

## Controls on Trace Element Partitioning Between Sphalerite and Galena

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There is an abundance of published trace element data for both sphalerite and galena in natural systems, yet the systematic partitioning behavior of trace elements between these minerals remains poorly constrained. Sphalerite and galena both have ionic structures in which the incorporation of trace elements is primarily governed by Goldschmidt's rules of substitution. These rules help explain the trends observed on grain-scale LA-ICP-MS trace element maps generated on assemblages containing sphalerite and galena from 13 different ore deposits. These deposits are representative of a range of different ore types, geologic environments, and physiochemical conditions of ore formation and subsequent syn-metamorphic remobilization and recrystallization.

As per Goldschmidt's rules, much of the LA-ICP-MS mapping data can be explained by simply taking into account the ionic radius of the trace element ion and corresponding vacancy in either sphalerite or galena. As such, there are predictable partitioning patterns during equilibrium crystallization that are independent of ore type, geological environment and physiochemical conditions that most trace elements appear to follow. The elements Mn, Fe, Co, Cu, Ge, Ga, Cd, In and possibly Hg all prefer sphalerite as host, while As, Se, Ag, Sb, Te, and Bi prefer galena. The LA-ICP-MS maps also highlight the more complicated partitioning behaviors of Sn and Tl. These elements are primarily concentrated in either sphalerite or galena in different assemblages.

The authors are unaware of ionic radius data for either Sn<sup>2+</sup> or Sn<sup>3+</sup> in tetrahedral or octahedral coordination, precluding prediction of the behaviour of these ions from Goldschmidt's rules. However, it does seem from results here that galena becomes the preferred host for Sn over sphalerite during syn-metamorphic recrystallization, supporting the conclusion reached by George et al (2015). When chalcopyrite is also present in an assemblage containing sphalerite and galena, it seems that Sn as well as Ga both move to chalcopyrite during recrystallization. Nevertheless, in lower temperature, non-recrystallised ores, the partitioning behavior of Sn would appear to vary as a function of as-yet unknown parameters, possibly including temperature. In the material studied here, Tl is primarily concentrated within galena. This is expected when one considers the ionic radius of Tl<sup>+</sup> (1.5 Å) compared to Pb<sup>2+</sup> (1.19 Å) in octahedral coordination, as in galena, in contrast to Zn<sup>2+</sup> (0.74 Å) in tetrahedral coordination, as in sphalerite (Shannon 1976). Only in one sample here is Tl preferentially hosted in sphalerite over galena.

In two samples from the Broken Hill deposit, NSW, which underwent syn-metamorphic recrystallization, compositional zoning was observed in both sphalerite and galena. Silver and Sb in galena, and Co in sphalerite, are depleted around grain rims and directly adjacent to fractures. Growth-zoned sphalerite or galena is normally exceptionally rare in recrystallized deposits due to high temperatures and ample time for grain-scale re-equilibration of trace elements. Thus the zoning here is considered the result of secondary leaching following fluid-rock interaction.