

# Geochemistry and Stable Isotope Composition of Hogarth and Caland Pit Lakes, Steep Rock Iron Mine, Northwestern Ontario, Canada

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## Abstract

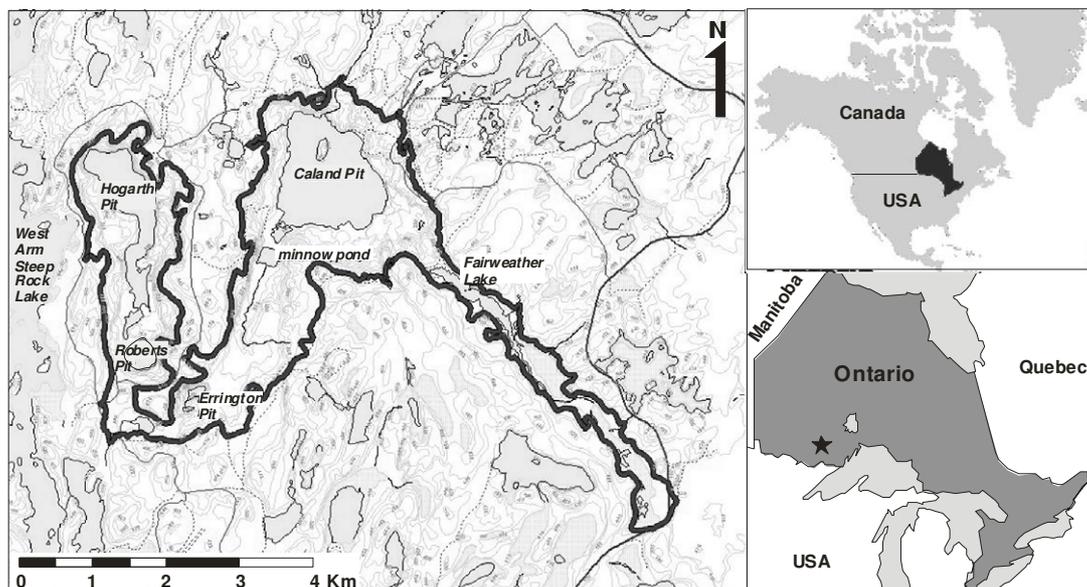
Caland and Hogarth pit lakes were formed after the closure and subsequent flooding of the Steep Rock iron mines, Ontario, Canada. The oxygen and deuterium isotopic composition of the pit waters define a linear trend consistent with non-equilibrium evaporation. The sulfur isotope composition of dissolved sulfate is similar for the two pit lakes and indicates derivation from pyritic lenses within the ore zone. The  $\delta^{18}\text{O}$  for dissolved sulfate indicates different mechanisms for pyrite oxidation. For Hogarth, sulfate is produced by anaerobic oxidation of pyrite by ground water; whereas Caland sulfate is produced by aerobic oxidation of pyrite by ground water. The carbon isotopic composition of DIC from Hogarth is similar to that isotopic composition of the carbonate wall rocks; whereas, DIC in Caland pit water is isotopically depleted due to exchange with DOC generated by fish farming activities.

**Key words:** sulfur isotopes, oxygen isotopes, deuterium isotopes, carbon isotopes, DIC-DOC, pit lakes, pyrite oxidation, evaporation

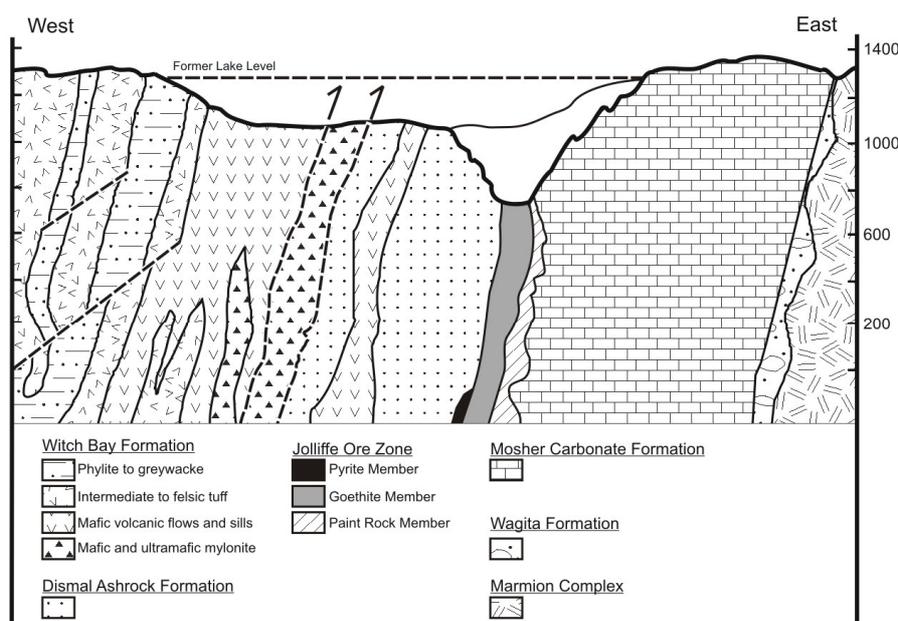
## Introduction

Flooding since 1979 of two open pits of the decommissioned Steep Rock iron mines near Atikokan, Ontario, has led to the formation of Hogarth and Caland pit lakes (Fig. 1). Although the geology of the two pits is similar (Fig. 2), there are distinct differences in terms of the water chemistry and quality between the two pit lakes. Hogarth is non-stratified, oxygenated and highly enriched in dissolved sulfate (1200-2000 mg/L), resulting in chronic sulfate toxicity. On the other hand, Caland, which until recently hosted a commercial fish farm, is non-toxic and has an upper oxygenated fresh water lens that overlies an anoxic and moderately saline (200-500 mg/L sulfate) water column. The objectives of this study are to use stable isotopes in order to: 1) to determine the source and reaction mechanisms responsible for the generation of the elevated sulfate contents; 2) nature of pH-buffering wall rock interactions; and, 3) compare the isotopic composition of pit lake waters to regional meteoric waters.

**Figure 1** Map showing location of Hogarth and Caland pit lakes. Black outline represents original lake level (prior to draining for mining), with 2001 pit water levels shown.



**Figure 2** Geological cross-section of Errington Pit (see Fig. 1; after Kusky and Hudleston, 1999)



## Methods

Samples of the pit lake waters were collected in March (during ice cover), August and November (prior to ice cover) 2006 for geochemical and stable isotopic analysis. The samples include depth profiles for the two lakes, local ground water and an adjacent lake (West Arm; Fig.1). In addition, pit wall rocks and surface waste dumps/tailings were also collected.

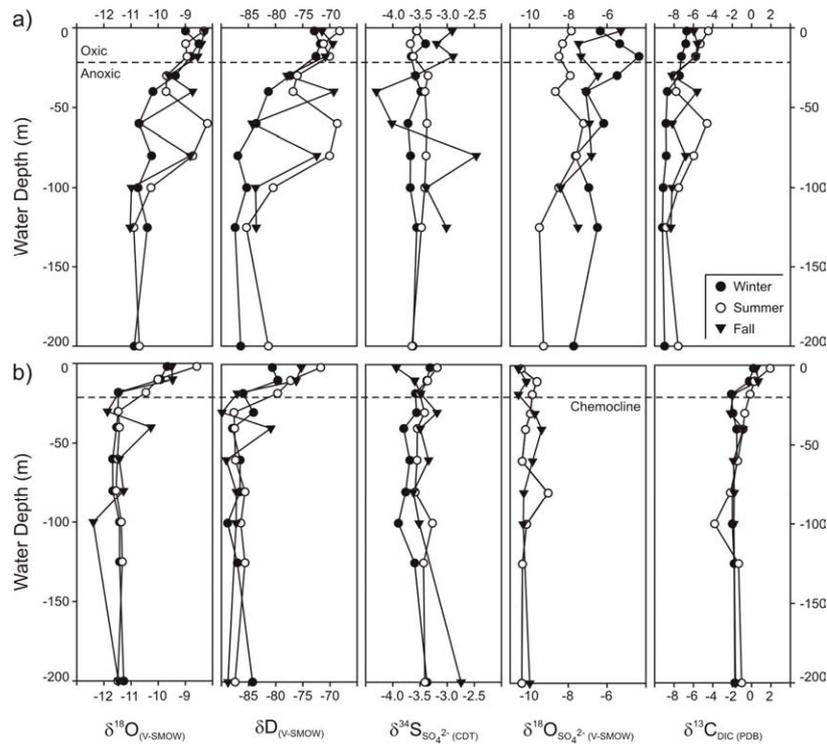
The chemical composition of the various waters was determined accordingly: 1) trace metal concentrations were measured on acidified samples using a Varian Vista Pro ICP-AES; 2) the concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  were determined by a DIONEX DX-120 dual channel chromatograph; and, 3) DOC concentrations were determined using a Skalar SAN-SYSTEM Autoanalyzer. All chemical analyses were performed at Lakehead University.

Stable isotopes analyses were performed at the University of Calgary Isotope Science Laboratory. Oxygen isotope analyses of water samples were performed using the  $\text{CO}_2\text{-H}_2\text{O}$  equilibration technique of Epstein and Mayeda (1953). Hydrogen isotope analyses of water were determined by chromium reduction (Nelson and Dettman, 2001). The  $\delta^{34}\text{S}$  ratio of dissolved sulfate (precipitated as  $\text{BaSO}_4$ ) and pure sulfide minerals and  $\delta^{13}\text{C}$  of carbonate wall rocks was determined using a Carlo Erba NA 1500 elemental analyzer interfaced to a continuous flow-isotope ratio mass spectrometry (CF-EA-IRMS). For the determination of bulk rock  $\delta^{34}\text{S}$  ratios, sulfur was extracted using THODE reagent (Thode et al., 1961) prior to CF-EA-IRMS analysis. The  $\delta^{18}\text{O}$  composition of dissolved sulfate (precipitated as  $\text{BaSO}_4$ ) was determined using a Finnigan MAT TC/EA interfaced to a CF-IRMS.  $\delta^{13}\text{C}_{\text{DIC}}$  of water was prepared by phosphoric acid digestion (McCrea, 1950) prior to IRMS analysis. All isotopic compositions are expressed in per mil notation relative to international standards ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ : V-SMOW;  $\delta^{34}\text{S}$ : CDT;  $\delta^{13}\text{C}_{\text{DIC}}$ : PDB). Analytical uncertainties are  $\pm 0.2\text{‰}$  for  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^{13}\text{C}_{\text{DIC}}$ ,  $\pm 2\text{‰}$  for  $\delta\text{D}$ ,  $\pm 0.7\text{‰}$  for  $\delta^{34}\text{S}$  and  $\pm 0.5\text{‰}$  for  $\delta^{18}\text{O}_{\text{sulfate}}$ .

## Results and Discussion

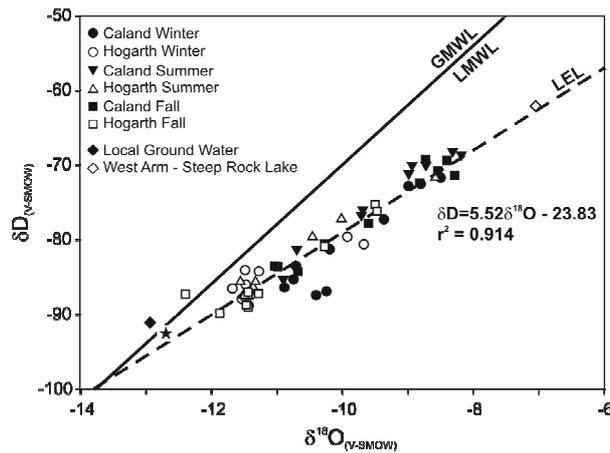
The stable isotope composition of pit waters with respect to water depth and season are provided in Figure 3. There are generally no systematic variations with season or with depth. The exception is  $\delta^{18}\text{O}$  and  $\delta\text{D}$  which shows a rapid depletion within the epilimnion of each, with more uniform values characterizing the hypolimnion. Specific differences between the two lakes include: 1) Caland pit water is slightly enriched and displays a wider range in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  relative to Hogarth; 2)  $\delta^{34}\text{S}_{\text{sulfate}}$  is similar for the two lakes, but Caland has slightly elevated and more variable  $\delta^{18}\text{O}_{\text{sulfate}}$  compositions; and, 3) Caland is depleted in  $\delta^{13}\text{C}_{\text{DIC}}$  in comparison to Hogarth. Caland and Hogarth waters plot along a linear trend to the right of the GMWL between values for Atikokan ground water/precipitation and the West Arm (Fig. 4).

**Figure 3** Seasonal depth profiles for the isotopic composition of a) Caland and b) Hogarth pit lakes.



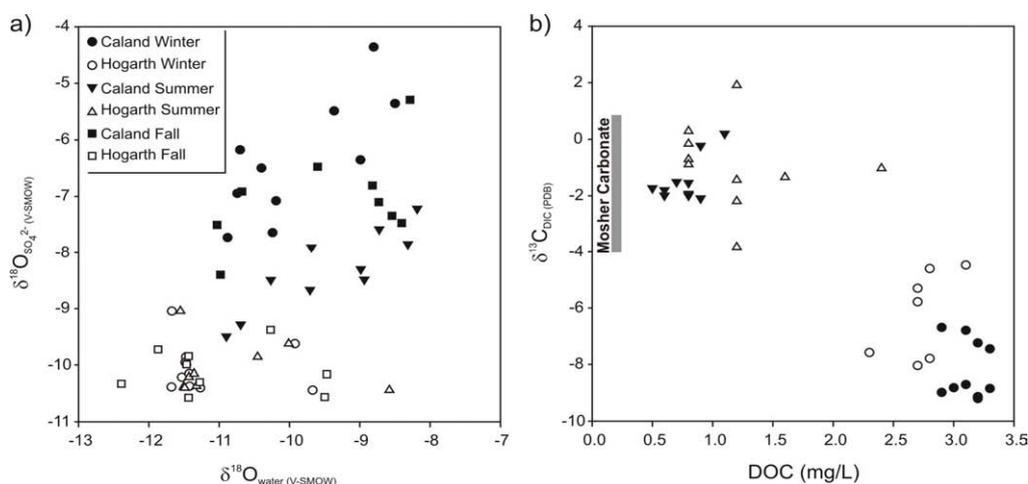
The trend in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  indicates that the waters in the pits have undergone minor to moderate amounts of evaporation (*c.f.* Gammons et al., 2005; Pellicori et al., 2005), which reflects that neither lake has any surface outflow even though water depths now exceed 200 m.

**Figure 4** The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  composition of Hogarth and Caland pit waters. The star corresponds to the amount-weighted mean annual values (1976-1980) for Atikokan precipitation and the LMWL is the local meteoric water line (Birks et al., 2003), which parallels the global meteoric water line (GMWL). LEL is the local evaporation line (this study).



The isotopic composition of sulfate is depleted relative to pyrite from the submerged ore zone and surface waste rocks ( $\delta^{34}\text{S} = -1.5$  to  $10\text{‰}$ ) and other pit wall rocks ( $\delta^{34}\text{S} = -1.6$  to  $4.9\text{‰}$ ), and is consistent with oxidation of ore zone pyrite, with subsequent fractionation due to precipitation of saturated sulfate minerals from the water column. The oxygen isotopic composition of dissolved sulfate indicates differences in the nature of sulfide oxidation between the two pit lakes (Fig. 5a). Hogarth sulfate is produced by anaerobic oxidation of pyrite, whereas the oxygen isotope composition of Caland sulfate is consistent with aerobic oxidation of pyrite (*c.f.* Pellicori et al., 2005).

**Figure 5** a) The  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$  isotopic composition of dissolved sulfate, and b)  $\delta^{13}\text{C}_{\text{DIC}}$  and DOC composition of Hogarth and Caland pit lakes.



The near neutral pH (6.4 to 8.5) of both pit lakes is the result of interactions with carbonate wall rocks. The carbon isotopic composition of DIC from Hogarth is similar to that isotopic composition of the carbonate wall rocks ( $\delta^{13}\text{C} = -4.0$  to  $0.6\text{‰}$ ; Fig. 5b). However, DIC in Caland pit water is more depleted and suggests either isotopic exchange with isotopically depleted DOC generated by fish farming activities or atmosphere exchange.

### Conclusions

1.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the pit waters plot along an evaporative trend that deviates from the local meteoric water line.
2. Sulfur isotopes indicate that dissolved sulfate for both lakes is derived from pyritic lenses within the submerged ore zone.
3. Dissolved sulfate in Hogarth is derived by anaerobic oxidation of pyrite, whereas the sulfate in Caland is derived by aerobic oxidation of pyrite.
4.  $\delta^{13}\text{C}_{\text{DIC}}$  compositions indicate that pit waters are pH-buffered due to interaction with carbonate wall rocks; however, depleted  $\delta^{13}\text{C}_{\text{DIC}}$  compositions of Caland reflect interaction with isotopically depleted DOC.

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