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book reviews

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Framboids are microscopic, subspherical aggregates of pyrite microcrystals, where the sulfide is mainly microbiological in origin: a framboid may contain fewer than 100 or more than 500 000 microcrystals. The sizes of the microcrystals span however a much smaller interval. Framboids are ubiquitous but require unique conditions to form. The book by David Rickard, world authority on sulfide chemistry, geochemistry, geomicrobiology, biogeochemistry and ore geology, opens the doors of this fascinating world. The importance of these minuscule aggregates cannot be underestimated, if we consider that *pyrite nanoparticles contribute a significant component of the nanoparticulate budget of the oceans [. . .] and may contribute up to 10% of the dissolved iron emanating from black smoker hydrothermal vents* (page 109).

The book consists of 13 chapters, preceded by a very useful synopsis (nine pages) presenting the main results in a nutshell, and followed by a list of symbols and abbreviations, a list of units, a glossary (12 pages), a rich bibliography (26 pages) and a detailed index (eight pages). It is a small encyclopedia of all that is known to date about framboids.

Chapter 1 (20 pages) is the *Introduction* which presents the study of framboids, whose principal features are detailed: microscopic size, spheroidal shape, equant and equidimensionality of the microcrystals building up a framboid, their ubiquitous distribution, as well as a short history of their discovery and investigation.

Chapter 2 (26 pages) presents the *Framboid Sizes*, whose distribution is log-normal and varies between less than 2 and more than 200 µm in diameter, although 95% lie between 2.9 and 12.3 µm. As the reliability of the measurement of the size of such small objects is an issue, a detailed discussion describes various errors occurring in the literature in particular the stereological error (error in converting the measure of 2D sections in 3D spheres). Although 99% of framboids are between 2.0 and 17.7 µm in diameter, a statistically significant difference in size is observed between freshwater and marine framboids.

Chapter 3 (16 pages) deals with *Framboids Shapes*. After an introduction on how to evaluate the sphericity and the deviations from it, the effects of gravity are briefly presented, followed by a detailed discussion of the results of these effects, namely the polyhedral morphology which could be revealed only once the microscope technology was sufficiently advanced.

Chapter 4 (28 pages) is devoted to *Microcrystal Morphology*, which is composed, essentially, of modified octahedra and cubes. Because framboid microcrystals seem stable over geologic time periods, no correlation exists between the size of the constituent microcrystal and the geological age of the framboid. After a reminder about the various crystal forms known for pyrite, where the symbol ⟨⟩ is incorrectly used instead of {} for the indices of the forms (Table 4.3; note that the correct symbol is used instead in Table 6.1), we learn that the most common form of pyrite microcrystals in framboids is the octahedron, the least common of the three basic forms (cube, pyritohedron and octahedron), suggesting a peculiar formation mechanism (which is presented in the second part of the book). Detailed analysis shows that the habit is actually that of a truncated octahedron, reflecting a decrease in the degree of supersaturation towards the end of the crystal growth. The association of framboids with organic material is discussed next, showing that the relation is quite complex. The sentence 'the object being observed is two dimensional' (page 73) is imprecise: it is the image of the object that is two dimensional, not the object itself.
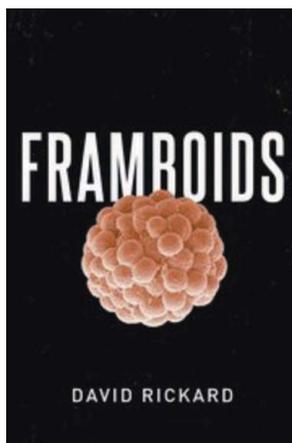
Chapter 5 (20 pages) is titled *Framboid Microarchitecture* and presents an in-depth analysis of how the microcrystals associate in a framboid. One of the main features of framboids is the uniformity of their constituent microcrystals, which leads to single or multiple domains of close-packed geometries, although the majority of framboids have eventually a disordered microstructure. The chapter discusses the topology of close packings while showing several micrographs of framboids sections. Several terminological imprecisions occur in this chapter. The term two-dimensional is incorrectly used instead of diperiodic (pages 91 and 95); the curious term 'simple *ccp*' (page 92) raises some questions about what could be a 'complex (non-simple) ccp': it would be better to avoid ambiguous terms that may direct the mind of the reader to different concepts ('simple cubic' is not *ccp*). One may also wonder why it was chosen to use the 'c-axis of the sphere'. The climax arrives at page 106, when reading about 'amorphous superlattices' (sic!) This is not an invention of the author but a quotation from a 2017 book; the absurdity of such oxymoron should however have been pointed out.

Chapter 6 (19 pages) presents *The Crystallography of Pyrite Framboids*. After a description of the crystal structure of pyrite, incorrectly described as 'the lowest cubic symmetry' (pyrite is hemihedral, not tetartohedral; it might be a typo for 'lower'), the investigation of pyrite framboids by powder X-ray diffraction and electron backscatter diffraction study is presented. We learn that the microcrystals in a framboid are not crystallographically oriented, so that framboids are not mesocrystals, as supposed in the past, but the result of an aggregation process. Indices of directions are incorrectly given as non-relatively prime integers (page 118).

Chapter 7 (24 pages) discusses *Organic Matter in Framboids*. After a relatively lengthy, but certainly interesting, historical excursus about old hypotheses, we learn that the abundant organic matter accompanying the microcrystal has several origins and is divided into biofilm and kerogen. It does not seem very clear whether any conclusion can be given about the time scale. On one hand we read that the organic matter is probably the result of early diagenesis (page 146), while on the other hand we read that *organic matter in framboids is contemporaneous with framboid growth and framboids grew within the organic matter* (page 152). A bit confusing . . .

Chapter 8 (16 pages) deals with *Framboid Mineralogy* but is actually devoted to non-pyritic framboids. These objects do exist, but represent a minority of framboids. The pre-requiste – equant and equidimensional microcrystals – is characteristic of cubic crystals and cannot be obtained from marcasite, which is orthorhombic. Framboids, or at least aggregates presenting similarities to framboids, have been found for greigite, copper sulfides, sphalerite and oxides. A table summarizing the results would have been most welcome.

Chapter 9 (22 pages) discusses *Framboid Geochemistry* and requires the reader to have some additional background knowledge on the subject compared with the previous chapters. The trace elements in framboids represent *a snapshot of the local trace element concentration in the fluids at the time* (page 185) of formation, which opens the door to indirectly probing the environment where the framboids formed. However, the distribution of trace elements between framboids, pyrite crystals and the host rock differs with the elements, which makes any conclusion less easy. Framboids also give a more accurate representation of the sulfur isotopic composition, which they retain over geologic time.

Chapter 10 is the longest (31 pages) and deals with *Pyrite Framboid Formation Chemistry* and discusses at length the possible reaction mechanisms. It is not possible to give a short summary of the very detailed content of this chapter, which is a mine of information.

Chapters 11 (13 pages) and 12 (27 pages) present the nucleation and the growth of pyrite microcrystals leading to framboids. Framboids require a huge supersaturation to produce what is known as burst nucleation: a huge number of nuclei form, which then grow to similar sizes through a drastic reduction of the supersaturation. The reader is reminded of the classical nucleation theory and we learn that framboids form from homogeneous nucleation, whereas pyrite crystals do so from heterogeneous nucleation. The decrease in supersaturation is related to the change in morphology, from the less-stable forms (dodecahedron, pyritohedron, octahedron), to the more-stable ones (cube, truncated cube). Various growth mechanisms (screw dislocation, particle attachment, Ostwald ripening) are compared and the effects of temperature and pH are discussed.

The last chapter (20 pages) discusses *Framboid Self-Assembly and Self-Organization* and culminates this fascinating journey by presenting various models about the mechanism by which microcrystals aggregate into a framboid. Oriented attachment is excluded, because the forces acting on microcrystals should be strong enough to bring them together, but not too strong to prevent reorientation. The minimization of the surface energy, with a contribution from the entropic maximization, seems to be the key factor.

The proof-reading process was very careful, as shown by the very low number of typos:
- Chapter 3 instead of chapter 2 at page 20;
- *Pa*3 instead of *Pa$\bar{3}$* on page 114 and in Table 10.1;
- *Fd*3*m* instead of *Fd$\bar{3}$m* in Table 10.1.

David Rickard has condensed in a relatively small book (about 350 pages) a wealth of information which makes it a reference text certainly for many years to come; information I could summarise only to a very small extent. The subject is fascinating and overlooked outside the circle of specialists. Some conclusions could have been summarized at the end of each chapter, although the synopsis at the beginning of the book is already of great help. An in-depth study would certainly require some considerable effort; as with every reference book, readers will certainly go back time and again when they need to deepen their understanding of some particular aspect.