

## A high-resolution paleoclimate reconstruction using C and N isotopes in a subarctic environment, northern Canada

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The Tibbitt-to-Contwoyto Winter Road (TCWR) is the sole overland route servicing diamond mines north of the city of Yellowknife, Northwest Territories (NWT), Canada. Because the majority of the TCWR traverses frozen lakes, late freezing or early thawing of these lakes can drastically shorten the transportation season, imparting significant economic consequences on mining operations. Such was the case in 2006, when a warm and stormy winter season associated with an El Niño Southern Oscillation (ENSO) event resulted in a significant and costly reduction of shipments to the mines. As the use of the TCWR is projected to increase in the coming years, planners and policy makers require a sound scientific understanding of past regional climate variability upon which to base their development strategies. Previous research has been valuable in gaining a broad understanding of regional long-term climate change; however, no research has provided a climate record with a resolution high enough to identify medium- to short-term climate phenomena that might be affecting this region (e.g. sub-decadal ENSO cycles and the decadal-scale Pacific Decadal Oscillation [PDO]).

This study is an integral component of a larger-scale study designed to develop a comprehensive database of high-resolution paleoclimate data for the NWT, using a variety of proxies. As part of the larger study, freeze cores were taken in 2010 from 10 lakes along the TCWR and sliced at 1-mm intervals using a custom-designed freeze core microtome. We report here the results of preliminary bulk <sup>13</sup>C and <sup>15</sup>N isotope analyses, taken at 1-cm intervals throughout the Danny's Lake and Horseshoe Lake cores. Higher-resolution analysis is underway for sections of the Danny's Lake core in order to identify short-term climate cycles. Additionally, C and N isotopic compositions are currently being analysed for surface sediment samples of over 90 lakes scattered along a latitudinal gradient throughout the NWT. These data will be used to create a paleoclimatic transfer function, which will correlate spatial variations in isotope values to climate parameters, and provide a means of using temporal variations in these isotopes down-core to quantitatively reconstruct past climate change.

Preliminary results from the Danny's Lake core show clear trends in isotopic compositions for both C and N isotopes and suggest distinct stages of lake evolution. Previous to 6700 BP, there are large long-term fluctuations in isotope values, which may be related to significant variations in vegetation or lake water levels. At 6700 BP, a sudden change in trends, as well as a sharp colour change in the sediment, suggest a significant and abrupt shift in lake dynamics, the source of which is currently under investigation. A positive correlation between the C/N ratio, %C, and %N from 6700-4000 BP suggests an increase in terrestrial organic matter input to the lake. This increase stops at 4000 BP and is stable to the present. Comparison of these preliminary results to the paleoclimatic transfer function will provide greater insight into the causes of these trends.

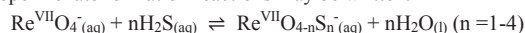
## Influence of mineral surfaces on Re speciation in sulfidic porewaters

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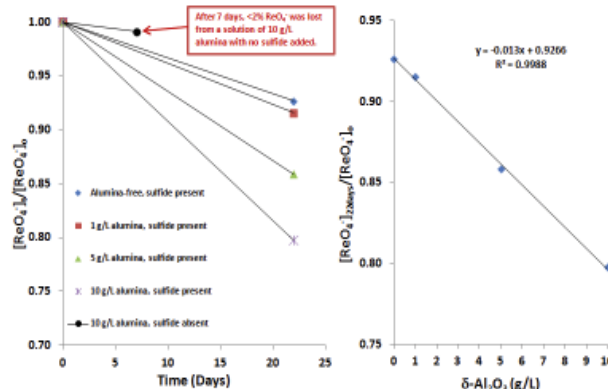
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### Introduction

The thioperrhenate anions may be important species in the chemical pathway to Re deposition within sulfidic waters. Thioperrhenate formation reactions may be written:



Because of their immense areas and hydrated properties, oxide surfaces are known to influence various environmentally relevant reactions within porewaters of soils and sediments [1,2]. Mineral catalysts have been shown to greatly enhance the rate of thiomolybdate reactions [1]. To test the conjecture that thioperrhenate reactions are also catalyzed by oxide surfaces, solutions were prepared to contain 0 to 10 g/L  $\delta\text{-Al}_2\text{O}_3$ , 10  $\mu\text{M}$   $\text{ReO}_4^-$  and 10 mM  $\Sigma\text{S}^{2-}$  at pH = 7.0.  $\text{ReO}_4^-$  remaining in the filtered solutions after 0.2 and 22 days was quantified using ion chromatography (IC) with suppressed conductivity detection.



**Figure 1:** Left: loss of  $\text{ReO}_4^-$  from test solutions over time. Right: loss of  $\text{ReO}_4^-$  after 22 days as a function of  $\delta\text{-Al}_2\text{O}_3$  mass loading.

### Conclusion

The left panel of the figure shows an increasing rate of  $\text{ReO}_4^-$  loss as the mass loading of  $\delta\text{-Al}_2\text{O}_3$  increases. Closed circles indicate <2% of initial  $\text{ReO}_4^-$  is lost from analogous sulfide-free suspensions; observed losses in the sulfidic suspensions cannot be due to adsorption of  $\text{ReO}_4^-$ . The right panel shows the loss of  $\text{ReO}_4^-$  after 22 days exhibits linearity with increasing mass loading. These data demonstrate that  $\delta\text{-Al}_2\text{O}_3$  enhances the rate of a sulfidation reaction(s) involving  $\text{ReO}_4^-$ . Further inquiry is required for definitive identification of reaction product(s). These results may help to explain observations that Re removal only occurs below the sediment-water interface in temporally anoxic basins, even when the overlying water column is also sulfidic [3].

[1] Vorlcek & Helz (2002) *Geochim. Cosmochim. Acta* **66**, 3679-3692.

[2] Lan, Deng, Kim & Thornton (2007) *Geochem. Trans.* **8**:4 doi: 10.1186/1467-4866-8-4.

[3] Chappaz, Gobeil & Tessier (2008) *Geochim. Cosmochim. Acta* **72**, 6027-6036.