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The marine barite saturation state of the world's oceans

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Abstract

This paper addresses the question of the eventual control of barium concentration in seawater by an equilibrium with barite. For this, we have used a new thermodynamic model to compute the barite saturation index of ocean waters, mainly from GEOSECS data. Our results show that equilibrium between barite and seawater is reached in a number of places: cold surface waters of the Southern Ocean, waters at intermediate depths (2000–3500 m) in the Pacific, deep waters (2000–3500 m) of the Gulf of Bengal. The only samples for which a slight barite supersaturation is found are the surface waters at GEOSECS station G89 in the Weddell Gyre. Besides these locations, the rest of the world's oceans is undersaturated, as was established by Church and Wolgemuth [Church, T.M., Wolgemuth, K., 1972. Marine barite saturation, Earth Planet. Sci. Lett. 15 35–44.]. There is a return to undersaturation of the water column at depths of about 3500 m in the Pacific and of about 2500 m in the Southern Ocean. The reverse is found for GEOSECS station 446 in the Gulf of Bengal for which the highest Ba concentrations can be found at depth: surface waters are undersaturated and equilibrium is reached below 2000 m. Finally, we briefly discuss the role of biogenic and inorganic processes on barite formation in the ocean as well as the influence of strontium substitution in marine barites.

Keywords: marine barite; saturation; world ocean; oceanography; thermodynamics; aqueous solutions

1. Introduction

Barite particles are a universal component of suspended matter in the oceans and have a biogenic origin (Dehairs et al., 1980, 1990; Bishop, 1988). Correlations between alkalinity and dissolved Ba and Si concentrations in seawater also support a biogenic origin for these particles (see discussion and references in McManus et al., 1994; Paytan and Kastner, 1996). The question of the eventual limitation of the barium concentration of ocean waters by the inorganic precipitation of barium sulfate (barite) has been addressed by Chow and Goldberg (1960) and by Church and Wolgemuth (1972). From the limited data and the thermodynamic models available at that time, Chow and Goldberg (1960) concluded that ‘‘the saturation values of barium are not approached in surface ocean waters but may be reached at greater depth’’ while Church and Wolgemuth (1972) showed that the ‘‘Ba concentration of the entire seawater column in the Eastern Pacific and probably

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most of the world's oceans seems to fall below the barite saturation curve.'' Such assumptions have been commonly accepted and referred to since then (see, e.g., Bertram and Cowen, 1997). More recently, Falkner Kenisson et al. (1993) have found that the anoxic Black Sea deep waters exceed saturation with respect to pure barite by at least a factor of two. Because of the potential use of barium as a tracer of oceanic circulation, it is important to know all the factors controlling its concentration in the oceans. The concentration of chemical elements likely to be used as geochemical tracers is the result of molecular diffusion, advection (transport) and chemical reactions. In this paper, we investigate the eventual limitation of Ba concentration in the ocean by an equilibrium with solid barium sulfate. Conversely, undersaturation of seawater with respect to barium sulfate indicates where barite can dissolve and where barium could be remobilized.

A large body of data on the distribution of Ba in the oceanic water column has been collected since Church and Wolgemuth's paper. In the same period, the development of Pitzer's ion interaction approach for the thermodynamic properties of electrolyte solutions has triggered the construction of a new generation of solubility models of great interest for the earth sciences (see Weare, 1987; Pitzer, 1991 for reviews). Above all, demonstrating equilibrium between a solid and an aqueous phase is a challenge to solution chemistry and to the way of calculating the thermodynamic properties of the aqueous phase. Using Pitzer's formalism, we have built a new solubility model for barite in electrolyte solutions from 0 to 200°C and to 1 kbar (Monnin, 1999). Here, we apply this model to barium concentrations in seawater samples collected during various oceanographic cruises (mainly GEOSECS) to calculate the saturation state of the world's oceans with respect to barium sulfate.

2. Calculation of the barium sulfate saturation index in seawater

The barite saturation index is the ratio of the barium sulfate ionic product to the barite solubility product:

$$SI = Q/K_{sp}. \tag{1}$$

The expression of the barite solubility product as a function of temperature and pressure is given by Monnin (1999). The ionic product Q is defined as:

$$Q = m_{Ba^{2+}(aq),F} \cdot m_{SO_4^{2-}(aq),F} \cdot \gamma_{M^{2+}(aq),F} \cdot \gamma_{SO_4^{2-}(aq),F} \tag{2}$$

where $m_{Ba^{2+}(aq),F}$ and $m_{SO_4^{2-}(aq),F}$ designate the molalities of the free barium and sulfate aqueous ions and $\gamma_{Ba^{2+}(aq),F}$ and $\gamma_{SO_4^{2-}(aq),F}$, their activity coefficients. In this work, we use a thermodynamic model of the Na–K–Ca–Mg–Ba–Sr–Cl–SO_4–H_2O system based on Pitzer's equations (Monnin, 1999). In this model, only $BaSO_4$(aq), $SrSO_4$(aq) and $CaSO_4$(aq) are treated as weak electrolytes, i.e., interactions between Ba^{2+}(aq), Sr^{2+}(aq) and Ca^{2+}(aq) and aqueous sulfate are taken into account by an explicit association equilibrium between the free ions and the $BaSO_4^0$(aq), $SrSO_4^0$(aq) and $CaSO_4^0$(aq) ion pairs. All other types of interactions within the aqueous phase are accounted for by interaction parameters in Pitzer's expressions for the activity coefficients. Such an approach has been termed a 'hybrid' model (Whitfield, 1975) or 'extended Pitzer formalism' (Clegg and Whitfield, 1995).

So the relationships between the actually measured concentrations (labeled T for total in Eq. (3)) of aqueous barium and sulfate and the molalities of the free ions and the ion pairs are:

$$\begin{aligned} m_{Ba^{2+}(aq),T} &= m_{Ba^{2+}(aq),F} + m_{BaSO_4^0(aq)} \\ m_{SO_4^{2-}(aq),T} &= m_{SO_4^{2-}(aq),F} \\ &\quad + m_{BaSO_4^0(aq)} + m_{CaSO_4^0(aq)} + m_{SrSO_4^0(aq)}. \end{aligned} \tag{3}$$

The activity coefficients of the aqueous species are calculated at a given temperature from Pitzer's parameters for that temperature, while the effect of pressure is accounted for by the integration of partial molal volumes (Monnin, 1989). Compressibility effects are neglected (Millero, 1979; Monnin, 1990), so the calculation of the barite ionic product requires that of the distribution of species (also called speciation) between free ions and ion pairs. This is done by solving the mass conservation expressions (Eq. (3) above) along with expressions of mass action law for the $BaSO_4^0$(aq), $SrSO_4^0$(aq) and $CaSO_4^0$(aq) complexes.

Undersaturation is indicated by a saturation index smaller than 1 and supersaturation by a SI greater

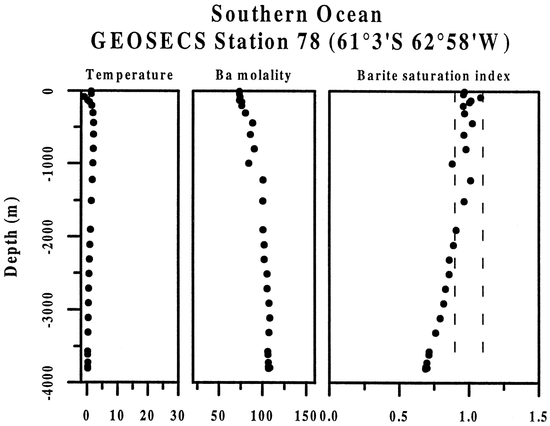

Fig. 1. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 78 in the Atlantic sector of the Southern Ocean. Barite equilibrium in surface waters is also found at GEOSECS stations 74, 76 and 91.

than 1. Equilibrium is reached for SI = 1.0, which never occurs in the mathematical sense. In practise, one has to define a saturation index range within which equilibrium is assumed to be reached. For example, Langmuir and Melchior (1985) arbitrarily chose an error band of $\pm 1/20 \log K_{sp}$ [for a saturation index defined as $\log(Q/K)$], which amounts to considering that barite is at equilibrium when Q/K is between 0.3 and 3. Ideally, the width of this range should reflect the uncertainties on the various quantities used to calculate the saturation index: analytical errors on measured concentrations and errors on all thermodynamic model parameters. The evaluation of such uncertainties is difficult. Moreover, these uncertainties are not independent of the investigated temperature and pressure ranges. Thermodynamic models based on Pitzer's equations (as all semi-empirical approaches) are better constrained for conditions where experimental data are the most numerous, i.e., 25°C and 1 bar. Model performances can, nevertheless, be evaluated a posteriori by comparing model predictions to experimental data not used in the model parameter calculations. This was done in a previous paper (Monnin, 1999) where we have shown how the solubility model used here can predict barite solubility in electrolyte solutions up to moderate concentrations (typically 1 M, often more), 200°C and 1 kbar within experimental uncertainty (Monnin, 1999). Here, we assume that equilibrium between barite and an aqueous solution is achieved when the barite saturation index is within the range 0.9–1.1. This is equivalent to admitting that the model can predict barite solubility in seawater and electrolyte solutions within 10% of measured values.

3. The world ocean saturation state with respect to pure barium sulfate

As raw input data, we use in situ temperature, depth, salinity and total barium concentration as commonly reported in oceanographic tables. Depth is readily converted to pressure. Molalities of the major seawater components are calculated from the sample salinity and from the composition of standard 35‰ seawater taken from Clegg and Whitfield (1991). The Ba concentration (mol/kg seawater) is transformed into Ba molality (mol/kg H_2O).

In Figs. 1–11, we have plotted temperature, Ba concentration and barite saturation index vs. depth. We have treated all GEOSECS stations (about 50) for which Ba concentrations are available (Ostlund et al., 1987).

It turns out that a few distinctive patterns of barite SI vs. depths emerge, each being representative of a distinct ocean basin. Here, we give the list of the stations (Table 1) that fall within one single type, but we selected only one representative plot. Besides the

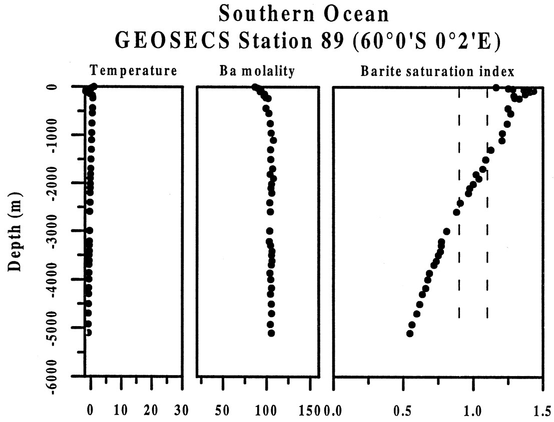

Fig. 2. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 89 in the Atlantic sector of the Southern Ocean. The slight supersaturation of surface waters is also found at GEOSECS stations 82 and 287.

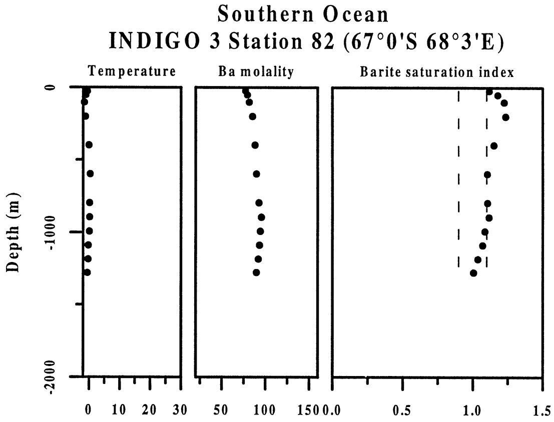

Fig. 3. Temperature, barium molality and barite saturation index vs. depth for INDIGO 3 station 82 in the Indian sector of the Southern Ocean. The water column is either at slightly supersaturated or at equilibrium down to the seafloor.

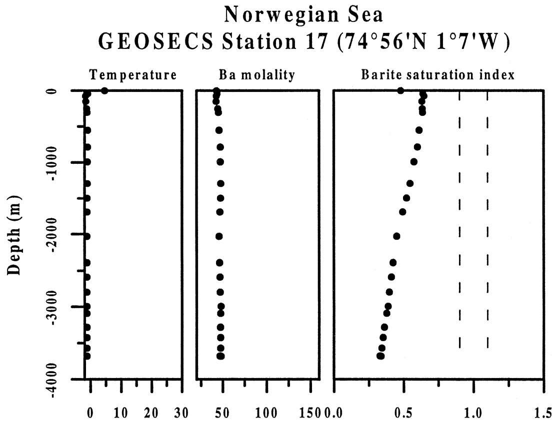

Fig. 5. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 17 in the Norwegian Sea.

GEOSECS atlas itself, a map of the locations of the GEOSECS stations can be found in many papers (e.g., Campbell, 1983). The following observations can be made.

(1) In the Southern Ocean (roughly south of 50°S), surface waters are cold (Figs. 1 and 2). They are either at equilibrium with barite (south of the Atlantic: stations 74, 76, 78, 91; Fig. 1) or slightly supersaturated (Atlantic sector: stations 82, 89 and Pacific sector: station 287; Fig. 2). At these locations, the water column becomes undersaturated at depths between 1500 and 2500 m, which we had already observed from the INDIGO 3 cruise data (Jeandel et al., 1996). It can be seen in Figs. 1 and 2 that temperature and the Ba concentration become constant at depth. The transition from barite saturation to undersaturation is solely due to the effect of pressure on both the barite solubility product and the activity coefficient of aqueous barium sulfate (see

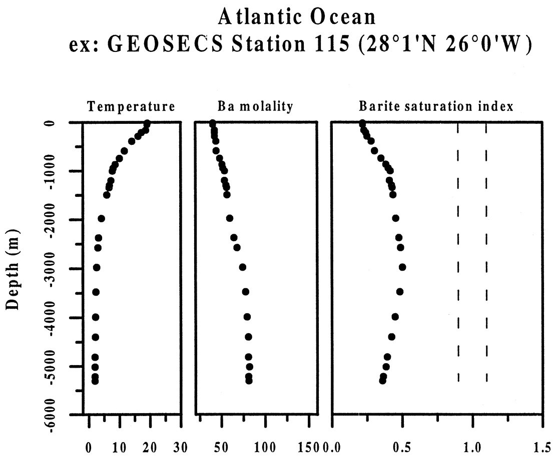

Fig. 4. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 115. This station is taken as representative of the Atlantic Ocean from 45°S to 60°N as the same barite saturation state has been found at GEOSECS stations 3, 11, 18, 19, 23, 29, 33, 37, 40, 48, 54, 56, 60, 93, 103, and 111.

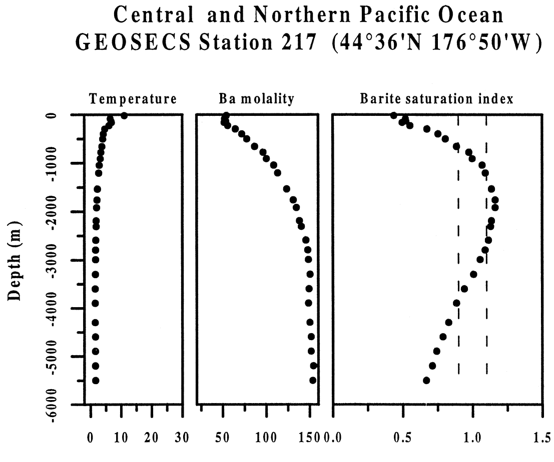

Fig. 6. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 217. This station is taken as representative of the Pacific Ocean from 45°S to 50°N as the same barite saturation state has been found at GEOSECS stations 204, 212, 217, 215, 219, 224, 226, 227, 241, 263, 296, 331, 337 and 343.

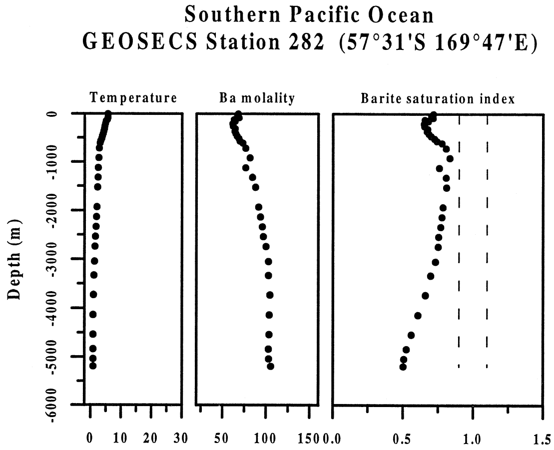

Fig. 7. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 282 situated north-east of New Zealand. The same pattern has been found for station 293 in the Southern Pacific, but also at station 429 located at the same latitude in the Southern Indian Ocean.

Monnin, 1999 for a discussion). Station G89 is the only station showing oversaturation in the upper 1500 m. As yet, we do not have a straightforward explanation for this situation. However, dissolved Ba profiles measured during subsequent expeditions (ANTX-6, 1992; CIVA-1, 1993) in the same general area as station 89 (unpublished results; Cattaldo et al., in preparation) do not show the elevated dissolved Ba concentrations reported for station 89 by Ostlund et al. (1987).

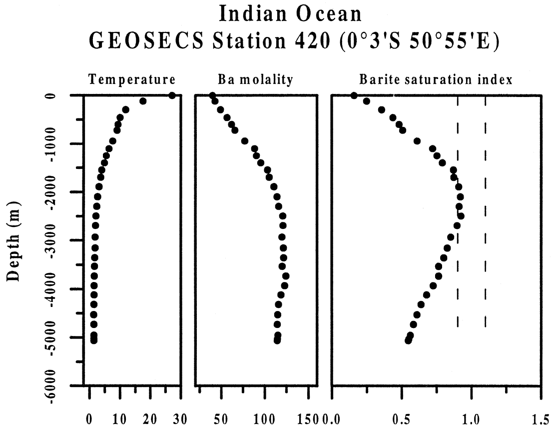

Fig. 8. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 420 in the Indian Ocean. The results for GEOSECS stations 418 and 424 are the same. The same pattern has been found for station 293 in the Southern Pacific, but also at station.

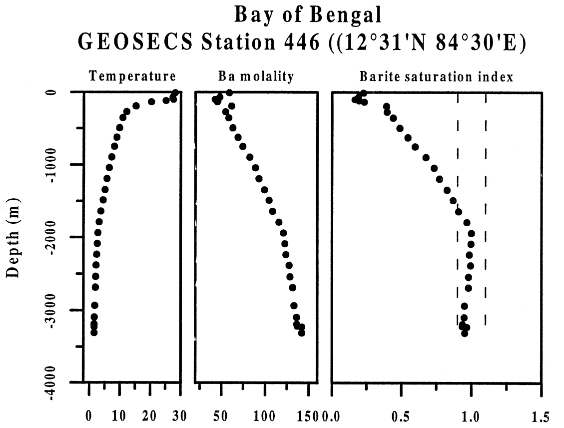

Fig. 9. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 420 in the Bay of Bengal showing barite saturation for deep waters.

INDIGO 3 stations, I82 and I83, are located above the continental shelf (see the map in Jeandel et al., 1996). The Ba data are given by Dehairs and Goyens (1990). The water column at these stations is slightly supersaturated from the surface down to the seafloor (Fig. 3).

(2) The Central and Northern Atlantic Oceans are undersaturated at all depths (GEOSECS stations 3, 11, 18, 19, 23, 29, 33, 37, 40, 48, 54, 56, 60, 93,

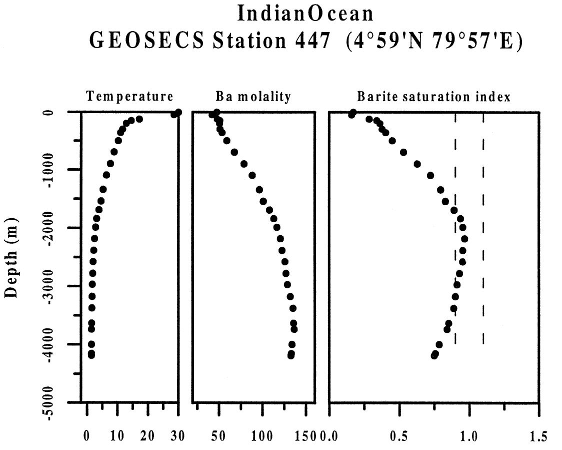

Fig. 10. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 447 south of Ceylon. There is a return to undersaturation near the seafloor.

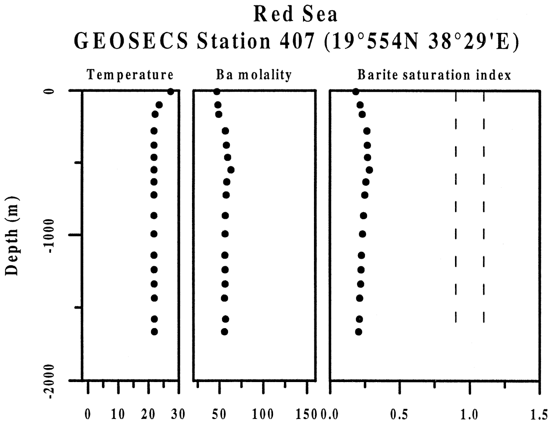

Fig. 11. Temperature, barium molality and barite saturation index vs. depth for GEOSECS station 407 in the Red Sea.

103, 111, 115; Fig. 4). At GEOSECS station 17 in the Norwegian Sea, waters are cold and have a low barium concentration (about 50 nmol/kg; Fig. 5). This leads to barite undersaturation.

(3) Fig. 6 (pertaining to GEOSECS stations 204, 212, 217, 215, 219, 224, 226, 227, 241, 263, 296, 331, 337 and 343) shows that surface waters in the Central and Northern Pacific are undersaturated. At these locations, the barite saturation index increases with depth from the surface to a maximum value of 1.2. Saturation is reached at depths between 1000 and 3500 m, with a return to undersaturation below about 3500 m. In contrast to other stations in the Pacific (Fig. 6) or the Southern Ocean (Figs. 1 and 2), we have found that the whole water columns at GEOSECS station 293 (52°S 178°W South-East of New Zealand) and station 282 (57°S 169°E, south of New Zealand) are undersaturated with a maximum SI of 0.7 (Fig. 7). Despite their low latitude, these stations are still situated north of the Polar Front in

Table 1
Locations of the GEOSECS and INDIGO 3 stations investigated in this work

	Station	Location	Station	Location
GEOSECS Southern Ocean	74	55°S 50°W	82	56°S 24°W
	76	57°S 68°W	89	60°S 0°E
	78	61°S 62°W	287	69°S 173°W
	91	49°S 11°E		
INDIGO 3 Southern Ocean	82	67°0′S 68°3′E		
GEOSECS Atlantic Ocean	3	51°N 41°W	48	4°S 29°W
	11	63°N 35°W	54	15°S 29°W
	18	70°N 0°W	56	21°S 33°W
	19	64°N 5°W	60	32°S 42°W
	23	60°N 18°W	93	41°S 18°E
	29	35°N 47°W	103	24°S 8°E
	33	21°N 54°W	111	2°S 14°W
	37	12°N 50°W	115	28°N 26°W
	40	3°N 38°W		
GEOSECS Pacific Ocean	204	31°N 150°W	241	4°N 179°E
	212	30°N 159°W	263	16°S 167°W
	215	37°N 177°W	296	44°S 167°N
	217	44°N 176°W	331	4°S 125°W
	219	53°N 177°W	337	4°N 124°W
	224	34°N 151°W	343	16°N 122°W
	226	30°N 170°E	282	57°S 169°E
	227	25°N 170°E	293	52°S 178°W
GEOSECS Indian Ocean	418	6°N 64°E	445	8°N 86°E
	420	0°S 5°E	446	12°N 84°E
	424	12°S 53°E	447	5°N 79°E
	429	47°S 57°E		
GEOSECS Red Sea	407	19°N 38°E		

sub-Antarctic waters (Orsi et al., 1995). At these two locations, the SI vs. depth plot (Fig. 7) is similar to that for the Atlantic depicted in Fig. 4.

(4) The shape of the SI vs. depth curves for the Indian Ocean (GEOSECS stations 418, 420 and 424) is similar to that for the Pacific, but saturation is merely approached at intermediate depths with a maximum saturation index of 0.9 (Fig. 8). The same pattern is found at station 429 (47°S 57°W) as was found for stations 282 and 293 located at the same latitude in the Pacific, i.e., waters are undersaturated.

(5) At stations 445 and 446 situated in the Bay of Bengal, the Ba concentrations are among the highest recorded in the GEOSECS data. The Ba concentration increases linearly from about 50 nM in surface waters to about 100 nM at a depth 2000 m (Fig. 9). Below this depth, the increase in Ba content is still linear, but with a lower slope. Our calculations reveal that surface waters are markedly undersaturated (Fig. 9). Perfect barite equilibrium is reached at depths below 2000 m up to the seafloor at 3500–3800 m. This peculiar situation may be linked to the supply of large amounts of Ba to the Bay of Bengal by the Ganges–Brahmaputra. This supply has been attributed to Ba desorption from clay minerals (Carroll et al., 1993) or to a submarine discharge of groundwater (Moore, 1997), although these two processes have been documented from data collected in shallow waters far north of the location of the GEOSECS stations. Broecker et al. (1980) have observed nutrient concentrations in deep and benthic waters at station 446, higher than those found at stations further south. They attributed this to the respiration and dissolution of organic matter that is being transported down the slope of the Ganges fan, rather than originating directly above and falling vertically. Recently, Schäfer et al. (1996) proposed a similar transport scenario to explain the large particle flux intercepted by sediment traps deployed in the deep northern Bay of Bengal. Dissolution of (or Ba desorption from) these particles could possibly lead to the high Ba concentrations found in deep waters at these locations.

At GEOSECS station 447 (south of Ceylon), our results show that the water column is saturated between 2000 and 3500 m, and then undersaturated below 3500 m up to the bottom at 4300 m (Fig. 10). This undersaturation at depth corresponds to a slight decrease in the Ba concentration below about 3700 m (Fig. 10).

(6) The Red Sea (station 407) is undersaturated with a saturation index of about 0.3 (Fig. 11). This is due to warm temperatures (above 20°C) and low Ba contents (about 50 nmol/kg) from the surface down to the seafloor.

4. The energetics of barite formation in the oceans: the role of biogenic and inorganic processes

The picture of the saturation state of the world oceans with respect to pure barium sulfate emerging from our results challenges the earlier statements of Chow and Goldberg (1960) and of Church and Wolgemuth (1972). First of all, equilibrium is reached in a number of places: cold surface waters of the Southern Ocean, waters at intermediate (2000–3500 m) depths in the Pacific, deep waters (2000–3500 m) of the Gulf of Bengal. When supersaturation is found, the saturation indices are still very close to unity. Indeed, the highest saturation index ($Q/K = 1.45$) is found for the surface waters at GEOSECS station 89 in the Southern Ocean in the Weddell Gyre. Apart from the above locations, the rest of the world's oceans is undersaturated.

Barite crystals have been found in the whole water column in the Atlantic Ocean (Dehairs et al., 1980). This contradicts our finding of seawater undersaturation at these locations. The formation of these crystals has been shown to be correlated to biota (Bertram and Cowen, 1997) and to 'a-biotic' precipitation in biogenic aggregates (Dehairs et al., 1980; Bishop, 1988; Stroobans et al., 1991). Living organisms responsible for barite precipitation have not yet been clearly identified in pelagic settings (Bertram and Cowen, 1997) It nevertheless appears that such organisms, if existing, have to follow an energetically unfavorable pathway in order to produce these crystals: they precipitate barite from undersaturated solutions. An example of such a process has already been clearly identified: Acantharians form celestite in ocean waters although seawater is unambiguously undersaturated with respect to strontium sulfate (Bernstein et al., 1992).

In fact, barite crystals in the ocean are not pure: they contain variable quantities of Sr although their

Sr contents generally reach only a few percent (Dehairs et al., 1980). It has been suggested that ''ocean waters in which pure barite appears to dissolve may actually be saturated with respect to (Ba,Sr)SO_4 of intermediate composition'' (Hanor, 1969). Substitution of strontium for barium in $BaSO_4$ has also been invoked to resolve the contradiction implied by the inference of barite dissolution in supersaturated Black Sea waters (Falkner Kenisson et al., 1993). It has also been suggested to explain the discrepancy between calculated barite solubility in seawater at 25°C and 1 bar and experimental values (Monnin and Galinier, 1988). Cation substitution in barites has been investigated by Church (1979) in a series of experiments that showed that the equilibrium value for Sr substitution in barite should be, at most, a few mole percent. Solubility measurements require that equilibrium is attained from both sides (supersaturation and undersaturation) in order to ensure that the dissolving solid has the same composition as the precipitating one. When solid solutions are involved, this reversibility is very difficult to obtain experimentally. Church (1979) states that precipitation of so-called synthetic marine barites during the ''more rapid addition [of solution] allows greater substitution [of Sr for Ba]''. In other words, the degree of substitution depends on the initial degree of supersaturation of the reacting solution and that equilibrium values obtained this way are not unambiguous. In a recent study, Prieto et al. (1993) used Lipmann's diagrams to show that solid barium sulfate in equilibrium with strontium-rich aqueous solutions must be an 'extremely strontium-poor solid solution' and that very high supersaturations must be achieved to reverse the pattern predicted at equilibrium. Our calculations point out the proximity of equilibrium between ocean waters and pure barite. Noting that strontium is about 1000 times more concentrated than Ba in ocean waters, the solid at equilibrium must be virtually pure barium sulfate when equilibrium is reached between seawater and barite, if we follow the conclusions of Prieto et al. (1993). This may explain the fact that our results show that the world oceans are, in any case, either at, or not too far from equilibrium with respect to pure barium sulfate. An extensive study of Sr distribution in marine barites as a function of pure barite saturation index would bring some insight into this problem.

The results depicted in Figs. 1, 2, 6, 8 and 10 show that Pacific and Southern Ocean waters at equilibrium with barium sulfate become undersaturated at greater depths where the dissolution of pure barium sulfate crystals become possible. So we propose to define a barite lysocline located between 3000 and 4000 m in the Pacific Ocean and between 2000 and 3000 m in the Southern Ocean. The whole Atlantic Ocean is undersaturated and the Indian Ocean is an intermediate case between the Atlantic and the Pacific Oceans.

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