

The genesis of phosphatic nodules in the Toyoma Formation, Northeastern Japan

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Various phosphatic and carbonate rocks occur in the Permian Toyoma Formation. Morikiyo & Matsunaga [1] reported the isotopic ratios of calcite, pyrite and apatite in these rocks and concluded that the rocks were formed by sulfate reduction. However, the $\delta^{34}\text{S}$ of pyrite was reported for the total rock; therefore, this reasoning requires reconsideration. The $\delta^{34}\text{S}$ of individual pyrite grains in the phosphatic rocks was re-analyzed using high-resolution secondary ion mass spectrometry. Intergranular differences in the $\delta^{34}\text{S}$ of rock samples are as large as 38‰. $\delta^{34}\text{S}$ is correlated to the morphology of pyrite; framboidal pyrite has low $\delta^{34}\text{S}$, whereas euhedral pyrite has high $\delta^{34}\text{S}$. It is thus possible to determine the stage of diagenesis in which each rock type was formed by considering the total rock pyrite $\delta^{34}\text{S}$ and the modal proportion of the pyrite types. The phosphatic nodules were formed at the earliest stage in all of the rocks in the Formation. The source of phosphorus is inferred to be fish scales and bones, according to the Y, La, and Ce contents. Therefore, points to be clarified are: 1) the reason for dissolution of biogenic phosphate debris, and 2) the cause of apatite precipitation after the dissolution of the debris. At the time of deposition, the occurrence of trace fossils shows that surface sediments were not anoxic, rather that sediments inside were anoxic. Thus, the upward diffusion of H_2S from the underlying sediment resulted in surface sediment containing sulfur-oxidizing bacteria, which grew and produced sulfuric acid and caused the dissolution of phosphate debris. As burial of the sediment progressed, the former surface layer became anoxic, initiating sulfate reduction, which led to the precipitation of apatite.

[1] Morikiyo & Matsunaga (2001) Abstr. 11th Goldschmidt Conf. #3066.

Arsenic(III) polymerization upon sorption on iron(II,III)-(hydr)oxides surfaces:

Implications for arsenic mobility under reducing conditions

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Arsenic is a toxic metalloid involved in important health issues due to its presence as a water pollutant in many parts of the world. A major control of the aqueous concentration, mobility, and cycling of arsenic is its sorption to and desorption from iron oxides surfaces. The modes of arsenic sorption to the surface of Fe(III) (oxyhydr)oxides have been extensively documented by XAFS and RAXR and include both inner- and outer-sphere monomeric surface complexes.

In contrast, recent investigations of arsenic-iron systems under anoxic conditions have revealed that As(III), the toxic reduced form of arsenic, tend to form polymeric surface complexes, and surface precipitates at the surface of Fe(II,III) hydr(oxides). EXAFS and HRTEM studies of the bioreduction products of As-doped iron-oxyhydroxides have revealed that As(III) sorbs as oligomeric species at the surface of $\text{Fe}(\text{OH})_2$ and green-rusts [1,2]. These new types of As(III) surface complexes are consistent with the bonding geometry of As(III) in ferrous arsenite minerals. We have also recently shown that As(III) forms surface precipitates at high surface coverage on magnetite nano-particles, although tightly bound monomeric surface complexes form at low surface coverage [3].

Adsorption of As(III)-oligomers to Fe(II,III) (oxyhydr)oxide surfaces may help limit As(III) mobility in reducing Fe(II)-rich groundwaters. However, the relatively high solubility of As(III)-surface precipitates forming at high surface coverage on nanomagnetite particles should be taken into account for designing magnetite-based water-treatment processes.

[1] Ona-Nguema *et al.* (2009) *GCA*, **73**, 1359-1381. [2] Wang *et al.* (2008) *GCA* **72**, 2573-2586. [3] Morin *et al.*, in preparation.