

## Crystallographic and fluid compositional effects on the halogen (Cl, F, Br, I) incorporation in pyromorphite-group minerals

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### ABSTRACT

Pyromorphite-group minerals (PyGM), mainly pyromorphite [Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl], mimetite [Pb<sub>5</sub>(AsO<sub>4</sub>)<sub>3</sub>Cl], and vanadinite [Pb<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>Cl], are common phases that form by supergene weathering of galena. Their formation is strongly influenced by processes at the Earth's surface and in the soil overlying a lead deposit, and they incorporate high amounts of halogens, mostly Cl and, in some cases, F. The abundance of Br and I in natural PyGM and their potential as process tracers during surface and sub-surface fluid-rock interaction processes has not been investigated in detail due to analytical difficulties. We, therefore, developed methods for the simultaneous determination of Cl, F, Br, and I in PyGM for (1) powdered bulk samples via combustion ion chromatography (CIC) and (2) compositionally zoned crystals by means of secondary ion mass spectrometry (SIMS).

Our study is based on well-characterized samples of pyromorphite (N = 38), mimetite (N = 16), and vanadinite (N = 2) from Schwarzwald (Germany). Natural pyromorphite incorporates more I (up to 26 µg/g) than mimetite (up to 2 µg/g) and vanadinite (up to 1 µg/g), while Br contents are higher in mimetite (up to 20 µg/g) and vanadinite (up to 13 µg/g) compared to pyromorphite (less than 4 µg/g). These results are unexpected, as mimetite and vanadinite have longer As/V-O bonds giving them larger unit cells and larger polyhedral volumes for the Cl site in the Pb<sub>2</sub> octahedron than pyromorphite. Accordingly, pyromorphite was expected to preferentially incorporate Br rather than I, but the opposite is observed. Hence, halogen chemistry of PyGM is probably not governed by a crystal-chemical control (alone) but by fluid composition. However, the exact reasons remain enigmatic. This idea is corroborated by spatially resolved SIMS analyses that show that many pyromorphite-group minerals are strongly zoned with respect to their halogen mass ratios (e.g., Br/Cl, Br/I mass ratios). Furthermore, variations in halogen abundance ratios do not correlate with Ca/Pb, P/As, or P/V ratios and therefore may record alternating and season-dependent environmental parameters including biological activity, vegetation density, physico-chemical soil properties, and rainfall rate. We suggest that the zonation reflects multiple single fluid flow episodes and, hence, records surface processes. However, further experiments concerning the fractionation of halogens between fluid and PyGM are needed before halogen ratios in pyromorphite-group minerals can be used as reliable monitors of fluid-driven processes.

**Keywords:** Bromine, iodine, combustion ion chromatography, pyromorphite, mimetite, vanadinite