

# DISTRUBUTION OF FERRIHYDRITE IN SEDIMENTS AND ITS ROLE IN REGULATING GROUNDWATER ARSENIC EXPOSURE POTENTIAL

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The environment plays a key role in regulating the concentration of environmental toxins such as arsenic. Minerals are the matrix on which contaminants are retained, affecting both their aqueous concentrations and the transport properties. In some cases, minerals serve as either electron acceptors and donors for a variety of biogeochemical processes that affect the mineral form, surface area, and reactivity of sediments. This critical role is well established, yet surprisingly little is known about the distribution of some of the most important minerals in regulating arsenic concentration. Here, we quantify the concentrations of ferrihydrite in a variety of settings, and study the relationship between its concentration and dissolved arsenic levels from a variety of arsenic-affected environments. Ferrihydrite is a metastable mineral that only somewhat crystalline, and is highly reactive for both adsorption and microbially-mediate reduction. Its presence is often controversial given this metastability, yet the retention of arsenic and other ions is often not easily modeled with low surface area Fe minerals. Using a combination of sequential extractions and X-ray absorption spectroscopy to identify these phases, we find that there is clear evidence for the persistence of ferrihydrite or other poorly crystalline Fe(III) phases even in tropical environments where rapid Fe cycling often is assumed to convert it to hematite and goethite. We attribute the stability of these nanoparticulate forms of Fe(III) to the presence of adsorbed silicate or phosphate or other phases on the mineral surface in these environments. A critical factor in the identification of this phase involves the differentiation of crystalline minerals that have distinct, but variable spectral signatures depending on factors such as morphology and particle size. The distribution of ferrihydrite and Fe(III) in sediments also appears affect As speciation, possibly by affecting Fe reduction. While ferrihydrite is found, it often appears to be less effective at minimizing aqueous As levels than crystalline oxides.

# A new look on the barium cycle: Stable barium isotope fractionation in ODP sediments and calibration experiments

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We show by the analysis of the stable barium isotope composition ( $^{137}\text{Ba}/^{134}\text{Ba}$ ) of natural marine barite ( $\text{BaSO}_4$ ), that significant isotope fractionation takes place in the marine biogeochemical barium cycle. We have combined previous measurements of the S and O isotopic composition with new Ba isotope ratio determinations. We find that biogenic marine barites separated from sediments collected in different parts of the world's Ocean with ages up to about 55 million years fall within a close range and have isotope ratios comparable to recently reported value for continental barium-bearing minerals (von Allmen et al., 2010). Whereas, cold seep barites, show isotope values close to modern biogenic barite, marine hydrothermal samples are enriched in the lighter isotope. Highest  $^{134}\text{Ba}$ -enrichments are found in authigenic barite minerals formed above black shales in the deep sediments of ODP Leg 207 that are depleted in sulfate due to AOM-triggered microbial sulfate reduction.

Laboratory experiments were conducted to investigate the potential of different low-temperature reactions to result in barium isotope discrimination. These reactions include adsorption of dissolved Ba on  $\text{MnO}_2$  and kaolinite, and the precipitation of anhydrous  $\text{BaCO}_3$  and  $\text{BaSO}_4$  under different experimental conditions (reaction process and temperature). The Ba minerals were generally enriched in light Ba compared to the aqueous solution, to magnitudes depending on precipitation conditions.

As an important finding, we can conclude that diagenetic barites at ODP Leg 207 record coupled transport induced isotope discrimination, probably superimposed by desorption/adsorption processes in the sulfate-depleted part of the sediment column. Despite the relatively short residence time, the barium isotopic composition of primary barites seem to have been relatively constant through the past 55 m.y.

It should be noted that S and O measurements of a Cambrian barite sample from China showed the influence of microbial sulfate reduction and were accompanied by a depletion in the heavy Ba isotope comparable to our findings from ODP Leg 207.

[1] von Allmen et al. (2010) Chemical Geology 277, 70-77.