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AN OCCURRENCE OF THE ASSEMBLAGE, NATIVE SULFUR-COVELLITE-"$Cu_{5.5x}Fe_xS_{6.5x}$", AUCANQUILCHA, CHILE

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ABSTRACT

A mineral with composition near to Cu_5FeS_6 has been found associated with native sulfur and covellite in the volcanic sulfur deposit at Aucanquilcha. Microprobe, optical and X-ray powder diffraction data match closely a previously reported occurrence at Nukundamu, Fiji. Comparison with equilibrium synthesis by Kullerud and others indicates formation in the temperature range 434–482°C.

INTRODUCTION

Electron probe microanalysis (Lévy, 1967; Sillitoe and Clark, 1969) of naturally-occurring, supergene idaite has cast considerable doubt on the equation (Frenzel, 1959) of this not uncommon sulfide with the phase of general formula $Cu_{5.5x}Fe_xS_{6.5x}$[1] (Yund, 1963), which has been synthesized by Merwin and Lombard (1937), Roseboom and Kullerud (1958), and Yund and Kullerud (1966). Idaite has been shown to have the composition Cu_3FeS_4, or Cu_3FeS_{4-x}, and there is as yet no evidence of solid solution in nature between this and more copper-rich compositions. The well-established X-ray powder data ($a=3.77_7$ Å; $c=11.18$ Å; Yund, 1963) for hexagonal $Cu_{5.5x}Fe_xS_{6.5x}$ are only with difficulty reconciled with those of natural idaite (Frenzel, 1959, 1963), and Lévy (1967) has suggested that Frenzel's original powder data may be adequately fitted to a stannite-type, tetragonal cell. A difference in crystal structure between these phases is supported by the dissimilar reflectivity dispersion profiles of natural idaite (Lévy, 1967; Sillitoe and Clark, 1969) and the synthetic "Cu_5FeS_6" of Merwin and Lombard (1937; in Lévy, 1967).

Frenzel and Ottemann (1967) have, on the other hand, presented microprobe data for a *hypogene*, idaite-like mineral from Nukundamu, Fiji, indicating a composition close to Cu_5FeS_6. Hexagonal cell parameters of $a=3.78_0 \pm 0.001$ Å and $c=11.18_7 \pm 0.003$ Å were determined for this sulfide, clearly allying it to the synthetic $Cu_{5.5x}Fe_xS_{6.5x}$ phase. In order to avoid confusion, Sillitoe and Clark (1969) have recommended that the name idaite be retained for the probably tetragonal, and still imperfectly characterized natural sulfide occurring, as originally described by Frenzel (1959), in zones of supergene oxidation, with the implication that the more copper-rich phase reported by Frenzel and Otte-

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[1] This formula, while not entirely satisfactory, will be used hereinafter to avoid confusion in reference to published data.

mann is in fact a new mineral. A phase with the Cu_3FeS_4 composition has yet to be synthesized under dry conditions in the system Cu—Fe—S, although Frenzel (1959) probably formed this mineral in low temperature, hydrothermal experiments approximately simulating the supergene oxidation environment. Conversely, the "idaite" he synthesized (1960) at 400°C in an alkali halide medium may correspond to $Cu_{5.5x}Fe_xS_{6.5x}$.

A second occurrence of a mineral with a composition close to Cu_5FeS_6, and clearly comparable to that synthesized by Yund and Kullerud (1966) and earlier workers, is reported in this note.

Sulfides in the Aucanquilcha Sulfur Deposit

The Aucanquilcha sulfur deposit (Lat. 21°14′S.; Long. 69°24′W.), lying at 6,000–6,100 m a short distance west of the Chile-Bolivia frontier in Antofagasta Province, Chile, has long been known for the presence in the ore of small amounts of copper sulfides, dominantly covellite (*e.g.*, Ruiz, 1965). The covellite forms small (generally <50 cm), irregularly-shaped masses associated with native sulfur cementing andesitic tuffaceous material in a volcanic vent. Volcanism and mineralization are generally considered to be of Quaternary age, but may be appreciably older.

The unusual association, covellite+native sulfur, is here undoubtedly of hypogene origin, and supergene oxidate minerals are absent. Microscopic examination of covellite-rich aggregates has shown that this sulfide is represented by the optically normal variety, albeit with a rather pale bluish coloration in plane-polarized light, assuming a strong purplish hue under oil immersion. No areas exhibiting "blue-remaining" properties are observed. The covellite yields a normal X-ray powder pattern, including the several weak lines which are absent in patterns of the higher-symmetry ***blaubleibender*** modification (Moh, 1964; Sillitoe and Clark, 1969).

The covellite forms irregular, anastomosing networks of veinlets, fringes and patches, rimming and cementing angular fragments of strongly bleached andesitic lavas and tuffs. The native sulfur has a generally similar textural role, and exhibits relatively smooth contacts with the covellite. Neither mineral extensively veins the other, although locally sulfur has apparently overgrown nodules of covellite; such sulfur is, however, intimately intergrown with further covellite. These minerals appear to have formed over essentially the same period in the course of post-volcanic hydrothermal activity, but the smoothly curving grain boundaries exhibited by the sulfur when in contact with the covellite may indicate that the sulfide in part crystallized in equilibrium with liquid sulfur.

A second opaque mineral occurs in association with the covellite, forming occasional minute to moderate-sized, highly elongate laths, with lengths of up to 1,200 μm. This mineral displays extreme bireflectance in air from brownish-pink, through yellowish pink, to pale gray, and a similarly egregious anisotropism, from pale green to gray-green. The laths exhibit straight extinction, and both bireflectance and anisotropism are slightly enhanced under oil immersion, but with no appreciable color changes.

These striking optical properties are, at least superficially, similar to to those of supergene idaite, but the Aucanquilcha mineral lacks, in plane-polarized light, the reddish-orange colors, and, under crossed nicols, the bright, yellowish greens which have been found to be characteristic of idaite from the Copiapó region of northern Chile (Sillitoe and Clark, 1969).

The laths of this mineral are interlaminated with covellite plates where that sulfide forms fringes or combs around andesitic fragments, and in many zones the two minerals extinguish simultaneously. A very small proportion (~5 vol. percent) of the grains of the pinkish-gray mineral have been partially or wholly pseudomorphosed by mesh-like intergrowths of normal covellite and minute equigranular grains of an isotropic, pyrite-like phase. This alteration is not, however, shown by grains completely enclosed by covellite. Examples of grain contact of the covellite, native sulfur, and the idaite-like mineral are quite common in the specimens examined.

X-ray powder studies, using a Nonius Guinier—de Wolff quadruple-focussing camera, and Co-Kα radiation and, as an external standard, silicon, were carried out on a fairly pure aggregate of grains of the pinkish-gray mineral, removed by drilling from a polished surface. A small amount (probably less than 10 vol. percent) of covellite was present in the sample, but the stronger lines due to this contaminant could be distinguished, permitting the identification of a powder pattern closely matching that given by Yund (1963) for synthetic $Cu_{5.5x}Fe_xS_{6.5x}$. All reflections listed by Yund with relative intensities greater than 5 (max. 100), and with $d > 1.50$ Å, were recognized, including the three low-angle lines at $d \simeq 11.2_0$, 5.6_0, and 3.73_0 Å not recorded by Frenzel (1959) in his powder data for natural idaite. No additional lines which could not be ascribed to covellite were observed. Hexagonal cell parameters of $a = 3.77_8 \pm 0.002$ Å and $c = 11.18_3 \pm 0.003$ Å were calculated, corresponding closely to the values determined by Yund (1963).

ANALYTICAL DATA

Electron probe microanalysis of this mineral lends further support to its identification as the hexagonal $Cu_{5.5x}Fe_xS_{6.5x}$ phase of Yund and others. The analysis was carried out on an A.R.L. AMX microprobe, in co-operation with the late Merle Crozier of this department. An optically normal, hypogene bornite ($a = 10.950 \pm 0.001$ Å) from Mina Manto Esperanza, Copiapó, Chile, and the associated normal covellite were used as standards. The bornite was found to be compositionally homogeneous on a microscopic scale, and was taken to have the stoichiometric composition, Cu_5FeS_4, a not unreasonable assumption made in earlier analytical studies of copper-iron sulfides (Sillitoe and Clark, 1969), and supported by previous microprobe analyses of hypogene bornites from this area (*ibid.*). The Aucanquilcha covellite, unlike much normal, supergene covellite in northern Chile, is free from iron (*i.e.* < 0.01 weight percent), and its optical properties and unzoned nature were accepted as evidence for stoichiometry (Kullerud, 1965).

During the analysis of the Aucanquilcha sulfide, a coarse-grained, *supergene* idaite, formed through the oxidation of the Manto Esperanza bornite, was also analyzed, to ensure comparability with the earlier studies cited above. No additional elements (*e.g.* Se) were detected in either sulfide or in the native sulfur.

The rather small corrections for absorption, "atomic number effect" and characteristic fluorescence were calculated according to the schemes of Duncomb and Shields (1966), Duncomb and Reed (1967), and Reed (1965), respectively. The results of the microprobe analysis are presented in Table 1, together with comparative data for compositionally contiguous minerals.

It will be seen from these data that the Aucanquilcha sulfide has a composition falling very close to that of the synthetic ternary phase prepared by Roseboom and Kullerud (1958) and Yund and Kullerud (1966), but differing appreciably from that of supergene idaite from the Copiapó region. The calculated composition, which may be expressed as

TABLE 1. ELECTRON PROBE MICROANALYSES OF THE AUCANQUILCHA SULFIDE AND CONTIGUOUS PHASES IN THE $Cu_{5.5}FeS_{6.5}$—Cu_3FeS_4 REGION OF THE SYSTEM Cu-Fe-S

	$Cu_{5.5}FaS_{6.5}$	Aucanquilcha sulfide	"idaite" Nukundamu[a]	Cu_5FeS_6	idaite Mina Manto Esperanza	Cu_2FeS_4
Cu	56.94	56.7±0.4	56.3	56.14	51.1±0.5	50.87
Fe	9.11	9.5±0.6	9.8	9.87	15.6±0.6	14.90
S	33.95	33.9±0.5	33.7	33.99	33.3±0.5	34.23
Total	100.00	100.1	99.8	100.00	100.0	100.00

[a] Frenzel and Ottemann (1967)

$Cu_{5.28}FeS_{6.25}$, is slightly more iron-rich than $Cu_{5.5}FeS_{6.5}$, but has a Cu:Fe atomic ratio exceeding the 5:1 found for the similar mineral from Nukundamu by Frenzel and Ottemann (1967). Quantitative analysis of the fine-grained, intergrown phases apparently resulting from the breakdown of this sulfide was not possible, but their identification as covellite and pyrite was confirmed.

DISCUSSION

The very similar compositions and X-ray powder patterns of the sulfides from Aucanquilcha and Nukundamu are convincing evidence for their identity, and it is considered that these phases are correlative with the "$Cu_{5.5x}Fe_xS_{6.5x}$" of Yund (1963). The natural sulfide apparently exhibits a slight degree of solid solution, particularly with respect to Cu:Fe ratio, but there is no indication that such solid solution extends to the Cu_3FeS_{4-x} region in which idaite *proper* falls. Increasing Cu:Fe ratio is apparently accompanied by a slight decrease in the hexagonal cell parameters.

The Aucanquilcha native sulfur—covellite—"$Cu_{5.5x}Fe_xS_{6.5x}$" assemblage may be directly compared to the known equilibrium phase relations in the sulfur-rich, iron-poor region of the system Cu—Fe—S (Roseboom and Kullerud, 1958; Yund and Kullerud, 1966). Covellite and $Cu_{5.5x}Fe_xS_{6.5x}$ are stable, respectively, below 507±3°C (Kullerud, 1965) and 501°C (Roseboom and Kullerud, 1966) in the presence of vapor, but tie-lines connect the two sulfides and liquid sulfur only between 482°C, the lower stability limit of the assemblage, bornite s.s.—sulfur, and 434°C, at which temperature a tie-line is established between covellite and pyrite (Roseboom and Kullerud, 1958). The observed mineral assemblage in the Aucanquilcha deposit, therefore, appears to have formed in part within a narrow temperature range, and has rather precise geothermometric implications, an unusual feature for naturally-occurring copper-iron sulfides.

The apparent breakdown of a proportion of the ternary sulfide to covellite+pyrite may also be explained in terms of phase equilibria in the system Cu—Fe—S, and presumably represents partial re-equilibration on cooling to below 434°C. The assemblage, covellite+Cu_5FeS_6 +pyrite, occurs in the Nukundamu deposit (Frenzel and Ottemann, 1967), which therefore probably formed below 434°C. The slightly differing compositions of the Aucanquilcha and Nukundamu ternary sulfides may indicate that the hexagonal phase has a more iron-rich composition when in equilibrium with covellite below 434°C than at higher temperatures.

It may be noted that the (Cu, Fe)S_2 phase recently confirmed from natural assemblages by Kajiwara (1969) and synthesized at 225°C by Shimazaki (1969), is not represented in the ores under discussion. The stability relations of the disulfide phase are still undefined, and there is as yet no evidence that solid solution extends as far as the Cu—S join under geologically reasonable pressures.

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