1 Introduction

Germanium is a strategic metal used in high-tech industry for the manufacture of optical fiber, infrared vision device, and semiconductor and for the catalysis of PET plastics. Sphalerite (ZnS) may contain hundreds ppm of germanium and is considered as the main germanium carrier. MVT (Mississippi Valley Type) deposits are a major source of sphalerite in the world. This paper investigates the distribution of germanium in sphalerite from MVT in Tennessee, USA.

MVT deposits in Tennessee are divided in two mining districts: the Middle Tennessee Mine (MTM) district in the center of the state, located in the Cincinnati Arch, which consists in three mines Cumberland, Elmwood and Gordonsville and the East Tennessee Mine (ETM), located in Appalachian Basin, represented by Coy, Young and Immel mines.

An average of 300 ppm Ge is observed in sphalerite concentrates from MTM against around 10 ppm in sphalerite concentrates from ETM. The main goal of this paper is to study the distribution of germanium in sphalerite from MVT in Tennessee, USA.

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2 Geological Setting

According to Kyle (1976), MVT from MTM and ETM are hosted in Paleokarst formed between the dolomitic Mascot Formation (Lower Ordovician) and the limestone of the Kingsport Formation (Lower Ordovician). In both districts, the mineralization consists of low iron sphalerite with traces of galena, pyrite, fluorite and barite (Kyle, 1976). The main differences between sphalerite from both districts concern its color, ranging from reddish-brown in MTM to pale yellow in ETM, its trace element contents and its general habit, ranging from well crystallized and coarse-grained in MTM to poorly crystallized and fine-grained in ETM. ETM district is located in the Appalachian basin, a foreland basin formed during Appalachian orogeny. The MTM district is located in the Cincinnati Arch, which is a structural high between the eastwards Appalachian basin and westwards Illinois basin.

3 Results

3.1 EMPA and LA-ICP-MS

Sphalerite composition from the two districts (ETM and MTM) was determined by electronic microprobe (EMPA) and Laser Ablation coupled to ICP-MS. In sphalerite from MTM, data has revealed two groups of trace elements that compete for their substitution in sphalerite: a first group with Ga, Ge and Cu with a correlation Cu vs (Ga+Ge) close to 1 and a second group with Fe and Cd with a ratio close to 1. These correlations can be interpreted by the following substitution equation: Cu\(^{2+}\) + Ga\(^{3+}\) ↔ 2Zn\(^{2+}\); 2Cu\(^{2+}\) + Fe\(^{2+}\) + Ge\(^{4+}\) ↔ 4Zn\(^{2+}\) and Fe\(^{2+}\) + Cd\(^{2+}\) ↔ 2Zn\(^{2+}\).

In ETM, the trace element contents are below the EPMA limits of detection. LA-ICP-MS reveals that even in low content, Cu-Ga and Ge are present (with an average of 145, 140 and 15 ppm respectively). The Cu vs (Ga+Ge) correlation is lacking, but there is a correlation between Fe and Cd similar to that of MTM.

3.2 EMPA cartography

EMPA cartography has revealed a crystallographic...
control of trace elements distribution with preferential incorporation of Ga, Ge and Cu following (011) growing bands and Fe, Cd following (010) growing bands (Fig 1).

3.3 Lead isotopes

The Pb isotopic compositions of galena and sphalerite in all the deposits are relatively homogeneous in each mining districts and are typical of a crustal source for the ore lead. However a significant difference is observed between districts suggesting a different source of lead. (Fig 2).

4 Discussions

Analysis by electronic microprobe and LA-ICP-MS have revealed a crystallographic control of traces elements incorporation with two group of traces (Fe/Cd and Ga/Ge/Cu) but also a different trace elements content between the two districts (ETM and MTM). This difference was also revealed by lead isotopes which show that the source of metals in the two districts is not the same. As the two districts do not belong to the same basin, it is possible that they were not linked to the same mineralized event.

Regional studies on MVT deposits at the scale of NE America have revealed the existence of two MVT brine provinces: an Appalachian province and a Midcontinental one (Kesler et al., 1996). Furthermore, MVT deposits in the Appalachian basin have no germanium while all MVT in the Midcontinental region are characterized by high grade of germanium (Hall and Heyl, 1968; Heyl and Jolly, 1968; Viets et al., 1992; Leach et al., 2010). These data were summarized in a map presenting the geographic distribution of the two MVT provinces (Fig. 3).

5 Conclusion

Sphalerites from MTM and ETM are characterized by different contents in trace elements. MTM sphalerites are enriched in Ge, Ga, Cu, Fe and Cd whereas ETM one are only enriched in Fe and Cd, with minor concentration of Cu Ga and Ge. When present, the incorporation of these traces elements in sphalerite is crystallographically controlled.

This distinction is not limited to MVT deposits from Tennessee but can be enlarged to MVT deposits from NE America. Two metallogenic provinces can be identified: the Midcontinental province where MVT are enriched in Ge and the Appalachian one, where MVT are...
characterized by low Ge content. Based on lead isotope compositions of sulfides and Na-Cl-Br systematics in fluid inclusions, it appears that the different content in trace elements observed in MVT deposits at the NE America scale is genetically linked to two different ore fluid sources.

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