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ALPHA-ARSENIC SULFIDE, FROM MINA ALACRÁN, PAMPA LARGA, CHILE

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ABSTRACT

Two distinct modifications of AsS occur in the Alacrán Ag-As-Sb vein deposit in northern Chile. Of these, one, which crystallized early in the development of the deposit, apparently corresponds to the high temperature α-AsS polymorph (Hall, 1966), not previously documented from natural assemblages. Realgar which occurs as euhedral crystals in median vein cavities is similar, but not identical to "normal" realgar, or β-AsS, from other localities. The relationships between the two forms are poorly-defined, but neither exhibits instability on exposure to light or to infrared radiation.

INTRODUCTION

The inter-relationships of the polymorphic forms of AsS have received considerable attention in recent years (*e.g.* Cahoon, 1965[1]; Hall, 1966; Roland, 1966), but several interesting problems remain unsolved and the published data are in part inconsistent. The high temperature, probably triclinic (Cahoon, 1965), α polymorph is stable in the system As-S only between its melting point at 307±5°C (Hall, 1966) and 256±5°C (Hall, *op. cit.*), or 252±2°C (Roland, 1966), in the presence of vapor. This phase may be preserved for at least two years in the laboratory (Roland, 1966) and Hall and Yund (1964) briefly report its occurrence in ores. Cahoon (1965), Hall (1966), and Roland (1966), on the other hand, found only the low temperature, monoclinic, β polymorph in specimens of realgar from many localities. The present note records the occurrence of α-AsS at a long-known locality for realgar, the Pampa Larga mining district, near Copiapó, Atacama Province, Chile (Segerstrom and Parker, 1959; Parker, Salas and Pérez, 1963).

THE MINA ALACRÁN DEPOSIT

Realgar is an important constituent of the barite-quartz-calcite veins formerly worked for silver at the small Mina Alacrán (27°36′S; 70°11′W). The dominant ore minerals in these mineralogically complex veins include stibnite, pyrite, realgar, orpiment, and native arsenic and silver, in association with minor galena, chalcopyrite, and pitchblende (Parker, Salas and Pérez, 1963). Specimens from the dumps and accessible adit exposures of the mine have since been found by the author to

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[1] B. G. Cahoon, Polymorphism of arsenic sulfide (AsS), in C. S. Hurlbut, Jr., *Research on chemistry and physics of inorganic systems under extreme high pressure and temperature,* Harvard University, Final Rept. Dec. 1965, 42–51 (available from Harvard University).

contain, in addition to the above, an unusual suite of minerals including greigite, smithite (Parker, Salas and Pérez record "sulfosales de plata"), arsenolamprite (Clark, 1970), sphalerite (in part, arsenian), arsenopyrite, acanthite, and high realgar.

The mineralization, probably of lower Paleocene age (Sillitoe, Mortimer and Clark, 1968), has suffered only moderate oxidation since the Pliocene incision of the Quebrada La Cortadera, in which the mine lies, into the Upper Miocene Atacama Pediplain (Clark *et al.*, 1967), and these assemblages represent a hypogene paragenesis. Parker, Salas and Pérez (1963) state that the native arsenic is a product of supergene enrichment, but microscopic examination does not support this contention.

OCCURRENCE OF REALGAR (β-AsS)

Realgar, exhibiting well-formed monoclinic crystals where lining cavities, is widespread both in the Mina Alacrán veins and, in association with pyrite, as disseminations in the granodiorite wall-rocks. It is characteristically associated with granular orpiment and with massive or botryoidal native arsenic; in conformity with the phase relations in the system As-S, orpiment is not observed in actual contact with arsenic.

Whether massive or crystalline, the realgar occurring on the surfaces of specimens collected from the dumps of the mine or from the walls of the adit has a strong reddish-orange hue, markedly richer than that of most museum specimens of this mineral. Specimens which have presumably been exposed to sunlight for at least twenty years and those from underground, which have long been subject to oxidizing agencies, but only sporadically to light energy, are megascopically identical. Indistinguishable X-ray powder patterns were yielded by specimens from the dumps and by material from the adit which had been at once transferred to light-tight boxes when collected. In both cases, the patterns (Table 1) were identical to that found by Hall (1966) for synthetic β-AsS (realgar) annealed at 250°C. Careful examination using a Guinier-de-Wolff multiple-focussing camera failed to reveal the several additional lines Hall recorded for *natural* realgar from Allchar, Macedonia (his Table 1).

The powder patterns of the Mina Alacrán realgar showed no significant changes after grinding under toluene for periods of up to two minutes, and have in all cases remained unchanged on exposure to sunlight for over two years. Similarly, exposure to infrared radiation in an evacuated tube for three hours caused no structural modification.

Arsenolite (As_2O_3) is fairly widespread as a superficial oxidation product in this deposit, thinly coating native arsenic in some zones, and has

TABLE 1. PARTIAL X-RAY POWDER DATA FOR LOW AND HIGH REALGAR, MINA ALACRÁN[a]

Low realgar (β-AsS)		High realgar (α-AsS)	
d (Å)	*I*	*d* (Å)	*I*
6.02	3	6.74	1
5.75	4.5	5.72	7
5.40	10	4.96	6
4.65	2	4.86	2
4.28	2	4.65	1
4.05	2	4.18	2
3.75	1	3.91	4
3.68	2	3.41	1
3.61	1	3.37	0.5
3.20	8	3.30	1
3.08	3	3.17	4
3.00	4	3.07	4
2.93	6	2.98	10
2.88	3	2.95	6
2.84	2	2.88	8
2.79	1	2.81	3
2.73	6	2.74	3
2.71	3	2.71	1
2.65	1		

[a] Patterns taken on an X-ray diffractometer, using silicon ($a=5.4305$ Å) as external standard; peak heights measured graphically.

been detected by X-ray study of the outermost portions of a realgar aggregate closely associated with arsenic. In this instance, however, it appears to constitute a transported supergene phase, and also coats adjacent arsenic-free greigite.

OCCURRENCE OF α-AsS

In view of the conflicting observations which have been presented on the effect of light on realgar, an attempt was made to examine material which had not been exposed prior to X-raying. Two realgar-bearing specimens from the Mina Alacrán dumps were broken open, and realgar grains occurring in their interiors were immediately separated, gently crushed, and X-rayed on a diffractometer. At first, only restricted angular ranges were traversed, to minimize the possibility of structural changes over the longer periods required for a complete wavelength scan, but it soon became evident that the powder pattern yielded by the realgar was suffering no significant change as a result of exposure. However, all realgar from the central zones of the two specimens surprisingly exhibited (Table 1) the powder pattern characteristic of the synthetic high temperature, α polymorph (Cahoon, 1965; Hall, 1966), with no additional or omitted lines.

The α-AsS in these specimens shows only a slightly paler, more yellowish color in hand specimen than the realgar from this deposit. It forms irregular masses and veinlets, not exceeding ~2 mm in thickness, and exhibits no crystal faces under high-power binocular examination. In polished sections, prepared using cold-setting resins and lead-lap polishing techniques, its optical properties are in general not noticeably different from those of realgar in this and other deposits. Thus, its medium-gray color in plane-polarized light in air is appreciably darkened under oil immersion, and a proportion of the grains are distinctly bireflectant in air. The mineral exhibits very strong, yellowish internal reflections, which are, however, generally slightly paler than those shown by normal realgar.

Vickers micro-indentation hardness values of from 53 to 66 were obtained on randomly-oriented grains using a Leitz Durimet-Pol hardness tester and a 15-gram load; this range in part slightly exceeds that found for realgar by previous workers (*cf.* McLeod and Chamberlain, 1969), but similar values were yielded by the associated normal realgar. Measurement of reflectivity in air at 546 nm using a Vickers-EEL Digital Microphotometer and the Carl Zeiss neutral glass (N.G. 1) and SiC standards, yielded values of between 19.5 and 21.3 ± 0.8 percent, whereas the low realgar gave somewhat lower values, in the range $18.2-20.6 \pm 0.8$ percent (*cf.* McLeod and Chamberlain, 1969). The rather high standard errors in these determinations resulted from the presence of very small microscopic flaws in the surface areas examined.

Exposure of the α-AsS to sunlight in both evacuated and open tubes for two years at 25°C has led to no changes in X-ray powder pattern.

The nature of the spatial transition from β- to α-AsS in these specimens is poorly-defined. The samples consist of portions of one-half of a narrow vein section, ranging from a median string of cavities to beyond the contact with the wall-rock some 8–10 cm away. The realgar on the surface of the specimens occurs as a coating and crystals on the walls of the cavities, whereas the α-AsS is concentrated in the interstices of barite plates immediately against the wall of the vein. No realgar occurs in the intervening 5–8 cm section of the vein, so that the two forms are here physically separated.

The possibility that the development of the realgar resulted from exposure of the high temperature polymorph to light and/or oxidizing agencies cannot be wholly discounted, but it is noteworthy that the outer vein sections in which the α-AsS occurs clearly represent an early phase of hydrothermal deposition, preceding that in which the central portions developed, and characterized by a distinct ore mineral assemblage. A more detailed description of the mineral assemblages in this deposit is in preparation, but in the present context it may be mentioned that the α-AsS occurs in contact with antimony-free smithite (β-$AgAsS_2$; Hall, 1966), orpiment, and arsenolamprite, the orthorhombic modification of native arsenic. Neither smithite nor arsenolamprite occurs on the walls of the median cavities. Although the association smithite+α-AsS+ orpiment cannot represent equilibrium in the system Ag-As-S at any temperature, because β-$AgAsS_2$ is stable only between 320±5°C [Hall, 1966; Roland (1966) has 313±2°C to 415°C], the presence of this sulfosalt in the border sections of the veins is indicative of comparatively high temperatures of formation. The assemblage Ag_2S (now acanthite, but in part exhibiting cubic crystal morphology)+native arsenic is also represented in the outer parts of the veins, suggesting that ore deposition commenced at temperatures at least as high as ~355°C (Hall, 1966).

Discussion

The observations summarized here are not readily correlated with those of previous workers on the AsS polymorphs. Roland (1966), however, concluded that α-AsS might be preserved in nature through the quenching of ore fluids in near-surface volcanic or sub-volcanic environments. The site of deposition of the Mina Alacrán ores cannot be delimited precisely, but a consideration of the Lower Tertiary erosional regime of the region suggests that mineralization may have taken place at rather shallow depths, perhaps not exceeding 1–2000 m. The restricted vertical extent of *hypogene* ore-shoots associated with Lower Tertiary granitic intrusions in this immediate area is further suggestive of near-surface deposition as a result of rapid cooling of hydrothermal solutions on contact with ground waters, while the tourmaline-breccia pipes in the nearby Cabeza de Vaca pluton are distinctly sub-volcanic in appearance.

The low-temperature realgar occurring in the central parts of the veins does not exhibit the "porphyroblastic" texture which Roland (1966) has observed in α-AsS inverted from the high temperature polymorph, and is here considered to have crystallized, below ~250°C, as a primary phase. The well-formed monoclinic crystals locally developed by the realgar are also indicative of primary formation at low temperature. Unfortunately, the α-AsS does not show diagnostic crystal forms in this deposit. The possibility that the metastable preservation of α-AsS might in this instance be due to an anomalous composition may probably be excluded; X-ray fluorescence analysis of several grain aggregates failed to detect any minor elements in amounts greater than 0.000_9 weight percent. The realgar is also free from minor elements. Electron microprobe analysis of several grains of the two realgar modifications, employing metallic As and pyrite as standards, yielded sensibly indistinguishable compositions in the range $AsS_{0.97-1.1}$ (this formula has no present structural significance). These preliminary data do not exclude the possibility that α- and β-AsS have slightly, but significantly differing compositions, which might perhaps be inferred from the apparently *lower* symmetry of the higher-temperature form, but place approximate limits on any departure from stoichiometry.

The freshness of the β-AsS specimens collected from this mine was wholly unexpected, in view of Cahoon's (1965) observations. That author examined realgar from "Pampa Larga, Capiapo [sic], Chile," probably from Mina Alacrán or the nearby Mina Descubridora. He found that this realgar, presumably collected many years ago, broke down on exposure to sunlight in an open tube after only one month. The powder pattern of the breakdown product differed from those of arsenolite and of Hall's (1966) "γ-AsS", an apparent third AsS polymorph, but was also yielded by the alteration products of realgar from Getchell, Nevada. Cahoon further effected the complete obliteration of all realgar powder reflections by the exposure of crushed material from another locality to sunlight for only seven hours, but he could not determine whether the alteration was a result of oxidation or of inversion to a new AsS polymorph.

These results are in apparent disagreement with those of Hall (1966), who observed that natural and synthetic β-AsS is converted to γ-AsS on exposure to infrared radiation *in vacuo* below 133°C, and has identified γ-AsS in the yellowish coating on natural realgar specimens. They are also hard to reconcile with the present observations on realgar from Mina Alacrán. As pointed out above, the specimens from the dumps of this mine do not show the yellow-orange alteration product occurring on most museum specimens of realgar, and the β-AsS shows no evidence of instability despite its exposure to sunlight and oxidizing agencies for a considerable period. The specimens from Pampa Larga studied by Cahoon (1965) must either have differed in some key respects from those collected by the author, or, possibly, may have been exposed to light for a very much longer period (that is, $\gg$20 years). The very rapid breakdown of realgar recorded by Cahoon is, in any event, unexplained. At the same time, γ-AsS is apparently absent in the Mina Alacrán realgar.

Present knowledge of the polymorphism of arsenic monosulfide is incomplete. Careful study of natural realgar, collected from fresh underground exposures and stored under controlled conditions, is clearly required, as is further X-ray and chemical examination of the synthetic analogues.

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