Geophysical Research Abstracts
Vol. 16, EGU2014-7620, 2014
EGU General Assembly 2014

Could organic phosphorus compounds contaminate the analysis of phosphate oxygen isotopes in freshwater matrices?

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Variation in the stable isotope composition of oxygen within dissolved phosphate ($\delta^{18}O_p$) represents a novel and potentially powerful environmental tracer, providing insights into the sources of phosphorus and the extent to which phosphorus from different sources is metabolised. The analysis of $\delta^{18}O_p$within freshwater matrices requires isolation of the phosphate ion from possible sources of contaminant oxygen within the bulk matrix, prior to pyrolysis (usually of a silver phosphate precipitate) and analysis of the oxygen isotope composition. The majority of published research uses co-precipitation of phosphate with brucite ($Mg(OH)_2$) as an initial step in the isolation of the phosphate ion. However, freshwater matrices also contain a wide range of organic phosphorus compounds, including adenosine 5'-triphosphate (ATP) and phosphonates such as 2-aminoethylphosphonic acid. In this paper, we initially examine the potential for co-precipitation of organic phosphorus compounds with brucite. Our data indicate that ATP, sodium pyrophosphate and inositol hexakisphosphate are almost entirely removed from solution through co-precipitation with brucite, whilst glucose-6-phosphate and 2-aminoethylphosphonic acid are less readily co-precipitated. Subsequently, we assessed the potential for acid-hydrolysis of organic phosphorus compounds during re-dissolution of the brucite precipitate, using a range of acid systems. Our data indicate that up to 17% of ATP and up to 5% of sodium pyrophosphate can be hydrolysed by concentrated acetic acid, yielding fresh phosphate ions in solution. Our findings have potentially significant implications for analysis of $\delta^{18}O_p$because the fresh phosphate ions produced following acid hydrolysis will be subjected to inheritance and kinetic isotope fractionations, likely altering the bulk $\delta^{18}O_p$ within a freshwater sample.