

## $^{18}\text{O}^{18}\text{O}$ and $^{17}\text{O}^{18}\text{O}$ in the atmosphere

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The isotopic composition of atmospheric  $\text{O}_2$  reflects the balance between photosynthesis, respiration, and the hydrologic cycle over millennial timescales. The Quaternary oxygen-isotope budget in atmospheric  $\text{O}_2$ , however, is under-constrained, and measurements of the  $^{18}\text{O}^{18}\text{O}$  and  $^{17}\text{O}^{18}\text{O}$  content in the atmosphere will provide additional information.

For instance, the tendency for  $^{18}\text{O}^{18}\text{O}$  and  $^{17}\text{O}^{18}\text{O}$  bonds to form upon photosynthesis is expected to be insensitive to the isotopic composition of the source water, as C-O bond ordering in carbonates has been shown to be independent of the isotopic composition of carbonate source water [1]; water has no O-O bonds to pass on, so photosynthetic  $\text{O}_2$  cannot inherit a bond-ordering signature from its source water.

Oxygen consumption via respiration, in contrast, is expected to alter the bond ordering in  $\text{O}_2$ . Microbial respiration and photorespiration fractionate oxygen isotopologues in a manner similar to Knudsen diffusion, leaving the residue between +14-30‰ and +7-15‰ enriched in  $\delta^{18}\text{O}$  and  $\delta^{17}\text{O}$ , respectively [2,3] resulting in the well-known atmospheric Dole effect. If the mass dependence of respiration mimics that of diffusion, then  $^{18}\text{O}^{18}\text{O}$  and  $^{17}\text{O}^{18}\text{O}$  in the fractionated residue should be depleted relative to the stochastic distribution [1]. Thus, the Dole effect may manifest itself as a depletion in  $^{18}\text{O}^{18}\text{O}$  and  $^{17}\text{O}^{18}\text{O}$  relative to the stochastic distribution in atmospheric  $\text{O}_2$ .

We examined the exceedingly rare  $^{18}\text{O}^{18}\text{O}$  and  $^{17}\text{O}^{18}\text{O}$  isotopic variants of  $\text{O}_2$  in tropospheric air. We find that these species are enriched relative to the stochastic distribution of isotopes – opposite in sign from signatures predicted to be imposed by the biosphere. We demonstrate, with laboratory experiments, that bond ordering in atmospheric  $\text{O}_2$  is likely governed by autocatalytic  $\text{O}(^3P) + \text{O}_2$  isotope-exchange reactions that cycle through the atmospheric  $\text{O}_2$  reservoir on decadal timescales. Our analysis of the atmospheric budget suggests that trends in O-O bond ordering over geologic time may be sensitive to tropospheric  $\text{O}(^3P)$  concentrations, tropopause temperature, and stratosphere-troposphere exchange flux, offering constraints on the abundance of short-lived trace gases and the strength of circulation in the ancient atmosphere.

[1] Eiler, J. M. (2007) *Earth Planet. Sci. Lett.* **262**, 309-327.

[2] Guy, R. D. *et al.* (1989) *Planta* **177**, 483-491.

[3] Kiddon, J., *et al.* (1993) *Global Biogeochem. Cycles* **7**, 679-694.

## Characterizing the dissolved organic composition of water in the oilsands region via FT-ICR MS

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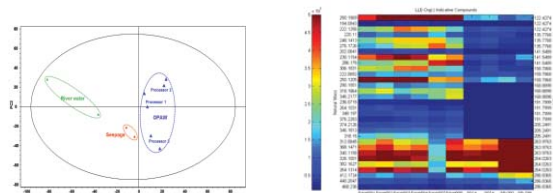
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### Introduction

Ultrahigh-resolution FT-ICR MS (Fourier Transform – Ion Cyclotron Resonance) is an emerging technique to characterize complex compositions of thousands of organic compounds dissolved in water and provide the potential to help identify impacts of oilsands development on aquatic environments. Here, we present a case study demonstrating the distinct compositional differences in the organic profiles of various water types collected in the region, which highlights the potential of FT-ICR MS in characterizing and profiling water for environmental monitoring and water resources management.

### Results and Discussion



**Figure 1: a) the score plot of PCA of FT-ICRMS results acquired in negative mode demonstrating distinctions and differences among various types of water. b) heatmap showing proposed key indicative compounds for each water type.**

The FT-ICR MS analyses after Liquid-Liquid Extraction of oil sands process affected waters (OPAW) and river water lead to the successful detection of up to 7,300 compounds in water samples. The organic-rich OPAW and seepage samples analyzed in this study showed a wide range of organic compositions. Distinct patterns of mass distribution and elemental composition can be linked to the type of water. Principle Component Analysis (PCA) showed clear separation trends and groupings among various water types (Figure 1a). Further statistical analysis via Partial Least Square Discrimination Analysis (PLS-DA) proposed a series of homologues indicative of each water type (Figure 1b). The distinctive organic profile of industrially processed water as compared to background organics suggests great potential in applying FT-ICR MS in water resources management and aquatic environmental monitoring.