Experiments on direct precipitation from Precambrian seawater

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Iron-rich, silica-rich and anoxic conditions of Precambrian seawater favor the formation of Fe-Si-O-OH-gels as primary sedimentary products. These may crystallize to ferrous layered silicates (e.g. greenalite, stilpnomelane) and coagulate to microgranules during early diagenesis, resulting finally in banded iron formations [1, 2]. Experimental studies on gel and subsequent mineral formation are however scarce.

Therefore, we have performed anoxic batch experiments at different concentrations of SiO_2(aq) (200-1650 μM) and Fe^{2+} (100-1000 μM). The oxygen was removed by boiling coupled with N_2-flushing and reduced with sodium dithionite. A constant amount of Mg^{2+} (100μM), K^+ (100μM) and Al^{3+} (10μM) was used to promote the formation of potential iron-silicates. Well soluble chlorides and sulfates were used as primary chemicals. The solutions were stored for several days in the dark and the gelatinous precipitates were subsequently centrifuged and vacuum dried.

X-ray diffraction (XRD) reveals that the samples from the chloride series are amorphous. However, peaks of magnetite and a chlorite group mineral ($d_{002} \cong 7$Å) appeared after a mild temperature treatment (72 h at 50°C). The sulfate series consistently show wide peaks from mackinawite (FeS) and greigite (Fe_3S_4) without temperature treatment. Transmission electron microscopy (TEM) of representative samples from both series show amorphous SiO_2 as the main phase with small particle size of less than 50 nm. Interestingly, a significant amount of Fe adsorbed to the silica was detected by EDX analysis and could be transformed to nanocrystalline magnetite after short irradiation with a focused electron beam. All experiments with elevated sulfur concentrations show additionally fibrous mackinawite and isometric greigite.

In conclusion, the experiments show that the precipitation of amorphous silicates also binds a significant amount of iron from the solution by adsorption because of its large surface area. If sulfur is available, it forms iron sulfides which will be transformed to pyrite during diagenesis. Any formation of crystalline Fe-silicates must involve a slightly elevated temperature, however, the recrystallization was quite fast even at a very moderate (~50°C) temperature.

[1] Klein (2005) *American Mineralogist* **90**, 1473-1499. [2] Rasmussen et al. (2013) *Geology* **41**, 435-438.