

TERNARY SOLID SOLUTIONS IN THE SYSTEMS Cu-As-S,
MINA EL GUANACO, TALTAL, CHILE

A. H. CLARK, *Department of Geological Sciences,
Queen's University, Kingston, Ontario,*

AND

A. MORAGA B., *Instituto de Investigaciones Geológicas,
Antofagasta, Chile.*

ABSTRACT

Electron-probe microanalysis has confirmed the occurrence of extensive Cu-As-S solid solutions in the El Guanaco deposit, northern Chile. The solid solutions are compositionally intermediate between enargite and djurleite, and represent diffusion fronts which developed in the supergene enrichment of the former sulfide.

INTRODUCTION

Electron-probe microanalytical studies (Clark, Clark, and Sillitoe, 1968; Sillitoe, 1969) of sulfide assemblages formed by the supergene enrichment of pyrite and chalcopyrite in copper deposits of northern Chile have confirmed the existence of extensive solid solutions falling within the chalcopyrite-bornite and bornite-digenite regions of the system Cu-Fe-S. These phases represent diffusion fronts which developed at an intermediate stage in the replacement of copper-poor sulfides by djurleite and chalcocite, and have resisted equilibration, through exsolution, to the phase equilibria stable at normal temperatures (Yund and Kullerud, 1966) for periods of at least 12.6 m.y. (Clark *et al.*, 1967b; Sillitoe, Mortimer and Clark, 1968). Comparable, and presumably metastable, solid solutions have now been found to have formed in the replacement of enargite by supergene djurleite in the El Guanaco gold-copper deposit, 100 km ENE of Taltal, Chile. One of us (A.M.) is engaged in a detailed study of the geology of this complex polymetallic hydrothermal center of probable Tertiary age.

The specimens examined were not precisely localized, but had recently been taken from the intermediate levels of the La Guanaca workings, surfacing close to the summit of the mountain at the core of the mineralized area. The enriched ore occurs as narrow (0.5–1 cm) branching veinlets cutting a white aphyric, rhyolitic rock, and in hand-specimen has the steely-gray appearance characteristic of "massive chalcocite" in the north of Chile. The hypogene ore exposed at lower levels of the mine consists, at least in part, of structurally similar veinlets of essentially monomineralic enargite, which often forms acicular euhedra

projecting into clay-filled cavities. Minor chalcopyrite, pyrite and jordanite (confirmed by X-ray diffraction and microprobe studies) are associated with the enargite. The lower stability limits of enargite and jordanite lie at $320 \pm 20^\circ\text{C}$ (Skinner, 1960; Barton and Skinner, 1967), and $< 250^\circ\text{C}$ (Roland, 1968), respectively, and this association presumably represents a stable assemblage which formed above 320°C .

In polished section (all sections were mounted in cold-setting media) the enriched assemblages are seen to comprise highly corroded remnants of elongate enargite grains embedded in djurleite. The latter yields a complex X-ray powder pattern essentially identical to that found by E. H. Roseboom Jr. (pers. commun., 1966) for djurleite from an unknown locality, differing slightly from that given by Morimoto (1962) for a specimen from the Rendaiji mine, Japan. Djurleite has been found to be the predominant constituent of "massive chalcocite" ores in the Copiapó region (Lat. 26° - 29° S.), although the relationships of these two, probably distinct, modifications of this mineral, both of which are widespread in this area, remain obscure (Clark *et al.* 1967a; Sillitoe, 1969).

Cu-As-S SOLID SOLUTIONS

Optical and electron microprobe studies indicate that the metasomatic enargite-djurleite contacts in the La Guanaca ores are generally well-defined, neither mineral showing compositional variations in the vicinity of their interface. Both sulfides here exhibit their normal optical properties (*e.g.* Uytendogaardt, 1951; Sillitoe, 1969). Locally, however, the djurleite is seen to be separated from the enargite by continuous or discontinuous fringes of an optically inhomogeneous phase, which has a greenish-grey color in plane polarized light (in air), and a white-light reflectivity somewhat greater than that of enargite but lower than that of djurleite. In oil immersion, the greenish tint is enhanced, and a distinct bireflectance is evident. This intermediate phase exhibits contacts with the adjacent sulfides which are sharp and clearly-defined at low magnification (to $\times 360$), but are gradational at higher power. The inner boundary of the intermediate phase against enargite is extremely serrated, and micro-veinlets penetrate the outer zones of grains of the hypogene mineral. These greenish-grey haloes average 5 - $30 \mu\text{m}$ in width, but occasionally attain 200 - $300 \mu\text{m}$.

Qualitative electron microprobe examination of these assemblages, carried out using an Associated Research Laboratories AMX instrument, in co-operation with the late Merle Crozier, shows that the phase intervening between the enargite and djurleite is indeed compositionally intermediate between them. With the exception of minor antimony (~ 0.5 - 1.0%) in the enargite, no elements other than copper, arsenic,

and sulfur were detected in the assemblage, and the intermediate phase must be considered to represent solid solution in the system Cu-As-S . Scans across the replacement contacts for $\text{Cu K}\alpha$, $\text{As K}\alpha$, and $\text{S K}\alpha$ radiations reveal gradients in the concentrations of these elements from the inner to the outer boundaries of the gray-green phase (Fig. 1), although this zonation is characterized by abrupt discontinuities in several areas. The solid solutions are consistently interrupted close to the contact with the surrounding djurleite by a compositional hiatus, marked by a slight change in color from a greenish- to a pale bluish-gray. The optical properties of the djurleite are maintained with appreciable solid solution of arsenic.

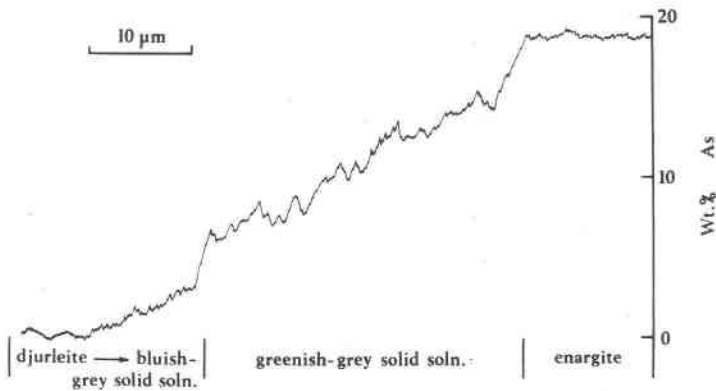


Fig. 1. Electron microprobe traverse for $\text{As K}\alpha$ radiation across enargite—djurleite contact zone. La Guanaca mine, Taltal, Chile.

Although the qualitative scans demonstrate the existence of a wide range of solid solution, in terms of the system Cu-As-S , they do not confirm that the intermediate phase has a composition which, though variable, remains colinear with enargite and djurleite. Preliminary semi-quantitative analyses were therefore made of a compositionally homogeneous "plateau" area within one halo, using the associated enargite and djurleite as standards for copper and sulfur. The composition of the copper sulfide was assumed to be $\text{Cu}_{1.97}\text{S}$ (Takeda *et al.*, 1967), while the enargite was taken as Cu_3FeS_4 , an assumption supported by the recent microprobe studies of Levy (1967). The composition of this zone was estimated to be approximately $\text{Cu}, 54.2$; $(\text{As } 15.2)$, $\text{S}, 30.6$ (in wt.%), which falls close to the $\text{Cu}_3\text{AsS}_4\text{-Cu}_{1.97}\text{S}$ join. This tentative analysis does not, of course, prove that the solid solutions have compositions lying on this join in all zones, although this is suggested by the rather

consistent relations observed between the intensities of Cu $K\alpha$, As $K\alpha$ and S $K\alpha$ radiations.

Attempts to separate pure samples of the intermediate phase for X-ray powder study have met with only partial success. Material drilled from polished section, and which had previously been shown to have an arsenic-rich compositional range, yielded a diffuse powder pattern comprising only the stronger lines of enargite, with minor but inconsistent angular displacements. This suggests that at least the inner zones of the Cu-As-S solid solutions may be regarded as conforming to the enargite-type structure. No isotropic areas were observed within the intermediate phase, and the tennantite structure is apparently not assumed.

DISCUSSION

There is little doubt that the phase, or phases, occurring between enargite and djurleite in the La Guanaca ores are directly comparable to the Cu-Fe-S solid solutions found in similar textural environments elsewhere in northern Chile, and that they represent a "frozen" stage in the supergene replacement of the enargite. The phase relations in the system Cu-As-S are still imperfectly known, even at high temperatures, but Skinner (1960) apparently found no evidence of extensive solid solution in the enargite region of the Sb-free system. In this respect, the Cu-As-S solid solutions are perhaps more anomalous than those involving Cu, Fe, and S, in view of the extensive solid solution which exists in the system Cu-Fe-S at elevated temperatures (Yund and Kullerud, 1966). The supergene "chalcopyrite-bornite" and "bornite-digenite" solid solutions observed in ores of this region exhibit several compositional hiati, which may reflect structural transitions in the corresponding high-temperature phases. Similarly, the compositional break between arsenian djurleite and the more arsenic-rich solid solutions found in the present study may indicate the approximate stability limit of a copper-arsenic sulfide having the djurleite structure. In general, however, there is no reason to expect that these extensive metastable supergene solid solution should bear any relationship to the stable phase equilibria in the system Cu-As-S.

Their preservation for considerable periods in the near-surface environment must incite caution in the interpretation of the compositional relationships of sulfides formed under supergene, or even low temperature hypogene conditions in terms of sub-solidus phase equilibria. Random sectioning of the alteration haloes in the La Guanaca specimens has exposed areas of the solid solution phase apparently occurring as discrete inclusions in djurleite, and the temptation to regard such intergrowths as resulting from the equilibrium co-precipitation of the two minerals is strong. The La Guanaca enargite-djurleite solid solution

phases are superficially similar to, and might be confused with, the so-called "green enargite" of Scheiderhöhn (1922), which has recently been shown to be mercury-bearing and to contain less sulfur and copper than stoichiometric Cu_3AsS_4 at one locality by Bächtiger, Bayer and Corlett (1968).

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Manuscript received, March 17, 1969; accepted for publication April 8, 1969.