Antimony in the As-Fe-O system: size or valence-shell chemistry?

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Antimony (Sb) is classified as a priority pollutant, but the risks posed by exposure to Sb can be mitigated by the precipitation of minerals with low bioaccessibility. The major source of Sb is mine wastes, in which Sb almost always occurs with arsenic (As). One of the most common As-bearing minerals in these wastes is scorodite ($FeAsO_4.2H_2O$), which has the lowest bioaccessibility of common As-bearing mine waste minerals. Antimony and As have many chemical similarities (they both are metalloids occurring in Group 15 of the Periodic Table) and substitute for one another in several minerals. We therefore investigated to what extent and how Sb is taken up in scorodite.

We analysed 36 natural scorodite samples (kindly provided by several museums) by microprobe for their As and Sb contents. The maximum concentration of Sb found was in a sample from Bredda Head, Isle of Mann, with an As:Sb wt. ratio of 100:1. Given that the analogous crustal abundance ratio is 10:1 As:Sb [2], we draw the conclusion that scorodite is likely not a host for Sb and, additionally, most likely actively excludes it.

Using the scorodite synthesis method of [1], we prepared 9 samples with varying concentrations of Sb, as well As-only and Sb-only end members. XRD analysis suggests that the end members are scorodite and tripuhyite ($FeSbO_4$), and that the intermediate members are not Sb-substituted scorodite, but instead are mixtures of scorodite and tripuhyite, with tripuhyite becoming more stable with increasing amounts of Sb in the synthesis. For example, at a molar ratio of 60 % As to 40 % Sb, tripuhyite dominates over scorodite. Chemical digestion of the series became increasingly difficult with increasing Sb content. We conclude that, despite the chemical similarities of As and Sb, Sb is not taken up in scorodite (perhaps due to its larger ionic radius compared to As), and that tripuhyite is a highly stable and perhaps underestimated environmental Sb-sink.

[1] Paktunc, D. *et al* (2008) *Geochim. Cosmochim. Acta* **72**, 2649-2672. [2] WebElements.com. Accessed 02/02/14.