

PhD thesis
THE MECHANISMS OF FORMATION OF PYROMORPHITE
IN THE PRESENCE OF CERUSSITE

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Abstract

Environmental pollution by heavy metals has been intensively studied for many years. In the case of lead, the attention of scientific world is still focused on the neutralization of the most toxic, ionic form. In the environment, this element most often occurs as particulate matter including minerals galena PbS , cerussite $PbCO_3$ or anglesite $PbSO_4$. These minerals are relatively soluble and dissolve upon weathering releasing ionic lead to the environment.

The aim of this study was to precisely determine the mechanisms of crystallization of most insoluble lead phases during the reaction of cerussite dissolution in the presence of phosphate-containing solutions, as well as to characterize the factors which control the reaction path and products. The effects of chloride and carbonate ions, pH, temperature and concentration of ions were studied in particular. This basic research focused on experimental study in the field of environmental mineralogy, concerning various chemical components in a wide range of pH and temperature. Analytical and computer modeling methods for identification of solution composition and solid phases were carefully selected for precise interpretation of the processes leading to transformation of lead carbonates into lead phosphates.

The results show that transformation of cerussite into pyromorphite is chemically favored and takes place via dissolution-precipitation mechanism. The main factor which determines the formation of a new phosphate phase is pH. In acidic solution as well as in the pH above 7, pyromorphite $Pb_5(PO_4)_3Cl$ or hydroxypyromorphite $Pb_5(PO_4)_3OH$ tend to precipitate. In the pH range between 5 and 7, $Pb_3(PO_4)_2$, $PbHPO_4$ and pyromorphite are formed. The local micro-environment in the reaction front at the surface of dissolving cerussite is different than in bulk solution so phases theoretically unstable can crystallize. For the first time, the precursor in the reaction cerussite-pyromorphite was identified and characterized. With time, metastable $Pb_3(PO_4)_2$ recrystallizes into hydroxypyromorphite.

A very important innovative result of this study is the evidence that in the presence of chloride ions the reaction in the wide range of pH leads solely to the formation of pyromorphite $Pb_5(PO_4)_3Cl$. This is a result of a significant difference in solubility. This means that, in contrary to many previous publications, the environmental importance of the hydroxyl form of pyromorphite is insignificant. The common presence of chloride ions in rainwater, soil solutions and natural or waste surface waters makes the formation of $Pb_5(PO_4)_3OH$ less likely.

The mechanisms of the reaction and key factors which were identified and explained for the first time based on the example of lead minerals are universal and the proposed interpretation applies to

other systems in nature and technology. For the first time, the effect of carbonate and chloride ions on the reaction mechanism, its rate and formation of new mineral phases was determined. This aspect has been the subject of controversy and is a hot research topic in the literature due to the significant impact on the optimization of remediation technologies.

Described mechanisms of reactions are extremely important in environmental protection. The formation of fine crystalline phases on the surface of the dissolving mineral that does not armor the surface of cerussite allows the reaction to proceed until the entire cerussite crystal has been dissolved. The results allow better understanding of the mechanisms of transformation of minerals that occur in the environment and stability of lead minerals in the environment, particularly in the context of widely used method of lead immobilization with the use of phosphate fertilizers. In the soil, where lead minerals (eg, cerussite), ionic lead, chloride and carbonate compounds coexist, various lead compounds may crystallize. This is of great importance for the development of methods for the disposal of heavy metals. It is necessary to perform comprehensive studies on the thermodynamic stability of the lead phases observed in this study for the optimization of remediation methods.

Moreover, the presence of carbonate ions in the hydroxyl pyromorphite structure has been observed. It was also found that the substitution of carbonates in the pyromorphite $Pb_5(PO_4)_3Cl$ structure is absent or negligible. It is the novelty on the current knowledge on the possibilities of substitution of these ions in the structure of lead apatites and on their environmental role. Substitutions of carbonate ions usually decrease the stability (increase the solubility) of apatites. Therefore, it is very beneficial for the effectiveness of remediation procedures that such a process does not occur in the case of lead immobilization by means of transformation of soluble phases into a stable pyromorphite.

Key words: pyromorphite, cerussite, hydroxypyromorphite, immobilization, lead, dissolution-precipitation mechanism