Rates of hydroxyapatite formation and dissolution in a sandstone aquifer: Implications for dynamic phosphate behaviour within an agricultural catchment

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Phosphorus concentrations within water bodies have strict targets under the European Union Water Framework Directive. The headwaters of the Hampshire Avon in southern England, in the Vale of Pewsey is an agricultural catchment underlain by Upper Greensand (UGS), and flanked by Upper and Lower Chalk. P concentrations in the river are high, and work is underway to investigate the geological versus agricultural origins of this material. It is hypothesised that due to the agricultural nature of the catchment and the release of $CaCO_3$-rich waters to the UGS from weathering and dissolution of surrounding Chalk, that hydroxyapatite, $Ca_5(PO_4)_3(OH)$, would precipitate into the pore space of the UGS. Under different chemical conditions, hydroxyapatite would likely dissolve, representing an anthropogenic P flux to headwaters, which may be an important source of anthropogenic P to the catchment.

To investigate hydroxyapatite precipitation and dissolution kinetics, we conducted batch experiments to precipitate the mineral onto sand grains, which was then dissolved in a continuous-flow reactor under various conditions. We also modelled the reactive transport of P along a 1D flow path to simulate hydroxyapatite precipitation and dissolution.

Hydroxyapatite rapidly precipitated onto sand grains from an alkaline solution that had high concentrations of Ca and P, thus representing a secondary anthropogenic P mineral if the P is sourced from fertiliser. The dissolution rate of the sand-bound mineral is strongly pH dependent, likely representing the acidic dissolution mechanism of hydroxyapatite. However, within the UGS, pore waters are often close to equilibrium, which results in the dissolution rate having a stronger dependence on the P concentration than on pH. Reactive transport models demonstrate that P behaviour is dynamic, as hydroxyapatite is able to both precipitate and dissolve along a 1D flow path, thus representing an anthropogenic flux of P.