

Idaite from the Skouriotissa Massive Sulfide Orebody, Cyprus: Its Composition and Conditions of Formation

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Abstract

Idaite occurs at the contact of massive sulfide ore with overlying well-bedded, ochreous sediments at Skouriotissa, Cyprus. It occurs as rims around, and fracture fillings in, chalcopyrite and is invariably rimmed with covellite. The optical properties of the Skouriotissa idaite are comparable with those described by Frenzel (1959) for supergene idaite from the Ida mine, Southwest Africa. Electron probe microanalyses indicate a composition Cu_3FeS_4 . This composition is in agreement with that suggested by Levy (1965) and by Sillitoe and Clark (1969) for idaite comparable in all respects with the Skouriotissa idaite. The idaite was probably formed during oxidative leaching of chalcopyrite by descending ferric sulfate-bearing acid solutions produced during the submarine oxidation of pyrite to goethite of the ochre.

Introduction

Idaite, after its first identification and description by Frenzel (1959) as a supergene sulfide formed by the alteration of bornite in the Ida mine, Southwest Africa, stimulated the interest of many mineralogists. Since then its occurrence has been reported from many parts of the world, *e.g.* Argentina (Brodtkorb, 1961), Perú (Kobe, 1961), Japan (Takeuchi and Nambu, 1961), Yugoslavia (Grafenauer, 1963), Germany (von Gehlen, 1964), France (Lévy, 1965), Norway (Krause, 1965), India (Rao, 1965), Austria (Tufar, 1967), Fiji (Frenzel and Ottemann, 1967), Chile (Sillitoe and Clark, 1969), Spain (Martin Calvo, 1969), and Cyprus (Constantinou, 1972).

There is some controversy about the chemical composition of idaite. Frenzel (1959) suggested a composition Cu_5FeS_6 for the mineral because its X-ray diffraction pattern was similar to that given by Merwin and Lombard (1937) for a synthetic phase with Cu_5FeS_6 composition. Yund (1963) suggested a general formula $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x}$, whereas Lévy (1965) suggested the formula Cu_3FeS_4 based on electron probe analyses. Frenzel and Ottemann (1967) analyzed a coarsely crystalline hypogene "idaite-like" mineral from Fiji with an electron probe and found that its composition approached stoichiometric Cu_5FeS_6 ; on the other hand Sillitoe and Clark (1969) reported electron probe analyses which agreed with the stoichiometric Cu_3FeS_4 composition suggested by Levy (1965) but Ramdohr (1969) gave a formula Cu_5FeS_6 for idaite. More recently Ottemann and

Frenzel (1971), on the basis of 11 electron probe analyses of supergene idaite from different localities, concluded that its composition ranges from Cu_5FeS_4 to Cu_5FeS_6 . Clark (1970) reported the occurrence at Aucanquilcha, Chile, of a mineral with a composition near Cu_5FeS_6 associated with native sulfur and covellite and with optical as well as X-ray diffraction properties matching closely with those of the phase synthesized by Yund and Kullerud (1966), Yund (1963), Merwin and Lombard (1937) and, presumably, observed by Frenzel and Ottemann (1967) from Nakundamu, Fiji. This phase is regarded as a new mineral by Sillitoe and Clark (1969) and by Clark (1970) and different in nature from idaite as originally described by Frenzel (1959).

A supergene origin for idaite through the oxidation of bornite by chloride-rich ground water in acid conditions was suggested by Frenzel (1959), whereas Takeuchi and Nambu (1961), Grafenauer (1963) and Krause (1965) suggested that the alteration of bornite to idaite represents an intermediate stage in the formation of enriched copper ores. Sillitoe and Clark (1969) propose a formation of idaite through the action on bornite of ferric sulfate-bearing solutions in the oxidized zone above the water table.

The data on the Skouriotissa idaite presented in this paper are part of a detailed study of the geology, mineralogy, and geochemistry of the Cyprus massive sulfide ores (Constantinou, 1972). Eight orebodies were studied, but idaite was found to occur only at Skouriotissa. Polished sections of idaite were investigated with standard optical methods using a

Reichert Zetopan ore microscope; the reflectance of idaite was measured using the *Reichert Reflex* spectral microphotometer described by Singh (1965). The Skouriotissa idaite was also examined by electron probe microanalysis using a *Cambridge MkI* microanalyzer with an excitation voltage of 25 kV and a 0.33A specimen current. Allowance was made for background radiation, and, using the method of T. Kelly (personal communication) modified from the alpha correction method of Trail and Lachance (1966), the quantitative data obtained were corrected for errors caused by absorption, detector deadtime, atomic number effect, background fluorescence, and characteristic fluorescence. For comparison a specimen was examined by a *GEOSCAN* microanalyzer and the B.M.-I.C.-N.P.L. computer programs (Mason, Frost, and Reed, 1969) were used for the calculation of corrections. Spectrochemically pure metals were used as Cu and Fe standards for both instruments; pyrite with 53.45 percent S and synthetic ZnS were used as S standards for the *CAMBRIDGE MkI* and the *GEOSCAN*, respectively.

The Skouriotissa Orebody

The Skouriotissa orebody (Fig. 1) was exploited extensively by the Phoenicians, Greeks, and Romans, as is indicated by the two millions tons of ancient slag lying in its vicinity. Mining activities lapsed between the decline of the Roman Empire and 1914 when the orebody was rediscovered by drilling. Ore reserves exceeded 6×10^6 tons of ore containing 48 percent sulfur, 2.5 percent copper, and minor zinc (Bruce, 1948). The orebody has the form of a lens (670 m long, 350 m wide and 1 to 50 m thick) which fills a shallow basin at the top of the Troodos Pillow Lavas. It is conformable with the surface of the pillow lavas; the lava-ore contact is sharp, and barren lavas succeed massive ore over a distance of less than 2 cm.

The orebody is overlain by a thick cover of sedimentary rocks; the top of this cover is occupied by massive reef limestone underlain by marls and chalks of the Pakhna Formation; this in turn is underlain by argillites and umber of the Perapedhi Formation (Constantinou, 1972). The umber, a

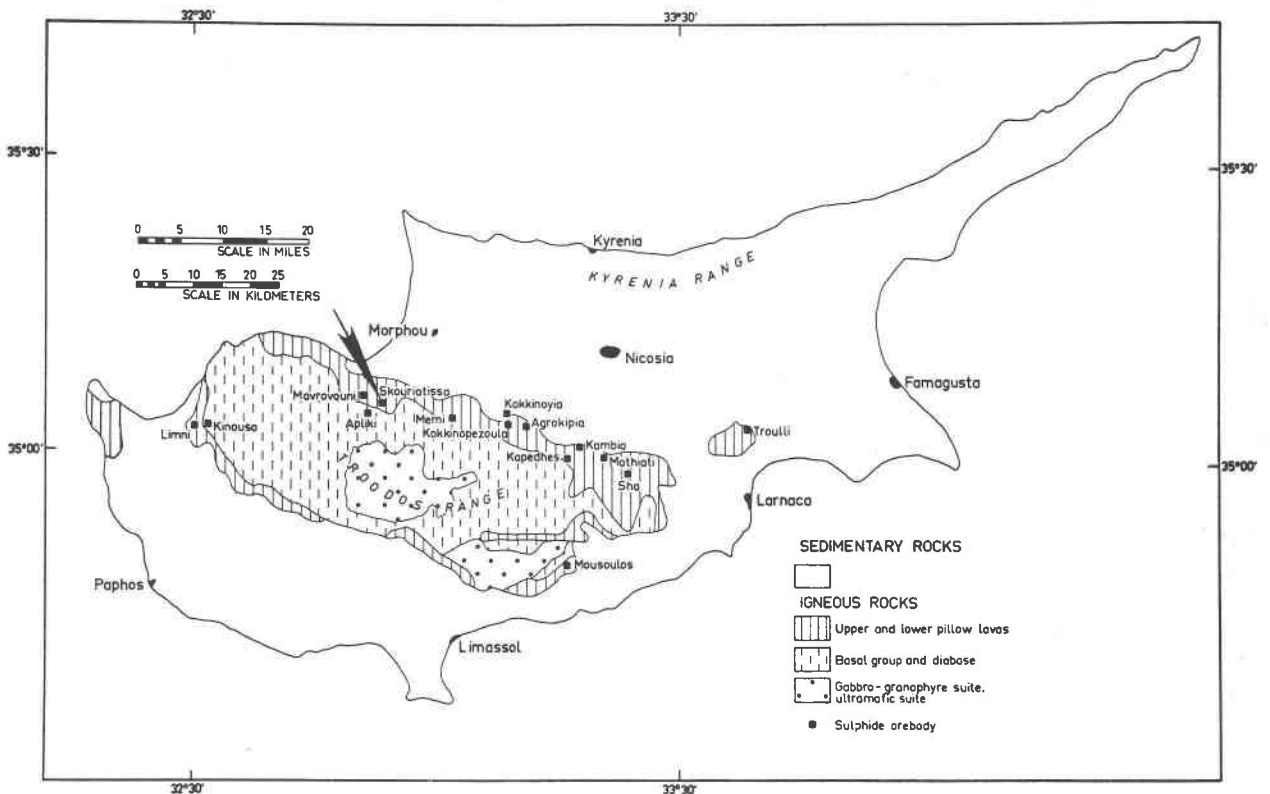


FIG. 1. Location of major sulfide orebodies in the Troodos Pillow Lava Series, Cyprus. Modified from Cyprus Geological Survey map.

manganiferous iron-rich sediment, in places rests unconformably on the finely bedded sediments of the Ochre Group. The latter is a stratigraphic unit proposed by the writer to include the well-bedded brown and red hematitic ochres (manganese-poor, iron-rich sediments) which are interbedded with well-bedded cherts, clayey tuffs and sulfides, and which were long confused with the overlying umbers (Constantinou and Govett, 1972).

A post-Miocene 350° trending normal fault with a downthrow of about 25 m to the west divides the orebody into the western and eastern zones. Most of the ore has a characteristic conglomeratic structure and high porosity, but in the lower part the ore is hard and compact and has low porosity. The predominant mineral is pyrite followed by chalcopyrite and minor amounts of sphalerite. The forms and textures of these minerals, particularly those of pyrite, show great variation. The secondary mineral assemblage is more complex and includes covellite, digenite, blaubleibender covellite, chalcocite, monoclinic pyrrhotite, bornite, and mackinawite in decreasing order of abundance. Below a massive gossan at the western end of the orebody, there are zones of stockwork mineralization where the dominant secondary minerals are tenorite, paramelaconite, delafossite, and cuprite, and less commonly native copper.

The Skouriotissa Idaite

The idaite at Skouriotissa occurs at the top of the ore at the eastern zone near its contact with the overlying sediments of the Ochre Group, which in

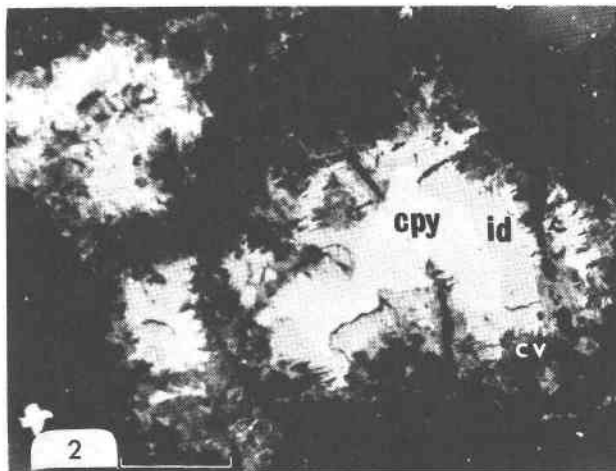


FIG. 2. Chalcopyrite (cpy) rimmed by idaite (id), in turn rimmed by covellite (cv). Reflected plane polarized light. Scale bar = 300 microns.

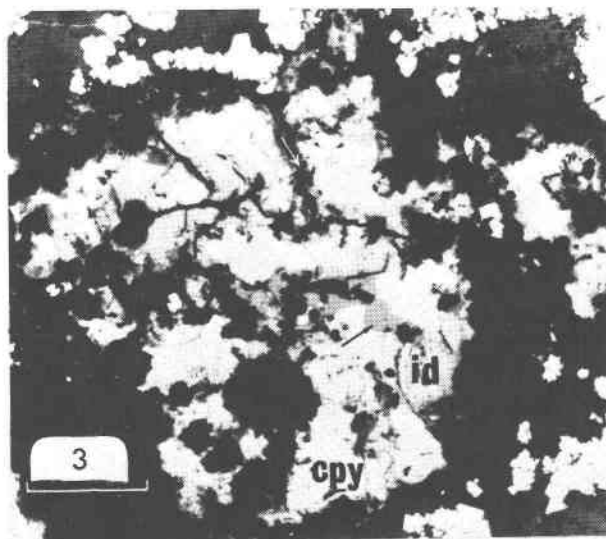


FIG. 3. Idaite (id) as rim around chalcopyrite (cpy) or in fractures in chalcopyrite. The outer part of the idaite rim is altered to covellite. At point indicated by black arrow near center of picture, is a sphalerite grain in chalcopyrite. Pl, reflected plane polarized light. Scale bar = 300 microns.

this location consist of alternating bands of sulfide, red hematitic ochre, and chert. The red hematitic ochre consists of regularly repeated bands of goethite mixed with varying proportions of pyrite. Graded bedding is common, with coarse pyrite grains concentrated at the base of the individual bands. Polished section studies indicate that the pyrite in the goethite bands is invariably corroded and replaced by goethite. The cherts consist of regularly repeated bands of cryptocrystalline silica mixed with varying proportions of pyrite. In the cherts the pyrite is corroded and replaced by silica.

The ore in contact with the ochre is enriched in copper, chalcopyrite cementing intensely corroded pyrite, and/or euhedral unzoned pyrite. The chalcopyrite is typically rimmed with normal covellite often mixed with blaubleibender covellite, particularly in samples which contain digenite as an alteration product of chalcopyrite. Covellite is also found in the form of veinlets filling fractures in chalcopyrite.

The idaite occurs in this zone of copper enrichment as rims of variable thickness around chalcopyrite (Figs. 2, 3, 6), as fracture-fillings in the chalcopyrite, and as rare *discrete* anhedral grains greater than 500 m in size (Fig. 4). The idaite-chalcopyrite contact is usually sharp (Figs. 2, 4). Whereas idaite has been frequently reported from supergene alteration of

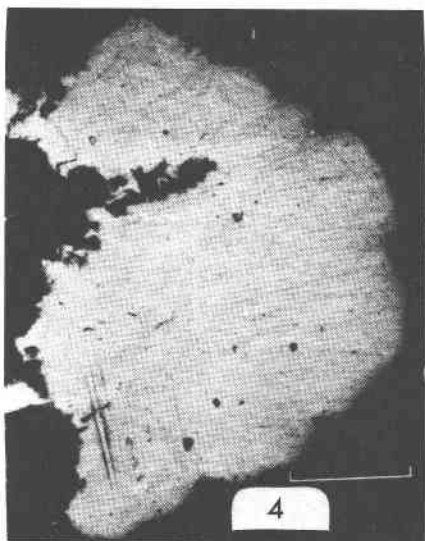


FIG. 4. Large anhedral grain of idaite surrounded by a thin rim of covellite (not visible here but visible in Figure 5) in a matrix of cryptocrystalline silica. Scale bar = 300 microns.

bornite, in Skouriotissa this association was not observed. In Figure 6 a chalcopyrite grain is rimmed with idaite which is in turn rimmed by covellite, whereas an adjacent bornite grain is rimmed by digenite which is in turn surrounded by a mixture of normal and blaubleibender covellites. The idaite is invariably altered to form thin rims of covellite and veins of covellite along fractures in the idaite.

In reflected light the color of Skouriotissa idaite,

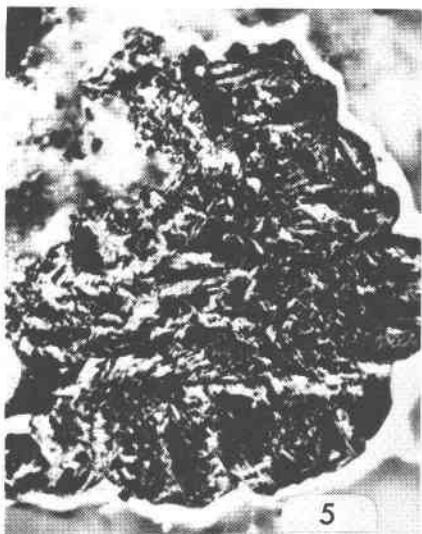


FIG. 5. High anisotropy of the idaite shown in Figure 4, Nicols crossed. Scale bar = 600 microns.

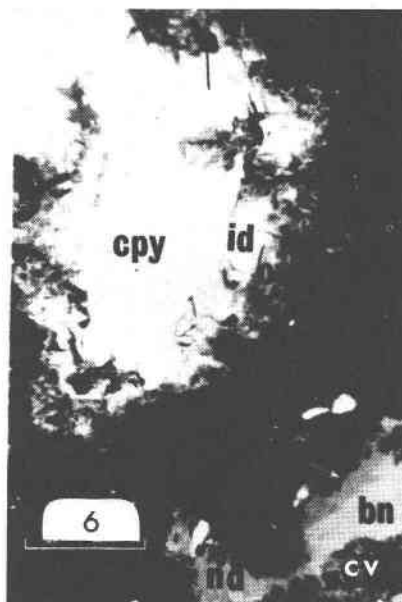


FIG. 6. Chalcopyrite (cpy) replaced by idaite (id) in turn replaced by covellite (cv). At bottom right bornite (bn), replaced by digenite (nd) in turn replaced by covellite (cv). Scale bar = 400 microns.

depending on the section orientation, ranges from red-orange, similar to that of bornite but slightly darker, to yellowish light-gray similar to that of chalcopyrite but slightly darker. In oil immersion the differences in color with the section orientation are enhanced. Its reflectance at 589 nm is from 23 to 32 percent. It has an extremely high anisotropism with colors ranging from pale green to yellow green in air. Lamellar twinning exhibiting a parquet-type orientation is common (Fig. 5).

Electron probe microanalyses of the Skouriotissa idaite (Table 1) show that its average composition (Table 2) is very close to prior analyses and to stoichiometric Cu_3FeS_4 , the formula suggested by Levy (1965) and Sillitoe and Clark (1969). This average composition does not conform to Cu_5FeS_6 , the formula suggested by Frenzel (1959) or to $\text{Cu}_{5.5}\text{FeS}_{6.5}$, the general formula suggested by Yund (1963).

The evidence obtained from the five electron probe analyses of idaite from Skouriotissa does not support the more recent suggestion by Ottemann and Frenzel (1971) that the composition of idaite ranges from Cu_3FeS_4 to Cu_5FeS_6 . Their conclusion was based on 11 analyses of idaite from different localities. However, in addition to the 5 spot microanalyses a number of X-ray scanning images and microprobe line scans across many areas of the analyzed grains

indicate that the Skouriotissa idaite is very homogeneous with respect to copper, iron, and sulfur.

Conditions of Formation

Field relationships and mineralogical and geochemical data strongly suggest that the finely-bedded brown and hematitic ochres overlying the Skouriotissa orebody are the accumulated products of submarine oxidative leaching of the underlying sulfide ore when exposed on the sea floor (Constantinou, 1972; Constantinou and Govett, 1972, 1973). Seawater is generally highly oxidizing and has a pH of 7.0 to 8.0; iron cannot exist in seawater in the ferrous state. Even with concentration 0.1 ml oxygen per liter (one of the lowest recorded concentrations in normal seawater) the oxidation potential is +0.6V at pH 8.0. According to Garrels and Christ (1965), the theoretical upper Eh limit for pyrite at pH 8.0 is -0.2V, whereas according to Sato and Mooney (1960) the measured Eh limit for pyrite is +0.4V. Thus, even assuming the latter figure, pyrite (the main constituent of the Skouriotissa ores) when exposed to seawater even with a very low concentration of dissolved oxygen would oxidize to goethite, with ferric sulfate as an intermediate product. The Skouriotissa idaite was probably formed by oxidative leaching of chalcopyrite by descending sulfate-bearing solutions.

During the oxidative leaching process, chalcopyrite probably alters to idaite by loss of iron. The rim of idaite acts as a protective layer inhibiting complete transformation of chalcopyrite to idaite. As oxidative leaching continues, iron is further leached out of the outer part of the idaite rim to form a rim of covellite. The rim of covellite again acts as a protective layer inhibiting further leaching of idaite. Finally the outer part of the covellite rim is dissolved by further leaching and its position is taken by goethite which

TABLE 2. Average Composition of the Skouriotissa Idaite (1) Compared to That Reported by (2) Levy (1965) and by (3) Sillitoe and Clark (1969), and to That for Various Formulae Suggested for Idaite

	Cu	Fe	S	Total
	Weight Percent			
(1) Mean of 5 analyses	51.34	14.5	33.66	99.5
(2) Mean of 4 analyses	49.85	15.08	34.6	99.53
(3) Mean of 3 analyses	52.78	15.63	33.6	102.01
Cu_3FeS_4	50.87	14.90	34.23	100.00
Cu_5FeS_6	56.14	9.87	33.99	100.00
$\text{Cu}_{5.5}\text{FeS}_{6.5}$	56.94	9.11	33.95	100.00

precipitates by hydrolysis of ferric sulfate from the oxidizing solutions. The goethite layer in turn protects the rest of covellite from further dissolution. This mechanism offers a plausible explanation for the well defined chalcopyrite-idaite-covellite zoning found in the Skouriotissa ores. In other words successive leaching of iron under oxidative leaching conditions produces phases in which the ionic ratio of copper to sulfur becomes 1 to 1 and which are more stable under these conditions.

Sillitoe and Clark (1969) first stressed the importance of ferric-sulfate-bearing solutions in the oxidation of bornite to idaite in the Copiapó district, Chile. They suggested that these solutions had been derived from the supergene oxidation of pyrite and chalcopyrite in the oxidized zone above the water table. At Skouriotissa ferric-sulfate-bearing solutions were also responsible for the oxidation of chalcopyrite to idaite but were of submarine origin. Supergene oxidation processes did not affect the zone of the Skouriotissa ore in which the idaite was found because it was protected from such processes by the impermeable cover of argillites and marls overlying it.

Summary and Conclusions

In Cyprus the mineral idaite has to date been found only at the top of the eastern zone of the Skouriotissa massive sulfide orebody, near the contact of the ore with the overlying well-bedded red hematitic ochre. It is found as rare discrete anhedral grains, as rims around chalcopyrite, and as ramifying veinlets filling fractures in chalcopyrite. Chalcopyrite-idaite contacts are abrupt. The idaite is invariably rimmed with covellite.

The optical properties of the Skouriotissa idaite compare with those first described by Frenzel (1959)

TABLE 1. Electron Probe Analyses of the Skouriotissa Idaite Using Geoscan (1) and Microscan 1 (2,3,4,5) Microanalyzers

Idaite Sample	Cu	Fe	S	Total	Formula
	Weight Percent				
(1)	50.7	14.6	35.7	101.0	$\text{Cu}_{3.04}\text{Fe}_1\text{S}_{4.25}$
(2)	51.7	14.7	32.7	99.1	$\text{Cu}_{3.09}\text{Fe}_1\text{S}_{3.88}$
(3)	49.4	13.9	32.9	96.2	$\text{Cu}_3\text{Fe}_1\text{S}_4$
(4)	52.2	14.7	33.1	100.0	$\text{Cu}_{3.15}\text{Fe}_1\text{S}_{3.96}$
(5)	52.7	14.6	33.9	101.2	$\text{Cu}_{3.17}\text{Fe}_1\text{S}_{3.96}$

for supergene idaite from the Ida mine, Southwest Africa. Electron probe microanalyses indicate it to be very homogeneous and near stoichiometric Cu_3FeS_4 , the formula reported by Levy (1965) and by Sillitoe and Clark (1969) for comparable idaite.

The well-bedded ochres which overlie the Skouriotissa orebody are considered to be the accumulated product of submarine oxidative leaching of the underlying sulfide ore. The main stages involved in the oxidation of pyrite to goethite, which is the chief constituent of ochre, are: $\text{FeS}_2 \xrightarrow{\text{oxide}} \text{FeSO}_4 + \text{H}_2\text{SO}_4 \xrightarrow{\text{oxide}} \text{Fe}_2(\text{SO}_4)_3 \xrightarrow{\text{hydrolysis}} \text{Fe}(\text{OH})_3 \xrightarrow{\text{dehydration}} \text{FeOOH}$. Part of the ferric sulfate produced as an intermediate product was carried in solution down to the lower levels of the orebody and oxidized the pyrite, chalcopyrite, and other sulfide minerals of the ore. The idaite was formed by solid-state transformation of chalcopyrite to idaite during oxidative leaching caused by descending ferric sulfate-bearing acid solutions. Through the same process the idaite was partly transformed to covellite.

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