American Mineralogist, Volume 99, pages 1133–1146, 2014

Major, minor, and trace element composition of pyromorphite-group minerals as recorder of supergene weathering processes from the Schwarzwald mining district, SW Germany

Gregor Markl[1,*], Michael A.W. Marks[1], Johannes Holzäpfel[1] and Thomas Wenzel[1]

[1]Mathematisch-Naturwissenschaftliche Fakultät, Fachbereich Geowissenschaften, Universität Tübingen, Wilhelmstrasse 56, D-72074 Tübingen, Germany

Abstract

More than 150 samples of pyromorphite, mimetite, vanadinite, and minerals of the hedyphane-group (which collectively are summarized here under the term PyGM for pyromorphite-group minerals) from the Schwarzwald mining district, southwest Germany, have been analyzed by electron microprobe and LA-ICP-MS. In this largest study of its kind, the relations of PyGM composition to host rock and fluid compositions and the amount of solid solution between the various end-members were investigated. In addition, we report the colors of the many analyzed mineral compositions. Here is a list of the most important results.

• Pyromorphite and mimetite are completely miscible.

• At conditions of the oxidation zone in ore deposits, the solvus between pyromorphite and vanadinite appears to asymmetrical with up to about 3 mol% of vanadinite component in pyromorphite and up to about 39 mol% of pyromorphite component in vanadinite in cases where both minerals coexist.

• Due to a lack of suitable samples, the solvus between vanadinite and mimetite could not be completely constrained, but we report vanadinite analyses with up to 12 mol% mimetite and 8 mol% pyromorphite component.

• There is complete miscibility between pyromorphite and phosphohedyphane and between mimetite and hedyphane.

• F-rich varieties appear only to exist in hedyphanes and phosphohedyphanes, while pyromorphites, mimetites, and vanadinites are Cl- or OH-dominated.

• We report for the first time analyses suggesting the occurrence of an OH-end-member corresponding to mimetite.

• While pyromorphites are preferably green and mimetites yellow, this is not at all a diagnostic feature, as many exceptions exist; major elements are not correlated at all with the color of a specific crystal.

• Most PyGM are strongly zoned and display, for example, significant variations in Ca that are likely to be related to variations of the compositions of various fluid pulses from which the crystals formed.

• PyGM composition is generally uncorrelated with host rock composition, but PyGM enrich other metals like REE, Cr, Sb, Bi, or U up to a factor of 10^6; therefore, they can be regarded as very sensitive recorders of the metal inventory of an oxidation zone and they even record metals only present as traces in the primary ore deposit very reliably.

• REE patterns of PyGM show significant variability even at one location; this may suggest that each zone of a PyGM crystal records the REE pattern of a single fluid pulse or it may indicate fractionation of the REE during PyGM growth. In the absence of conclusive data, the former possibility appears the more likely one.

• PyGM are extremely efficient filters for heavy metals from supergene solutions in and in the vicinity of ore deposits.

Keywords: Pyromorphite, mimetite, vanadinite, fluorophosphohedyphane, hedyphane, trace elements, solid solution, "hydroxylmimetite"