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SILVER-BEARING INCLUSIONS IN "ARGENTIFEROUS" GALENA FROM THE SILVERMINE DISTRICT IN SOUTHEASTERN MISSOURI

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ABSTRACT

Galena from Sn–W greisen veins in the Silvermine district of southeastern Missouri contains between 1 and 3 kg/tonne Ag and carries trace amounts of Bi, Sb, Sn, As, Fe, Cu, Zn and Au (up to 11 g/tonne). Such galena, long considered argentiferous, has been examined optically at 1250× and by SEM up to 12,500×. It clearly contains two types of minute inclusions: round blebs and rods. Their distribution in rows suggests an exsolution origin. Optical properties and electron-microprobe/SEM-EDS analyses indicate that one of the cryptic phases is argentiferous tetrahedrite containing variable amounts of silver (up to approximately 15%) and the other is a Cu–Fe–Sn–S mineral, very likely mawsonite. Neither phase has been previously reported from this locality. Repeated analyses of homogeneous domains within the galena failed to detect any silver above the limits of detection of the electron microprobe (approximately 0.02%).

Keywords: "argentiferous" galena, argentiferous tetrahedrite, Silvermine district, Missouri.

SOMMAIRE

La galène des filons de greisen à Sn–W du district de Silvermine, dans le Sud-Est du Missouri, contient de 1 à 3 kg Ag par tonne et des traces de Bi, Sb, Sn, As, Fe, Cu, Zn et Au (jusqu'à 11 g/tonne). Depuis longtemps considérée comme galène argentifère, elle est ici examinée par microscopie optique (1250×) et par microscopie électronique à balayage (12500×). Elle contient deux types d'inclusions infimes: en globules et en bâtonnets, alignés suivant des droites; leur distribution fait penser à une origine par exsolution. Les propriétés optiques et les résultats d'analyses à la microsonde et par dispersion d'énergie d'un spectre au microscope électronique montrent la présence d'une tétraédrite argentifère à teneur d'argent variable (jusqu'à environ 15%) et d'un minéral de Cu, Fe, Sn et S, mawsonite très probablement. C'est la première fois qu'on signale ces deux espèces dans cette région. Des analyses répétées de domaines homogènes montrent que la quantité d'argent que peut contenir la galène est inférieure au seuil de détection par microsonde électronique (environ 0.02%).

(Traduit par la Rédaction)

Mots-clés: galène "argentifère", tétraédrite argentifère, district de Silvermine, Missouri.

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INTRODUCTION

The Silvermine district, so named for minor production of silver during the late 19th century, lies 14 km west of Fredericktown, Missouri, on the St. Francis River in northeastern Madison County (Fig. 1). Data on the geology and general mineralogy of the district are given in Lowell & Gasparrini (1982). The presence of silver in the district has been known since 1855 when the property was first worked as mineral land. In a study of the ore-dressing work on the then-active Einstein vein, Wilson (1879) reported for the first time that nearly all the silver is carried in galena; he presented five fire assays of purified galena running between 1 and 3 kg/t Ag. The apparent absence of silver minerals in the ore as inclusions in the galena led him and subsequent investigators to conclude that the galena carried its silver values in solid solution. Argentiferous galena from the district was thereafter reported by Haworth (1888), Keyes (1895), Tarr (1921), Singewald & Milton (1929), Tolman (1933a, b), Kidwell (1946), Lowell (1976), Lowell & Tobey (1976) and Lowell & Kurz (1977). Recently, Hagni (1981) described five silver-bearing minerals from the district: argentiferous tennantite, antimonpearceite, argentiferous chalcopyrite, a Ag–Cu–Bi sulfide and argentiferous galena, which replaces the other four carriers.

In the Silvermine district, galena occurs in irregularly distributed masses ranging from a few to 50 mm in diameter in association with other vein sulfides, particularly pyrite. It is always a minor constituent in sulfide-rich zones and rarely forms masses larger than 1 cm in size. Many examples of galena replacing or filling fractures in the other sulfides can be observed, but the mineral also occurs as inclusions in pyrite, sphalerite and chalcopyrite, which are not fracture-related. Most of the galena thus appears to be late in the sulfide paragenesis, but some overlap with other phases probably occurs. Available assay-data for silver in galena-rich and galena-poor samples, as well as the findings by Hagni (1981), indicate that silver is not exclusively confined to galena, as assumed by previous authors.

METHOD OF STUDY

The initial procedure used to determine

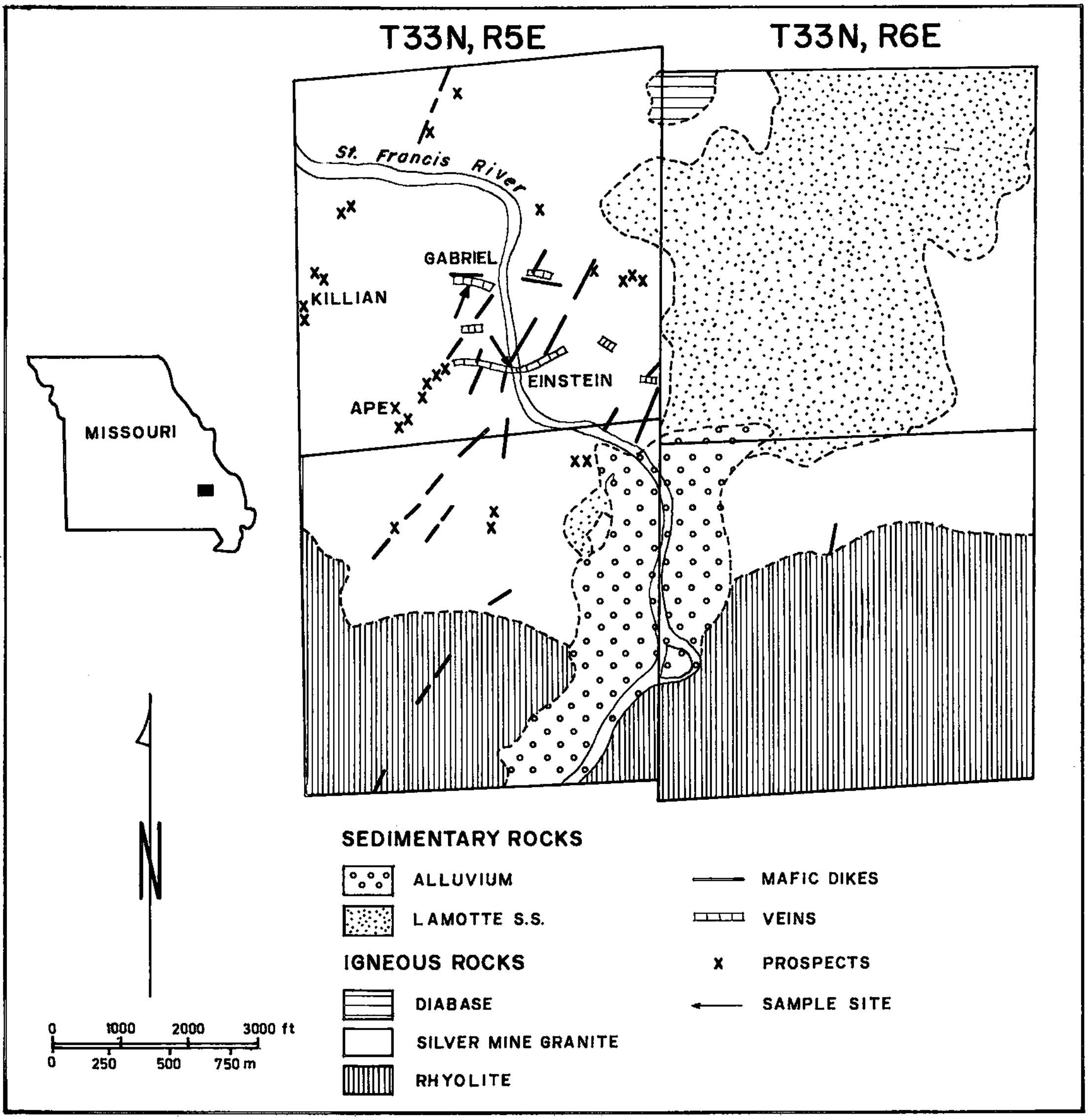

FIG. 1. Index map and geological map of the Silvermine district (after Lowell & Gasparrini 1982).

homogeneity in the galena involved chemical etching in nitric acid, using techniques described by Scott (1976), followed by examination in oil and air using reflected light. These techniques failed to bring out any cryptic phases despite the large number of samples examined.

Unetched polished mounts were next examined with an SM-LUX-POL Leitz microscope by using oil immersion, reflected light and magnifications of 500× and 1250×. At these magnifications, a number of minute but discrete particles that had escaped detection by conventional ore-microscopy became visible. The particles were photographed, and the largest were qualitatively analyzed by electron microprobe to confirm that they were not galena. Because most of them are too fine for an acceptable analysis by microprobe, the inclusions were then examined at magnifications up to 12,500 times in a scanning-electron microscope equipped with a solid-state detector for energy-dispersion analysis (SEM-EDS) (Fig. 2). This procedure led to the identification of the individual grains based on optical properties and chemistry, as described in Gasparrini (1980) and Lefebvre & Gasparrini (1980).

Following these determinations and findings, inclusion-free areas within the galena were quantita-

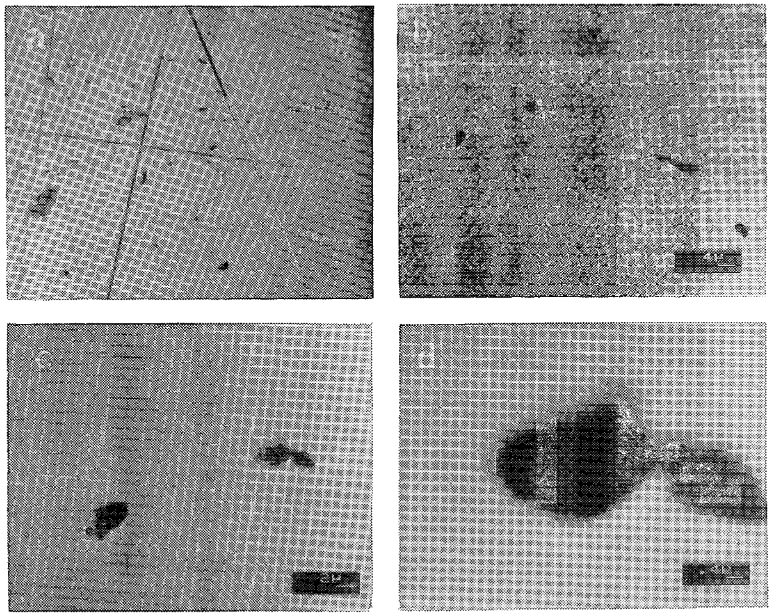

FIG. 2. Grains of tetrahedrite and mawsonite as seen at the highest optical-microscope magnification of 1250× (a), and at magnifications of 1250× (b), 2500× (c) and 12,500× (d) in the SEM. The particles appear to be aligned in a row and show elongate shapes suggesting coherent exsolution, perhaps along a crystallographic direction in the galena. Tetrahedrite is light grey, mawsonite, dark grey.

tively analyzed for silver in the electron microprobe by using wavelength-dispersion techniques. This study involved (i) a peaking of the spectrometer at the silver $L\alpha$ wavelength on a standard of metallic silver, and (ii) a comparison of the counts emitted at that wavelength position by a standard of silver-free galena with the counts emitted by the galena under study. The advantage of this technique over the traditional one, in which the counts emitted by the sample are compared with those emitted by the silver in a standard of known composition, lies in the elimination of the need for a determination of the background; the average number of counts obtained from the silver-free galena is the silver background on the sample under study. Determination of silver concentrations in galena is a delicate operation that may give erroneous results if not accurately conducted, for several reasons including the following: 1) The shape of the spectrum at the silver $L\alpha$ wavelength position, when using an ADP diffracting crystal, or other crystal with a similar range of wavelengths, is such that it requires background determinations on both sides of the peak. If not performed accurately, such determinations may give incorrect values interpreted as peak counts. 2) Background values for silver in galena are normally high owing to the matrix effect caused by lead. These may be interpreted as silver peak counts. 3) The *M* spectrum of the lead includes peaks emitting within the energy range of the *L* spectrum of the silver. These peaks of lead may be interpreted as emitted by the silver.

RESULTS AND CONCLUSIONS

The combined ore microscope - SEM - microprobe study show that the galena contains cryptic inclusions of two different minerals, argentiferous tetrahedrite and a Cu–Fe–Sn–S mineral, very likely mawsonite. The occurrence of these minerals at the Silvermine locality was first reported by Gasparrini & Lowell (1983). Tetrahedrite, $(Cu,Ag,Fe)_{12}Sb_4S_{13}$, which forms the more common and larger of the two types of inclusion, occurs as grains that vary in size from a fraction of a micrometre (only seen when using the higher SEM magnifications) up to several micrometres (visible under optical microscope with magnifications less than 500×). The grains of tetrahedrite are round or smoothly elongate and occur both as isolated grains and in groups. In the latter case, the particles are aligned in rows and usually show an elongate shape (Fig. 2). Both of these features suggest coherent exsolution, perhaps along crystallographic directions in the galena. The determinations of composition of the tetrahedrite by the SEM show very little arsenic and variable amounts (up to 15%) of silver.

The Cu–Fe–Sn–S mineral, believed to be

mawsonite, $Cu_6Fe_2SnS_8$, is much less abundant than the tetrahedrite (in a ratio of 1:5 to 1:10) with which it is usually associated. The two phases occur in composite grains or in linear groups (Fig. 2). The average size of the mawsonite is 1 to 2 micrometres. Its chemical composition is constant and lacks detectable silver. In addition to the mawsonite, one grain of stannite, Cu_2FeSnS_4, 20 micrometres in size, was found attached to silicate gangue in a galena concentrate.

The microprobe study shows that no detectable silver is present in the inclusion-free areas of the galena (detection limits with wavelength–dispersion spectrometry: approximately 0.02%). To confirm this finding, six additional grains of galena were reanalyzed for silver by Dr. Gunter Springer, at the Falconbridge microprobe laboratory. Dr. Springer's findings are in agreement with the authors' conclusions.

Based on the results of the electron-microprobe analyses and on the presence of silver in micrometre-scale inclusions of tetrahedrite, we conclude that most, if not all, of the silver is hosted by discrete particles of tetrahedrite and is not in solid solution in the galena. We think it likely that many samples of so-called *argentiferous galena* would likewise be discredited by studies based on ultrahigh-magnification optical microscopy, SEM–EDS and careful work by electron microprobe. Detection of such minute silver-bearing phases by these methods could be important in the extractive metallurgy of Ag–Pb ores.

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