

Uptake of Barium from Vermiculite by the Bacterium *Pseudomonas fluorescens* - New Indications for Barium as a Palaeoproxy

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Abstract: The apparent association of biogenic barite (BaSO_4) and organic matter in marine sediments has given support to the idea of using Ba as a proxy for palaeoproductivity. Despite this general acceptance only a few unicellular organisms (acantharian, diatoms) are known to incorporate barium. In this work, we show that the bacterium *Pseudomonas fluorescens* is able to take up barium. Because natural seawater harbors numerous bacteria many of which may take up Ba, this uptake of Ba explains why it may be considered a palaeoproxy. The introduction of this article reviews briefly what is known to date of Ba as a palaeoproxy, and what is known about bacterial interaction with Ba. Like other trace elements such as Fe, Mn and Sr, Ba can be extracted from vermiculite by *Pseudomonas fluorescens* and some mutants derived from it. Barium, therefore, seems to be as important a factor in bacterial metabolism as iron or other trace elements. The incorporation of Ba by living bacterial cells in the marine environment and its release from these cells upon their death and subsequent decay can contribute to Ba accumulation in marine sediments.

Keywords: Barium, bacterial metabolism, marine sediments, palaeoproductivity.

INTRODUCTION

The first description of the use of barium as a proxy for biological palaeoproductivity based on its association with the decomposition of organic matter and its enrichments in marine sediments was published by Goldberg and Arrhenius [1]. Since then this particular concept has been used by numerous authors (e.g. [2-14]).

Several authors [4, 15, 16] point to a fundamental aspect of the use of barium as a geochemical proxy: Ba seems to be an ideal proxy because barite (the main carrier of barium) is not as labile as organic matter or carbonate. The biogeochemical cycle of carbon has a major influence on the Earth's climate system. Variations in atmospheric CO_2 are assumed to result from changes in ocean productivity by the burial of carbon derived from the atmosphere into the sediment, continental weathering, CO_2 degassing from volcanoes, CO_2 production at mid-ocean ridges and LIPS (Large Igneous Provinces). Therefore, to estimate present and past primary production concerning sediments, sediment proxies other than organic matter or carbonate are needed. These sediment proxies have to reflect a strong correlation between productivity and their distribution in the sedimentary record.

The suitability of barium as a proxy of oceanic palaeoproductivity is nowadays widely accepted, at least for oceanic areas outside the direct influence of terrigenous and hydrothermal inputs (e.g. [4, 9, 17-20]).

Barium distribution in seawater is characterized by surface water depletion and deep water enrichment (e.g. [21, 22]) or lowered concentrations in surface waters without reaching depletion [19, 23, 24]. Barium exhibits a nutrient-like profile which is indicative of Ba transport in biological debris (e.g. [3, 25, 26]). The association of Ba with biogenic particles is supported by the fact that sediments underlying highly productive surface waters are considerably enriched in Ba (see [1, 2, 4, 7, 8, 27-29]). In Dehairs *et al.* [8] it is stated that barite micro-crystals are an ubiquitous component of oceanic suspended matter and its biologic production in surface waters and their subsequent dissolution with depth plays a major role in the oceanic Ba cycle (see also [19, 24]). In Chow and Goldberg [27] it is considered that the formation of barite could take place in supersaturated microenvironments composed of biogenic detritus [6-8, 19, 24, 28, 30].

Several observations indicate that biochemical processes are involved in the formation of BaSO_4 in the water column. It has been suggested by Dehairs *et al.* [8] that uptake of Ba by organisms and their debris is a vital mechanism for the accumulation of barium. In Turekian [31] the particular distribution of Ba in sediments is described and explained by the production of barium sulphate crystals in association with biological activity. Moreover, the Ba content of suspended matter is positively correlated with plankton activity [32].

The involvement of barite in some biological processes has been confirmed by the observation of barite crystals within the protoplasm of abyssal benthic Rhizopoda of the class Xenophyophorida [33, 34]. Active intracellular production of barite is known to occur for some marine and freshwater algal and protozoan species [35-38] as well as in

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bacteria [39]. It has also been shown that barite crystal formation occurs in association with phytoplankton activity [28, 40, 41].

Various other organisms were proposed to incorporate Ba in their life processes. In Bernstein *et al.* [25, 42, 43] the incorporation and subsequent release after decay of Ba from marine protozoans of the genus *Acantharia*, which secrete skeletal and cystic structural structures composed of celestite (SrSO_4) is documented. Other authors have also reported the presence of traces of barium in acantharian celestite [44-46]. Because of the good correlation between dissolved barium and silicon within the water column, the distribution of both elements is often proposed to be governed by the dissolution of Ba-enriched siliceous frustules, e.g. from diatoms [7, 47-53]. In Ganeshram *et al.* [54] and Sternberg *et al.* [55] details about the experimental uptake of barium by phytoplankton and diatoms are presented, respectively. In Dehairs *et al.* [14] the bacterial influence of barium accumulation in marine sediments is first described.

Müller [56] represents one of the few articles ever published about the uptake of trace metals by a bacterium (*Pseudomonas fluorescens* strain CHA0 and mutants derived from it) from geological material like clay. The attention was turned to the removal of trace metals from clay minerals because clay minerals are omnipresent in natural soil, subsoil and rocks including marine sediments. Bacteria are also able to sequester trace elements in their cell wall and to release them again (e.g. [57, 58]). Macronutrients like K, Na, Ca, Mg, Al and NH_4 as well as trace element micronutrients like V, Mn, Fe, Co, Ni, Cu or Zn are widely found in bacterial metabolites. Because of their low concentrations in most environments, metals and trace elements require organic ligands for their transport. Besides Fe, trace elements like Cu, Zn and Mn seem to play a major role in biocontrol activity of bacteria (e.g. [59, 60]). Experimental results indicate a net uptake of barium by all the bacterial strains used for these investigations. Barium, therefore, appears to play an important role in bacterial metabolism as does iron and other trace elements. In contrast to barite (BaSO_4 , the main mineral carrier of Ba), all carbon bearing products of metabolism are nonpermanent. Consequently bacteria exhibit a major source of barium available for sedimentary accumulation. The objective of this study was to show definitively that the incorporation of barium during bacterial metabolism and its release upon decay of the prokaryotes leading to accumulation of barium in sediments.

MATERIALS AND METHODS

Sample Preparation

Vermiculite supplied by Thermex, Austria, was used for all the experiments. Prior to use, the vermiculite was expanded by heating with concentrated H_2O_2 (30%), in order to remove all organic material, and crushed with a mixer and either oven (60°C) or air dried. The dry vermiculite was ground in a mortar down to a particle size range from 1 to 80 μm .

A 30 g-quantity of vermiculite was dispersed in 1 L of growth medium containing 25 mM NaH_2PO_4 , 25 mM Na_2HPO_4 (buffer to maintain the pH throughout the

experiments at about 6.8), 7.6 mM $(\text{NH}_4)_2\text{SO}_4$, 1.7 mM NaCl, 10 mM glucose and 10 mM mannitol. The growth of *Pseudomonas fluorescens* during the experiments was monitored by measuring the optical density of the slurries with and without bacteria by UV spectroscopy.

After a two week incubation period the vermiculite was freed from the bacteria by ultrasonic sound treatment of five minutes. The supernatant was removed after centrifugation and the vermiculite air dried. Fused glasses of the vermiculite samples were prepared by mixing a 5:1 ratio of flux ($\text{Li}_2\text{B}_4\text{O}_7$) and the finely ground samples for the analysis of trace elements by Laser Ablation ICP-MS.

XRF and LA-ICP-MS

XRF analysis of the fused glasses in order to determine major elements to be used as internal standards for LA ICP-MS were carried out routinely at the Institute for Mineralogy and Petrography at ETH Zürich using a wave-length dispersive X-ray fluorescence spectrometer (WD-XRF, Axios, PANalytical).

The LA ICP-MS analyses of major, minor and trace elements were performed using a pulsed 193 nm ArF Excimer laser (Lambda Physik, Germany) with a homogeneous beam delivery prototype system similar to a Geolas (Microlas, Germany) in combination with an ELAN 6100 DRC (Perkin Elmer, Canada) ICP-MS [61].

Data analysis was undertaken using the software LAMTRACE and in-house spreadsheets following methods previously described [62, 63].

Limits of detection were calculated for each element and established at three times the standard deviation of the background signal (measured before laser ablation) divided by element sensitivity during the respective ablation.

A complete description of the procedures established for the batch experiments and the analytical procedure has been published [56, 64, 65].

RESULTS

Originally we examined our vermiculite samples for the presence of 30 trace elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, W, Tl, Pb, Bi, U). All trace elements with the exception of barium were presented and discussed in Müller [66]. The results of the analyses of barium are published separately because of the significance of this element as a palaeoproxy.

As soon as the concentration of a particular element in vermiculite mixed with bacteria is statistically significantly lower than in the original vermiculite and the abiotic control, the interpretation is that the element has been taken up by the microbes. The supernatant solution was scanned by AAS (Perkin Elmer 1100) for a variety of trace elements but no significant content concerning the trace elements of interest were detected. For a complete description of the analytical procedures established for the batch experiments and the analytical procedure see [56, 64, 65].

All the secondary metabolites produced by the wild type CHA0 and the various mutants show the ability to complex a variety of these trace elements (see tables 1 and 2 in Müller [56]). Whereas macronutrients like C, O, N, H, P, Ca, Mg, K, S, Na and Cl constitute the bulk of the bacterial cells (e.g. [67, 68]), many trace elements and metals are found specifically in proteins: Among those are V, Mn, Fe, Co, Ni, Cu, Zn and Ba [69]. Table 1 exhibits the results of the LA ICP-MS analysis of barium. Fig. (1) illustrates these results of the statistical analyses. All the bacterial strains incorporated barium in trace amounts. The distribution pattern of the barium uptake by the microbes is very similar to those for Fe, Mn, Sr, Y, La and Ce (for details see Müller [56]).

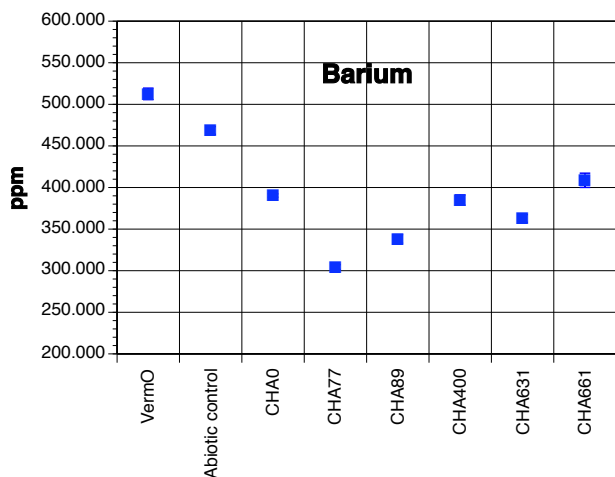


Fig. (1). Barium concentrations with their respective error bars (proportional to the standard deviation which is commonly smaller than the symbol) for all of the samples analyzed.

DISCUSSION AND CONCLUSION

In the introduction of this article a brief review of what is known to date of Ba as a palaeoproxy, and what is known about bacterial interaction with Ba was given. Therefore, the discussion will be focused on the incorporation of Ba as a trace element on bacterial metabolism and to illustrate this way the new insights of Ba to be used as a paleoproxy.

Müller [56] described the uptake of various trace elements (Mn, Fe, Co, Cu, Zn, Sr, Y, Zr, La, Ce, U) by *Pseudomonas fluorescens* strain CHA0 and its genetic derivatives. The uptake of barium, as outlined above, completes this picture. Different alternatives concerning incorporation of trace elements by bacteria include: (1) uptake of trace elements into the cells or cell walls; (2) incorporation in coatings on the clay mineral; (3) storage of

elements in biofilm and (4) incorporation of trace elements in proteins, enzymes and other products of bacterial metabolism. All these mechanisms concerning barium deserve consideration as the inclusion of barium in bacterial metabolism and the further release of Ba upon decay of the procaryotes presents a basic process for its accumulation in sediments and the use of Ba as a palaeoproxy.

In Vahrenkamp [70] a comprehensive overview concerning metals in life processes is provided. Like other metals, barium can either be toxic (as soluble compound) or harmless (in the form of the hardly soluble mineral barite (BaSO₄)).

Unfortunately, little is known about the role of barium in bacterial cells because Ba is not as frequently used as a trace element for life processes by bacteria as are Na, K, Ca, Mg, and Fe but it nevertheless an important share concerning bacterial metabolism. To illustrate this fact, it is pointed out that almost all of the most abundant elements within the earth’s crust exhibit a lower atomic number (30) than zinc which, in turn, is the last element of the first transition row of the periodic table of the elements. Only Rb, Sr, Zr and Ba are more commonly than Zn within the earth’s crust. The most abundant elements within the earth’s crust play a major role concerning the metabolism of all sorts of life forms [70].

In Goytain and Quamme [69], ACDP2 (ancient conserved domain protein) is reported to be a divalent metal transporter including Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺, Sr²⁺ and Ba²⁺. The ACDP family proteins are conserved in some form from bacteria to man and women (see also [71]). In Goytain and Quamme [69] the authors concluded also that the cellular accumulation and intracellular distribution of the above mentioned divalent cations may be changed with magnesium deficiency. The interaction between several heavy elements (Al, Ba, Cd, Co, Cr, Cs, Cu, Fe, Ga, Mn, Ni, Rb, Pb, Si, Sn, Sr, Ti, U, and Zn) and three different *Bacillus* isolates were studied in [72]. The ability to interact with the elements mentioned was investigated in vegetative cells and spores of *Bacillus* strains as well as those of the corresponding reference strains *B. cereus* ATCC 4415, *B. megaterium* NRRL B5385, and *B. sphaericus* NCTC 9602. Cells and spores were capable of taking up Ba. *B. sphaericus*/JG-A12 and *B. cereus*/JG-A30 shared almost the same binding capability to each particular metal ion involved in the experiments including Ba.

In Dong *et al.* [73], the authors published an article about the adsorption of lead, cadmium, copper, zinc and barium on freshwater surface coatings. Ba is reported to be the least adsorbed element among those used in the study. In Xiong *et al.* [74], six deep-sea proteolytic (decomposing) bacteria taken from Aleutian margin sediments (a deep-sea environment), which produced different proteases (enzymes

Table 1. Concentration (in ppm) and confidence interval for barium as determined by LA ICP-MS in vermiculite. The original vermiculite is denoted VermO. Vermiculite from blank slurries (containing the nutrient medium and vermiculite only) is named abiotic control. The vermiculite altered by the bacteria is labelled according their genetic name CHA0, CHA631, CHA77, CHA89, CHA400 and CHA661). All concentrations are averages of three measurements per glass pill.

	Verm0	Abiotic Control	CHA0	CHA77	CHA89	CHA400	CHA631	CHA661
Barium	513±6.92	469±4.62	390±2.03	304±2.9	338±5.11	385±6.14	363±4.71	409±8.55

which hydrolyze proteins), were studied. Various cold-adapted proteases were formed by the bacteria *Pseudoalteromonas issachenkonii* as well as by the psychrophilic bacteria *Pseudomonas strain DY-A*. These specific bacteria are living permanently in cold environments ranging from the deep sea to mountain and polar regions. The authors tested the effect of different divalent cations on protease activity. Among these cations Ba exhibited an influence on the relative activity of protease E1.

To complete the overall picture, in a short excursus, the role of bacteria and their remnants in the geological record will be depicted. Deep drilling into the marine floor has uncovered a vast sedimentary ecosystem of microbial cells (e.g. [75]). The same authors show that in subsurface sediments within a wide range of oceanographic settings, intact polar membrane lipids (biomarkers for the presence of live cells) were attributable to archaea and bacteria. The widespread occurrence of extended hopanoids (class of compounds, that have various functions in prokaryotes) in sediments illustrates the importance of bacterial lipid contributions to geological materials [76]. Terrestrial and marine bacteria and archaea (and their remnants after decay) can be useful as biomarkers in palaeoenvironmental investigations (e.g. [77-79]). It is pointed out that biomarkers can also be associated with planktonic bacteria [80]. Biomarker analyses of anoxic marine sediments showed bacterial fatty acids with strong ^{13}C depletion that are likely products of sulphate-reducing bacteria [81].

The literature about barium involved in metabolic processes of bacteria remains scarce. In summary, it can be concluded that barium can be incorporated within various metabolic products or be involved in metabolic activities of bacteria and archaea. Barium, in turn, can be released from these forms of life upon their decay. If metabolic use of Ba by different forms of life (including freshwater and marine bacteria) could be demonstrated, the findings could lead to exciting new discoveries and to further support barium's use as a palaeoproxy.

CONFLICT OF INTEREST

The author confirms that this article content has no conflict of interest.

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