

## Isotopic signatures of Cu and Hg during weathering of tetrahedrite and chalcopyrite

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Chalcopyrite ( $\text{CuFeS}_2$ ) and tetrahedrite  $[(\text{Cu,Ag})_{10}(\text{Zn,Fe,Hg})_2(\text{Sb,As})_4\text{S}_{13}]$  are common copper-bearing minerals in ores, oxidation zones, and some mining waste. Weathering of tetrahedrite is especially of interest as it is usually considered as waste; among the multitude of elements that it contains, at least some of them belong to the 'penalty' elements, usually excluding the mineral from being a useful source of metals. We are investigating the processes that control weathering of both minerals in oxidation zones in Špania Dolina (Majzlan et al. 2018), Ľubietová and Rudňany (Slovakia).

The isotopic composition of copper ( $\delta^{65}\text{Cu}$ ) moves stepwise to heavier values as weathering progresses. Tetrahedrite in Rudňany has  $\delta^{65}\text{Cu}$  value of -1.15 ‰ and chalcopyrite -2.00 ‰ but malachite 2.25 ‰. Tetrahedrite in Špania Dolina has value of -2.45 ‰ but the secondary malachite attains values of up to 0.06 ‰ and azurite up to 4.29 ‰. Secondary sulfides (e.g., covellite,  $\text{CuS}$ ), as expected, are isotopically light, with  $\delta^{65}\text{Cu}$  down to of -6.83 ‰. These sulfides, observed and documented in reflected light and BSE images, participate in the redox cycling of copper and cause the isotopic shift in  $\delta^{65}\text{Cu}$ . Among the secondary oxysalts, only the rare tangdanite  $[\text{Ca}_2\text{Cu}_9(\text{AsO}_4)_4(\text{SO}_4)_{0.5}(\text{OH})_9 \cdot 9\text{H}_2\text{O}]$ , found in the vicinity of the weathering tetrahedrite, has  $\delta^{65}\text{Cu}$  values lower than the primary tetrahedrite, suggesting that it could be produced by copper release from the secondary sulfides. Most of this isotopically light copper, however, is probably lost to aqueous solution and carried away.

Weathering of mercurian tetrahedrite produces abundant powdery secondary cinnabar ( $\text{HgS}$ ). Secondary cinnabar is also found as rims on pyrite and chalcopyrite as the result of very high affinity of  $\text{Hg}^{2+}$  to reduced sulfur. Our working hypothesis that the mercury is quantitatively captured by the secondary cinnabar was refuted by investigation of the isotopic composition ( $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ) of the primary and secondary minerals. Very pronounced shifts between the primary tetrahedrite ( $\delta^{202}\text{Hg} = -1.27$  ‰) and secondary cinnabar ( $\delta^{202}\text{Hg} = 0.06$  ‰) could be explained either by Hg binding to thiol ligands, adsorption onto iron oxides or microbial methylation, according to the knowledge of principal mechanisms of Hg isotopic fractionation (Blum et al. 2014). There are hints that Hg adsorption to iron oxides could be the principal process; X-ray adsorption spectroscopy of bulk iron oxides indicates that the adsorbed Hg may be converted to cinnabar- or metacinnabar phase.

Blum, J.D., Sherman, L.S., Johnson, M.W., 2014: Mercury isotopes in earth and environmental sciences. *Annual Rev. Earth Planet. Sci.* 42, 249-269.

Majzlan, J., Kiefer, S., Herrmann, J., Števkó, M., Chovan, M., Lánczos, T., Sejkora, J., Langenhorst, F., Lazarov, M., Gerdes, A., Radková, A., Jamieson, H., Milovský, R., 2018: Synergies in elemental mobility during weathering of tetrahedrite  $[(\text{Cu,Fe,Zn})_{12}(\text{Sb,As})_4\text{S}_{13}]$ : Field observations, electron microscopy, isotopes of Cu, C, O, radiometric dating, and water geochemistry. *Chemical Geology* 488, 1-20.