2.7.14

Bacteria are redox active sorbants that do not template nucleating hydrous ferric oxide

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We have used various materials characterization methods to study the synthetic precipitation of hydrous ferric oxides (HFOs) prepared either in the absence (abiotic, a-HFO) or presence (biotic, b-HFO) of nonmetabolizing bacterial cells (*Bacillus subtilis* or *Bacillus licheniformis*, ~10^8 cells/mL) and under otherwise identical chemical conditions, starting from Fe(II) (10^{-2}-10^{-4} M) under open oxic conditions and at different pH (6-9). We have also performed the first Mössbauer spectroscopy (MBS) measurements of bacterial cell wall (*Bacillus subtilis*) surface complexed Fe, where Fe(III) was added to cells under various (open oxic) conditions. We find that non-metabolic bacterial cell wall surface complexation of Fe affects Fe speciation in at least two ways: (1) it can reduce Fe(III) to sorbed-Fe^{2+} by a proposed steric and charge transfer effect and (2) it stabilizes Fe(II) as sorbed-Fe^{2+} against ambient oxidation. The cell wall sorption of Fe occurs in a manner that is not compatible with incorporation into the HFO structure (different coordination environment and stabilization of the ferrous state) and the cell wall-sorbed Fe is not chemically bonded to the HFO particle when they coexist (the sorbed Fe is not magnetically polarized by the HFO particle in its magnetically ordered state). This invalidates the concept that sorption is the first step in a heterogeneous nucleation of HFO onto bacterial cell walls. Both the a-HFOs and the b-HFOs are predominantly varieties of ferrihydrite (Fh) yet they show significant abiotic/biotic differences: Biotic Fh has less intra-particle (including surface region) atomic order (MBS quadrupole splitting), smaller primary particle size (magneto-metry blocking temperature), weaker Fe to particle bond strength (MBS center shift), and no 6-line Fh (6L-Fh) admixture (pXRD, magnetometry). Given the nature of the differences between a-HFO and b-HFO and their synthesis condition dependences, several biotic precipitation mechanisms (template effect, near-cell environment effect, catalyzed nucleation and/or growth effect, and substrate-based coprecipitation) are ruled out. The prevailing present view of a template or heterogeneous nucleation barrier reduction effect, in particular, is shown not to be the cause of the large observed biotic effects on the resulting HFOs. The only proposed mechanism (relevant to Fh) that is consistent with all our observations is coprecipitation with and possible surface poisoning by ancillary bacteriagenic compounds. When transposed to natural settings, our findings have several possible biogeochemical implications regarding Fe cycling, in the photic zones of water columns in particular.

2.7.15

Silica colloid aggregation by cyanobacteria: A microbial silicification mechanism

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Active deposition of silica is an important geological process in many geothermal systems (e.g. New Zealand, Iceland, Yellowstone) where silica sinter terraces form. Comparable processes in the geologic past may also have been responsible for the formation of a wide range of ancient silica deposits such as stromatolites in the Archean. Field-based investigations have shown that in modern hot spring environments, silica sinters form in close spatial relation to microorganisms. However, the role which microorganisms play in sinter formation, and the mechanisms that control microbial silicification are poorly understood.

In this study, we investigated the interactions between nano-size silica colloids and the photosynthetic cyanobacteria *Calothrix*. The objective of this work was to assess the affinity of silica colloids to attach onto cyanobacterial surfaces and to determine if microbial silicification can occur through the aggregation of colloidal silica by microbial cell surface polymers.

Flow through experiments were conducted with *Calothrix* filaments cultured in BG11 media and silica colloids with an average diameter of 20 nm suspended in dilute electrolyte solutions. The accumulation of silica colloids around the cell surface was examined using transmission electron microscopy (TEM) and monitored as a function of time. Laboratory silicified cells were then compared with field samples of silicified cyanobacteria mats collected from hot springs in Iceland and New Zealand.

The experimental results indicate that silica colloids display a strong affinity for *Calothrix* surfaces. TEM analysis of cells exposed to silica colloids for 1 h show extensive colloid aggregate formation around the exopolymer sheath. Similarly, analysis of field samples by TEM revealed intact cells covered with silica spheroids around the extracellular sheath. Silification was observed to occur in successive stages, with silica colloid binding on the cell surface as the first step. Both laboratory and field results suggest that microbial surfaces can disrupt colloid stability and promote the aggregation of fine-grained particles via the attachment of colloids onto the polysaccharide sheath. In this way, microorganisms can act as a template which bind and accumulate colloidal sediment. Colloid-microbe interactions can therefore strongly impact sinter architecture and the mineralization of microorganisms in hot spring environments.