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Effects of phosphate on the solubility of schultenite $PbHAsO_4$ and mimetite $Pb_5(AsO_4)_3Cl$

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Schultenite $PbHAsO_4$ and mimetite $Pb_5(AsO_4)_3Cl$ belong to the most common lead arsenates in the polluted soils and sediments. Synthetic schultenite has been used in the past as a component of pesticides, herbicides, and fungicides. Mimetite occurs in the soils contaminated with the smelting wastes. It also forms by transformation of schultenite in the presence of Cl^- ions. Both minerals are metastable and can release the As and Pb into aquatic system.

Bioavailability of lead in contaminated soils can be reduced to insignificant levels by precipitation of pyromorphite $Pb_5(PO_4)_3Cl$ induced by phosphate amendments to soils containing Pb. We have examined the effect of phosphate ions on the solubility of schultenite and mimetite. The dissolution of $PbHAsO_4$ and $Pb_5(AsO_4)_3Cl$ was conducted in the presence and in the absence of phosphates and chlorides. The amount of K_2HPO_4 and KCl used in the experiments was calculated based on stoichiometry of pyromorphite and the amount of Pb present in the form of schultenite or mimetite. The samples of the synthetic lead arsenates were reacted with aqueous phosphate at various pH (2-7) for up to 8 months.

In the experiments with schultenite at pH = 3.5 the concentration of As(V) reached 45 μM/L in the absence and 1081 μM/L in the presence of phosphates, opposite to the concentration of Pb(II) which was 47 and 5 μM/L, respectively. This indicates that immobilization of Pb is associated with the release of As(V) into the solution. The dissolution of $PbHAsO_4$ is rapid, the bulk of the reaction occurrs within the first few hours of the experiments. Rapid dissolution of schultenite in the presence of PO_4^{3-} results in formation of secondary phase: very small hexagonal crystals, often in aggregates. They loosely cover surface of schultenite, which can indicate their homogeneus crystallization. EDS analysis indicates the presence of Pb, P, As, and Cl. This suggests the formation of $Pb_5(PO_4)_x(AsO_4)_{3-x}Cl$ pyromorphite-mimetite solid solutions.

In the experiments with mimetite at pH = 3.5 the concentration of As(V) reached 29 μM/L in the absence of phosphates and 74 μM/L in their presence. The concentration of Pb(II) was 45 and 0.2 μM/L, respectively. The dissolution of mimetite is slower than schultenite, the bulk of the reaction occurrs within the first few days of the experiments, with dissolution rates declining with time. Equilibrium was attained after 30 days. The surface of mimetite dissolved in the presence of PO_4 and Cl is covered by small, 0.2 to 1.0 μm long crystals. The position on the surface indicates their heterogeneous crystallization. EDS analysis reveals the presence of Pb, As, and Cl with small amounts of P. This suggests the formation of pyromorphite-mimetite solid solution with mimetite as the dominant phase. The driving force for the reaction is a difference in log K_{SP} of these minerals, which is relatively small (-79.6 for pyromorphite and and -76.3 for mimetite).

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