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Biologically induced nanomineralization: Specific biosignatures of biogeochemical relevance?

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Mineralization processes promoted by prokaryotic cells in various terrestrial environments are often generating minerals of nanometric sizes, first due to the characteristic sizes of the cells themselves. A first important question is that of the evolution of such biologically induced nanominerals by aggregation, recrystallization, or dissolution. For example, the occurrence of 1-3 nm ZnS particles at the vicinity of sulphate-reducing bacteria has been described by several authors but the processes by which these particles nucleate within or at the proximity of cells, and by which they aggregate to form clusters of ca 100 nm remain to be understood. The importance of such phenomena for detoxification and immobilization of heavy metals will be discussed.

A second question, general to all nanocrystals, is that of the stabilization of structures that differ from the bulk. The stabilization, in biological hydrothermal environments, of mixed valence ferrihydrites which normally should rapidly evolve to spinel-structured crystals will be described. The formation of nanometric-sized amorphous or crystalline metastable carbonates and phosphates by bacteria and the potential meaning of these processes for global carbonate and phosphate biomineralization will also be examined.

A third question is that of the exact relationships between the biological induced nanominerals and the cells. Cases in which the production of nanominerals obviously kill the cells will be investigated. Methods for studying the interface between micro-organisms and minerals with very high spatial resolution will be shown. We will discuss whether the covering of cell walls by 1-3 nm ferrihydrite domains clustered into ca 100 nm domains, as observed by several authors, is due to cell activity or to passive adsorption. A particular example will be shown in which cell metabolism is a consistent explanation.

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Structure and reactivity of nano-crystalline As-Fe oxy-hydroxides in acid mine drainage

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Nano-crystalline or “amorphous” iron oxy-hydroxides are kinetically favored with respect to stable crystalline phases in low temperature environments. Therefore, they frequently occur as transient phases in Earth’s surface environments. They exhibit very-high surface areas (few 100 cm²/g) and thus play a key role in the geochemical cycles of minor and trace elements able to sorb onto their surface or to be incorporated in their structure. However, macroscopic modeling of sorption/growth/dissolution reactions affecting these phases is still limited by our incomplete knowledge of the actual structures of these reactive mineral colloids.

In the present communication, we compare the molecular structures of natural “amorphous” As-rich iron precipitates to those of iron end-members. This work is based on EXAFS and XRD investigation of biogenic nano-crystalline precipitates collected in acid mine drainage waters exhibiting exceptional arsenic concentrations [i].

Our data evidences the poisoning effect of As(V) and As(III) against the initial growth of nano-sized iron oxy-hydroxides nuclei : AsO₄ tetrahedra and AsO₃ pyramids easily share corners with FeO₆ octahedra ; AsO₃-FeO₆ edge-linkages also occur. These reactions limits the formation of edge-sharing octahedra chains in the iron oxy-hydroxides and hydroxy-sulfates structures. In a context of high As arsenic concentration (molar As/Fe = 0.5 – 1), this reaction leads to the formation of nano-sized and highly soluble As-Fe mixed oxy-hydroxides. In the AMD studied, natural aggregation and rapid sedimentation of these As-rich colloids progressively lowers the dissolved arsenic concentration upstream. Schwertmannite and ferrihydrite can therefore precipitate downstream, as As concentration decreases and pH increases. The remaining dissolved arsenic progressively immobilizes by forming weakly soluble complexes onto the surfaces of these minerals.

Reference

- [1] Morin et al. (2003) Bacterial formation of tooeleite and mixed As(III)/(V)-Fe(III) gels in the Carnoulès acid mine drainage, France. A XANES, XRD and SEM study. *Environ. Sci. and Technol.* **37**,1705-1712.