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Recent (1930s) natural acidification and fish-kill in a lake that was an important food source for an Inuit community in northern Québec, Canada

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Abstract

Isiurqutuuq Lake was an important food source for the Inuit community of Akulivik (northern Québec, Canada) until the 1930s when the fish disappeared. Their disappearance was attributed to explosives used by prospectors. Modern lake water is acidic (pH 4.5), and most life forms are absent. A unit of sulphide-rich graphitic shale occurs throughout the watershed. The oxidation of sulphide minerals produces acidic water, rich in metals, including Zn, Cu and Ni. The lake is less than 15 m above sea level and close to the Hudson Bay coast. Ice sheets, which remained until about 8000 BP, depressed the region 150 m below the present levels, and when ice melted Isiurqutuuq Lake was part of the sea floor. Isostatic uplift exposed the sulphide zone on the north shore of the lake at ~2500 BP, followed by exposure of the lake. Weathering and oxidation of the sulphides was slow at the start, but increased steadily as frost heaving and fracturing permitted access of water and air to the sulphide zone. Diatom analysis of lake sediment cores reveals striking changes up-section. A clay unit at the base contains a marine-littoral diatom flora. Following uplift and marine regression, freshwater diatoms became established, dominated by circumneutral and alkaliphilous taxa. The subsequent appearance and increasing abundance of acidophilous diatoms reveal increasing acidification which culminates in the top 2 cm. The modern lake-bottom sediments are dominated by acidobiontic species that develop at pH values <5.5. This relatively late acidification is attributed to the initial buffering of acid by marine shells deposited when the lakebed was beneath Hudson Bay. Only when the shells were consumed did the lake become acidic. The scientific evidence is consistent with the observation of the Inuit population that the fish died out in the 1930s. Remediation of the problem is possible by neutralising the acid with modest addition in the lake of the abundant shell sand found in the Akulivik area.

Keywords: lake; acidification; fish; toxic; metals; diatom

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1. Introduction

Isiurqutuuq Lake, near Akulivik, northern Québec, Canada (Figs. 1 and 2), was an important source of Arctic char for the local Inuit population until the 1930s. At that time, the fish disappearance was attributed to explosive charges used by prospectors who visited the area in the years 1931 to 1933. Initial studies (Kaminski et al., 1995) confirmed the absence of fish and most other life forms in the lake and established that this was due to the water being acidic (pH 4.3).

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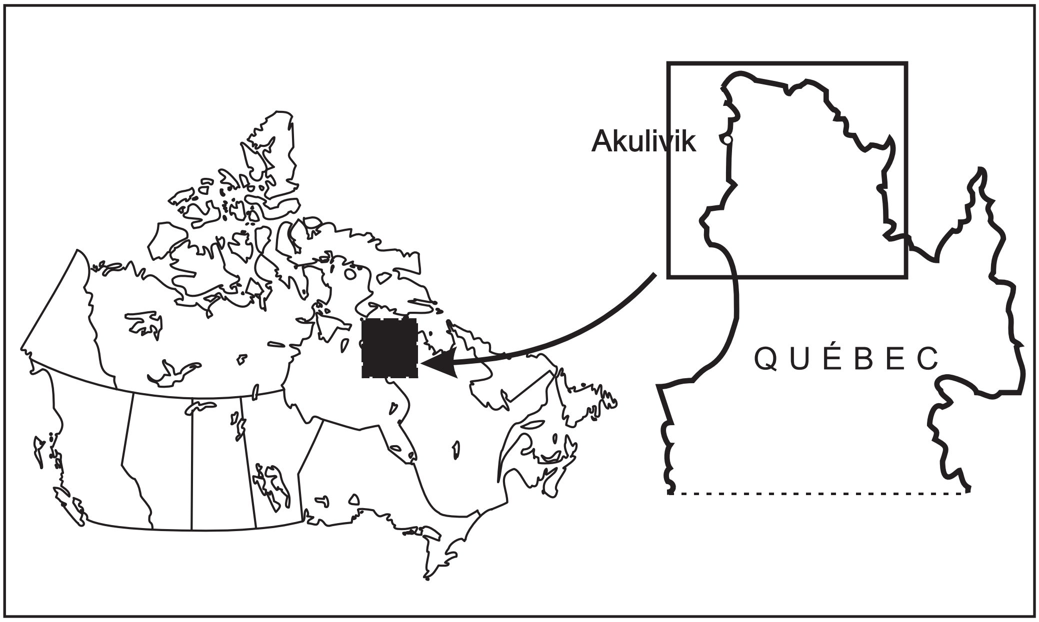


Fig. 1. Location map for Akulivik, northern Québec, Canada.

Fig. 2. Photograph of Isiurqutuuq Lake, looking east from the Kucyniak Massif.

The community of Akulivik wished to determine the cause of the acidification, and its possible remediation. At their request the area was visited in July–August, 1995. The 1995 study showed that acidification was caused by H_2SO_4 released by oxidation of sulphide minerals in a graphitic shale unit that occurs throughout the watershed (Cameron, 1995). Moreover, the lake and the most actively oxidising zones of the graphitic shale on the lakeshore are close to sea level. Because of rapid glacial rebound the graphitic shale could only have emerged above the sea in the last 2000–3000 years (Cameron, 1995). To explain why acidification and fish-kill only happened during this century, it was suggested that marine shells, abundant in the Akulivik area, initially buffered the acid entering the lake. When the $CaCO_3$ provided by the shells was consumed, the lake water became acidic. In April 1996, six cores were taken through the ice for the geochemical and diatom studies described below.

2. Isiurqutuuq Lake watershed

The watershed of the lake (Fig. 3) is long and narrow along the south slopes of the Kucyniak Massif. The lake is in a central position, with two main streams draining from the east and west. Isiurqutuuq Lake empties into the Chukotat River to the east. It has an area of 4.1 km^2 and is shallow (mean depth of 4 m reported by Kaminski et al., 1995). Basaltic volcanic rocks and dolerite sills, described by Baragar (1983), dip steeply to the north and underlie most of the watershed. Beneath the volcanic rocks, or within the dolerite, are beds of black, sulphide-rich graphitic shale. These sulphide-rich rocks occur mainly within a narrow zone (sulphide zone, Fig. 3), which attracted the interest of prospectors in the 1930s. In places, the sulphides occur as lenticular bodies that may be up to 10 m in width and hundreds of metres long (Gunning, 1933). The sulphide is mostly iron sulphide, which occurs mainly as pyrrhotite (FeS), with smaller

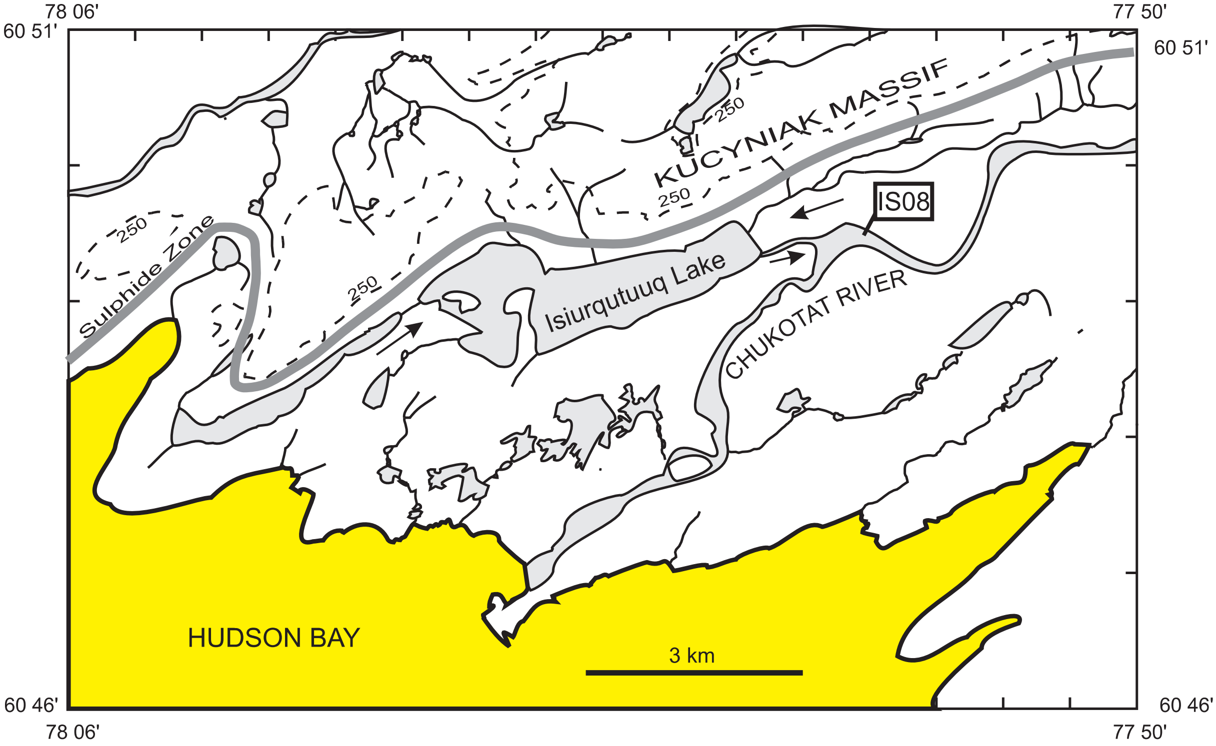


Fig. 3. Map of Isiurqutuuq Lake region. Arrows show direction of stream flow. Contour is for 250 ft. IS08 indicates location of water sample from Chukotat River.

amounts of pyrite (FeS_2). Analyses of metals in the waters suggest that there is also sphalerite (ZnS), chalcopyrite ($CuFeS_2$) and pentlandite (NiFeS).

3. Formation of gossan

On the north shore of Isiurqutuuq Lake is a large area of gossan (Fig. 4). This is the surface expression of a thick, lenticular zone of sulphide minerals within the graphitic shale. These sulphide minerals are being oxidised at depth. The gossan consists of soft, water-saturated, multi-coloured mud that contains boulders heaved to the surface by frost action. The mud is the residue remaining after physical and chemical processes have attacked sulphide minerals in the mineralised bedrock. The colours of the gossan (red, green and black) are due to the iron compounds that remain when the sulphur component has moved to the lake as sulphuric acid.

The Laurentide Ice Sheet (Dyke and Prest, 1987) depressed the region by about 150 m, and when it melted at ~8000 BP, marine waters invaded the area and reached that approximate elevation (Prest et al., 1967). Wave-washing limits measured along an east–west transect in the area (Prévost, 1987) revealed that marine waters attained various elevations, reaching almost 160 m at the western end of Smith Island (40 km west of Isiurqutuuq Lake), and 130 m on the Kucyniak Massif just north of the lake. Thus following deglaciation, the lake and its vicinity were below sea level, except for the highest points of the Kucyniak Massif to the north (Fig. 3). The postglacial emergence curve by Gray et al. (1993) for the Akulivik area shows an initial rapid uplift after melting of the ice, followed by a slower rate of emergence of about 0.6 m/100 years. Isiurqutuuq Lake's precise elevation has not been determined, but the 1 : 50,000 topographical map of the area shows that the 50-ft (15 m) contour passes through the gossan on the shore just north of the lake. Thus the sulphide unit emerged from the sea ~2500 BP and the lake later.

In the years following postglacial emergence (Fig. 5, top), only the outcropping glacially smoothed surface of the sulphide unit was available to oxidation and weathering. This generated only small quantities of H_2SO_4 and metals to be carried to the lake. With time, sulphide minerals dissolved along cracks and joints, providing access to water. Cycles of freezing and thawing fractured and split the rocks, greatly increasing the volume of sulphides accessible to water and O_2 (Fig. 5, bottom). The surficial layer (few cm) of frozen soil and rock melts in summer, resulting in the active layer through which water can flow. Oxidation of sulphide minerals produces heat. Once oxidation of the sulphide body

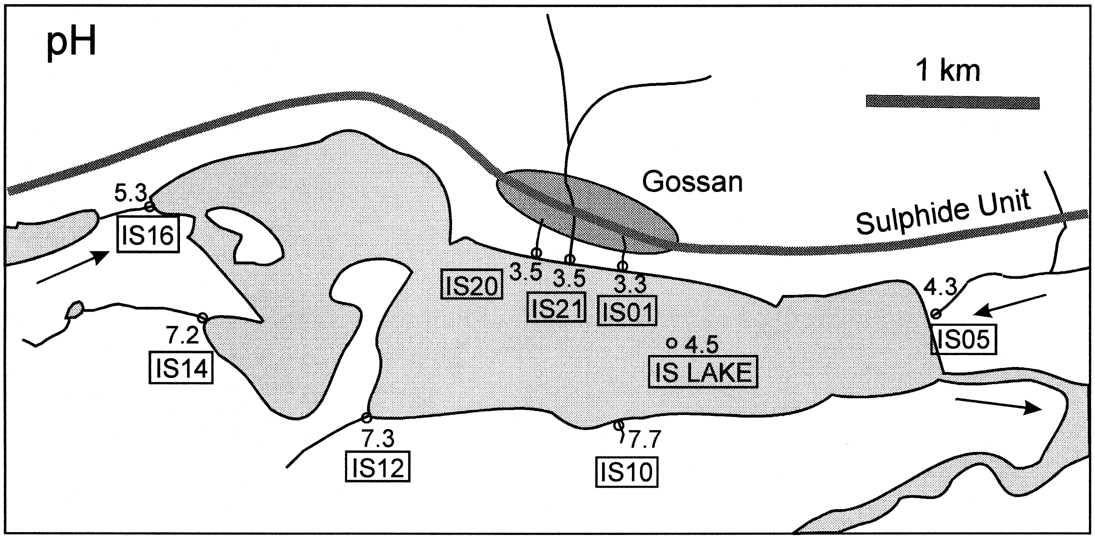


Fig. 4. pH of waters, Isiurqutuuq Lake. Sample numbers shown in box (see Table 1).

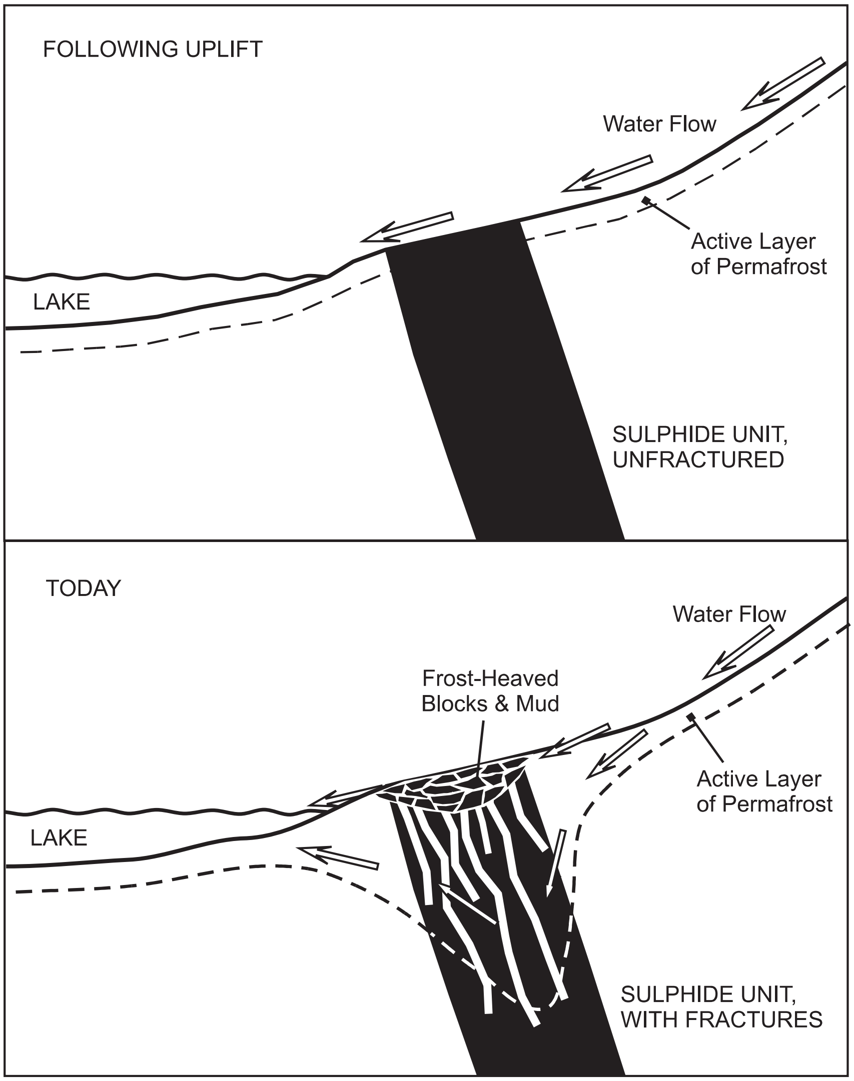


Fig. 5. Stages in the development of gossan, north shore Isiurqutuuq Lake.

was well established (Fig. 5, bottom), heat melted the permafrost to several m depth, which facilitated the flow of O_2-bearing water into the sulphide unit. Thus, the production of H_2SO_4 and metals and their subsequent flow into the lake water has gradually increased from 2500 BP to the present.

4. Sample collection and analysis

During the 1995 field visit, water samples were collected from streams entering the lake at several points, and also from the centre of Isiurqutuuq Lake. Based on the fact that waters of shallow northern Canadian lakes are well mixed due to frequent high winds (Cameron, 1979), the water sample collected from the centre of Isiurqutuuq Lake is considered representative of the basin's conditions. One water sample was also collected from the Chukotat River (IS08, Fig. 3), upstream from the outlet of the stream draining Isiurqutuuq Lake. This sample provides an estimate of the regional background concentration of metals in water. All waters were clear and were not filtered or acidified for preservation. The samples

Table 1
Analytical data for waters collected in the Isiurqutuuq Lake area

Sample	Medium	Area	pH	Cond.	Al	Fe	Mn	Co	Ni	Cu	Zn	Sr	Pb
IS01	Inflow stream	North	3.3	870	8600	4800	413	18.7	64	44	423	60	1.0
IS20	Inflow stream	North	3.5	590	7000	2800	453	13.9	56	67	269	33	6.8
IS21	Inflow stream	North	3.5	570	6500	7500	270	17.0	76	60	481	34	8.9
IS05	Inflow stream	East	4.3	180	1660	165	101	4.6	17	22	77	18.8	0.5
IS10	Inflow stream	South	7.7	80	56	17	0.2	<0.05	1.4	7	1.0	23	0.1
IS12	Inflow stream	South	7.3	160	18	310	1.4	0.09	1.9	3	3.0	33	0.2
IS14	Inflow stream	South	7.2	470	15	160	6.4	<0.05	1.2	4	1.0	80	0.2
IS16	Inflow stream	West	5.3	170	250	24	77	3.0	14	7	59	61	0.2
IS Lake	Isiurqutuuq L.	Lake	4.5	150	590	<5	114	2.1	7.7	8	34	26.7	0.3
IS08a	Chukotat R.	River	6.0	30	35	49	2.9	<0.05	0.8	1.4	0.8	10.4	<0.1
IS08b	Chukotat R.	River	6.0	30	33	50	2.8	<0.05	0.9	1.3	0.7	10.0	<0.1
IS18	Gossan seep	North	3.3	>2000	50000	530000	884	153	700	1600	2770	80	2.6
IS19	Gossan seep	North	3.0	>2000	82000	1150000	2530	195	950	860	5800	120	0.1
IS22	Gossan seep	North	3.3	570	14800	21400	554	39	227	108	1260	45	16.4

Concentrations in ppb, conductivity measured in μS cm^{-1}.

were immediately flown to the GSC, in Ottawa, for analysis. Methods used for the analysis of the trace constituents listed in Table 1 are described in Cameron et al. (1995). Sample IS08 (Chukotat River, Fig. 3) was analysed twice to provide an estimate of precision (see Table 1).

Core samples from Isiurqutuuq Lake were collected and sectioned over a 4-day period at the end of April, 1996. A gas-powered auger was used to drill through ice, which at the time was almost 2 m thick. Core samples up to 36 cm in length were collected in 2.5 inch ID acrylic plastic tubes. Core samples consisted mainly of grey or black clay below a thin (1–2 cm) layer of organic sediment. Cores were extruded from the tubes within 24 h of collection. The upper 10 cm was split into 10 samples each representing 1 cm of sediment. The lower sections were sampled in 5 cm increments. After drying, a portion of each sample was analysed by neutron activation analysis (Hoffman, 1992).

For diatom studies, sediment samples boiled in 10 ml of a 1 : 1 mixture of HNO_3 and H_2SO_4 for 20 to 30 min to remove organic matter (Mannion, 1982; Battarbee, 1986). The residue was washed seven times with distilled water to remove traces of acid, with settling periods of 8 to 16 h between washes. Slides for systematic counting were prepared by pipetting a homogeneous diatom suspension onto 18 × 18 mm cover glasses. The cover glasses were dried on a slide warmed at 75°C and mounted on permanent microscope slides using Naphrax as a mounting medium, diluted with 20% toluene. Identification and enumeration of diatoms was performed along systematic transects using a Leitz DM-RB microscope, equipped with a PL-Fluotar 100× oil-immersion objective and Leica L-Plan 10× oculars.

Diatom identifications are based on the monographs of Patrick and Reimer (1966), Patrick and Reimer (1975), Foged (1981), Germain (1981), Krammer and Lange-Bertalot (1986, 1988, 1991a,b) and Gasse (1986). To facilitate reading, authorities are not attached to the diatom species names in the text (a compiled list is available upon request). The nomenclature by Hustedt (1930) was retained for the genus *Fragilaria*. Identification of one of the dominant diatoms, *Fragilaria* (*virescens* v.) *exigua* Grunow in Cleve and Möller (1878), was done using Krammer and Lange-Bertalot (1991a), and hence we employed the name *Fragilaria exigua* (Grunow) Krammer and Lange-Bertalot (1991) they suggested (p. 137 of their monograph). However, as mentioned by Flower et al. (1996), the species name '*exigua*' utilised by Krammer and Lange-Bertalot (1991a) has to be considered illegitimate, as it is a later homonym. The correct species epithet is *Fragilaria exiguiformis* Lange-Bertalot (1993), which was validly published to rectify Krammer and Lange-Bertalot's (1991a) misuse of the name '*exigua*'. Here we decided to retain the species name *Fragilaria exigua* because it has been (and it is still) widely utilised in the diatom literature. Furthermore, a substantial taxonomical revision of this problematic diatom was recently done by Flower et al. (1996), who created one new genus and two new species (*Stauroforma exiguiformis* and *Stauroforma inermis*). Based on the morphological characteristics proposed in that revision, preliminary SEM investigations of our material revealed that both *S. exiguiformis* and *S. inermis* are present in the Akulivik core sediments. Our *Fragilaria exigua* therefore constitutes a grouping of these two newly described species. It is not an isolated case, however. SEM studies of material from Antarctica and Europe shows that in fact, most accounts of *Fragilaria exigua* are likely to comprise the two taxa, as their delineation is difficult to accomplish in light microscopy (Flower et al., 1996). Subsequent publications involving cores from the Akulivik region will follow this latest revision of the *Fragilaria exigua* group, by using SEM to clearly delineate both taxa (*S. exiguiformis* and *S. inermis*), and to establish their respective abundance in the sediment samples.

The pH spectrum applied to characterise each diatom species (acidobiontic, acidophilous, circumneutral/indifferent, alkaliphilous, alkalibiontic) follows the categorisation widely utilised in the literature, derived from the original classification system of Hustedt (1938–39). The assignment of a pH category to individual diatoms was achieved using the monographs listed above, references cited elsewhere in the text and several other papers (amongst others: Lowe, 1974; Dickman et al., 1984).

5. Acid and metal inflows to Isiurqutuuq Lake

The most acidic waters entering the lake are those that flow directly from the gossan on the north side of the lake (Fig. 4). Seeps directly on the gossan have even lower pH (Table 1). The east and west streams are also acidic. The east stream is important, because it has the highest flow and has a pH (4.3) that is lower than that of the lake (4.5). The rocks forming the south shore of the lake do not contain sulphide units and the waters entering from this side are neutral to alkaline (pH 7+, Fig. 4).

Metal contents, such as Zn (Fig. 6, Table 1), are highest in low pH waters. Very high metal contents are present in the seeps on the gossan. The streams that pass over the gossan carry these metals into Isiurqutuuq Lake. Metal contents in the east and west streams are lower, but still strongly anomalous compared to the regional background levels found in the Chukotat River. In contrast, streams draining the south shore of the lake contain only 1–3 ppb Zn, and similarly low contents of other metals. This reflects the non-mineralised nature of the rocks on this side of the lake.

Part of the metal entering the lake precipitates in the lake sediments, and part remains in solution. Table 2 shows mass balance calculations to estimate the metal remaining in solution. The areal extent of those parts of the watershed drained by streams from the north, east, south and west is first estimated (column 2). Since rain and snowfall can be considered uniform over the watershed, inflows are proportional to the area of each part of the watershed (column 3). For each element, the first column contains the

Table 2
Mass balance calculation on metals fluxes into Isiurqutuuq Lake

Watershed	Area		Sr		Fe		Al		Mn		Zn		Ni		Cu	
	(km^2)	(%)	(ppb)	(wt.)	(ppb)	(wt.)	(ppb)	(wt.)	(ppb)	(wt.)	(ppb)	(wt.)	(ppb)	(wt.)	(ppb)	(wt.)
North	5.3	14.0	42.5	5.9	5033	705	7367	1031	379	53	391	55	65	9.1	57	8.0
East	20.6	53.0	18.8	10.0	165	87	1660	879	101	53	77	41	17	9.0	22	11.7
South	3.0	7.7	45.2	3.5	162	12.5	30	2.3	2.7	0.2	1.7	0.1	1.5	0.1	4.7	0.4
West	5.6	14.0	60.5	8.5	24	3.4	250	35	77	10.8	59	8.3	14	2.0	7.0	1.0
Lake	4.1	11.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Summed inflows (ppb)				27.9		808		1948		117		104		20.2		21.0
Lake water (ppb)				26.7		<5		590		114		34		8		8
Lake water/inflows				0.96		<0.01		0.30		0.97		0.33		0.40		0.38

wt. = weighted concentration.

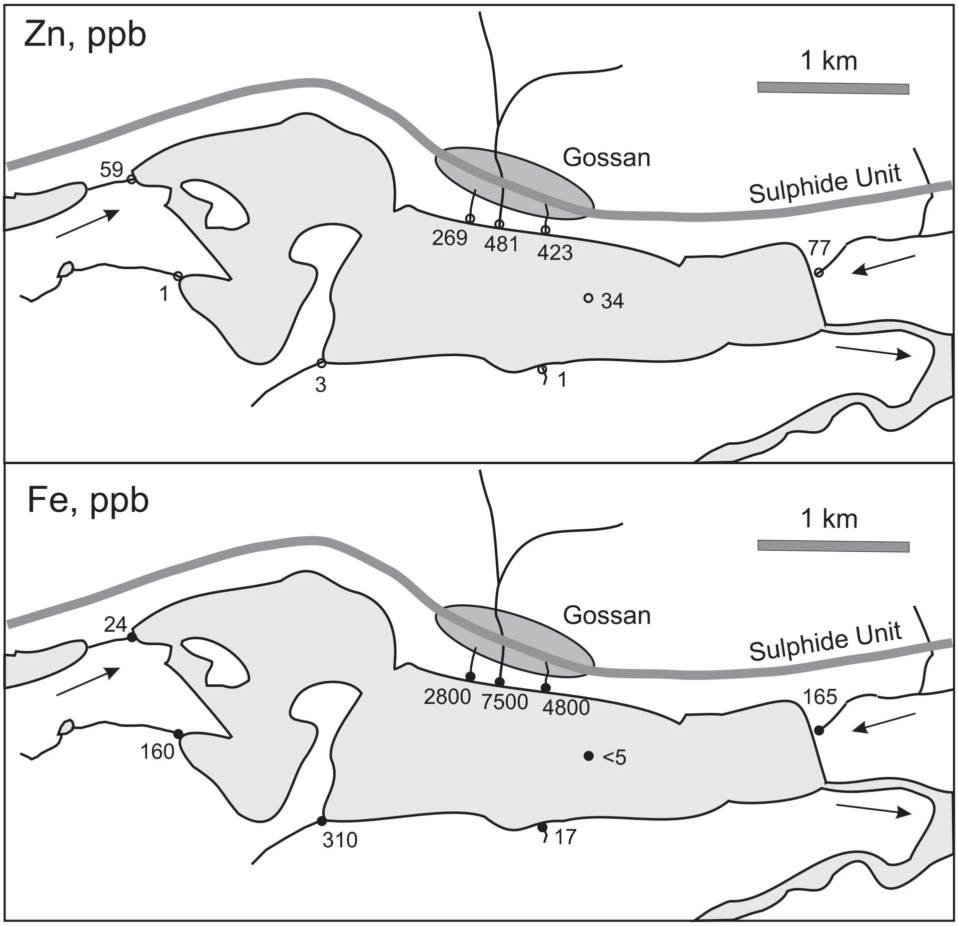


Fig. 6. Zinc and iron contents of stream and lake waters, Isiurqutuuq Lake.

inflow concentration for each part of the watershed, which required averaging the three streams entering from the north, and the three streams flowing from the south. Precipitation falling on the lake is considered to have negligible contents of the elements. In column 2, concentration is weighted by the area of each part of the watershed, then summed to estimate the concentration entering the lake from all streams. For a conservative element, such as Sr, the sum of the inflows should be equal to the concentration in the lake. This is the case (Table 2) and serves as a test for the method of calculating the mass balances of the various elements.

Manganese is also conservative, with all Mn entering the lake water remaining in solution. The solubility of Mn is increased by the low pH of the lake water. Other elements show non-conservative behaviour. All Fe entering the lake is precipitated (Fig. 6). This is most obviously shown by strong Fe-staining on the rocks and sand along the lakeshore below the north gossan. Precipitation of Fe hydroxides causes other metals (Zn, Ni, Cu) to co-precipitate. This accounts, in part at least, for the non-conservative nature of these elements, with only about one third of these metals added to the lake by stream inflow remaining in solution in the lake water. Freshly precipitated Fe hydroxides are an important natural cleanser of toxic metals.

6. Geochemistry of lake sediment cores

The location of the sediment cores are shown in Fig. 7 along with the depth from the top of the ice to

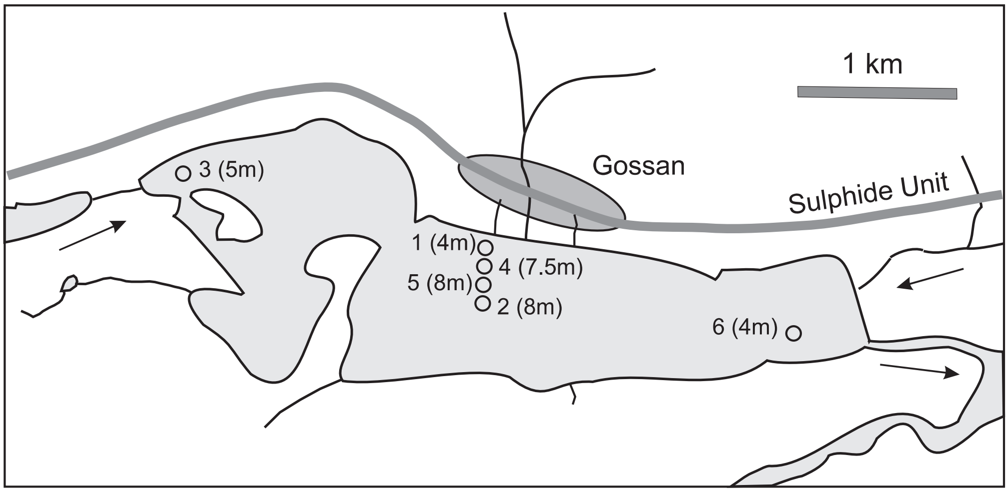


Fig. 7. Location of lake sediment cores, Isiurqutuuq Lake. After core number, depth from top of ice to sediment–water interface is shown in brackets.

the water/sediment interface of the lake bottom. For Cores 1 through 6, the core lengths were 15, 30, 26, 36, 33 and 25 cm, respectively.

Cores 1, 2, 4 and 5, extending from close to the gossan out to the middle of the lake, were similar in appearance; variation was noted in the thickness of three distinct layers of sediment. A silty layer at the top thinned from about 4 cm near shore to 1 cm at the centre of the lake. The surface of this layer had occasional plant fragments and a few small (<1 cm in length) bright red worms. Underneath the silty layer was a unit of light grey clay with rusty orange mottling, varying in thickness from 11 cm near shore (Core 1) to 35 cm in Core 4. Two cores taken closest to the centre of the lake (Cores 2 and 5) both contained light grey clay layers of about 26 cm, without mottling. At the base of Cores 2, 4 and 5, there was a few cm of a charcoal grey clay.

Two cores taken from the west and east ends of Isiurqutuuq Lake differed considerably from each other and from those taken perpendicular to the gossan zone. Core 3 was taken from the west end of the lake offshore from the stream inflow. An upper 2 cm layer of silt overlies a 8 cm layer of greyish-black clay. The base of the core consisted of the light grey clay with rusty orange mottling observed in the centre-lake cores. Core 6 from the east end of the lake has 5 cm of silt overlying a charcoal grey sand/clay mix graded into an olive grey sand.

In Fig. 8 the distributions of Al, Fe, Ni, Cu, Hg and Zn are shown for two cores, 2 and 5, collected near the centre of the lake. Iron and Al are uniform throughout the lengths of both cores, except at the top, where there is an enrichment of Fe. Mercury and Cu are also enriched in the upper part of the core, while Ni is depleted. Zinc is uniform over much of the length but decreases, along with Cu and Ni, below 20 cm depth. Enrichment of Fe and Mn in the upper part of lake sediments is a common phenomenon. Reducing conditions in deeper sediment reduce Fe^{3+} to Fe^{2+}. The Fe^{2+} form of iron is soluble and can migrate to the surface, to precipitate as Fe^{3+} hydroxides (Berner, 1980). Other elements may also dissolve at depth (Kersten and Forstner, 1989), then migrate upwards, to co-precipitate near the surface with the Fe^{3+} hydroxides. For example, decomposing organic material can render soluble Hg as methyl mercury. Enrichment of Hg in the near-surface sediment of northern lakes has also been attributed to long-distance atmospheric transport from both anthropogenic and natural sources (Farmer, 1991).

For all six sediment cores, we have calculated the average enrichment/depletion in the upper part of the sediment. For each element in each core the content in the topmost sediment was divided by the median content of the entire core. The products were then averaged over all six cores. The results show an average surface enrichment of 2.4 for Hg, 1.9 for Fe,

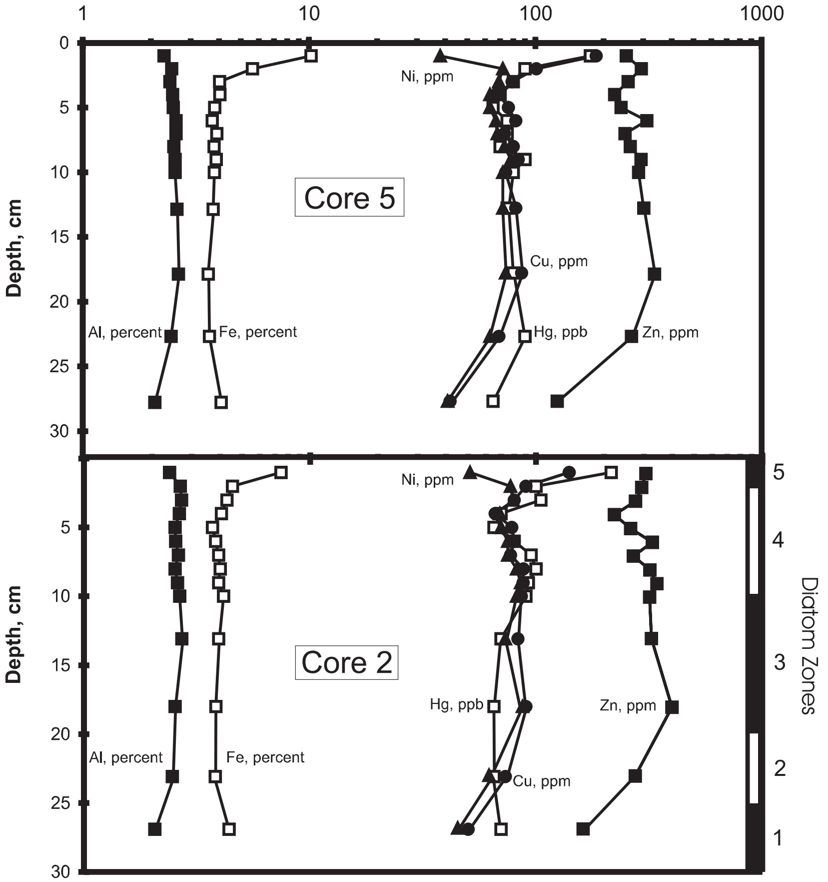


Fig. 8. Geochemical data for lake sediment Cores 2 and 5. For detail on diatom zones of Core 2, see Fig. 10.

and 1.5 for Cu and depletions of 0.9 for Zn, 0.8 for Mn, and 0.7 for Ni.

Broad relationships between cores are shown by the median element values (Fig. 9). The cores from the central portion of the lake (2, 4, 5) are finer grained and have the highest Al content, reflecting greater contents of clay minerals and other aluminosilicates. Core 6 has a lower Al content, indicating a higher amount of sand, similar to the sandy alluvial material forming the eastern shore of the lake. Cores 3 and 5, also near to shores (but not sandy shores), have intermediate contents of Al. There is a general correlation between Al and most other elements (Table 1) reflecting the higher element contents and greater sorption power of clay minerals and aluminosilicates over quartz sand. Thus for five of the cores there is a close correlation between Fe and Al (Fig. 9). The remaining core (Core 1) has a higher relative content of Fe. This core is closest to the gossan and the excess Fe reflects the precipitation of this element from Fe-rich stream waters. In addition, Hg is similarly rich in Core 1, presumably the result of similar processes. However, Zn does not show this effect.

7. Diatom studies

Core 2 was selected for diatom studies because it was collected from the central part of the lake (Fig. 7), and thus more likely to contain a complete section of lake sediment. The diatom analysis revealed five distinct floristic zones, shown in Fig. 10. Zone 1 at the base of the core (28 to 25 cm), consists of marine sediments deposited when the area was below sea level. Only marine diatoms

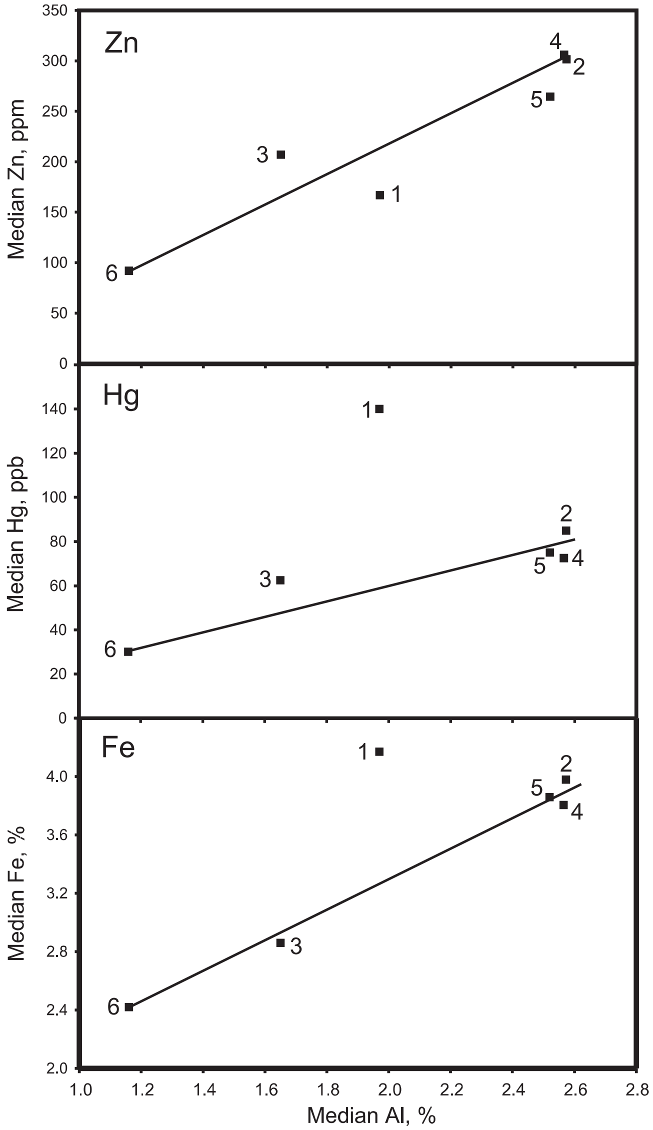


Fig. 9. Relationship of median Fe, Hg and Zn to Al for lake sediment cores. Core number is shown.

were found in this section of the core (Fig. 10). In Zone 2 (25 to 20 cm), there is an increase in freshwater diatoms. The mixture of freshwater and marine diatoms may indicate that the water was brackish. Alternatively, a distinct change from marine to freshwater conditions may have occurred during this time, but the 5 cm sediment increment for this portion of the core is too coarse to detect the transition. Zone 3 (20 to 10 cm) is characterised by alkaliphilous and circumneutral diatoms. The dominant diatom of Zone 3 is *Fragilaria exigua*, and it is accompanied by *Achnanthes pusilla*, *Frustulia vulgaris*, *Anomoeoneis vitrea*, and various species of *Fragilaria* (sensu Hustedt, 1930). Increasing acidification of Isiurqutuuq Lake is evident from 10 to 2 cm (Zone 4), as the alkaliphilous and circumneutral diatoms gradually decrease in abundance. Near the top of Zone 4, acidophilous diatom species (*Eunotia* spp., *Aulacoseira spp.*, *Eunotia exigua*, *Achnanthes marginulata*) dominate.

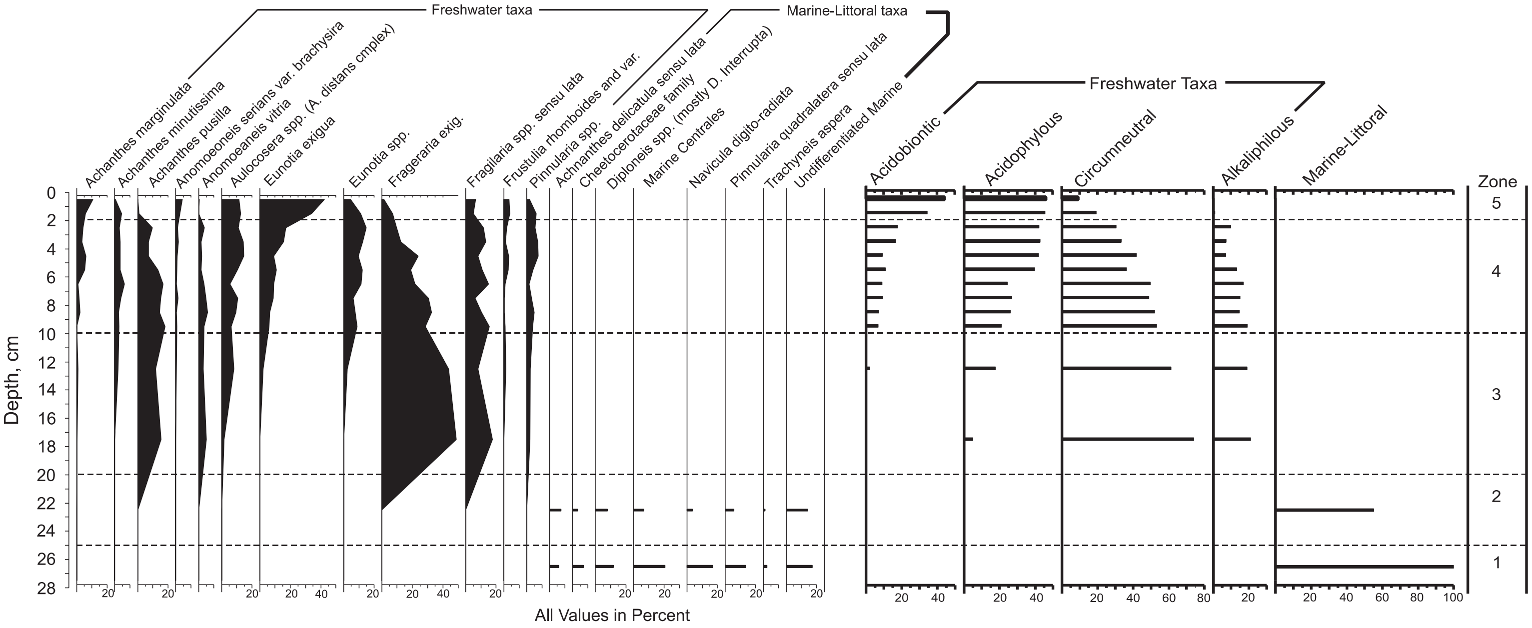


Fig. 10. Diatom diagram for lake sediment Core 2, from centre of Isiurqutuuq Lake.

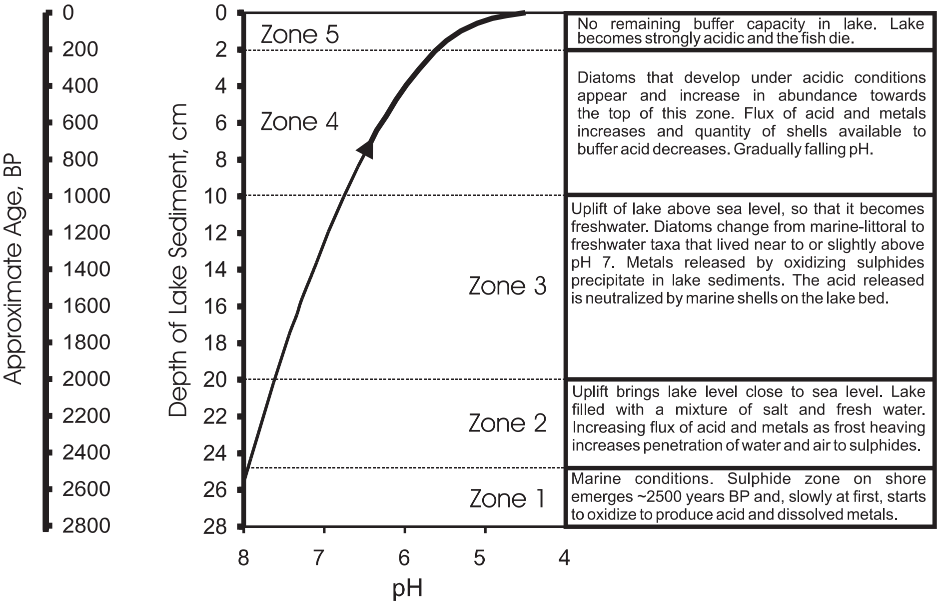
In Zone 5 (2 to 0 cm), the acidobiontic diatom *Eunotia exigua* markedly increase in abundance to dominate the modern lake-bottom sediments, representing nearly 45% of the diatom flora. Other acidophilous and acidobiontic diatoms experience a simultaneous increase in abundance (*Anomoeoneis serians* and varieties, *Frustulia rhomboides* and varieties, *Achnanthes marginulata*, as well as species of *Aulacoseira* and *Eunotia*). The presence of about 10% of alkaliphilous and circumneutral diatoms in the top cm of Core 2 may be explained by the three streams (pH 7+) flowing into Isiurqutuuq Lake (pH 4.5) along the southern shore (Fig. 4). Although the change from a marine to freshwater environment is evident in Zone 2 (25–20 cm), it is only in the upper 2 cm that strong acidification of Isiurqutuuq Lake occurred (Fig. 10). The sulphide zone on the shore of the lake emerged from the sea at about 2500 BP. Given this and the diatom evidence that the lake was close to sea level during the deposition of the 20–25 cm sediment increment, sediment deposition rates are estimated at about 1 cm/100 years. This indicates that the upper 1 cm increment, with the strongest evidence for acidification, was deposited within the past 100 years. This estimate is consistent with the observation that fish disappeared in the 1930s.

8. Discussion and conclusions

A summary of the changes in Isiurqutuuq Lake during postglacial emergence is given in Fig. 11. At 2500 BP that part of the sulphide zone now marked by a gossan emerged from the sea and weathering commenced. Release of H_2SO_4 and metals was slow at first, but increased as fracturing of the rocks permitted penetration of water and O_2 to attack the sulphide minerals. At 2500 BP, Isiurqutuuq Lake was still below sea level, and acid and metals flowing into the area were diluted and dispersed in sea water. Marine sediment continued to deposit, characterised by a distinctive marine diatom assemblage (Zone 1, Fig. 10).

With further uplift, the outlet of Isiurqutuuq Lake rose above sea level. During high tide and storms sea water flooded into the lake to mix with the freshwater influx from streams. These brackish water conditions are identified as diatom Zone 2, where both marine and freshwater species occur.

The next stage is diatom Zone 3 (Fig. 10), when Isiurqutuuq Lake and its inlet rose clear above the sea, away from the influence of marine waters. Marine-littoral diatom species were entirely replaced by alkaliphilous and circumneutral freshwater taxa. The optimum development of alkaliphilous diatom species



No remaining buffer capacity in lake. Lake becomes strongly acidic and the fish die.

Diatoms that develop under acidic conditions appear and increase in abundance towards the top of this zone. Flux of acid and metals increases and quantity of shells available to buffer acid decreases. Gradually falling pH.

Uplift of lake above sea level, so that it becomes freshwater. Diatoms change from marine-littoral to freshwater taxa that lived near to or slightly above pH 7. Metals released by oxidizing sulphides precipitate in lake sediments. The acid released is neutralized by marine shells on the lake bed.

Uplift brings lake level close to sea level. Lake filled with a mixture of salt and fresh water. Increasing flux of acid and metals as frost heaving increases penetration of water and air to sulphides.

Marine conditions. Sulphide zone on shore emerges ~2500 years BP and, slowly at first, starts to oxidize to produce acid and dissolved metals.

Fig. 11. Summary diagram of changes in Isiurqutuuq Lake during postglacial emergence.

is above pH 7, and circumneutral around pH 7 (e.g., Foged, 1970; VanLandingham, 1970; Lowe, 1974). Zone 3 marks the floristic dominance of *Fragilaria exigua*, which is considered a circumneutral diatom (e.g., Krammer and Lange-Bertalot, 1991a; Wolfe, 1996). It has also been reported from sixteen slightly acidic southern Québec lakes, displaying an abundance-weighted mean pH of 6.32 (Dixit et al., 1988). However, the pH characterisation of *Fragilaria exigua* found in the literature may be somewhat misleading. Flower et al. (1996) state that the two species created from ultrastructural delineation of *Fragilaria exigua* (*Stauroforma exiguiformis* and *S. inermis*) will doubtlessly exhibit different pH optima. As explained earlier, past accounts (including this paper) of *F. exigua* necessarily imply that grouping took place, as both *Stauroforma* species seem to frequently co-occur (Flower et al., 1996). Therefore the ecological preference of *S. exiguiformis* and *S. inermis* remains uncertain, firstly because they cannot be easily distinguished by light microscopy, and secondly because the proportion of each species in previous accounts of *F. exigua* cannot yet be determined precisely. Some preliminary but useful information on the autecology of *Stauroforma* species was obtained by Flower et al. (1996) when they re-examined selected published lake-datasets in which *Fragilaria exigua* had been reported as abundant. It seems like *Stauroforma exiguiformis* would be found in circumneutral to slightly acidic waters (~pH 6), whereas *S. inermis* would prefer waters of pH around and above 7. In the Akulivik material, it is conceivable that one of these new species may dominate over the other, and shifts in the dominance may even occur upcore. Therefore, if the dominant (*Fragilaria exigua*-derived) species of Zone 3 is *Stauroforma exiguiformis*, it would denote that conditions of the lake waters were slightly acidic, rather than circumneutral as our ecological characterisation suggests (Fig. 10). This would be in accordance with the clear increase in the contents of Zn, Cu and Ni from Zone 2 to the top of Zone 3 (Fig. 8). Whereas dissolved metals derived from the oxidising sulphides were dispersed in sea water in Zone 1, by Zone 3 these metals were confined to a freshwater lake and precipitated in the lake sediments. Alternatively, if the dominant diatom of Zone 3 is *Stauroforma inermis*, then the circumneutral to alkaliphilous characterisation of this zone (based on the diatoms found in the sediments) would be logical. This is also a plausible scenario, as Zone 3 contains a substantial number of alkaliphilous diatoms (*Achnanthes pusilla*, *Anomoeoneis vitrea*, etc.), combined with a near-absence of acidophils (e.g., *Eunotia* spp., *Frustulia rhomboides*, *Achnanthes marginulata*). But in this latter scenario, how could diatoms preferring waters ~pH 7 be flourishing when acidic, metal-rich waters were entering the lake from oxidising sulphides? First, as described above, the flux of metals and acid from oxidising sulphides increased gradually with time as the unit fractured and became more permeable. Second, when below sea level, it is likely that marine shells were deposited on the lake bottom. At Akulivik and extending inland are extensive deposits of shell sand, now being excavated and used as road fill. The $CaCO_3$ of the shell sand would have neutralised the acid until all this buffering material was consumed.

Increasing acidification of Isiurqutuuq Lake occurs in Zone 4 (10 to 2 cm). Alkaliphilous and circumneutral diatoms gradually decrease in abundance towards the top of this zone, where the diatom flora is dominated by acidophilous diatom species (optimum development below pH 7).

In the top 2 cm of Core 2 (Zone 5), the acidobiontic diatom *Eunotia exigua* is dominant (45%), accompanied by an increase in other acidophilous and acidobiontic taxa (e.g., *Frustulia rhomboides*, *Achnanthes marginulata*). Acidobiontic diatoms have an optimum development below pH 5.5 (Lowe, 1974). *Eunotia exigua* is known to be resistant to extreme acidity, such as low pH values of 2 to 3 (Renberg, 1986), and also to high concentrations of heavy metals (van Dam and Mertens, 1990). *Frustulia rhomboides* is an acidophilous/acidobiontic diatom that is present in the upper few cm of sediment. This species has been reported from Africa in areas affected by H_2SO_4 discharges coming from gold mines (Gasse, 1986).

Thus, although a transition from marine to freshwater conditions took place at about 20 cm depth in the sediment column, it was only during the deposition of the top 2 cm that conditions became strongly acidic. Arctic char fry and adults can resist pH values down to 4.6 (Iwata et al., 1990), but eggs of this fish species cannot survive in low pH conditions. Jagoe et al. (1984) observed 50% mortality after 96 h at pH 5.5. At Isiurqutuuq Lake, adult Arctic char likely survived throughout the gradual acidification of the lake (Zones 3 to 5, Fig. 10). However, the survival of char eggs was hampered (especially in the upper zone) because pH conditions were too low, which resulted in fish disappearance from the lake (top of Zone 5). Thus, the various scientific evidences are consistent with the observations of the Inuit population that the fish died out more than 60 years ago. In the 1930s, pH values, which had been in a steady decline for several hundred years, approached the present lake water value of 4.5.

Acid lakes are far from uncommon in northern Canada (Cameron, 1978, 1979, 1986). Glacial erosion stripped off old weathered surfaces to expose fresh sulphide-bearing rock to the atmosphere. In permafrost terrain, intense oxidation and frost heaving of these rocks combine to generate high fluxes of acid.

9. Remediation

The request by the Akulivik population to determine the causes of fish-kill, which prompted this study, also asked that there be consideration of remediation of Isiurqutuuq Lake, so that it could return to being an important food source.

When water from Isiurqutuuq Lake is titrated with a base (Na_2CO_3) an equivalent of 6.9 mg/l $CaCO_3$ is required to neutralise the acid. Kaminski et al. (1995) estimated the volume of the lake as 15.6×10^6 m^3, which would require the addition of 108 t of $CaCO_3$. There is a ready source of $CaCO_3$, tens of thousands of tonnes, as shell sand, on the beach at Akulivik. It would be necessary to add excess $CaCO_3$ to the lake to buffer future additions of acid. To estimate how much requires measurement of stream inflows (or outflow) to the lake. Kaminski et al. (1995) estimated the outflow as 205 l/s in August, 1994. Given the long winter, this number is likely higher than the average flow throughout the year. If average inflow and outflow is taken as 100 l/s, then annual inflow is 20% of the lake volume. Per year, 22 t $CaCO_3$ would be required to neutralise the acid inflow. If Arctic char did repopulate the lake, then the magnification of toxic metal inputs up the food chain becomes a concern. Dumping of shell sand on the gossan would inhibit oxidation of sulphides and reduce acid and metal inputs to the lake.

These calculations allow a broad estimate of the amount of $CaCO_3$ as shells in the lake bottom at the time of emergence, which initially buffered the acid entering the lake. The flux of acid to the lake has increased with time as frost heaving has made the sulphide unit more accessible to weathering. Thus, we take an average of 11 t $CaCO_3$/year to neutralise acid over the period after emergence. This would require shells on the lake bottom equivalent to 2 mm of $CaCO_3$ to neutralise acid inflows for 2000 years.

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