

In situ trace elemental analysis and fluid-inclusion microthermometry of sphalerite from Huize super large Pb-Zn deposit, southwest China: Constraints on trace elements substitution

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Huize deposit is a super large Pb-Zn deposit in Sichuan-Yunnan-Guizhou metallogenic province, Southwest China. The Huize deposit contains more than 7Mt metal reserves at average grade of 25-35wt.% Zn+Pb. The orebodies are mainly hosted within the dolostone of the Lower Carboniferous Baizuo Formation. Ore minerals of primary ores include sphalerite, galena and pyrite. Gangue minerals are calcite and dolomite.

In this study, we present in situ trace element analysis of sphalerite in different stages and different generations from Huize deposit, accompanied with the fluid-inclusion microthermometry, to discuss the substitute relation of trace elements in sphalerite.

According to the mineral assemblage and forming sequence, the sphalerite is identified as two stages including six generations. There are two distinct generations in the first stage ore, including dark-brown sphalerite (SphI-1) and light-brown sphalerite (SphI-2). Fluid inclusions of SphI-1 have relatively high the homogeneous temperature (270-375 [U+2103]), whereas SphI-2 fluid inclusions have lower homogeneous temperature (246.6-288.5 [U+2103]). The second stage consists of four generations, dark brown sphalerite (SphII-1) [U+FF0C] light brown sphalerite (SphII-2), orange-yellow sphalerite (SphII-3), and the last light yellow sphalerite (SphII-4). The homogenization temperature of the early three sphalerite generations are 304.5-400 [U+2103], 213.5-311.0 [U+2103] [U+FF0C] and 208.9-285.6 [U+2103], respectively. The fluid inclusions of SphII-4 are rare so that we analysis the homogeneous temperature (225.7-254.3 [U+2103]) of fluid inclusion of calcite (CcII) coexistent with SphII-4, which representatives SphII-4 depositional temperature.

SphI-1 sphalerite consists of two types. One is the successional sphalerite (SphI-11) and following SphII formation, and the other one is continuously pulsatile SphI-12 and following SphI-2 formation. SphII tend to occur as continuously growing sphalerite. Therefore, the ore-forming fluids in the process of sphalerite deposition include two supply types, continuous and pulsatile.

In general, sphalerite is enriched with Fe, Cd, Ge, and Cu in the early high temperature, while enriched with Ga in late temperature. It is notable that Fe and Zn show a liner negatively correlation ($R^2=-0.89$) in all sphalerite samples [U+FF0C] indicating Fe²⁺ is substitution with Zn²⁺ in sphalerite crystal structure. Cu and Ge in SphI-11 and SphI-12 present a positive correlation ($R^2=0.82$) and show a stronger correlation from SphII-2 to SphII-4 [U+FF08] $R^2=0.98$ [U+FF09], suggesting that there may be [Cu-Ge] ions as a substitute for Zn. Fe and Cd in SphI-1 and SphII-1 are positively correlated ($R^2=+0.75$, $R^2=+0.72$), while correlation in SphI-2, SphII-2, SphII-3 and SphII-4 are poorer. This association indicates that Fe and Cd substitute for Zn through an unknown incorporation way in the high temperature stage (SphI-1 and SphII-1), whereas in low temperature (SphI-2 and SphII-2 to SphII-4), the relationship between Fe and Cd is confusion.