



Biomineralization of Fe^{III}-oxides in geothermal environments: Relationship among aqueous geochemistry, microbial populations and solid-phase composition and structure

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The biomineralization of Fe-oxides is a common process in soils, sediments, and natural water systems. The role of microorganisms in Fe^{II} oxidation and subsequent biomineralization of Fe^{III} phases has been studied extensively in acid-mine waters and hydrothermal systems. Geothermal environments present a unique opportunity to study less-diverse microbial communities that may contain deeply-rooted functional attributes important in the oxidation of Fe^{II}, and where the environmental context of specific microbial populations may be established with greater clarity. Different Fe^{III}-oxide microbial mat solid phases were collected from approximately 10 geothermal systems with varying source water geochemistry. The solid phases were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) to determine Fe^{III}-oxide properties among different geothermal habitats. In addition, the distribution of 16S rRNA genes within these environments has been determined. The oxidation of Fe^{II} via O₂ is energetically favored (exergonic) in nearly all geothermal environments, and the thermodynamic favorability increases with increasing pH. However, the abiotic rate of precipitation of Fe^{III}-oxides becomes quite significant at pH values greater than 4.5, and may make a greater contribution to Fe^{III} mineralization in springs at pH 6-7. Indeed, there is more evidence of Fe^{II} oxidizing

chemolithotrophs in the acidic springs, where *Metallosphaera*, *Sulfobacillus*, *Acidimicrobium* and *Thiomonas*-like sequences have been recovered at numerous locations where the pH ranges from 2.5-4. The composition and structure of the Fe^{III}-oxide phases varies considerably across geothermal environments, partly due to the variation in aqueous chemistry among sites. For example, As^V-rich hydrous ferric oxides (HFO) are found in low pH springs where microbial arsenite oxidation yields soluble arsenate, which is then complexed to poorly-ordered nanoclusters of octahedral Fe-OH. In higher pH systems, As^V is not incorporated to the same degree and the resultant Fe^{III} oxides contain silicate rather than arsenate. The role of thermophilic chemolithotrophs in the formation of these Fe^{III} solid phases is under investigation, and cultivation is one of the additional approaches being used to confirm the role of specific populations shown to be relevant in these microbial mats. For example, a *Metallosphaera*-like isolate has been recently obtained from acidic springs in Norris Basin, YNP. This organism is related (~96 % across the full-length 16S rRNA gene) to known *Metallosphaera* sp., but clusters separately with some 40-50 environmental clones from a variety of YNP acidic sites. This organism has been shown to oxidize Fe^{II}, but does not biomineralize Fe^{III}-oxides around the cell wall as has been observed extensively within the actual mat samples. Additional cultivation work will attempt to establish other relevant thermophilic Fe^{II} oxidizers, and specifically identify those responsible for formation of mineralized structures around the cell.