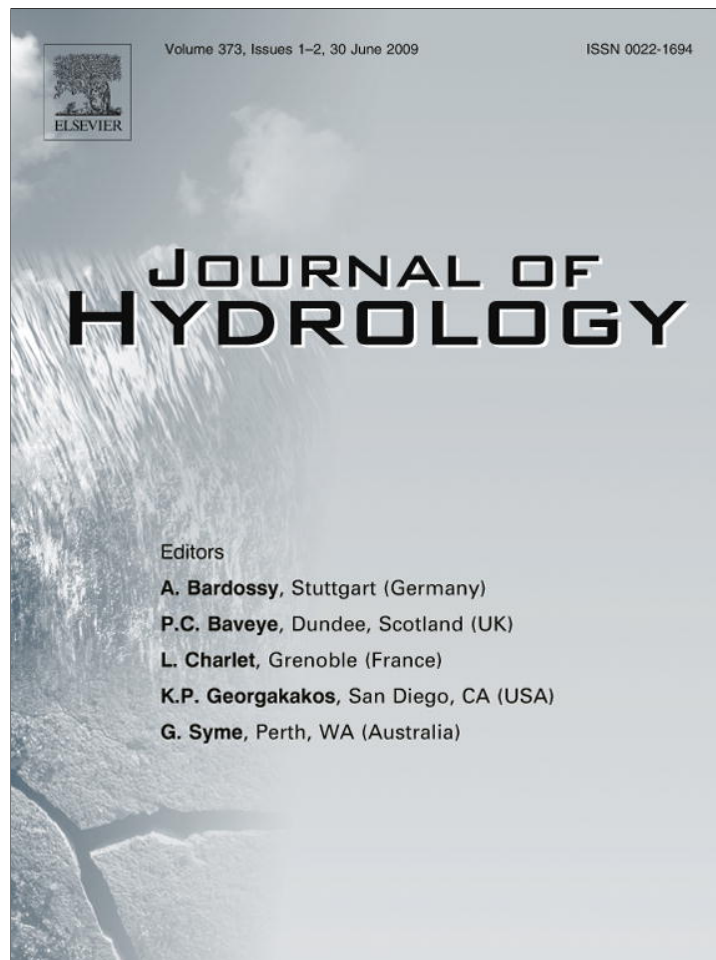


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Hydrogeochemistry of groundwaters in and below the base of thick permafrost at Lupin, Nunavut, Canada

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SUMMARY

Shield fluids are commonly understood to evolve through water–rock interaction. However, fluids may also concentrate during ice formation. Very little is currently known about groundwater conditions beneath thick permafrost in crystalline environments. This paper evaluates three possible Shield fluid evolution pathways at a crystalline Shield location currently under 500+ meters of permafrost, including surficial cryogenic concentration of seawater, in situ cryogenic concentration and water–rock interaction. A primary goal of this study was to further scientific understanding of permafrost and its role in influencing deep flow system evolution, fluid movement and chemical evolution of waters in crystalline rocks. Precipitation, surface, permafrost and subpermafrost water samples were collected, as well as dissolved and free gas samples, fracture fillings and matrix fluid samples to characterize the site. Investigations of groundwater conditions beneath thick permafrost provides valuable information which can be applied to safety assessment of deep, underground nuclear waste repositories, effects of long-term mining in permafrost areas and understanding analogues to potential life-bearing zones on Mars.

The study was conducted in the Lupin gold mine in Nunavut, Canada, located within the zone of continuous permafrost. Through-taliks beneath large lakes in the area provided potential hydraulic connections through the permafrost. Na–Cl and Na–Cl–SO₄ type permafrost waters were contaminated by mining activities, affecting the chloride and nitrate concentrations. High nitrate concentrations (423–2630 mg L⁻¹) were attributed to remnants of blasting. High sulfate concentrations in the permafrost (578–5000 mg L⁻¹) were attributed to naturally occurring and mining enhanced sulfide oxidation. Mine dewatering created an artificial hydraulic gradient, resulting in methane hydrate dissociation at depth. Less contaminated basal waters had medium sulfate concentrations and were Ca–Na dominated, similar to deeper subpermafrost waters. Subpermafrost waters had a wide range of salinities (2.6–40 g L⁻¹). It was unclear from this investigation what impact talik waters would have on deep groundwaters in undisturbed environments. In situ cryogenic concentration due to ice and methane hydrate formation may have concentrated the remaining fluids, however there was no evidence that infiltration of cryogenically concentrated seawater occurred since the last glacial maximum. Matrix waters were dilute and unable to affect groundwater salinity. Fracture infillings were scarce, but calcite fluid inclusion microthermometry indicated a large range in salinities, potentially an additional source of salinity to the system.

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Introduction

Research programs studying waters in crystalline rocks in the Canadian and Fennoscandian Shields have concluded that waters with total dissolved solids (TDS) ranging between 2 and 340 g L⁻¹ are derived from water–rock interactions with intrusion of sedimentary brines at Shield margins (Fritz and Frape, 1982;

Frape et al., 1984; Frape and Fritz, 1987; Gascoyne et al., 1987, 1989; Kamineni, 1987; Lahermo and Lampen, 1987; McNutt, 1987; Nordstrom and Olsson, 1987; Nurmi et al., 1988; McNutt et al., 1990; Ruskeeniemi et al., 1996; Bucher and Stober, 2000). However, it has also been hypothesized that these brines formed by cryogenic concentration of surficial marine and/or sedimentary waters with subsequent deep penetration during glacial times (Herut et al., 1990; Bein and Arad, 1992; Bottomley et al., 1999; Starinsky and Katz, 2003). This cryogenic seawater brine formation hypothesis implies that Canadian and Fennoscandian Shield brines

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have formed since the Pleistocene as part of a “highly dynamic flow” system (Starinsky and Katz, 2003). The Canadian and Fennoscandian Shields were affected by the glacial–interglacial cycle over the last 2 million years. Several glacial advances covered the entire outcrop area of both Shields, including the most recent Wisconsinian glaciation. During a glacial–interglacial cycle, permafrost formation is expected at the margin of advancing and receding glaciers.

Subsurface freeze–thaw cycles during permafrost formation and dissipation can concentrate solutes in the remaining fluids (e.g. Konrad and McCammon, 1990; Marion, 1995; Yershov, 1998). Further, the cold temperatures in permafrost can create a strong thermodynamic sink that may allow advection of water (and solutes) against the concentration gradient (Cary and Mayland, 1972; Gray and Granger, 1986; Perfect et al., 1991; Qiu et al., 1988). On a limited scale, fluid concentrations in the freezing front have been noted to become sufficiently high as to “leap” over solute pockets, resulting in alternating bands of high and low concentration fluids in frozen soils (Kay and Groenevelt, 1983; Romanov and Levchenko, 1989). Increased concentrations of carbonate, sulfate, sodium, magnesium and calcium in groundwaters found in the Siberian platform under thick permafrost has been attributed to in situ cryogenic concentration, although other processes including evaporation and halite dissolution have also influenced brine formation (Alexeev and Alexeeva, 2002, 2003; Shouakar-Stash et al., 2007).

The purpose of this study was to evaluate the three brine evolutionary pathways described above at a crystalline Canadian Shield location currently under cryogenic conditions. This was accomplished by conducting surface and subsurface hydrogeologic and geochemical characterization at a permafrost site that had been an active mine for over 20 years. To fully characterize the site, precipitation, surface, permafrost and subpermafrost water samples were collected, as well as dissolved and free gas samples, fracture fillings and matrix fluid samples. Potential hydraulic pathways through the permafrost were also explored with ground penetrating radar (GPR) and pressure measurements. Field activities conducted at the field site but not discussed in this paper are described in several reports (Ruskeenieni et al., 2002, 2004).

This investigation is directly applicable to several fields of research, as relatively little is currently known about groundwater conditions beneath thick permafrost in crystalline rock. For instance, Deep Geologic Repositories will potentially be constructed at depths of 500–1000 m within the crystalline rock of the Fennoscandian and Canadian Shield as part of the Finnish, Swedish and Canadian concepts for long-term isolation of nuclear waste (e.g. NWMO, 2005; Posiva, 2000; SKB, 1992, 2004; TVO, 1992). The large temporal scale (>1 million years) over which a safety case must demonstrate repository performance requires consideration of glacial and interglacial conditions which will alter the thermal, hydraulic and mechanical boundary conditions, potentially affecting engineered barrier systems, radionuclide mobility and groundwater flow system stability (e.g. Vieno and Ikonen, 2005). This project addresses this need having acquired further scientific understanding of permafrost and its role in influencing deep flow system evolution, fluid movement and chemical evolution of waters in crystalline rocks. Numerous new mining prospects are currently undergoing evaluation in Arctic Canada due to the renewed prospect of an ice-free Northwest Passage. This study also provides an evaluation of long-term influence of mining in permafrost environments. Further, determining natural and anthropogenic influences to geochemistry is important at any disturbed site when investigating natural processes. Recent investigations have also discussed the possible cold origins for life (Bada, 2004; Bada et al., 1994; Levy et al., 2000; Miyakawa et al.,

2002a,b; Price, 2007; Priscu and Christener, 2004). Water is the key to known life, and on other planets like Mars, would most likely be found trapped in or beneath permafrost (Clifford, 1993). However, an evaluation of the geochemical potential for life within and beneath permafrost in a tectonically inactive environment on Earth should be conducted before expensive missions to extraterrestrial planets.

Site description

The Lupin gold mine (65°45'29"N, 111°13'10"W) in Nunavut, Canada (Fig. 1), was active from 1982 to 2005. All mining activities were located underground, with workings extending to 1450 m below ground surface. The Lupin area is approximately 450 m above sea level, and relatively flat, with a height variation of 30–40 m. Current isostatic rebound in nearby regions is on the order of 6 mm yr (Stella et al., 2007).

Geology

The Lupin gold deposit is located in an Archean metaturbidite sequence that has been subjected to regional and contact metamorphism, resulting in a number of low to high grade metasedimentary rock types. Although the rocks are crystalline, the sedimentary origin makes this study site unique compared with greenstone belts and granitic locations previously examined on the Canadian and Fennoscandian Shields. Three major deformation phases were identified, resulting in a complex fold structure (Bullis et al., 1994). Amphibolite facies metamorphism from multiple intrusions and metamorphic events altered turbidite mudstones and greywackes to the crystalline rock types meta-greywacke/quartzite, phyllite and quartz-feldspar-gneiss (King et al., 1988; Ford and Duke, 1993; Bullis et al., 1994; Geusebroek and Duke, 2004). Peak metamorphism occurred between 2.680 and 2.585 Ga, however faulting caused contact metamorphism as late as 1.84–1.81 Ga (Geusebroek and Duke, 2004). Metamorphism imparted a high angle foliation (80–85°) or planar structural element to the lithological units at the site (Fig. 1). Metamorphic events and the orientation of the folds and foliation were suggested to influence groundwater flow and fracture orientations (Stotler, 2008). A more detailed overview of the metamorphic and structural history of Lupin is provided by Geusebroek and Duke (2004).

Permafrost

The site is well within the zone of continuous permafrost (Fig. 1). In the area of the Lupin mine, permafrost depth, defined by the 0 °C isotherm, currently extends between 400 and 600 m below ground surface (mbgs). Permafrost depth can vary due to differences in porosity and heat conductivity of the main rock types, as well as surficial features such as vegetation, snow cover or soil types (e.g. Kukkonen and Šafanda, 2001). Temperature measurements within the mine shaft indicated a permafrost depth of 541 mbgs. Extrapolation of the observed thermal gradient (16 mK m⁻¹) indicated the lowest rock temperature below the seasonally affected zone was ~–8 °C, somewhere between 50 and 80 mbgs. These observations were important when considering the potential for precipitation of various mineral phases during freezing.

The age or onset of permafrost formation at Lupin has not yet been determined. The results of the warmest climate scenario from an ensemble glacial systems modeling approach presented by Tarasov and Peltier (2007) indicated an 80% probability that permafrost completely melted at the site during the last glacial maximum, although relict permafrost cannot be completely ruled out.

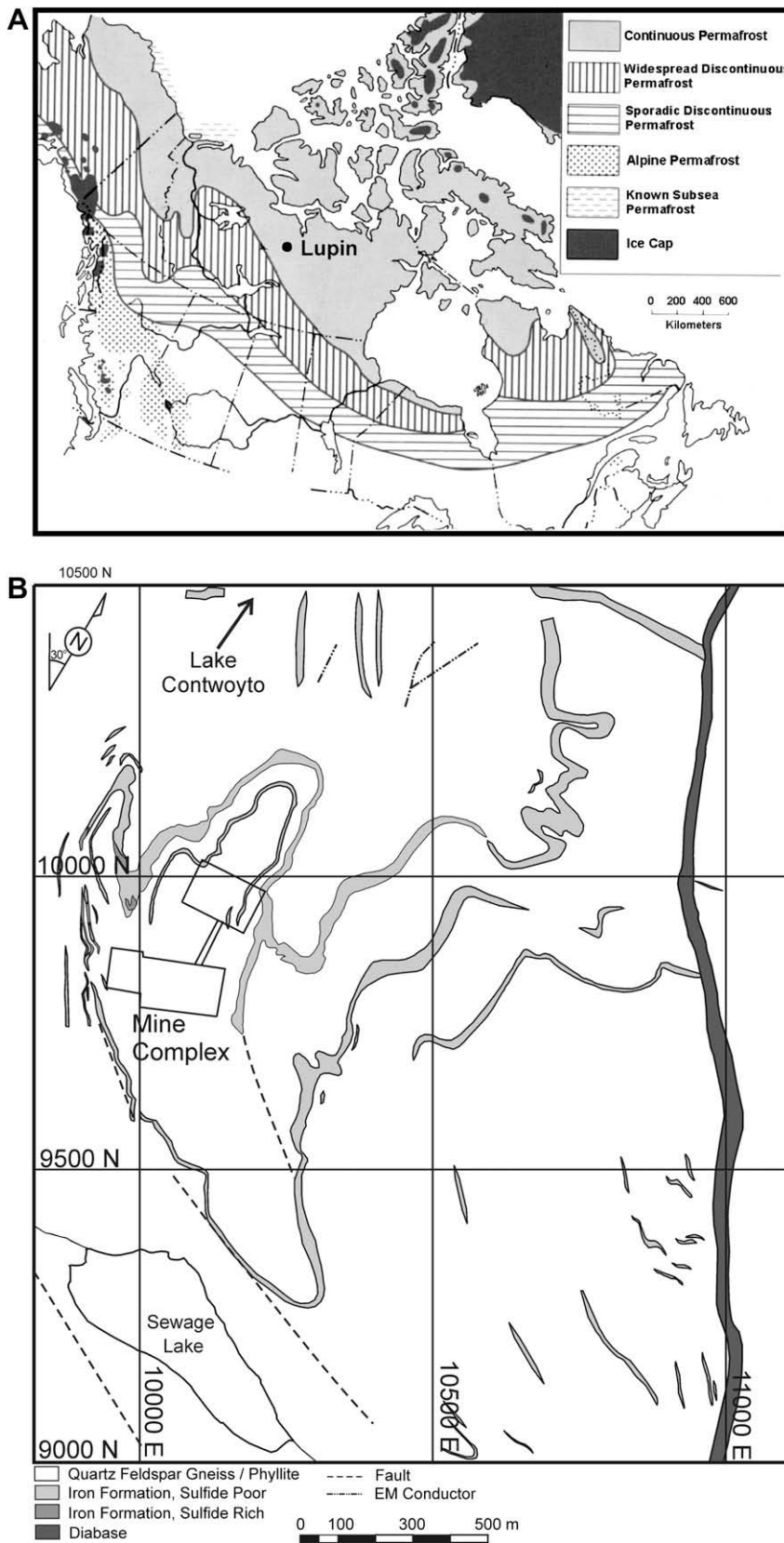


Fig. 1. (A) Location of Lupin (L) within Canada and zone of continuous permafrost (after Natural Resources Canada, 1995). (B) Surface geology of the study area (after King et al., 1989).

Permafrost at Lupin therefore likely started to form following the rapid retreat of the ice sheet at the start of the last periglacial

period, which began approximately 8000–6000 years ago (e.g. Smith et al., 2001).

Taliks

Taliks are unfrozen channels that may provide routes for discharging or recharging groundwaters through thick, continuous permafrost. Taliks, typically found beneath large watercourses where mean annual bottom temperatures remain above the freezing point (i.e. the watercourse does not freeze down to the bottom), are termed “hydrothermal taliks” (van Everdingen, 1976). Conditions favorable for the existence of a talik occur when water depth is $>2/3$ of maximum ice thickness (Mackay, 1992; Burn, 2002).

Of the many lakes in the Lupin area, Lake Contwoyto was of particular interest. It was 1.3 km from the Lupin mine, 100 km long, and ranged between 2 and 5 km wide near the mine. The lake bathymetry was uncertain, but its linear geometry suggested a fault-valley origin with deep fractured roots. Observations of the talik boundary beneath Lake Contwoyto were obtained through a GPR survey, and indicated a hydrothermal talik could be located 30–60 m from shoreline. The GPR methodology and results are described in detail in [Supplementary information](#).

The GPR results had important hydrogeologic implications. While deep permafrost may effectively seal many of the potential flow routes through crystalline bedrock, hydrothermal through-taliks in the area of the Lupin mine could provide hydraulic pathways through the permafrost.

Methods

Sample descriptions

Waters sampled at Lupin are grouped into the following categories: precipitation, surface water, permafrost zone fluids, fluids at the base of the permafrost, subpermafrost fluids and rock matrix fluids. Several precipitation samples were collected in October 2000 and June 2002, but additional data was available from earlier studies (Gibson, 1996; Gibson et al., 1999). Surface water samples were collected from lakes and flowing streams in June 2002. Permafrost waters were sampled from drips along a north–south trending, 1–2 m wide fault zone with cross fracturing bisected by the main mine access ramp (known as the “ramp fault”) between 250 and 540 mbgs. Beneath the permafrost, waters were primarily sampled from research and exploration boreholes. Boreholes are identified as *collar depth mbgs-borehole number*. Individual borehole construction details, including length, azimuth, diameter, dates drilled/sealed, are provided in [Supplementary material](#).

Matrix fluids were extracted from drilled core by crush and leach from the 550-112, 570-105 and 570-106 research boreholes and the 890-188 exploration borehole. Techniques and rationale for examining matrix pore fluids by crushing and leaching of core are detailed by Frapet et al. (2004), Smellie et al. (2003), Waber and Frapet (2002) and Waber and Smellie (2008). Briefly summarized, rock core was quickly rinsed in deionized water, then crushed ($<63 \mu\text{m}$), weighed and added to double-deionized nano-pure water in a solid to liquid ratio of 1 g to 1 mL. The mixture was put on a shaker for 24 h. The solution was then extracted from the rock particles by vacuum sieve. For the calculation of mass-solute-per-kg-of-rock, it was assumed that all available chloride was released into the fluid phase during the 24 h reaction period, which had proven sufficient due to repeated crush and leaching of samples in previous studies (Smellie et al., 2003).

Analytical methods

Precipitation, surface water, groundwater and crush and leach samples were analyzed for major and trace elements. Multiple

samples were collected from each sampling point over the 6 year study period in connection with other sampling activities (gases, microbes and dating) to observe any changes in groundwater chemical conditions, and to achieve as complete a characterization of the groundwater system as possible at any given sampling opportunity. Gas samples were collected using an inverted bottle headspace displacement method. Glass bottles (500 mL or 1 L) were filled with borehole fluid by placing nylon tubing from the borehole packer to the bottom of the bottle. The sample bottle was allowed to overflow into a container. Once the water level in the container topped the sampling bottle, the bottle was carefully inverted, keeping the bottle opening below the water surface. Gas then displaced the fluid in the sampling bottle, until only ~ 20 mL of borehole fluid remained. The bottles were sealed underwater. During transport and storage, bottles were kept upside down until analyzed.

Redox and oxygen concentrations were measured from six boreholes using a flow-through cell (Ruskeeniemi et al., 2004). A platinum electrode with a combined Ag/AgCl reference was used for redox measurements. The outflow rate from the borehole was between 1 and 1.5 L min^{-1} . The monitoring time varied from 20 to 55 h. Therefore, about 1–5 m^3 of water was removed during the monitoring cycle, and thus in principal the water volume in the holes changed at least 1–5 times. The pH and electrical conductivity values were recorded after the oxygen and redox values had stabilized (Table 1). Dissolved oxygen concentrations were below the detection limit (0.0 mg/L). Eh-values, ranging from -10 mV to 25 mV, were still slowly decreasing at the end of the measurement period. The field-measured pH-values are rather uniform (pH 8.2–8.6) for waters from all boreholes monitored. The pH values measured in laboratory are uniformly about two units lower than these in situ results, indicating atmospheric CO_2 diffusion into the sample occurred during transportation, and that pCO_2 levels in the groundwater were low or below atmospheric.

Field-filtered (0.45 μm) water samples were taken for the determination of physico-chemical parameters and ionic analysis in the Geolaboratory of the Geological Survey of Finland (GTK). A filtered and acidified (0.5 ml concentrated suprapure $\text{HNO}_3/100$ ml water) sample was taken for metal and trace element analyses. Electrical conductivity and pH were measured in the field and in the laboratory. Total alkalinity (as $\text{mmol HCO}_3^- \text{L}^{-1}$) was determined in the laboratory using an automatic titrator. No adjustments were made for atmospheric CO_2 diffusion during transport. The main anions, F^- , Cl^- , NO_3^- and SO_4^{2-} , were analyzed using ion chromatographic (IC) technique. All cations and other elements were analyzed by ICP-AES or ICP-MS technique. The detection limits for Ca, Na, K, Mg, Li and Sr of the ICP-MS/ICP-AES method are 100, 200, 10, 100, 0.1 and 0.1 $\mu\text{g/L}$, respectively. Charge balance errors in the samples reported are below 10%.

Tritium, $\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{37}\text{Cl}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ were analyzed at the University of Waterloo Environmental Isotope Laboratory (UW EIL). Tritium values were determined by the electrolytic enrichment method of Taylor (1977) and counted in a LKB Wallac 1220 Quantalus liquid scintillation counter, with a detection limit of 0.8 T.U. Deuterium determinations were made following the Mn reduction preparation method of Shouakar-Stash et al. (2000) and

Table 1
Redox (Eh) and dissolved oxygen values measured in flow-through cell.

Depth-borehole no.	Date	Eh (mV)	O ₂ (mg L ⁻¹)	pH	EC (mS/cm)
890-188	21-Feb-2003	24	0.0	8.34	545
1130-192	22-Feb-2003	-18	0.0	8.22	4430
1130-217	24-Feb-2003	-16	0.0	8.60	1370
1130-197	25-Feb-2003	11	0.0	8.48	1410
1130-181	27-Feb-2003	-10	0.0	8.43	1230

the Cr reduction method of Morrison et al. (2001) and analyzed on an Isoprime IRMS coupled with a Eurolecton elemental analyzer. Oxygen isotope analysis was performed on a Micromass 903 triple collector mass spectrometer using the preparation procedures of Epstein and Mayeda (1953) with Moser's (1977) modification. Analytical reproducibility of $\pm\delta^{18}\text{O}$ and $\pm\delta^2\text{H}$ are 0.2‰ and 2.0‰, respectively. Dissolved chloride was converted to CH_3Cl which was then analyzed for $\delta^{37}\text{Cl}$ on a dual inlet Isoprime IRMS following the method of Eggenkamp (1994), with an accuracy of $\pm 0.15\%$. Nitrates were separated from other anions using an ion-exchange resin column packed with Bio-Rad AG 1-X8 and combusted in EA-Isochrom-Carlo Erba continuous flow elemental analyzer-IRMS with a precision of $\pm 0.3\%$. Samples analyzed for $\text{NO}_3^-^{18}\text{O}$ were combusted with excess graphite to generate CO_2 which was then analyzed using a Dual Inlet Prism II MS, with an accuracy of $\pm 0.5\%$. $\delta^{34}\text{S}$ analyses were prepared following the method of Yanagisawa and Sakai (1983) and analyzed on a RoboProp-CN Europa Tracemass IRMS with an accuracy of $\pm 0.3\%$. Sulfate $\delta^{18}\text{O}$ was prepared by combustion of BaSO_4 which was analyzed on an HEKATECH high temp-EA-IsoPrime IRMS, with an accuracy of $\pm 0.3\%$, following the method of Shakur (1982). Chlorine-36 was analyzed by accelerator mass spectrometry at ETH in Zurich, Switzerland.

The Indiana University Stable Isotope Facility and the UW-EIL analyzed $\delta^{13}\text{C}$ using Micromass Isoprime and Finnigan MAT Deltas for $\delta^2\text{H}$ isotopes of gases. Accuracy and reproducibility of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ are typically $\pm 0.3\%$ VPDB and $\pm 5\%$ VSMOW, respectively. Gas compositions were analyzed at the UW Organic Geochemistry Laboratory; N_2 and CO_2 on a Fisher/Hamilton Gas Partitioner, Model 29 gas chromatograph, and alkane-hydrocarbons on a Varian 3800 gas chromatograph equipped with a flame ionization detector and capillary injection port. Detection limits for CO_2 , N_2 , C_1 , C_2 , C_3 , nC_4 and iC_4 are 0.5 mg/L, 30 mg/L, 0.3 $\mu\text{g/L}$, 0.2 $\mu\text{g/L}$, 0.2 $\mu\text{g/L}$, 0.8 $\mu\text{g/L}$ and 1.6 $\mu\text{g/L}$, respectively.

Samples for ^{14}C analysis were collected in 2 L glass containers. The containers were filled with water by holding tubing leading from the borehole at the bottom of the container, allowing the water to displace the air in a non-turbulent manner. The containers were allowed to over flow into a plastic bag for at least 6 L (three container volumes) and then sealed underwater to eliminate the possibility of air contamination. Carbon-14 was analyzed by accelerator mass spectrometry at Rafter Radiocarbon Laboratory in New Zealand. Stable carbon isotope samples ($^{13}\text{C}/^{12}\text{C}$) were prepared at the University of Waterloo EIL. The ^{14}C content is corrected for the $\delta^{13}\text{C}$ value and reported according to the conventions of Stuiver and Polach (1977).

Results

Complete analytical results and a description of crush and leach rock samples are provided in Supplementary material. Chemical trends with depth are presented in Fig. 2. Precipitation and surface waters in the Lupin area contained very low concentrations of most ions. These waters were dilute; with mean concentrations of sodium, 0.32 and 4.64 mg L^{-1} and calcium, 0.29 and 4.2 mg L^{-1} , for precipitation and surface waters, respectively. Precipitation samples were Na-dominated, but buffering by local surficial water/rock interaction resulted in Ca-dominated surface water samples. Total dissolved solids (TDS) (2.6–22.5 mg L^{-1}), chloride (0.2–3.5 mg L^{-1}), sulfate (0.1–10.6 mg L^{-1}) and nitrate (0.2–0.9 mg L^{-1}) concentrations in the precipitation and surface waters were also low (Fig. 2). In order of frequency, permafrost waters were Na-Cl, Na-Cl- SO_4 , or Na-Mg-Cl- SO_4 . Permafrost fluids had similar chloride concentrations as deeper subpermafrost groundwaters. Subpermafrost fracture waters were either Na-Ca-Cl or Ca-Na-Cl type. The subpermafrost water salinity varied up to 10 g L^{-1} within any one sealed borehole on the 1130 level during the study. Over

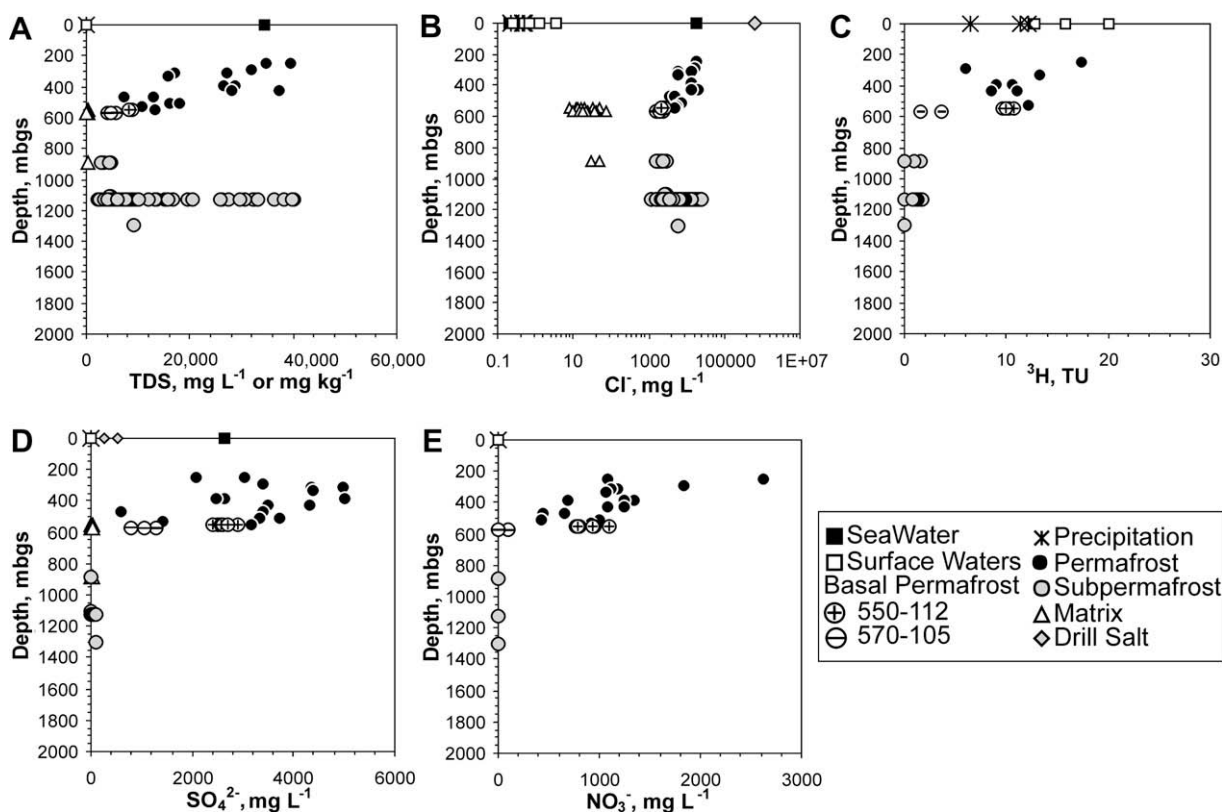


Fig. 2. Chemical trends with depth at Lupin (A) TDS, (B) Cl, (C) SO_4 , (D) NO_3 , and (E) ^3H .

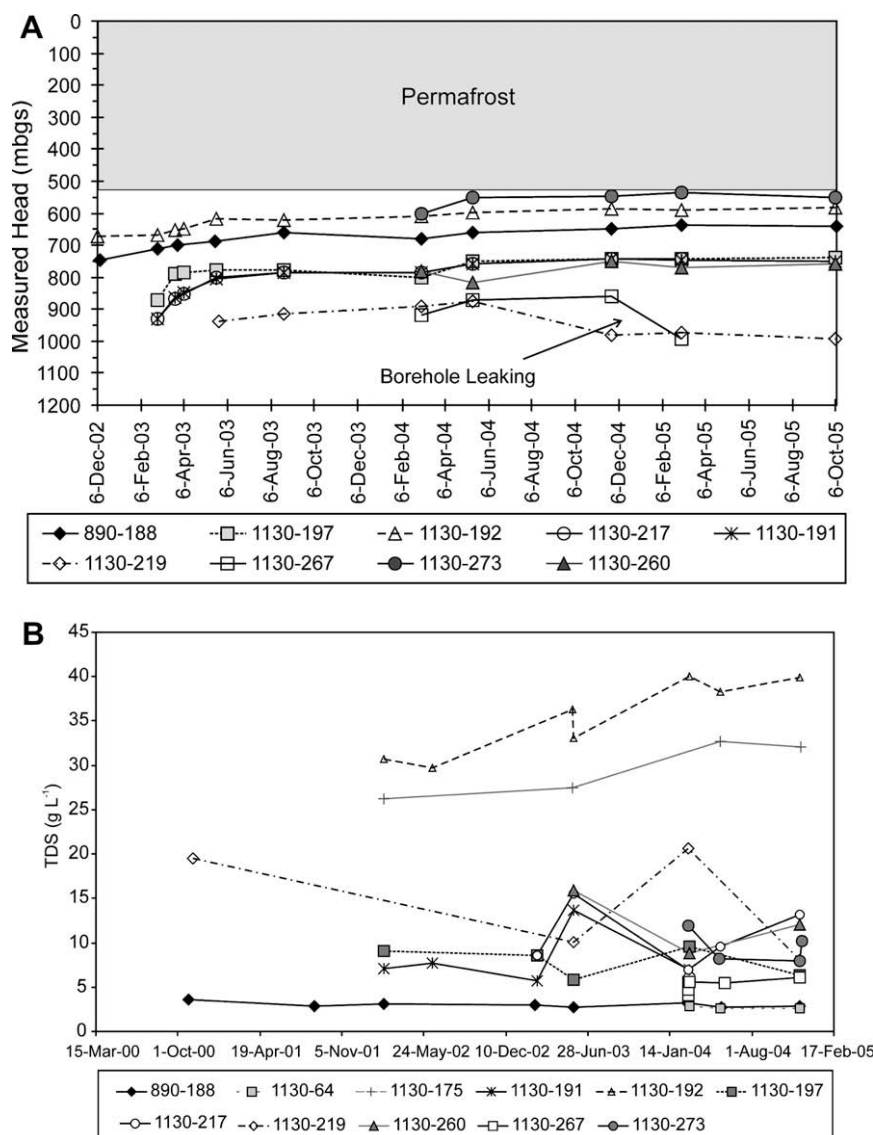


Fig. 3. Changes in pressure (A) and salinity (B) with time in boreholes from the subpermafrost zone of the Lupin Mine, Nunavut, Canada.

the 5 year period of the study, only waters from boreholes 890-188 and 1130-64 showed a constant TDS; while 1130-192 and 1130-175 both exhibited an increasing trend in TDS. The remaining boreholes sampled displayed no consistent TDS pattern. The fluids were divided into three groups of differing salinities; a high salinity water (~38 g L⁻¹), a medium salinity water (between 8 and 20 g L⁻¹), and a low salinity water (<5 g L⁻¹) (Fig. 3B). Crush and leach experiments on rock core (matrix fluids) from several boreholes yielded a very low salinity Na-Cl solution. The matrix fluids were Na-Cl type with the exception of one Ca-Cl type from the only sulfide-bearing amphibolite rock sampled (sample 570-106, 385 m). This sample had the largest Ca/Na ratio (6:1) of any fluid sampled at the Lupin site.

Stable isotopic composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$) of waters sampled are shown in Fig. 4. Precipitation $\delta^2\text{H}$ and $\delta^{18}\text{O}$ varied between -119‰ and -279‰ VSMOW and -15.7‰ and -37.6‰ VSMOW, respectively (not shown on graph, Gibson, 1996). Precipitation $\delta^2\text{H}$ - $\delta^{18}\text{O}$ values vary seasonally along the local meteoric water line (LMWL) which was estimated to be $\delta^2\text{H} = 7.32 \cdot \delta^{18}\text{O} - 4.46$ ($R^2 = 0.98$) from precipitation data collected by Gibson (1996). Reported stable isotopic values of surface waters were similar to other studies in this area of the Canadian Arctic (Rossi, 1999;

Gibson, 1996; Gibson et al., 1999; Gibson, 2002), and plotted along the defined Local Evaporation Line (LEL) ($\delta^2\text{H} = 5.37 \cdot \delta^{18}\text{O} - 52.4$) for surface waters in the Lupin area (Gibson et al., 1999). Stable isotopes of subpermafrost waters sampled at the Lupin mine generally plot in one area near and below the intersection of the LEL with the global meteoric waterline (GMWL) (Fig. 4). The deepest sample (1300-105) was in the center of the grouping. Unlike many other saline Canadian/Fennoscandian groundwaters (e.g. Frapet et al., 2004), none of the Lupin waters plotted above the GMWL.

Tritium values (Fig. 2E) ranged between 6 and 13 TU in precipitation samples and 14 and 21 TU in surface water samples. These values were similar to the tritium distributions reported over a limited geographical area in the region (Rossi, 1999). For an uncontaminated environment, the ^{36}Cl value for Lake Contwoyto ($1073.8 \times 10^{-15} \text{ }^{36}\text{Cl}\cdot\text{Cl}^{-1}$) was anomalously high (Fig. 5). However, similar values were reported in low chloride surface waters in the Antarctic dry valleys (Carlson et al., 1990). Lake Contwoyto had very low chloride content (3.5 mg L^{-1}); therefore any amount of ^{36}Cl would have a large influence on the $^{36}\text{Cl}\cdot\text{Cl}^{-1}$ value. The high ^{36}Cl value was likely attributable to proportionally large atmospheric chlorine contributions, low weathering rates and higher

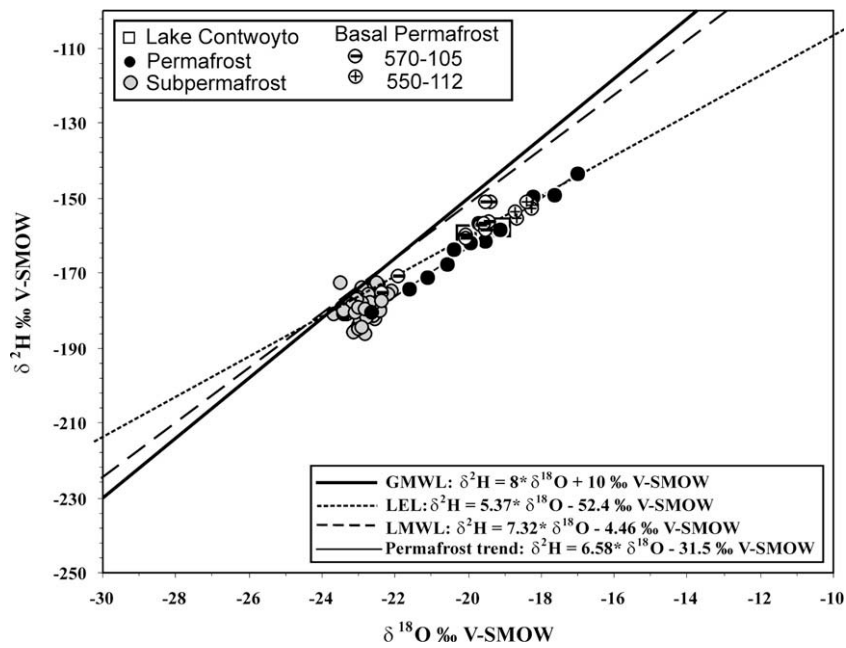


Fig. 4. Stable isotopic composition of Lupin Waters. LEL from Gibson et al. (1999), LMWL from Gibson (1996), GMWL after Craig (1961). Surface water samples are slightly hidden behind 570-105 and permafrost samples.

cosmic flux due to lowered atmospheric ozone (e.g. Carlson et al., 1990).

Discussion

Mine influence

Mining activity (such as dewatering) has introduced fresh surface waters into the mine and drilling within the permafrost necessitated the use of a drilling brine solution made from fresh lake water and imported NaCl salt (with low SO₄²⁻). According to mine personnel, at least one large spill of drilling brine solutions occurred within the upper part of the mine during past operations. Blasting introduced large quantities of nitrogen to the subsurface. As with any mine, dewatering operations have also affected the natural flow and pressure regime in the surrounding bedrock. In this section, the unique effects of mining in permafrost will be highlighted and discussed.

Mine brine

The dissolved load in permafrost fluids at the site (12.9–39.6 g L⁻¹) is higher than expected based on freezing experiments and investigations of Mackenzie Valley sedimentary hydrates under a similar permafrost thickness (Zhang and Frape, 2002; Matsumoto et al., 2005). Unlike the Na–Ca fluids found deeper in the site, permafrost fluids are Na-dominated (Fig. 6C). The relationships between Na and Ca, Br and Cl and Na/Ca and Br/Cl ratios indicate permafrost fluids trend towards the introduced drilling salt end member, compared with matrix and subpermafrost waters. The Br versus Cl plot and the Ca/Na vs. Br/Cl ratio plot (Fig. 6) also suggest the drilling salt used at the site resulted in the large salt load observed in the permafrost waters. High ³H concentrations (6.0–17.3 TU) also reflect the influence of water pumped down for mining activity (drilling brine, washing, etc.) (Fig. 2E).

³⁶Cl values also supported an imported salt source in permafrost fluids. Permafrost ³⁶Cl values have a signature similar to the drilling salt (<0.0014 × 10⁻¹⁵ ³⁶Cl·Cl⁻¹), and are much lower than measured in deeper subpermafrost waters (Fig. 5). As most salt is mined from salt domes with negligible U and Th, ³⁶Cl·Cl⁻¹ ratios less than 1 × 10⁻¹⁵ are typical for imported drilling salt (Bentley et al., 1986; Fabryka-Martin et al., 1987; Phillips, 2000). This

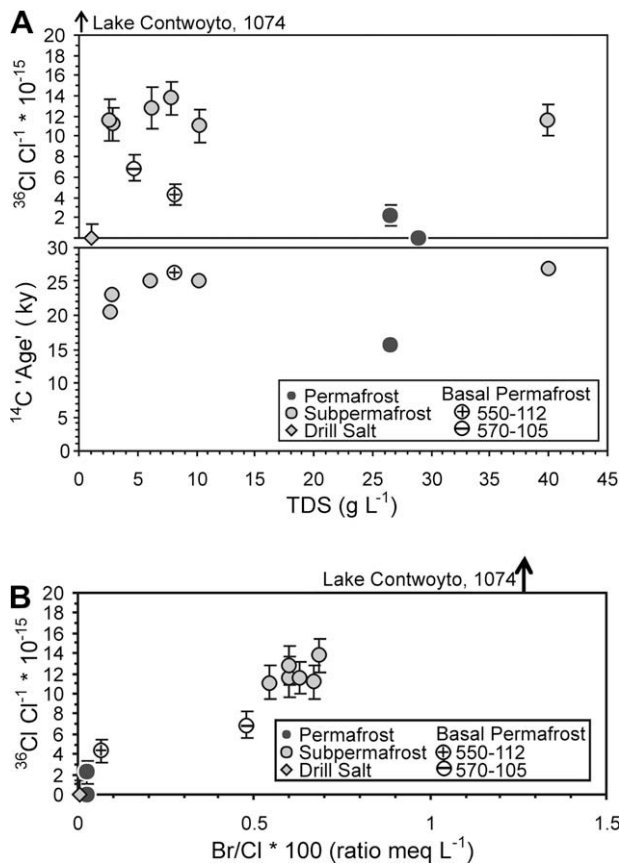


Fig. 5. Radioactive tracers (A) ³⁶Cl and ¹⁴C vs. TDS, (B) ³⁶Cl vs. Br/Cl × 1000 for waters sampled at the Lupin mine. Radiocarbon error is less than the size of the data point.

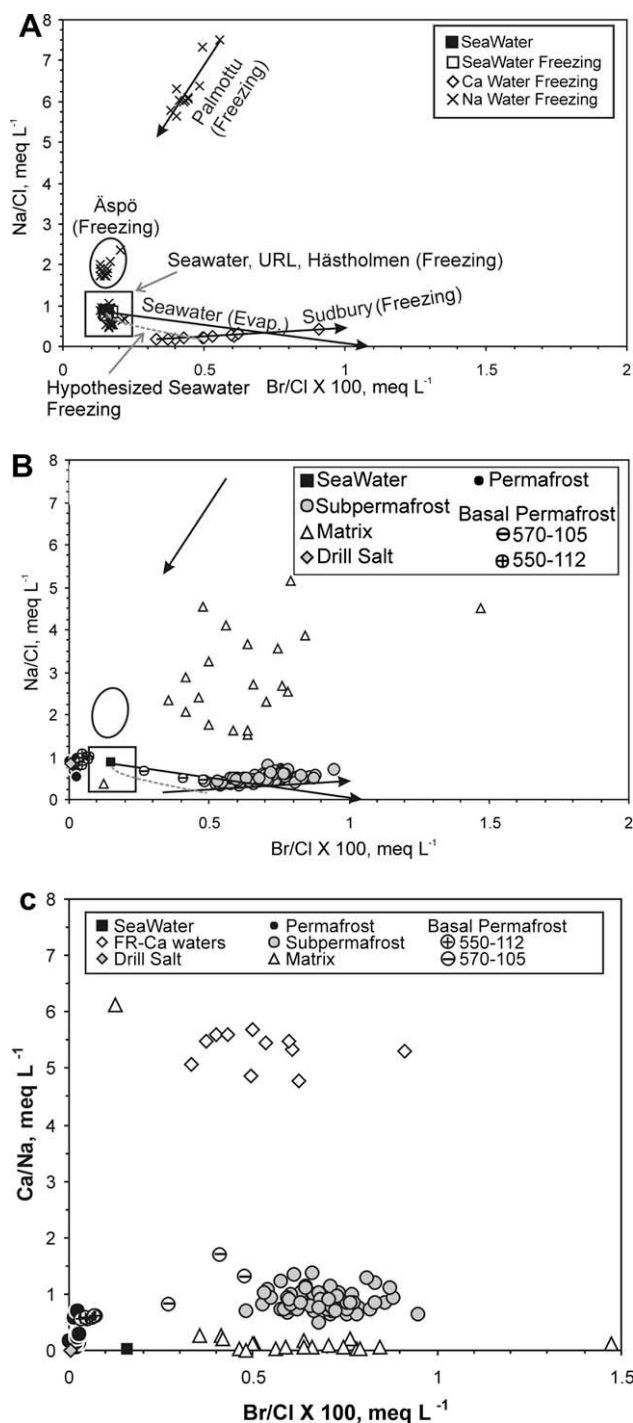


Fig. 6. Na/Cl vs. Br/Cl. (A) Trends for evaporating seawater (McCaffrey et al., 1987), brackish Sudbury Ca–Cl water freezing experiment (Frape et al., unpublished), Palmottu Na–Cl water freezing experiment (Zhang and Frape, 2002), Äspö Na–Cl–HCO₃ water freezing experiment (Zhang and Frape, 2002), are shown. Data inside the box include sea water, sea water freezing experiment results and hypothesized freezing trend (Herut et al., 1990), URL Na–Cl water freezing experiment results (Zhang and Frape, 2002) and Hästholmen freezing experiment results (Zhang and Frape, 2002). (B) Results from Lupin. (C) Ca/Na vs. Br/Cl for samples collected at Lupin.

indicated a majority of chloride sampled in the permafrost was introduced by mining activities.

Conversely, stable isotopic $\delta^{37}\text{Cl}$ ratios in the permafrost waters were similar to the matrix fluid, rather than the salt stored at the mine site (Fig. 7). It is possible the $\delta^{37}\text{Cl}$ in the drilling fluids were

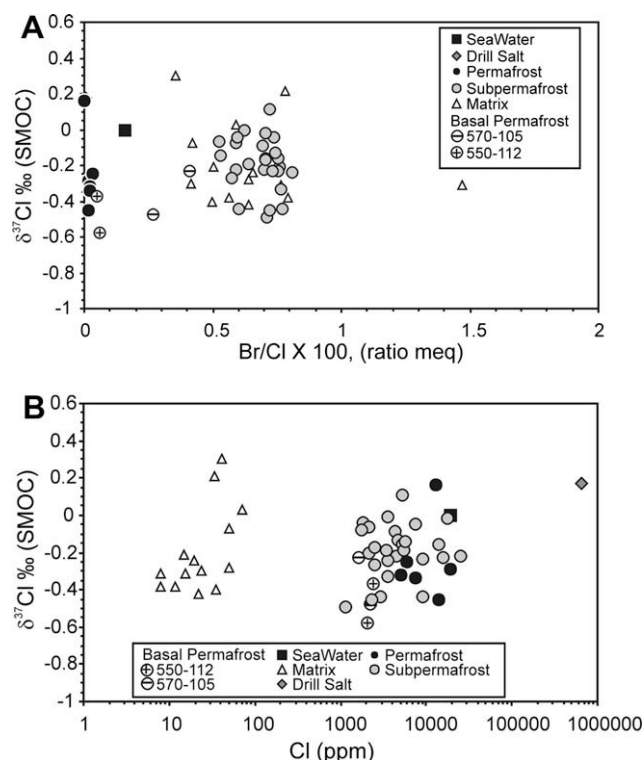


Fig. 7. $\delta^{37}\text{Cl}$ (A) vs. Br/Cl and (B) vs. Cl for samples collected at the Lupin mine.

fractionated by the freezing process. As saline water freezes, ^{37}Cl is preferentially incorporated into the ice, resulting in up to a 1‰ fractionation (Zhang and Frape, 2002). However, the fractionation was typically only observed experimentally in chloride incorporated into the ice, as chloride concentrations in the fluid reservoir were too large for the chloride mass to be affected. Therefore, freezing provided a rather unsatisfying explanation for the observed permafrost $\delta^{37}\text{Cl}$ variation. It was not possible to ascertain if the same salt source was utilized for mixing the drilling brine throughout the 20 years of mine operations prior to the research team's arrival. A change in salt source could also explain the observed variation of $\delta^{37}\text{Cl}$ ratios in permafrost fluids. In conclusion, the geochemical data (ionic ratios, ^3H and ^{36}Cl) indicated the chloride sampled in permafrost waters associated with the ramp fault was contaminated by the Na–Cl drilling brine.

Nitrate

High nitrate concentrations (423–2630 mg L⁻¹) were sampled in permafrost zone waters (Fig. 2D). Out of nearly fifty Canadian and Fennoscandian Shield sites previously studied, samples from only three mines (Macassa Mine in Kirkland Lake, ON; Sigma Mine in Val d'Or, PQ; and Con Mine in Yellowknife, NWT) have recorded nitrate concentrations over 100 mg L⁻¹, and only samples from Macassa had nitrate concentrations over 1000 mg L⁻¹ (Blomqvist, 1999; Blomqvist et al., 2000; Frape and Fritz, 1981, 1987; Frape et al., 1984, 2004; Gascoyne et al., 1987; Jones, 1987; MacDonald, 1986; Ruskeeniemi et al., 1996; Sherwood-Lollar, 1990).

Ammonium-nitrate was utilized at the Lupin mine for blasting, and was considered as a potential source of nitrate to the permafrost fluids. However, in studies at the Whiteshell Underground Research Laboratory site (URL) in Manitoba, only small increases in NO₃ concentrations were observed in fractures adjacent to blast sites, which then returned to pre-blast concentrations within two hours of the blast (Gascoyne and Thomas, 1997). Thus, the high nitrate concentrations at Lupin were intriguing.

To determine nitrate source, the nitrate isotopic composition was analyzed. The fluid $\delta^{15}\text{N}\text{-NO}_3$ (+2.62‰ to +11.73‰ AIR) and $\delta^{18}\text{O}\text{-NO}_3$ (−0.78‰ to +27.62‰ VSMOW) compositions were similar to ammonium-nitrate fertilizer compositions (Fig. 8) and mine water sampled in other mines (Mislowack et al., 2008). This suggested the increased nitrate concentrations were related to blasting compounds and residuals. The isotopic composition of ammonium-nitrate used by the mine for blasting was not analyzed (safety and security regulations prohibited its removal from site), but fertilizer and blasting ammonium-nitrate should have similar isotopic compositions.

Microbial studies in subpermafrost boreholes at Lupin isolated several denitrifying bacteria, however the bacteria were not obligate denitrifiers, and there was no direct evidence for denitrification in the subpermafrost waters (McGown et al., Submitted for publication). No information was available regarding the presence or activity of these microbes in the permafrost. $\delta^{15}\text{N}\text{-NO}_3$ ratios remained very similar in three repeat sampling events over 4 years, although $\delta^{18}\text{O}\text{-NO}_3$ ratios changed up to ~20‰ in some samples. These data, high nitrate concentrations, and a plot of $\delta^{15}\text{N}$ vs. $\ln[\text{NO}_3^-]$ (Fig. 8) suggested that denitrification was not an active or significant process in the permafrost. Subpermafrost nitrate concentrations were too low for isotopic analysis, and it could not be determined whether the low concentrations in the subpermafrost were due to denitrification, low redox conditions preventing the formation of nitrate, isolation from mining activities, or some other process.

Sulfate

Increased dissolved sulfate concentrations (578–5000 mg L^{−1}) were observed in permafrost fluids compared with subpermafrost fluids (1–41 mg L^{−1}). Three possibilities were investigated to determine the source: (1) importation of sulfate with the drilling brine (2) dissolution of sodium sulfate precipitated due to permafrost formation or (3) oxidation of iron formation sulfide minerals. Sulfate concentrations and SO₄/Cl ratios in the drill salt were much lower than observed in permafrost fluids, and were therefore not considered to be the sulfate source in the permafrost fluids. In Siberian Platform permafrost, crystallization of hexahydrate (MgSO₄·6H₂O, eutectic −4.8 °C) and mirabilite (Na₂SO₄·10H₂O, eutectic −3.5 to −8.2 °C) was considered a sulfate source (Alexeev and Alexeeva, 2003). At Lupin, the minimum temperature

(−6.8 °C at 87 mbgs) was low enough for the precipitation of both hexahydrate and mirabilite. Although Mg concentrations were much higher in permafrost (239–1150 mg L^{−1}) than subpermafrost fluids (6–366 mg L^{−1}), permafrost sodium concentrations were clearly related to drill brine inputs (Fig. 6B). If the permafrost SO₄^{2−} were related to dissolution of hexahydrate and mirabilite, a component of sodium would be distinct from the drilling brine. Precipitation of mirabilite was expected to have the same effect on hydrogen and oxygen isotope fractionation as ice formation (Stewart, 1974), thus the relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ was not able to further constrain the potential for mirabilite precipitation.

However, sulfur isotopic evidence suggested oxidation of sulfide minerals in the iron formation and in other lithologies resulted in the increased permafrost SO₄^{2−} concentrations. Isotopic values for the sulfide mineral end members were reported in Table 2. One sample from the 440 m level had a value of −33.2‰ CDT. The sample was mostly chalcopyrite but contained considerable impurities. The other samples were more typical of sulfides in this type of geological environment (e.g. Rye and Rye, 1974), with $\delta^{34}\text{S}$ values between −2.5‰ and 12.5‰ CDT.

In most environments, a biologically mediated sulfide to sulfate transition is accompanied by a $\delta^{34}\text{S}$ depletion of 2.0–5.5‰ (Toran and Harris, 1989). Therefore, the oxidation of sulfides was considered a conservative process with only a very minor depletion of the sulfide isotopic value. Examination of Fig. 9 showed the $\delta^{34}\text{S}\text{-SO}_4$ measured within the permafrost ($\delta^{34}\text{S}\text{-SO}_4$: −1.8 to +2.9‰ CDT) reflected the abiogenic oxidation of pyrite ($\delta^{34}\text{S}_{\text{pyrite}} = -2.5‰$ CDT) in the permafrost groundwaters. However, both sulfide oxidizers and reducers were isolated in Lupin groundwaters McGown et al., Submitted for publication, and the sulfur isotopic value of the chalcopyrite sample (−33.2‰ CDT) indicated microbial sulfate reduction may have occurred in the past. Thus, in a process similar to acid mine drainage, in situ oxidation of permafrost sulfate has resulted in acidification of permafrost waters (pH range: 3.2–7.6).

Table 2
 $\delta^{34}\text{S}$ of sulfide minerals associated with calcite filled fractures from the Lupin mine.

Sample depth (m)	Mineral	$\delta^{34}\text{S}$ (‰ CDT)
300	Pyrite, some chalcopyrite	−2.5
440	Chalcopyrite	−33.2
475	Pyrite	12.5
490	Pyrite, some chalcopyrite	2.1

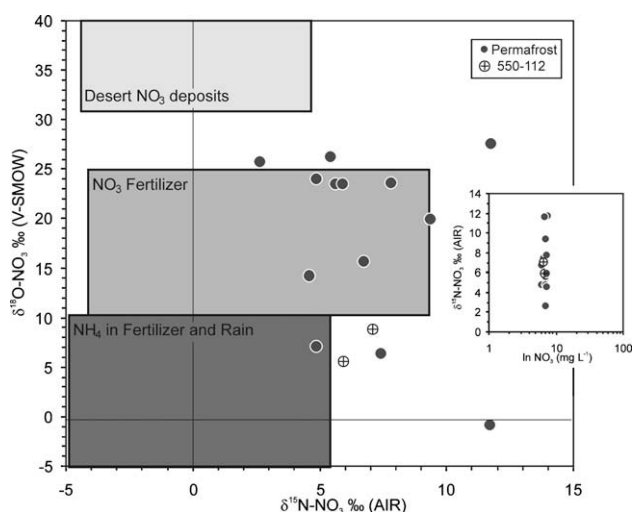


Fig. 8. Stable isotopes of nitrate in Lupin groundwaters. Boxes showing typical desert and fertilizer values after Kendall and Aravena (2000). Inset box is a semi-log plot of $\delta^{15}\text{N}$ vs. $\ln[\text{NO}_3^-]$.

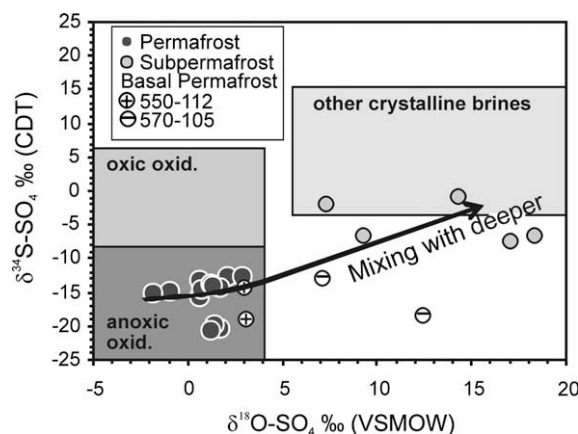


Fig. 9. Stable isotopes of sulfur in Lupin groundwaters. Crystalline brine sulfate values are from Fritz et al. (1994). Justification of the oxic and anoxic boxes provided in the text.

Analysis of $\delta^{18}\text{O}$ was conducted to try to determine if sulfide oxidation was a naturally occurring process, or induced by mining activities. The two most probable sources of oxygen in sulfate in permafrost fluids are oxygen bound to water molecules and gaseous or dissolved oxygen in groundwater ($\delta^{18}\text{O}\text{-SO}_4\text{-Atmospheric} = +23.7\text{‰}$ VSMOW, Kroopnick and Craig, 1972). Abiogenic fractionation of $\delta^{18}\text{O}$ from atmospheric or dissolved oxygen into sulfate is -10‰ (VSMOW), but fractionation associated with SO_4 derived from the H_2O molecule is only -3‰ (Krouse and Mayer, 2000). The $\delta^{18}\text{O}\text{-SO}_4$ ratios in the permafrost fluids (-12‰ to -16‰ VSMOW) indicated the most important source of oxygen for SO_4^{2-} is from H_2O molecules, although a very small component of the oxygen could be from atmospheric or dissolved oxygen. Combined with the slightly acidic conditions and saturated water conditions, a very low fractionation was favored ($+2\text{‰}$ to $+4\text{‰}$) (Toran and Harris, 1989). With a water $\delta^{18}\text{O}$ value of -17‰ to -20‰ , the sulfate in the permafrost zone should have had values identical to those seen at the site. Fig. 9 shows the sulfate in water within this zone was a result of local sulfide oxidation under anoxic conditions. While oxidation was likely enhanced by the mining activity, it was probably also naturally occurring. However, it was not possible to determine to what degree oxidation increased due to mining activities.

The sulfur isotopic fractionation accompanying mirabilite and hexahydrate precipitation were unknown; however, a maximum 2.4‰ CDT fractionation of $\delta^{34}\text{S}$ was reported as gypsum precipitated during seawater evaporation (Raab and Spiro, 1991). It is likely a similar isotopic fractionation occurs during mirabilite and hexahydrate precipitation. Therefore, it was not likely precipitation of mirabilite and hexahydrate could account for the large isotopic sulfur fractionation ($\sim 20\text{‰}$) between permafrost and subpermafrost waters, although precipitation of oxidized sulfides within the permafrost cannot be ruled out. Lower SO_4^{2-} values in the subpermafrost are related to microbial sulfate reduction McGown et al., Submitted for publication. In conclusion, high SO_4^{2-} concentrations may or may not be enhanced due to mining activities;

regardless they are a result of oxidation of naturally occurring sulfide in the rocks.

Dewatering operations and hydraulic pressures

Large differences in hydraulic pressures were observed in the eight closely spaced sealed boreholes on the 1130 m level and in borehole 890-188 (Figs. 3A and 10). This indicated that the boreholes were either not interconnected, or only poorly connected. Based on the calculated groundwater table derived from hydraulic pressure measurements, the boreholes were divided into three groups (Figs. 3A and 10): high (890-188, 1130-192 and -273), medium (1130-191, -197, -217 and -260) and low (1130-219 and -267).

There was no or little correlation between TDS and pressure (Figs. 3 and 10). As an example, the two boreholes with the highest pressures, 1130-273 and 1130-192, were among the lowest ($8\text{--}12\text{ g L}^{-1}$) and the highest (38 g L^{-1}) TDS measured at the site, respectively, while waters from the remaining boreholes displayed no consistent pattern in TDS. As individual boreholes were opened and hydraulic pressures decreased, TDS and temperatures also decreased. This was attributed to the presence and dissociation of gas hydrates, which were inferred to occur in the area, and will be discussed further later in the paper (Stotler et al. Submitted for publication). As gas hydrates dissociate, an endothermic reaction occurs, lowering temperatures. At the same time, TDS decreases as the fresh waters in the crystalline hydrate structure are released (Haackel et al., 2004; Hesse, 2003; Hesse and Harrison, 1981; Hesse et al., 2000).

The TDS and pressure data suggested the boreholes were intersecting and connecting different fracture networks of very different salinities and densities. The variations in pressure and TDS suggested two to three once independent fracture systems were connected by the boreholes. It was hypothesized that higher TDS water is pushed up from depth. As boreholes were sealed, this water replaced the less dense water in the boreholes and fracture networks. In most boreholes, these waters mixed to varying degrees relative to fracture network transmissivities. When mine

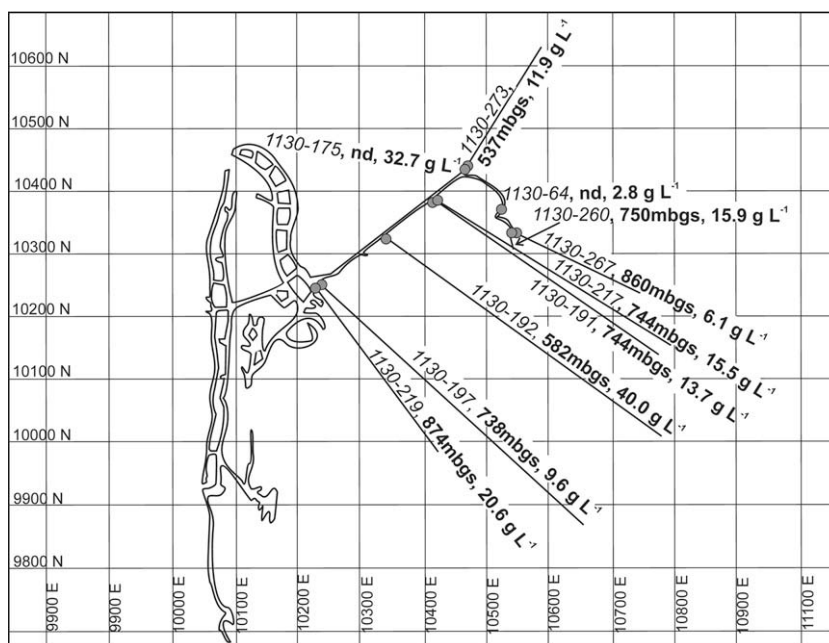


Fig. 10. The Lupin mine 1130 m level plan and drillhole location map. Boreholes are labeled with Borehole number, the highest measured Hydrostatic Pressure (depth of the equivalent fresh water table), and highest measured total dissolved solids (grams per liter). Borehole 1130-175 is drilled downwards 920 m and 1130-64 is drilled upwards 30 m.

work extended below the permafrost, dewatering conducted by the mine depressurized the area immediately surrounding the mine (Stotler et al. Submitted for publication). The drawdown caused by mine dewatering may have encouraged the downward flow of relatively dilute permafrost and/or talik water in these fractures.

Evolution of waters at the Lupin site

Although permafrost fluids were generally found to be contaminated by mining activities, little or no indication of contamination was observed in deep subpermafrost fluids. Over time, fluids from one basal permafrost research borehole (570-105) sampled an increasing proportion of uncontaminated fluid. Here, the data collected will be analyzed to determine any information can be gained about the fluid evolutionary pathway.

The “cryogenic freezing of seawater” hypothesis

Several important observations from this permafrost study were not consistent with the cryogenic formation of crystalline brines from seawater hypothesis (Starinsky and Katz, 2003). First, Lupin waters do not have the chemical signature predicted by the seawater freezing hypothesis. As shown in Fig. 6, the relationship between Na/Cl and Br/Cl ratios for subpermafrost Lupin groundwater was significantly different from seawater evaporation (McCaffrey et al., 1987), hypothesized seawater freezing (Herut et al., 1990), and the hypothesized freshwater dilution trends (Starinsky and Katz, 2003). The extrapolated seawater freezing trend formed the basis of the cryogenic formation of brines from seawater hypothesis (Starinsky and Katz, 2003). Significantly, fluids at Lupin were not as concentrated as predicted by this hypothesis.

Additional information provided by age tracers (He, ^{36}Cl) also suggested Lupin brine formation occurred before the last glacial cycle, contrary to the Starinsky and Katz (2003) hypothesis. While ^{14}C ages did indicate a recharge event during the last glacial advance, there was no apparent correlation of ^{14}C age with salinity. If the saline waters at Lupin formed through freezing on the surface in a glacially-created lagoon, there would be a clear correlation between salinity and ^{14}C age, as the most saline fluids would have formed within the ^{14}C methodology. Further, the presence of methane hydrates throughout the glacial cycle would significantly reduce the permeability and porosity of the rock, slowing transport of surficially derived brines. Therefore, the combined data strongly suggests surficial seawater freezing has not affected deep subsurface waters at Lupin.

Four age tracers (^3H , ^{14}C , ^{36}Cl and He) were analyzed in the deep waters and indicate waters of at least three different ages are mixing. Samples from approximately half of the subpermafrost boreholes monitored occasionally contained minor amounts of tritium ($0.8 < 2$ T.U.) during the 7 year sampling period, with the exceptions of 1130-176, -192, -195, -260, -273 and 1300-105 (Fig. 2E). However, tritium concentrations were typically below detection. The length of time subpermafrost boreholes were purged prior to sealing would suggest negligible drill fluid influence. Radiogenic carbon isotopic evidence (Fig. 5A) from four boreholes indicated a recharge event around 25,000 ybp, roughly the same time as glaciers were forming over the site. The boreholes sampled a wide range of salinity ($3\text{--}40\text{ g L}^{-1}$), thus salinity did not correlate with dateable carbon. The high He concentrations suggest a component of water with between 50 and 500 million years of radiogenic accumulation (McGown et al. Submitted for publication). Nucleogenic ^{36}Cl production in crystalline rocks is typically less than $50 \times 10^{-15}\text{ }^{36}\text{Cl}\cdot\text{Cl}^{-1}$, and generally between 10×10^{-15} and $30 \times 10^{-15}\text{ }^{36}\text{Cl}\cdot\text{Cl}^{-1}$ (Bentley et al., 1986; Phillips, 2000; Cecil, 2000). Although subsurface nucleogenic ^{36}Cl production was not determined at Lupin, ^{36}Cl values in subpermafrost

waters are within the range expected for equilibration with subpermafrost nucleogenic production. Thus, the Cl^- in the subpermafrost system is likely older than the 0.5–1 million year limit of the ^{36}Cl dating method (Phillips, 2000).

Low dissolved bicarbonate values may have been indicative of a lack of carbonate/water interaction, and calculated saturation indices of calcite were typically near saturation in deep waters. Calcite mineralization (CaCO_3) was sparse, and the thin calcite veins were not observed to be producing water. Recent models have suggested most groundwater recharge during glacial periods would occur as glaciers form, rather than from glacial meltwater during retreat (Lemieux, 2006; Lemieux et al., 2008). Direct influences from glaciation on Lupin groundwater chemistry were unclear, but radiogenic carbon (^{14}C) suggests a recharge event of some kind may have occurred at ~ 25 ky, supporting the conclusions of Lemieux et al. (2008). Although ^{14}C -ages indicated a recent recharge event within the last 20,000 years, dissolved ^{36}Cl and high He concentrations indicate a residence time on the order of millions of years (McGown et al. Submitted for publication).

In situ freezing

Although the subpermafrost samples do not follow the hypothesized seawater freezing pathway presented by Herut et al. (1990) (Fig. 6A), modification of subpermafrost waters in situ by freezing cannot be completely ruled out. Several different Canadian and Fennoscandian Shield type brackish fluids were experimentally frozen, including a Sudbury Ca–Cl-type fluid (Zhang and Frape, 2002). The deep Lupin waters follow a similar slope to the frozen Ca–Cl Sudbury water (Fig. 6A). Similar trends were observed at other Canadian Shield sites which may be related to paleo-permafrost (Stotler, 2008).

The wide range of stable isotope ratios and the slight deviation away from the global meteoric waterline (GMWL) and LMWL observed in permafrost water samples reflect the mixing of introduced surface waters from drilling with natural permafrost waters. Stable isotopic values of permafrost waters plot linearly along and slightly below the LEL, with a slope of 6.58‰ and 7‰ VSMOW range in $\delta^{18}\text{O}$ (Fig. 4). In laboratory experiments, frozen waters were found to plot linearly with slopes between 4.32 and 7.44 (Souchez and Jouzel, 1984; Zhang and Frape, 2002). The sampled permafrost waters plot along a similar slope, but originate near the LEL. This was attributed to mixing between natural frozen waters and the drill waters. Large amounts of ice and hoarfrost were observed in many of the mined openings in the permafrost zone, indicating freezing was an on-going process. Even though considerable evaporation likely occurs in open areas of the mine as a result of the strong ventilation, the relationship of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ did not indicate evaporation as a significant process in the permafrost waters. Although the permafrost samples were mixtures of introduced and natural fluids, the effects of freezing were noticeable in stable isotopic compositions.

Evidence concerning the origin and occurrence of methane and other hydrocarbon gases and the formation of methane hydrates in the Lupin area are discussed extensively in a companion paper (Stotler et al. Submitted for publication). Similar to ice formation, important hydrogeologic implications of methane hydrate formation include the potential for sealing of porosity, fracture space, and permeability, elevated ion concentrations and relative depletion of ^2H and ^{18}O in associated groundwater, (e.g. Burt and Williams, 1976; Hesse, 2003; Hesse and Harrison, 1981; Hesse et al., 1985; Kleinberg et al., 2003; Trofimuk et al., 1974; Ussler and Paull, 1995, 2001). Water chemistry can be affected by the ion-exclusion process to the base of hydrate formation, which can be well below the base of the permafrost (e.g. Sloan, 1998). Due to the low permeability of crystalline rocks, methane in these environments may be trapped in gas pockets well beneath the base

of the permafrost, as permafrost does not have to be the primary gas trapping mechanism. Depending on the gas concentration and distribution within the rock mass, several ion exclusion zones may then form within crystalline permafrost. Since gas was only found at certain depths well below the base of permafrost at Lupin (between 890 and 1130 m), up to three ion exclusion zones could form, including at the base of ice-bonded permafrost, and both above and below individual methane hydrate formation zones. However, directly beneath hydrothermal through-taliks, thermal conditions would likely be outside the range of hydrate stability.

Permafrost fluids were too contaminated to determine if in situ freezing affected the ionic chemistry of the permafrost and basal permafrost fluids. The maximum salinities were observed at the site in deeper fluids well below the zone of mine contamination. While these fluids were saline (40 g L^{-1}), they were almost an order of magnitude less concentrated than known Shield fluids (325 g L^{-1} , Frapete et al., 2004). This suggests that in situ freezing processes were not the primary evolutionary mechanism responsible for concentrating these other Shield brines.

Water–rock interaction

The subpermafrost fracture waters at the Lupin mine were more saline ($2.2\text{--}40.0 \text{ g L}^{-1}$) and generally more enriched in calcium than the matrix waters ($0.09\text{--}0.38 \text{ g kg}^{-1}$) (Fig. 6B). It was possible the matrix fluids of sulfide-bearing amphibolites, which had a high Ca/Na ratio, increased the calcium content of the waters relative to the phyllite rock mass, which had significantly lower Ca/Na ratios. Br/Cl ratios and $\delta^{37}\text{Cl}$ in subpermafrost waters are indistinguishable from the matrix waters (Fig. 7). Low matrix salinities at Lupin were similar to those found at High Lake, another Canadian Shield site located in permafrost approximately 90 km north of Lupin (Stotler et al., 2008b). However it was not possible with the limited dataset to determine whether the low matrix salinity was related to site specific (local) or periglacial/glacial processes (e.g. freeze out, cold temperature gradients affecting solute transport or dilute glacial water flushing). The lack of matrix salts would mean that for most parameters, the rock pore fluid would likely be unable to substantially overprint the geochemical signature of saline fluids found in faults.

It was also possible rock salinity was concentrated in fracture minerals. In some crystalline rock environments, a major portion of rock salinity has been attributed to fluid inclusions, and subglacially precipitated calcite has been reported in the literature (Hanshaw and Hallet, 1978; Nordstrom and Olsson, 1987). Fracture infillings at Lupin were generally scarce, potentially limiting their influence on fluid chemistry. Isotopic composition ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) and fluid inclusion microthermometry analyses were performed on a number of hand specimens and drill core fracture calcite samples to determine inclusion salinity and characteristics of the fluid from which it formed. Descriptions of Lupin fracture filling minerals, isotopic composition, and fluid inclusion microthermometry data are provided with [Supplementary material](#).

Several different fluid inclusion assemblages (FIA) were observed in the calcites from the Lupin site. Homogenization temperatures (T_h) indicate all calcites formed at temperatures greater than 73°C . One FIA consisted of only liquid phase inclusions. A second FIA consisted of liquid and gas phase inclusions. The liquid was a high salinity ($>26\%$), Ca/Mg fluid, with homogenization temperatures between 73 and 147°C . The next FIA observed consisted of three phase Na–Cl inclusions with salinities between 31% and 36% and homogenization temperatures between 250 and 271°C . Another FIA consisted of a low salinity ($<3\%$) fluid, with homogenization temperatures between 132 and 148°C . Finally, there was a FIA consisting of what are believed to be CH_4 inclusions. Often, multiple sets of FIA were found in the same fluid inclusion chip, in what appeared to be the same crystal, indicating a boiling

system at the time of crystallization. The high salinity Ca/Mg fluid inclusions could have provided a source of high salinity and calcium for the subpermafrost waters.

The measured calcite isotopic compositions had the largest range of any Canadian or Fennoscandian Shield site studied (Fig. 11A) (Blyth 1992, 2004; Blyth et al., 2000, 2004; Frapete et al., 1992). One especially large subhorizontal calcite vein, found at the 540 level, along the access ramp, had a particularly wide range of values ($\delta^{13}\text{C}$: -2.08‰ to $+30.09\text{‰}$ and $\delta^{18}\text{O}$: -14.49‰ to -6.29‰). The samples were among the most enriched $\delta^{13}\text{C}$ sampled in the Canadian or Fennoscandian Shields, although Ylivieska, Outokumpu, Stripa and Gidea were also relatively enriched ($+20\text{‰}$ PDB) (Blyth 1993, 2004; Blyth et al., 2000, 2004, 2009; Frapete et al., 1992).

Oxygen isotopic compositions and T_h of the calcite emplacement waters were interpreted following the methods of Blyth et al. (2000, 2004) to determine the isotopic composition of the fluid from which the calcites formed. Some of the most saline inclusions, with the highest homogenization temperatures, were likely emplaced by a heavy water ($\delta^{18}\text{O} > +10\text{‰}$ SMOW, Fig. 11B). Another FIA appeared to have been carried by a slightly lighter water, 0‰ SMOW $> \delta^{18}\text{O} > -10\text{‰}$ SMOW. Finally, a FIA appeared to crystallize from an extremely light water, -20‰ SMOW $> \delta^{18}\text{O} > -30\text{‰}$ SMOW. Although this water was isotopically light, similar to cold climate precipitation, homogenization temperatures greater than 80°C and inclusion salinities of greater than $20 \text{ wt.}\%$ indicated this was still a higher temperature hydrothermal fluid. The hydrothermal or metamorphic origin of the calcites suggested they were greater than one billion years in age, possibly as old as peak ($2.5\text{--}2.7 \text{ Ga}$) or retrograde ($1.84\text{--}1.81 \text{ Ga}$) metamorphism, and not of glacial origin. Further comparison of the microthermometric data with isotopic data (Fig. 11) showed no further trends or patterns.

The sampled dissolved load is much greater in the fracture waters than the matrix waters, thus the rock matrix was not likely able to substantially overprint fracture water chemistry. However, some calcite fluid inclusions have sufficient salinity to account for the observed TDS in the most saline deep waters.

Conceptual model

The complete conceptual model for the Lupin area is presented in Fig. 12. A thin active layer only affected the upper $\sim 1\text{--}8 \text{ m}$. Small lakes froze completely and had no taliks, while other larger and deeper lakes (300 m wide) contained open taliks. Larger lakes ($>500 \text{ m}$ wide), including Lake Contwoyto, had hydrothermal through-taliks. Permafrost fluids were mixtures of drilling salt, blasting remnants and natural fluids. Introduction of mine-brine, mine-induced drawdown and gas hydrate melting complicated direct investigation into the effects of in situ freezing effects, but there were indications that in situ freezing of formation waters affected the groundwater chemistry. Basal permafrost waters had similar salinities as the most dilute deep subpermafrost waters. Elevated sulfate in the basal subpermafrost waters was a result of natural and mining enhanced oxidation of sulfides in the rock. Under the right conditions of fracture/foliation interconnection, intersection with taliks, and a hydraulic gradient (i.e. due to mine dewatering activities), a hydraulic pathway may allow for the recharge of fresh talik waters to depth. Given that many of the horizontal boreholes cut almost perpendicular across the foliation and intercepted numerous geological structural elements, it was possible that the small amounts of dilute water observed in some of the deep saline water zones were transported to depth under these conditions. However, although a downward gradient for dilute talik water was provided by mine dewatering, there was no evidence of the contaminated permafrost fluids at depth. Therefore, the primary dilute water source at the 890 and 1130 m levels was likely

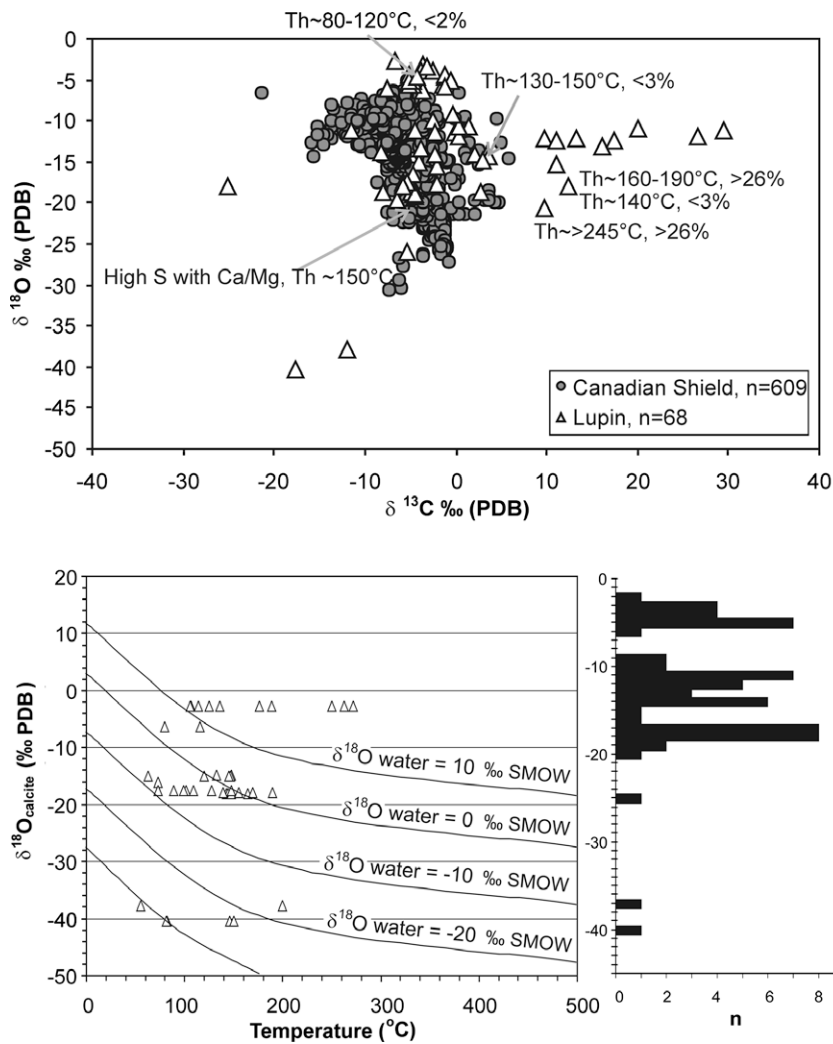


Fig. 11. Lupin calcites with microthermometry data (A) vs. Canadian Shield calcites (Jones, 1987; Frapce et al., 1992; Blyth, 1993) and (B) isotopic thermometric plot for Lupin calcites.

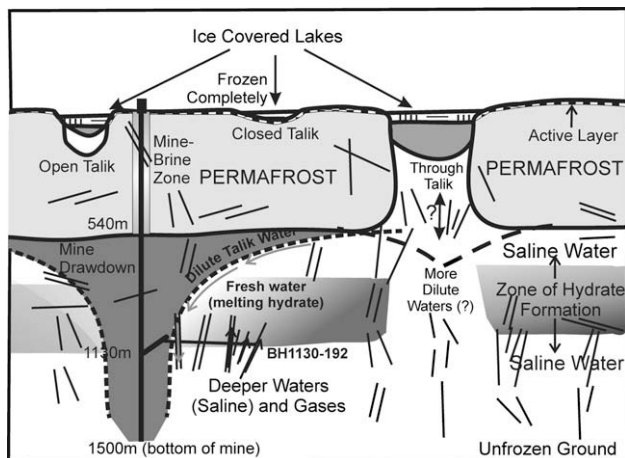


Fig. 12. Hydrogeologic conceptual model of the Lupin area.

melting gas hydrates, due to anthropogenic mine depressurization. Methane hydrates would not exist beneath hydrothermal through-taliks, due to the warmer subsurface temperature conditions. Methane hydrate formation should cause similar ionic fractiona-

tions as ice formation. Thus, while ice formation within the permafrost is not necessarily the cause of the observed ionic trends in the subpermafrost, the methane hydrate formation process is a type of freezing with similar geochemical effects to residual fluids. The varied ages from different age dating methodologies indicate mixing of fluids is occurring.

Conclusions

Geochemical data from the Lupin site clearly show the contaminated permafrost water is distinct from the subpermafrost water, however the degree to which freezing modified the chemistry at the site is difficult to quantify. The observed deep groundwater chemistry at Lupin did not evolve as cryogenically concentrated of seawater. Large variation of the isotopes of chlorine, hydrogen and oxygen was apparent in the permafrost. For hydrogen and oxygen isotopes, this was attributed to freezing of the introduced drill brine.

Although various geochemical parameters suggest the waters associated with the “ramp fault” sampled in the permafrost have been heavily affected by mining activities, natural geochemical components are observed as well. Much of the dissolved load analyzed in the permafrost waters was from the use of drilling brine for work in the permafrost areas by mine personnel. Nitrate

accumulation was a result of blasting activities and its persistence was due to oxic to suboxic conditions. Some constituents (i.e. SO_4^{2-}) within the permafrost may have been a result of natural processes, although it is unclear to what extent formation was influenced by mining operations.

For hydrogeologic modeling, permafrost in areas with numerous large lakes should be treated as a leaky confining layer, rather than a completely impermeable barrier. Although ice and methane hydrate formation in deep permafrost may seal many potential flow routes in the crystalline bedrock, through-taliks can form tube-like conduits through frozen ground. The presence of through-taliks beneath Lake Contwoyto and several smaller lakes in the area was suspected. It was unclear from the investigation what impacts taliks would have on waters at depth at an undisturbed location. Many large lakes in the Canadian and Fennoscandian Shields, including Lake Contwoyto, appear to be associated with fracture zones. Thus taliks may provide the hydraulic pathways, if not the gradients, required for recharge through permafrost.

There are several implications of this research for deep geologic radioactive waste disposal. Even considering the contamination, brines were not found at Lupin at repository depth. Thus, in situ freeze-out during permafrost/methane hydrate formation is not considered to be able to create such strongly concentrated fluids. Deep (~1 km) recharge of glacial meltwater was not ruled out, although artificially induced hydraulic gradients from mining appeared to cause mixing of fluids of different ages at the sample depths. An upper limit to potential fluid salinities during methane hydrate formation should be investigated. A repository placed in an area currently influenced by permafrost conditions would need to constrain the effects of hydrate and permafrost dissociation due to heat generated from the repository. Thermal modeling should constrain the possibility for heat generated by the repository to create a hydrothermal talik through permafrost. Should hydrothermal taliks form due to repository heat, understanding how taliks affect deep groundwater flow system evolution in permafrost environments would become critical for safe radioactive waste disposal in northern countries.

This research also had several important implications for exploring for subsurface life on other planetary bodies. Fluid and gas present beneath thick permafrost in tectonically inactive environments can provide vital nutrients and a medium necessary for life to exist. Although lake-formed hydrothermal taliks would not be a feature on an extraterrestrial body such as Mars, if a pressure or chemical talik were to form, hydrologic connections to the surface through the permafrost may also be created.

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for the Lupin mine and Antero Lindberg supervised the diamond drillings. Field and technical assistance was provided by various members of the funding agencies, including Runar Blomqvist, Kimmo Lehto, Lena Moren and Paul Degnan. We also acknowledge two anonymous reviewers and Prosun Bhattacharya for comments that improved the manuscript.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhydrol.2009.04.013.

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