

## PhD Thesis

# VARIATION OF THERMODYNAMIC PROPERTIES OF PYROMORPHITE-VANADINITE AND MIMETITE-VANADINITE SOLID SOLUTION SERIES

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### Abstract

The aim of this PhD thesis is a synthesis of apatites: pyromorphite  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ , mimetite  $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ , vanadinite  $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$  and solid solutions of the series pyromorphite-vanadinite  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}-\text{Pb}_5(\text{VO}_4)_3\text{Cl}$  and mimetite-vanadinite  $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}-\text{Pb}_5(\text{VO}_4)_3\text{Cl}$  and determination of their thermodynamic properties. Obtaining of strictly defined phases during the synthesis will allow to determine very precisely the solubility product  $K_{\text{sp}}$ , enthalpy formation  $\Delta H_f$ , Gibbs free energy  $\Delta G_f$ , entropy  $\Delta S$  and the heat capacity  $C_p$ . Information obtained through research on the formation of the solid solution series pyromorphite-vanadinite and mimetite-vanadinite and determination of the effect of isomorphic substitution on the thermodynamic properties of studied phases, will be used to understand the mechanisms formation and transformation of these minerals in the environment.

It was found that pyromorphite, mimetite and vanadinite as well as solid solutions of pyromorphite-vanadinite and mimetite-vanadinite series can crystallize from low-temperature aqueous solutions, i.e. under hypergeneric conditions. The pyromorphite-vanadinite and mimetite-vanadinite series are continuous isomorphic series, and the isomorphic substitutions in the apatite structure in these series cause systematic changes in their thermodynamic properties. Thermodynamic variations of the studied phases can be linked to the regularities of changes in their structure and chemistry. This work is based on laboratory experiments (synthesis, dissolution experiments) and instrumental analysis of solids and solutions. The solid phases obtained during the synthesis were characterized using x-ray powder diffraction (XRD), scanning electron microscopy with microanalysis (SEM/EDS), infrared absorption spectroscopy (FTIR) and Raman spectroscopy. Aqueous solutions were characterized using atomic absorption spectroscopy (AAS) and UV-Vis spectrophotometry.

Synthetic sediments were identified by XRD as pyromorphite, mimetite, vanadinite and their solid solutions. Diffraction peaks of solid solutions systematically shifted as a result of replacing  $\text{PO}_4$  by  $\text{VO}_4$  and  $\text{AsO}_4$  by  $\text{VO}_4$ . Systematic changes of the unit cell parameters were also observed depending on the chemical composition of the sample. This situation indicates the equivalent position of  $\text{TO}_4$  tetrahedra in the structure of lead apatite. Observations made with SEM show that for both ranks the sediments precipitated mainly in the form of hexagonal

heaps, and the grain size did not exceed 1  $\mu\text{m}$ . For solid solutions of the pyromorphite-vanadinite series, on the MIR spectra both the bands originating from vibrations carried out in the  $\text{PO}_4$  tetrahedron and the vibrations in the  $\text{VO}_4$  tetrahedron were observed. For solid solutions of the mimetite-vanadinite series, infrared spectra also have a mixed character. On the Raman spectra of the solid solutions of the pyromorphite-vanadinite series, the characteristic bands of vibrations in the tetrahedra  $\text{PO}_4$  and  $\text{VO}_4$  were observed. A similar situation occurs in the case of solid solution mimetite-vanadinite series. In spectra bands characteristic for vibrations in  $\text{AsO}_4$  and  $\text{VO}_4$  tetrahedrons can be observed. The Raman spectra and mid-infrared MIR allowed to observe the banding caused by substitution. The position of the bands of the tested phases differs depending on the ratio  $\text{P}/(\text{P}+\text{V})$  and  $\text{As}/(\text{As}+\text{V})$  in the structure of the solid. This is due to differences in atomic masses of replacing anions.

The thermodynamic properties of pyromorphite, mimetite, vanadinite and solid solutions of pyromorphite-vanadinite and mimetite-vanadinite series were calculated based on the results of the dissolution experiments. Dissolution of pyromorphite and mimetite was congruent. Vanadinite and other phases from the pyromorphite-vanadinite and mimetite-vanadinite series were incompletely dissolved. During the dissolution of the studied minerals, chervetite  $\text{Pb}_2\text{V}_2\text{O}_7$  precipitated from the solution. Nevertheless, it was possible to calculate the solubility constants of all tested phases. All calculations were carried out for the state of equilibrium between sediment and solution. A comparison of the  $\log K_{\text{sp}}$  of pyromorphite, mimetite and vanadinite showed that vanadinite is less soluble than pyromorphite and mimetite. In the ranks of pyromorphite-vanadinite and mimetite-vanadinite, the  $K_{\text{sp}}$  value for solid solutions increases linearly with increasing content of P or As in the apatite structure. It was also noticed that the solubility of solid solutions of pyromorphite-vanadinite and mimetite-vanadinite series increases with decreasing pH and temperature increase, while the chemical composition of the solid has a very large effect on the solubility constant. Thermodynamic constants such as enthalpy  $\Delta H_f$ , Gibbs free energy  $\Delta G_f$ , entropy  $\Delta S$  and heat capacity  $C_p$  were determined using the curvilinear model  $\log K_{\text{sp}}$  from the temperature according to the regression curve ( $\log K_{\text{sp}} = A - B/T + D \log T$ ). The variability of the above thermodynamic constants within both series was non-linear.