The Occurrence of Cd and Tl in the Sphalerite from El Losar del Barco Mine (Ávila, Spain): a Potential Environmental Hazard

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INTRODUCTION.

Sphalerite is the chief ore of zinc in all sulfide-rich base metal deposits. A broad range of trace and minor elements, some of them highly toxic (notably Cd, but also, Tl, As, Hg, etc), can occur in this mineral, often at levels that may pose an environmental hazard in abandoned ore dumps and mine tailings.

Sphalerite is generally considered less reactive than pyrite but dissolution rates for the two minerals may neverthless be comparable. Unlike pyrite, sphalerite may even continue dissolving in a non-oxidizing conditions (Acero et al., 2007), increasing, therefore, the risk of toxic element release into the environment.

The Santa Manolita mine in El Losar del Barco (Ávila, Spain) is a small mining exploitation, abandoned several decades ago. In this area some waste rock piles, where sphalerite is a very abundant mineral, and vestiges of the mineral processing plant are still visible. This deposit is characterised by Pb-Ag (galena) and Zn (sphalerite) hydrothermal-type mineralization in quartz veins embedded in biotitic granite with high silicification (Mapa Geológico y Minero de Castilla y León, 1997).

The aim of this work is to characterise the sphalerite from this mining area to identify its toxic element content and to assess if this mineral is responsible for the contamination detected in a research study in progress in this area.

MATERIALS AND METHODS.

Studied samples correspond to vein-breccia fragments with dark brownish crystals of sphalerite showing a variable grain size (from millimeter to centimeter). These samples were studied by X-ray diffraction, polarizing microscopy and electron microprobe analysis. The analysed elements are S, Fe, Zn, Cd, Tl, Ga, Se and Te.

RESULTS AND DISCUSSION.

X-Ray Diffraction.

Five powder diffractograms of sphalerite were obtained showing its typical d-spacings: 3.12(1), 1.91(0.75), 1.63(0.50), 1.24(0.18) and 1.10(0.15).

Polarizing microscopy.

Sphalerite appears in euhedral to subhedral crystals, very cracked, and sometimes corroded, embedded in quartz and carbonates, along with subordinate galena, pyrite and chalcopyrite. Relicts of zonation and patches of different colour (colourless, yellow, orange, reddish, brownish and black) and twins are present (Fig. 1).

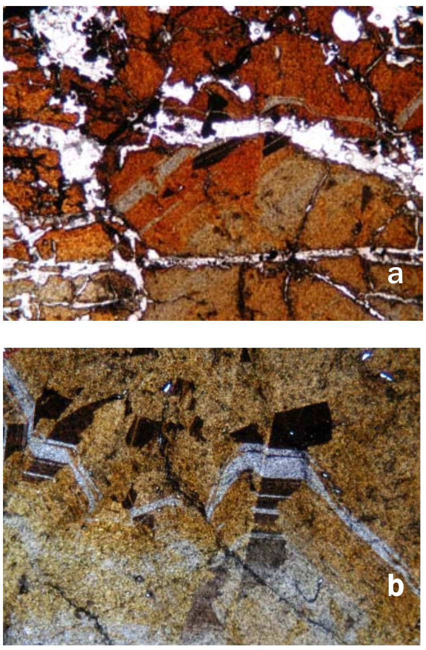

fig 1. Photomicrographs in polarized transmitted light (PP 2.5X) of cracked banded-sphalerite (a) and twinned sphalerite with relicts of zonation (b)..

Electron microprobe analysis.

Forty punctual analyses were performed on several sphalerite crystals of the same and different samples. Analyses were carried out on zones/patches of different colour.

Electron microprobe data are comprised in the following ranges (wt%): 32.0-34.8 for S, 0.454-6.68 for Fe, 58.4-66.7 for Zn, 0.054-0.655 for Cd, n.d.-0.266 for Tl, n.d.-0.291 for Ga, n.d.-0.055 for Se and n.d.-0.094 for Te. The corresponding mean values (wt%) are as follows: 33.2 for S, 3.31 for Fe, 63.3 for Zn, 0.27 for Cd, 0.05 for Tl, 0.05 for Ga, 0.01 for Se and 0.02 for Te. Representative analyses are shown in Table 1. Such data indicate the compositional inhomogeneity of these elements in the studied sphalerite crystals.

The usual Zn content in sphalerites is comprised in the range 41-67% (Deer et al., 1962). The sphalerite from El Losar del Barco displays a relatively high Zn content, with a mean value (63.3%) really close to the upper limit range.

Iron is almost always present in natural sphalerite. Concentrations range from trace levels up to more than 15% (Lepetit et al., 2003). The sphalerite of our study displays a relatively high Fe content (up to 6.68%). The higher is the Fe content, the darker is the colour displayed by the mineral. A dark black colour (marmatite) normally indicates high Fe contents (> 6%) (Cook et al., 2009).

Sphalerite is the chief ore of Cd with extensive solid solution at higher temperature. Cadmium contents are commonly rather uniform in a given deposit, typically within the 0.1-0.5% range, although sometimes higher (Cook et al., 2009). The El Losar del Barco sphalerite displays Cd contents (up to

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0.66%) that exceed the typical range, with a mean value (0.27%) in the upper zone range. This element has been detected in all of the performed analyses. Similar values have been found by Martínez-Frías (1991) in sphalerite samples from SE Spain. No relation has been found between Cd content and mineral colour. The high Cd content represents a serious threat to surrounding ecosystems if geoenvironmental conditions promote the weathering of this mineral, as cadmium is one of the most hazardous trace elements.

S	Fe	Zn	Cd	Tl	Ga	Se	Te	total	colour
33.8	*4.45*	*61.2*	*0.306*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*99.8*	*orange*
34.1	*4.11*	*61.6*	*0.655*	*0.054*	*n.d.*	*n.d.*	*0.061*	*100.6*	*black*
34.8	*6.68*	*58.4*	*0.506*	*n.d.*	*n.d.*	*0.029*	*n.d.*	*100.5*	*black*
33.7	*0.813*	*65.5*	*0.505*	*0.068*	*0.052*	*0.044*	*0.094*	*100.7*	*yellow*
32.7	*0.454*	*66.7*	*0.185*	*n.d.*	*0.030*	*n.d.*	*0.014*	*100.0*	*colourless*
32.8	*3.97*	*62.0*	*0.066*	*n.d.*	*0.291*	*0.020*	*0.006*	*99.2*	*brown*
32.9	*3.44*	*62.8*	*0.054*	*n.d.*	*0.039*	*n.d.*	*n.d.*	*99.3*	*yellow*
32.0	*3.68*	*63.6*	*0.272*	*n.d.*	*0.000*	*0.055*	*n.d.*	*99.6*	*orange*
32.6	*3.31*	*63.8*	*0.131*	*0.190*	*0.078*	*0.014*	*n.d.*	*100.2*	*red*
33.2	*4.16*	*62.3*	*0.406*	*0.266*	*0.011*	*0.012*	*n.d.*	*100.3*	*black*

Table 1. *Representative microprobe analyses of sphalerite (wt%) from the El Losar del Barco mine.*

Thallium is normally associated with sulfide minerals and is often found in mineralized areas interspersed with sulfide deposits (Zitko, 1975). The majority of world thallium production is derived from zinc smelting (Nriagu, 1998), suggesting that sphalerite is a major host for this element. Kelley et al. (2004) showed that Tl concentrations sequentially decrease with deposition from 126 ppm in early brown sphalerite to < 37 ppm in yellow-brown and red-brown sphalerite, although up to 355 ppm are reported from tan-colored sphalerite. A Tl mean content about 500 ppm has been found in our study, with values rising up to 2660 ppm. Analogous concentrations are reported by Martínez-Frías (1991) in sphalerite samples from SE Spain. The weathering of these sphalerites and the consequent Tl release entail a serious risk to environment as Tl is more toxic to mammals than Cd, and even Hg (Nriagu, 1998).

A high negative correlation (R^2=0.90) is found between Zn and Fe+Cd+Tl (Fig. 2), proving the Zn substitution by these other three metals.

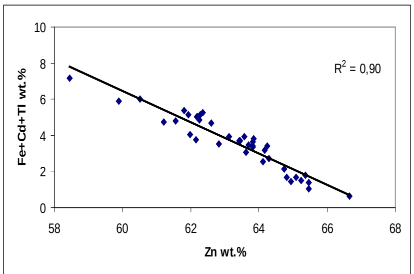

fig 2. *Negative correlation between Zn and Fe+Cd+Tl in the sphalerite from the El Losar del Barco mine.*

Sphalerite is an important source of gallium whose concentration tend to be higher in low-temperature, carbonate-hosted replacement deposits. Concentrations from several hundreds of ppm to 2000-3120 ppm have been reported in very low-Fe-sphalerites (Melcher et al., 2006). In that from the El Losar del Barco Ga is present in most of the performed analyses with a mean value about 500 ppm.

Orberger et al. (2003) showed sphalerite Se values from hundreds to thousands of ppm. This element has not been detected in most of the studied samples, and where detected its content varies from 40 to 550 ppm.

Concerning Te, this element has been only also detected in some samples and in low contents (about 200 ppm on average).

CONCLUSIONS.

The high contents of Cd and Tl in the sphalerite rock wastes from the El Losar del Barco mining area represent a potential environmental hazard, especially if geoenvironmental conditions favour their release. Proper planning should be undertaken to manage these wastes.

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