Precursors in hydrothermal reaction of single cerussite $PbCO_3$ crystals with phosphates.

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In the presence of phosphate ions in solution, cerussite $PbCO_3$ crystals transform into lead apatite through dissolution/precipitation mechanism. This is analogous to calcite $CaCO_3$ conversion into hydroxylapatite $Ca_5(PO_4)_3OH$. Experiments are often run at higher temperature to speed up the process. This may, however, alter the mechanism of the reaction since formation of metastable $Pb_3(PO_4)_2$ is favored upon heating. In the autoclave experiments, fragments of cerussite crystal ca. 2 mm in size were placed into 2M $(NH_4)H_2PO_4$ solution (pH=7) in teflon bomb, then heated to 140 ºC for several days. Dissolution of cerussite and formation of $Pb_5(PO_4)_3OH$ (hydroxylpyromorphite, HPY) is expected in this setup. In the presence of 0.67M NH_4Cl, formation of $Pb_5(PO_4)_3Cl$ (pyromorphite, CPY) was observed. The experiments were repeated several times stopping the reaction at various stages. In the free-chlorine system, cerussite in contact with phosphate ions gets immediately covered by a thin crust of relatively coarse-crystal (~5μm in size) HPY. After heating in the autoclave, the layer of very fine crystalline $Pb_3(PO_4)_2$ develops underneath in the expense of cerussite. With time (ca. 5 days), this transforms into HPY. This sequence indicates formation of precursor phase in the transformation of cerussite into lead hydroxylapatite. In the Cl-rich system, a thin layer of relatively coarse-crystal CPY (up to 1 μm in size) also precipitates at ambient temperature and a layer of fine crystalline $Pb_3(PO_4)_2$ develops underneath at 140°C. To our surprise, within 1-2 days of heating this transforms into HPY regardless the presence of Cl in the system. Only later, HPY converts into CPY.

The results indicate that at neutral pH and hydrothermal conditions, transformation of cerussite into lead apatites goes throught precursor stage: formation of $Pb_3(PO_4)_2$. Therefore, high-temperature experiments do not simulate the environmental conditions. At current stage of knowledge it is assumed that the mechanisms of transformation of $Pb_3(PO_4)_2$ into HPY and HPY into CPY are similar to their analoques in calcium apatite systems. The role of carbonate ions as potential inhibitors of pyromorphite formation at hydrothermal conditions is under investigation.

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