American Mineralogist, Volume 87, pages 176–180, 2002

Icosahedral domain structure of framboidal pyrite

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ABSTRACT

A new type of framboidal pyrite, with icosahedral domains, is described in this study. Examining the microcrystals on sections of framboids from various localities using a scanning electron microscope, we found pentagonal and trigonal patterns. These are made up of rectangular and fan-shaped domains, and octahedral microcrystals are regularly linked by sharing of edges in each domain. These symmetrical arrangements are interpreted to be different sections of icosahedrally arranged framboids which are composed of twenty tetrahedral domains. Thus some pyrite framboids are not spherical, but are fundamentally icosahedral both in appearance and internal structure. The formation of the icosahedral framboids might be related to the initial nucleation rate and the number of microcrystals within each framboid.

INTRODUCTION

Framboidal pyrite is a microscopic pyrite aggregate which has a unique raspberry-like shape and occurs mostly in ancient sedimentary rocks, modern marine and lacustrine sediments, and anoxic water columns (Love and Amstutz 1966; Sweeney and Kaplan 1973; Perry and Pedersen 1993; Ross and Degens 1974). One of the characteristic features is that, without exception, individual framboids are composed of microcrystals of uniform size and shape. This suggests homogenous nucleation of the initial microcrystals. There have been a number of studies on the on the genesis of framboids and the following chemical reaction has been suggested: disordered mackinawite $\rightarrow$ ordered mackinawite (Fe_9S_8) $\rightarrow$ greigite (Fe_3S_4) $\rightarrow$ pyrite (FeS_2) (Schoonen and Barnes 1991a, 1991b; Wilkin and Barnes 1997). The latter suggest that the framboidal shape might have formed at the greigite stage as a result of a magnetic accretion of greigite microcrystals (Wilkin and Barnes 1997). However, Butler and Rickard (2000) synthesized framboidal pyrite directly from iron (II) monosulfide without forming greigite as an intermediate material. This suggests the possibility of two different processes, formation via greigite and direct pyrite formation from the initial material.

Framboidal pyrite shows regular or irregular arrangements of internal microcrystals and the regular packing has been interpreted as body-centered cubic or approximately closest cubic packing (Love and Amstutz 1966; Kalliokoski and Cathles 1969; Rickard 1970). Some framboids consist of different subdomains of ordered microcrystals (Rickard 1970). Morrissey (1972) and Skripchenko and Berber'yan (1976) reported polygonal arrangements of microcrystals from sections of framboids and suggested that framboidal pyrite might have a polyhedral rather than a spherical form. However, the three-dimensional distribution of microcrystals in framboids has not previously been discussed in detail.

EXPERIMENTAL METHOD

We examined pyrite framboids from five muddy sediments (Miocene ~ Holocene in age) and four modern reductive sediments for comparative studies of the internal structure (Table 1). All the specimens were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specimens used for stereomicroscopic observations were residues obtained from the muddy sediments by sifting fine sand with a 200 mesh sieve. The specimens for SEM and TEM observations were framboidal pyrite and greigite grains which were picked from the residues. The SEM observations were performed using JSM5310LVB (JEOL) and JSM5600 instruments equipped with Energy Dispersive Spectrometers (EDS: ISIS310, Oxford Instruments) and operated at 15 kV. Large framboid specimens were sectioned with tweezers under the stereoscope, and small specimens were buried in epoxy resin on slides and were polished to make thin sections. All the specimens were coated with Au or C. The TEM observations were carried out using a JEM200CX (JEOL) instrument equipped with an EDS (Voyager IV, Noran Instruments) unit and operated at 200 kV. The specimens were prepared by crushing framboid grains which were part of the same specimens used for SEM observations.

RESULTS AND DISCUSSION

Nature of framboidal pyrite in the examined samples

Compared with the framboids from modern sediments, the framboids from Pleistocene sediments are much larger with average diameters of 30 to 80 μm and a maximum diameter of 120 μm. They may be divided into two types based on shape: spherical single framboids and polyframboids. The term "polyframboid" was suggested by Love (1971) and represents aggregates of numerous framboid units. Microcrystals of both

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0003-004X/02/0001–176$05.00

TABLE 1. Locations and geological ages of samples used in this study and presence of icosahedral domain structures

Sample	Location	Age	I.D.S.*
	Sedimentary rocks		
Shirone Drilling core	Shirone City, Niigata Prefecture, Japan	Holocene	O
Kanai Drilling core	Kanai Town, Niigata Prefecture, Japan	Holocene	O
Teradomari Formation	Shiroiwa, Niigata Prefecture, Japan	Miocene	O
Uonuma Formation	Oguni Town, Niigata Prefecture, Japan	Pleistocene	O
Udenaha muddy sediments	Udenaha, Okinawa Prefecture, Japan	Pleistocene	O
	Modern sediments		
Lake Harutori	Kushiro City, Hokkaido Prefecture, Japan	Present	X
Mitarase Lagoon	Akatsuka, Niigata Prefecture, Japan	Present	Δ
Sakata Lagoon	Akatsuka, Niigata Prefecture, Japan	Present	Δ
Septiba Bay	Septiba, Brazil	Present	X

* I.D.S: Icosahedral domain structure in framboidal pyrite. O = presence, Δ = rare presence, X = absence.

types are almost octahedral in shape and are arranged in dense packings.

Framboidal pyrite in modern unconsolidated sediments (lower 4 samples in Table 1) is frequently found in wood fragments, the inside of diatoms, and rarely as single particles in the sediments. They mostly range in size from 5 to 20 μm, and even the largest one is less than 30 μm in diameter. Most framboids from modern sediments are composed of cubic ~ cuboidal microcrystals arranged in irregular and loose packings. However, some of them consist of densely packed octahedral microcrystals.

Wilkin et al. (1996) argued for a relationship between framboid diameter (D) and microcrystal diameter (d). They observed that the D/d ratios of framboids from two modern sediments fell within a range from 5 to 30, although clear correlation could not be found in D and d values. On the contrary, the D and d values of all framboids used in this study exhibit clear correlations (Fig. 1). The D/d ratios of framboids from Holocene sedimentary rocks (e.g., Shirone) are generally higher than those of framboids from modern sediments (Fig. 1). The D/d ratios of framboids dominated by cubic ~ cuboidal microcrystals are low. In contrast, framboids composed of octahedral microcrystals, even those from modern sediments, show high D/d values. These differences may reflect the formational environments of each framboid, for instance the surrounding redox conditions, nucleation time and rate of growth of initial microcrystals, etc.

Most framboids used in this study consist of nonmagnetic pyrite microcrystals. The framboids from Shirone drill core are exceptional in that half are weakly magnetized. The TEM, EDS, and electron diffraction (ED) studies revealed that most of the microcrystals in magnetic framboids have ferromagnetic greigite microcrystals in their central parts. A similar occurrence was reported from Late Neogene sediments in New Zealand (Roberts and Turner 1993).

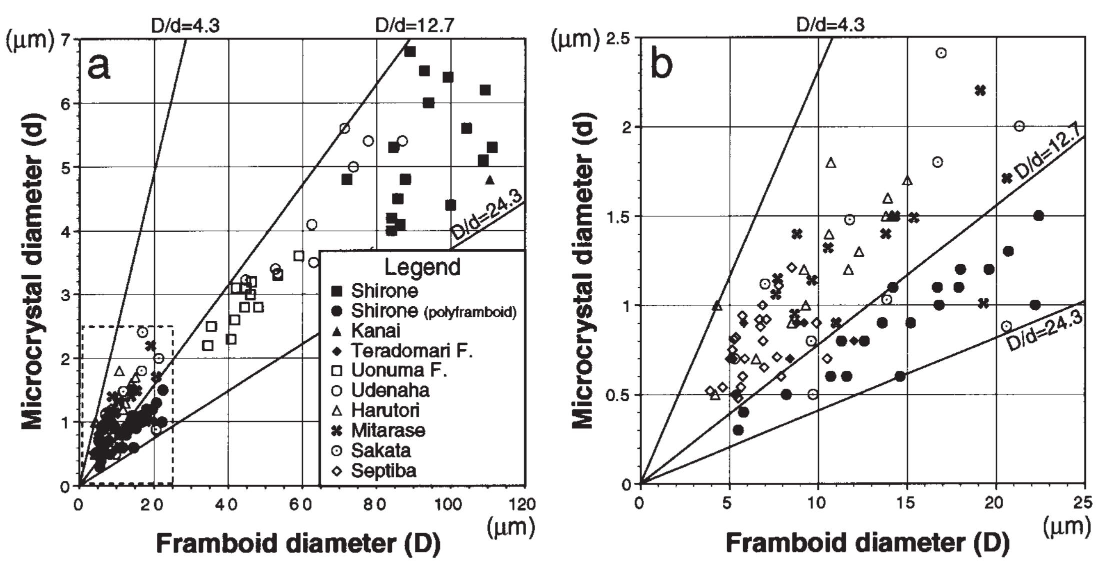

FIGURE 1. (**a**) Relationship between framboid diameters (D) and microcrystal diameters (d) of various pyrite framboids used in this work. The D/d ratios almost fall within two different ranges, D/d = 4.3 ~ 12.7 and D/d = 12.7 ~ 24.3. The D/d ratios of most framboids from Holocene to Pleistocene sedimentary rocks are plotted within the latter range. (**b**) Enlarged figure of the square area in (**a**), indicated by dotted lines.

Arrangements of pyrite microcrystals in framboids

Framboids from Holocene to Pleistocene sediment samples from five localities were examined by SEM. The results indicate that the octahedral microcrystals are arranged in a regular fashion. A notable feature is that the octahedral microcrystals are linked together by shared edges. We found two types of two-dimensional arrangements: "Pattern A" and "Pattern B" (Fig. 2). In "Pattern A" each octahedral microcrystal makes lattice-like arrangements. The microcrystal arrangement in "Pattern B" consists of two kinds of triangles which are (111) faces of octahedral microcrystals and the voids between them. In "Pattern B," the microcrystals of the next upper layer are sited directly above the tetrahedral voids which are formed by four adjacent edge-sharing octahedra of the lower layer.

Considering all information from these two-dimensional arrangements, it is possible to construct a three-dimensional schematic structure (Fig. 2c). The arrangements can be interpreted as accumulations of the octahedral layers ("Pattern B") similar to cubic close packing of spheres. Such a regular arrangement of microcrystals in framboidal pyrite was reported by Kalliokoski and Cathles (1969). Note that individual faces of the microcrystals never come into contact.

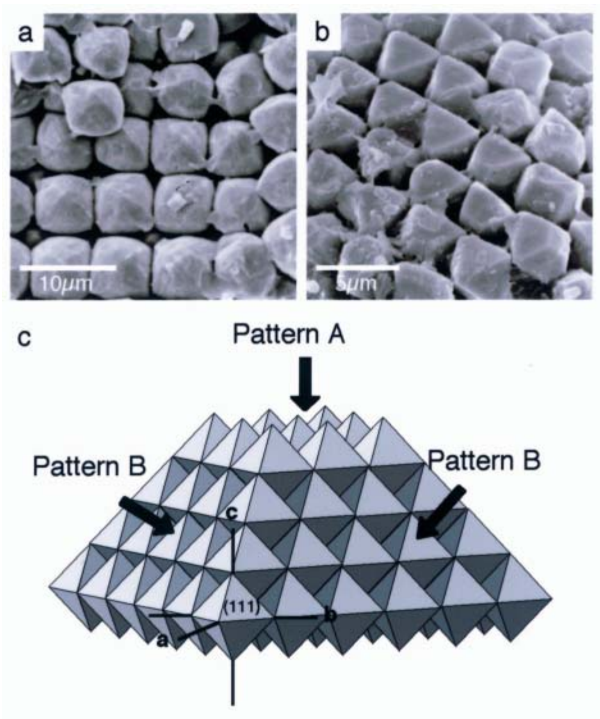

FIGURE 2. Arrangement of microcrystals in framboidal pyrite. (**a**) SEM image of a two-dimensional arrangement of octahedral microcrystals in a framboid from Shirone drill core (62m). The microcrystals are arranged in a lattice-like pattern ("Pattern A"). (**b**) Another regular arrangement ("Pattern B") of microcrystals in a framboid from Shirone drill core (27m). (**c**) Three-dimensional schematic packing structure of microcrystals in framboids. "Pattern A" is the view perpendicular to the crystal axes of microcrystals, and "Pattern B" is the view down [111].

Domain structure in framboid

We found through the course of this study that microcrystals are arranged in discrete domain structures with different orientation in most framboids. On some sections, the microcrystal arrangements are trigonal as shown in Figure 3a. They consist of a triangular domain (colored blue) in the center, three rectangular (or trapezoidal)-like domains (colored red) in contact with the sides of the central triangle, and fan-shaped domains (colored blue) between the rectangular domains. In the central triangular domain, individual microcrystals show (111) of the octahedra and such arrangements correspond to "Pattern B" of Figure 2. On the other hand, the arrangements in the rectangular domains correspond to "Pattern A." The fan-shaped domains between two rectangular domains are regarded as "Pattern B," although they are actually subdivided into six subtly different directional "Pattern B" domains by a bisector of the angle between the rectangles. Consequently, such arrangements indicate distributions with threefold symmetry.

Pentagonal arrangements of microcrystals are also found in the other sections (Fig. 3b) Similar pentagonal arrangements of framboids are reported from Rammelsberg Banderz (Devonian) in Germany (Love and Amstutz 1966), Carboniferous

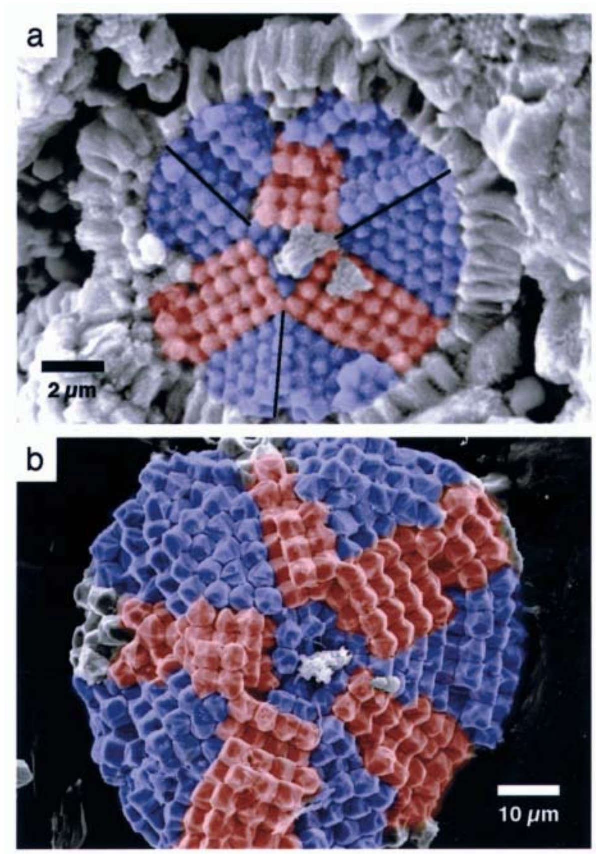

FIGURE 3. SEM image of symmetrical domain structures on sections of framboids. (**a**) Trigonal arrangement of microcrystals on the section of a framboid (polyframboid, Shirone drill core, 31m). The outermost crust is composed of secondary pyrite. (**b**) Pentagonal domain structure on the section of a framboid from Shirone drill core (62m).

limestones at Tynagh, Ireland (Morrissey 1972), and modern freshwater canal sediments in the U.K. (Large et al. 2001). The pentagonal arrangements consist of a pentagonal domain (colored blue) in the center, five rectangular (or trapezoidal)-like domains (colored red) in contact with the sides of the pentagon, and fan-shaped domains (colored blue) between each rectangular domain. In the five rectangular domains, the microcrystals show arrangements like "Pattern A." In the fan-shaped domains, they arrange as in "Pattern B." Although individual framboids were sectioned carefully with tweezers so that all the microcrystals would keep their original arrangements, the section planes were not always perfectly even. Therefore, in such cases, the oblique effects of microcrystal arrangements should also be taken into consideration. We checked the patterns of microcrystals carefully for such declined sections.

Icosahedral domain structure

SEM observations of various two-dimensional sections of framboids revealed the three-dimensional arrangement of the domain structures (Fig. 4). This figure shows examples of two different sections: "Section 1" and "2" of a framboid. There is a trigonal domain in the center of each section and the triangle on "Section 2" is larger than that of "Section 1." We interpret that the trigonal domain observed in this study represents a different cross section of one tetrahedron unit, with an apex in the center of the framboid (Fig. 4). "Section 1" is likely the inner part and "Section 2" is probably the outer part of a tetrahedron unit. Twenty tetrahedral domains are adjacent to each other, stacked by packing on three faces out of four. Thus, the tetrahedral domains define the shape of an icosahedron. The icosahedral form composed of particles is known for some radiolarians (Haeckel 1904), some viruses (Horne et al. 1959), and micro clusters [e.g., fullerene: C_{60}, C_{70} (Kroto et al. 1985)] in nature. An icosahedron has six fivefold axes at each apex and ten threefold axes at each face (Fig. 5). Therefore, perpendicular sections to axes through each apex and the core of the icosahedron show a fivefold symmetrical domain distribution as shown in "Section B" of Figure 5, and this corresponds to Figure 3b. Parallel sections to each trigonal face of the icosahedron show threefold symmetrical distributions as shown in "Section A," and this corresponds to Figure 3a. In each tetrahedral unit, the arrangement of octahedral microcrystals approaches cubic closest packing as shown in Figure 4, where each face of a tetrahedral unit corresponds to (111) of the octahedral microcrystals, and the edges correspond to the [100] direction. Such a densely packed icosahedral material composed of numerous particles has not previously been seen in nature, because the above-mentioned examples form the skeletal frameworks around empty interiors.

As shown in Table 1, the icosahedral domain structure was commonly found in most pyrite framboids from Holocene to Pleistocene sedimentary rocks and some framboids from modern muddy sediments. A characteristic commonality of the icosahedral framboids is that the microcrystals are always octahedral in shape and the *D/d* ratio of the icosahedral framboids is invariably larger than that of irregular framboids which consist of cubic ~ cuboidal microcrystals. This fact suggests that formation of the icosahedral domain structure might be related to the initial nucleation rate and growth time of microcrystals and the number of microcrystals formed within one framboid. In addition, given the frequent occurrences of the icosahedral framboid in older sediments, there are some possibilities that the icosahedral structure might form in response to external pressure (e.g., compactions of the surrounding sediments),

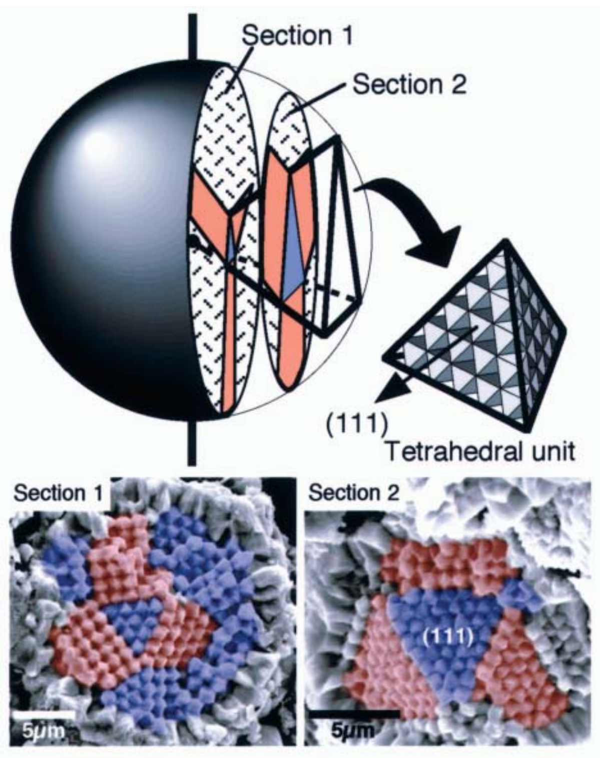

FIGURE 4. Three-dimensional distribution of each domain in a framboid. The two SEM images of the sections of framboids correspond to two different sections of one tetrahedral unit. The rectangular domains (colored red) are interpreted as sections parallel to two parallel edges of the tetrahedral unit. Both SEM images show pyrite framboids from Shirone drill core (31m).

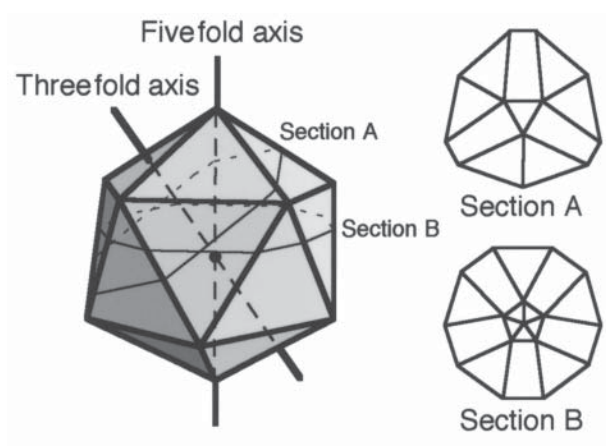

FIGURE 5. Symmetry of an icosahedron and its sections.

which accelerates rearrangement of the microcrystals to achieve denser structures. Although Wilkin and Barnes (1997) proposed a model for framboid formation that proceeds via the magnetic accretion of greigite particles, this is probably not essential (Butler and Rickard 2000). The detailed formation mechanism of framboid still remains uncertain. Our discovery of the icosahedral structure, which is regarded as a dynamically stable structure in framboidal pyrite, may help to clarify the self-organization process of framboid formation.

ACKNOWLEDGMENTS

We thank S. Akiyama of the Department of Mathematics, Niigata University for helpful discussions, T. Ito of Hokkaido University of Education, I. Kobayashi, and K. Yasui of Niigata University for providing samples used in this work, and J.F. Banfield of the University of Wisconsin-Madison and G.R. Shi of Deakin University for their critical reading of the manuscript. This study was supported in part by a Grand-in-Aid for Scientific Research (A) (no. 12304035) from the Ministry of Education, Japan.

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MANUSCRIPT RECEIVED MARCH 20, 2001
MANUSCRIPT ACCEPTED AUGUST 13, 2001
MANUSCRIPT HANDLED BY LEE A. GROAT