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, As₄S₃. 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.

INTRODUCTION

Mina Capillitas, in Catamarca Province of northwestern Argentina, shows complex and variable parageneses that formed episodically from hydrothermal solutions (Máquez-Zavalia 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 (As₄S₃; 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 Andalgala, in the Province of Catamarca (27°27'S, 66°30'W). The deposit consists of a series of epithermal polymetallic high-sulfidation veins (Máquez-Zavalia 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...
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 duranussite 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 duranussite 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-Zavalia (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 duranussite, and the small spheres are sphalerite.

This mode of occurrence of duranussite 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 duranussite at Mt. Washington copper mine, Vancouver Island, British Columbia, but gave no further information. The duranussite 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-
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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.

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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 CuKα 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).

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X-ray powder-diffraction data for duranusite from Mina Capillitas, Argentina.

114.6 mm Gandolfi camera, CuKα radiation ($λ = 1.5406$ Å), visually estimated intensities.
Durianusite 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, \( \alpha = 90 \)°, \( \beta = 90 \)°, \( \gamma = 90 \)°. These data are in good agreement with JCPDS #25-1479 for durianusite. Table 1 lists the X-ray data for durianusite.

**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 durianusite at Mina Capillitas is close to that from Duranian, 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 durianusite. However, because most grains and laths of durianusite 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 durianusite 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 durianusite 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 durianusite.

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 (As₂O₃) 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).

**DISCUSSION AND CONCLUSIONS**

The occurrence of realgar with sphalerite and durianusite 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 durianusite 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 durianusite. Sphalerite deposition continued for some time after the formation of durianusite, as revealed by the development of sphalerite hemispheres over the surface of sphalerite–durianusite 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.

**ACKNOWLEDGEMENTS**

This investigation was conducted during an external fellowship given to one of the authors (MFMZ) by the Consejo Nacional de Investigaciones Cientificas y Tecnicas (CONICET) de la Republica Argentina. The authors are specially grateful to Ing. F.P. Alvarez, who provided the samples, and to the Department of Geological Sciences of the University of Manitoba and Virginia Polytechnic Institute and State University, where the studies were carried out. The authors also thank J.K. McCormack and J.H. McCarthy for their helpful comments, and R.F. Martin for invaluable improvements to the manuscript.

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Received March 10, 1999, revised manuscript accepted August 24, 1999.