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Triple oxygen isotope systematics of phosphates

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Oxygen isotope analyses of phosphate are widely used to investigate paleoenvironmental conditions (most prominently paleo-temperatures from conodonts or fish teeth), as well as biogeochemical processes and phosphorous cycling both in terrestrial and aquatic systems. Beyond conventional $\delta^{18}O_{PO4}$, triple oxygen isotope ($\Delta'^{17}O_{PO4}$) analyses now open up new areas of research e.g. including the reconstruction of ancient air O_2, which can be used to estimate paleo-pCO_2 and paleo gross primary productivity [1]. These applications heavily rely on model parameters such as the equilibrium triple oxygen isotope curve for the phosphate-water system and on accurate normalization to the VSMOW-SLAP scale.

We have conducted enzymatic assay experiments with pyrophosphatase at variable temperatures to attain an empirical equilibrium curve. The respective Ag_3PO_4 is analyzed using two independent methods. One is based on the combination of i) high temperature combustion in a TC/EA, ii) conversion of CO to CO_2 using high-voltage glow discharge and iii) triple oxygen isotope analysis via the *Aerodyne Research Inc.* TILDAS CO_2spectrometer [2,3]. This so called "TORCH" method has been validated for sulfates, organics and water, allowing for direct calibration to VSMOW-SLAP scale using the same analytical approach [3]. The second method is based on the laser fluorination approach commonly used for silicates and a range of other materials, including bioapatite [4]. Highly reproducible data is achieved by i) conversion of Ag_3PO_4 to $Ba_3(PO_4)_2$, followed by ii) laser fluorination using an air-lock sample introduction system that prevents cross-contamination. Normalization to VSMOW-SLAP scale is achieved indirectly via silicate standards. Results from both techniques will be discussed in comparison to recent literature data, presenting phosphate standard data [5,6,7] and pyrophosphatase experiments [8].

The final equilibrium curve is subsequently used for interpreting $\Delta'^{17}O_{PO4}$ Conodont element data also reported in this conference (Bagherpour et al. 2026_session 13e).

[1] Feng et al. (2025), *PNAS*; [2] Bajnai et al. (2023), *G3*; [3] Zahnow et al. (2026) *Anal. Chem.*, [4] Feng et al. (2022), *GCA* ; [5] Ellis and Passey (2023), *Chem. Geol.*; [6] Ellis et al. (2025), *Anal. Chem* [7] Wostbrock et al. (2026) *Rapid Comm.*; [8] Sambuichi et al. (2025), *Prog. Earth Planet. Sci.*