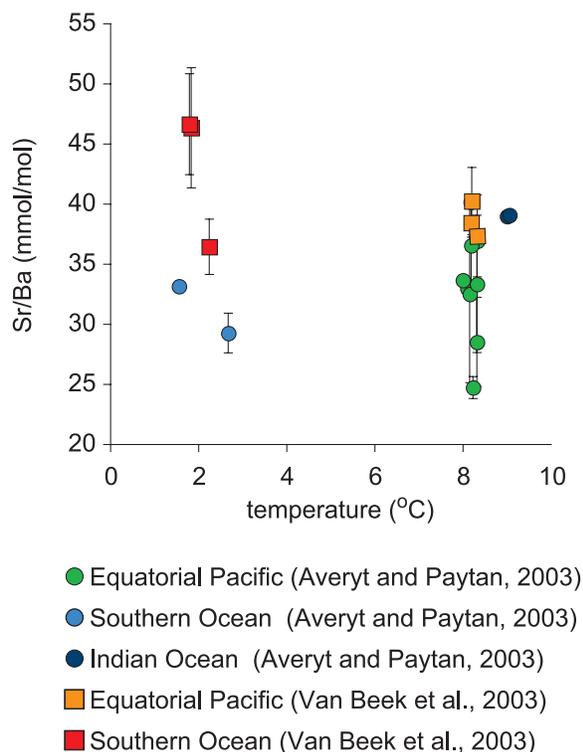
● Equatorial Pacific (Averyt and Paytan, 2003)
● Southern Ocean (Averyt and Paytan, 2003)
● Indian Ocean (Averyt and Paytan, 2003)
■ Equatorial Pacific (Van Beek et al., 2003)
■ Southern Ocean (Van Beek et al., 2003)

Figure 1. Error bars represent the range of all the measurements (different samples) at a given location. The average of all [Sr/Ba]$_{barite}$ measurements published is 36.6 mmol/mol, and the standard error is 2.1 mmol/mol (95% confidence) [*Averyt*, 2005]. Ocean temperature data at 500 m depth are based on annual climatology data as found in the World Ocean Atlas 1998 [*Conkright et al.*, 1998].

We identify several factors that may increase the variability in measurements of the Sr/Ba ratios (and therefore the D_{Sr}) in marine barite, including [Sr]$_{SW}$ variations of 2–3% [*de Villiers*, 1999], spatial variation within a crystal (6%), the presence of accessory minerals (up to 20%) in barite sample separates, among others. Thus, although not explicitly stated, any application of the partition coefficient in our work would necessitate that the reported error ($\pm 6.4 \times 10^{-6}$) be considered as it represents the "natural variability" of the [Sr/Ba]$_{barite}$ and of Sr partitioning into this phase. Only systematic changes that are distinct and greater than this error envelope should be considered in paleoreconstruction of seawater Sr fluctuations.

[3] Recognizing that spatial and temporal temperature variations should be considered seriously in paleoceanographic reconstructions, the effect of temperature on [Sr/Ba]$_{barite}$ in the ocean has been

investigated in further work [*Averyt*, 2005]. Subsequent to the publication of our work (2003), *Van Beek et al.* [2003] reported additional measurements of Sr/Ba ratios of core top marine barite. Figure 1 shows the relationship between all the [Sr/Ba]$_{barite}$ data available compared with temperature in the overlying water column temperature of the overlying water at the depth of maximum barite formation ($\sim$500 m). The choice to use the temperature at 500 m is based on ample data indicating that this is the approximate depth where the majority of marine barite precipitation occurs in the ocean [*Dehairs et al.*, 1980, 1991, 1992; *Bishop*, 1988; *Dymond et al.*, 1992]. Statistical analyses show that the compiled weighted average of all [Sr/Ba]$_{barite}$ measurements at each location are not significantly related to temperature. Moreover, the [Sr/Ba]$_{barite}$ of sample residues extracted from different ocean basins (equatorial Pacific, Southern Ocean, Indian Ocean) are not distinct despite the large range of seawater temperatures.

[4] In addition, *Averyt* [2005] evaluated the effects of temperature on D_{Sr} in barite using thermodynamic calculations of the stability of barite solid solutions over the range of chemical and physical conditions expected within microenvironments where barite precipitates. The details of this model analysis are too complex to discuss in this short response but are given by *Averyt* [2005]. The results suggest that although the composition of barite precipitated from a fluid of a given Sr/Ba ratio is influenced by temperature, fluid composition plays a much larger role than temperature in determining the extent of Sr substitution into barite.

[5] *Monnin and Cividini* [2006] recently published a calculation of the distribution of Sr in barite, using the Sr and Ba concentrations in seawater samples and the equilibrium Sr mole fraction of the solid solution from a Lippmann's diagram. Interestingly, we note that the partition coefficient for Sr in barite reported by *Monnin and Cividini* [2006] of 4.2×10^{-5} is quite similar to ours (2.9×10^{-5}), despite differences in our approach and our decision to incorporate any temperature effect in the error associated with the partition coefficient, rather than as an independent variable. Indeed, the similarity of these values is surprising given the variable processes occurring within a natural, oceanic regime that contribute to our empirically derived calculation. This suggests that our assumptions [*Averyt and Paytan*, 2003] are relatively robust.

[6] In addition, *Monnin and Cividini* [2006] find that "the Sr in barite varies only slightly with temperature of the sample." Consequently, on the basis of the best available data, the temperature within the range of present day oceans does not seem to be the most important factor controlling the incorporation of Sr into barite. This implies that consideration of seawater temperature variations through time will also likely be unimportant for paleoapplications.

[7] While we recognize the complications of developing and applying empirical distribution coefficients for use in paleoceanographic reconstructions, these are still the most practical and relevant tools we have; and if used with the understanding of the associated limitations and assumptions, these empirical values provide valuable information that could not be obtained otherwise.

References

Averyt, K. B. (2005), Strontium and calcium in marine barite, Ph.D. thesis, Stanford Univ., Stanford, Calif.

Averyt, K. B., and A. Paytan (2003), Empirical partition coefficients for Sr and Ca in marine barite: Implications for reconstructing seawater Sr and Ca concentrations, *Geochem. Geophys. Geosyst.*, *4*(5), 1043, doi:10.1029/2002GC000426.

Bishop, J. K. B. (1988), The barite-opal-organic carbon association in oceanic particulate matter, *Nature*, *332*, 341–343.

Conkright, M., S. Levitus, T. O'Brien, T. Boyer, J. Antonov, and C. Stephens (1998), World Ocean Atlas 1998 CD-ROM Data Set Documentation, internal report, *Tech Rep. 15*, p. 16, Natl. Oceanogr. Data Cent., Silver Spring, Md.

Dehairs, F., R. Chesselet, and J. Jedwab (1980), Discrete suspended particles of barite and the barium cycle in the open ocean, *Earth Planet. Sci. Lett.*, *49*, 528–550.

Dehairs, F., N. Stroobants, and L. Goeyens (1991), Suspended barite as a tracer of biological activity in the Southern Ocean, *Mar. Chem.*, *35*, 399–410.

Dehairs, F., W. Baeyens, and L. Goeyens (1992), Accumulation of suspended barite at mesopelagic depths and export production in the Southern Ocean, *Science*, *258*(5086), 1332–1335.

de Villiers, S. (1999), Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans, *Earth Planet. Sci. Lett.*, *171*, 623–634.

Dymond, J., E. Suess, and M. Lyle (1992), Barium in deep-sea sediment: A geochemical proxy for paleoproductivity, *Paleoceanography*, *7*, 163–181.

Monnin, C., and D. Cividini (2006), The saturation state of the world's ocean with respect to $(Ba, Sr)SO_4$ solid solutions, *Geochim. Cosmochim. Acta*, *70*, 3290–3298.

Van Beek, P. J., J. Reyss, P. Bonte, and S. Schmidt (2003), Sr/Ba in barite: A proxy of barite preservation in marine sediments?, *Mar. Geol.*, *199*, 205–220.

Wang, D., X. Lu, and S. Xu (2007), Comment on "Empirical partition coefficients for Sr and Ca in marine barite: Implications for reconstructing seawater Sr and Ca concentrations," by Kristen B. Averyt and Adina Paytan, *Geochem. Geophys. Geosyst.*, *8*, Q01008, doi:10.1029/2006GC001456.