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# Extent of Fluorapatite Precipitation in Systems Co-Equilibrated with Calcite and Fluorite

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The presence of excessive levels of fluoride (F) in the groundwaters of India and other countries poses a serious threat to human health as groundwater is heavily relied upon for consumption. The source of F in these aquifers is typically considered to be geogenic where F-bearing minerals like fluorite ($CaF_{2(s)}$) contained in the sediments are in dynamic equilibrium with carbonate-bearing minerals like calcite ($CaCO_3$) Among the several methods to remove F from groundwater, precipitation of F as fluorapatite ($Ca_5(PO_4)_3F_{(s)}$), a highly insoluble and thermodynamically stable mineral, by critical calcium (Ca) and phosphate ($PO_4$) amendments has gained recent attention. Previous studies have demonstrated that in the presence of calcite and $PO_4$, F can be precipitated as $Ca_5(PO_4)_3F_{(s)}$ but the role of $CaF_{2(s)}$ which is also present in such systems has not been investigated. The goal of this study was to evaluate the effectiveness of calcite as a source of Ca when $PO_4$ was added externally to precipitate $Ca_5(PO_4)_3F_{(s)}$ in the presence of $CaF_{2(s)}$. Initially, batch experiments were performed to co-equilibrate $CaF_{2(s)}$ and calcite in 8 mg $L^{-1}$ of F-containing water prepared in ultrapure water in the absence of $PO_4$. Samples were regularly collected and analyzed for pH and F measurements till the system achieved equilibrium with respect to F. Experiments were setup in triplicate and for homogenous mixing orbital shaker was used. Additionally, batch experiments were carried out by adding $PO_4$ in the form of $NaH_2PO_4$. To check the removal efficiencies, varied concentrations of $PO_4$ were taken as 0-100 mM. Filtered samples were acidified for ICP-MS analysis to measure Ca and P concentrations. At the end of the experiments, the solids were collected after centrifugation and freeze-drying, and characterized using XRD, SEM-EDS and FTIR. Results indicated the formation of $Ca_5(PO_4)_3F_{(s)}$ as the primary mechanism for F removal and an optimal $PO_4$ concentration to achieve such removal was identified. The inferences from this study will likely help in devising methods for in situ treatment of F-polluted water and may offer a prompt solution to groundwater affected by endemic geogenic pollution for decades.