



Disruption of the geochemical metal cycle during mining: Multiple isotope studies of lake sediments from Schefferville, subarctic Québec



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ABSTRACT

Iron mining in Schefferville (1939–1977) in subarctic Quebec has left behind large numbers and quantities of tailing deposits. The impact of past mining activity on aquatic ecosystems in the Schefferville area has been studied using geochemical and isotopic (Pb, Zn and Fe) analyses of lake sediments, ore deposits, tailings and epiphytic lichens. Analysis of two sediment cores from Lakes Dauriat and Oksana reveals that the surface geochemical cycle of the Schefferville area has been profoundly disturbed by anthropogenic activity such as mining. Disturbances were particularly abrupt at the transitions from pre-mining to mining and mining to post-mining periods. Elemental and isotopic analyses of the lake sediments reveal four different end-member contributions to the lake sedimentation, with changes in terms of sources and source contribution observed throughout the sedimentation history. End-members were identified using Pb, Zn and Fe isotopes and are consistent for each element. Lead isotope ratios vary from highly radiogenic ($^{206}\text{Pb}/^{204}\text{Pb} = 27$) to less radiogenic ($^{206}\text{Pb}/^{204}\text{Pb} = 17.7$) from the bottom to the top of the sediment cores. Iron isotope compositions vary from -0.2% to 1% , the latter value remaining constant throughout the sedimentary history of Lake Oksana. A systematic difference in the Zn isotope ratios of the two lakes is also observed, and can be explained by local differences in basin lithology. In order to identify pollution sources, samples from ores and tailings and epiphytic lichens were measured as proxies of mining activity, lithology, and atmospheric deposition, respectively.

The impact of anthropogenic activity is clearly evident in the sediment records and results from mining activity, as well as local urban and industrial activities (waste water inputs). Long-range atmospheric deposition also accounts for some of the variations in isotopic composition measured in the sediments. The systematic coupling of Pb isotopes with Zn or Fe isotopes allows us to identify and constrain the metal sources that contributed to sediment contamination. This study demonstrates that disturbance due to mining activities is very effective in rapidly modifying lake sediment composition. Though the disturbances remained local in terms of geographic extent, the damage to the aquatic ecosystem has been significant and may persist for decades.

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1. Introduction

Mining operations produce negative impacts on the environment through the generation of mineral and other wastes that are transported across the land and through the atmosphere. This waste includes products used for ore extraction, as well as waste rock and anthropogenic waste associated with mining activities. The environmental impacts associated with mining mostly result from mechanical damage to soils, ecosystems and landscapes and from the effects of acid mine drainage (Dudka and Adriano, 1997). Large amounts of dust are emitted into the atmosphere during ore extraction, pre-treatment (crushing) and transport, especially in open pits, which generate significantly

more atmospheric pollution than underground mines (Dudka and Adriano, 1997). Ore-processing by smelting and refining releases many trace elements in particulate and gaseous forms (Dudka et al., 1995; Simonetti et al., 2004). These particles are later deposited in terrestrial and aquatic environments via dry and wet deposition (Baron et al., 2006; Sivry et al., 2008). In aquatic ecosystems, trace elements released by mining activity are found in both water and sediments. The concentrations of chemical elements in sediments usually increase significantly at the beginning of mining activity and then, as leaching of metals into aquatic systems is a relatively slow process, peak in the post-mining period (Dudka and Adriano, 1997).

Prior to the mining, the Schefferville area was occupied by nomadic people (Humphrys, 2013) such as the Montagnais and the Naskapis (Barbeau, 1987). The first mining company was officially launched in 1947, for Fe ore extraction, but mining exploration is known to have started during the early 20th century. The town of Schefferville was

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built during the same period, in parallel with the development of the mines. To transport and market the ore, a railway was constructed, connecting Schefferville with Sept-îles (Humphrys, 2013). Schefferville experienced almost exponential growth up until the beginning of the 1980s. Wastewater was drained into Lake Dauriat, located in the town centre, until 1975, when a wastewater treatment plant was built. However, fierce competition from mining companies in Brazil and Australia, led to a decline in ore mining and growth of the city was halted. The Schefferville mines eventually closed in November 1982 (Barbeau, 1987). However, due to a relatively recent inflation in the price of iron, mining activity around Schefferville restarted in June 2011.

The mining of metals has the potential to disturb the surface geochemical cycle of metals, resulting in significant increases in the concentrations of trace and toxic elements in the environment (Thornton, 1996). Metal concentrations and isotopic compositions analysis of archives are very useful for obtaining information on trace element contamination. Lake sediments are particularly useful records of changes in metal inputs to the environment (Gallon et al., 2005; Thapalia et al., 2010), being formed through a combination of atmospheric deposition, deposition from the watershed's drainage system and precipitation of organic and mineral matter from the water column. Epiphytic lichens provide a proxy for atmospheric deposition alone, and can therefore complement sediment records for source identification.

The use of Pb isotopes for identifying sources of contamination has become routine in the last few decades (Graney et al., 1995; Weiss and Shoty, 1999; Simonetti et al., 2000; Monna et al., 2004; Cloquet et al., 2015). This is largely because Pb isotopes are not altered by chemical or physical processes (Ault et al., 1970). Lead does not fractionate and therefore retains the isotopic composition of its source. Identification of past Pb source contamination has been studied in sediments (Nedjai et al., 2011; Thevenon et al., 2011) and peat bogs (Weiss and Shoty, 1999; Baron et al., 2005). The use of epiphytic lichens in trees has also proved very effective for identifying long-range atmospheric transport (Carignan and Gariépy, 1995; Carignan et al., 2002).

Zinc (Zn) and Iron (Fe) isotopic compositions can be used in addition to Pb because, unlike Pb, these can be modified by a range of different processes. With the advent of Multicollector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), the analytical precision of Zn (Albarede, 2004; Cloquet et al., 2008) and Fe (Dauphas and Rouxel, 2006) isotope ratio measurements has become smaller than the natural variations. This has opened up new opportunities for the study of the biogeochemical cycling. Zn emitted into the atmosphere through smelting and refining is enriched in the lighter Zn isotopes, whereas Zn in tailings and slags is enriched in the heavier Zn isotopes (Cloquet et al., 2006b; Dolgoplova et al., 2006; Sivry et al., 2008; Sonke et al., 2008; Mattielli et al., 2009). Distinctly light $\delta^{66}\text{Zn}$ values have been measured in urban runoff (Cloquet et al., 2006b; Chen et al., 2008; Chen et al., 2009). The identification of different mining periods has been achieved using Zn isotopes (Borrok et al., 2009; Thapalia et al., 2010), demonstrating that Zn isotopes can be used as tracers of environmental contamination. In addition, iron is the sixth most abundant element in the universe and represents 35% of the Earth's mass. It is also the main ore present in the Schefferville area. These three isotopic systems are therefore complementary and can provide different types of information on pollution sources.

In this study, we report the down-core changes in the geochemical and isotopic (Pb, Zn and Fe) composition in two sediment cores from two lakes in the Schefferville area (Lake Dauriat and Lake Oksana). Lake Oksana was chosen specifically because of its remoteness from the mining area in that it has therefore recorded the integrated signal of atmospheric pollution (as opposed to proximal mining activities), 2) Lake Dauriat was selected because of its proximity to the town of Schefferville. This lake therefore provides an integrated signal of the impacts of different types of urban pollution (gas, sewage, municipal waste etc.). In order to determine the chemical and isotopic compositions of the different metal sources in the Schefferville area lakes, geochemical

and isotopic analyses were performed on epiphytic lichens (current atmospheric signal of the study area), as well as on ore deposits and tailings (anthropogenic signals related to the past Fe mining).

A combination of climatic change (i.e., warming of arctic regions and melting of permafrost) and growing economic pressure (i.e., Quebec's *Plan Nord*), has made areas like the Schefferville region increasingly accessible and attractive to mining companies. The main objective of this research is to gain a better understanding of the multiple disturbances that have affected the dynamics and kinetics of the surficial geochemical cycles of metals associated with mining activities in northern landscapes like the Schefferville area.

2. Study site

Lakes Dauriat (54°48'17.52"N, 66°49'27.31"W) and Oksana (54°47'35.85"N, 66°47'16.05"W) are located near the town of Schefferville (Fig. 1), in the New Québec Orogen (NQO), also known as the Labrador Trough. The NQO is located on the border of the Superior and Churchill geological provinces (Clark and Wares, 2004). It is composed of rocks of Lower Proterozoic age (ca 2.2 to 1.8 Ga) comprising three sedimentary facies (two of which are volcanic in origin and the other metamorphic in origin). These sequences contain orthoquartzites, dolomites, iron formations, greywackes and conglomerates of sedimentary rocks (Dimorth, 1981). The sedimentary rocks of the Schefferville area were deposited in marine and fluvial environments (Clark and Wares, 2004). The area lies partly within the Sokoman formation and partly within the Ruth formation. During the end of the Lower Proterozoic, the Sokoman formation and underlying rocks were faulted and folded. The rocks of the Schefferville area are mainly composed of quartz, iron oxides and carbonates that have been chemically precipitated. During its formation, the ore from the Schefferville area was a taconitic-poor iron ore (25–30% Fe). During the Mesozoic, the experienced meteoric leaching resulted in a decrease in Si/Fe and Si/Mn, thereby making the ore exploitable (60% Fe; Leslie and Bourque, 1984). The Schefferville iron ore is composed of two main types of deposit: the ore call “soft ore” and the “rubble ore”. The “soft ore” mainly consists of hydroxides (limonite and goethite). The “rubble ore” is mainly formed from/ of goethite originating from the fragmentation and cementation of the “soft ore” (Leslie and Bourque, 1984).

The Schefferville area is located in a forest-tundra vegetation zone (Plan Nord, 2011) mainly composed of lichens (*Cladonia*), dwarf birch (*Betula nana*), shrubs of the genera *Kalmia* and *Vaccinium* and crowberry (*Empetrum nigrum*), as well as black spruce (*Picea mariana*) and white spruce (*Picea glauca*) trees. The catchments of lakes and rivers are mostly occupied by larch (*Larix laricina*) (Journaux and Taillefer, 1957).

The climate of the region is subarctic, characterised by long and cold winters and short but relatively warm summers (Government of Quebec, 2010). Between June and August, the three warmest months, the average monthly temperature is around 10 °C. Near the town of Schefferville, the prevailing wind direction is northwest with an average speed > 15 km/h throughout the year (Environment Canada, 2011).

3. Materials and methods

Two sediment cores from Lakes Oksana and Dauriat were initially drilled in 1999. The two lakes were sampled again in March 2012 in order to complete the sediment chronology of the last fifteen years. Sediment cores were collected with a short Aquatic Research Instruments percussion corer (40 cm length), in roughly the middle of the lakes. The water column measures 3.5 m at Lake Dauriat and 12 m at Lake Oksana. Lake Dauriat has one tributary (south of the lake) and one effluent (north-west of the lake). The core was collected from outside the draining network. Lake Oksana is a “Kettle lake” i.e., has no tributary or effluent. Cores were mainly composed of thin and sandy sediments and organic matter. The colour of the Lake Dauriat sediment changed from brown to black along the length of the core, reflecting the change

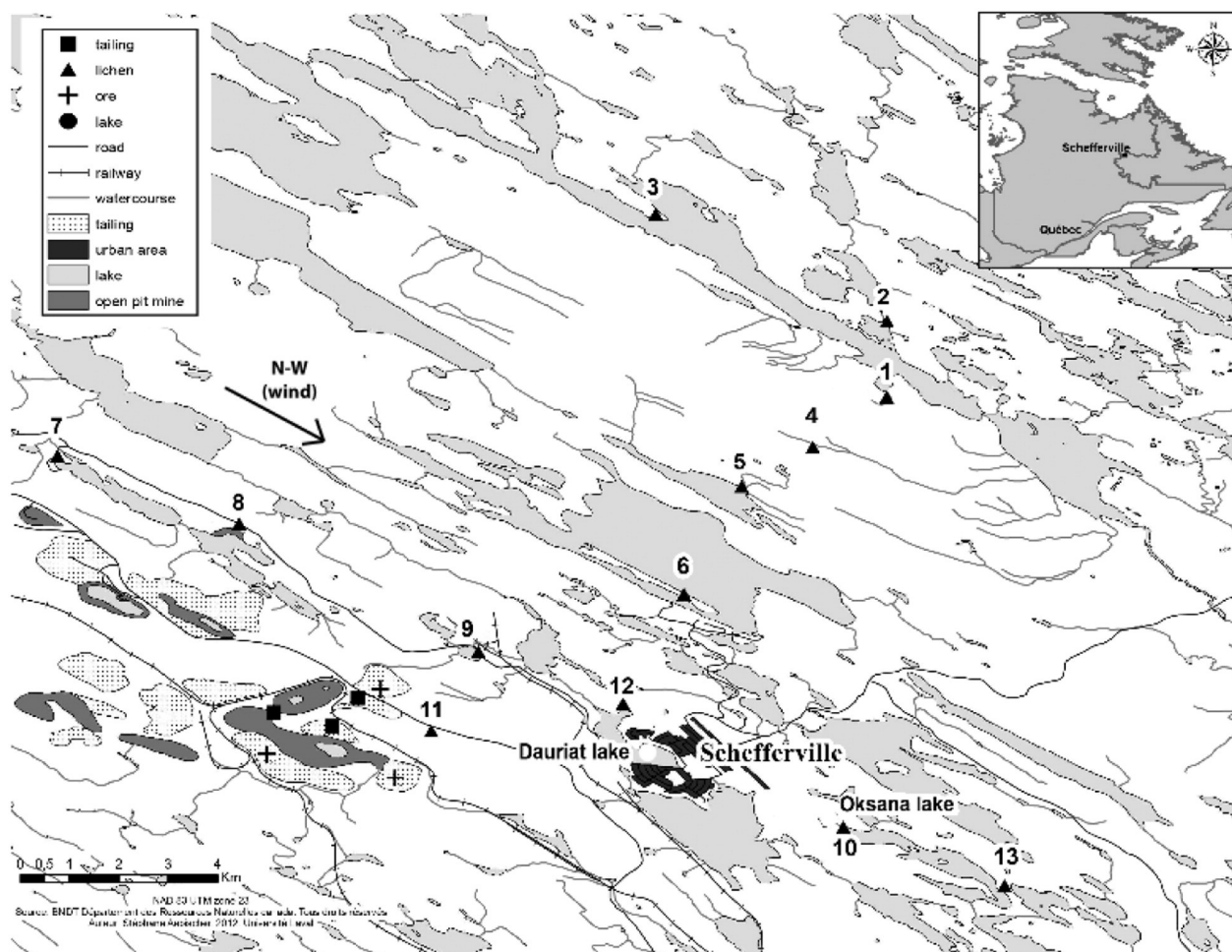


Fig. 1. Map showing the location of the town of Schefferville and the various sampling sites in the surrounding area.

from pre-mining to post-mining periods, whereas the Lake Oksana sediments were uniformly green-black in colour.

Epiphytic lichens of the genus *Bryoria* were collected by hand from young Larch and spruce tree branches (≤ 5 years old) using pre-cleaned latex gloves and then stored in sealed bags. Ore and tailing deposits were sampled in old open pits with pre-cleaned latex gloves and also stored in sealed bags. Tailings were sampled around the open pits and represent the non exploitable part of the ore. Samples were lyophilized and finely ground (particle size less than $80 \mu\text{m}$) in an agate mortar.

Lake sedimentation rates were estimated using ^{210}Pb and ^{137}Cs dating techniques. Dating was performed at the radiochronology laboratory of Centre for Northern Studies (CEN) at Université Laval, using the High-Purity Germanium detector method. The Constant Initial Concentration (CIC) and Constant Rate of Supply (CRS) models were used to date sediments.

Chemical analyses were performed at the Service d'Analyse des Roches et des Minéraux (SARM) at the Centre National de la Recherche Scientifique – CNRS (Nancy, France). An Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Elemental Icap 6100) and an Inductively Coupled Plasma Mass Spectrometer (ICP-MS Thermo Elemental X7) were used for determining concentrations of major elements and trace elements, respectively. Samples were prepared and measured following the procedure of Carignan et al. (2001). In brief, samples were melted by alkaline fusion (using LiBO_2) and the fusion product was then dissolved in diluted nitric acid (see SARM website for further information about detection limits and precision).

Isotopic analyses were performed using a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS, Thermo Scientific Neptune Plus) at CRPG, Nancy. Isotope samples were completely digested on a hot plate at 120°C using various mixtures of acids (HNO_3 , HCl and HF , as well as hydrogen peroxide for lichens). Once dissolved, the chemical elements of interest were isolated using ion exchange chromatography. Isolation of Pb was performed on a chromatographic column containing AG1-X8 200–400 mesh resin (Cloquet et al., 2006a). After being fixed in HBr 0.8 M, Pb was recovered in HCl 6 M. Isolation of Zn and Fe was achieved on a chromatographic column (biored polyprop 2 ml) containing AG MP-1 resin (modified from Maréchal et al., 1999), with Fe eluted first with HCl 0.5 M and Zn then recovered with HNO_3 0.5 M. Total procedural blanks were also determined and were found to be negligible (300 pg Pb, 15 ng Zn and 10 ng Fe) compared to the amount of elements contained in the samples.

International standard solutions were measured to correct for instrumental drift. SRM 981 was used for Pb with addition of TI SRM 997, IRMM-3702 was used for Zn analyses doped with Cu IRMM 976, and IRMM-014 was used for Fe analyses. Iron was measured using the standard-sample bracketing technique (Marin-Carbonne et al., 2011; Liu et al., 2014) and Zn and Pb were measured using both external normalisation and the standard-sample bracketing technique. Iron isotopes were measured in medium resolution in order to resolve ArO and ArOH and to control potential ArN isobaric interferences on Fe masses. Reference materials were measured in order to monitor potential alterations of the isotopic composition of the samples throughout the procedure. The isotopic compositions of the GSD-10 (river sediment), BCR-482

(lichen) and BCR-1 (basalt) were determined and corresponded to literature data within uncertainties. In addition, during Zn measurements, JMC_{lyon} was frequently measured over IRMM-3702 and yielded $\delta^{66}Zn_{JMC_{lyon}} = -0.27 \pm 0.07\%$ (2 times standard deviation, $n = 23$). These results are consistent with both literature data and previous results obtained and can therefore be regarded as showing long term reproducibility. The Zn results presented in this study are reported relative to IRMM 3702 and 0.27‰ must therefore be added in order to match the JMC_{lyon} scale. Since individual sample measurements of Zn and Fe usually provided better precision, we chose to apply a 2sd of 0.1‰ to all measurements and for the discussion of the results.

4. Results

4.1. Epiphytic lichens

Lichens are excellent indicators of air quality and pollution sources as human disturbances have a measurable impact on these organisms. These effects can be easily measured in lichens because of their slow metabolism and absorption of airborne particles without selection (e.g., Gough and Erdman, 1977; Déruelle and Lallemand, 1983), and epiphytic lichens are therefore commonly used proxies for atmospheric fallout. The measured Pb and Zn concentrations, Pb enrichment factors (EF) and Pb and Zn isotope ratios of epiphytic lichens are listed in Table 1. Lead concentrations in lichens range from 0.8 to 5.6 $\mu\text{g/g}$. The Pb concentrations of epiphytic lichens appear to decrease with increasing distance from the town and/or the Schefferville mines (Fig. 2). Zinc concentrations in the same lichens range from 29.7 to 88.7 $\mu\text{g/g}$. A negative trend is also observed between Zn concentration and distance from the town. However, no clear trend is observed with distance from the mines, suggesting that the town is the only source of Zn here. Moreover, Pb and Zn sources appear to be partly decoupled. Enrichment factors are used to assess the origins of the chemical elements found in organic and inorganic compounds and are calculated as follows (Klos et al., 2011) using Taylor and McLennan (1995) values:

$$EF-Pb_{\text{lichens}} = (Pb/Al)_{\text{lichens}} / (Pb/Al)_{\text{crust}}$$

Aluminium entering the atmosphere is rarely of anthropogenic origin, and generally has a crustal composition. The $EF-Pb_{\text{lichen}}$ values in this study are all >10 , ranging from 15.8 to 155.3, which means that 90% to 99% of the Pb contained in these lichens comes from anthropogenic sources.

The Pb isotopic compositions of the epiphytic lichens are relatively homogeneous (average $^{206}Pb/^{207}Pb = 1.153$, $SD = 0.003$), except for three samples (1 + 2, 6 and 8) that have $^{206}Pb/^{207}Pb$ values of 1.21, 1.11 and 1.17, respectively (Table 1). Unlike Pb concentrations, no trends are observed in Pb isotope ratios with distance from the town or mines.

The Zn isotopic composition of epiphytic lichens, expressed as $\delta^{66}Zn$, varies from -0.07 to 0.47% , the average and median values being

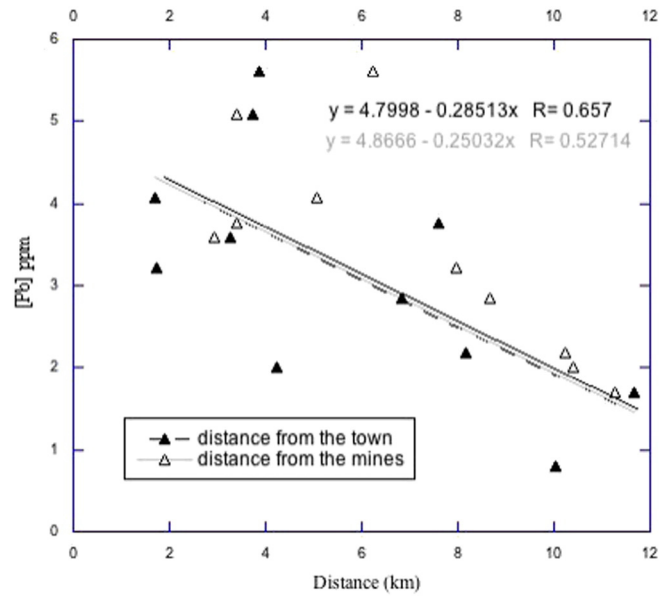


Fig. 2. Lead concentrations in epiphytic lichens in relation to the distance of the town and the mines of Schefferville.

0.27‰ and 0.30‰. Like Pb, there appears to be no significant relationship between Zn isotope composition and distance from the town or mines. Only three of the lichen sites measured (4 + 5, 7 and 10) have a $\delta^{66}Zn$ value different from 0.3‰ within uncertainties, and these are not the same sites as those reported for Pb. Of note, there does not appear to be a geographical relationship between any of the anomalous points or sites identified, neither for Pb nor for Zn.

Of the different isotopic systems studied in lichens here, Fe presents the most homogeneous composition. The $\delta^{56}Fe$ values vary between 0.08‰ and 0.21‰, with an average of 0.1‰ and median of 0.12‰. The $\delta^{56}Fe$ reported in lichens from the study area can be considered identical within 0.1‰ with the exception of sites 1 + 2 (0.21‰) and 7 (0.19‰).

4.2. Ore and tailings

Chemical concentrations are more homogeneous in the tailings than in the ore samples (Table 2). The Fe ore concentrations are high, between 30% and $>66\%$ (average = 46%), while the tailings have lower Fe concentrations, from 20% to 40% (average = 32%). In contrast, Zn ore concentrations (25 ppm or less) are lower than in tailings (53–58 $\mu\text{g/g}$, average = 55.5). The Pb ore concentrations (3.45–7.95 $\mu\text{g/g}$) with an average of 6.3 ppm are also lower than in tailings (15–22 $\mu\text{g/g}$, average = 17.8 $\mu\text{g/g}$).

Lead, Fe and Zn isotope compositions were determined on three ore samples and three tailing samples (Table 2) and were found to be heterogeneous in the three isotopic systems. The Pb isotope ratios are

Table 1
Concentrations, enrichment factors (EF) and Pb and Zn isotopic compositions of epiphytic lichens.

Sample ID	Lat. N	Long. W	Altitude (m)	Zn (ppm)	Pb (ppm)	EF – Pb	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$\delta^{66}Zn$	$\delta^{56}Fe$
1 + 2	54°52'16"	66°46'26"	471	43.67	2.19	16	18.908	15.599	37.62	1.21407	0.30	0.17
3	54°54'21"	66°48'58"	479	61.60	1.70	109	18.105	15.675	38.08	1.15251	0.30	0.07
4 + 5	54°51'41"	66°47'30"	562	78.61	2.85	69	17.830	15.514	37.52	1.14895	0.15	0.10
6	54°50'8"	66°48'43"	491	42.33	5.61	155	17.244	15.521	36.94	1.11075	0.39	0.13
7	54°51'39"	66°55'42"	513	29.72	0.80	32	17.897	15.516	37.63	1.15293	-0.07	0.21
8	54°50'54"	66°53'50"	524	37.96	3.75	27	18.229	15.578	37.87	1.17015	0.29	0.13
9	54°49'29"	66°51'8"	521	28.97	5.09	55	18.080	15.592	37.78	1.15966	0.35	0.07
10	54°47'37"	66°47'15"	530	88.70	3.21	89	17.902	15.566	37.61	1.14996	0.47	0.12
11	54°48'38"	66°51'36"	593	70.33	3.59	79	17.980	15.585	37.69	1.15362	0.31	0.12
12	54°48'50"	66°49'31"	502	36.01	4.07	56	18.001	15.580	37.70	1.15537	0.27	0.05
13	54°46'50"	66°45'20"	501	64.50	2.00	68	17.950	15.546	37.69	1.15469	0.25	0.11
BCR 482							17.605	15.568	37.48	1.13089	-0.32	-0.02

Table 2

Pb, Zn and Fe concentrations and lead and zinc isotope ratios of ore and tailings.

Material	Lat.N	Long.W	Altitude (m)	Fe (ppm)	Zn (ppm)	Pb (ppm)	Al ₂ O ₃ (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	δ ⁶⁶ Zn	δ ⁵⁶ Fe
ore	54°29'8"	66°31'23"	607	308,077	<L.D.	7.6	0.20	18.005	37.45	1.1549	0.19	0.91
ore	54°29'8"	66°31'23"	607	669,348	<L.D.	3.5	0.39	17.737	37.37	1.1395	0.75	1.47
ore	54°29'8"	66°31'23"	607	424,117	25.6	8.0	0.16	19.613	37.97	1.2219	0.53	0.91
tailing	54°29'8"	66°31'23"	607	379,736	58.4	21.6	11.53	25.346	40.33	1.5522	−0.06	0.19
tailing	54°29'2"	66°31'26"	615	199,346	54.4	15.8	8.76	24.016	40.25	1.4813	0.27	0.58
tailing	54°29'6"	66°31'55"	616	396,244	53.8	16.1	8.53	25.311	41.44	1.5424	0.45	0.62

more radiogenic in the tailing samples (²⁰⁶Pb/²⁰⁴Pb between 25.34 and 24.01) than in the ore samples (²⁰⁶Pb/²⁰⁴Pb between 17.74 and 19.61) and there is negligible scatter in the values. The Zn isotope ratio values (δ⁶⁶Zn) are significantly higher in the ore samples (δ⁶⁶Zn between 0.19‰ and 0.75‰, average = 0.49‰) than in the tailing samples (−0.06‰ and 0.45‰, average = 0.22‰). The same can be observed for Fe isotope ratio values. The δ⁵⁶Fe of ore samples range between 0.90‰ and 1.48‰ (average = 1.10‰), whereas tailing samples display values of + 0.18‰ up to 0.62‰ (average = 0.46‰).

4.3. Lake sediments

4.3.1. Dating

The age-depth chronology of the lake sediment cores was established using ²¹⁰Pb analyses and radioactive markers (¹³⁷Cs) using an Excel macro (Tremblay and Bouchard, 2010). The CRS sedimentation model was selected for the whole of the lake Oksana core sampled during the 2012 field mission. A linear regression was derived from this model to date the sediments sampled in 1999 and a sedimentation rate of 0.083 cm/y was determined. The Lake Dauriat sediments sampled in 1999 were dated by Laperrière et al. (2007, 2009). An average sedimentation rate of 0.93 cm/year (−λ/slope) was calculated for the last decade surface sediments of Lake Dauriat (sampled in 2012).

4.3.2. Elemental variations

Lake Dauriat was selected for study because of its proximity to the town of Schefferville (Fig. 1) and its lake sediments have indeed recorded human disturbances associated with the town's construction and development (Table 3). The concentrations of Fe, Pb and Zn in the lake sediments increased significantly during the active mining period (1939–1977) (Table 3) and Al normalisation revealed an anthropogenic origin for these variations with clear Pb/Al, Fe/Al and Zn/Al ratios increase during the mining period and clear decreases during the post-mining period, yet without ever reaching pre-mining period concentrations.

Table 3Zr/Th ratios, Pb, Zn, Fe and Al concentrations, Al₂O₃ %, and Pb, Fe and Zn isotopes of lake Dauriat.

Z (cm)	Year	Zr/Th	Pb (ppm)	Zn (ppm)	Fe (ppm)	Al ₂ O ₃ (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	δ ⁵⁶ Fe	δ ⁵⁷ Fe	δ ⁶⁶ Zn	δ ⁶⁸ Zn
0.25	2012	13.2	79	415	159,820	8.50	18.171	15.617	37.773	2.0788	1.1635	0.00	0.01	0.13	0.27
1.75	2011	13.7	81	436	161,954	8.54	18.151	15.625	37.782	2.0815	1.1617	−	−	0.12	0.24
3.75	2008	12.9	85	451	162,164	8.61	18.132	15.606	37.730	2.0809	1.1618	−0.23	−0.38	0.14	0.29
5.75	2006	13.2	84	440	162,094	8.66	18.154	15.612	37.769	2.0805	1.1628	−	−	0.13	0.27
7.75	2004	23.8	89	462	160,764	8.88	18.152	15.618	37.774	2.0810	1.1623	0.02	0.07	0.18	0.35
16	1997	11.8	103	408	166,710	8.43	18.116	15.609	37.744	2.0835	1.1606	0.14	0.17	0.07	0.13
20	1993	11.5	106	368	162,198	8.71	18.105	15.600	37.724	2.0836	1.1606	0.08	0.19	−0.02	−0.05
22	1990	11.4	121	322	162,372	8.94	18.084	15.595	37.717	2.0856	1.1596	0.09	0.13	−0.02	−0.03
24	1988	11.1	132	405	163,248	8.40	18.052	15.600	37.722	2.0896	1.1572	0.02	0.12	−0.04	−0.09
26	1985	11.2	147	318	166,640	8.43	18.044	15.601	37.725	2.0907	1.1566	−0.11	−0.12	−0.02	−0.06
30	1980	10.0	119	319	176,956	8.28	17.733	15.570	37.429	2.1107	1.1389	−0.07	−0.1	0.01	0.02
34	1974	7.3	149	661	185,104	9.49	17.707	15.567	37.334	2.1084	1.1375	−0.07	−0.09	−0.02	−0.11
36	1970	8.1	136	334	236,128	8.64	18.038	15.598	37.730	2.0917	1.1564	0.04	0.06	−0.08	−0.17
38	1965	8.3	93	588	255,082	8.30	18.013	15.589	37.701	2.0930	1.1555	−0.02	−0.09	−0.01	−0.02
42	1950	9.1	75	631	128,100	12.33	18.019	15.595	37.713	2.0930	1.1555	0.17	0.27	0.01	0.01
44	1939	14.0	45	263	103,746	11.50	18.865	15.673	38.192	2.0245	1.2037	0.24	0.23	−0.12	−0.24
46	1930	15.5	16	111	97,662	10.89	20.387	15.815	39.352	1.9303	1.2891	0.27	0.34	0.08	0.15
48	1920	14.9	15	109	98,340	11.12	20.149	15.786	39.268	1.9489	1.2764	0.34	0.47	−0.03	−0.06
50	1900	15.5	14	112	99,808	11.22	20.633	15.845	39.689	1.9236	1.3021	0.35	0.62	0.06	0.13

Lake Oksana was also chosen for its proximity to the mines but it is located far enough from the mines that it received no direct sedimentation. The Oksana lake sediments have therefore recorded the atmospheric fallout associated with the extraction and transport of iron ore. Zinc concentrations and Zn/Al ratios appear to have increased during the mining period (Table 4), whereas Fe and Pb concentrations and Fe/Al and Pb/Al ratios unexpectedly decreased during the same period, although the mining period is represented by only one sample. In contrast, Pb and Fe concentrations and Pb/Al and Fe/Al ratios appear to have peaked around the middle of the 19th century after a constant increase, with Zn and Zn/Al ratio being at a minimum at this time.

Together, these changes suggest a variation in the detrital input to the sediments. Additional evidence for changes in the detrital input is apparent from the Zr/Th ratio. Since both Zr and Th are found in detrital minerals, two major changes in detrital input appear to have had an impact over the past 120 years in Lake Dauriat (Table 3), the first at the beginning of the mining period and the second towards the end. The Zr/Th profile varies less in the Lake Oksana sediments (Table 4). Note that a short-lived, rapid, and significant change in the Zr/Th ratio occurred in 2004 in the Lake Dauriat sediments. This event is also recorded in the Oksana sediments, where a small increase in the Zr/Th ratio can be seen in the 2003 sample. Such transitions have already been highlighted for Lake Dauriat using a paleolimnological approach (Laperrière et al., 2007).

In addition to measurements of elemental concentrations, we also performed analyses of Pb, Zn, and Fe isotopes in the sediments, the results of which are detailed below.

4.3.3. Lead

Analyses of Oksana and Dauriat lake sediments show large Pb isotope ratio variations along the cores, from radiogenic compositions at the base (e.g., ²⁰⁶Pb/²⁰⁴Pb ratio up to 27) to less radiogenic ratios (e.g., ²⁰⁶Pb/²⁰⁴Pb close to 17.7) at the top. This observation once again suggests contributions from multiple sources over time in both lakes (Fig. 3). In detail, a marked decrease to less radiogenic Pb isotope ratios

Table 4
Zr/Th ratios, Pb, Zn, Fe and Al concentrations, Al₂O₃ %, and Pb, Fe and Zn isotopes of lake Oksana.

Z (cm)	Year	Zr/Th	Pb (ppm)	Zn (ppm)	Fe (ppm)	Al ₂ O ₃ (%)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁷ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁴ Pb	²⁰⁸ Pb/ ²⁰⁶ Pb	²⁰⁶ Pb/ ²⁰⁷ Pb	δ ⁵⁶ Fe	δ ⁵⁷ Fe	δ ⁶⁶ Zn	δ ⁶⁸ Zn
0.5	2009	12.6	31	102	51,842	1.62	18.777	15.801	38.338	2.0418	1.1882	0.89	1.30	0.36	0.72
1.5	2003	13.2	42	105	54,870	1.74	18.685	15.649	37.941	2.0306	1.1940	0.83	1.20	0.11	0.21
5	1964	13.0	28	170	36,839	1.41	18.752	15.638	37.865	2.0192	1.1992	1.04	1.50	0.08	0.17
9	1917	12.2	49	96	57,081	1.77	18.614	15.618	37.896	2.0357	1.1919	1.03	1.55	0.07	0.16
13	1870	13.4	65	85	64,893	1.63	18.505	15.607	37.911	2.0486	1.1857	0.98	1.38	0.28	0.56
15	1847	13.2	82	108	62,529	1.76	18.438	15.606	37.929	2.0571	1.1815	0.93	1.41	0.29	0.60
19	1799	11.5	49	119	51,051	1.77	19.058	15.679	38.208	2.0048	1.2155	1.09	1.60	0.26	0.51
21	1776	10.3	29	115	50,947	1.72	19.596	15.747	38.300	1.9544	1.2445	0.95	1.50	0.37	0.78
25	1729	11.2	10	106	48,911	1.70	22.240	16.066	38.820	1.7455	1.3843	1.13	1.82	0.34	0.69
29	1682	10.3	9	97	48,100	1.71	23.774	16.262	39.069	1.6432	1.4621	0.95	1.41	0.37	0.82
33	1635	11.4	5	96	40,217	1.91	26.315	16.583	38.314	1.4559	1.5870	0.94	1.42	0.29	0.57
37	1587	10.8	4	86	52,716	1.90	27.200	16.691	38.071	1.3996	1.6297	1.05	1.48	0.32	0.64

is highlighted between 1930 and 1940 in the Lake Dauriat sediments. ²⁰⁶Pb/²⁰⁴Pb decreases from values of around 20 to a value of about 18. The decrease in the ²⁰⁶Pb/²⁰⁴Pb ratio is accompanied by an increase in the Pb flux. Between 1940 and the top of the sediment core (2012), the ²⁰⁶Pb/²⁰⁴Pb ratio remains stable, except for during the 1970s where a decrease (from 18 to 17.7) followed by an increase is observed. Large variations in the ²⁰⁶Pb/²⁰⁴Pb ratio, to less radiogenic values, are recorded at the base of the Lake Oksana core. ²⁰⁶Pb/²⁰⁴Pb decreased from 27 during the 1600s to values of around 18.5 during the 1840s. Highly radiogenic Pb compositions are supported by high U/Pb ratios at the bottom of the sampled core (not shown). Since 1840, the ²⁰⁶Pb/²⁰⁴Pb ratio has remained largely stable, with a slight trend to more radiogenic values observed in the surface sediments (2012).

4.3.4. Zinc

Zn isotopic values vary less systematically than Pb isotopic values. The total variation in δ⁶⁶Zn recorded in the lake sediments is 0.5‰ (from −0.1‰ to 0.4‰). The δ⁶⁶Zn values of the Lake Oksana sediments are more positive (0.4‰ to 0.1‰) than those of Lake Dauriat (0.2‰ to −0.1‰) (Fig. 4, Tables 3, 4). The δ⁶⁶Zn profile of Lake Dauriat sediments is constant (within uncertainties) during the pre-mining and active mining periods (average = 0‰). δ⁶⁶Zn values only increase in the surface sediments (modern sediment) of the core. During the post-

mining period, the δ⁶⁶Zn values are systematically higher (average = 0.14‰). A similar profile is observed in the Lake Oksana sediments. The pre-mining period, from about 1600 to 1900, displays a constant δ⁶⁶Zn of around 0.3‰. In contrast, sediments covering the period 1900–2000 show depletion in heavier Zn isotopes (around 0.1‰). The post-mining period is characterised by enrichment in heavier Zn isotopes (up to 0.35‰). In this lake, the top sediments have the same δ⁶⁶Zn value as the deeper sediments and a comparable Zn/Al ratio.

4.3.5. Iron

The Fe isotopic values are different in Dauriat and Oksana lake sediments and cover a total range of more than 1‰ (from −0.2‰ to +1‰). The Fe isotope ratios of the Oksana lake sediments remain constant (within uncertainties) at a δ⁵⁶Fe of 1‰ (Fig. 5a, Table 4). As it was observed for Zn, δ⁵⁶Fe values are higher in Lake Oksana than in Lake Dauriat. In Dauriat sediments, significant variation in δ⁵⁶Fe is observed during the different periods (Fig. 5b). During the pre-mining period, δ⁵⁶Fe values were constant around 0.3‰ and then a slow depletion in heavier isotopes of up to −0.1‰ occurred during the active mining period. During the mining to post-mining transition, δ⁵⁶Fe shows a change towards the heavier isotopes, with values up to 0.15‰, followed by a rapid change towards the lowest values (0.8‰ and −0.2‰ for Oksana and Dauriat, respectively) in the early 2000s.

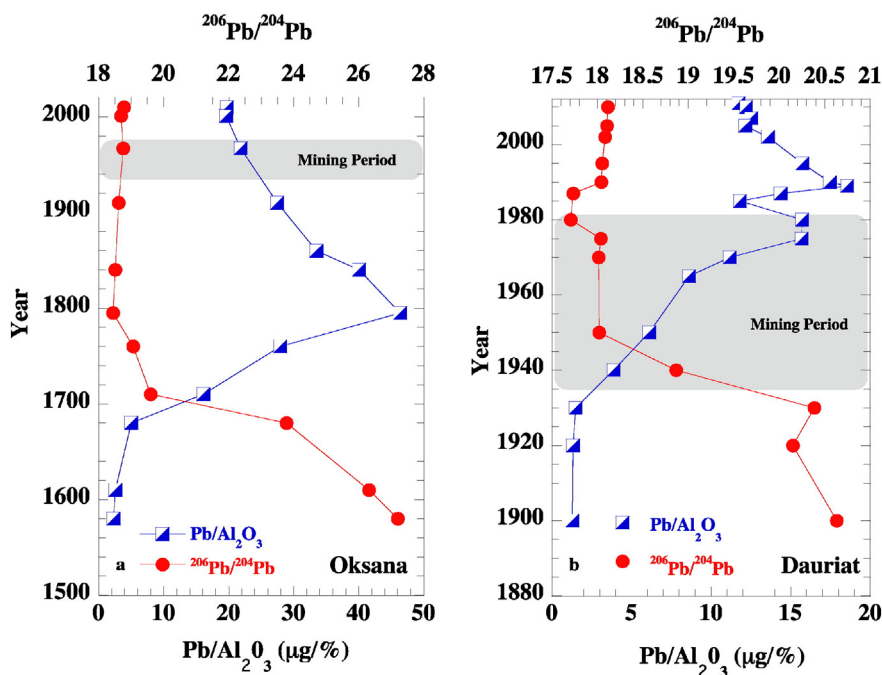


Fig. 3. Variation in the chemical (Pb/Al₂O₃, dots) and isotopic composition (²⁰⁶Pb/²⁰⁴Pb, squares) in the sediments of lakes Dauriat and Oksana during the pre-mining, the mining and the post-mining periods (left panel: lake Oksana, right panel: lake Dauriat).

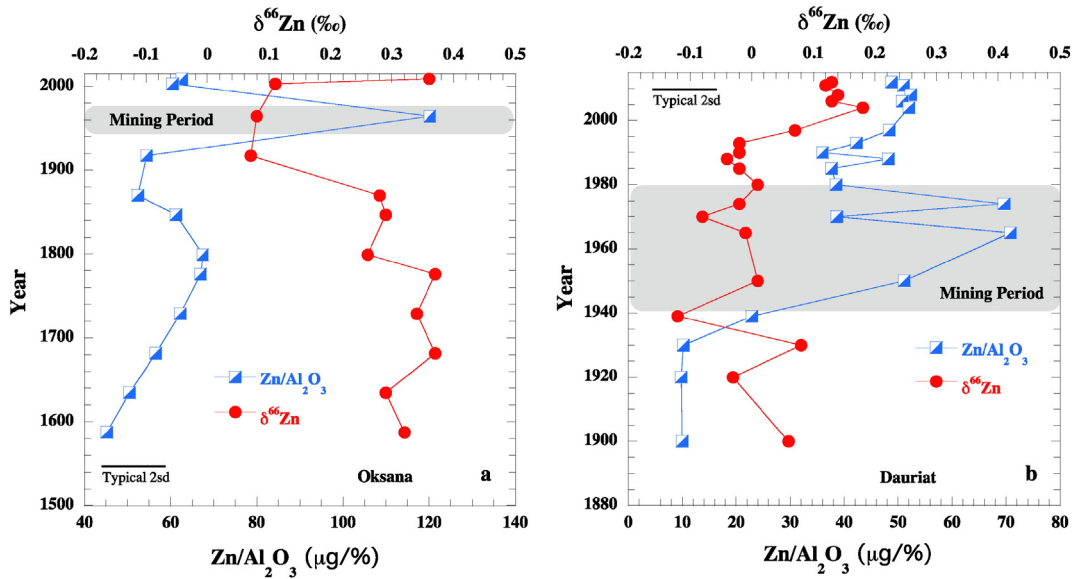


Fig. 4. Variation in chemical (Zn/Al_2O_3 , dots) and isotopic composition ($\delta^{66}Zn$, squares) in the sediments of lakes Dauriat and Oksana during the pre-mining, the mining and the post-mining periods, a) lake Oksana, b) lake Dauriat. Grey area represents the commercial mining period.

5. Discussion

To better constrain the anthropogenic effect on the isotope ratios, the data obtained from lichens, ores and tailings are reported in the mixing diagrams. Tailings are assumed to represent an average of the local lithology. Ores represent local concentrations of Pb with fluid circulation and are used as a proxy for mining activities. In addition, lichen Pb isotope ratios, which are proxies for atmospheric deposition, are also reported. Here, the two lakes provide different information due to differences in sediment accumulation rates at the two locations.

5.1. Lake Oksana

Oksana sediments do not provide a satisfactory temporal resolution for the transition period but have recorded the older history. Oksana reveals an early change towards non-radiogenic Pb isotopes (before 1900), with a shift from 27 to 18.5 in terms of $^{206}Pb/^{204}Pb$ (Table 4). Such a large shift is interpreted as a change in atmospheric deposition,

with the addition of increasing amounts of Pb from anthropogenic sources. This might be due to increased local activity around the mines before the industrial exploitation, however, the variation is probably better explained by long-range atmospheric deposition from European activities leading up to the peak associated with the industrial revolution, as has already been observed in previous studies (Gallon et al., 2005, 2006) of Canadian lakes. This can also explain the large variations in Pb flux (Fig. 3). To explain the Pb isotope ratio variations observed in the lake sediment core (Fig. 3), at least two sedimentary sources are required. Moreover, in the $^{206}Pb/^{204}Pb$ vs $^{207}Pb/^{204}Pb$ diagram (Fig. 6a), the Pb isotopic values seem to be aligned. In such tri-isotopic diagrams, a mixture of two sources of distinct composition forms a straight line, the sources being at the extremities of the line. However, the line is not perfectly straight (Fig. 6b) suggesting the presence of at least a third end-member. This is also confirmed by the Al_2O_3/Pb vs $^{206}Pb/^{204}Pb$ mixing diagram (Fig. 7). One of these three end-members is represented by the geogenic source. A further end-member, with less radiogenic Pb and lower Al_2O_3/Pb ratios is also

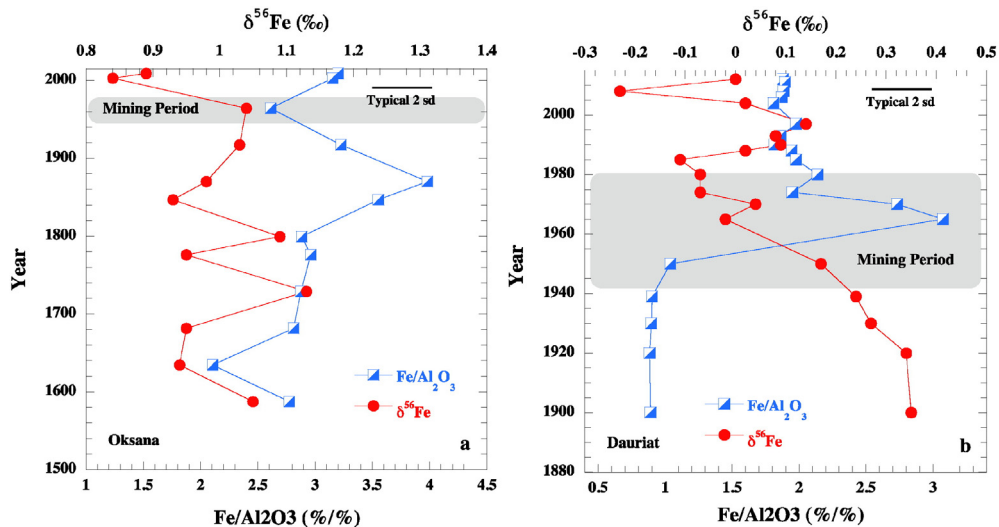


Fig. 5. Variation in chemical (Fe/Al_2O_3 , dots) and isotopic compositions ($\delta^{56}Fe$, squares) in the sediments of lakes Dauriat and Oksana during the pre-mining, mining and post-mining periods, a) lake Oksana, b) lake Dauriat.

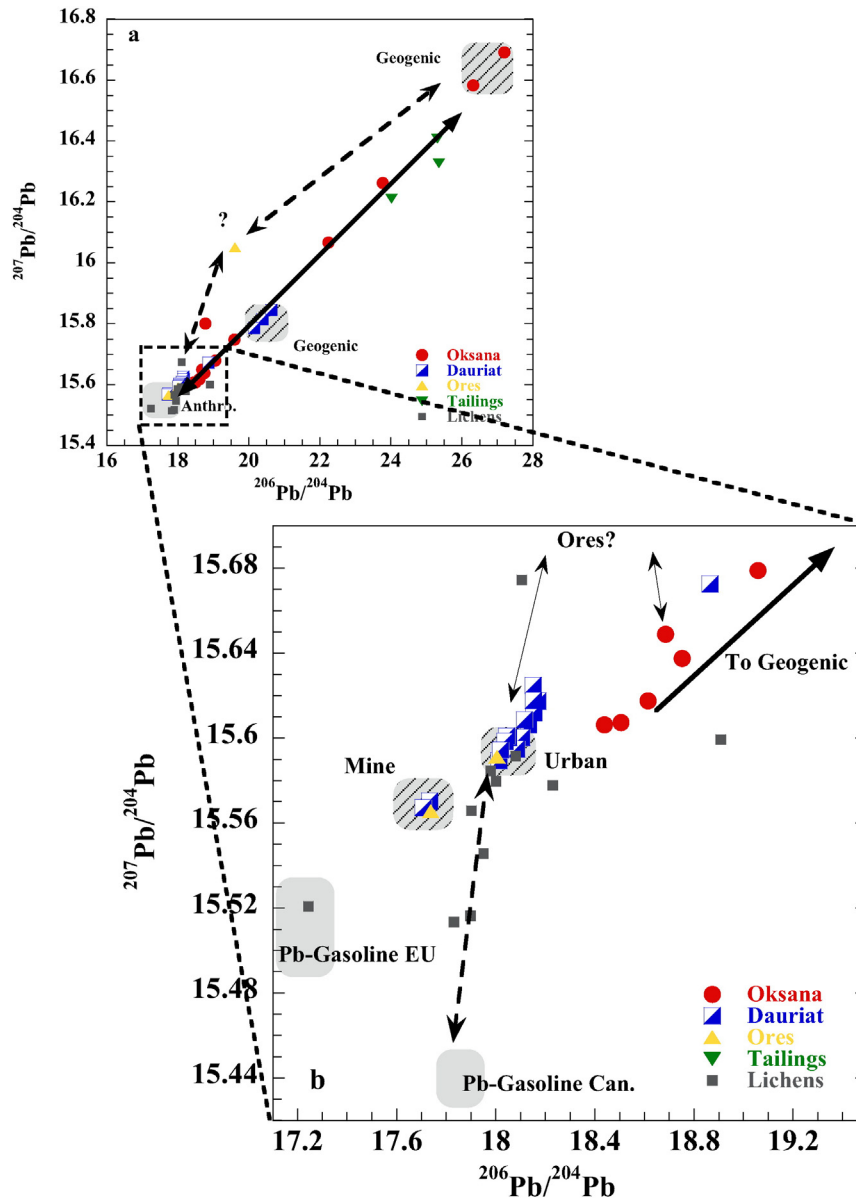


Fig. 6. $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ tri-isotope diagram for lake sediments (Oksana and Dauriat), lichens, ores and tailings. End members are represented with grey areas.

required and is likely linked to anthropogenic activities (e.g., urban activity, leaded gasoline from the EU and or Canada, and mining). The impacts of mining activities on atmospheric deposition in Lake Oksana sediments are rapidly overprinted by long-range atmospheric deposition.

The decrease in the Pb flux and the trend towards radiogenic Pb in surface sediments coincides with the end of Pb addition from motor vehicle gasoline in North America and the cessation of mining activity. During the post-mining period, the $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of surface sediments remain similar, indicating a constant and stable input of Pb regardless of the sediment.

In order to better constrain the end-member origins, Zn isotopes were measured and reported in a mixing diagram (Fig. 8a). Two end-members are required to explain the Zn isotopes of Oksana sediments. These two end-members can be explained by the lithology and by an additional end-member that is better represented by aerosol deposition, as recorded in the lichens. However, a mining, urban or industrial contribution cannot be excluded. The pre-mining sediments are characterised by a constant $\delta^{66}\text{Zn}$ value of 0.3‰ within uncertainties, reflecting the lithology. The $\delta^{66}\text{Zn}$ measured here are consistent with

previous values reported for various types of rocks in different environments (e.g., Viers et al., 2007; Pons et al., 2013) and can be explained by the local geological composition of the watersheds, as was already discussed for Pb. At the beginning of the mining period, the Zn isotopic composition of Oksana sediments shifts towards lighter values by more than 0.2‰. This variation is easily linked to anthropogenic activities in that mining, as well as urban and industrial activities, usually leads to depletion in heavier Zn isotopes (John et al., 2007; Sivry et al., 2008; Sonke et al., 2008; Mattielli et al., 2009). In contrast to Pb, Zn is heterogeneous in the ores and tailings across the study in terms of both isotopic composition and Zn/Al₂O₃ ratios. Even though the average values are consistent with the local lithology, the significant heterogeneity in the Zn data prevents us from going any further in our interpretation of the mixing diagram. The post-mining period is characterised by enrichment in heavier Zn isotopes in sediments. Such variation can be attributed to present-day atmospheric deposition and is consistent with the isotope ratios measured in lichens sampled in the area (Table 1).

The average values of $\delta^{56}\text{Fe}$ in Oksana sediments are relatively constant at around 1‰ ± 0.1‰. Although the more recent Oksana sediments were affected by a short-lived, high-intensity event that

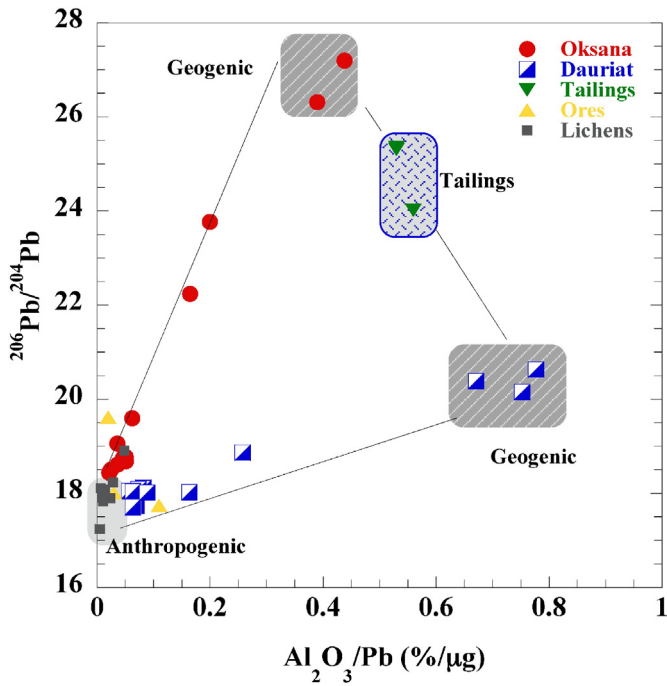


Fig. 7. $\text{Al}_2\text{O}_3/\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratios of lichens, ore, tailings and lake sediments (Oksana and Dauriat).

resulted in slightly lighter $\delta^{56}\text{Fe}$ values, the Oksana sediments did not record any significant and/or systematic variations in terms of $\text{Fe}/\text{Al}_2\text{O}_3$ or $\delta^{56}\text{Fe}$. This relative homogeneity can be explained by the high flux of Fe from the lithology to the sediment. This is further supported by the large inputs of Fe that are recorded in the entire Oksana sediment core, from the bottom of the core (the earliest sediments) to the top, and the consequently relatively limited input from the other end-members through time, which thus had negligible impact on these sediments.

5.2. Lake Dauriat

The Lake Dauriat sediments can also be described by mixing between at least three end-member sources (Figs. 6, 7). One of these

end-members is again represented by the lithology. However, this end-member is different to the Oksana geogenic end-member (Fig. 7). In Lake Dauriat, the bottom sediments have again recorded a change towards a less radiogenic composition that began prior to the onset of active mining. This variation is consistent with long-range atmospheric deposition from Europe, as was described for Lake Oksana; however, the impact of early mining and the growth of the town of Schefferville, as well as the impact of North-American industrial activities cannot be neglected. The values measured for $^{206}\text{Pb}/^{204}\text{Pb}$ (17.7 to 18.1) during the mining period in Lake Dauriat are slightly less radiogenic than those in Lake Oksana (~18.7). This difference is easily explained by contributions from urban and mining activities, which would have had more impact on the Lake Dauriat sediments. At that time, the city had no wastewater treatment system and wastewaters were instead drained into the lake. Such deficiencies in the town's infrastructure are likely one of the main causes of the increasing concentrations of chemical elements during the mining period. The abrupt excursion to less radiogenic values at the beginning of the mining period indicates the occurrence of a short-lived and rapid change in Pb sources. Values of $^{206}\text{Pb}/^{204}\text{Pb}$ during this period (1970–1980) are relatively low ($^{206}\text{Pb}/^{204}\text{Pb} = 17.720 \pm 0.013$, $^{206}\text{Pb}/^{207}\text{Pb} = 1.138 \pm 0.001$) and are close to those measured at the smelter in Rouyn-Noranda (R-N; $^{206}\text{Pb}/^{207}\text{Pb} \approx 0.993$). However, the lead emitted by this plant was not detected in a lake located 300 km from the smelter in an earlier study (Gallon et al., 2006). Given that Schefferville is located several hundred kilometres from the R-N smelter and in the same north-east direction as some of the previously studied lakes, a significant record of R-N smelting activities in the Schefferville area lakes would not be expected. The change in isotope ratio is therefore probably better explained by the construction of the wastewater plant, which, as a consequence, would have reinforced the mining signal recorded in the Lake Dauriat sediments by suppressing the urban signal. However, this period was also characterised by a peak in atmospheric Pb due to the use of leaded gasoline. Lead isotopic values in lake Dauriat surface sediments ($^{208}\text{Pb}/^{204}\text{Pb}_{\text{Dauriat}} = 37.727 \pm 0.011$; $^{206}\text{Pb}/^{204}\text{Pb}_{\text{Dauriat}} = 18.124 \pm 0.03$) are comparable to the values of long-range Pb atmospheric deposition ($^{208}\text{Pb}/^{204}\text{Pb} = 37.666$; industrial Canadian Pb) measured in lichens sampled in other parts of northern Quebec (Carignan et al., 2002), as well as the lichens sampled in this study area. The decrease in Pb concentrations of epiphytic lichens with increasing distance from the mines and town of Schefferville (Fig. 2), indicates that

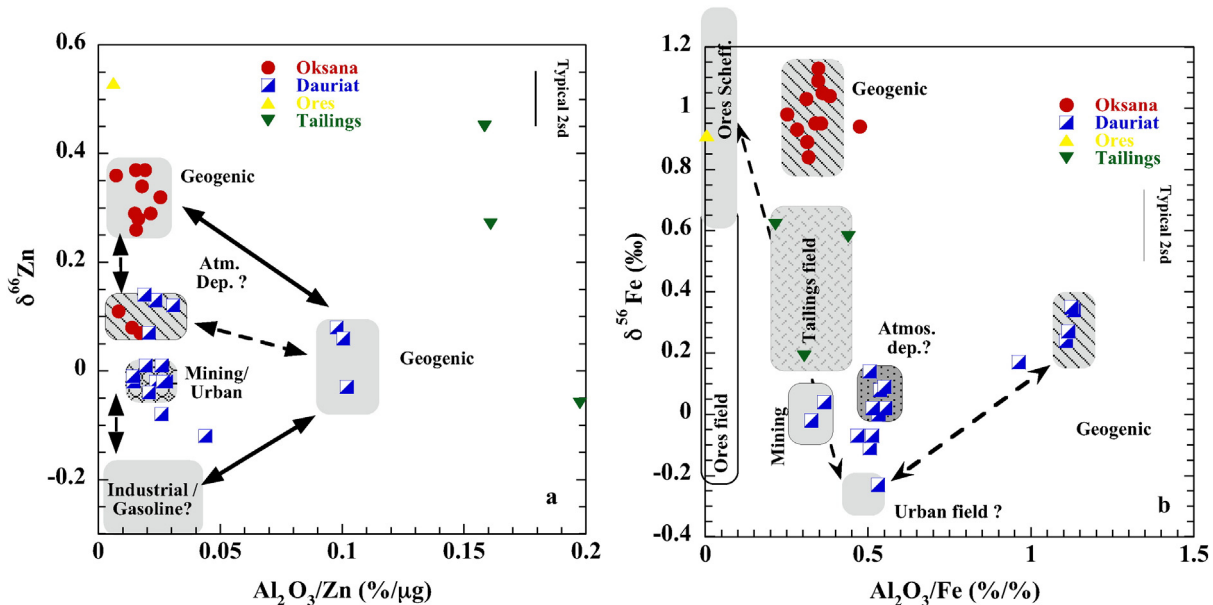


Fig. 8. $\text{Al}_2\text{O}_3/\text{Zn}$ vs $\delta^{66}\text{Zn}$ (a), $\text{Al}_2\text{O}_3/\text{Fe}$ vs $\delta^{56}\text{Fe}$ (b) ratios of lichens, ore, tailings and lake sediments (Oksana and Dauriat).

anthropogenic and mining activities generate Pb pollution in the vicinity of the mines and the town. The homogeneity of Pb isotopic values in epiphytic lichens reflects a short-term constant source of Pb. Samples with extreme values may have experienced different exposure to aerosols than the other lichens sampled, for example as a result of differences in forest cover and/or wind exposure. A local point source could also explain such extreme values. The average $^{206}\text{Pb}/^{207}\text{Pb}$ value obtained is similar to that of Canadian air emissions from industries ($^{206}\text{Pb}/^{207}\text{Pb} = 1.150$; Carignan and Gariépy, 1995), suggesting that the majority of the lead found in epiphytic lichens around Schefferville is derived from long-range Canadian atmospheric pollution. However, given the observed temporal changes, the Pb isotope ratios measured in the surface sediments cannot be explained by atmospheric deposition or geogenic end-members alone. The origin of this end-member remains unclear but might be related to the recent restart of mining activity.

The average $\delta^{66}\text{Zn}$ value for the pre-mining period in Dauriat sediments is 0.05‰. This value is different from the Lake Oksana sediments and can be explained by differences in the local geological composition of the watersheds of Lakes Oksana and Dauriat, as was proposed for Pb. Although the two lakes are located only around 4 km apart, the north-west orientation of the NQO geological unit means that the two watersheds have different geologies. When isotope ratio values are plotted in a mixing diagram (Fig. 8b), at least three end-members are required to explain the observed Zn distribution. During the mining period, no significant change in the Zn isotope ratios is observed. In contrast, there is an increase in the $\text{Zn}/\text{Al}_2\text{O}_3$ ratio, suggesting that the Zn flux during this period had a similar isotopic composition to the lithology. The post-mining period is characterised by enrichment in heavier Zn isotopes in the sediments. This can be attributed to present-day atmospheric deposition and is consistent with the isotope ratios measured in lichens sampled in the area (Table 1). With regards to Fe, the Dauriat sediments during the pre-mining period have a $\delta^{56}\text{Fe}$ value of $0.32\text{‰} \pm 0.08\text{‰}$. Once again, this value differs from that of the Oksana sediment. The $\delta^{56}\text{Fe}$ values are consistent with values previously reported for different lithologies in different environments (e.g., Beard et al., 2003; Dauphas et al., 2004; Poitras and Frey, 2005). The same end-members described previously are revealed in the Fe mixing diagram, with mining/anthropogenic activities causing a shift in the isotope ratios towards lighter values, and with atmospheric deposition shifting ratios towards heavier values in the surface sediments. This implies that atmospheric deposition is represented by $\delta^{56}\text{Fe}$ of around 0.2‰. This value is identical to those reported for the lichens analysed in this study ($\delta^{56}\text{Fe}$ of 0.1‰ to 0.2‰ (Table 1)). Moreover, in recent studies, Fe atmospheric deposition was shown by Labatut et al. (2014) to vary from 0.3 to 0.4‰ and was estimated by Conway and John (2014) to reach up to 0.7‰. These values perfectly explain the variation recorded in the two Arctic lakes in this study.

5.2.1. Multi-isotope approach

In order to test the coherence between the different end-members defined for Pb, Zn and Fe, diagrams reporting Pb isotopes as a function of $\delta^{66}\text{Zn}$ and $\delta^{56}\text{Fe}$ are presented (Figs. 9, 10). In this isotopic space, the end-members should plot in the place defined for each isotopic system individually. In fact, coupling Pb and Fe isotopes in this way represents a new way of constraining/examining the different end-members that contribute to the sedimentation. Oksana sediments, characterised by homogeneous $\delta^{56}\text{Fe}$ values (within uncertainties), produce a well-defined trend in Pb–Fe isotope space. Although it can be explained using Pb alone, the data dispersion indicates a change in the sedimentation sources of the lake, with the contribution of lead being more important than that of Fe. This may be due to long-range atmospheric deposition associated with the industrial revolution during the pre-mining period. At that time, the amount of Pb emitted to the atmosphere increased substantially without any significant input of Fe. In addition, because the local lithology has a very high Fe content,

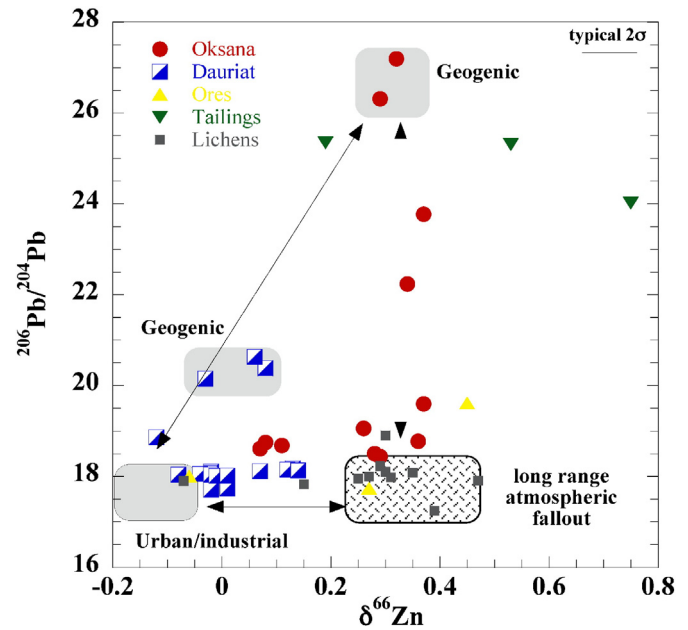


Fig. 9. $\delta^{56}\text{Fe}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of Oksana and Dauriat lake sediments, lichens, ores and tailings.

the impact of iron inputs from other sources would have been limited. For Pb, in contrast, the balance is reversed and the inputs from atmospheric Pb deposition are significantly higher than those from the local lithology. In addition and unlike Fe, Pb isotope ratios exhibit considerable heterogeneity, thus explaining the decoupling of Fe and Pb sources during the pre-mining period in Oksana sediments. The Fe–Pb isotope plot is thus better explained with a hyperbolic mixing curve than with a linear mixing line (Fig. 10). For Zn, the difference with Pb is less pronounced but the explanation also works perfectly (Fig. 9).

Dauriat sediments show a pre-mining impact, with variations in isotopic composition observed for both Pb and Fe. In Fig. 10, atmospheric deposition can be clearly identified as the end-member influencing this change, and this is supported by the Pb and Fe isotope measurements

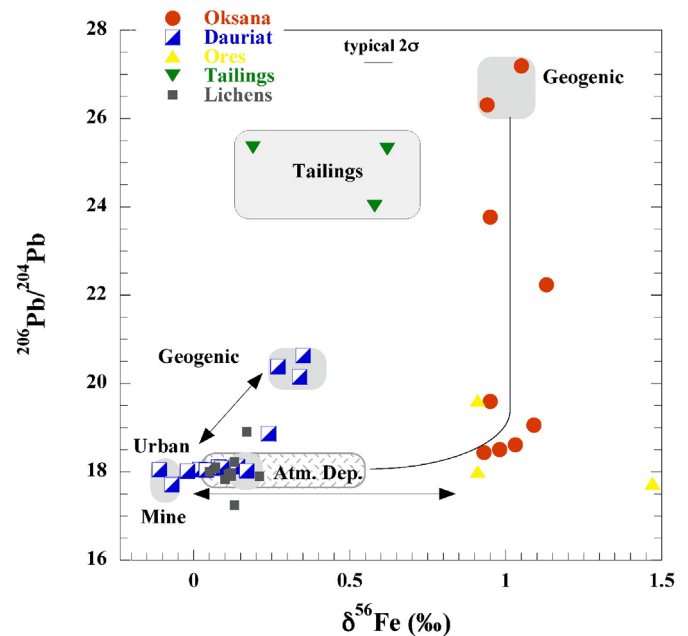


Fig. 10. $\delta^{66}\text{Zn}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of lichens, ore, tailings and lake sediments (Oksana and Dauriat).

in lichens. Furthermore, early mining activity cannot account for much of the sedimentation in Dauriat at that time. The mining end-member, clearly identified in the diagram, is likely responsible for most of the variation recorded at the beginning of the mining period. However, the ores reported in this study do not seem to have been those exploited at the time as they plot in the Oksana sediment field rather than in the mining field. Nevertheless, the heterogeneity between the different ores reported here and in the literature (Flament et al., 2008), combined with the significant difference between ores and tailings, suggests a large range of potential ores in the area. The mining signal is then rapidly overprinted by the urban impact, which becomes the most important source of sedimentation to the lake for much of the mining period. The hypothesis is also coherent in the Pb–Zn isotopic space (Fig. 9). After this period, the most recent sediments are again clearly dominated by atmospheric deposition. The same end-members for this period plot perfectly on the Pb vs Zn isotope ratio diagram, with a value of 0.3–0.4‰ constrained for the $\delta^{66}\text{Zn}$ of atmospheric deposition, as measured in sediments and epiphytic lichens. These values are heavier than those previously reported for modern atmospheric deposition in other studies (Cloquet et al., 2006a, 2006b; Sonke et al., 2008; Chen et al., 2009; Mattielli et al., 2009), yet are consistent with values recorded in peat bogs (Weiss et al., 2007). This suggests that the $\delta^{66}\text{Zn}$ values of the atmospheric deposition are variable across the surface of the planet.

6. Conclusion

Elemental and isotopic analysis of sediment cores from two lakes in the Schefferville area show that the surface geochemical cycle has been disturbed by mining activity. Variations in sedimentary sources can be identified. Elemental analysis of sediments from Lake Dauriat, located close to the city, shows the impacts of human activities in urban settings, whereas analysis of sediments from Lake Oksana, located outside the direct influence of the city, provides information on the effects of Fe ore extraction and transport. In lake sediments affected by mining (Oksana) and urban pollution (Dauriat), metal concentrations have generally been higher during the current post-mining period than they were during the pre-mining period.

Lead, Zn and Fe isotopic analyses of Lake Oksana and Dauriat sediments have allowed the sediment sources associated with different stages/phases within the mining period to be identified. An early disturbance during the pre-mining period is explained by long-range atmospheric deposition. The other sedimentary sources identified are the local geogenic sources during the pre-mining period (a different source at each lake), an urban and a mining source during the mining period (1939–1977), and a modern long-range atmospheric deposition source during the post-mining period (1977–2012). The sources were identified by comparing previously published records with analysis of complementary materials that serve as their proxies (ores, tailings and lichens). Long-range atmospheric deposition is consistent with Canadian and U.S. industrial emissions during the mining and post-mining periods, but a contribution from European aerosols during the pre-mining period cannot be excluded.

On the basis of this study, mining can be seen to have had a profound impact on at least Lake Dauriat in the Schefferville area. Furthermore, the transition from the pre-industrial steady state to the perturbed mining state was very fast. In contrast, the transition between the mining and post-mining periods was much slower and more subtle as it was somewhat masked by long-range air pollution from Canadian and U.S. industry, thereby ensuring that metal concentrations are higher during the post-mining than the pre-mining period. A return to the natural balance appears to be a difficult and lengthy process; however, initiating measures aiming at the restoration of abandoned mine sites should accelerate it. A better understanding of the potential disturbances and impacts on the global bio-geo-cycles is essential for effective decision-making in managing present and future mining activities in the Arctic and subarctic regions in an environmentally sustainable manner.

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