Biotic and abiotic controls of the barium distribution in the Southern Ocean water column

T. Cattaldo
F. Dehairs
Department of Analytical Chemistry, Vrije Universiteit Brussel, Pleinlaan 2, B-1050, Brussels, Belgium

C. Jeandel
UMR5566 ,CNES-GRGS, 18, Ave E. Belin, 31401 Toulouse Cx 04, France

C. Monnin
Laboratoire de Géochimie, Université Paul Sabatier, 38, Rue des 36 Ponts, 31400, Toulouse, France

N. Metzl
Laboratoire de Physique et Chimie Marine, URA 2076/CNRS, Université Pierre et Marie Curie, T. 24-25, 4 Place Jussieu, 75230 Paris Cx 05, France

Besides mixing, the dissolved barium distribution in the oceanic water column is controlled to a significant extent also by particle–solute interaction. *In vitro* uptake experiments involving diatom cultures suggest that passive uptake prevails over active uptake. The overall effect of these processes is that barium behaves as a non-limiting nutrient element with ratios of dissolved over particulate concentrations varying between 100 and 1000. Uptake of barium by plankton particles eventually results in the formation of barium sulphate (baryte). There is increasing evidence that this baryte formation is closely linked with the formation of micro-environments composed of detrital organic matter, in which $BaSO_4$ saturation is eventually reached during the process of bacterial decay (Bishop, 1988; Dehairs *et al.*, 1980). This mechanism sets the link between oceanic baryte and oceanic productivity and as a result oceanic baryte is now increasingly recognised to represent a good proxy for palaeoproductivity (Francois *et al.*, 1995).

Using an extensive data set obtained mainly from the Southern Ocean we investigated the different main processes affecting the oceanic barium cycle. For particulate barium in surface waters regional variability can be important and this is clearly associated with variation of planktonic production and biomass such as occurring, for instance, across the Polar Front Zone (PFZ). We observed that on a time scale of approximately three weeks water column stocks of micro-crystalline baryte co-vary with seasonal change in surface water productivity (Dehairs *et al.* 1997). This phase lag of about three weeks is consistent with the time lapse required for baryte to be formed during *in vitro* experiments using decaying detritus from a diatom culture. This process of baryte formation is invoked, next to advective transport, to explain the occurrence of a conspicuous dissolved barium minimum in the upper water column (temperature minimum waters) of the PFZ in the Indian sector. Using mass balance calculations in which advective and diffusive transport of dissolved barium is taken into account, a barium consumption term is calculated (~ 1 μmol m^{-2} d^{-1}) which is similar to estimates of barium uptake rates and baryte production rates for the mesopelagic water column. This stresses the original role of plankton activity in the oceanic barium cycle. The synthesised baryte can be released back into the water column as discrete micro-crystals at breakdown of the carrying biogenic aggregate phase or can be transported to the sediments when associated with large and fast settling aggregates such as fecal pellets. Those crystals released into the water column may evenually redissolve, depending on ambient $BaSO_4$ saturation conditions. Calculations of baryte saturation conditions (Jeandel *et al.*, 1996; Monnin *et al.*, 1997) indicate significant undersaturation (saturation index $\leqslant 0.75$) for the entire water column in the Sub-Tropical and Sub-Antarctic zones. South of the PFZ, however, baryte saturation conditions are reached in the upper 1000 m (53°S) to 2000 m (65°S) of water column (saturation index between 0.9 and 1.05). Below these depths undersaturation conditions again prevail with the exception of Antarctic slope and shelf region, where conditions of $BaSO_4$ saturation may reach down to the seafloor. Thus, it appears that for a large part of the Southern Ocean deep water column, conditions prevail that favour dissolution of the water column released baryte micro-crystals. Using a multiple end-member mixing model, intermediate and deep water column dissolved barium profiles were reconstructed as resulting from pure conservative mixing. By comparing these results with observed concentrations the effect of conservative mixing versus production-consumption is evaluated and compared with conditions of $BaSO_4$ saturation. This approach allows to constrain the uncertainties associated with the thermodynamic and hydrodynamic model calculations.

Overall our results contribute to a better understanding of the oceanic cycle barium, which is an essential step for proper utilisation of baryte as a proxy for past productivity.

References

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