

## An experimental investigation of U(IV) aqueous complexation with citric acid, NTA and EDTA

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Within anoxic near surface aqueous settings where  $\text{UO}_{2(\text{cr})}$  may be released an opportunity to encounter and complex with organic acids may occur. Reactions between  $\text{UO}_{2(\text{cr})}$  and ligands may promote the solubility and mobility of uranium. Published results describing complexation of U(IV) and organic ligands are extremely limited and inconsistent [1]. This study aims to identify the U(IV)-ligand species formed during complexation reactions and to derive  $K_{\text{sp}}$  values from the reactions. Organic ligands investigated in this study include citric acid, nitrilotriacetic acid (NTA) and ethylene diamine tetraacetic acid (EDTA). Solubility studies were conducted at 25°C inside a Coy<sup>®</sup> type B glove box anaerobic chamber containing a mixed 95% $\text{N}_2$ /5% $\text{H}_2$  atmosphere. Batch solubility experiments, approached from undersaturation, were completed for pH 5 to 10 with acid concentrations ranging from 1nM to 100mM in 0.01 M NaCl.  $\text{Eu(II)Cl}_2$  was added to suppress oxidation of U(IV) to U(VI). Analysis of the solubility data revealed that exposure to citric, NTA and EDTA had little effect on  $\text{UO}_{2(\text{cr})}$  solubility. Solubility varied within an order of magnitude when compared to hydrolysis of the  $\text{UO}_{2(\text{cr})}$  mineral used in this study. The log activity of the  $\text{UO}_{2(\text{cr})}$  hydrolysis yielded a value of -5.43. Under all measured conditions of organic ligand concentration, the data consistently show an increase in uranium concentration to a median log U activity of -4.69. The observed solubility of  $\text{UO}_{2(\text{cr})}$  in the presence of chelating organic ligands is inconsistent with expected values based on literature data, possibly due to inefficient controls on oxidation [2]. Further research, with solubility approached from the oversaturation direction will likely be required to fully minimize  $\text{O}_2$  potentials. Although the solubilities values are higher than expected, these experiments suggest that strong chelating agents will have little effect on  $\text{UO}_{2(\text{cr})}$  solubility.

[1] Rai *et al.* (1990) *Inorganic Chemistry* **29**, 260-264.

[2] Lasaga (1995) *Reviews in Mineralogy* **31**, 23-81.

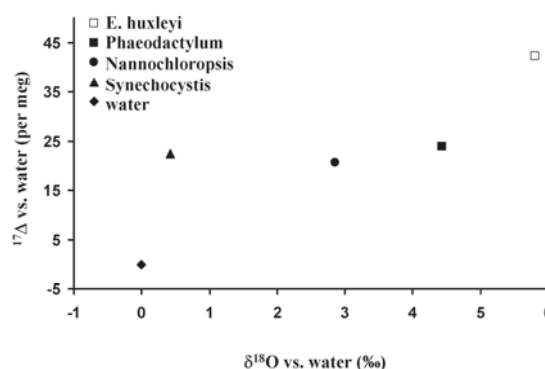
## The effect of marine photosynthesis on $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ of atmospheric $\text{O}_2$

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Atmospheric  $\text{O}_2$  is enriched in  $^{18}\text{O}$  with respect to ocean water. The magnitude of this enrichment (Dole effect) is 23.9‰ [1]. Currently, the enrichment is attributed to isotope effects of respiration and evapotranspiration. It is assumed that marine phytoplankton produces photosynthetic  $\text{O}_2$  of similar composition to seawater and thus does not contribute to the Dole effect. Here we show (see figure) that this assumption is wrong and that with exception of cyanobacterium (*Synechocystis* [2]) different types of marine phytoplankton produce  $\text{O}_2$  enriched in  $^{18}\text{O}$  by up to several ‰ with respect to the substrate water. As well, the  $^{17}\text{O}$  anomaly of this  $\text{O}_2$  is 20 to 40 per meg greater than in the substrate water.



Our new observation of  $^{18}\text{O}$  enrichment by marine photosynthesis shows that the oceanic contribution to the Dole effect is much larger than previously assumed. This will help closing an important gap between the observed Dole effect and its modeled magnitude.

[1] Barkan & Luz (2005) *RCM* **19**, 3737-3742. [2] Helman *et al.* (2005) *Plant Physiol.* **138**, 2292-2298.