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The saturation state of the world's ocean with respect to $(Ba,Sr)SO_4$ solid solutions

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Abstract

Barite is commonly found in suspended matter in ocean waters and in marine sediments. The calculation of the barite saturation index of the world's ocean waters has shown that the vast majority of the oceans are undersaturated with respect to pure barium sulfate, equilibrium being reached at a few locations like the Southern Ocean surface waters, deep waters of the Bay of Bengal or intermediate waters of the Pacific [Monnin, C., Jeandel, C., Cattaldo, T., Dehairs, F. 1999. The marine barite saturation state of the world's oceans. *Mar. Chem.* **65** (3–4), 253–261.]. It is thus paradoxical to commonly find barite in a globally undersaturated ocean. Strontium is the most common impurity in natural barite. It is often suggested that the Ba content of ocean waters is controlled by equilibrium with Sr-substituted barite, and not with pure $BaSO_4$. In order to address this problem, we have used the GEOSECS data (49 stations, 1404 data points) to calculate the saturation index of substituted barite in the world's ocean using Lippmann's description of thermodynamic equilibrium between a solid solution and an aqueous solution for the $(Ba,Sr)SO_4$ system. Recent studies indicate that the $(Ba,Sr)SO_4$ solid solution is most likely regular and continuous. The calculated saturation indices of the regular solid solution (with the interaction parameter A_0 equal to 1.6) are closer to those of pure barite than those calculated for the ideal solid solution. Conclusions previously reached for the pure barite case are not changed: the saturation state of ocean waters with respect to a regular solid solution is very close to that of pure barite. Sr-substitution for Ba in barium sulfate does not bring barite at equilibrium. When equilibrium is reached, the degree of Sr substitution of Ba amounts to only a few mole percent of Sr. Equilibrium values of the Sr content of the solid solutions in the intermediate (0.2–0.8) range are found for ocean surface waters where the Ba/Sr ratio is low, but as these waters are undersaturated, such solids are not stable in the water column. This provides another reason for the bimodal distribution of $(Ba,Sr)SO_4$ solid solutions in nature, on top of that induced by the large ratio of the end member solubility products. Equilibrium is found for cold waters (i.e. for temperatures below 5 °C) having a Ba content greater than about 70 nmol/kg. The distribution coefficient of Sr in barite can be calculated from the Ba and Sr concentrations of these samples and from the equilibrium Sr mole fraction of the solid solution obtained from Lippmann's diagram. It was found independent of pressure and it varies only slightly with the temperature of the sample. For the regular solid solution (with $A_0 = 1.6$), it is:

$$10^5 D^{\mathrm{Ba}}_{\mathrm{BaSO_4}}(\mathrm{regular}) = 10^5 \left[\frac{\dfrac{m_{\mathrm{Ba^{2+},aq}}}{m_{\mathrm{Sr^{2+},aq}}}}{\dfrac{x_{\mathrm{BaSO_4,SS}}}{x_{\mathrm{SrSO_4,SS}}}} \right] = 0.227t + 3.753.$$

This expression (which has been established for temperatures below 5 °C) can be used to directly calculate the composition of solid solutions at equilibrium with a given seawater sample, or conversely to know the Ba content of seawater at equilibrium with a given $(Ba,Sr)SO_4$ solid solution.

1. Introduction

In the ocean, the correlation between dissolved barium and biointermediate elements like alkalinity and silica

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(Chan et al., 1977; Jeandel et al., 1996), and the fact that Ba can be preserved as refractory barite in the sedimentary record have generated numerous studies for the use of this element as a proxy in paleoceanography. The presence of barite is commonly reported in suspension in the water column (Jacquet et al., 2004; Sternberg et al., 2005) and in sediments (Van Beek et al., 2003). On the other hand, thermodynamic calculations have established that the world ocean is globally undersaturated (Monnin et al., 1999; Rushdi et al., 2000). This paradox underlines the question of the mode of formation of marine barite and their stability in the marine environment.

There is an obvious role of living organisms in barite formation (see the discussion in Sternberg et al., 2005), some living organisms being able to directly form barite within their cells (Gooday and Nott, 1982). It is also commonly accepted that barite saturation can be reached in microenvironments of decaying organic matter (Dehairs et al., 1987). On the other hand, Acantharia build their skeleton with strontium sulfate (celestine), which incorporates as much as 10 mol% of barium (Bernstein et al., 1992). Celestine formation by Acantharia is a case of mineral formation in a thermodynamically unfavorable pathway. When these organisms die, their skeletons dissolve in the surrounding water (which is largely undersaturated with respect to celestine), and barium is then released to the aqueous phase. This leads to a local enrichment of barium and therefore to the inorganic formation of barite, that may in turn incorporate some strontium (Bernstein et al., 1992).

This latter mode of formation of marine barite directly addresses the influence of impurities on barite stability. It can be shown that a solution at equilibrium with a solid solution is always undersaturated with respect to the pure end members, although this undersaturation may be very slight when the difference between the endmember solubility products is large (Glynn and Reardon, 1990). It can then be postulated that the world ocean, which is globally undersaturated with respect to pure $BaSO_4$ (Monnin et al., 1999), may in fact be at equilibrium with Sr-substituted barite. This would provide an explanation of the barite paradox.

The geological/oceanographic problem is that of the stability of barite in the marine environment. Modeling first translates this problem into the calculation of the solubility (or equivalently the saturation index) of a solid phase used as a model for natural barite in a model system for seawater. Marine barites (the natural products, with their impurities, crystal defects, poor crystallinity, etc.) have been represented so far by pure solid barium sulfate (Monnin et al., 1999; Rushdi et al., 2000), although the question of Sr-substitution in marine barite has often been addressed (see below). Thermodynamic models for seawater are numerous. They can differ by the number of species they take into account, by the methods used to calculate the thermodynamic properties of the dissolved species and by the temperature, pressure and concentration ranges they can account for. A lot of effort has been made to improve our ability to calculate the thermodynamic properties of electrolyte solutions in general, and natural waters like seawater in particular. Among many others, Monnin (1999) has elaborated a model based on Pitzer's ion interaction approach to calculate the solubilities of barite and celestine in the $Na–K–Ca–Mg–Ba–Sr–Cl–SO_4–H_2O$ system as a function of solution composition, temperature and pressure. This model has been used by Monnin et al. (1999) to address the problem of barite stability in seawater by calculating the saturation state of barite in the world ocean using mainly the GEOSECS data base. It could be objected that the $Na–K–Ca–Mg–Ba–Sr–Cl–SO_4–H_2O$ system does not take into account dissolved species or compounds (like carbonate or bicarbonate, low molecular weight organic acids, colloids, etc.; Putnis et al., 1995) that may build complexes with aqueous barium in seawater, therefore changing its thermodynamic properties. Strong complexing generally lowers the total activity coefficients of dissolved electrolytes. This would lead to a decrease in the barite saturation index, thus worsening the barite paradox. The extension of the description of the aqueous phase at the level of accuracy reached by models based on Pitzer's ion interaction approach should be given some attention, despite the large research effort its requires.

The influence of strontium substitution on barite stability in the marine environment has been addressed in early papers on this topic (Hanor, 1969; Church and Wolgemuth, 1972). We here take advantage of recent progress in the study of aqueous solution–solid solution systems (Glynn and Reardon, 1990; Konigsberger and Gamsjager, 1992; Prieto et al., 1993; Prieto et al., 1997; Glynn, 2000; Astilleros et al., 2003). The present work presents the calculation, based on Lippmann diagrams, of the saturation state of the world's ocean with respect to, and the composition of, Sr-substituted barite at equilibrium with seawater. These calculations have been carried out for the 1404 seawater samples collected at the 49 GEOSECS stations for which the Ba content is reported (Ostlund et al., 1987), which provides a view of the global ocean.

2. Depicting thermodynamic equilibrium in the Lippmann diagram

By analogy with classical temperature–composition phase diagrams, Lippmann (Lippmann, 1980, 1982) has constructed a diagram that allows the calculation of the composition of solid solutions at equilibrium with aqueous solutions. We write here the various expressions for the case of a $(Ba,Sr)SO_4$ solid solution. The general theory can be found in Glynn (2000); Glynn and Reardon (1990) and Lippmann (1977, 1980, 1982). The conditions for thermodynamic equilibrium can be expressed as: