

Constraints on the solid solubility of Hg, Tl, and Cd in arsenian pyrite

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ABSTRACT

Arsenic-rich (arsenian) pyrite can contain up to tens of thousands of parts per million (ppm) of toxic heavy metals such as Hg, Tl, and Cd, although few data are available on their solid solubility behavior. When a compilation of Hg, Tl, and Cd analyses from different environments are plotted along with As in a $M(\text{Hg, Tl, and Cd})\text{-As}$ log-log space, the resulting wedge-shaped distribution of data points suggests that the solid solubility of the aforementioned metals is strongly dependent on the As concentration of pyrite. The solid solubility limits of Hg in arsenian pyrite—i.e., the upper limit of the wedge-shaped zone in compositional space—are similar to the one previously defined for Au by Reich et al. (2005) ($C_{\text{Hg,Au}} = 0.02C_{\text{As}} + 4 \times 10^{-5}$), whereas the solubility limit of Tl in arsenian pyrite is approximated by a ratio of $\text{Tl}/\text{As} = 1$. In contrast, and despite a wedge-shaped distribution of Cd-As data points for pyrite in Cd-As log-log space, the majority of Cd analyses reflect the presence of mineral particles of Cd-rich sphalerite and/or CdS. Based on these data, we show that arsenian pyrite with M/As ratios above the solubility limit of Hg and Tl contain nanoparticles of HgS, and multimetallic Tl-Hg mineral nanoparticles. These results indicate that the uptake of Hg and Tl in pyrite is strongly dependent on As contents, as it has been previously documented for metals such as Au and Cu. Cadmium, on the other hand, follows a different behavior and its incorporation into the pyrite structure is most likely limited by the precipitation of Cd-rich nanoparticulate sphalerite. The distribution of metal concentrations below the solubility limit suggests that hydrothermal fluids from which pyrite precipitate are dominantly undersaturated with respect to species of Hg and Tl, favoring the incorporation of these metals into the pyrite structure as solid solution. In contrast, the formation of metallic aggregates of Hg and Tl or mineral nanoparticles in the pyrite matrix occurs when Hg and Tl locally oversaturate with respect to their solid phases at constant temperature. This process can be kinetically enhanced by high-to-medium temperature metamorphism and thermal processing or combustion, which demonstrates a retrograde solubility for these metals in pyrite.

Keywords: Mercury, thallium, cadmium, arsenic, pyrite, nanoparticles