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DURANUSITE, PRODUCT OF REALGAR ALTERATION, MINA CAPILLITAS, ARGENTINA

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Abstract

Realgar, AsS, occurs as disseminated grains within layers of banded rhodochrosite of the Mina Capillitas, an epithermal deposit in the Province of Catamarca, Argentina. The realgar has been altered by deuteric solutions to form the rare mineral duranusite, As_4S. Duranusite is associated with crusts and small hemispherical bodies of nearly pure sphalerite. Duranusite occurs as thin lamellae and filaments intimately intergrown with sphalerite.

Keywords: duranusite, realgar, epithermal deposit, Mina Capillitas, Argentina.

Sommaire

Le réalgar, AsS, se présente en grains disséminés dans des couches de rhodochrosite à Mina Capillitas, gisement épithermal dans la province de Catamarca, en Argentine. Des solutions deutériques ont réagi avec le réalgar pour produire la duranusite, minéral rare de composition As_4S. Elle est associée à des croûtes et des amas hémisphériques de sphalérite presque pure. La duranusite forme de minces lamelles et des filaments en intercroissance intime avec la sphalérite.

(Traduit par la Rédaction)

Mots-clés: duranusite, réalgar, gisement épithermal, Mina Capillitas, Argentine.

Introduction

Mina Capillitas, in Catamarca Province of northwestern Argentina, shows complex and variable parageneses that formed episodically from hydrothermal solutions (Márquez-Zavalía 1988). Arsenic sulfide mineralization occurs as realgar, heretofore described in only two localities in Argentina (Angelelli *et al.* 1983, de Brodtkorb & Gay 1994), and as its alteration product, duranusite (As_4S; Johan *et al.* 1973). This is the first occurrence of duranusite outside its type locality of Duranus, France. The arsenic sulfides are disseminated in one portion of the banded rhodochrosite for which Mina Capillitas is famous. The main objective of this paper is to document the new occurrence of this rare mineral and give the results obtained during this study.

Geological Setting

Mina Capillitas is situated in Andalgalá, in the Province of Catamarca (27°27'S, 66°30'W). The deposit consists of a series of epithermal polymetallic high-sulfidation veins (Márquez-Zavalía 1988) that formed during episodic volcanism in the upper Miocene – lower Pliocene (5 ± 0.5 Ma). The veins strike generally ENE or WNW, and are associated with advanced argillic and "sericitic" alteration.

The Nueve vein, where the association of realgar with duranusite was found, was one of the first mined and was among the most important and widely exploited veins in the deposit. This vein consists of many smaller veins that pinch, swell and anastomose. Ore shoots are generally located in the strongly silicified and argillized

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areas; the nature of the wall rock does not affect the thickness of the vein system. The Nueve vein is known to extend 270 meters and has an average thickness of 60–80 cm. In the portion of the vein where realgar and duranusite occur, there are two main parageneses separated by an episode of brecciation: a) enargite – pyrite – chalcopyrite – rhodochrosite, and b) sphalerite – galena – rhodochrosite – "capillitite" (a brown variety of rhodochrosite). The wall rock here is rhyolite, and the vein strikes N60°W and dips 55–85°S.

Occurrence

Realgar and duranusite occur in localized irregular patches on and within rhodochrosite (Fig. 1) at the +83 level of the Nueve vein. These minerals were formed during the sixth of seven stages of mineralization defined by Márquez-Zavalía (1988).

Realgar occurs as nearly equant grains 1–2 mm across scattered within banded rhodochrosite. Most of the grains of realgar are anhedral, but a few were found that display faces with parallel (probably [001]) striations. The color of the realgar varies with the degree of preservation and its orientation, from deep red to orange-red to bright yellowish orange. The presence of realgar was confirmed by optical characteristics, X-ray diffraction and electron-microprobe analyses. Many of the grains are not just red to orange, but also contain an intermixed black phase. Binocular microscopic examination revealed that the grains that contain black material are partly dissolved or corroded, and that the black phase exists primarily around voids developed in the realgar. It was also apparent that abundant small hemispherical grains coat many of the surfaces of the black phase (Figs. 2, 3, 4). Reflected-light examination revealed that the black material is actually an intergrowth of sphalerite and duranusite, and the small spheres are sphalerite.

This mode of occurrence of duranusite is similar to that at the type locality at Duranus, France (Johan *et al.* 1973, Fleischer 1975). Anthony *et al.* (1990) mentioned an additional occurrence of duranusite at Mt. Washington copper mine, Vancouver Island, British Columbia, but gave no further information. The duranusite from Mina Capillitas occurs in this vein as filaments associated with altered realgar, as does the type material.

Optical Properties

In reflected light, realgar is grayish white in color and exhibits low bireflectance and pleochroism (gray-

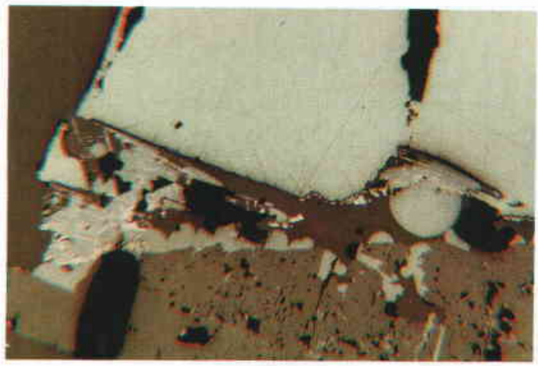

FIG. 2. Reflected-light photomicrograph of realgar (lighter gray phase at top) with intergrown duranusite (thin white lamellae) and sphalerite (intermediate gray phase in spherical masses) and with rhodochrosite (darker gray phase at the bottom). The width of the field of view is approximately 0.6 mm.

FIG. 1. Realgar crystals in a matrix of banded rhodochrosite. Duranusite occurs in the darker margins of the realgar grains. The sample is approximately 1 cm from bottom to top.

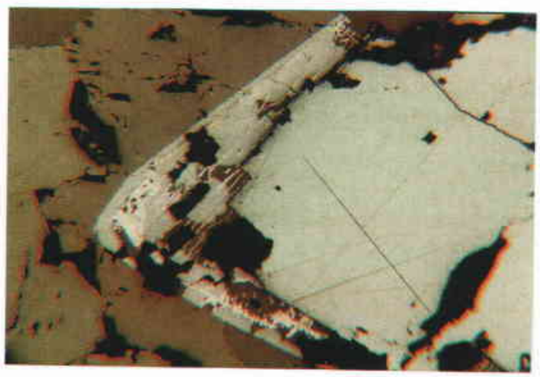

FIG. 3. Reflected-light photomicrographs of a grain of realgar (light grey phase at right) overgrown by a mixture of sphalerite and duranusite (white lamellar phase within the sphalerite) and surrounded by rhodochrosite (darker phase). The width of the field of view is approximately 0.6 mm.

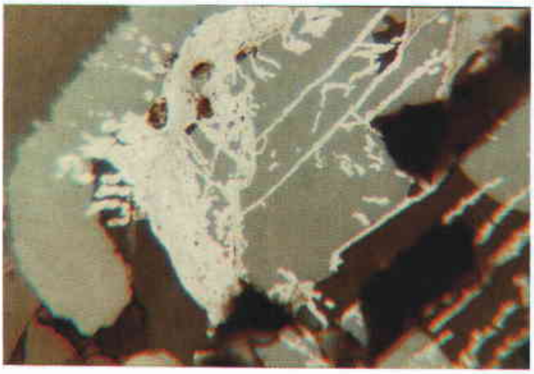

FIG. 4. Detail from Figure 3.

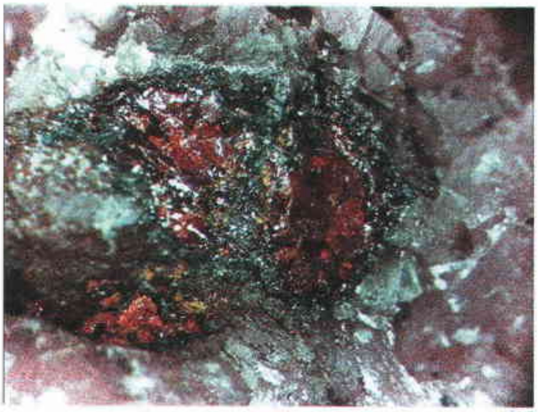

FIG. 5. Grain of realgar (bright red) with overgrowth of intermixed sphalerite and duranusite (black) and set within a matrix of banded rhodochrosite (pink). The width of the field of view is approximately 3 mm.

FIG. 6. Cavity within banded rhodochrosite and from which a grain of realgar has apparently been dissolved. Small spherules of sphalerite, intergrown with duranusite, now lie within the cavity. The width of the cavity is approximately 1 mm.

ish white to grayish white with a bluish hue). Abundant deep red, orange and yellow internal reflections obscure most other optical properties. Reflectivity was measured in air using pure silicon as a standard, as described in Pauly (1986), and the values obtained are in good agreement with those of Criddle & Stanley (1986). Many minute pseudosecondary and secondary fluid inclusions (<2 μm) occur along healed fractures in the realgar.

In reflected light, duranusite is white, with a very low bireflectance and pleochroism. It occurs as thin, high-reflectivity filaments, lamellae, and very small globular masses that are intergrown with sphalerite around the margins of realgar grains (Figs. 5, 6). Sphalerite is present as a nearly continuous coating over parts of the realgar, in spherical aggregates up to 100 μm in diameter. In cross section, there are concentric growth-zones clearly visible within many of the sphalerite grains; this sphalerite fluoresces orange under short-wavelength ultraviolet light.

X-RAY CRYSTALLOGRAPHY

The X-ray powder-diffraction pattern for both realgar and duranusite were obtained using Cu$K\alpha$ radiation with a Ni filter. X-ray data for the duranusite were obtained with a 114.6-mm Gandolfi camera, using a small amount of the mineral separated under the stereomicroscope.

Realgar has a monoclinic symmetry, space group $P2_1/n$ (Buerger 1935). Unit-cell parameters for a sample of Mina Capillitas realgar, refined from powder-diffraction data using CELREF (Appleman & Evans 1973), are: a 9.333(3), b 13.562(3), c 6.593(2) Å, β 106.32°, V 800.0(3) Å^3. These data are in good agreement with the findings of Buerger (1935).

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR DURANUSITE FROM MINA CAPILLITAS, ARGENTINA

hkl	d_{obs}(Å)	d_{calc}(Å)	I/I_0	*hkl*	d_{obs}(Å)	d_{calc}(Å)	I/I_0
010	6.74	6.74	20	121	2.387	2.392	50b
011	5.61	5.62	100	113	2.306	2.293	20
002	5.05	5.04	70	123	1.984	1.983	80
012	4.04	4.05	30	130	1.905	1.901	10
100	3.588	3.570	50	131	1.872	1.875	20
021	3.198	3.200	50b	200	1.794	1.797	60
111	3.022	3.030	40	124	1.760	1.755	30
102	2.924	2.920	80	211	1.709	1.706	30b
022	2.803	2.800	60	034	1.678	1.680	10
112	2.683	2.683	50	212	1.639	1.632	10
004	2.524	2.530	10	140	1.526	1.527	20
120	2.387	2.392	50b				

114.6 mm Gandolfi camera, Cu$K\alpha$ radiation (λ = 1.5406 Å), visually estimated intensities.

Duranusite is orthorhombic; its space group has not been determined. Unit-cell parameters refined from powder data using CELREF (Appleman & Evans 1973) are: *a* 3.588(3), *b* 6.742(6), *c* 10.095(9) Å, *ù* 244.2(3) Å^3. These data are in good agreement with JCPDS #25-1479 for duranusite. Table 1 lists the X-ray data for duranusite.

Chemical Composition

Electron-microprobe analyses of realgar (Table 2) reveal that it is quite pure. It contains only a small and irregularly distributed amount of iron (up to 0.29%).

The chemical composition of the duranusite at Mina Capillitas is close to that from Duranus, except that it seems to contain zinc, in quantities that even surpass 3 wt% (Table 2). The microprobe beam was adjusted to approximately 1 μm in diameter for the analysis of duranusite. However, because most grains and laths of duranusite are only 5 to 10 μm in width (and extend to unknown depth in the polished sections), it is not possible to ascertain if the zinc reported is actually a component of the duranusite itself or a result of the electron-beam excitation volume, including a portion of the surrounding sphalerite. However, the zinc values obtained were reasonably consistent and did not show any tendency to be higher near margins of the duranusite or in thinner grains. Furthermore, we have never observed polishing contamination on the surface of polished sections. Accordingly, we believe that the zinc is actually in the duranusite.

The analysis of sphalerite reveals only very small and irregular amounts of arsenic, manganese and iron (Table 2). Some of the spherulitic sphalerite is concentrically zoned; the lighter bands observed under reflected light correspond to areas slightly enriched in Mn.

Examination with a scanning electron microscope revealed that some exposed surfaces of realgar are partially coated with small crystals of arsenic oxide. Although we do not have confirmatory data, we believe that these are crystals of arsenolite (As_2O_3) because the mode of occurrence and shape of the crystals match well with the description given by Dana & Ford (1932) and Roberts *et al.* (1990).

TABLE 2. THE COMPOSITION OF REALGAR, DURANUSITE AND SPHALERITE FROM MINA CAPILLITAS, ARGENTINA

Mineral	Duranusite			Realgar			Sphalerite		
	#29	#37	#40	#16	#18	#21	#32	#34	#61
As wt%	87.06	88.40	90.57	68.39	68.21	69.06	0.13	0.09	0.12
S	7.76	7.54	8.27	30.42	32.03	31.62	31.12	32.62	32.45
Zn	3.18	3.11	1.38	0.00	0.00	0.00	67.99	65.54	66.53
Fe	0.91	0.11	0.02	0.29	0.00	0.06	0.34	0.38	0.00
Mn	0.04	0.01	0.00	0.00	0.00	0.00	0.03	0.00	0.00
Total	98.96	99.17	100.24	99.09	100.24	100.73	99.61	98.63	99.10
As atom%	79.06	80.55	81.23	48.90	47.68	48.29	0.09	0.06	0.08
S	16.48	16.05	17.33	50.82	52.32	51.66	48.07	50.16	49.82
Zn	3.31	3.24	2.00	0.00	0.00	0.00	51.51	49.45	50.10
Fe	1.11	0.14	0.00	0.28	0.00	0.05	0.30	0.33	0.00
Mn	0.05	0.02	0.00	0.00	0.00	0.00	0.03	0.00	0.00

Electron-microprobe data.

Discussion and Conclusions

The occurrence of realgar with sphalerite and duranusite in banded rhodochrosite at Mina Capillitas may be interpreted in terms of paragenetic relationships. The distribution of the grains of primary realgar within at least six different layers of rhodochrosite indicates that there was episodic precipitation of arsenic sulfide. The alteration of realgar with release of arsenic to form duranusite appears to have been simultaneous with the deposition of the sphalerite, and was perhaps caused by the same fluids that precipitated the sphalerite. This would account for the intimate intergrowth of sphalerite and duranusite. Sphalerite deposition continued for some time after the formation of duranusite, as revealed by the development of sphalerite hemispheres over the surface of sphalerite–duranusite intergrowths. Subsequent to the final development of the sulfides, there was some minor oxidation, which resulted in the formation of minor amounts of arsenic oxide on some exposed surfaces of realgar.

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