

## Oxygen isotopes in phosphate as a tracer for sources and pathways of catchment P in stream water

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We present oxygen isotope measurements on dissolved inorganic phosphate (DIP) from stream water and rural sewage to trace and quantify the contribution of different sources of P to the total P discharge from catchments with different landuse in South Sweden. Recent studies by Elsbury *et al.* [1] proved that  $\delta^{18}\text{O}_\text{P}$  values can be an efficient tool to study sources and transport pathways for dissolved phosphate.

Sampling, sample handling, and isotope measurements were done similar to the procedures described by McLaughlin *et al.* [2], but adapted to the specific chemistry of the different water types. Due to significant concentrations of DOC in the water samples, they were shaken with activated carbon powder prior to filtering in order to remove organic matter (modified after Gruau *et al.* 2005 [3]).

Preliminary results showed, that the household sewage could be clearly distinguished from the stream waters by the  $\delta^{18}\text{O}_\text{P}$  values of DIP. Depending on the catchment, the  $\delta^{18}\text{O}_\text{P}$  of freshwater varied from +7 to +10 ‰, whereas sewage samples showed significantly higher  $\delta^{18}\text{O}_\text{P}$  values of +12 to +14 ‰, all values reported relative to VSMOW.

Phosphate in fresh water with low DIP concentrations is expected to be in equilibrium with ambient water ( $\delta^{18}\text{O}_\text{w} = -16$  to  $-12$ ‰), whereas wastewater contains high concentrations of DIP, is not in equilibrium, and thus reflects the isotope signature of the source. More isotope measurements, particularly on wastewater, fresh water from different catchment areas, and soluble phosphate in soils/sediments will be used when modelling the dynamics of phosphorus losses from the studied catchment areas.

[1] Elsbury *et al.* (2009) *Environ. Sci. Technol.* **43**, 3108–3114. [2] McLaughlin *et al.* (2004) *Limnol. Oceanogr. Methods* **2**, 204–212. [3] Gruau *et al.* (2005) *Water Research*, **39**, 232–238.

## Investigation of Ca-Pb-P-As solid solutions in apatite

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Alternative to often impractical, expensive, and short term remediation techniques, *in situ* heavy metal stabilization has been investigated for about three decades as a potential method of environmental remediation. Precipitation of apatite group minerals,  $^{\text{IX}}\text{M}_1^{\text{VI}}\text{M}_2^{\text{III}}(\text{VO}_4)_3\text{X}$ , has been shown to be an effective means for incorporation of a number of heavy metals and radionuclides, e.g. Pb, Cd, Cu, Ni, Sr (90), Y (90), U, because of their ability to incorporate numerous elements and their low solubilities. Additionally, apatite crystallization has the potential to immobilize polyanions such as  $\text{AsO}_4$  and  $\text{VO}_4$ .

In this study the extent of possible solid solutions of apatites in Ca-Pb-P-As-OH-Cl system at 25 and 80°C, and ambient pressure has been investigated. The syntheses were conducted by rapid mixing or dropwise addition of aqueous solutions at constant or varying pH. The results show that under the conditions studied solid solutions among potential endmember compositions in this system did not form and reactions yield precipitation of pyromorphite  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ , hydroxylpyromorphite  $\text{Pb}_5(\text{PO}_4)_3\text{OH}$ , hydroxylapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ , mimetite  $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ , hydroxylmimetite  $\text{Pb}_5(\text{AsO}_4)_3\text{OH}$  and johnbaumite  $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$  end members, with some additional phases, e.g. schultenite  $\text{PbHAsO}_4$ ,  $\text{PbHPO}_4$ ,  $\text{CaHAsO}_4 \cdot x\text{H}_2\text{O}$ . Johnbaumite precipitates only at elevated temperatures and guerinite  $\text{Ca}_5(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2 \cdot 9(\text{H}_2\text{O})$  is the main Ca-arsenate forming at low temperatures. Low temperature formation of hydroxylapatite is preceded by precipitation of brushite  $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ , which with time or upon heating recrystallizes to hydroxylapatite. Brushite was the only apatite group precursor phase found in the investigated system.