"FRAMBOIDAL" CHALCOCITE
FROM WHITE PINE, MICHIGAN

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ABSTRACT

"FRAMBOIDAL" CHALCOCITE FROM WHITE PINE, MICHIGAN

By

Nancy Alyanak

Chalcocite with nuclei occurs throughout the mineralized zone at White Pine, Michigan. They are more abundant in the well-laminated, black, fine-grained lithologies than in the massive lithologies. The nuclei are similar to the framboidal texture commonly observed in pyrite associated with sediments. The chalcocite nuclei can only be observed after the polished section has been etched and stained with a weak hydrochloric acid and potassium ferrocyanide solution--a stain very sensitive to low concentrations of iron.

The scanning electron microscope shows that microcysts at least as small as .2 microns are found in each nucleus. Microcrysts within a well-defined circular or elliptical nucleus are densely packed, with a few scattered microcrysts in the surrounding grain. However, the microcrysts are less densely packed where the nucleus occupies the entire grain. All gradations between the dispersed and densely packed microcrysts are found.

In polished section these nuclei are either circular, elliptical or conform to the shape of the grain, with a median circular diameter of four microns and a median elliptical long axis of eight microns. It is concluded that the framboidal cores are biaxial prolate ellipsoids. Using Wicksell's method, the size frequency distribution for the minor axis of the framboids was calculated and then compared to known size frequency distributions of framboidal pyrite.

Two origins are possible for the framboidal chalcocite: (1) replacement of framboidal pyrite, and (2) formation of primary framboidal chalcocite. To evaluate the first alternative the pyrite zone and the fringe zone were examined for framboids like those in the chalcocite. None were found, supporting the second model.

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INTRODUCTION

Nuclei in chalcocite grains from White Pine, Michigan occur throughout the ore body and can be observed in polished section after etching and staining with hydrochloric acid and potassium ferrocyanide. Detailed examination with the scanning electron microscope showed that these cores are framboids and are similar to pyrite framboids which have been found in black shales from Precambrian to recent. Although pyrite is by far the most common mineral that is framboidal, other sulfides and oxides have been found with this texture.

By definition, a framboid is an aggomeration of small grains, called microcrysts, into a sphere or ellipsoid (Love & Amstutz, 1966). The chalcocite would fit this definition and as described below the size distribution of the chalcocite framboids is similar to those found in pyrite.

Once the framboidal nature of the chalcocite has been established, their origin is important in understanding the origin of the mineralization at White Pine. Although this texture can be produced inorganically in pyrite (Berner, 1969), many workers interpret it as an indication of sulfate reducing bacteria. Recent studies on the requirements of biogenic sulfides (Trudinger, 1972) describe an environment compatible with that represented by the Nonesuch Shale. Sulfide fractionation studies (Burnie, 1972) also support a biogenic origin for the Nonesuch sulfides. Any theories on the origin of the chalcocite must be compatible with the formation of framboids.

Two origins for the framboidal chalcocite must be considered: either they represent replaced pyrite framboids or they are primary chalcocite. In this paper the occurrence and distribution of the framboidal chalcocite is documented and then the nature of the chalcocite is compared with the pyrite immediately above the mineralized zone.

GEOLOGIC SETTING

The ore body at White Pine Mine, Ontonagon Co. Michigan is a classic example of a strata bound ore deposit. The mineralized zone lies at the base of the Upper Keweenawan Nonesuch Shale, an organic rich series of sandstone, siltstone, and shale about 600 feet thick at White Pine. The Copper Harbor Formation, 2300 to 5500 feet of conglomerate and red sandstone, underlies the Nonesuch. The Middle Keweenawan Portage Lake Lava Series underlies the Copper Harbor and is well known for native copper deposits 20 to 80 miles to the northeast. The top of the Nonesuch grades into the overlying Freda Sandstone, 500 feet of siltstone and shale.

The mineralization occurs in a 25 foot zone within the Lower Nonesuch and Upper Copper Harbor. The lithologic units in this zone have been informally named the Lower Sandstone, the Parting Shale, the Upper Sandstone, and the Upper Shale. Each of these four have been subdivided into subunits. The subunit terminology shown in Figure 1 will be used in this paper.

The highest percent copper (about 3) mineralization occurs in Domino, Thinly, and Upper transition. Both Domino and Thinly are thinly laminated black shale and siltstones rich in organic material. The Upper Transition grades into Thinly and also contains shale beds. Copper mineralization of 1 to 2 percent is found in Dark Gray Massize and UZV. Both of these subunits are gray, massively bedded siltstones. Most of the copper is in finely dispersed grains of chalcocite. A little native copper also occurs at the base of the mineralized zone.

The Nonesuch Shale is located on the axis of the Iron River syncline, which trends NE-SW on the south flank of the Lake Superior basin. Dips in the syncline are low to the south but steep on the north side where the syncline meets the Porcupine Mt. uplift. Along the western margin of the mine the White Pine fault strikes NW and dips steeply to the NE. The displacement to the NE of the mine is much greater (3000 to 5000 miles) than to the SE (240 ft.). Many other faults are known in the area.

The mineralization in the Lower Nonesuch at White Pine has been thoroughly discussed by Ensign and others (1968), White and Wright (1954, 1966), and Brown (1971).

METHOD OF OBSERVATION

The framboidal centers in the chalcocite are only visible after the polished section has been stained with a solution of 250 ml. water, 2 ml. concentrated hydrochloric acid, and .1 ml. saturated potassium ferrocyanide solution. The thin section is immersed in the stain for 20 seconds, then rinsed with distilled water and allowed to air dry. This stain is sensitive to low concentrations of iron (Feigl, 1958). The relative concentration of iron in chalcocite can be told by the color of the stain. This color ranges from yellow at the lowest (about .5%) through purple (about .8%), deep to light blue (about 1.5%) to light green (about 2%) at the highest concentration recorded. Most chalcocite stains shades of blue. Not all chalcocite contains enough iron to react with the stain.

Under a reflected light microscope the framboidal cores usually appear as circles and ovals of beige surrounded by blue stained chalcocite (Figure 2). Not all stained chalcocite grains have cores in cross section. This either could be an effect of a random section, or not all stained grains have cores. Unstained grains never have cores.

SHAPE AND STRUCTURE

The framboids can best be observed with the scanning electron microscope. The framboids were first located with the ore microscope on a polished and stained section. Photographs show that the cores are spheres or ellipsoids filled with smaller microcrysts at least as small as .2 micron (Figure 3). In some framboids the microcrysts appear to be small platelets while in others they appear to be more equidimentional. However between framboids the size of these microcrysts varies, and in the samples studied ranged from smaller than .1 microns to .5 microns. At 20,000 magnification the microcrysts appear to be a mixture of small euhedral grains and platelets (Figure 4). It is not possible with this resolution to determine the size of the possible smaller microcrysts.

In some chalcocite grains the framboidal core is in higher relief than in others (Figure 5). This is probably due to differing hardness of the core and different responses of the framboid to the etching. Occasionally a framboid is plucked out in the preparation of the thin section (Figure 6).

Microcrysts in cores with well defined circular or elliptical cross section are densely packed. In these well defined cores, the cross sectional shape of the framboid is independent of the shape of the grain (Figure 3). These well defined cores are made up of

densely packed microcrysts and the rim surrounding these cores contain dispersed microcrysts. The number of microcrysts, from the edge of the core to the edge of the grain appear to decrease exponentially (Figure 5). In some grains the core entirely occupies the grain--that is, there is no rim surrounding the framboids (Figure 7).

The shapes of the cores are variable with most being circular or elliptical, while some approximate the shape of the grain in which they occur. All gradations exist between a grain with a well defined core and a grain with a core that completely fills the grain (Figure 8).

The circular or elliptical shape of the cores on polished section indicates that the framboids are probably ellipsoids in three dimensions. In a sample of 350 core sections there are too many (50%) circular sections for the true shape to be a triaxial ellipsoid. In the same sample the apparent long axis of the ellipse is longer than the apparent short axis. From this data it is concluded that the framboids are biaxial prolate ellipsoids.

COMPARISON WITH OTHER FRAMBOIDS

By definition, a framboid is a sphere or ellipsoid made up of microcrysts. The scanning electron microscope photographs show that the well defined oval and circular sections of cores have this framboidal structure, but the dispersed cores do not. They are made up of microcrysts, but are not spheres or ellipsoids. Framboidal cores have rarely been observed in the literature (Rust, 1935). Thus the behavior of the microcrysts during the growth of the surrounding grain can only be surmised. Since one can see microcrysts breaking away from the well defined, definitely framboidal cores, it seems reasonable to assume that the now dispersed cores were once proper ellipsoidal framboids.

Framboids have been observed with transmitted light microscope after separation from unconsolidated sediments (Love, 1967), in polished section with reflected light, and in thin section by reflected and transmitted light (Lougheed, 1973). Of these methods, the polished section with reflected light is the only possible one for the chalcocite cores. The microcrysts in the cores are too small for clear resolution under a light microscope and comparison with other framboids is made on the SEM photography and the size distribution, to be discussed later.

Some workers have found ordered packing of microcrysts in the pyrite framboids. No order is apparent in these photographs.

SIZE FREQUENCY DISTRIBUTION

The cores are of various sizes with discrete circular cores rarely having a diameter greater than 23 microns. In the elliptical cores the short axis is rarely longer than 23 microns and the long axis 26 microns. In cases where the core approximated the shape of the grain, the limit of size is the size of the grain. These cores are up to 100 microns long. The size distribution of these was not attempted, since all size distribution methods require an assumed shape.

Because of the number of circular sections encountered, the shape of the discrete framboids can be assumed to be a biaxial prolate ellipsoid and therefore a relatively easy method for the size frequency distribution of the minor axis can be used. This method was developed by Wicksell (1925) for spheres and later extended by him to special cases of ellipsoids (1926). It is the only method that does not assume constant axial ratios or a given eccentricity (Underwood, 1970).

Wicksell requires the following assumptions: (1) Prolate ellipsoid of revolution, (2) Unimodal distribution, (3) Random distribution in space, (4) Random orientation of axes, (5) Orientation independent of size, (6) eccentricity independent of size.

The shape of the size frequency distribution obtained using this method is easily comparable to that measured directly by other workers for spherical pyrite framboid (Love, 1967) (Figure 9). This size frequency distribution of the chalcocite cores falls easily into the known size distribution of pyrite framboids, further evidence that the cores are actually framboids.

LITHOLOGIC DISTRIBUTION

Although framboidal chalcocite grains are found throughout the mineralized zone, they are not equally abundant in all lithologies. Detailed studies of samples from a vertical column (Longwall) show that the framboidal chalcocite grains are most common in the finer grained laminated lithologies--Lower Transition-Domino, Upper Transition-Thinly and Top Zone. The massive, less well laminated, ore bearing lithologies contain fewer framboidal grains.

There is no stratigraphic or lithologic correlation with the two core types. Well defined cores and dispersed cores can be found adjacent.

COMPOSITION

The framboidal cores were originally observed because of the difference in response between core and the surrounding grain to the iron sensitive stain. From the color of the stain it was not apparent whether the core contained more or less iron than in the matrix. Microprobe traces on five selected cores were made to determine relative concentration of iron. The slides were prepared by polishing, staining, and coating with carbon.

The difference in amount of iron between rim and core varies among grains from a core 2.4 times more iron rich to cores with a very slight increase of iron (Figures 10a, 10b, 10c, 10d, 10e). Cores with well defined circular and elliptical shapes (a, b, c, d) and dispersed cores (e) show increasing iron.

Although the microprobe traces show increasing iron, this may not be the actual case. The higher iron content in the core may be due to more iron absorbed to the very high surface area of the microcrysts. Furthermore most of the framboids stand above the plane of the section (i.e., high relief) and are closer to the detectors. This would result in higher count rates. For these reasons it is not possible to determine if the core contains more or less iron than the surrounding grain, only that a difference exists.

In order to avoid this possible stain-composition interaction two other stains were tried: an a-a' dipyridyl stain (Feigl, 1958) and an ammonium dichromate stain (Einaudi, 1970). Neither were sensitive enough to detect framboids. The time consuming procedure of hunting through unstained grains under the microprobe was also attempted unsuccessfully. Carbon concentration was also found to be greater in the core than in the rim. Three microprobe traces were made for carbon (Figures 10a, 10d, 10e). This increase could also be due to high surface area and high relief of the cores since all of the sections were carbon coated.

Potassium was also found to be more concentrated in the core than in the rim (Figures 10a, 10d). Although potassium is in the stain, it is not active in the color Prussian blue. However, the possibility that potassium increases due to preparation does exist.

It is interesting to note that the sulfate reducing bacteria thought to be responsible for framboids require trace amounts of Fe, K, and C (Postgate, 1965).

ORIGIN OF FRAMBOIDS

Whatever the origin proposed for chalcocite grains, either replaced pyrite or primary, the formation of framboids must be included. Most workers believe that framboidal texture indicates the activity of sulfate reducing bacteria (Berner, 1970). The bacteria reduces the sulfate to sulfide, which forms H_2S and combines with metals. In the case of pyrite formation, a variety of FeS compounds form with pyrite as the final product (Berner, 1970).

Pyrite framboids have been produced inorganically by Berner (1969) by bubbling H_2S gas through NaOH solutions, then adding $FeSO_4 7H_2O$ to the resulting NaHS solution. In natural environments the bacteria would supply the gas.

The idea of primary chalcocite has been criticized in the past by Davidson (1962) and by Boothe and Mercer (1963) on grounds of copper toxicity to bacteria. However, Temple and LeRoux (1964) have shown that fatal copper concentration depends on the rate of H_2S production. If a bacteria colony can produce enough H_2S to precipitate the copper before it is toxic to the bacteria, then primary chalcocite framboids can develop.

If the framboids are biogenic then the Nonesuch sediments must meet the requirements of bacterial growth. Trudinger and others (1972) and Temple (1964) state that the requirements of bacteria are an anerobic, reducing condition with a slight acid to slight alkaline pH and a supply of organic material. The environment of deposition of the Nonesuch Shale is compatible with the sediment type one would expect to find bacteria in.

Further evidence for an organic origin for the sulfate at White Pine is given by a sulfur isotope study conducted by Burnie et al. (1972) which indicates that the sulfur isotopes are produced by biogenic activity.

DISCUSSION

The origin of the chalcocite in White Pine has long been debated. Authors have used it as an example of a syngenetic deposit and as an epigenetic deposit. Recent work has favored the epigenetic model (Brown, 1971; White, 1971). These conclusions were based on an irregular mineral fringe zone that cut lithologic units at a shallow angle and on zoning at the fringe (Brown, 1971). Ore bearing solutions were thought to have come from the Copper Harbor Conglomerate below. Recent work by Vogel and Ehrlich (personal communication) has shown that the fringe cutting is no more irregular than a given depositional unit.

One way to test the replacement model is to look at the pyrite zone above the mineralized zone. If the chalcocite has replaced the pyrite, then since the detailed framboidal structure is preserved, all details of the pyrite morphology should be preserved. Pyrite from the unmineralized zone, only centimeters above the chalcocite, was studied. Nine samples scattered throughout the mine area were used.

There are indeed framboids in the pyrite. Two types were found during examination of the pyrite and fringe zone. The first is made up of euhedral microcrysts of pyrite much larger (3 to 4 microns) than the microcrysts in the chalcocite framboids (less than .2

micron) (Figure 11). These pyrite framboids are also larger than the chalcocite framboids. These framboids fit the definition of framboid but are not similar to chalcocite framboids in the mineralized zone.

The second type of pyrite framboid is much smaller, 3 to 4 microns in diameter (Figure 12). The microcrysts are various irregular shapes and sizes from 1.25 to 1 micron across. The outermost microcrysts are wedge shaped and fit together closely. Both microcryst and framboid are much smaller in this type than in the previous type. Although these also fit the definition of framboid, they are not similar to the chalcocite framboids.

Since both of these pyrite framboid types are made of microcrysts considerably larger than the chalcocite microcrysts, the possibility exists that the chalcocite microcrysts resulted from dispersion of pyrite type microcrysts during nucleation of the chalcocite grain. The pyrite microcrysts were examined for possible internal structure using the same methods as those used on the chalcocite cores. No internal structures were found, indicating that the chalcocite did not form from pyrite microcrysts.

Along with framboids, lenses of euhedral grains, often triangular in cross section, are found in the pyrite zone. These lenses are much larger than the framboids, up to 3 or 4 mm. in length, although smaller irregular groups of euhedral grains, about the same size as the framboid are also found and may be due to random sectioning of the larger lenses. It is possible that the framboid is also a chance of circular section of these irregularly shaped clouds, since irregular groups of euhedral grains are much more common than circular groups.

Detailed comparisons of the pyrite framboids and the chalcocite framboids were made. The two types of framboids observed in pyrite were not found in the chalcocite grains. Furthermore, the euhedral grains, so abundant in the pyrite are virtually absent in the mineralized zone.

The fringe itself (measured in millimeters) is a texturally very complicated zone with replacement of pyrite by bornite and digenite (Brown, 1971). However, this is only millimeters thick and is obviously the interface between two geochemical environments.

CONCLUSION

Two origins are possible for these framboids--primary deposition and secondary replacement of pyrite. If the chalcocite framboids are replaced pyrite, similar pyrite framboids should be present above the mineralized zone. Alternately, euhedral clusters and framboids like those of pyrite above the mineralized zone should also be found in chalcocite within the mineralized zone. Nothing of either case is apparent, supporting a primary origin for the framboidal chalcocite.

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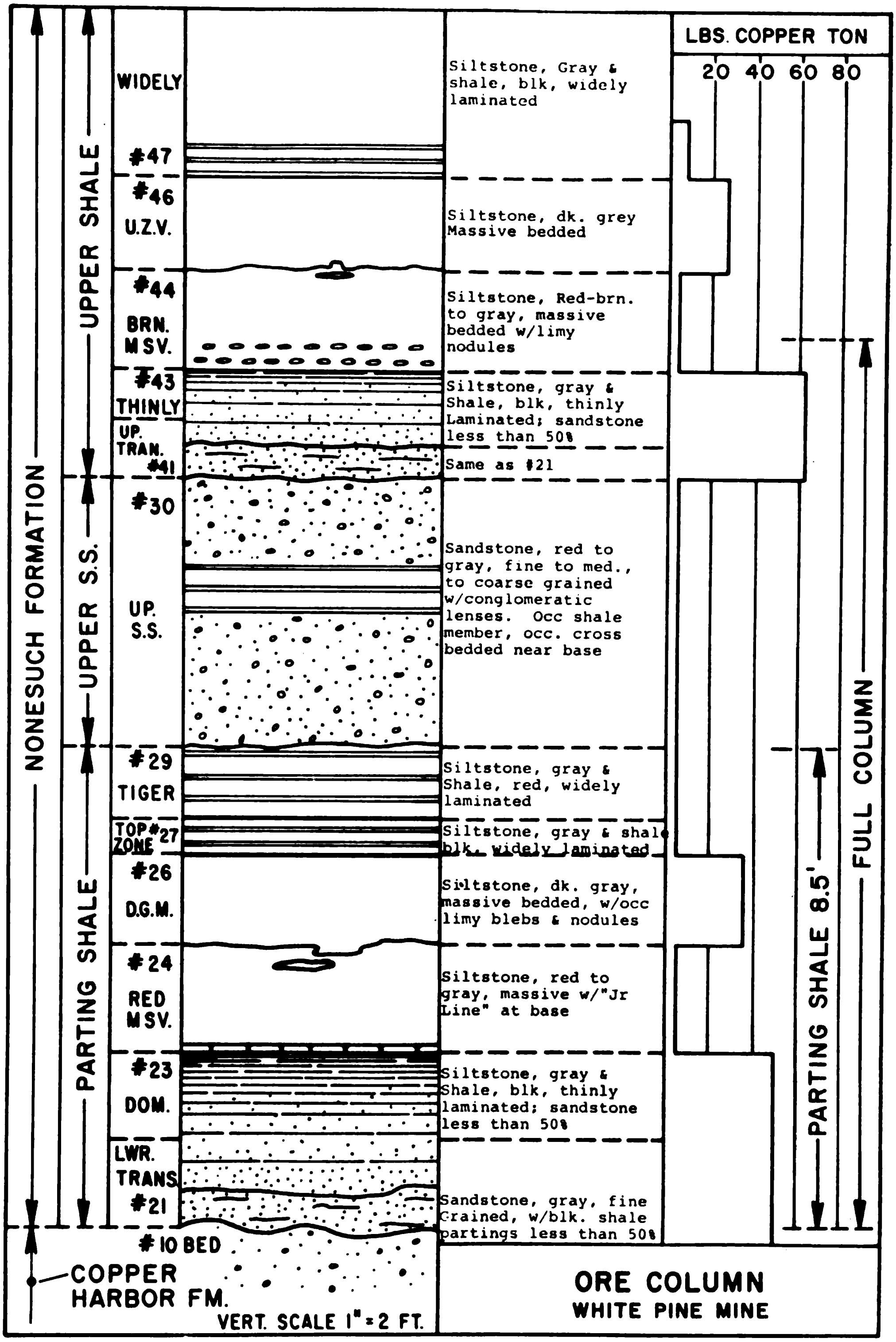


Fig. 1. Lithologic column at White Pine.

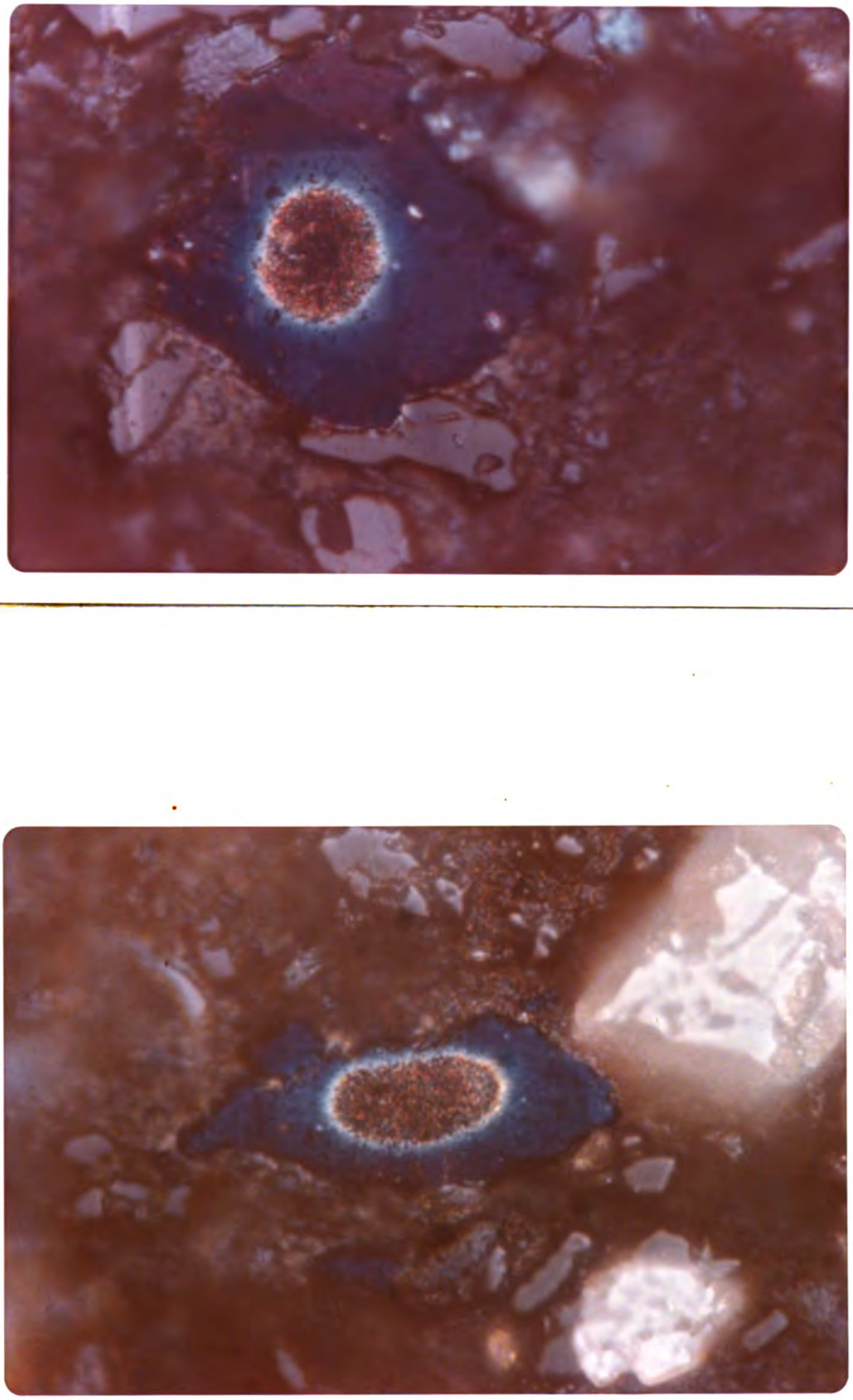
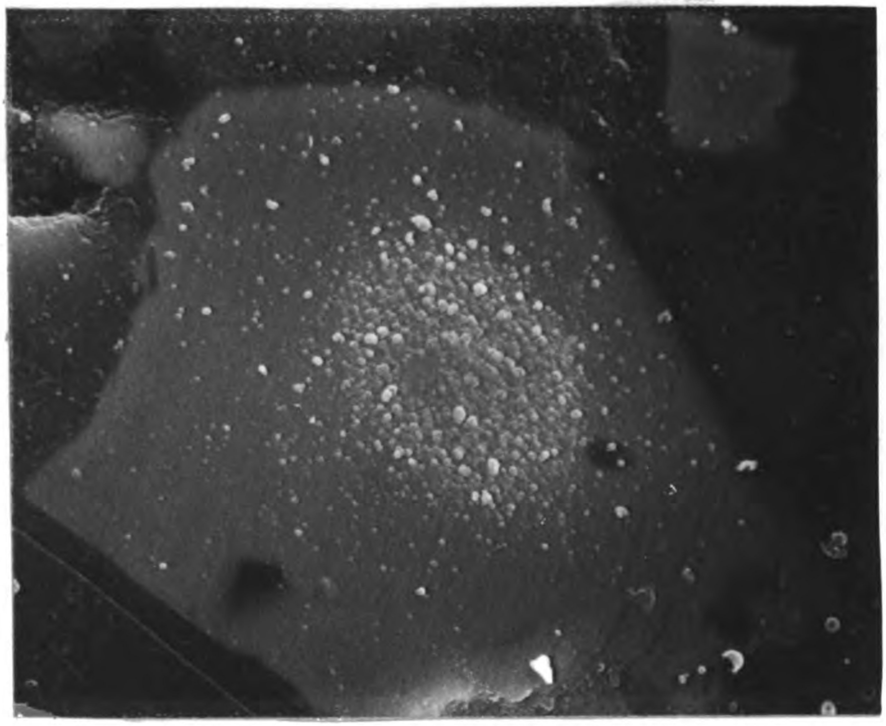


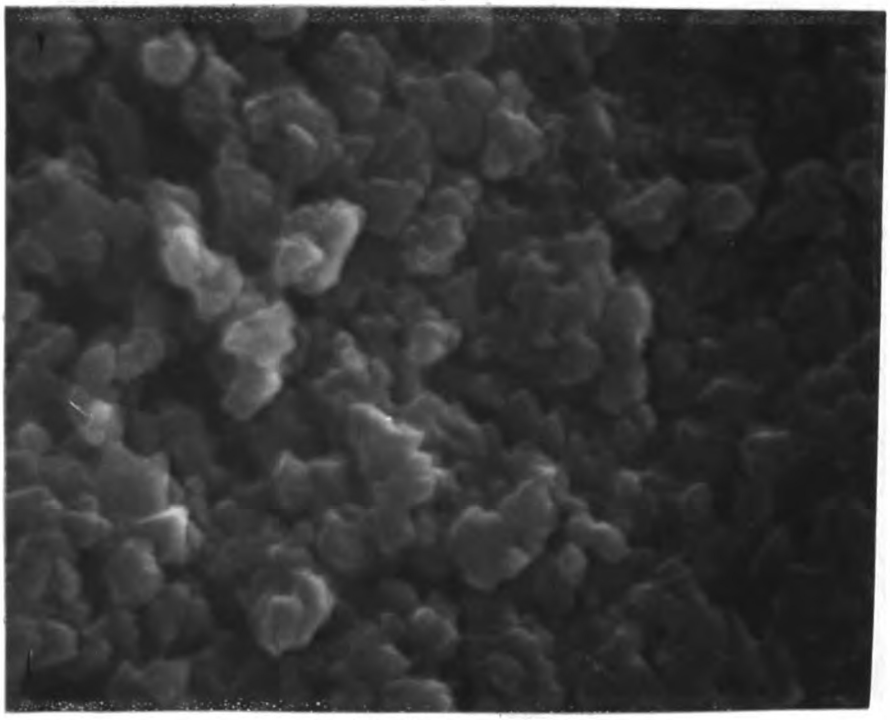
Fig. 2. Oval and circular framboidal cores in stained grains under reflected light (1 cm = 10 μ).



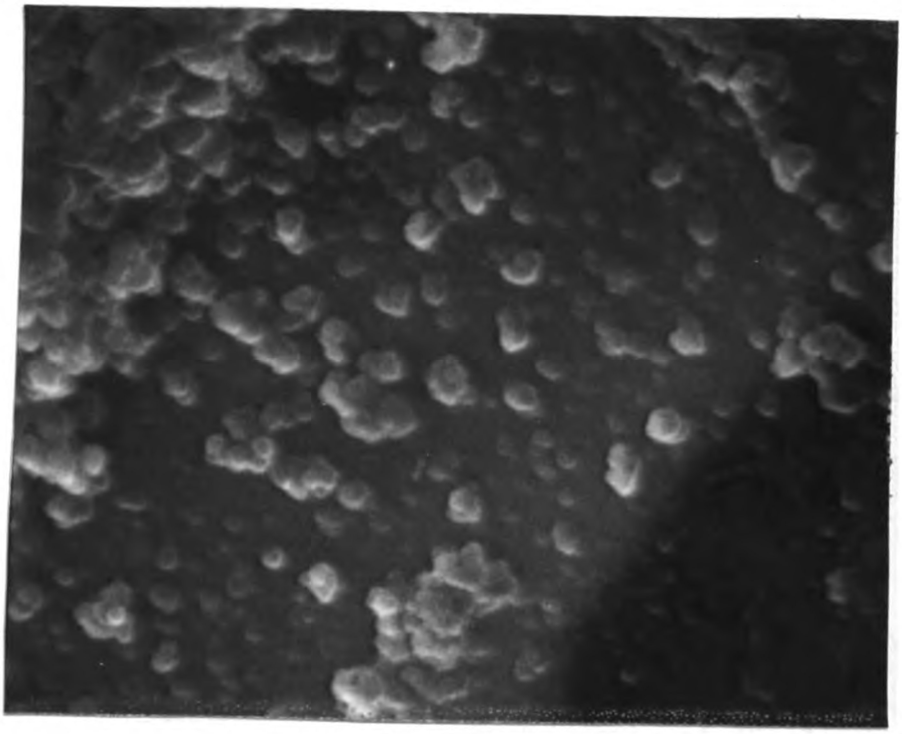
Circular core

Oval core

Fig. 3. SEM photos of two cores (1 cm = 10 μ).



Oval core



Edge of circular core in upper left (note microcrysts in matrix).

Fig. 4. Detail of cores in Fig. 3 (1 cm = .5 μ).

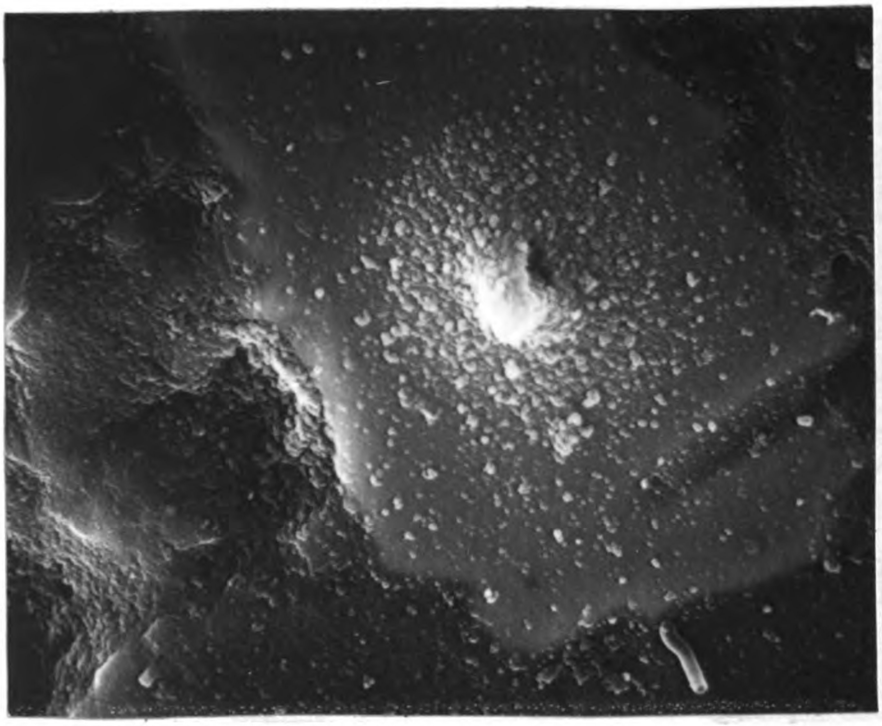


Fig. 5. Especially high relief in core. Compare to those in Fig. 3 (1 cm = 2 μ).

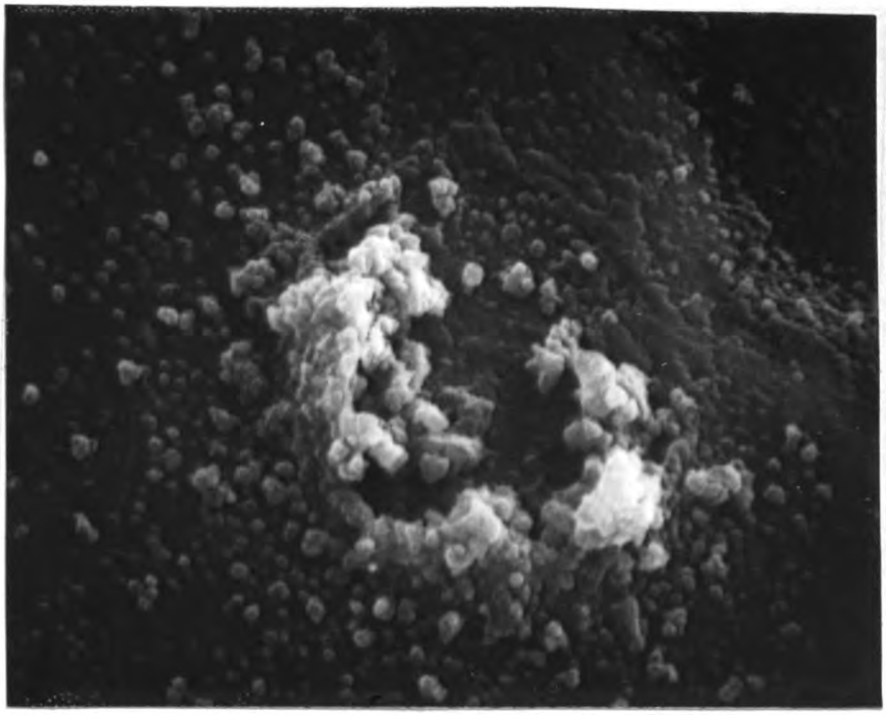
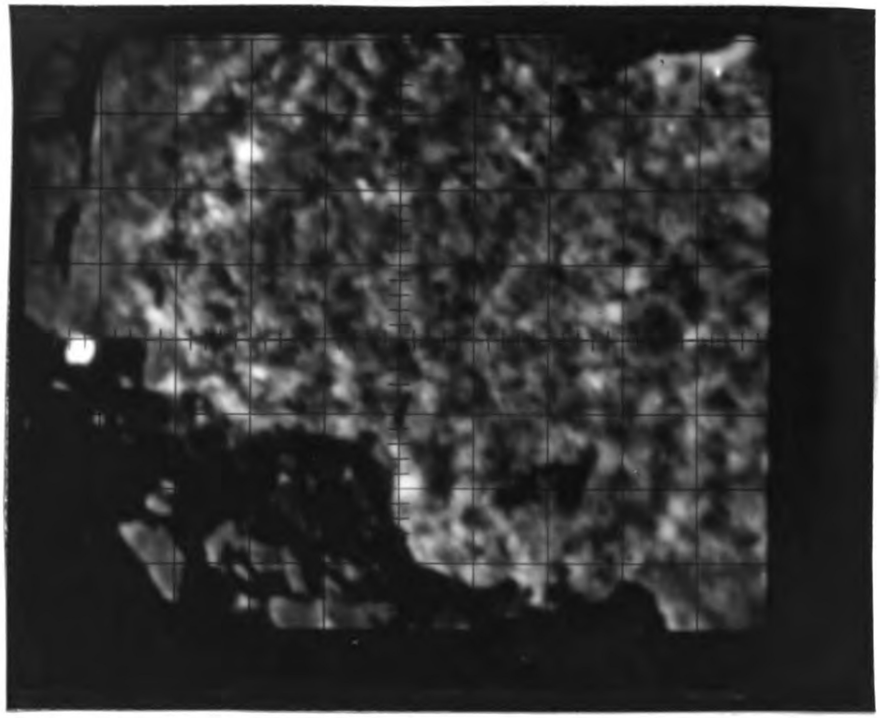


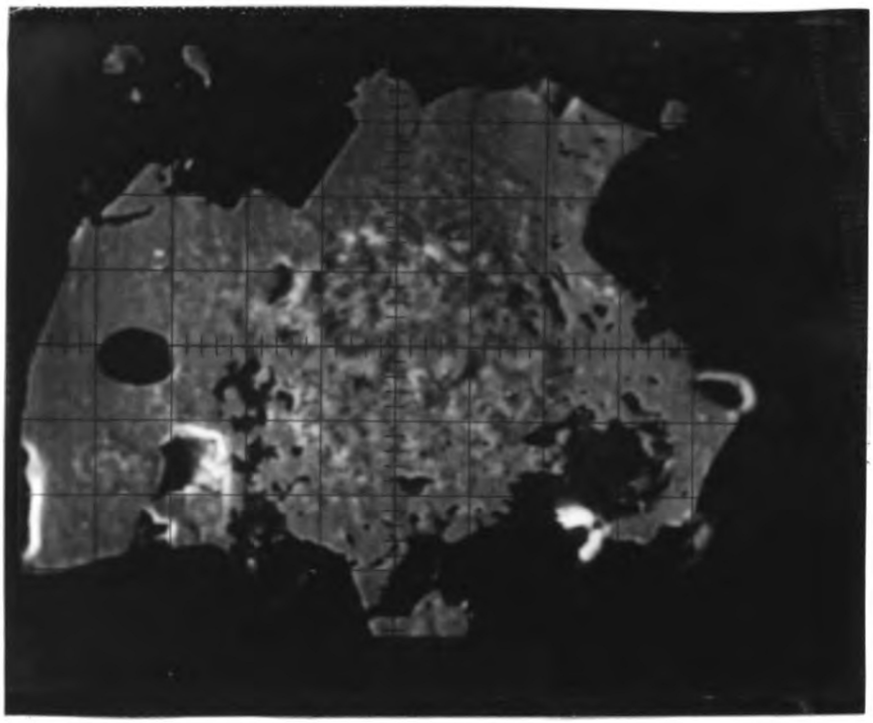
Fig. 6. Framboidal core plucked out during preparation (1 cm = 1 μ).

(1 cm = 10 μ)

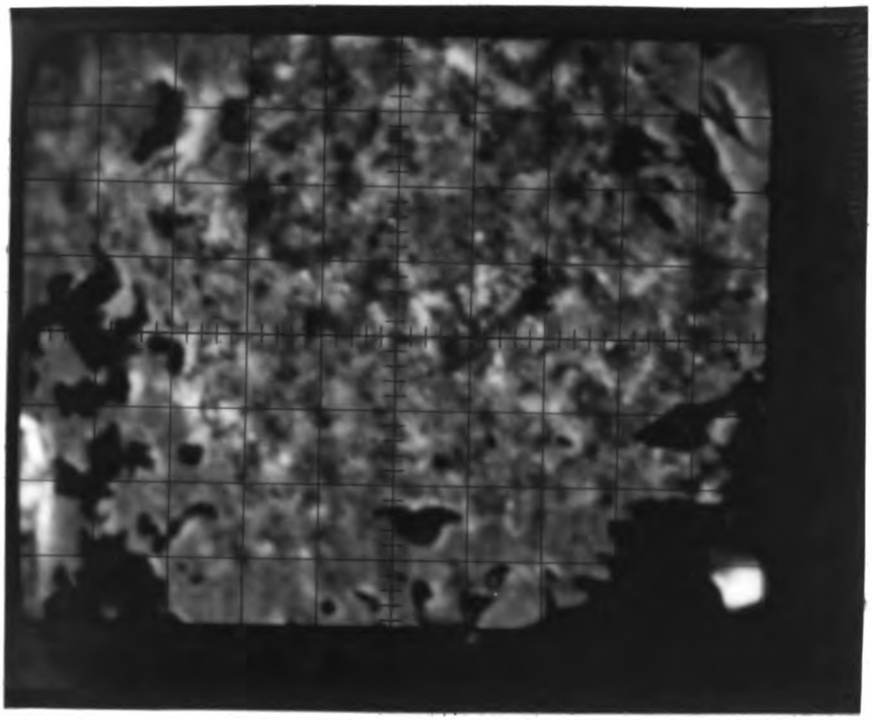


Detail of above (1 cm = 5 μ).

Fig. 7. Core that occupies most of its grain (microprobe photo).



(1 cm = 10 μ).



Detail of above (1 cm = 5 μ).

Fig. 8. Core that almost occupies its grain (microprobe photo).

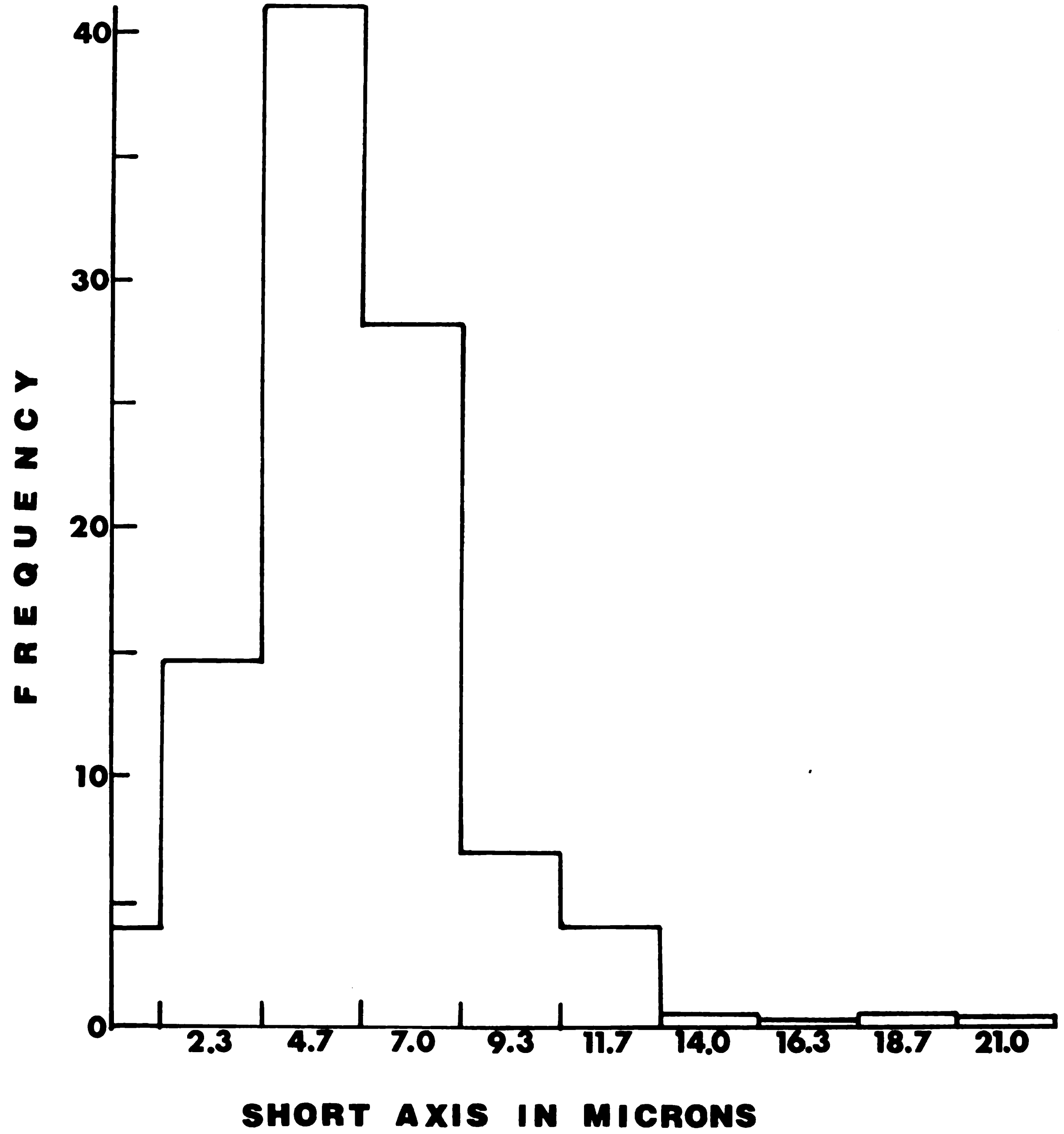


Fig. 9. Size frequency distribution of chalcocite framboidal cores.

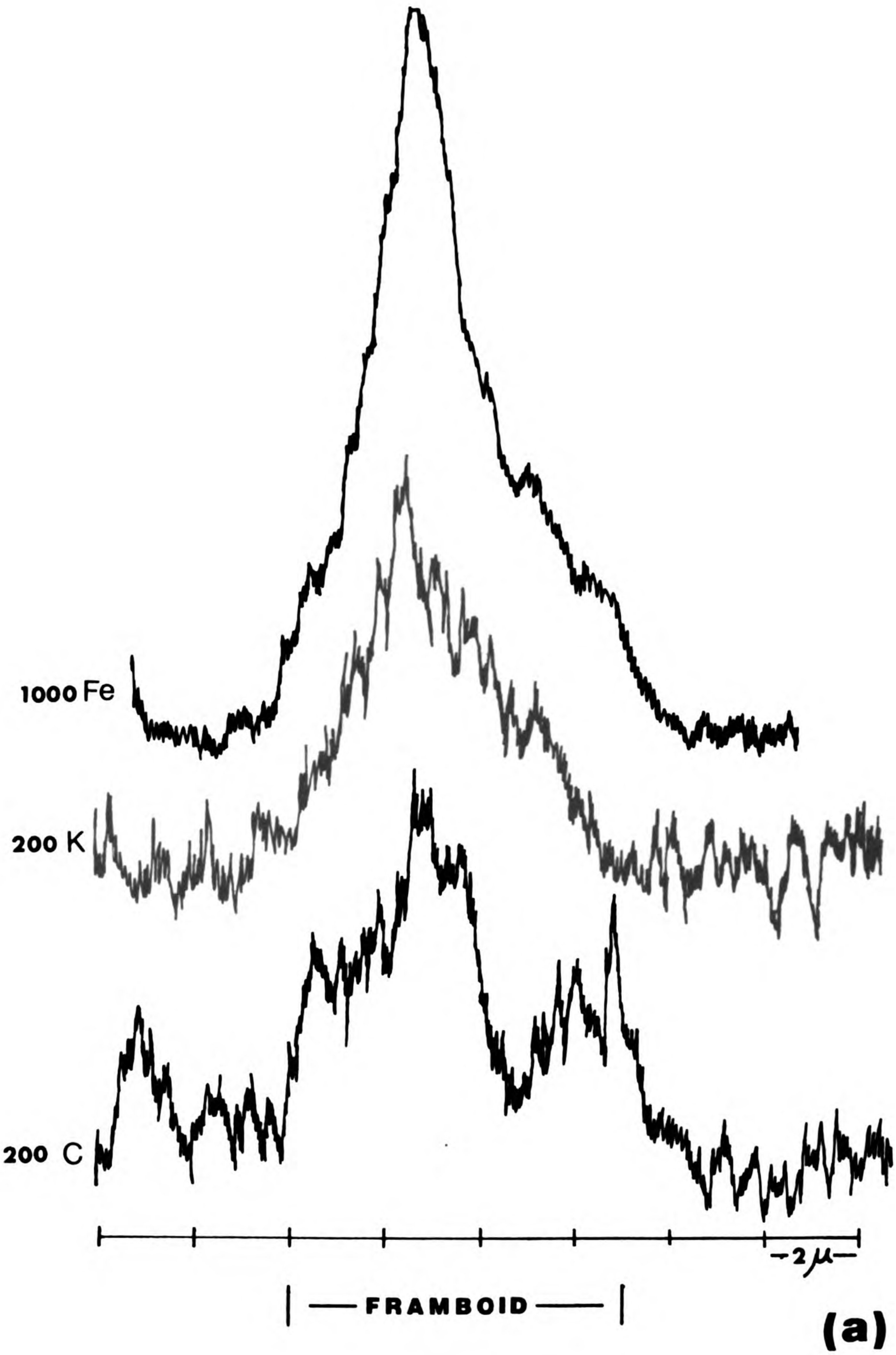


Fig. 10a. Microprobe traverse of elliptical framboidal core for Fe, K, and C (counts per second are given).

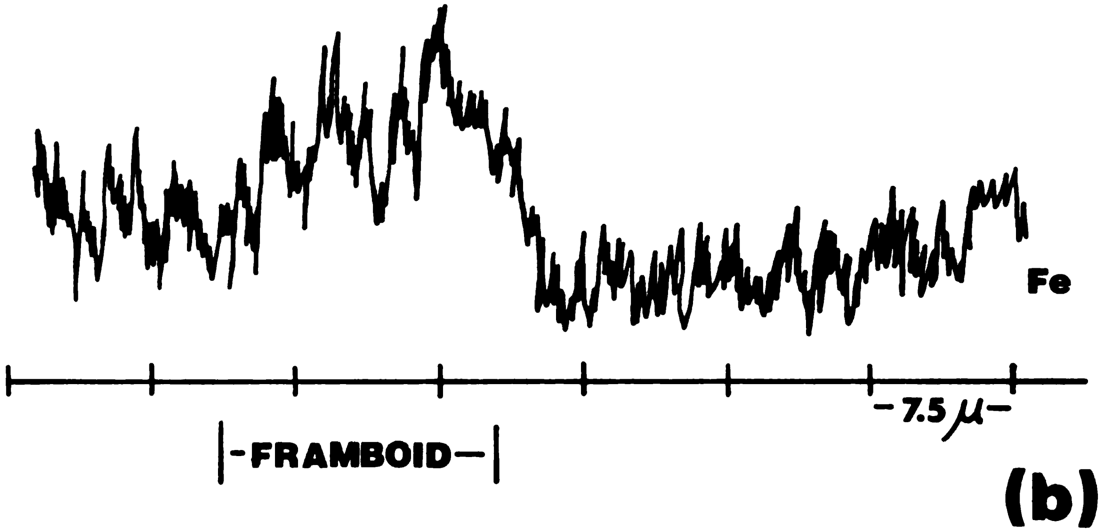


Fig. 10b. Microprobe traverse of circular framboidal core shown in Fig. 2 for Fe.

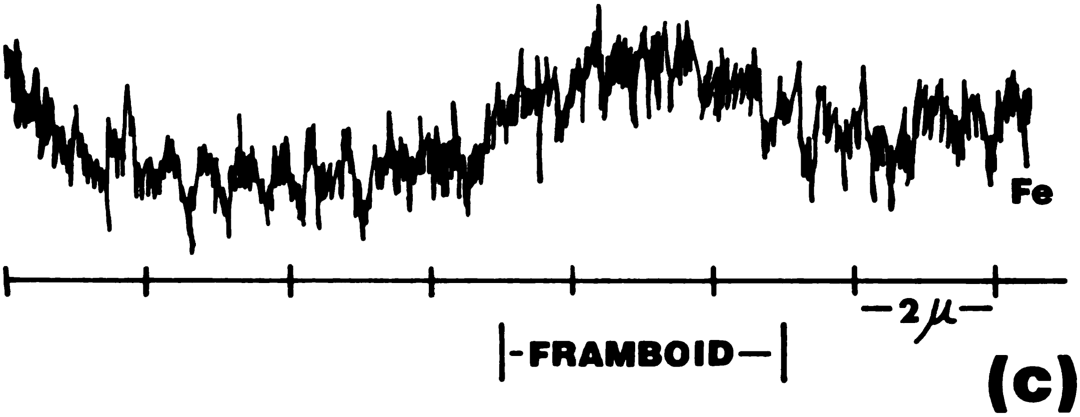


Fig. 10c. Microprobe traverse of circular framboidal core for Fe.

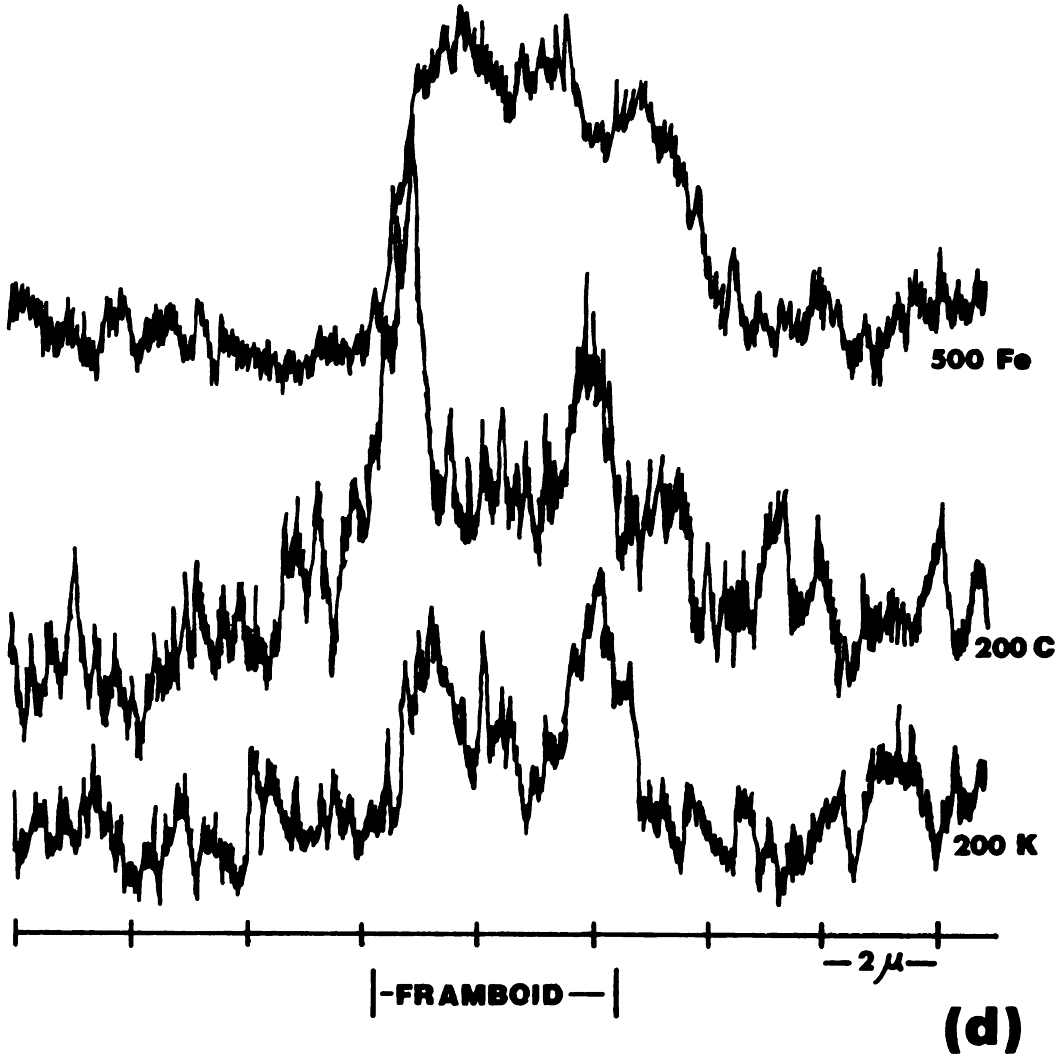


Fig. 10d. Microprobe traverse of circular framboidal core for Fe, C, and K (counts per second are given).

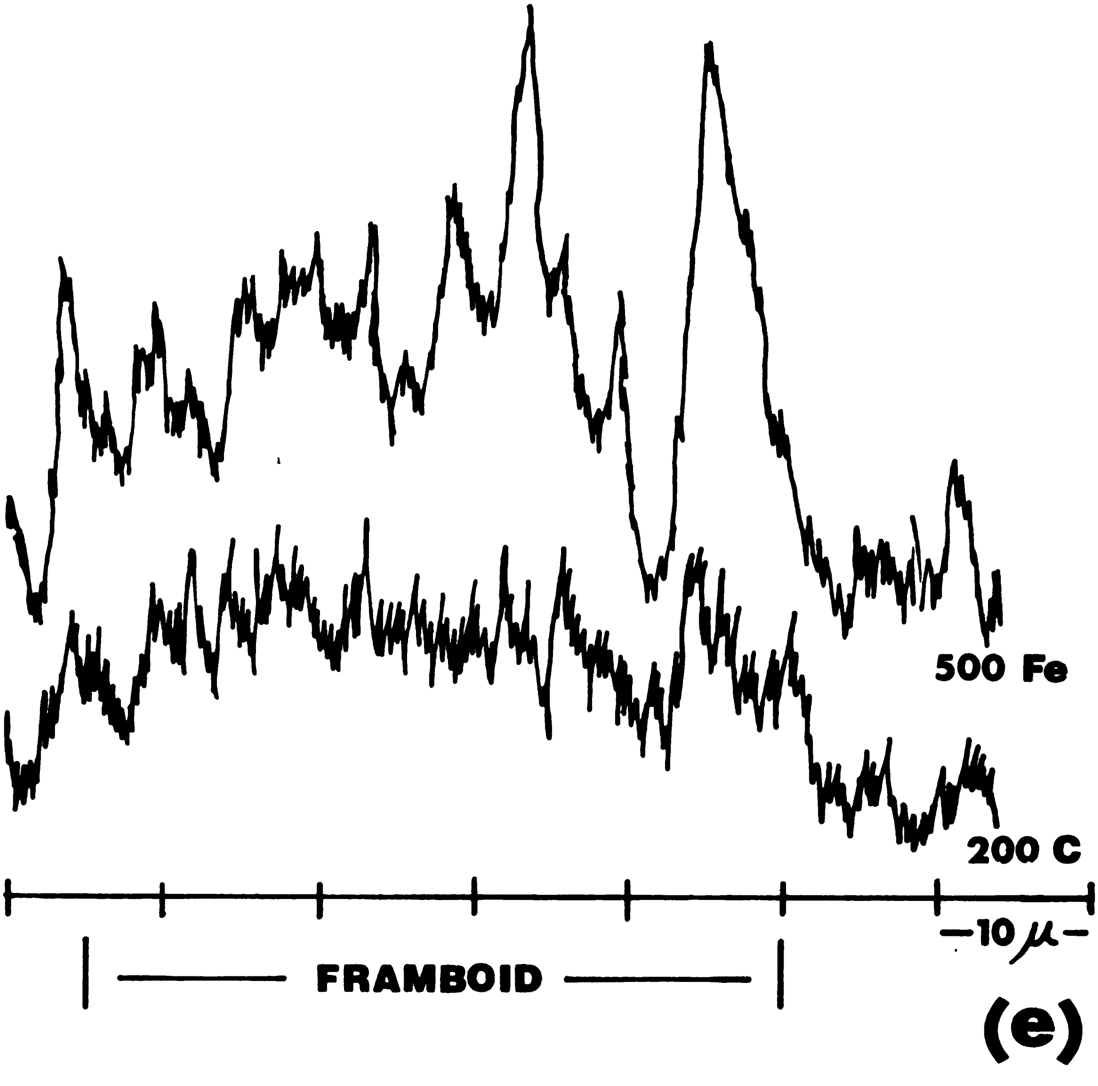


Fig. 10e. Microprobe traverse of framboidal core shown in Fig. 8 for Fe and C (counts per second are given).

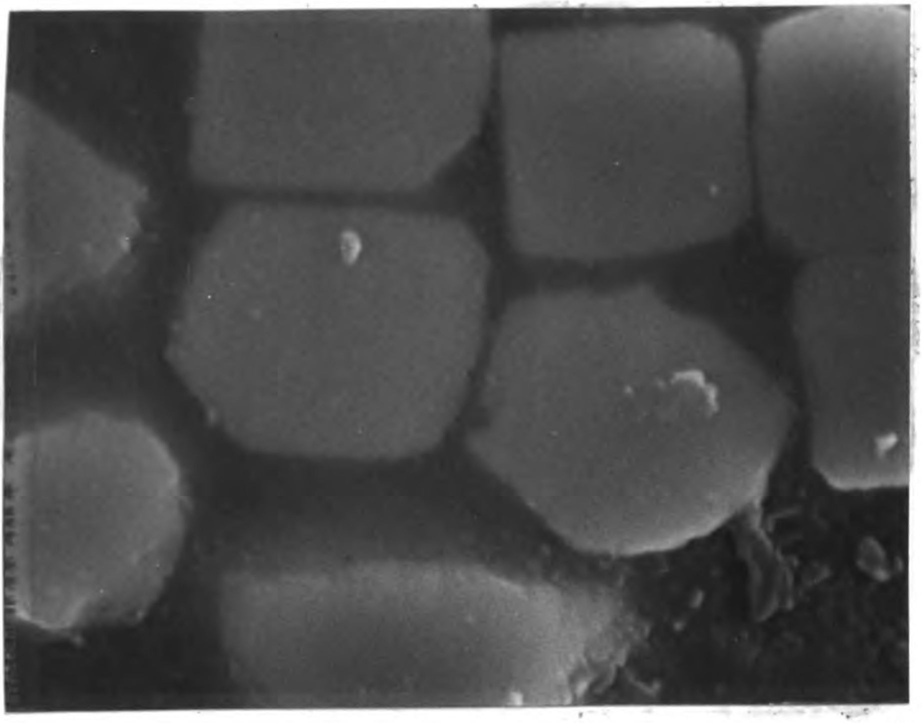


Fig. 11. Euhedral microcrysts in pyrite framboid (1 cm = 1 μ).

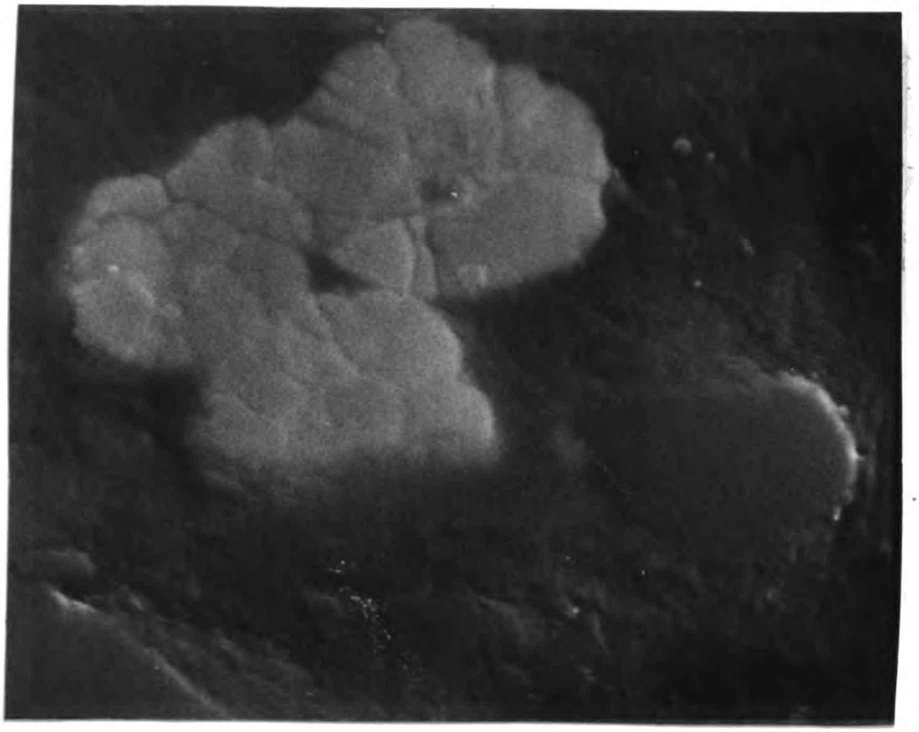


Fig. 12. Wedge shaped microcrysts in pyrite framboid (1 cm = 1 μ).