Mechanisms of replacement reactions of single cerussite $PbCO_3$ crystals by pyromorphite, mimetite and vanadinite

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Formation of thermodynamically stable phases like pyromorphite $Pb_5(PO_4)_3Cl$, mimetite $Pb_5(AsO_4)_3Cl$ and vanadinite $Pb_5(VO_4)_3Cl$ are common in the environment. It is hypothesised here that lead carbonate $PbCO_3$, cerussite, can be readily replaced by polycrystalline lead apatites. This process is analogous to the calcium carbonate – calcium hydroxylapatite system, where such transformation is observed. However, the mechanisms of formation of pyromorphite, mimetite and vanadinite in the presence of cerussite are unknown.

The aim of this study was to experimentally determine the mechanism of the transformation of cerussite to pyromorphite, mimetite and vanadinite and the conditions under with these phases can form. The parameters of the experiments include pH (alkalic or acidic), the presence or absence of chloride ion, and temperature (140 or 5 °C). Experiments were carried out in order to produce partially reacted crystals to provide information about structural and textural relationships between parent and product phases. Cerussite crystals were put into 2M $(NH_4)H_2PO_4$, 2M $(NH_4)H_2VO_4$ or 2M $(NH_4)H_2AsO_4$ to form pyromorphite, vanadinite and mimetite, respectively.

X-Ray powder diffraction was used to identify and characterize the reaction products. Microstructural relationship between parent and product phases were determined by scanning electron microscopy (SEM-EDS) and electron microprobe analysis.

In every case single cerussite crystal were replaced by pollycrystaline pyromorphite, mimetite and vanadinite through dissolution of $PbCO_3$ followed by precipitation of lead apatite. In acidic conditions formation of shultenite $PbHAsO_4$ or phospho-shultenite $PbHPO_4$ were also observed. Products of the reaction in every case are porous, allowing fluid transport to the reaction interface. At all temperatures the product phase and its morphology are the same. Interface coupled dissolution-precipitation mechanisms are confirmed by the textural relationships.

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Vertical lithofacies changes of the Jeonchong tuff cone in the Miocene Eoil Basin, SE Korea: Implication of a series of eruptive and depositional processes

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The Miocene Eoil Basin, SE Korea, contains abundant volcanic and volcaniclastic deposits because of active volcanism during basin formation. The Jeonchon tuff cone refers to an about 25 m-thick sequence of basaltic lapilli tuff in the central part of the basin. The tuff cone is underlain by pahoehoe lavas (the Lower Eoil Basalt), lacustrine mudstone, and mouth-bar sandstone in ascending order, indicating hydrovolcanic eruption in a shallow lake. It is composed of seven sedimentary facies: massive tuff breccia (TBm), crudely stratified lapilli tuff (LTb), inverse-to-normally graded lapilli tuff (LTin), normally graded lapilli tuff (LTn), massive coarse tuff ($_C$Tm) and massive medium to fine tuff ($_M$Tm & $_F$Tm). It can be divided into five depositional units (unit I to V in ascending order) based on facies characteristics and componentry. Unit I, about 4 m thick, consists of quartz-bearing massive tuffs ($_M$Tm & $_F$Tm), suggesting contact-surface steam explosivity within mouth-bar sand. Unit II, about 1.5 m thick, consists of graded lapilli tuffs (LTin & LTn) with abundant accidental basalt clasts, suggesting bulk-interaction steam explosivity within the Lower Eoil Basalt and deposition from pyroclastic surges and ballistic fallouts of basalt clasts. Unit III consists of tuff breccia (TBm; about 3.5 m thick) and overlying stratified lapilli tuff (LTb; about 0.5 m thick), which are interpreted to have resulted from debris flows and Surtseyan fallouts associated with vent-widening explosions. Unit IV, 0.8 m-thick and composed of massive coarse tuff ($_C$Tm), suggests remobilization of pyroclasts by debris flows during volcanic quiescence. Crudely stratified lapilli tuff (LTb) of Unit V, about 15 m thick, is interpreted to have formed by sustained Surtseyan finger jets without further excavation of the substrate. The vertical lithofacies changes suggest that the Jeonchon tuff cone experienced a series of eruptive and depositional processes during growth because of the changes in depositional environments, types of the substrate (sand vs. lava), and vent geometry.

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