

## SYNCHROTRON-BASED X-RAY DIFFRACTION OF THE PYROMORPHITE-VANADINITE AND MIMETITE-VANADINITE SERIES

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Pyromorphite  $Pb_5(PO_4)_3Cl$ , mimetite  $Pb_5(AsO_4)_3Cl$  and vanadinite  $Pb_5(VO_4)_3Cl$  (commonly called: lead apatites) are minerals isostructural with apatite. In-situ chemically induced precipitation of pyromorphite and mimetite has recently gained a considerable attention as a cost effective reclamation method of soils and wastes contaminated with Pb(II) and As(V). The unique crystal structure and chemistry of these minerals, however, allow for numerous substitutions of both metal cations and anionic complexes [1]. Natural pyromorphites and mimetites usually contain substituted  $VO_4^{3-}$ ,  $AsO_4^{3-}$  and  $PO_4^{3-}$ . This suggests that pyromorphite, mimetite and vanadinite tend to form solid solutions which are relatively stable in environment. [2]. There are several reports on the response of the lead apatites structure to cationic substitutions, however, the knowledge about anionic substitutions which strongly influences the environmental stability of these minerals is sparse. Detailed crystal-chemical study of pyromorphite – mimetite solid solution series has been recently reported by Flis *et al.*, 2010. The performed structural Rietveld refinement of the synchrotron-based data allowed for precise determination of structural parameter of the series including: cell dimensions, ionic bond lengths and angles as well as anionic site occupancies. To date, the only X-ray diffraction studies regarding vanadate substitutions in the lead apatite series is reported by Baker *et al.* [3]. He reports that pyromorphite-vanadinite and mimetite-vanadinite solid solution series are complete. His X-ray data, however, is not supported by the chemical analysis of synthesised solids. Furthermore pyromorphite-mimetite-vanadinite solid solution series are prone to serve peak overlapping and characterized by subtle structural changes among adjacent members. Thus, detailed crystal-chemical studies of these minerals demand high resolution X-ray radiation source.

In order to supplement existing data, a number of compounds covering a wide range of compositions between pyromorphite-vanadinite and mimetite-vanadinite end members were synthesized from aqueous solutions by drop-wise mixing of the respective chemical reagents. The syntheses were carried out at 90°C and pH = 3. Products were characterized by SEM coupled with EDS chemical microanalyser, as well as synchrotron-based X-ray diffraction. Diffraction experiments were carried on the dedicated high-resolution high-throughput powder diffractometer at Sector 11-BM B of the Advanced Photon Source, Argonne National Laboratory,

USA. Analyses were performed at room temperature using monochromatic radiation of the wavelength of 0.42 Å. Intensities of the diffracted X-rays were collected on a 12-element Analyzer/Detector System offering supreme resolution and greatly reduced data collecting time [4]. Raw data from each of the 12 detectors was calibrated, merged and reduced using in-house routine. The diffraction data was analyzed by Rietveld method using the computer program GSAS and EXPGUI. The background was modeled using Chebyshev polynomials of the first kind. Apatite starting atomic parameters came from the refinement based on neutron data in P63/m of Holly Springs hydroxylapatite.

The use of the dedicated high-resolution, high-throughput diffraction beamline 11-BM allowed for quick collection of data of a quality unavailable on any conventional radiation source. The results from Rietveld refinement confirm that the pyromorphite-vanadinite and mimetite-vanadinite solid solution series are continuous. Unit cell parameters vary linearly with anionic substitutions and they depend primarily on chemical properties of constituting anions. The refinement of the occupancies of the anionic position in the mineral structure of all synthesized compounds was in good agreement with the theoretical composition of the samples based on the chemistry of the starting solutions. The results supplement characteristics of environmentally important mineral series.

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