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MINERALOGICAL NOTES

CUPRIAN GALENA SOLID SOLUTIONS, ZAPALLAR MINING DISTRICT, ATACAMA, CHILE

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ABSTRACT

A phase resembling galena, but with lower reflectance and greater hardness, occurring in galena-djurleite ores in the Arco de Oro deposit, is shown by electron probe microanalysis to be a copper-lead sulfide with up to *ca.* 13 weight percent copper. The phase is isostructural with galena, and is considered to represent a metastable cuprian galena solid solution formed during an episode of supergene sulfide enrichment.

Microscopic examination of specimens from the Arco de Oro mine, a small working in the Zapallar Cu-Pb-Zn-Ag-Au camp (Lat. 27°35.7′ S.; Long. 70°0′ W.), Atacama Province, Chile, has revealed the existence of significant variations in the white-light reflectance of galena grains. Numerous subhedral and euhedral crystals of this mineral exhibit highly reflectant cores passing outwards to rims of the same color, but with slightly lower reflectance.

The boundaries between areas of optically-normal galena and the anomalous marginal zones are generally gradational, but in some sections phases of differing reflectance occur in immediate juxtaposition. Several discrete grains appear to consist entirely of the optically anomalous phase. The reflectance variations are observed only in specimens which display the effects of supergene sulfide enrichment, here represented by the development of thin rims of sectile djurleite around aggregates of the hypogene minerals. The cleavage-controlled replacement of galena by this copper sulfide is well shown in several sections. The anomalous phase or phases form irregular layers between galena and djurleite, but also occur in galena aggregates apparently not in contact with djurleite.

Both the galena and the less reflectant phase are a slightly bluish-white in color, and totally isotropic, The spectral reflectances of the normal galena and of several areas of the associated phase were measured in air on a Vickers-EEL digital microphotometer, equipped with a Schott "Veril" continuous-band filter and a photomultiplier detector unit, and using a Carl Zeiss silicon carbide standard (no. 048), calibrated by the Commission on Ore Microscopy of the International Mineralogical

TABLE 1

Composition, spectral reflectance, micro-indentation hardness and unit-cell edge of cuprian galena solid solutions, Chile.

Composition				Reflectance in air (± 0.1nm)				Micro-indentation hardness	Unit-cell edge
Pb	Cu	S	Total	470	546	589	650	(VHN_{25})	Å
weight per cent									
86.60	-	13.40[1]		45.4	42.5	41.9	42.2	72-81 (74)[2]	5.930 ± 0.002
81.1	4.5	14.2	99.8	45.1	42.2	41.8	42.0	79-87 (84)	
79.7	6.3	13.7	99.7	44.6	41.9	41.6	41.8	82-89 (85)	5.924 ± 0.003
75.9	9.7	14.0	99.6	43.6	41.4	41.3	41.6	87-96 (91)	5.922 ± 0.003
73.7	11.5	14.3	99.5	43.5	41.2	41.2	41.4	86-98 (93)	5.920 ± 0.002
Galena, Niederfischbach, Germany (Hausmann and v. Gehlen, 1970)									
				45.5	42.4	41.8	42.1	70-81 (VHN_{100})	

[1] assumed composition; Bi 0.1-0.2 weight per cent, Ag 0.1 per cent.

[2] range and mean of ten indentations.

Association. No corrections were made for the secondary effects of glare, which have been found to be very minor with this apparatus.

The optically anomalous phase is found to be slightly and variably less reflectant than galena at all wavelengths in the visible spectrum (Table 1). The dispersion curves of galena and the less reflectant phase are similar in profile, but diverge at lower wavelengths (*i.e.*, below 520 nm). Bireflectance was not detected (*i.e.*, R_g does not exceed R_p by more than 0.1 percent) in the galena or in any grain of the anomalous phase. The reflectance values obtained for galena from this deposit are in close agreement with those recently reported by Hausmann and von Gehlen (1970) for an unanalysed specimen of that mineral from Niederfischbach, Germany.

Micro-indentation hardness measurements, made on a Leitz Durimet-Pol instrument, using a 25p load and a 15 sec. indentation period, revealed a marked increase in hardness in the anomalous phase relative to galena and with decreasing reflectance (Table 1). Maximum hardnesses of (VHN_{25}) 110 ± 5 were obtained on this phase.

Electron probe microanalysis of several areas of the less reflectant galena-like mineral showed it to contain, in addition to major lead and sulfur, variable concentrations of copper. No other elements were detected (limit of detection generally *ca.* 0.1 weight per cent). Scanning on the Cu-Kα peak showed tht the anomalous phase contains up to *ca.* 13

weight percent Cu, and revealed several galena grains with a gradational enrichment in copper towards their outer margins.

In order to established the relations between composition and physical properties of the anomalous phase, quantitative analyses were made of four sensibly homogenous areas of the anomalous phase within the outer parts of several large, intergrown galena crystals, using the associated galena (Bi 0.1–0.2 weight percent; Ag 0.1 percent; Cu, Fe, and Se not detected) and djurleite (assumed composition $Cu_{1.96}S$) as standards.

The four analyses yield reasonably acceptable totals (Table 1), and show the anomalous phase to be a copper-lead sulfide with a variable composition, in which increasing copper:lead ratio is accompanied by a progressive increase in micro-indentation hardness, and a decrease in reflectance.

Sufficient material for X-ray powder study could be drilled from three of the four analysed areas of this phase. Each gave a galena-type powder pattern. The unit-cell edges of the samples were determined from films prepared in a Debye-Scherrer-type Philips powder camera, with a 114.6 mm diameter, using the Nelson-Riley extrapolation (1945), and silicon ($a = 5.4305$ Å) as an internal standard. The associated galena yielded a cell-edge of 5.930 ± 0.002 Å, in close agreement with that reported for an unanalysed natural specimen by Berry and Thompson (1962), but significantly shorter than that (5.936 ± 0.001 Å) found for synthetic PbS by Swanson and Fuyat (1953) and Craig and Kullerud (1968). The three samples of the anomalous phase all yield appreciably shorter cell-edges, with an almost linear relationship between that dimension and the copper content (Table 1).

Discussion

The copper-lead sulfide phase occurring in the Arco de Oro deposit displays systematic trends in reflectance, micro-indentation hardness, and unit cell-edge with composition, and may be considered to represent a cuprian galena solid solution. The compositions of several areas of this phase fall close to the PbS-Cu_2S (or $Cu_{1.96}S$) join in the system Cu-Pb-S, and it contains, at the most, only traces of additional elements. It is inferred from the associated assemblages and local geomorphology that this phase formed during the supergene replacement of galena by djurleite *prior* to an Upper Miocene episode of pedimentation (Sillitoe, Mortimer, and Clark, 1968).

Craig and Kullerud (1968) have studied the phase relations in the system Cu-Pb-S at, and above 200°C, but found no significant solid solution of copper in galena at any temperature; it is considered unlikely that up to 13 weight percent copper would be taken into the galena

structure at 25°C. Further, the gradational nature of the properties of the Arco de Oro phase and its similarity to galena rule out the possibility that it represents a discrete ternary phase stable only at low temperatures.

It is suggested, therefore, that the Arco de Oro phase should be regarded as a metastable solid solution which has been preserved for a considerable period owing to the sluggish reaction rates in the presently extremely arid environment of the Atacama Desert. The occurrence of this and similar compositionally intermediate phases in supergene sulfide ores in this region (*e.g.*, Clark and Sillitoe, 1970) should encourage caution in the interpretation of supergene mineral assemblages in terms of experimentally-derived phase equilibria.

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THE REMOVAL OF POTASSIUM SILICOFLUORIDE FORMED IN THE DETERMINATION OF COESITE AND STISHOVITE[1]

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In the search for coesite and stishovite in shocked samples from craters such as the Ries Kessel in Bavaria, analytical difficulties are en-

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