



Experimental model of cerussite PbCO_3 transformation into phosphate phases at pH 3-11

Monika Kwaśniak-Kominek and Maciej Manecki

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Mineralogy, Petrography and Geochemistry, Krakow, Poland (monika.kwasniak@gmail.com)

Bioavailability of lead depends strongly on mineral speciation. Mobility of this toxic element is strongly reduced when lead in the form of relatively soluble phases (carbonates) is transformed into insoluble forms like phosphates. Despite the fact, that in-situ immobilization of Pb by phosphate amendment (phosphate-induced lead immobilization) is widely applied in remediation of polluted soils and waters, the mechanism of transformation of lead carbonate into lead phosphates is only recently under investigation [1]. Our understanding of this mechanism might in future allow for optimization of the methods applied in environmental engineering. Although the transformation of carbonate minerals into phosphate phases has been studied before, little is known of this system with Pb. There is no systematic study of the effect of pH on the mechanism and the reaction product.

The mechanism of cerussite reaction with phosphate solution at pH 3 – 11 was studied using fragments of natural gem-quality crystals from Morocco. The mineral was reacted with 0.1M PO_4^{3-} or a mixture of 0.1M PO_4^{3-} and 0.03M Cl^- either at 140 °C in the autoclave for 24 hours or at 8 °C in the cooler (for around 6 weeks). Reaction products were identified ex-situ by X-Ray diffraction (XRD) and micro Raman spectroscopy. Scanning electron microscopy and microprobe analysis (EMP) were applied to cut and polished crystals in epoxy.

The products of the reaction depend on pH. This dependency is the most pronounced in Cl—free environment. At low pH (below 6) phosphoshulterite PbHPO_4 and hydroxylpyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ (HPY) are formed while at alkaline range HPY is the only product. Pyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ (CPY) forms in the wider pH range. The replacement reaction proceeds through coupled dissolution-precipitation mechanism. The lead phosphate coating does not armor the surface resulting in complete replacement of cerussite grain by polycrystalline porous reaction products. There is evidence for formation of precursors at the reaction front, which later undergo transformation into final products. This is probably combine effect of carbonate dissolution associated with relatively slow diffusion of ions through porous coating, affecting both pH and saturation indices. High concentrations of carbonate ions result in CO_3^{2-} substitution in the structure of precipitating HPY. This is less pronounced or non-existing in the case of CPY precipitating in the presence of Cl^- .

Monika Kwaśniak-Kominek was partially financed from AGH-UST grant No. 15.11.140.329. Maciej Manecki was financed from research grant No. NCN 2011/01/M/ST10/06999.

[1] Wang L., Putnis CV, Ruiz-Agudo E., King HE, Putnis A. Coupled Dissolution and Precipitation at the Cerussite-Phosphate Solutions Interface: Implications for Immobilization of Lead in Soils, Environmental Science & Technology, 2013.