

Deciphering the mechanisms of pyrite formation in pure cultures of sulfate-reducing bacteria

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Pyrite (FeS_2) is the most abundant metal sulfide at Earth's surface and is ubiquitous in modern and ancient sediments. As sulfide production is mainly driven by sulfate-reducing microorganisms, it is assumed that pyrite found in the past sediment record is biogenic and could be used as a biosignature. However, most of the studies of sulfate-reducing bacteria in pure cultures report the formation of metastable iron sulfides such as mackinawite (FeS) or greigite (Fe_3S_4), instead of pyrite. Hence, we lack an understanding of the role played by sulfate-reducing bacteria in sedimentary pyrite formation.

Here, we present results from pure cultures of *Desulfovibrio desulfuricans* in the presence of different sources of iron (dissolved Fe^{2+} or amorphous Fe^{III} -phosphate nanoparticles). We monitored iron and sulfur speciation, as well as phosphate and organic acid concentrations over one month. Moreover, we characterized the minerals produced in the cultures down to the atomic scale, using

a multi-analytical approach including X-ray diffraction, Fe K-edge X-ray Absorption Spectroscopy, Scanning and Transmission Electron Microscopy and Scanning Transmission X-ray Microscopy at C K-edge and Fe $L_{2,3}$ -edges.

As reported in the literature, a rapid precipitation of amorphous iron sulfide occurred in the cultures. But noteworthy, biogenic sulfide reduced Fe^{III} -phosphate leading to the formation of vivianite ($\text{Fe}_3^{\text{II}}(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) in addition to iron sulfides. We identified conditions upon which amorphous FeS evolved into well-crystallized mackinawite then greigite and finally pyrite. We will discuss the mechanisms of pyrite formation and implications for the search of biosignatures.