

Experimental study of synthetic pyrite framboids and other morphologies

H. OHFUJI, I. BUTLER AND D. RICKARD

Department of Earth Sciences, Cardiff University,
Park Place, Cardiff, CF10 3YE, UK (ohfujih@cf.ac.uk)

Framboids are microscopic sub-spheroidal clusters of microcrysts (normally pyrite) which often display extraordinary degrees of self-ordering. They represent one of the most abundant pyrite textures found in natural sediments. The mechanism of framboidal self-organization remains unsolved. Eleven laboratory syntheses of pyrite framboids have previously been reported. A critical review of these reports shows that the textures produced are not unequivocally framboidal.

We repeated these experiments and re-examined the reaction products. Then, we further investigated some experiments⁽¹⁻³⁾, using better defined experimental conditions to investigate the relationship between the pyrite morphologies produced and synthetic conditions. Four pyrite morphologies were observed in the products, which we classed as (i) single euhedral crystals, (ii) framboid-like aggregates (Fig. 1A), (iii) spheroidal particles (Fig. 1B) and (iv) acicular aggregates (Fig. 1C). We found a strong correlation between pyrite morphologies and the presence of (or amount of introduced) S°. In the presence of excess S°, pyrite morphologies changed from euhedral and framboid-like to spheroidal or acicular aggregates. There is a possibility that not only redox state but also sulfide concentration and sulfur speciation in solution might play an important role in determining pyrite textures produced.

Detailed examination of the framboid-like pyrite reveals that many have massive or concentric internal structures rather than discrete microcrysts (Fig. 1D). This implies that some synthetic framboid-like products might not be true framboids. We conclude that attempts to understand the self-organization mechanism of framboids requires careful examination of the internal structure of the products.

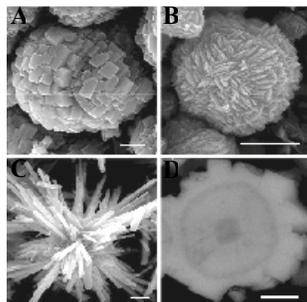


Figure 1. Morphologies of synthetic pyrite (scale: 1µm)

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Siderite in Archean sedimentary rocks: Evidence for a CO₂-rich and CH₄-poor atmosphere

HIROSHI OHMOTO¹ AND YUMIKO WATANABE¹

¹ Astrobiology Research Center and Dept. of Geosciences,
The Pennsylvania State University, University Park, PA,
USA (ohmoto@geosc.psu.edu)

A currently popular atmospheric evolution model postulates CH₄, as well as CO₂, was a main greenhouse gas prior to ~2.2 Ga ago (e.g., Catling et al., 2001; Kasting et al., 2001). Rye et al. (1995) developed this model from a simple thermodynamic analysis of the stability relation of two minerals (greenalite and siderite): greenalite + 3CO_{2(g)} + 2H₂O = 3 siderite + 2H₄SiO_{4(aq)}. By assuming greenalite was stable, but not siderite, in pre-2.2 Ga soil-forming environments, they concluded the *maximum* pCO₂ in the atmosphere at this time was ~10^{-1.4} atm. Subsequently, a revised climatic model (Pavlov et al., 2001) suggests values ~1,000 ppm CH₄ (~10⁻³ atm) and ~2,500 ppm CO₂ (~10^{-2.6} atm) for the atmosphere about 2.75 Ga.

We have conducted multi-dimensional thermodynamic analyses of the Fe-SiO₂-CO₂-O₂-H₂O system. Results indicate: (1) The stable minerals in well-aerated environments at pO₂ > 10^{-6.0} atm are goethite and Fe³⁺-bearing silicates. (Note all atmospheric evolution models postulate pO₂ > 10^{-1.5} atm.); and (2) Minesotaitite, not greenalite, may become a stable mineral at very low pO₂ (<10^{-6.5} atm) and low pCO₂ (<10^{-1.6} atm) conditions. Thus, Rye et al.'s (1995) pCO₂ value becomes meaningless for constraining the pre-2.2 Ga atmospheric composition.

Siderite becomes stable at pO₂ <10^{-6.5} atm and pCO₂ >10^{-1.6} atm at 25 °C. Such conditions are created only in subsurface anoxic water bodies (e.g., semi-closed basins; soils) where H₂ generates from decomposing organic matter by anaerobic organisms. This formational environment of siderite is consistent with the δ¹³C values of >2.2‰ siderite-rich carbonates, which range from -23 to 2‰ (mean = -8.2‰); in comparison, δ¹³C values of calcite-rich carbonates average 0.2‰. Utilizing these carbon isotopic data, we have further constrained the *minimum* pCO₂ of the pre-2.2 Ga atmosphere was ~10^{-1.7} atm (>55 times the present atmospheric level). This pCO₂ alone, without CH₄, could have provided the necessary greenhouse effect to compensate the lower solar flux and maintain liquid oceans in the Archean. This CO₂-rich atmosphere was also an important reason for the abundance of siderite-rich banded iron formations before ~1.8 Ga.

References

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