

26. A PRELIMINARY DESCRIPTION OF MICROCRYSTALLINE PYRITE FROM THE NANNOPLANKTON OOZE AT SITE 251, SOUTHWEST INDIAN OCEAN

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ABSTRACT

Microcrystalline pyrite from Site 251, on the Southwest Branch of the Indian Ocean Ridge, was examined by reflected light microscopy, scanning electron microscopy, and electron microprobe.

The pyrite consisted of indistinct (poorly defined) clusters of discrete crystallites and framboids (2-35 μ in spheroid diameter) in approximately equal proportions. The constituent crystallites, from 0.2-0.3 μ in size, were uniformly octahedral. In addition to pyrite, coccoliths and discoasters were found, as was the mineral gypsum. These are interpreted in terms of the genesis of the pyrite. It is concluded that the major source of iron for pyrite formation in calcareous nannoplankton ooze environments is unlikely to have been that previously advocated for sediments in general, namely, clastic iron minerals and clay fraction iron; rather, it is proposed that the nannoplankton was the source. Since it is also proposed that the nannoplankton provided the organic substrate for the bacteria responsible for pyrite formation, it follows that authigenic microcrystalline pyrite concentrations in chalk environments will only be found at horizons formed where relatively high nannoplankton concentrations existed.

INTRODUCTION

Microscopic pyrite from Site 251 (Sample 251A-11-1, 118 cm) was examined by reflected light microscopy and scanning electron microscopy (SEM). X-ray scanning photographs for calcium, iron, and sulfur were obtained with an electron microprobe.

The pyrite occurs within nannoplankton ooze sediments as indistinct (poorly defined) collections of octahedral microcrystallites; as framboids, which are commonly aggregated into cohesive clusters, but which are also found as discrete spheroids; and as thin, continuous layers of unordered octahedra. Extensive literature exists on the subject of microcrystalline sedimentary pyrite, especially framboidal pyrite which is the most abundant form of iron sulfide in sedimentary rocks. After reviewing this literature, it is concluded that the uniformity of grain size and the preponderance of the octahedral form of pyrite described here is unusual, although admittedly only a small sample was available for study. The most recent review of microcrystalline pyrite (Love and Amstutz, 1966) cites 104 papers which describe the widespread geographical and stratigraphical occurrence of framboids. These authors described framboids in terms of their morphology as did Rickard (1970) more recently. Before further describing the Site 251 occurrence, it is necessary to present a brief outline of the morphological characteristics currently employed to define framboidal pyrite.

The term framboid was coined by Rust (1935) to define "...clusters of tiny pyrite cubes and grains, the whole with a spheroidal outline." A modern definition,

as a result of the examination of framboids by many workers using reflected light microscopy and, in the last few years, SEM, will, of necessity, include many characteristics not noted by Rust. Such a definition can be more precise, unfortunately it cannot be as concise.

FRAMBOID MORPHOLOGY

The features to be described comprise the following: the external shape, the surface texture and size, the constituent crystallite shape and size, and the limits on each characteristic, beyond which the framboid, by definition, merges into some ill-defined crystal aggregate.

External Shape: Despite their name, framboids are not raspberry shaped. They have been described as spheroidal (Rust, 1935) and spherular (Vallentyne, 1963), the latter implying spherical to subspherical form. Love (1967) used the word ovoid for some of the subspherical forms. This must mark the subspherical limit of truly framboidal shape.

Surface Texture: It may be rough or smooth. As Love and Amstutz (1966) put it "...they may be rounded off as if to fit against an unseen outer wall,..." This perfect rounding may be explained by the action of a retaining/restraining outer membrane, or "sac" identified by Sweeney and Kaplan's (1973) SEM study of framboids.

Size: Statistical studies of various framboid assemblages indicated, until recently, that the size range for individual framboids was from 1 to 100 μ . Very much larger (up to 250 μ) framboids were found by Sweeney

and Kaplan (1973) in the basin sediments off the coast of Southern California, although they report that most framboids were smaller than 20μ in diameter. Love and Amstutz (1966) cite earlier papers which showed that framboids from various sources display a unimodal size distribution. They supported this with their observations on the Chattanooga Shale, where a positively skewed, unimodal distribution, peaking at around $5\text{--}6\mu$ was found. Love (1967), studying modern sediments from the wash (England) and Richard (1970) studying framboids in the sedimentary rocks of the Tynagh ore deposit, Eire, also found single mode distributions with peaks at $3\text{--}4\mu$ and 4μ , respectively.

It is tempting to use these consistent data in a definition of framboid assemblages, but until a wider spectrum of assemblages have been examined, neither size range nor distribution can be regarded as diagnostic.

Crystallite Shape and Size: The constituent crystallites of any one framboid appear to display only one crystal habit. All the pyrite of the present investigation is octahedral. Previously, octahedral forms had been described by Honjo et al. (1965), Kalliokoski and Cathles (1969), and Sweeney and Kaplan (1973). Cubic forms are figured by the latter authors and by Love and Amstutz (1966).

The major problem in identifying crystal habits has been that until the development of the SEM it was necessary to interpret the habit from the plane surface of a polished section. For example, Love and Amstutz interpreted the hexagonal sections in their specimens as being sections through pyritohedra and Skripchenko (1971) interpreted triangular outlines, in his specimens, as tetrahedra. Tetrahedral pyrite must be suspect. Such triangular outlines can, however, be interpreted as sections through, or faces of, octahedra (Plate 1, Figure 1).

The most consistent characteristic of framboids is that the constituent crystallites of any one framboid are approximately equidimensional. A review of the literature reveals only one exception to this rule, and this exception is in the unusually large framboids reported by Sweeney and Kaplan (1973). In these, smaller crystallites were intermixed in a framework of larger crystals.

With respect to size, Rickard (1970) has suggested that a maximum limit should be set on the ratio of crystallite size to spheroid diameter of 1:10.

Finally, the constituent crystallites may, or may not, be geometrically ordered. Five patterns were recognized by Love and Amstutz (1966) from polished sections. These were: unordered patterns, square patterns, hexahedral patterns, irregular to six-sided patterns, and linear patterns. They interpreted the first three, somewhat speculatively, as structurally random, cube structure, open-packed pyritohedra, and close-packed pyritohedra, respectively.

When all these data are considered it becomes possible to redefine pyrite framboids as follows:

A framboid consists of a microscopic aggregate of discrete, equant, morphologically (usually) single-habit, crystallites which may be packed randomly, or with some geometric regularity, to form a microscopic

spheroid in which the maximum ratio of crystallite size to spheroid diameter is 1:10. The surface of the spheroid may be smooth, or uneven; uneven, that is, within the limits imposed by spheroidicity.

The author agrees with Rickard (1970) that a qualifying adjective be used when there is any departure from the basic form. However, some special cases exist that justify the introduction of a new term. For example, when individual framboids compound to produce a larger spheroid, a new term is in order. Such compound forms were called "Rogenpyrits" by Fabricius (1961), unfortunately, this has genetic as well as morphological implications. Therefore, Love's (1971) entirely morphological term, polyframboid, is to be preferred. Polyframboids were found by Love to range in diameter from 35μ to 900μ .

MICROCRYSTALLINE PYRITE, SAMPLE 251A-11-1, 118 cm

Morphology

It was not feasible to prepare a sieved fraction of the sediment because of the limited amount of material available. Consequently, some of the nannoplankton ooze was mounted in cold-setting epoxy resin and polished. The remainder was mounted, using double-sided adhesive tape, on SEM stubs and gold coated. The polished mounts were examined in oil with the reflected light microscope using $\times 40$ and $\times 100$ oil immersion objectives.

The microscopic pyrite consisted of cohesive clusters of framboids, discrete framboids, and poorly defined clusters of discrete octahedra. It was impossible to conduct a statistical analysis of the various types, but visual estimates suggest that the formless clusters of octahedra are about equiproportional with the framboid/framboid aggregates. The term *nebuloid* is proposed for the apparently formless, structureless clusters of discrete crystallites.

Nebuloids

In polished section the triangular outlines of individual octahedra are grouped to form chainlike or filamentous lines, sometimes as small as one crystal thick. These filaments may be curved or straight and are often connected to concentrated clusters of randomly organized octahedra.

At the very high optical magnification used, depth of focus is obviously small, but when crossed nicols are used and the focus adjusted up and down, the octahedral form of the crystallites is recognizable. Unfortunately, the photomicrographs cannot show more than the triangular sections. Plate 1, Figure 1, is a typical nebuloid cluster. The size of the constituent octahedra measured varied from 0.5μ to 3μ .

Framboids

The diameter of the framboids fell within the size range $2\mu\text{--}35\mu$, the majority being between 3μ and 5μ . The constituent crystallites ranged from 0.2μ , in the case of the 2μ framboids (just within Rickard's crystallite-to-

spheroid ratio of 1:10), to about 2μ . It was noticeable that crystallite size was consistent for any one framboid, but was usually not constant from one framboid to another, even in a group of the same diameter. All the framboids were spheroidal, but none had a perfectly circular outline. Plate 1, Figures 2, 3, and 4 typify the forms at the lower end of the size range. It can be seen that there is no detectable sign of geometric regularity in the ordering of crystallites in any of the framboids. In section, their surfaces are well rounded and yet one framboid in Figure 2 shows clearly the peripheral octahedra, which, apparently, were not impeded in their growth.

Plate 1, Figures 3 and 4, show the groundmass in which many of the aggregated framboids are found. It can be seen that microcrystalline pyrite is intimately mixed with some gray, low-reflecting mineral. Under crossed nicols the gray mineral is translucent bright red and yellow. Any crystallinity is unresolvable, even at the highest optical magnification. The individual crystallites in some of the framboids are separated, perhaps cemented, by this material. Figure 3 also shows a framboid pair closely resembling a sectioned toroid. It is considered similar to the Doppelkugeln of Fabricius (1961). The stellate cluster of pyrite in the matrix prompts the question whether it might be a framboid in the process of degeneration, or the "petrified" remains of a youthful stage in framboid growth. Such strictly genetic questions will be discussed in a subsequent paper.

The largest framboids in the sample were poorly spheroidal, approximating to Love's (1967) ovoids in form, others were tear shaped (Plate 1, Figure 5). The constituent crystallites of these $30\text{--}35\mu$ framboids were between 0.8μ and 2μ in size. It is easy, after studying Figure 5, to be convinced that it is a compound spheroid. The simplest interpretation is that there is a smaller spheroid (secondary) at the pointed end which has been assimilated into the larger (primary) spheroid, while at the same time retaining a degree of circular ordering of its crystallites. Other similar framboids will have to be examined before this interpretation can be verified.

The SEM investigation confirmed that all the pyrite in the sample was octahedral. It also revealed that much of the pyrite was included in unordered layers or thin plates. These fragmented layers—a certain amount of comminution was necessary in the preparation of the mounts—were up to 0.2 mm thick and 1 mm along an edge. Plate 2, Figure 1, shows the flat, granular surface of one aggregate layer and Plate 2, Figure 2, a higher magnification photograph of a representative part of the same surface, reveals that the pyrite is only organized so as to present an even flat surface. There is no indication that the pyrite is cemented. When an edge of the layer was examined, some of the octahedra were seen to be similarly cement free (Plate 2, Figure 3). However, patches of crystallites were found that had a clearly defined coating layer, or cement (Plate 2, Figures 4 and 5). Voids in the aggregate, which from their outline can be seen to have contained octahedra (Figure 5), partially retain an extremely thin layer of coating material (as

little as 0.05μ thick). In the case of framboidal aggregates, some display a microscopically thick layer of material which coats the constituent crystallites (cf. Sweeney and Kaplan, 1973), while others are completely "clean." Plate 2, Figures 6, 7, and 8, all of the same area but at progressively higher magnification, show this layer very clearly. Figure 6 also shows that framboids retain their spheroidal form even when they are surrounded by nebulous clusters of discrete crystallites. These clusters would almost certainly be described as nebuloids when viewed with an optical microscope.

The coating material described here is presumably similar to the red and yellow, translucent groundmass noted in the reflected light study (Plate 1, Figures 3 and 4). It was impossible to establish its composition by any known analytical technique because of its extremely fine size. It was possible, however, by means of the electron microprobe, to establish which major elements were present in the framboid clusters.

Electron Microprobe Examination

The framboid cluster, parts of which are shown in Plate 1, Figures 3 and 4, was found to be typical. As anticipated, only iron and sulfur were found in substantial amounts, although minor localized concentrations of calcium were also found. X-ray scanning photographs were taken of this 0.35-mm aggregate, for the three elements, and are presented in Plate 3, Figures 1, 2, and 3. It can be seen that iron is distributed uniformly (Plate 3, Figure 1), sulfur forms definite circular spots (Plate 3, Figure 2) outlining the position of individual framboids, and calcium shows up as small concentrated blebs. At higher magnifications (Plate 3, Figures 4 and 5) the homogeneity of the iron concentration is maintained and the sulfur spots clearly outline the framboid centers. Since neither sulfur nor calcium are found in any concentration between sulfur spots, whereas iron is, it is clear that the red and yellow groundmass material is iron rich, conceivably an iron-oxide phase. Unfortunately, the electron microprobe used for these studies was not equipped for oxygen determination. Qualitative, if rather ambiguous, support for the groundmass material being an iron-oxide phase was found in the reflected light study. One 10μ diameter spheroid, with the same optical characteristics as the groundmass, was located: it was not framboidal and is best interpreted as an iron-oxide spheroid, closely resembling those described by Loughheed and Mancuso (1973) from the Negaunee Iron Formation, Michigan.

"Gangue" Material

This account of the microcrystalline pyrite would not be complete without a summary of the major constituents of the sediment in which the pyrite, which forms a proportionally minor part, was found.

The fossils present include coccoliths and discoasters. Apart from calcite, the only other mineral identified, gypsum, is particularly common. It occurs in prismatic and flattened crystal groups (Plate 4, Figure 1) in which individual crystal sizes of up to 150μ are common. In addition, rosettes up to 1 mm in section (Plate 4, Figure 2) are found. Pyrite layers are often intimately

associated with the gypsum. The presence of so much fossil debris and the abundance of gypsum may be particularly significant in terms of the genesis of microcrystalline pyrite in these sediments.

DISCUSSION

Two separate but related questions must be asked when considering the formation of framboids and microcrystalline pyrite in sediments and sedimentary rocks. These are, firstly, how and why did pyrite form and, secondly, how and why did it form framboids and nebuloids. Since this is essentially a morphological study, it is sufficient to outline very briefly how the Site 251 material fits the established data. Before doing so the main morphological characteristics of the assemblage will be restated: microcrystalline pyrite in nebuloid forms and framboids is associated with fossil nannoplankton and abundant gypsum in a nannoplankton ooze sediment.

Origin of Pyrite in the Sediment

Early diagenetic pyrite in Recent sediments is well established as resulting from the reaction of iron from clastic iron minerals (Kaplan et al., 1963; Berner, 1964b, c, d) and clay minerals (Carroll, 1958), with hydrogen sulfide and elemental sulfur produced by bacterial sulfate reduction (Berner, 1969, 1970).

With respect to formation of pyrite in a calcareous nannoplankton ooze environment, where clastic iron minerals and clay fraction iron would be expected to be of relatively low concentration, it is necessary to look for other sources of iron. It is proposed that a major source of iron is to be found in the nannoplankton for, as Harvey (1937-38) stated, there is "...little more ionic iron in a cubic metre of water than found in a diatom of moderate size." This proposal is under investigation and will form the basis of another contribution.

It has been shown that the organic fraction of sediments is an inadequate source of sulfur for pyrite formation and that the single most important source is the reduction of sulfates from the overlying seawater (Kaplan et al., 1963). However, to provide sufficient sulfate, it was necessary to invoke the idea of a sulfate gradient in seawater and sediment (Berner, 1964a). Further, it was shown that nonbacterial sulfate reduction of marine waters does not occur (Berner, 1970). Thus, as Berner (1970) showed, the essential requirements for the production of microcrystalline pyrite in normal marine waters are that there is (a) organic matter for the metabolism of sulfate-reducing bacteria; (b) diffusion, and the establishment of a diffusion gradient of sulfate into the sediment; and (c) sufficient reactive iron concentrated in iron minerals and clays or, as postulated here, in the nannoplankton. An extremely elegant seven-stage model was produced by Berner (1970) to explain pyrite formation. It is unnecessary to repeat it in full, but some of the points will be described.

The initial step in the production of pyrite is the formation of noncrystalline iron monosulfide by the reaction of hydrogen sulfide with iron. The limiting factors are, therefore, the rate of production of hydrogen sulfide and/or the amount of reactive iron available. As the process develops, some of the

hydrogen sulfide is oxidized to give elemental sulfur which slowly reacts with the iron sulfide to form pyrite. Oxidation is accomplished either inorganically or by sulfur-oxidizing bacteria. In the presence of oxygen, which could be introduced by agitation after storm currents, or by burrowing organisms, part of the elemental sulfur would be reoxidized to sulfate. As Berner envisaged it, the formation of pyrite framboids would require several years in such an environment. In the case of Site 251, the abundance of gypsum could be explained as the product of the reaction of sulfate ions with calcite, the sulfate ions being supplied by the diffusion gradient established in the production of pyrite, both processes being early diagenetic. The pyrite formed in the way described by Berner, with difference that, in this instance, the nannoplankton provided both the organic substrate for the sulfate-reducing bacteria and, probably, most of the iron.

Origin of Framboids and Microcrystalline Pyrite

The answers offered by many authors to the questions of how and why microcrystalline pyrite, particularly framboidal pyrite, should form, are many and varied. It is beyond the scope of this paper to review them. Several recent studies have included such reviews, along with new proposals for the reasons for the formation of framboids. These include, Love (1967, 1971); Kalliokoski and Cathles (1969); Rickard (1970); stated the position very well when he concluded that "...Framboid formation may proceed through several different pathways, including pseudomorphism of immiscible organic globules, of spherular organic coacervates, possibly of single-celled microorganisms and by the infilling of gaseous vacuoles. It is impossible to say how much any one of these mechanisms contributes to framboid formation."

Clearly, with the assemblage here described, in which nebuloid crystallite clusters and framboids are intimately intermixed, the problems of interpretation are increased. Until a more detailed study is undertaken, none of the above proposals is supported.

SUMMARY

The microcrystalline pyrite from Site 251 (Sample 251A-11-a, 118 cm) displays a distinctive, uniformly octahedral, habit. It occurs as poorly defined clusters of individual octahedra (for which the term nebuloid is proposed) of grain size 1μ to 3μ and as framboids of spheroid diameter 2μ to 35μ composed of discrete octahedral crystallites from 0.2μ to 2μ in size. Some of the framboids and nebuloids were coated with an extremely thin (as little as 0.05μ) layer of an indeterminate material. It is tentatively suggested that this material is an iron oxide.

It is proposed that the iron necessary for the production of pyrite was provided largely by the nannoplankton which were found in association with the pyrite. The once organic constituents of these fossils are interpreted as having provided the sulfur for the pyrite production. Gypsum was formed by the reaction of sulfate ions introduced during the pyrite formation, with calcium carbonate from the sediment.

The presence of framboidal and nebuloidal pyrite in the chalks and oozes of the Indian Ocean Ridge is to be expected wherever a sufficient concentration of microorganisms is found.

ACKNOWLEDGMENTS

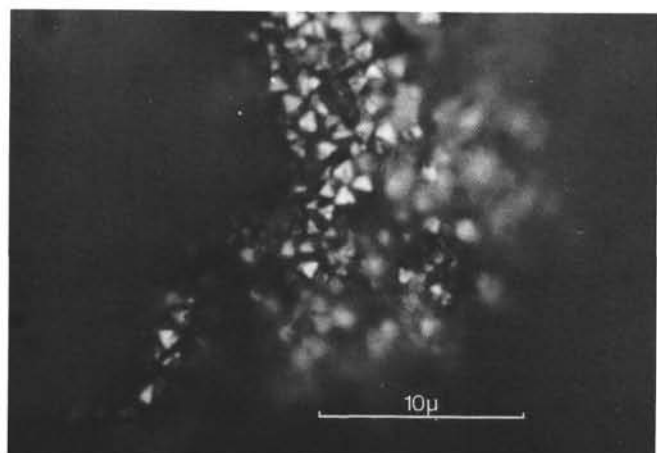
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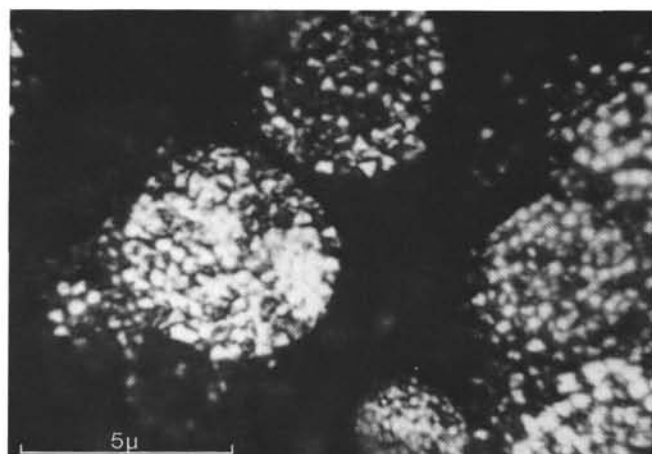
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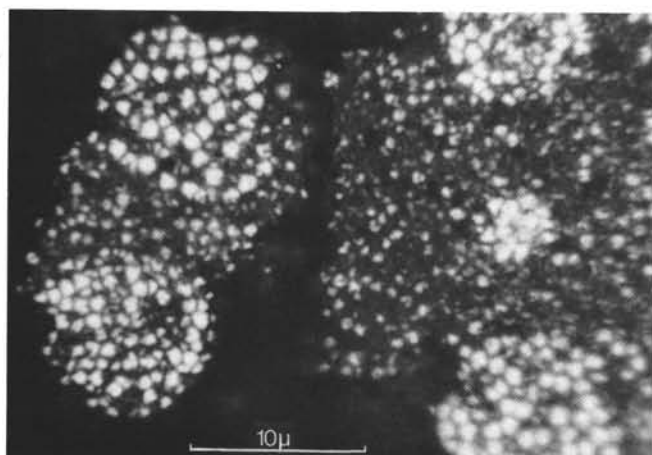
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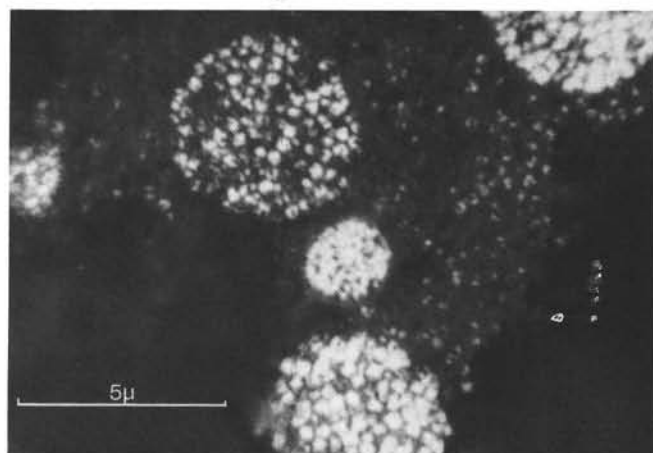
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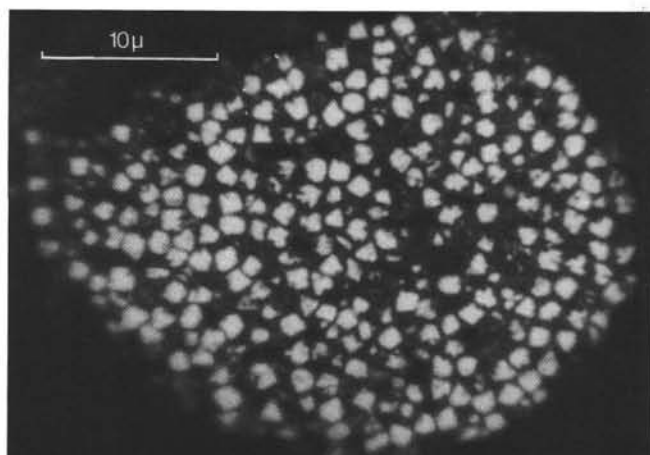
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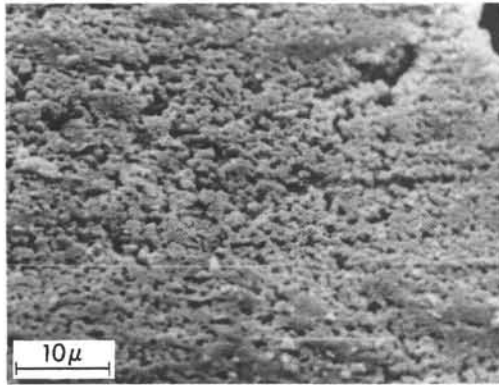
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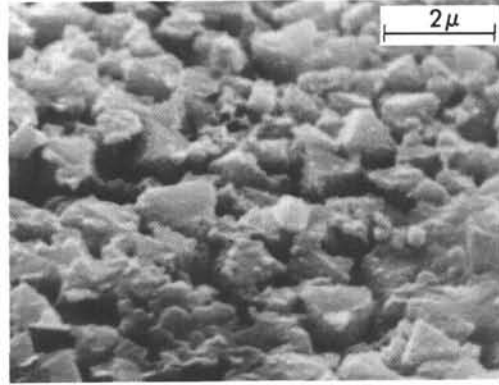
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Reflected light optical photomicrographs of polished sections of nebulous octahedral pyrite and framboidal pyrite from Sample 251A-11-1, 118 cm.

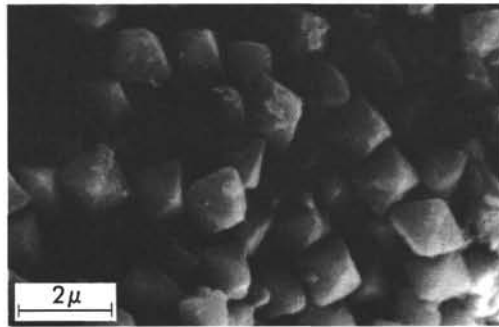
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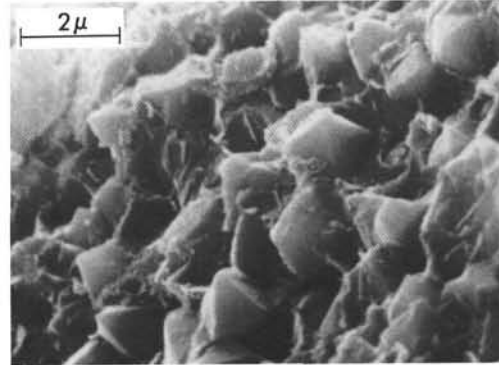
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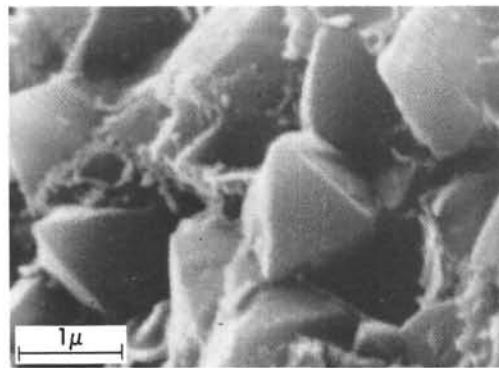
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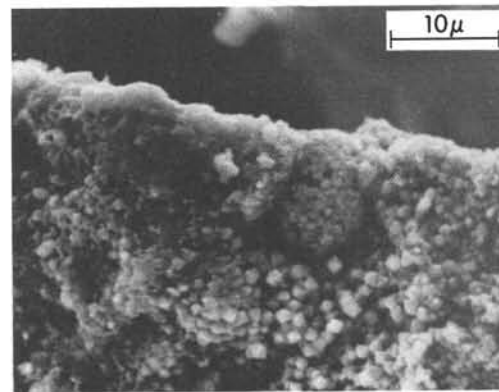
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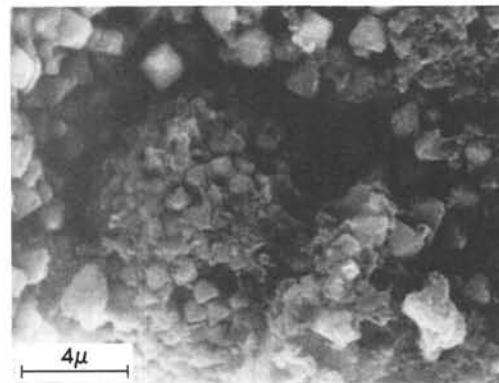
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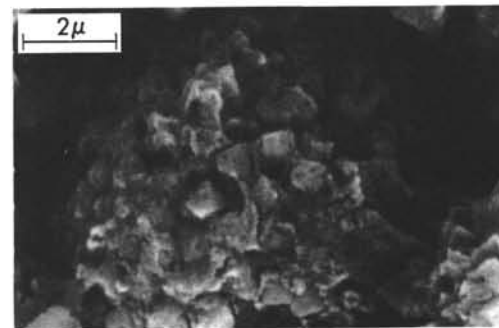
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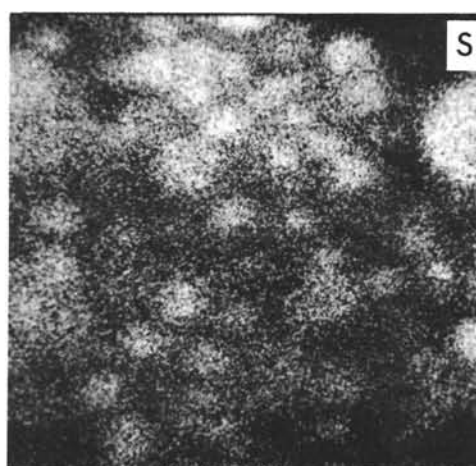
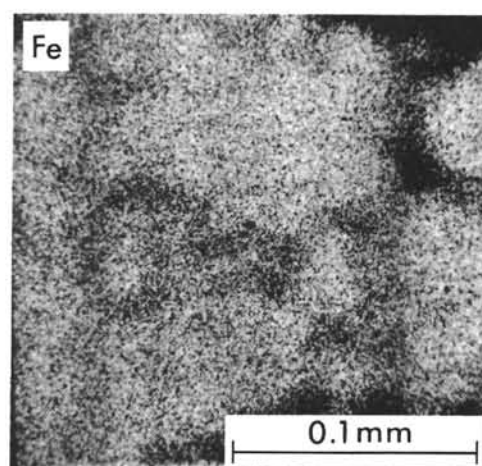
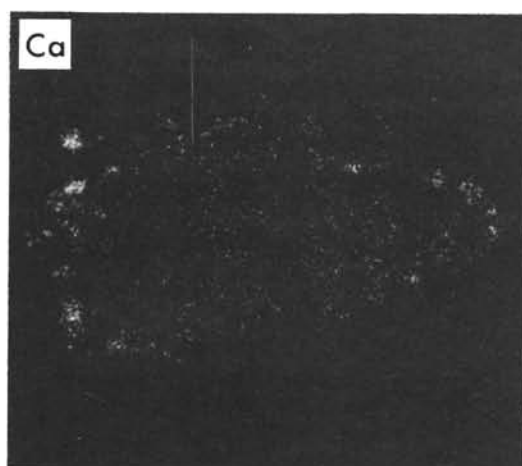
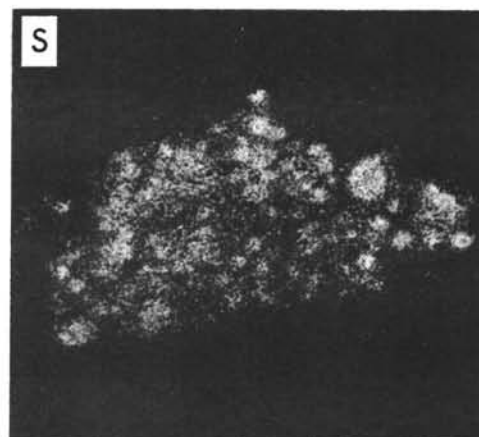
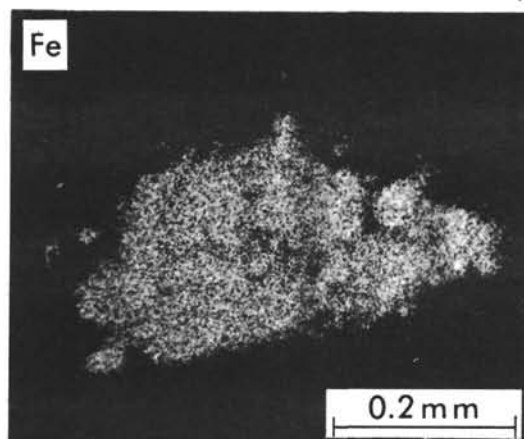
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SEM photographs by H. A. Buckley of microcrystalline octahedral pyrite and framboidal pyrite from Site 251 (gold coating).

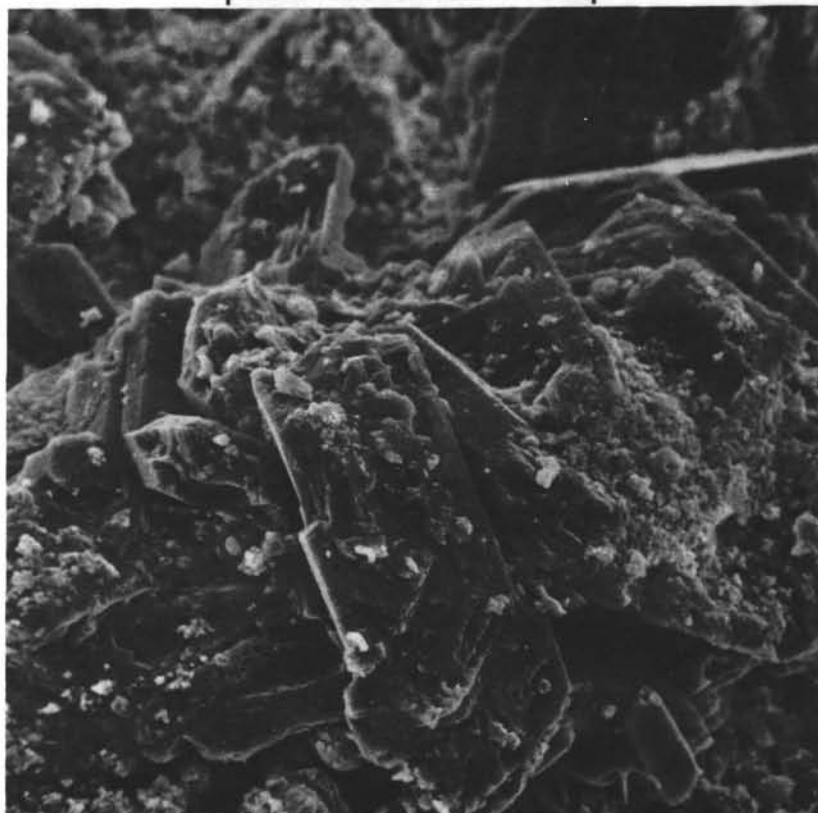
PLATE 3



X-ray scanning photographs by A. M. Clark of an aggregated cluster of framboids from Site 251, for iron, sulfur, and calcium.

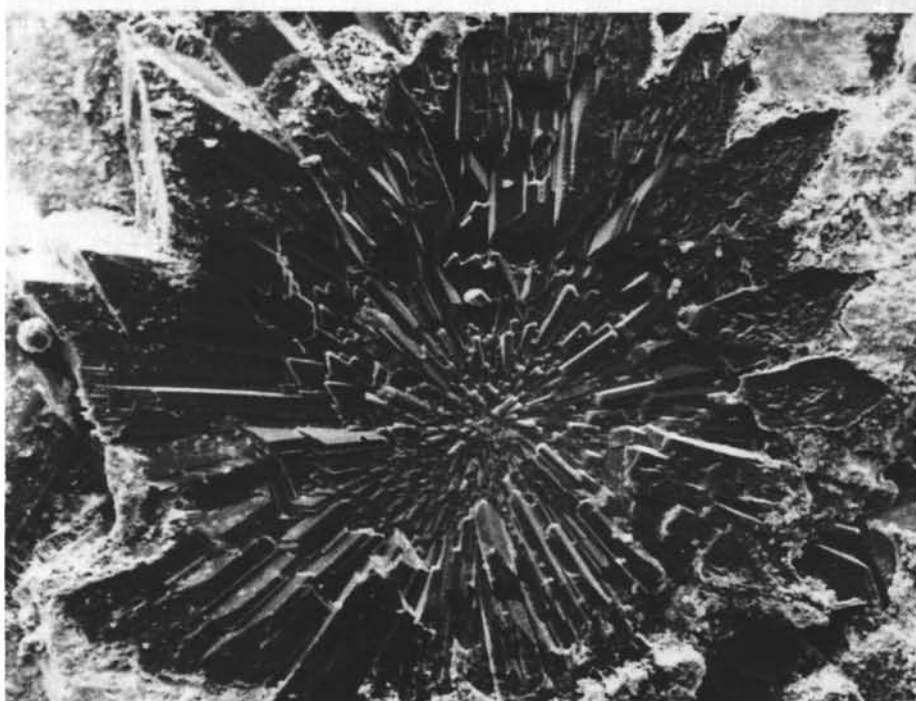
PLATE 4

100 μ



1

1.0mm



2

SEM photographs by H. A. Buckley of gypsum crystals from Site 251 (gold coating).