

preservation to insulation from supergene solutions and oxidate phases by the surrounding native copper. This is the first recorded natural occurrence of a brass.

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CUPRIAN SPHALERITE AND A PROBABLE COPPER-ZINC SULFIDE,  
CACHIYUYO DE LLAMPOS, COPIAPÓ, CHILE

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## ABSTRACT

Preliminary data are reported for two supergene sulfides from northern Chile. One, apparently a cuprian sphalerite (*nil* to  $15 \pm 2$  percent Cu.), formed as an intermediate stage in the replacement of sphalerite by djurleite. The second, with a composition close to  $\text{Cu}_3\text{ZnS}_4$ , was a product of the breakdown of the first phase during a subsequent oxidation episode.

## INTRODUCTION

Although few natural mineral assemblages conform strictly to the ternary system, Cu—Zn—S, phase relations in this system could have a significant influence on the inter-relationships between ferroan sphalerite-

ite solid solutions and both copper- and copper-iron sulfides. In an investigation of the system Cu—Zn—S, Craig and Kullerud (1969) could not confirm the existence of discrete ternary sulfides at 800°, 500° or 400°C, but found that up to 7 weight percent Zn enters the high-temperature chalcocite-digenite solid solution. The observed solid solubility of copper in sphalerite, however, did not exceed one percent, even at 800°C, in agreement with the conclusions of Toulmin (1960). Moh (1960), on the other hand, had previously reported the formation of small amounts of an optically distinctive phase in association with covellite in an experimental study of the CuS—ZnS join at 400°C. By analogy with “idaite,” a composition of  $Cu_5ZnS_6$  was tentatively assigned to this product. Two other, even less well-defined, phases, were observed.

In view of these conflicting results, Craig and Kullerud (1969) requested that Moh repeat his experiments, using the same (? the original) starting materials. In doing so, the latter reported the formation of “idaite” and other phases falling beyond the system Cu—Zn—S, and concurred with the suggestion that his earlier results were influenced by impurities in his reactants. G. Kullerud (written communication) reports that the copper used by Moh contained about 10 percent Fe and much oxygen. In this note we would like to present some preliminary observations on supergene sulfides from northern Chile which suggest that a ternary copper-zinc sulfide may actually exist in nature.

#### SUPERGENE ALTERATION OF SPHALERITE IN THE CACHIYUYO DE LLAMOS DISTRICT

Minor iron-free sphalerite occurs in association with chalcopyrite, pyrite, molybdenite, and galena in the hypogene ores in several small mines in the Cachiuyuyo de Llampos district ( $\sim 27^{\circ}6' S.$ ;  $70^{\circ}0' W.$ ), near Copiapó, in Atacama Province. These deposits, probably of Lower Tertiary age, had been affected by at least one episode of supergene sulfide enrichment prior to 12.6 m.y. B.P., and have subsequently been oxidized in the course of the further dissection of the area (Sillitoe, Mortimer and Clark, 1968; Sillitoe, 1969).

Supergene enrichment here involved the replacement of chalcopyrite, pyrite, sphalerite, and galena by massive djurleite. Grain contacts between sphalerite and djurleite normally appear sharp when viewed in polished sections, but in some specimens from the 25 m level and dumps of Mina San Samuel, and from Mina Flor del Llano, an intermediate zone of a pale blue, slightly anisotropic phase intervenes between the hypogene and supergene sulfides. These zones, up to 75  $\mu m$  in width, exhibit diffuse boundaries against sphalerite, but show well-defined contacts with the surrounding djurleite. Electron probe microanalysis of

such zones shows them to consist of a strongly zoned, copper-zinc sulfide, with a Cu:Zn ratio increasing away from the sphalerite cores. The blue phase, like both the sphalerite and djurleite, contains no iron (*i.e.*  $\leq 0.01$  weight percent), and no additional minor metals were detected.

Semi-quantitative analysis, using the associated djurleite (assumed composition  $\text{Cu}_{1.97}\text{S}$ ) as a standard, yielded maximum copper contents of  $\sim 2\text{--}4$  weight percent in most zones, but showed that the blue phase locally contains as much as  $15 (\pm 2)$  percent copper. In all cases, there is an abrupt compositional change at the contact with the zinc-free djurleite. Zinc and copper exhibit an inverse concentration relation, and comparison with the original sphalerite indicates that the blue phase maintains a metal:sulfur atomic ratio of approximately unity, and may probably be regarded as a cuprian sphalerite. X-ray study of material drilled from polished section, and comprising the blue phase, sphalerite, djurleite, and covellite, revealed no lines which could not be ascribed to the last three sulfides, but the very large number of lines yielded by the djurleite could have prevented detection of the weak pattern of an additional mineral.

#### SUPERGENE OXIDATION ASSEMBLAGES

The initial stages of supergene oxidation of these mixed, hypogene-supergene sulfide assemblages has resulted, as elsewhere in the Copiapó region (Sillitoe and Clark, 1969), in the alteration of djurleite to more copper-poor sulfides, here largely normal covellite. The covellite has subsequently been transformed in part to intergrowths of malachite and goethite. In one polished section of ore from the dumps of Mina San Samuel, such covellite of oxidation origin has penetrated through a djurleite rim mantling a residual aggregate of sphalerite grains, and has replaced much of the intermediate cuprian sphalerite zone. Where this occurs, the covellite is intimately associated, not only with minor goethite, but with several minute laths or needles of a very soft opaque mineral with strong bireflectance, from medium-yellow to pale whitish-cream (in air), and extreme anisotropism, from bright apple-green to pale gray. The laths do not exceed  $20 \mu\text{m}$  in length and  $5 \mu\text{m}$  in width, and exhibit a close parallelism with the associated, predominant covellite.

These striking optical properties are reminiscent of those of idaite from this region (Sillitoe and Clark, 1969), and, to a lesser extent, of the probably distinct " $\text{Cu}_{5.5x}\text{Fe}_x\text{S}_{6.5x}$ " phase (Yund, 1963). However, microprobe analysis of several of the larger grains of this mineral failed to reveal more than traces of iron ( $\leq 1$  percent), and this content may reasonably be ascribed to the associated goethite. The mineral clearly contains major copper, zinc, and sulfur, but its small grain-size and poor polishing

characteristics prevent wholly satisfactory quantitative analysis. Estimation, by comparison with the associated djurleite, and iron-free sphalerite, yields approximate copper, zinc, and sulfur contents of  $50 \pm 3$ ,  $16.7 \pm 2$ , and  $35 \pm 4$  weight percent, respectively. No gross compositional variations were evident between several grains.

#### DISCUSSION

The assemblages briefly described above comprise minerals which conform unusually closely to the system Cu—Zn—S. The cuprian sphalerite zones formed as a result of sulfide enrichment are undoubtedly analogous to the compositionally variable solid solutions which have been observed at the metasomatic contacts between several other hypogene sulfides and supergene djurleite or chalcocite in northern Chile (*e.g.* Clark and Moraga, 1969). The replacement of sphalerite by djurleite in these deposits appears to have involved an initial introduction of small or moderate amounts of copper into the sphalerite. The experimental data of Toulmin (1960) and Craig and Kullerud (1969) indicate that such solid solutions do not correspond to stable phases in the system Cu—Zn—S, and the adoption by the blue phase of a slight anisotropism perhaps reveals a significant distortion of the sphalerite structure.

The compositionally discrete sulfide mineral formed in the course of the replacement of the cuprian sphalerite by covellite presents greater difficulties for interpretation. The microprobe analysis indicates an approximate composition in the general  $\text{Cu}_3\text{ZnS}_4$ — $\text{Cu}_5\text{ZnS}_6$  region of the system Cu—Zn—S, more closely approaching the more copper-poor formula A rough colinearity with sphalerite and covellite is apparently maintained. The optical properties of this mineral are, by analogy with the Cu—Fe—S system, not inappropriate for a phase with this general stoichiometry, and they are certainly very similar to those of the poorly-defined phase synthesized at 400°C by Moh (1960). This phase has, however, been subsequently shown to be "idaite" (Craig and Kullerud, 1969), and the similarities in the properties of the Cachiuyo sulfide and of the synthetic product must be considered to be wholly coincidental.

The copper-zinc sulfide briefly described in this note, if a discrete, stable phase in the system Cu—Zn—S, must have an upper thermal stability limit at some temperature below 400°C (Craig and Kullerud, 1969). If a composition of, or close to  $\text{Cu}_3\text{ZnS}_4$  is confirmed by more precise analysis, it would appear that this supergene sulfide represents the zinc-analogue of idaite, *sensu stricto* (Sillitoe and Clark, 1969).

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CHEMICAL DIFFERENCES AMONG THE SERPENTINE  
"POLYMORPHS": A DISCUSSION

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ABSTRACT

Many of the serpentine mineral analyses treated statistically by Page (1968) do not conform to the standards he proposed for characterisation of the specimen or for completeness of analysis. When these unsatisfactory analyses are omitted the remainder are inconsistent with Page's conclusions that lizardite has relatively high  $\text{SiO}_2$  and low  $\text{Al}_2\text{O}_3$  contents and that antigorite has relatively large numbers of trivalent tetrahedral ions. They are consistent with his other conclusions that relative to one another chrysotile is low in  $\text{Al}_2\text{O}_3$ , lizardite is low in  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and antigorite is high in  $\text{SiO}_2$  and low in  $\text{MgO}$  and  $\text{H}_2\text{O}+$ . It is further shown that chrysotile and lizardite contain  $\text{H}_2\text{O}+$  in excess of the ideal formula, antigorite has the highest  $\text{FeO}/(\text{FeO}+\text{Fe}_2\text{O}_3+\text{Al}_2\text{O}_3)$  and lizardite the lowest. The extents of substitution by Fe and Al tend to be in the order chrysotile < lizardite < 6-layer serpentine, though the ranges overlap, and substitution in antigorite extends over the range of all the other species.

INTRODUCTION

In a recent paper under the above title, Page (1968) has examined statistically the possibility of differences between the chemical composi-

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