Framboidal Pyrite: Self Organisation in the Fe-S System

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Introduction

Framboidal pyrite is common in sediments and low temperature ore deposits. Numerous studies have sought to develop a model which explains all the features of the texture; to date, no model has achieved this aim. Generally, framboids are defined as spheroidal or sub-spheroidal aggregates of many (10^2-10^5) equant, equidimensional pyrite microcrystals. A striking structural feature of framboids is the development of ordered close packed arrays of microcrystals, either throughout the framboid or within domains.

Wilkin and Barnes (1996, 1997), synthesised framboidal pyrite by ageing precipitated FeS with aqueous sulphide in the presence of low O_2 concentrations. They interpreted their data to suggest that framboid formation is dependent upon the rate of formation of the magnetic thiospinel, greigite (Fe_3S_4), and the degree of FeS oxidation. The involvement of greigite has lead to the development of a model which involves precipitation of FeS, conversion to greigite (by Fe loss rather than sulphidation), magnetic aggregation of greigite microcrystals and conversion to pyrite.

Butler and Rickard (in press) have synthesised framboidal pyrite via the oxidation of FeS by hydrogen sulphide in the absence of O_2, and without involvement of greigite as an intermediate. There is, however, a strong dependence upon the Eh at which the reaction system is initially poised, and framboids were not formed in strongly reducing systems (Eh < -250 mV). In the light of new experimental data, textural features of natural framboidal pyrite may be re-evaluated to assess the validity of formation models.

Framboidal Structures

Wilkin *et al.*, (1996), among others, have noted the correlation of the ratio of microcrystal to framboid diameter (nucleation density) and the redox conditions in which they formed. Thus, in a given deposit, small framboids have small microcrystals and large framboids have proportionally larger microcrystals. Figure 1a shows framboidal pyrite filling a fossil plant cell, with framboids of similar nucleation density, but different diameter closely juxtaposed. Framboids never display bimodal microcrystal size distributions, and aggregation models require that such relationships be formed by multiple discrete microcrystal-framboid forming events.

Figure 1b shows a framboid with a close packed ordered array of cubo-octahedral microcrystals sharing a common orientation. More commonly, ordered micro-architectures occur without microcrystal orientation. However, the form shown here is not unusual. Figure 1c shows a polyhedral framboid. Polyhedral forms, either pyritohedral or cubo-octahedral, are best developed in framboids with close packed microcrystal arrays.

Figure 1d illustrates truncation of the surface microcrystals of a framboid. Again, this is not ubiquitous, but is most commonly seen in framboids with close packed micro-architectures. Framboids are characteristic of "open volume" precipitation, and are not associated with surface limiting structures. Where limiting structures are present (e.g. wrapping clay textures or overgrowths), they post-date framboid formation.

Framboid Formation

Self-organisation is the "autonomous passage of a system from an unpatterned to a patterned state without the intervention of an external template" (Ortoleva *et al.*, 1987). The laboratory synthesis of framboids (Wilkin and Barnes 1996, Butler and Rickard, in press) is consistent with abiotic formation without a structural template. The results of Butler and Rickard (in press) indicate that greigite is not an essential framboid precursor. The conversion of FeS to FeS_2, via Fe_3S_4 by Fe loss is a solid state process, and conversion of 20-30nm precipitate particles of FeS is not associated with particle growth (Butler *et al.*, 1999) required for framboidal microcryst formation.

We consider that the autonomous passage towards a patterned state (i.e. conversion of FeS precipitate to FeS_2 framboid) proceeds via sequential nucleation and growth of pyrite microcrystals by oxidation of $FeS_{(aq)}$ by $H_2S_{(aq)}$ (Butler and Rickard; in press). An ordered polyhedral framboidal can be regarded as a single pyrite crystal composed of a mosaic of individual blocks. Microcryst orientation and ordering is controlled by spatially periodic nucleation at or close to microcrystal edges and apices. Rapid microcrystal growth permits long-range inhibition of nucleation in the immediate vicinity of a growing microcrystal. Pyrite supersaturation controlled by Eh and pH determines relative nucleation versus growth rates, and so the microcrystal nucleation density. The spheroidicity of framboids remains a problem. Generally, spherical surfaces are related to bodies minimising surface area. It is possible that spheroidicity and associated microcrystal truncation is related to surface tension effects.
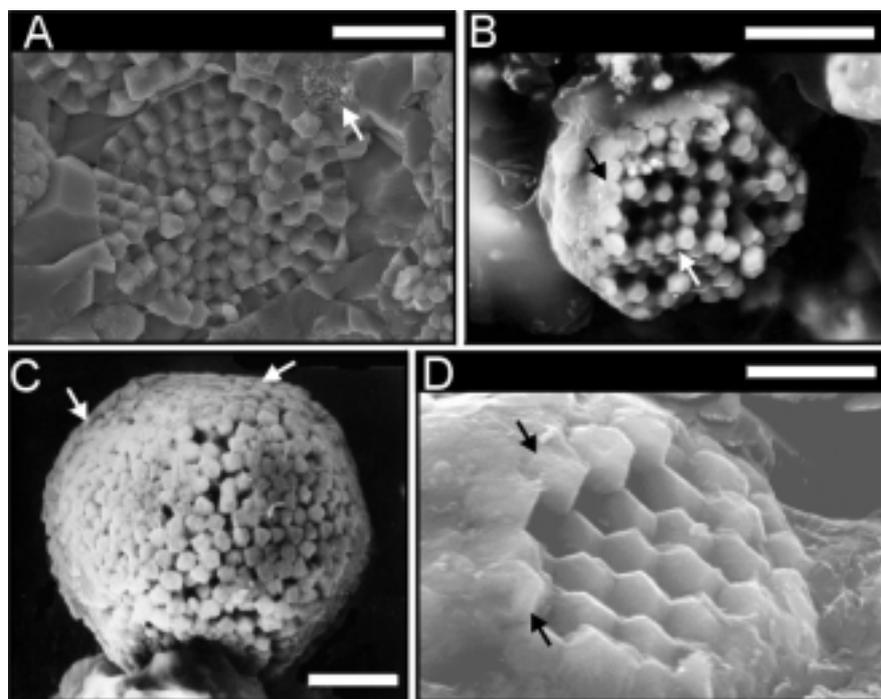
Figure 1: A) Closely juxtaposed large and small (arrowed) framboids in a fossil plant cell display similar nucleation densities. Note that the large framboid appears to be polyhedral rather than spheroidal. Scale bar = 5μm. B) The fractured framboid is composed of a close packed array of cubo-octahedral microcrystals sharing a common spatial orientation (light arrow). Note also the truncated microcrystals at the framboid surface (dark arrow). Scale bar = 5μm. C) A polyhedral framboid (straight edges and flat faces arrowed). In this case the form seems to be pyritohedral. Scale bar = 5μm. D) Truncated microcrystals at a framboid surface, although there is no boundary structure visible. Note also the close packed and shared microcryst orientation. Scale bar = 2μm.

Butler I.B., Rickard D. and Oldroyd A., *Proc. 9th Annual V.M. Goldschmidt Conference. LPI Houston*, 46-47, (1999).

Butler I.B. & Rickard. D., *Geochimica et Cosmochimica Acta*, (in press).

Ortoleva P., Merino E., Moore C. and Chadham J., *American Journal of Science*, **287**, 979-1007, (1987).

Wilkin R.T., Barnes H.L. and Brantley S.L., *Geochimica et Cosmochimica Acta*, **60**, 3897-3912, (1996).

Wilkin R.T. and Barnes H., *Geochimica et Cosmochimica*, **60**, 4167-4179, (1996).

Wilkin R.T. and Barnes H.L. 1997, *Geochimica et Cosmochimica Acta*, **61**, 323-339, (1997).