

Baryte stability in ocean waters and in marine sediments: a thermodynamic approach

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The question of the eventual limitation of the barium concentration of open ocean waters has been addressed by Church and Wolgemuth (1972) who, from the limited data and the thermodynamic models available at that time, proposed that 'the Ba concentration of the entire seawater column in the Eastern Pacific and probably most of the world's oceans seems to fall below the baryte saturation curve'. This statement has been widely accepted. In order to reconsider the problem of baryte stability in marine environments in light of the now available large body of data on Ba concentration in natural waters, a new model of baryte solubility in the Na-K-Ca-Mg-Ba-Sr-Cl-SO₄-H₂O system has been built (Monnin, 1995, 1998). It is based on Pitzer's formalism for the properties of the aqueous phase and on revised values of the baryte solubility product as a function of T and P. It is duly parametrized from baryte solubility data in simple electrolyte solutions taken from the literature. Its validation (testing of model predictions against data) shows that baryte solubility can be predicted within experimental accuracy from 0 to 200°C and to 1 kbar for moderately concentrated solutions (up to about 2M). This model is here used to calculate the baryte saturation index (Q/K) in ocean waters and in interstitial waters of oceanic sediments from aqueous solution compositions and in situ measured temperatures and pressures.

Baryte saturation state of the world's ocean

Monnin *et al.* (1998) have used data for about 50 GEOSECS stations for which Ba concentration in

seawater is reported. We find that equilibrium between baryte and seawater (i.e. Q/K between 0.9 and 1.1) is reached in a number of places: cold surface waters of the Southern Ocean, waters at intermediate depths (2000–3500m) in the Pacific, deep waters (2000–3500 m) of the Gulf of Bengal. The only location for which a slight baryte supersaturation is found are the surface waters at GEOSECS station G89 in the Weddell Gyre (Q/K ≈ 1.5). Besides these locations, the rest of the world's ocean is undersaturated. There is a return to undersaturation of the water column at depths of about 3500m in the Pacific and of about 2500m in the Southern Ocean. The reverse is found for GEOSECS station 446 in the Gulf of Bengal: surface waters are undersaturated and equilibrium is reached below 2000m. Also our results are in agreement with those of Falkner *et al.* (1993) who found that the Black Sea anoxic deep waters are supersaturated (Q/K ≈ 2).

Baryte stability in marine sediments

During ODP Leg 168, interstitial water samples have been collected by squeezing sediment cores retrieved in 10 holes drilled along a 100 km transect in the Eastern flank of the Juan de Fuca ridge. In situ temperatures range from 2° at the seafloor to a maximum of 63°C at the sediment-basement interface. Pressure is around 300 bar. Major elements have been analysed on board the Joides Resolution (Davis *et al.*, 1997). About 200 samples were analysed for Ba and Sr by ICP-MS in Toulouse. There is an overall control of the aqueous Ba

concentration by an equilibrium with BaSO₄, throughout the sediment column, as indicated both by the fact that, when sulphate drops to low concentrations, Ba is high, and vice versa, and by our calculations. The porewater Ba concentration can be very large, reaching as much as 300 μM/kg at site 1027, which makes it larger than that of Sr. We find that, near the sediment-water interface at all sites, there is an increase in the baryte saturation index (up to 5 to 10) with a return to equilibrium at a few tens of meters below seafloor, as best seen at site 1028. This baryte supersaturation at the top of the sediment column does not exist at sites 1030 and 1031 where upwelling of high-sulphate low-alkalinity basaltic fluids wipes out the effect of diagenetic reactions (like sulphate reduction). At sites where sulphate concentration drops below 1mM/kg, there is a significant baryte supersaturation (Q/K up to 15) in the zone of sulphate depletion. At site 1026, we found baryte undersaturation at depths corresponding to sandy layers for which there was no core recovery for the 1027 site located only a few km away from 1026. Porewater samples close to the sediment-basalt interface are in general at equilibrium with baryte, although the basaltic fluid sample collected with the WSTP tool at site 1026, is largely undersaturated (Q/K ≈ 0.2) at the in situ conditions (63°C, 300 bars). Calculations carried out for sites 717 and 718 in the Bay of Bengal (ODP Leg 116) show the same features: general baryte equilibrium with zones of baryte supersaturation.

Several reasons can be invoked to explain this supersaturation: 1) artifacts in the ODP porewater sampling procedure (sediment squeezing), 2) re-equilibration of the solution with baryte at room temperature, 3) impurities in baryte enhancing its

solubility, 4) slow baryte precipitation kinetics at low temperature and in situ pressure, 5) complexation of aqueous barium by a ligand not taken into account in the model, leading also to an increase in solubility. The fact that we are able to show that equilibrium is reached rules out 1) and 2). Prieto *et al.* (1993) have shown that solid barium sulphate in equilibrium with strontium-rich solutions must be an extremely strontium-poor solid solution, which excludes the role of impurities to explain the observed supersaturation. The fact that we find zones of baryte supersaturation at the top of the sediment column at the beginning of the organic matter transformation favours the idea that a barium-complexing ligand may be released into solution. It cannot be a carbonate species because the observed supersaturation is not linked to the alkalinity increase due to sulphate reduction, but may be to some organic compound produced by the transformation of organic matter in anoxic environments.

References

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