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ARSENIAN SPHALERITE FROM MINA ALCARÁN,  
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## ABSTRACT

Bright pink sphalerite from the arsenic-rich Alacrán deposit, with  $a=5.4110 \pm 0.0003 \text{ \AA}$ , is shown by electron-probe microanalysis to contain only traces of iron but  $1.7 \pm 0.3$  weight percent As.

## INTRODUCTION

The literature contains numerous reports of appreciable solid solution of arsenic in sphalerite (e.g. Schroll, 1953; Fleischer, 1955), but the analytical evidence remains largely unconvincing. Moss (1955; and in Hey, 1955, Frondel, 1967) proposed that the mineral voltzite has the general composition  $(\text{Zn,As})\text{S}$  or  $\text{Zn}(\text{As,S})$ , but Frondel (1967) subsequently found no evidence to support this suggestion. Most recent electron-probe microanalyses of sphalerite do not record even traces of arsenic. However, Herzenberg (1932, 1933) found 0.64 weight percent arsenic by chemical analysis of a raspberry-red sphalerite-like mineral from Llallagua, Bolivia, which he named *gumucionite*. Later workers (e.g. Hey, 1955) have assumed that this material represents a mixture of sphalerite and realgar but no further work appears to have been carried out on the original or similar specimens. The present note describes the occurrence of an apparently similar, and demonstrably arsenic-bearing sphalerite.

## SPHALERITE IN THE ALACRÁN DEPOSIT

Sphalerite is a minor constituent of the mineralogically complex, polymetallic Alacrán vein deposit (Parker, Salas and Pérez, 1963), in the Pampa Larga mining district of northern Chile (Lat.  $27^{\circ}36'S$ .; Long.  $70^{\circ}11'W$ .). It occurs, however, in at least three paragenetic contexts: (1) in association with early arsenopyrite, pyrite, stibnite, smithite,  $\alpha\text{AsS}$  (Clark, 1970a) and arsenolamprite (Clark, 1970b), among other minerals; (2) with late-stage greigite, pyrite, native arsenic, realgar, and orpiment; and (3) rarely, as free-standing crystals in vugs, in association with realgar and orpiment.

Sphalerite generations 1 and 2 have a brownish-black appearance in hand-specimen, and have been found by X-ray fluorescence and electron-probe microanalysis to contain, respectively, 8–9 mole percent FeS, and  $7.5 \pm 0.5$  percent FeS (when in contact with greigite and pyrite) to

$4.2 \pm 0.5$  percent FeS (in association with pyrite alone). The third generation, however, has a bright reddish-pink color, and is shown by spectrographic analysis to contain only traces (0.0X percent) of iron, in addition to unusually small amounts of cadmium and manganese (both 0.00X percent).

#### PINK SPHALERITE

This late-stage sphalerite exhibits minute, translucent tetrahedrons, overgrowing calcite rhombs and rosettes. Thin crusts and occasional crystals of realgar and crusts of orpiment occur in contact with the sphalerite, and the three sulfides appear to have crystallized simultaneously. Native rhombohedral arsenic, pyrite, and greigite probably formed at the same stage in the vein filling, but have not been observed to occur in contact with the pink sphalerite, which apparently crystallized in an arsenic-rich, but essentially iron-free micro-environment. The lustrous crystals are extremely brittle, and crumble at the touch of a needle. They show no color zoning in hand-specimen or in polished section, where they are characterized by intense, roseate internal reflections, and are readily distinguished from the iron-bearing sphalerites in the Alacrán ores.

X-ray powder patterns of this mineral confirm its identification as a cubic sphalerite, with less than 10 percent hexagonal packing (Smith, 1955; Short and Steward, 1959). The unit-cell edges of two crystals were measured in a 114.49 mm-diameter X-ray camera, using the Straumanis film mounting technique and Cu-K $\alpha$  radiation, and by extrapolation of back reflection lines to  $2\theta = 180^\circ$  by the Nelson and Riley (1945) function. Concordant values of 5.4110 and  $5.4111 \pm 0.0003$  Å were obtained, which are significantly greater than that found for pure  $\beta$ ZnS by Kullerud (1953;  $5.4094 \pm 0.0001$  Å, in Skinner and Barton, 1960) and Skinner and Barton ( $5.4093 \pm 0.0002$  Å; 1960).

#### ANALYTICAL DATA

The unusual optical properties of this sphalerite prompted an analytical study. Qualitative spectrographic and X-ray fluorescence analysis of clean, hand-picked crystals revealed that, although containing only traces of iron, the mineral is apparently rich in arsenic ( $>1$  weight percent). The possibility that the arsenic might be present as discrete inclusions of realgar or orpiment was investigated by electron-probe microanalysis of several intergrown crystals. Arsenic was confirmed as a constituent of the sphalerite, and no inclusions of arsenic sulfides were detected. Wavelength scanning across each of the crystals shows that the arsenic is homogeneously distributed. An arsenic content of  $1.7 \pm 0.3$  weight percent was determined, using the associated realgar (assumed

to be stoichiometric AsS) as a standard. In *in vacuo* heating experiments, the arsenian sphalerite broke down to a honey-yellow sphalerite and probable realgar in four hours at 200°C, but persisted without a change in color or in cell edge at 150°C for 32 hours. Annealing in the presence of magnesium metal for 42 hours at 150°C resulted in no increase in cell edge (*cf.* Skinner and Barton, 1960), so the arsenian sphalerite is apparently free from oxygen. The response of this phase to heating suggests that it contains no organic component (*cf.* Frondel, 1967).

#### DISCUSSION

On the basis of the observations summarized here, it is tentatively suggested that an arsenian sphalerite solid solution, probably of the form Zn(As,S), is a stable phase in the system As-Zn-S at low temperatures (below approximately 200°C). The earlier-formed, iron bearing sphalerite coexisting with arsenopyrite, pyrite, and native arsenic in this deposit contains no arsenic (*i.e.* <0.01 percent), suggesting that either the solubility of arsenic in sphalerite decreases with increasing temperature in the system As-Fe-Zn-S or, more probably, that such substitution is prevented by even minor amounts of iron.

The Mina Alacrán arsenian sphalerite in some respects resembles the "gumucionite" of Herzenberg (1932, 1933). However, it forms euhedral crystals in contrast to the botryoidal, fibrous habit of the material from Llallagua, which exhibited violent decrepitation and expulsion of water at low temperatures. Herzenberg considered the red coloration of "gumucionite" to be due to arsenic sulfide, but the present study suggests that this striking feature may be an inherent property of arsenian sphalerite.

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#### A NEW TECHNIQUE IN THERMOLUMINESCENCE PHOTOGRAPHY

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#### ABSTRACT

A simple and sensitive method has been developed to produce photographs of thermoluminescence in minerals. Placing an X-irradiated mineral in direct contact with a photographic emulsion forms images with a sensitivity comparable to photomultiplier tubes and with resolution of particles 10  $\mu\text{m}$  in size. Some geological and paleontological applications are also discussed.

#### INTRODUCTION

Photography, in the usual sense, of thermoluminescing minerals is complicated by the typically low light intensity involved. Although the film may be exposed over the entire time a sample is being heated, physical limitations allow only a small fraction of the light produced to enter the camera. The success of investigations (for example Roach, 1968, p. 591; and Fremlin, 1968, p. 407), utilizing the photograph of strongly thermoluminescent materials, indicates the desirability of a method allowing its extension to low intensity cases. The method described below, although restricted to a smaller temperature range, is quite simple and provides sensitivities comparable to that of a photomultiplier tube.

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