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Hypogene and Supergene Cobalt-Copper Sulfides, Carrizal Alto, Atacama, Chile

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Abstract

The supergene replacement of an intermediate member of the linnaeite-carrollite series by djurleite in the Carrizal Alto deposits has resulted in the development of microscopic intermediate zones consisting of essentially stoichiometric carrollite (Co_2CuS_4) and lesser amounts of a cobalt sulfide mineral. The latter, with the approximate composition $Co_{0.86}S$, exhibits physical properties and an X-ray powder pattern corresponding to synthetic β $Co_{1-x}S$. It clearly formed at normal temperatures, despite the experimental evidence for the instability of the β-phase below *ca* 460°C.

Introduction

Microscopic examination of a hand-specimen from the dumps of the now-abandoned, but once highly productive, Carrizal Alto copper camp, Atacama Province, northern Chile (Lat. 28° 5.5′ S; Long. 70° 55′ W; Ruiz, 1965, pp. 211–214), has revealed the occurrence of an unusual association of sulfide minerals whose compositions essentially conform to the system Co-Cu-S. The effects of supergene alteration of a cobalt-copper sulfide are well shown in this specimen, which contains a phase similar or identical to synthetic hexagonal (β) $Co_{1-x}S$, perhaps corresponding to the poorly-defined and generally discredited mineral, jaipurite (*viz*, Palache, Berman, and Frondel, 1944).

The cobalt-rich minerals were emplaced as narrow (1–12 mm) veins in altered dioritic country rock, and are now preserved largely as fragments in late-stage calcite-ankerite vein material. The ore mineral assemblage is remarkably poor in iron and nickel, and is quite distinct from the pyrrhotite-pyrite-chalcopyrite-arsenopyrite association which constituted much of the ore worked at this camp. Its precise provenance in the mine is unknown.

Grains of the hypogene ore minerals are locally cross-cut and mantled by "massive chalcocite," which formed during an episode of supergene sulfide enrichment ante-dating the local development of the Atacama Pediplain in the Upper Miocene (Sillitoe, Mortimer, and Clark, 1968; Clark *et al*, 1967), and consists entirely of djurleite. No effects of supergene oxidation, *sensu stricto*, are observed in the hand-specimen under discussion, but heterogenite and cuprian heterogenite of oxidation origin (*cf* Clark, 1970) have been confirmed as thin coatings on several other ore specimens from the Carrizal Alto dumps.

Hypogene Assemblage

The hypogene vein material is almost monomineralic, consisting of a sulfide of the linnaeite series associated with very minor amounts of pyrite, chalcopyrite, and bornite. The dominant constituent forms coarse intergrowths of blocky, subhedral grains exhibiting an irregular, rectangular cleavage. Grains not in immediate contact with djurleite contain no oriented inclusions which could be considered suggestive of exsolution, and the sparse inclusions of bornite and pyrite have irregular, bleb-like forms.

The linnaeite-type phase is completely isotropic, and exhibits a slightly pinkish-white color in plane-polarized reflected light in air and oil; it takes an excellent polish. Its Vickers micro-indentation hardness, determined for 15 grains with a Leitz Duriment instrument and a 100p load, shows (Table 1) a restricted range from 390 to 425 (average, 405). The reflectances of six grains at the four standard wavelengths (Table 1) were determined in air with a Vickers-EEL digital microphotometer, equipped with a continuous-band interference filter and a photomultiplier detector, and using the calibrated Carl Zeiss silicon carbide and tungsten carbide standards issued by the I.M.A. Commission on Ore Microscopy. No bireflectance was detected and only minor reflectance differences were found between the grains examined (Table 1).

The foregoing physical properties are in general agreement with those reported for linnaeite-group minerals, although quantitative values for reflectance and hardness do not appear to have been recorded for analyzed intermediate members of the linnaeite-carrollite series. The reflectance dispersion curve of the Carrizal Alto mineral lies at lower values but is similar in form to those found for siegenite by Petruk, Harris, and Stewart (1969) and for polydymite by E. A. J. Burke (Uytenbogaardt and Burke, 1969). Previous records of the micro-indentation hardness of linnaeite-type minerals (Uytenbogaardt and Burke, 1969) show wide variations for each subspecies, perhaps as a result of compositional variations in the specimens examined.

Electron microprobe analysis confirms the identity of this mineral as a member of the linnaeite-carrollite solid solution series, as defined by Tarr (1935) and by Vokes (1967). Using as standards synthetic chalcocite ($Cu_{2.00}S$), covellite ($Cu_{1.00}S$), metallic cobalt, and a natural cobaltian pentlandite (composition $Co_{6.2}Ni_{1.2}Fe_{1.9}S_8$) from Outokumpu, Finland, a composition of $Co_{0.79}Cu_{0.22}S_{1.2}$, or $(Co,Cu)_3S_{3.62}$ was determined (Table 2); only traces of nickel and iron are present. No variations in Co:Cu ratio could be detected within individual grains or between grains. No indication of the presence of a second phase intergrown with the thiospinel was detected during the microprobe and optical study. Examination using a Nomarski interference-contrast attachment revealed no zonal or irregular hardness heterogeneities. The sulfur content is apparently distinctly lower than that required to satisfy the formula M_3S_4, lending support to the suggestions of Tarr (1935), Darnley and Killingworth (1962), and Vokes (1967), among others, that some natural linnaeites are sulfur-deficient. The experimental evidence for discrete solid solution in the thiospinel phase in the system Co-S is, however, ambiguous (Elliot, 1965), and there is apparently no information on the phase relationships in this region of the ternary system Co-Cu-S.

X-ray powder patterns of this mineral are of the linnaeite type, and a unit-cell edge of 9.468(5) Å was obtained, using an X-ray diffractometer (Cu$K\alpha$ radiation; $\lambda = 1.5418$ Å), and metallic silicon (5.4306 Å) as an internal standard. No previous determinations of the cell parameters of analyzed *intermediate* members of the linnaeite-carrollite subseries appear to have been reported, but the determined parameter is significantly greater than that reported for synthetic Co_2CuS_4 by Bouchard, Russo, and Wald (1965; see below).

TABLE 1. Physical Properties of Carrollites A and B and $\beta Co_{1-x}S$

Mineral	Reflectance (%) (in air) 470nm	546nm	589nm	650nm	VHN range	VHN mean
carrollite A	41.3- 41.5	43.2- 43.3	43.9- 44.5	45.3- 45.7	390- 425	405 (100p)
carrollite B	40.7- 41.0	41.5- 42.0	42.7- 43.2	43.2- 43.7	373 387	385 (100p)
$\beta Co_{1-x}S$: R_p	38.8	36.0	34.0	30.8	224- 245	238 (10p)
R_g'	42.4	40.7	39.2	36.1		

For the purpose of discussion, this hypogene phase will hereinafter be referred to as "carrollite A", although it may be more precisely characterized as a cobaltian carrollite.

Supergene Assemblage

The minor supergene djurleite (confirmed by X-ray powder study) in the hand-specimen under discussion developed largely through replacement of carrollite A. Where grains of the hypogene sulfide are surrounded by djurleite, the mutual contacts are highly irregular and, in several areas, these minerals are separated by an intermediate phase. The latter is optically similar to the original carrollite, being isotropic and pinkish-white in color, but is detectably darker in both air and oil. It forms rims up to 2.5 mm in width, with microscopically-sharp contacts against the djurleite and, probably, against carrollite A. It everywhere contains small (<0.25 mm), and irregularly-vermicular inclusions of a second, optically-distinct, anisotropic mineral.

Carrollite B

Microprobe analysis (Table 2) of the supergene isotropic mineral reveals it to have a composition

TABLE 2. Compositions of Carrollites A and B and $\beta Co_{1-x}S$

Mineral	Co (weight per cent)	Cu	S	Total
carrollite A	46.2	14.2	39.0	99.4
carrollite B	38.2	20.5	41.5	100.2
$\beta Co_{1-x}S$	63.80	∿0.2*	36.05	99.85

*probably in associated carrollite.

closely approaching stoichiometric Co_2CuS_4, the generally accepted formula for carrollite *sensu stricto*; it will herein be termed "carrollite B." The anisotropic phase is a cobalt sulfide (Table 2), apparently free of copper and other metals.

Carrollite B is slightly softer and less reflectant than carrollite A (Table 1), the reflectance dispersion curve retaining the form of that of other linnaeite-type minerals. Solid solution of copper in linnaeite is inferred to cause significant decreases in reflectance and micro-indentation hardness, at least over the compositional range represented by the Carrizal Alto phases. This conclusion is in agreement with the data compiled for the thiospinel minerals by Vaughan, Burns, and Burns (1971), who interpret the trends in physical properties in the linnaeite-carrollite series as resulting from increasing electron occupancy of the anti-bonding σ^* molecular orbitals with increasing copper substitution.

In contrast to the hypogene phase, carrollite B shows no significant sulfur-deficiency. That naturally-occurring carrollite attains a copper-cobalt atomic ratio of 1:2 is implied by the work of Darnley and Killingworth (1962) and Richards (1965, *in* Notebaart and Vink, 1972). Vaughan *et al* (1971) suggest that more copper-rich compositions cannot exist, owing to the instability of the Cu(II) oxidation state.

The X-ray powder pattern of carrollite B is again of the linnaeite type, and yields a unit-cell edge of 9.480(5) Å (114.6 mm camera) in reasonable agreement with the value reported for an unanalyzed specimen of this mineral by R. M. Thompson (*in* Berry and Thompson, 1962). If the cell edge of 9.435 Å found for linnaeite by L. G. Berry (*in* Berry and Thompson, 1962) corresponds to pure Co_3S_4, it would appear that there is a positive relationship between unit-cell parameter and copper content in the linnaeite-carrollite sub-series. This trend approximately parallels that found by Bouchard *et al* (1965) for synthetic thiospinels, but lies at significantly higher levels. This apparent discordance between the cell dimensions of natural and synthetic phases is unexplained.

Anisotropic, Blue-Gray, Cobalt Sulfide

The anisotropic mineral occurring as inclusions in carrollite B exhibits a distinctly bluish-gray color in air, and is slightly darker in oil-immersion. It is moderately bireflectant in air and distinctly so in oil. Reflection pleochroism, from medium bluish-gray to whitish-gray, is faint in air and in oil. The mineral is less reflectant and appreciably softer than the enclosing carrollite, and took a mediocre polish. Anisotropism is intense, with purplish-blue colors developed in most grains at the positions of maximum illumination. A poor cleavage or parting in one direction is shown by several grains; no twinning is observed. The micro-indentation hardness (Table 1) for this phase, determined from four of the larger grains using a 10p load, is in the range 224-245. However, these values should be regarded as approximate, and perhaps overestimated, because of the highly irregular contacts with the enclosing carrollite. Values for R_g' and R_p were determined for six grains; the extreme readings are given in Table 1.

Electron microprobe analysis of several of the small inclusions, using natural cobalt pentlandite and metallic cobalt as standards, shows that the mineral contains, at the most, only traces of copper (max. 0.2 percent). Since wavelength scans reveal an apparent enrichment in copper in the immediate vicinity of the contacts with the carrollite, it is concluded that the mineral is essentially copper-free. The almost identical cobalt and sulfur contents determined for three grains were averaged to yield (Table 2) a composition of $Co_{0.96}S$ (omitting the Cu); the departure from stoichiometry should be regarded as an approximate estimate. However, it is clear that this mineral contains less cobalt than cobalt pentlandite, and more than linnaeite. The distinctly anisotropic nature of the phase precludes its mis-identification as either of those two isotropic minerals, or as cattierite.

On this basis, it was tentatively inferred that the Carrizal Alto mineral corresponds to the fairly well-defined synthetic phase, hexagonal $Co_{1-x}S$ (Lundqvist and Westgren, 1938; Rosenqvist, 1954). Kuznetsov and co-workers (Elliot, 1965) confirm that this "β-phase" possesses a NiAs-type structure, and a solid solution range, comparable to that of pyrrhotite, resulting from omission of cobalt atoms. At least one superstructure (β'), reflecting the ordering of lattice vacancies, has been reported (Kuznetsov *et al.*, JCDPS X-ray Powder Data File Card no. 19-366) for the composition "$CoS_{1.097}$". X-ray powder investigation of the inclusions, using a 114.6 mm camera, was hampered by their small size and irregular form, but several small samples drilled from the polished section, when combined, yielded a powder pattern showing the major lines of carrollite with several additional reflections. The latter (Table 3) correspond closely with the most intense lines of

$\beta Co_{1-x}S$ (NiAs-structure) as reported by Kuznetsov *et al.* (JCPDS Card no. 19-365). Although several lines characteristic of the β' superstructure would presumably be masked by stronger carrollite reflections, the relative intensities of the additional lines, and the spacings, particularly of the two lowest-angle lines, would appear to rule out the presence of the modification. It is concluded, therefore, that the anisotropic mineral represents the β-phase proper.

Microprobe analysis of the djurleite enclosing the intermediate intergrowths described above show it to contain only traces of cobalt (*ca* 0.2 wt percent), and that only within 50 μm of the inner contact.

TABLE 3. Partial X-Ray Powder Data for Natural and Synthetic $Co_{1-x}S$

$Co_{1-x}S$, Carrizal Alto		$\beta Co_{1-x}S$[1] (synthetic)			$\beta' Co_{1-x}S$[2] (synthetic)		
d(obs.) Å	I[3]	d Å	I	hkl	d Å	I	hkl
					5.40	2	102
					4.60	2	103
					3.20	4	211
2.94	25	2.931	20	100	2.891	20	300,204
					2.789	2	213
2.54	25	2.543	20	101	2.523	35	303,205
					2.254	4	215
					2.195	4	305
1.950	100	1.945	100	102	1.931	100	008,206
					1.854	4	412
					1.792	2	413,405
1.690	30	1.694	35	110	1.744	4	500
					1.679	35	330
		1.495	10	103			
		1.412	10	112,201			
		1.299	10	004		and many additional lines to ...	
1.280	20	1.276	20	202			
		1.200	5	211			
		1.189	10	104			
		1.118	5	203			
		1.108	5	210			
1.033	40	1.083	10	211			
		1.030	55	114			
1.016	45	1.019	55	212	1.015	100	636

[1] XRPD CArd 19-365; [2] XRPD CArd 19-366; [3] relative intensities estimated visually.

Discussion

In the specimen under discussion, the supergene replacement of an intermediate member of the linnaeite-carrollite series has led to the development of a more copper-rich carrollite, approaching stoichiometric Co_2CuS_4 in composition. The excess cobalt has been locally concentrated as a copper-free, or copper-poor, cobalt sulfide, with compositional and crystallographic properties which match those of the $\beta Co_{1-x}S$ phase in the system Co-S. The lack of significant compositional variations in these minerals is interpreted to indicate that, although they have formed at an intermediate stage of a supergene, sulfide-enrichment process—under conditions characterized by the development and preservation of definitely metastable, and compositionally variable phases (*cf* Clark and Sillitoe, 1971)—they constitute an assemblage stable under essentially normal temperatures and at atmospheric pressure. The sharp composition discontinuity between carrollite B and djurleite may indicate that the composition of the former represents the copper-rich limit of the linnaeite series, at least at low temperatures (*cf* Vaughan *et al*, 1971).

The cobalt sulfide mineral in this assemblage is considered to represent a natural analogue of the $\beta Co_{1-x}S$ phase. The original description of the "CoS" mineral, jaipurite, by Mallet (1880, *cited in* Palache, Berman, and Frondel, 1944, p. 242) was sketchy, lacking adequate information on physical properties and composition. As a consequence, jaipurite has been generally discredited as a natural species. This caution has apparently been justified by Rosenqvist's (1954) conclusion that $Co_{1-x}S$ (his δ-phase) is unstable in the system Co-S below *ca* 460°C. This phase did not persist in experimental runs of appropriate composition between 450°C and 400°C, and no significant changes in H_2/H_2S ratio (or sulfur fugacity) were detected in low temperature runs near this composition. At 400°C, Rosenqvist observed the gradual breakdown of $Co_{1-x}S$ to Co_9S_4 in runs of up to a month's duration, an adequate demonstration of the instability of the β-phase at that temperature, although, earlier, Lundqvist and Westgren (1938) had inferred that the "CoS_{1-x}" phase exhibits only polymorphic changes at low temperatures.

The formation of $Co_{1-x}S$, rather than cobalt pentlandite or linnaeite, at temperatures well below 460°C in the wholly unmetamorphosed Carrizal Alto deposit, is clearly in conflict with the phase relationships presented by Rosenqvist. The small amounts of copper which may be present in the mineral would probably be insufficient to affect significantly the stability relationships of the β-phase. The possibility remains that the β-phase again becomes stable at some temperature below 400°C. However, the evidence presented here for the natural occurrence of $\beta Co_{1-x}S$ will require amplification before the mineral name jaipurite can be considered worthy of reassessment. Unless new studies of the type-material reveal the existence of the $\beta Co_{1-x}S$ phase, the Carrizal Alto cobalt sulfide should probably be considered to be a new mineral species.

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