Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Solid-phase speciation and post-depositional mobility of arsenic in lake sediments impacted by ore roasting at legacy gold mines in the Yellowknife area, Northwest Territories, Canada



Christopher E. Schuh^{a,*}, Heather E. Jamieson^a, Michael J. Palmer^{b,1}, Alan J. Martin^c

^a Queen's University, Department of Geological Sciences and Geological Engineering, Kingston K7L 3N6, Canada

^b NWT Cumulative Impact Monitoring Program, Government of the Northwest Territories, Yellowknife X1A 2R3, Canada

^c Lorax Environmental Services Limited, Vancouver V6J 3H9, Canada

A R T I C L E I N F O

Handling Editor: Dr. R. Seal Keywords: Arsenic trioxide Giant Mine Yellowknife Ore roasting Lake sediments

ABSTRACT

Arsenic (As) concentrations in lake sediments in the Yellowknife region, Northwest Territories, Canada, are elevated from the weathering of mineralized bedrock and/or from the aerial deposition of arsenic trioxide (As₂O₃) generated via the roasting of arsenical gold ores at the now-defunct Giant Mine and other historical roasting operations in the area. Sediment cores were collected from shallow- and deep-water sites in two lakes located downwind of Giant Mine to determine the origin of As in sediments and understand how As concentrations and solid-phase speciation vary with sediment depth and spatially with changes in water depth and sediment texture. Deep-water cores were dated using ²¹⁰Pb and ¹³⁷Cs methods. Select sediment intervals were chosen for polished section preparation and analyzed using scanning electron microscopy (SEM)-based automated mineralogy, electron microprobe analysis (EMPA), and synchrotron-based microanalyses to characterize As-hosting solid phases. Sediment redox conditions and the post-depositional mobility of As at the shallow-water sites were assessed by sampling sediment porewaters using dialysis arrays (peepers). At the shallow-water sites, maximum sediment As concentrations occur at the sediment-water interface. In contrast, maximum As concentrations in the deep-water cores occur at sediment depths > 15 cm. Dating using ²¹⁰Pb and ¹³⁷Cs methods indicates that the As-rich horizons at both deep-water sites are coincident with the period of maximum emissions from the Giant Mine roaster. Four predominant As-hosting solid phases were identified: anthropogenic As2O3 from stack emissions, and authigenic realgar, As-bearing Fe-oxyhydroxide, and As-bearing framboidal pyrite. The contribution of arsenopyrite to total sediment As concentrations was negligible, suggesting that elevated As concentrations are largely derived from ore roasting. In near-surface sediments at the shallow-water sites, the dominant host of As is Fe-oxyhydroxide. Congruent porewater profiles for As and Fe indicate that the postdepositional mobilization of As is governed by the reductive dissolution of As-bearing Fe-oxyhydroxide. Deepwater sediments are enriched in As₂O₃ that has persisted for more than 60 years. The presence of authigenic Asbearing sulphides suggests that the partial dissolution of As₂O₃ leads to the formation of less bioaccessible phases where reduced sulphur (S) is available. The distributions of As-hosting solid phases at the shallow- and deepwater sites are interpreted to be both directly and indirectly influenced by water depth. Fine-grained As₂O₃ particles are less likely to persist in shallow-water areas and typically accumulate in deep-water zones as a result of sediment-focusing processes. Fine-grained organic matter also preferentially accumulates in deeper areas, which influences redox gradients in porewater, the stability field for As-bearing Fe-oxyhydroxide, and the depth of authigenic As-bearing sulphide precipitation.

1. Introduction

Arsenic (As) is an element of environmental concern due its potential to cause toxic effects in humans and other organisms (Mitchell, 2014). The roasting of gold-bearing arsenopyrite (FeAsS) ore at historical gold mines in the Yellowknife area, Northwest Territories, Canada, has resulted in a complex legacy of As contamination in the region. Giant Mine, the largest producer of gold in the region, roasted

* Corresponding author.

https://doi.org/10.1016/j.apgeochem.2017.10.025



E-mail address: c.schuh@queensu.ca (C.E. Schuh).

¹ Current address: Carleton University, Department of Geography and Environmental Studies, Ottawa K1S 5B6, Canada.

Received 9 May 2017; Received in revised form 6 October 2017; Accepted 31 October 2017 Available online 10 November 2017 0883-2927/ © 2017 Elsevier Ltd. All rights reserved.



Fig. 1. Map showing simplified bedrock geology (Wright et al., 2006) and sample-site locations relative to the City of Yellowknife and the former roasters at Giant Mine and Con Mine, Northwest Territories, Canada. Inset map shows the location of the study area within Canada. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

refractory gold ores from 1949 to 1999 (Fig. 1). Roasting on site commenced in 1949 and was conducted at 500 °C over two stages to oxidize As and sulphur (S) and convert gold-bearing arsenopyrite to gold-bearing iron (Fe) oxides amenable to cyanidation (Walker et al., 2015). During this process, a volatile gas phase of As, arsenic trioxide (As₂O₃), was produced, and eventually condensed to a dust with the crystal structure of arsenolite (Wrye, 2008; Walker et al., 2015; Bromstad et al., 2017). This reaction is given in Equation (1).

$$2\text{FeAsS} + 5\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 + 2\text{SO}_2 \tag{1}$$

Stibnite (Sb_2S_3) and antimony (Sb)-bearing sulphosalts were also present in the ore roasted at Giant, which produced a gaseous Sb-phase that was incorporated in the structure of As_2O_3 during crystallization (Riveros et al., 2000; Fawcett and Jamieson, 2011).

From 1949 to 1951, stack emissions were released directly to the atmosphere, with airborne As releases estimated at 7.5 tonnes per day (tpd) (Indigenous and Northern Affairs Canada, 2016). In 1958, a baghouse facility was constructed to collect As_2O_3 dust, reducing airborne emissions to 0.2–0.3 tpd. By 1963, a more efficient roaster system, involving two parallel electrostatic precipitators, was installed

and remained in operation until ore processing ceased at Giant in 1999. Over the course of mine life, more than 20,000 tonnes of As_2O_3 were released as stack emissions from the Giant roaster, approximately 86% of which were released before 1963 (Wrye, 2008). Arsenic trioxide, which is more soluble and bioaccessible than naturally occurring arsenopyrite (Plumlee and Morman, 2011), has potentially accumulated in the sediments of surrounding lakes, some of which are used for fishing and recreation by Yellowknife residents (Jamieson, 2014).

Arsenical gold ores were also roasted at the nearby Con Mine (1938–2003) (Fig. 1), though in lesser abundance than at Giant due to the predominantly free-milling nature of the gold. Ore roasting at Con began in April 1942 but was halted in November 1942 due to wartime restrictions, and did not resume until 1948 (Moir et al., 2006). Roasting operations permanently ceased in 1970 as ores extracted from deeper in the mine became more free-milling and less refractory (Jones, 1976), and pressure oxidation was initiated to process the refractory ore in the early 1990s (Wright, 1992). From 1948 to 1970, approximately 2500 tonnes of As_2O_3 were released to the atmosphere as stack emissions from the Con Mine roaster (Hocking et al., 1978). Due to the longer duration and larger scale of operation of the Giant Mine roaster, however, it is generally considered to have had a much greater impact in the

Yellowknife region with regards to the aerial extent and magnitude of As_2O_3 deposition (Walker, 2006).

Arsenic concentrations in Yellowknife area lake sediments may be elevated as a result of geogenic input from the weathering of mineralized bedrock and/or as a result of anthropogenic input from ore roasting at Giant Mine and other historical roasting operations in the region. For this reason, the focus of recent studies has been on establishing both geochemical background and baseline for As in lake sediments and surface waters in the Yellowknife region. Galloway et al. (2017) sampled near-surface lake sediments from 95 lakes in the Yellowknife area and found As concentrations ranging from 6.3 mg kg $^{-1}$ to > 10,000 mg kg⁻¹. These values exceed the Canadian Interim Freshwater Sediment Quality Guideline of 5.9 mg kg^{-1} (Canadian Council of Ministers of the Environment, 2002). The highest sediment As concentrations were measured in lakes located downwind of the Giant Mine roaster, results that may be consistent with the aerial deposition of As₂O₃ from stack emissions. Geogenic As is expected to be in the form of arsenopyrite, or possibly As-bearing Fe-oxyhydroxide formed from the weathering of arsenopyrite. In contrast, anthropogenic As from stack emissions is expected to be dominantly As₂O₃, which has potentially accumulated in lake sediments through historic aerial deposition or from continued runoff from terrestrial sources where it had been initially deposited.

Post-depositional changes may have affected the speciation of all As-hosting solid phases, regardless of whether they were introduced geogenically or anthropogenically to the sediments. These changes are largely controlled by adsorption, dissolution, and precipitation reactions, which are in turn largely controlled by microbially-mediated redox pathways. Iron oxyhydroxide, and to a lesser extent manganese (Mn) oxyhydroxide, often forms in sediments in oxidizing conditions prevalent near the sediment-water interface and can sequester dissolved As through sorption and co-precipitation reactions (Dzombak and Morel, 1990; Wavchunas et al., 1993; Dixit and Hering, 2003). The progressive burial of these phases over time, however, may result in the release of As to porewaters if As(V) bound to the oxyhydroxide surface is reduced to As(III) or by reductive dissolution of the host oxyhydroxide (Smedley and Kinniburgh, 2002). In reducing environments, dissolved As can be sequestered in the solid phase through sorption and co-precipitation reactions involving authigenic sulphides such as realgar (AsS or As₄S₄), orpiment (As₂S₃), and pyrite (FeS₂) (Bostick and Fendorf, 2003; O'Day et al., 2004; Lowers et al., 2007).

The spatial and depth distribution of As-hosting solid phases in lake sediments may also be influenced by sediment focusing, which describes the tendency of fine-grained particles to be redistributed from shallow-water zones to deeper areas of a lake basin (Blais and Kalff, 1995). Sediment resuspension, transportation, and mixing processes, including wave-induced turbulence, are strongest near the water surface and lose strength with increasing water depth (Mackay et al., 2012). As a result, fine-grained sediments are resuspended and transported away from shallow-water areas, and accumulate in deep-water zones where they are no longer influenced by these processes. In relatively shallow lakes, however, wave-induced mixing can still occur in areas with relatively large fetch to depth ratios (Håkanson, 1977). Bioturbation by benthic organisms can also mix and resuspend sediments, and has been shown to be a direct cause of As redistribution in soils (Covey et al., 2010). The spatial and depth distribution of As in sediments, therefore, is a result of both sedimentary and geochemical processes.

The primary objective of this study was to characterize and quantify the distribution of As-hosting solid phases in sediments from Long Lake and Martin Lake, two lakes in the Yellowknife area located downwind of Giant Mine. The specific objectives were to (1) determine whether sediment As concentrations are elevated from the aerial deposition of stack emissions or from the weathering of mineralized bedrock, (2) compare the concentrations and distributions of As-hosting solid phases in shallow- and deep-water environments, and (3) investigate whether As-hosting solid phases have undergone post-depositional changes that may affect the risk As-enriched sediments pose to human and ecological health. The results of this study are expected to be broadly applicable to other lacustrine environments affected by As contamination and will provide valuable information to support risk assessment.

2. Methods

2.1. Study area

The predominant wind direction in the Yellowknife area is east to west (Pinard et al., 2008), and lakes located to the west of the former Giant Mine roaster have been the most impacted by the aerial deposition of stack emissions in the region (Galloway et al., 2017; Palmer et al., 2015). Long Lake is located approximately 5 km southwest of Giant (62° 28' 18.12" N, 114° 25' 39.72" W) (Fig. 1). The lake has a surface area of 115 ha, an estimated maximum basin depth of 7 m, is mostly bound by granitoids, and is best described as "terminal" in that it is not connected to any downstream lakes (Martin and Soranno, 2006). Fred Henne Territorial Park is located at the eastern end of the lake and features a constructed beach, boat launch, and campground. The Yellowknife Golf Club, which features sand fairways, is located near the southwestern shore. Recent sampling indicates that the concentration of dissolved As in surface water during summer is approximately 40 µg L⁻¹ (Palmer et al., 2015).

Martin Lake is located approximately 5 km northwest of Giant and is a popular fishing and recreation area for Yellowknife residents (62° 31' 36.84" N, 114° 26' 34.8" W) (Fig. 1). The lake is 285 ha in area, has an estimated maximum basin depth of 5 m, and is predominantly bound by granitic bedrock. The lake has well-defined throughflow and is part of the Baker Creek system, which flows through the Giant Mine property and drains into Yellowknife Bay in Great Slave Lake approximately 7 km downstream of the outlet of Martin Lake. The concentration of dissolved As in Martin Lake surface water during summer is approximately 20 µg L⁻¹ (Palmer et al., 2015).

2.2. Sample collection and preparation

The fieldwork component of this study was carried out in July 2015. Sediment cores were collected using a Glew gravity corer (Glew, 1989) and transparent polycarbonate core tubes 7.5 cm in diameter and 60 cm in length. To capture differences in sediment As concentrations and solid-phase speciation associated with water depth, sediment cores were collected at shallow- and deep-water sites in both lakes (Fig. 1). In Long Lake, sample sites were located at water depths of 0.7 m (Long Lake Peeper Core - LLPC) and 5.8 m (Long Lake Core Deep - LLCD). In Martin Lake, cores were collected at water depths of 1.1 m (Martin Lake Peeper Core - MLPC) and 3.5 m (Martin Lake Core Deep - MLCD).

Collected sediment cores were immediately covered in opaque plastic bags to avoid photo-oxidation reactions during transport back to the laboratory. Long Lake cores were held for approximately 10-20 min prior to extrusion, while Martin Lake cores were held for approximately 1-2 h because of the lake's more remote location (Fig. 1). Extrusions were performed in a N2 atmosphere and the top 30 cm of sediment cores were extracted in 0.5 cm (0-10 cm), 1 cm (10-20 cm), and 5 cm (20-30 cm) intervals. Sediment samples for bulk elemental analysis were first sub-sampled and dried. Arsenic-rich sediment horizons identified by bulk elemental analysis, and sediments from the base of each deep-water core (sample LLCD-32 and sample MLCD-32 for Long Lake and Martin Lake, respectively), were then subsampled and dried in a N2 atmosphere to preserve solid-phase As speciation (Huang and Ilgen, 2006). Polished sections (30 µm thickness) were then made for subsequent characterization of As-hosting solid phases using scanning electron microscopy (SEM)-based automated mineralogy, electron microprobe analysis (EMPA), and synchrotron-based micro X-ray fluorescence (µ-XRF) and micro X-ray diffraction (µ-XRD). There was

insufficient sample volume to prepare polished sections for the sediment intervals immediately below the sediment-water interface for the shallow-water cores. Polished sections were instead prepared using sediments from 1.5 to 2 cm depth (sample LLPC-04 and sample MLPC-04 for Long Lake and Martin Lake, respectively). Similarly, a polished section was prepared using sediments from 2.5 to 3 cm depth in the LLCD core (sample LLCD-06) instead of LLCD-07 due to insufficient sample volume. A 230 Å carbon coating was applied to polished sections prior to analyses to minimize surface charging. The deep-water cores (LLCD and MLCD) were also subsampled for radiometric dating.

The post-depositional mobility of As in shallow-water sediments was assessed by sampling sediment porewaters using high resolution dialysis arrays (peepers) (Martin and Pedersen, 2002; Andrade et al., 2010; Fawcett et al., 2015). Prior to deployment in the field, peepers were cleaned with dilute Sparkleen™, rinsed with deionized water (DIW), soaked overnight in 0.5% ultra-pure HNO₃, and rinsed again with DIW. Peeper cells were then filled with DIW and covered with a 0.45 µm Sterlitech[™] polyethersulfone filter membrane. Peepers were then sealed in their DIW-filled cases and deoxygenated by periodic bubbling with ultra-pure N2 for approximately three weeks. Two sets of peepers were installed within 1 m of the shallow-water core sites in both study lakes (Fig. 1) by manually pushing the peepers, back-toback, into the sediments. Peepers were left to equilibrate with sediment porewaters for approximately two weeks. After removal, the location of the sediment-water interface was visually verified and peepers were placed back in their N2-purged cases. The cases were covered in opaque plastic bags during transport back to the laboratory. Holding times for peepers were the same as those for sediment cores described above.

Porewater samples were extracted from peeper cells by pipetting in a N₂-purged glove box. New pipette tips were used for each cell to avoid cross-contamination. For the Long Lake peepers, two rows of cells were combined vertically and sampled to a sediment depth of approximately 22 cm. Martin Lake peeper cells were subsampled at higher resolution (i.e. cells were not combined vertically) and sampled to a sediment depth of approximately 11 cm. Samples to be analyzed for trace metal (oid) concentrations were pipetted into N₂-purged, clear 8 mL highdensity polyethylene (HDPE) bottles and preserved with 8 M HNO₃. Amber-coloured 8 mL HDPE bottles were used for samples for inorganic aqueous As speciation and preserved with 12 M HCl. Both pH and Eh were measured immediately after extraction using a YSI 556 MPS. Samples were refrigerated for approximately one week prior to analyses.

2.3. Analyses

2.3.1. Sediment geochemistry

The elemental concentrations of 127 sediment sub-samples from all cores were determined at the Analytical Services Unit (ASU) at Queen's University. Samples were digested using aqua regia and subsequently analyzed for a 29-element suite including As using an Agilent Vista-PRO CCD inductively coupled optical emission spectrometer (ICP-OES). Antimony (Sb) concentrations were determined using an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) to achieve a lower detection limit. The volatilization and loss of reduced species of As and Sb during aqua regia digestion has been documented (Tighe et al., 2004, and references therein). In this study, average As recoveries for certified reference materials, which consisted of marine sediment (MESS-3) and contaminated soil (SS-2), were 96% and 103%, respectively. Recovery values between 80 and 120% are considered acceptable (Chen and Ma, 1998). Recovery calculations for Sb could not be performed due to the similarity between the Sb concentration in certified reference material SS-2 (1.02 mg kg⁻¹) and the method detection limit (1.0 mg kg $^{-1}$). Previous studies (Tighe et al., 2004; Chen and Ma, 1998), however, have shown that recoveries of Sb using aqua regia digestion for soils and sediments are typically within the acceptable range. Data quality was ensured by analyzing two sets of duplicates, a

certified reference material, and a blank for every 14 samples analyzed. Instrument calibration checks were also run to check specific standards, at the beginning of analyses, and throughout the analyses at a minimum of every 20 samples.

2.3.2. Radiometric dating

Sediment cores collected from the deep-water sites in both lakes (Fig. 1) were examined for the gamma-ray ²¹⁰Pb, ²¹⁴Bi, and ¹³⁷Cs signatures to determine the age of sediment intervals using methods described in Binford (1990). Dating was completed at the University of Ottawa using an Ortec High Purity Germanium Gamma Spectrometer. Certified Reference Materials obtained from the International Atomic Energy Association (Vienna, Austria) were used for efficiency corrections, and results were analyzed using ScienTissiME software.

2.3.3. Characterization of arsenic-hosting solid phases

Mineral liberation analysis (MLA) is an automated SEM-based software program that allows for the relative abundance of minerals in a sample to be quantified through a combination of backscatter electron (BSE) image analysis and energy-dispersive X-ray spectroscopy (EDS) (Gu, 2003; Fandrich et al., 2007; Buckwalter-Davis, 2013). For this study, automated mineralogy was conducted using a FEI Quanta 650 FEG ESEM operating under high vacuum. Operating conditions included a beam current of 10 nA and an accelerating voltage of 25 kV. Backscattered electron images used in the analyses were standardized to a copper (Cu) imaging standard. Image resolution was set to 1000 μm^2 to achieve a pixel-micrometre size of 0.51 $\mu m/pixel.$ To quantify the relative proportion of As-hosting solid phases, sparse phase liberation analysis (SPL) mode was used. The SPL measurement mode selectively identifies bright phases (i.e. As-hosting solid phases) and their external mineral associations by using a user-defined BSE greyscale range, and therefore does not provide bulk mineralogy information (Fandrich et al., 2007). The grevscale range used was 120-255. Most X-ray spectra were collected in point X-ray analysis (XBSE) mode, though a pixel-spaced X-ray analysis (GXMAP) measurement trigger with a 2-µm-pixel spacing was applied to increase the count rate on phases likely to contain only trace amounts of As, namely Fe-oxyhydroxide. The acquisition time per X-ray spectrum was 12 ms but was increased to 36 ms during GXMAP mode to enhance potential As peaks. The mineral reference library used for phase classification contained Xray spectra for both discrete As minerals (As₂O₃, arsenopyrite, As-sulphides) and potential As-hosting solid phases (Fe-oxyhydroxide, pyrite). The bulk mineralogy of each sample was also determined using X-ray modal analysis (XMOD), which is a point-counting method in which mineral identification is determined by collecting single X-ray spectra at counting points over a grid (Fandrich et al., 2007). This method, however, only provides the percentages of the mineral components of each sample, and does not yield information relating to the shape and area of each particle (Fandrich et al., 2007).

To produce a discernible peak in the EDS spectrum, elements must form approximately 3% of the solid phase being analyzed (Pirrie and Rollinson, 2011). Therefore, the As concentrations of Fe-oxyhydroxide and pyrite, solid phases suspected to contain As concentrations below detection using EDS, were determined using a JEOL JXA-8230 electron microprobe operating in wavelength-dispersive (WDS) mode. Arsenic trioxide grains were analyzed to determine their Sb content. Iron-free As-sulphides were also analyzed to determine the As/S ratio and identify the solid phase. The operating conditions (beam current, accelerating voltage, and beam diameter) and standards (lines, detector crystals, and counting times for both peaks and background) used in the analyses of each solid phase are summarized in Table 1. Atomic number, absorption, and fluorescence corrections were applied to all measured intensities.

Synchrotron-based μ -XRF element maps and μ -XRD patterns were collected using a monochromatic beam at undulator beamline 13-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory

Table 1

Summary of operating conditions and standards used in electron microprobe analysis (EMPA).

Solid Phase	Operating conditions (beam current, accelerating voltage, beam diameter)	Standards (lines, detector crystals, counting times for peaks and background)
Fe-oxyhydroxide	10 nA, 15 kV, 3.5 μm	As (synthetic FeAs ₂ , L α , TAP, 120 s) Fe (Fe ₂ O ₃ , K α , LiFL, 20 s) Ca (synthetic MgCaSi ₂ O ₆ , K α , PET, 40 s) Si (synthetic MgCaSi ₂ O ₆ , K α , TAP, 40 s) Mn (MnSiO ₂ , K α , LiFL 30 s)
Pyrite	30 nA, 15 kV, < 1 μm	As (synthetic FeAs ₂ , La, TAP, 240 s) Fe (FeS ₂ , Ka, LiFL, 10 s) S (FeS ₂ , Ka, PET, 10 s)
Arsenic trioxide	5 nA, 15 kV, 3.5 μm	As (synthetic FeAs ₂ and As ₂ S ₃ , La, TAP, 10 s) Sb (Sb ₂ S ₃ , La, PET, 60 s)
Arsenic sulphide	10 nA, 15 kV, < 1 μm	As (synthetic FeAs ₂ , Lα, TAP, 10 s) S (Fe ₇ S ₈ , Kα, PET, 10 s)

(Chicago, IL, USA). Polished sections were mounted on a sample stage positioned 45° to the incident beam. X-ray fluorescence from samples was measured using a Hitachi 4-element Vortex ME4 silicon drift diode detector positioned at 90° to the incident beam and connected to a Xspress 3 digital X-ray multi-channel analyzer system. A Perkin Elmer XRD1621 digital flat panel detector placed 400 mm from the sample and operating in transmission mode was used to measure XRD. Compositional XRF maps and XRD patterns were collected using an incident beam energy of 17.5 keV and a two-dimensional, continuous mapping mode in which the sample stage was scanned continuously through the beam. Frame rates from 50 to 100 ms per pixel were used to collect mapping data. Dioptas (Prescher and Prakapenka, 2015) software was used to calibrate and integrate XRD data and to subtract background produced by the glass sample slides. X-ray diffraction patterns were further refined for phase identification using HighScore Phus.

2.3.4. Solid-phase arsenic speciation calculations

The relative contribution of each As-hosting phase to total As concentrations was calculated using the following formula (Van Den Berghe et al., 2017):

$$As_{\%}^{h_{\chi}} = \frac{V^{h_{\chi}} * \delta^{h_{\chi}} * C_{As}^{h_{\chi}}}{\sum_{h=1}^{n} m_{As}^{h}} * 100$$
⁽²⁾

where $As_{\infty}^{h_x}$ is the relative contribution, by mass, of a particular host phase, h_x , to the total As concentration, V^{h_x} is the volume of the host phase in μm^3 , δ^{h_x} is the density of the host phase, $C_{A_x}^{h_x}$ is the concentration of As associated with the host phase, and $\sum_{h=1}^{n} m_{A_x}^{h}$ is the total mass of As in all As-hosting phases. Because SEM-based automated mineralogy is a two-dimensional technique in that it only provides the areas of particle surfaces exposed on the surface of the polished section, phase volumes were calculated by multiplying the total area on the polished section of each phase by an assumed sample thickness of 1 μm . Mineral densities used in each calculation were obtained from the Mineralogical Society of America (2016). Arsenolite, realgar, and goethite (α -FeOOH) were used as model compounds for As₂O₃, As-sulphide, and Fe-oxyhydroxide, respectively.

2.3.5. Porewater geochemistry

Porewater samples were analyzed for a 25-element suite of metal (oid)s including As and Sb using ICP-MS. The analytical method used was based on Standard United States Environmental Protection Agency (EPA) Method 200.8. The inorganic speciation of dissolved As in porewaters was determined using hydride generation atomic absorption spectrometry (HG-AAS) in accordance with Standard EPA Method 1632.

3. Results and discussion

3.1. Elemental concentrations in sediments

In Long Lake, the solid-phase concentrations of As, Sb, and other redox-sensitive elements that may be involved in the release and sequestration of As by sediments (Fe, Mn, and S) are markedly different between cores from the shallow- and deep-water sites (Fig. 2; Supplementary Data Table S1). At the shallow-water site (LLPC), where sediments are predominantly sandy, the highest concentration of As (90 mg kg⁻¹) occurs at the sediment-water interface, with values steeply declining over the uppermost 3 cm of the sediment column. Below 3 cm, As and Sb concentrations drop to levels near or below detection limits. Sediment profiles for Fe, Mn, and S are similar to those for As and Sb, with maximum concentrations also occurring at the sediment-water interface (Fig. 2).

In comparison, the deep-water core in Long Lake (LLCD) is characterized by finer-grained sediments, visible organic matter, and higher concentrations of As and Sb. Two As concentration maxima are apparent: a 1000 mg kg⁻¹ peak occurring between 3 and 4 cm depth (sample LLCD-07), and a 1500 mg kg⁻¹ peak occurring 17–18 cm below the sediment-water interface (sample LLCD-28), both of which are more than an order of magnitude higher than the shallow-water maximum (Fig. 2; Table S2). The solid-phase distribution of Sb, which is also associated with stack emissions, follows a similar pattern and is also substantially elevated when compared to the shallow-water core. Peak concentrations of Fe and Mn overlap with the shallower As maximum but decrease with depth and are not elevated in association with the deeper As maximum. Two peaks in S concentrations coincide with the As peaks.

Arsenic concentration profiles in the Martin Lake cores are generally similar to the profiles in the Long Lake cores (Fig. 2; Table S3). The concentration of As (430 mg kg⁻¹) in the shallow-water core (MLPC) is highest at the sediment surface and is almost five times higher than in sediments from the Long Lake shallow-water core (LLPC). Sediments from MLPC are more fine-grained than the sediments at LLPC, containing abundant silt, clay, and organic matter. Antimony and Mn follow similar trends to As at MLPC, with the highest concentrations occurring at the sediment surface before concomitantly decreasing with depth. In the LLPC core, the concentrations of Fe and S decrease with depth. Similar trends are absent in the concentration profiles of these elements in the MLPC core (Fig. 2).

Two sediment intervals from the deep-water core in Martin Lake (MLCD) are enriched in As (Fig. 2; Table S4): a 320 mg kg⁻¹ peak in near-surface sediments (sample MLCD-01), and a 560 mg kg⁻¹ peak occurring between 20 and 25 cm depth (sample MLCD-31). The highest concentrations of Sb and S are associated with the deeper As maximum, whereas the highest concentration of Mn occurs in association with the As maximum at the sediment-water interface. The concentration of Fe is elevated in association with both As peaks.

3.2. ²¹⁰Pb and ¹³⁷Cs dating of sediments

Dating of sediments from the LLCD core using ²¹⁰Pb methods suggests that the As peak 17.5 cm below the sediment-water interface is coincident with the period of maximum emissions from the Giant Mine roaster (1949–1951) (Fig. 2; Table S5). When operations began at Giant in 1949, roaster products were emitted directly to the atmosphere at a rate of 7.5 tonnes per day (tpd) until the first emission controls were implemented in 1951 (Indigenous and Northern Affairs Canada, 2016). However, the occurrence of elevated As concentrations in sediment



Fig. 2. Solid-phase concentrations of As, Sb, Fe, Mn, and S from sediment cores extracted from shallow- and deep-water sites in Long Lake and Martin Lake. Note that As concentration profiles for the Long Lake cores (LLPC and LLCD) are plotted on different scales. In the deep-water cores from both lakes, ²¹⁰Pb-derived timelines show important dates, and associated errors, related to the timeline of ore roasting at Giant Mine. The approximate depth of sediment intervals corresponding to dates discussed in the text are indicated by dashed lines.

horizons below the 18.5 cm interval (Fig. 2), which is inferred to have been deposited prior to the onset of ore roasting in the Yellowknife area, suggests that As derived from stack emissions has been remobilized and/or redistributed following its initial deposition. Andrade et al. (2010) similarly observed both upward and downward post-depositional remobilization of As in sediment cores collected from Yellowknife Bay (Fig. 1). In a study from Lake Tantaré, Quebec, in which the only input of As was atmospheric deposition associated with domestic coal combustion, Couture et al. (2008) found the maximum sediment As concentration to occur in an interval slightly below the horizon corresponding to the period of maximum coal usage in the early 1950s, and attributed this to the downward migration of dissolved As into more reducing zones where it was immobilized through coprecipitation and/or sorption reactions involving authigenic sulphides. Other potential redistribution processes include wave-induced turbulence and bioturbation (Håkanson, 1977; Covey et al., 2010).

In comparison, ²¹⁰Pb dating suggests that the As maximum located 3–4 cm below the sediment-water interface at LLCD occurs in sediments

deposited after ore roasting had ceased at Giant in 1999 (Fig. 2). The highest solid-phase concentrations of Fe and Mn, elements that often accumulate at oxic-anoxic boundaries in sediments (Smedley and Kinniburgh, 2002; Dixit and Hering, 2003), also occur in this interval, suggesting that As is being remobilized from the deep-core enrichment and accumulating with Fe- and Mn-oxyhydroxide phases in the oxic interfacial sediment horizons. The ¹³⁷Cs-derived timeline, however, suggests that this core has experienced some degree of physical mixing, which may have also influenced the As-concentration profile. The height of atmospheric fallout from nuclear weapons testing occurred in 1963, and therefore only one peak in ¹³⁷Cs activity is expected to occur in an undisturbed sediment core (Appleby, 2001). Two maximum ¹³⁷Cs activities occur at depths of 8.25 cm and 12.5 cm in the LLCD core, indicating that mixing has occurred. Although the LLCD core was collected from one of the deepest areas within the lake basin, the relatively large fetch to depth ratio at this site suggests that sediments may still be influenced by wave-induced turbulence (Håkanson, 1977).

At MLCD, the deep-core As enrichment occurs at 20-25 cm

sediment depth. Because these sediments were extruded as a single 5 cm section, the age resolution for this interval was very low and did not yield a reliable ²¹⁰Pb date. Arsenic concentrations, however, decrease sharply above the maximum at approximately 16.5 cm sediment depth, which is coincident with 1967 \pm 6.5 years (Fig. 2; Table S6). Stack emissions from the Giant roaster declined during the 1950s as more efficient control measures were installed. By 1963, stack emissions had been reduced to 0.1 tpd (Indigenous and Northern Affairs Canada, 2016). Furthermore, the highest ¹³⁷Cs activity, which is expected to correspond to 1963 (Appleby, 2001), also occurs in this horizon. These results suggest that the deep-core As enrichment occurs in sediments deposited prior to 1963 and reflects the period of maximum stack emissions from the roaster at Giant Mine.

Similar to the near-surface As enrichment in the LLCD core, the near-surface As peak at MLCD occurs in sediments deposited after ore roasting had ceased at Giant in 1999 (Fig. 2). The single ¹³⁷Cs maximum suggests that less mixing has occurred in the MLCD core than in the LLCD core. The formation of the near-surface As peak in MLCD can therefore be attributed to the post-depositional accumulation of As in association with diagenetic Fe- and Mn-oxyhydroxides (Andrade et al., 2010), or from the continued deposition of As-hosting solid phases from elsewhere in the lake basin and/or catchment.

The preceding discussion highlights the shortcomings of using concentration profiles of As and other diagenetically mobile elements as time markers in recently deposited sediments, as indicated by several others (Boudreau, 1999; Couture et al., 2008; Andrade et al., 2010). Moreover, relying on only the results of radiometric dating to understand these profiles, especially when mixing has occurred, is challenging. In the Yellowknife area and others affected by ore roasting, identification of the predominant As-hosting solid phases is necessary in order to conclude, with any degree of certainty, whether As was introduced geogenically or anthropogenically to the sediments.

3.3. Arsenic-hosting solid phases

Four predominant As-hosting solid phases were identified by SEMbased automated mineralogy in the sediments of Long Lake and Martin Lake: As₂O₃, As-sulphide, As-bearing Fe-oxyhydroxide, and As-bearing framboidal pyrite (Fig. 3). While hundreds of particles of these phases were identified, only six small ($< 5 \mu m$ diameter) arsenopyrite grains were found, indicating that it is not a major As-hosting solid phase in either study lake. Discrete, secondary Mn-oxyhydroxide was also not identified as an important host of As.

Arsenic trioxide particles, ranging in diameter from ~ 2 to 30 μ m, were identified by SEM-based automated mineralogy in sediments from deep-water zones in Long Lake (samples LLCD-06 and LLCD-28), and from both shallow- (sample MLPC-04) and deep-water (samples MLCD-01 and MLCD-31) zones in Martin Lake. Arsenic trioxide grains were not found in the shallow-water zone of Long Lake (LLPC). Arsenolite, the most common crystal form of As₂O₃, can form naturally from the oxidation of arsenopyrite and other As-bearing ore minerals (Drahota and Filippi, 2009), though it is unlikely to precipitate naturally in the water-saturated conditions found in lake sediments because it is highly soluble (Pokrovski et al., 1996; Nordstrom et al., 2014). Furthermore, Riveros et al. (2000) reported the solubility of As₂O₃-rich dust from Giant Mine as 11,000 to 15,000 mg L⁻¹ based on laboratory measurements of samples from the mine. This suggests that the As₂O₃ found in sediments from both study lakes is of roaster origin. Curiously, As₂O₃ from the Giant roaster has persisted in lake sediments despite its high solubility (Van Den Berghe et al., 2017), which is consistent with previous studies that found As₂O₃ to persist for more than 50 years in outcrop soils on the Giant Mine property (Wrye, 2008; Bromstad et al., 2017). Like the particles found in soils, the As₂O₃ particles found in lake sediments show only subtle textural evidence of dissolution (Fig. 3a). The ability of As₂O₃ to persist in soils and sediments for more than 50 years might be best explained by the influence of Sb content on solubility, though this is not well documented (Jamieson, 2014). In a study to determine if marketable As₂O₃ could be recovered from the As₂O₃rich roaster dust stored underground at Giant, Riveros et al. (2000) postulated that only low-Sb As₂O₃ crystals produced in the Giant roaster dissolve readily in water at temperatures < 100 °C.

Electron microprobe analysis of four As_2O_3 particles from Long Lake and Martin Lake sediments yielded Sb concentrations ranging from below detection (~0.07 wt%) to 0.27 wt%, which are within the range



Fig. 3. SEM-BSE images of As-hosting solid phases associated with the As-rich sediment intervals identified in cores from Long Lake and Martin Lake. Corresponding μ-XRF element maps show As-Kα (red), Fe-Kα (green), and Sb-Lβ1 (blue) intensities. (a) As₂O₃ from MLPC-04. (b) Arsenic sulphide from LLCD-06. (c) Authigenic As-bearing Fe-oxyhydroxide from LLPC-04. (d) Arsenic-bearing framboidal pyrite from LLCD-06. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reported by Riveros et al. (2000). It is evident in the compositional μ -XRF maps (Fig. 3a) that even particles determined to contain Sb in concentrations lower than detection using EMPA do in fact contain trace amounts of Sb. The presence of Sb, which was also present in the ore roasted at Giant, provides additional evidence that these particles are of roaster origin. The rate of As₂O₃ dissolution in low-temperature water, which is characteristic of lakes in the Yellowknife area, has been documented to be very slow in several studies (Riveros et al., 2000; Yue and Donahoe, 2009; Nordstrom et al., 2014), and may also be a contributing factor that has allowed As₂O₃ to persist in the sediments of Yellowknife lakes for more than 60 years.

A discrete As-sulphide phase was identified by SEM-based automated mineralogy in all polished sections analyzed. This phase is easily distinguished from arsenopyrite based on the absence of Fe in both the EDS spectra and μ -XRF maps (Fig. 3b). Because Fe-free As-sulphide does not occur in association with mineralization (Coleman, 1957) or in any of the tailings streams at Giant (Walker et al., 2015; Fawcett and Jamieson, 2011), it is inferred to be an authigenic phase. Using X-ray absorption spectroscopy (XAS), Fawcett et al. (2015) identified an As (III)-S phase in the reduced horizons of a core extracted from a water body located on the Giant Mine property and concluded that its formation was the result of diagenetic processes.

Eleven As-sulphide particles in As-enriched samples from both lakes were examined using EMPA. Normalization of elemental weight percentages, which were low due to the small size of the particles $(< 10 \ \mu m)$, resulted in mean elemental mass concentrations ranging from 68.5 to 70.2% and 29.8-32.3% for As and S, respectively. The mean atomic ratio of As to S for all particles analyzed was approximately 1:1, suggesting that the As-sulphide phase is realgar (AsS or As₄S₄) rather than orpiment (As₂S₃). O'Day et al. (2004) documented the formation of a "realgar-like" As-sulphide under sulphate-reducing conditions in aquifer sediments that had received As inputs from a former pesticide-manufacturing facility. The µ-XRD analyses of 18 Assulphide grains in this study produced 2-D diffraction patterns with broad and diffuse rings, indicating short-range order in a poorly crystalline material (Jamieson et al., 2011). The As-sulphide phase identified in this study is best described as an amorphous, realgar-like precipitate.

Particles of authigenic Fe-oxyhydroxide were identified by SEMbased automated mineralogy in all samples and are spatially associated with organic matter (Fig. 3c). Authigenic Fe-oxyhydroxide was distinguished from detrital Fe-oxide based on grain morphology. Authigenic particles do not have a well-defined shape in BSE images (Fig. 4a), whereas detrital grains appear more angular and have better defined edges (Fig. 4b). Seven authigenic grains (23 spots) and three (six spots) detrital grains were analyzed using EMPA. The average As concentrations of authigenic Fe-oxyhydroxide and detrital Fe-oxide were determined to be 3 wt% and 0 wt%, respectively. A change in the As content of authigenic Fe-oxyhydroxide with depth is also apparent. Grains from near-surface sediments in both the shallow- and deep-water cores from Long Lake were found to have a mean As content of 4 wt%, whereas the mean As content of particles from the lower As enrichment in the deep-water core (LLCD) is 2 wt%. These results are consistent with the release of As to porewaters as conditions become more reducing with depth in the sediment column (Smedley and Kinniburgh, 2002). A difference between lakes was also evident, with particles from the near-surface As enrichment in the MLPC core having a mean As content of 2 wt%. Like the As-sulphide grains in this study, µ-XRD analysis of 27 authigenic Fe-oxyhydroxide grains produced diffraction patterns consistent with a poorly crystalline material. The amorphous nature of these grains suggests that they form as a result of microbial Fe oxidation, the products of which are poorly crystalline and fine-grained (micrometre-to nanometre-sized particles) (Benzerara et al., 2011). Although no discrete As-bearing Mn-oxyhydroxide particles were identified, the Mn content of authigenic Fe-oxyhydroxide ranged from 0 to 7 wt%.

Authigenic pyrite was also identified as a host of As in all samples. In these sediments, pyrite formed in situ was distinguished from its detrital counterpart based on texture. The authigenic variety occurs predominantly as framboids (Fig. 4c) whereas detrital pyrite is present as massive grains (Fig. 4d). Framboids form in low-temperature sedimentary environments in reducing conditions, often in the presence of decomposing organic matter and sulphate-reducing bacteria, and may incorporate dissolved As during their formation (Moore et al., 1988; Jambor et al., 2009). Electron microprobe analysis of 26 framboidal pyrites revealed that the average As content of these particles is 0.2 wt % in all samples, irrespective of their depth within the sediment column. Furthermore, the concentrations of As and S are inversely correlated, suggesting that As is substituting for S within crystallographic sites during framboid precipitation (Savage et al., 2000). Lowers et al. (2007) documented the assimilation of As into framboidal pyrite in sediments contained within sulphate-reducing horizons and similarly observed no change in the As content of framboids with sediment depth, and the substitution of As for S.

Realgar, As-bearing Fe-oxyhydroxide, and As-bearing pyrite are all less bioaccessible than As_2O_3 (Plumlee and Morman, 2011). These phases, which are interpreted to form from the partial dissolution of As_2O_3 , may represent an *in situ* mechanism for reducing the mobility and bioaccessibility of As from stack emissions in the sediments of Yellowknife lakes, so long as redox conditions are not altered in the sediment column.

3.4. Solid-phase speciation and post-depositional mobility of arsenic

3.4.1. Long Lake shallow-water site (LLPC)

Arsenic-bearing Fe-oxyhydroxide comprises 88% of the total As concentration in near-surface sediments (LLPC-04) at the shallow-water site in Long Lake (Fig. 5a; Table S7), which is indicative of oxidizing conditions. The shallow water location and predominance of coarsegrained sediments at this site are indicative of a high-energy environment from which the redistribution of finer sediments is common (Blais and Kalff, 1995). In the likely event that fine-grained As₂O₃ particles were originally deposited at this location, it is probable that wind-induced wave action, ice scouring in winter, and other mechanisms of erosion would limit their accumulation in shallow-water sediments. This process can explain the absence of a deep-core As enrichment at this site. The As-bearing authigenic Fe-oxyhydroxide particles in this sample are poorly crystalline to amorphous, suggesting they are recent precipitates (Ford et al., 1997; Ford, 2002; Dixit and Hering, 2003). The deposition of wind-blown and slope-eroded sand from the nearby Yellowknife Golf Club (Fig. 1), which was observed during sampling, may have also diluted sediment As concentrations at this site. Quartz comprises approximately 44% of the modal mineralogy at LLPC, which is indicative of sandy sediments. This value likely represents a combination of sand dilution from the golf course and within-lake sedimentary processes that concentrate sand-sized particles at this location.

The geochemistry of sediment porewaters at LLPC provides additional insight into the geochemical controls governing the distribution of As-hosting solid-phases and post-depositional mobility of As at this site. Porewater profiles of pH and Eh (Fig. 6; Table S8) confirm that conditions are oxidizing in near-surface sediments, and become progressively more reducing with depth in the sediment column. A sharp decrease in pH just below the sediment surface is also apparent, which is likely indicative of the oxidation of Fe(II), As(III), and other reduced species, which are acid-generating reactions (Nordstrom and Alpers, 1999; Jamieson et al., 2013; Nordstrom et al., 2014). As conditions become suboxic with depth and aqueous species are reduced, there is a concomitant increase in pH. This can likely be attributed to suboxic redox pathways that generate bicarbonate alkalinity such as Fe(III) reduction, Mn(IV) reduction, and sulphate reduction (Froelich et al., 1979; Boudreau, 1999).

The maximum porewater As concentration in LLPC sediments is



Fig. 4. Backscattered electron (BSE) images highlighting the textural arguments used to distinguish between authigenic and detrital Fe-oxyhydroxide and pyrite grains, respectively, and their associated As concentrations. (a) Authigenic As-bearing Fe-oxyhydroxide from LLPC-04. (b) Detrital Fe-oxide from MLCD-01. (c) Arsenic-bearing framboidal pyrite from MLPC-04. (d) Detrital pyrite from MLPC-04.

located approximately 10 cm below the maximum sediment As concentration (Fig. 7). Congruent porewater profiles for As and Fe indicate that the remobilization of As is governed by the reduction of As-bearing Fe-oxyhydroxide, which is the predominant solid-phase host of As at this location (Fig. 5a). Arsenate is the principal aqueous species in near-surface porewaters, but As(III) becomes dominant with depth (Fig. 8). The change from As(V)- to As(III)-dominated porewaters is roughly coincident with the change in redox conditions inferred from the pH and Eh profiles (Fig. 6). Additionally, the increase in As(III) with depth suggests that it is the principal species being remobilized from Asbearing Fe-oxyhydroxide. The scarcity of As(III) in near-surface porewaters implies that upwardly diffusing As(III) is oxidized to As(V) and/ or immobilized by Fe-oxyhydroxide before reaching the overlying water column.

3.4.2. Long Lake deep-water site (LLCD)

In sediments associated with the near-surface As maximum at the deep-water site in Long Lake (LLCD-06), realgar and pyrite account for 71% and 12% of the total As inventory, respectively (Fig. 5a; Table S9). The high relative proportions of these phases, which are interpreted to form from the partial dissolution of As_2O_3 (12%), are indicative of sulphate-reducing conditions. Arsenic-bearing Fe-oxyhydroxide, however, comprises ~5% of the total As concentration, suggesting that this interval may represent a natural redox boundary where both oxidized and reduced species are relatively stable. The elevated As concentrations and predominance of sulphides in the near-surface maximum can also be attributed to sediment focusing, as fine-grained As_2O_3 and organic matter are transported to zones of accumulation in deep-water areas. It is also likely that physical mixing processes, the occurrence of



Fig. 5. Schematic diagrams showing the relative contribution of each As-hosting solid phase to total As concentrations, as determined by automated mineralogy, in As-enriched sediment intervals in cores from (a) Long Lake and (b) Martin Lake. Vertical exaggeration is approximately 400x. Diagrams are not meant to be representative of the actual bathymetric features of each lake. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Profiles of pH and Eh across the sediment-water





which was evident based on ¹³⁷Cs dating, has influenced the distribution of As-hosting solid phases in this horizon.

Of all the samples analyzed in this study, the As-enriched sediment interval 17-18 cm below the sediment surface (LLCD-28) contains the highest number of As_2O_3 particles (47), suggesting that this As peak is in fact representative of the period of maximum emissions from the Giant Mine roaster. In this interval, As_2O_3 accounts for only ~30% of the total As concentration (Fig. 5a; Table S10), suggesting that the formation of realgar and pyrite, which comprise close to 70% of the total As concentration, is attenuating dissolved As and reducing its bioaccessibility under sulphate-reducing conditions. Authigenic Asbearing sulphides also account for approximately 90% of the total As concentration in the sediment layer at the base of the core (LLCD-32) (Table S11), which explains the occurrence of elevated As concentrations in sediments inferred by ²¹⁰Pb and ¹³⁷Cs dating to have been deposited many years before the onset of ore roasting in the Yellowknife area. The partial dissolution of As₂O₃ and subsequent release of As to sediment porewaters creates a concentration gradient that drives the downward diffusion of dissolved As into more reducing horizons, where it is sequestered through co-precipitation and/or sorption reactions involving authigenic sulphides. Sediments in this interval may have also been redistributed by physical mixing processes, since a particle of



Fig. 8. Percent composition of As(III) and As(V) in LLPC

and MLPC porewaters.

3.4.4. Martin Lake deep-water site (MLCD)

deposition of stack emissions.

As₂O₃ was identified, and its only logical source is from atmospheric

3.4.3. Martin Lake shallow-water site (MLPC)

The solid-phase distribution of As in near-surface sediments from the shallow-water site in Martin Lake (MLPC-04) is very different from that at the shallow-water site in Long Lake. In MLPC-04, As₂O₃ comprises 73% of the total As concentration, suggesting that this site is largely influenced by continued terrestrial loading. Additionally, the predominance of As-bearing sulphides (27%) (Fig. 5b; Table S12), the low proportion (< 1%) of As-bearing Fe-oxyhydroxide, and the finergrained character of the sediments indicate that conditions at this site are more reducing and lower energy than at LLPC. Compared to the LLPC site, which is relatively open (long fetch), the MLPC core was collected in a relatively calm bay (Fig. 1), and is therefore less likely to be influenced by wave action and erosion. It is also unlikely that total sediment As concentrations at MLPC have been diluted by wind-blown and slope-eroded sand, which may be important at the LLPC site. Modal mineralogy indicates that sediments are less sandy at this location, as quartz accounts for only 17% of the total particle inventory at MLPC. The absence of a deep-core As enrichment at MLPC similar to those found in the deep-water cores (Fig. 2) suggests that this site is not located in a purely depositional setting, but is likely still influenced by some within-lake erosional processes.

In Fig. 6, the same down-core trends in pH and Eh observed in LLPC porewaters are apparent in porewaters at MLPC, although redox conditions are more reducing in near-surface sediments at MLPC and the transition from oxidizing to reducing conditions occurs at shallower sediment depths. High dissolved As concentrations in porewaters can likely be attributed to the partial dissolution of As₂O₃ in near-surface sediments, however, congruent profiles of dissolved As and Fe in MLPC porewaters suggest that the reductive dissolution of As-bearing Feoxyhydroxide does release some As to solution at this site, albeit at shallower sediment depths than at LLPC. Hence, Fe-oxyhydroxide particles were not found to be major hosts of As in the 1.5-2 cm interval below the sediment surface in the MLPC core, owing to their dissolution under reducing conditions at this depth. Additionally, decreasing As concentrations below the porewater maximum at MLPC reflect the removal of As from pore solution by the precipitation of As-bearing sulphides, which are abundant at this site (Fig. 5b). Like at LLPC, As(V) is the principal aqueous As species in near-surface porewaters at MLPC, although As(III) becomes dominant at shallower sediment depths (Fig. 8; Table S13). The change from As(V)- to As(III)-dominated porewaters also occurs concurrently with the change in redox conditions inferred from the pH and Eh profiles (Fig. 6).

site in Martin Lake (MLCD-01), As₂O₃, Fe-oxyhydroxide, realgar, and pyrite account for approximately 64%, 21%, 7.5%, and 7.5% of the total As concentration, respectively (Fig. 5b; Table S14). The relative abundance of As₂O₃ in sediments near the sediment-water interface, which are interpreted to have been deposited after ore roasting ceased at Giant in 1999 (Fig. 2), suggests that particles from shallower areas within the lake basin, or possibly from terrestrial sources within the catchment, are still being eroded, transported, and deposited in deepwater zones. The partial dissolution of these particles, and potentially the upward diffusion of As from deeper in the core and/or precipitation from the overlying water column, results in the formation of As-bearing Fe-oxyhydroxide. The As peak at depth (MLCD-31), which is inferred by ²¹⁰Pb and ¹³⁷Cs dating to correspond to the period of maximum stack emissions from the Giant Mine roaster, consists almost entirely of Asbearing sulphides; realgar and pyrite account for 71% and 14% of the total As concentration, respectively. The relative proportion of As₂O₃ in MLCD-01 (75%) is higher than in MLCD-31 (16%) (Fig. 5b; Table S15), although the latter contains more than twice the number of As₂O₃ particles. Similar to the deep-water core from Long Lake, the majority of roaster-generated As_2O_3 (deposited > 60 years ago) at this site has likely dissolved and been sequestered in less bioaccessible solid phases. Moreover, authigenic As-bearing sulphides comprise > 85% of the total

As concentration in sediments from the base of the core (MLCD-32)

(Table S16), indicating that dissolved As is diffusing downward and

being immobilized through authigenic sulphide precipitation.

In sediments from the near-surface enrichment at the deep-water

4. Conclusions

The presence of As₂O₃ in high concentrations, a phase which is unlikely to form naturally in lacustrine environments, indicates that elevated As concentrations in sediments from Long Lake and Martin Lake are largely the result of historical ore roasting operations in the Yellowknife area. Arsenic introduced geogenically to the sediments is inferred to be negligible, as indicated by the low number of detrital arsenopyrite grains observed. The results of radiometric dating suggest that the majority of As was introduced to the sediments during the period of maximum roaster emissions at Giant Mine. It is clear from this study, however, that identifying the solid-phase hosts of As is essential to interpreting concentration profiles in sediments impacted by the roasting of As-bearing ores. It is striking that As₂O₃, which is highly bioaccessible, has persisted in lake sediments for more than 60 years, although there is evidence that its partial dissolution has resulted in the formation of less bioaccessible phases, including As-bearing Fe-oxyhydroxide and As-bearing sulphides.

The differences in sediment As concentrations and the distributions of As-hosting solid phases observed between shallow- and deep-water sites in both lakes can be attributed to a combination of sediment-focusing processes and redox conditions, which are related. As a direct influence of textural sorting, fine-grained particles of As₂O₃ are less likely to accumulate in higher-energy, shallow-water environments and tend to be redistributed to deeper areas. Deep-water areas also serve as preferential repositories for fine-grained organic matter. The accumulation rate of organic matter will in turn govern redox gradients in porewater, the stability field for As-bearing Fe-oxyhydroxide, and the depth of authigenic As-bearing sulphide precipitation. Arsenic trioxide in near-surface, shallow-water sediments is likely the result of continued deposition from terrestrial sources. Based on these observations. there are two types of solid-phase As peaks present in the sediments of Yellowknife lakes. In deep-water areas where fine-grained materials accumulate, As enrichments at depth can be attributed to the historic aerial deposition of stack emissions from the Giant Mine roaster, whereas As peaks in near-surface and shallow-water sediments are related to redox processes. Continued terrestrial weathering from the surrounding catchment is an ongoing source of As to both shallow- and deep-water sediments.

In shallow-water sediments, the post-depositional remobilization of As is governed by the reductive dissolution of As-bearing Fe-oxyhydroxide. The release of As to suboxic porewaters, predominantly as As (III), creates a concentration gradient that drives the upward diffusion of As toward the sediment-water interface where it is oxidized to As(V). The porewater profiles of As and Fe indicate that some upwardly diffusing As is attenuated by Fe-oxyhydroxide in near-surface sediments, although more work is necessary to determine the rate and magnitude of diffusive flux across the sediment-water interface into the overlying water column.

Acknowledgments

This project is in part funded by a Natural Sciences and Engineering Council of Canada (NSERC) Strategic Grant (Grant #309983638) awarded to Jules Blais (Principal Investigator), and H. E. Jamieson, John Smol, and Alexandre Poulain (co-Principal Investigators), by funds awarded to C. E. Schuh by the Northern Scientific Training Program (NSTP, Project #306001), and by the Government of the Northwest Territories Cumulative Impact Monitoring Program (GNWT-CIMP, Project #168). Synchrotron-based analyses were performed at GeoSoilEnviroCARS (The University of Chicago, Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation -Earth Sciences (EAR-1128799) and Department of Energy- GeoSciences (DE-FG02-94ER14466). This research used resources of the Advanced Photon Source (APS), a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The authors would like to extend thanks to Agatha Dobosz, Brian Joy, and Martin Van Den Berghe of Queen's University, the Analytical Services Unit (ASU) at Queen's University, Linda Kimpe of the University of Ottawa, Tony Lanzirotti and Matt Newville of APS, Taiga Environmental Laboratory, and Kirsten Maitland, James Blanchard, and Trey Madsen for their assistance in the field.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx. doi.org/10.1016/j.apgeochem.2017.10.025.

References

Andrade, C.F., Jamieson, H.E., Kyser, T.K., Praharaj, T., Fortin, D., 2010. Biogeochemical redox cycling of arsenic in mine-impacted lake sediments and co-existing pore waters near Giant Mine, Yellowknife Bay, Canada. Appl. Geochem 25, 199-211.

- Appleby, P.G., 2001. Chronostratigraphic techniques in recent sediments. In: Last, W.M., Smol, J.P. (Eds.), Tracking Environmental Change, and Chronological Techniques. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 171–204.
- Benzerara, K., Miot, J., Morin, G., Ona-Nguema, G., Skouri-Panet, F., Ferard, C., 2011. Significance, mechanisms and environmental implications of microbial biomineralization. C. R. Geosci. 343 (2–3), 160–167.
- Binford, M.W., 1990. Calculation and uncertainty analysis of ²¹⁰Pb dates for PIRLA project lake sediment cores. J. Paleolimnol. 3, 253–267.
- Blais, J.M., Kalff, J., 1995. The influence of lake morphometry on sediment focusing. Limnol. Oceanogr. 40 (3), 582–588.
- Bostick, B.C., Fendorf, S., 2003. Arsenite sorption on troilite (FeS) and pyrite (FeS2). Geochim. Cosmochim. Acta 67, 909–921.
- Boudreau, B.P., 1999. Metals and models: diagenetic modelling in freshwater lacustrine sediments. J. Paleolimnol. 22, 227–251.
- Bromstad, M.J., Wrye, L.A., Jamieson, H.E., 2017. The characterization, mobility, and persistence, of roaster-derived arsenic in soils at Giant Mine, NWT. Appl. Geochem 82, 102–118.
- Buckwalter-Davis, M.J., 2013. Automated Mineral Analysis of Mine Waste. M.Sc. Thesis. Queen's University.
- Canadian Council of Ministers of the Environment, 2002. Canadian sediment quality guidelines for the protection of aquatic life. In: Canadian Environment Quality Guidelines.
- Chen, M., Ma, L.Q., 1998. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. J. Environ. Qual. 27, 1294–1300.
- Coleman, L.C., 1957. Mineralogy of the giant Yellowknife gold mine, Yellowknife, NWT. Econ. Geol. 52, 400–425.
- Covey, A.K., Furbish, D.J., Savage, K.S., 2010. Earthworms as agents for arsenic transport and transformation in roxarsone-impacted soil mesocosms: a μ XANES and modeling study. Geoderma 156, 99–111.
- Couture, R.M., Gobeil, C., Tessier, A., 2008. Chronology of atmospheric deposition of arsenic inferred from reconstructed sedimentary records. Environ. Sci. Technol. 42, 6508–6513.
- Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37, 4182–4189.
- Drahota, P., Filippi, M., 2009. Secondary arsenic minerals in the environment: a review. Environ. Int. 35 (8), 1243–1255.
- Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. John Wiley & Sons, New York.
- Fandrich, R., Gu, Y., Burrows, D., Moeller, K., 2007. Modern SEM-based mineral liberation analysis. Int. J. Min. Process 84, 310–320.
- Fawcett, S.E., Jamieson, H.E., 2011. The distinction between ore processing and postdepositional transformation on the speciation of arsenic in mine waste and sediment. Chem. Geol. 283, 109–118.
- Fawcett, S.E., Jamieson, H.E., Nordstrom, D.K., McCleskey, R.B., 2015. Arsenic and antimony geochemistry of mine wastes, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. Appl. Geochem 62, 3–17.
- Ford, R.G., Bertsch, P.M., Farley, K.J., 1997. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. Environ. Sci. Technol. 31 (7), 2028–2033
- Ford, R.G., 2002. Rates of hydrous ferric oxide crystallization and the influence on coprecipitated arsenate. Environ. Sci. Technol. 36, 2459–2463.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., 1979. Early oxidation of organic matter in pelagic sediments of the east equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43, 1075–1090.
- Galloway, J.M., Swindles, G.T., Jamieson, H.E., Palmer, M., Parsons, M.B., Sanei, H., Macumber, A.L., Patterson, R.T., Falck, H., 2017. Organic matter control on the distribution of arsenic in lake sediments impacted by ~65 years of gold ore processing in subarctic Canada. Sci. Total Environ. http://dx.doi.org/10.1016/j. scitotenv.2017.10.048. (in press).
- Glew, J., 1989. A new trigger mechanism for sediment core sampling. J. Paleolimnol. 2, 241–243.
- Gu, Y., 2003. Automated scanning electron microscope based mineral liberation analysis: an introduction to JKMRC/FEI mineral liberation analyzer. J. Min. Mater. Charact. Eng. 2 (1), 33–41.
- Håkanson, L., 1977. The influence of wind, fetch, and water depth on the distribution of sediments in Lake Vänern, Sweden. Can. J. Earth Sci. 14, 397–412.
- Huang, J.H., Ilgen, G., 2006. Factors affecting arsenic speciation in environmental samples: sample drying and storage. Intern. J. Environ. Anal. Chem. 86 (5), 347–358.
- Hocking, D., Kuchar, P., Plambeck, J.A., Smith, R.A., 1978. The impact of gold smelter emissions on vegetation and soils of a sub-Arctic forest-tundra transition ecosystem. J. Air Pollut. Control Assoc. 28, 133–137.
- Indigenous and Northern Affairs Canada, 2016. Giant Mine Remediation Plan (History of Giant Mine).
- Jambor, J.L., Martin, A.J., Gerits, J., 2009. The post-depositional accumulation of metalrich cyanide phases in submerged tailings deposits. Appl. Geochem 24, 2256–2265.
- Jamieson, H.E., Walker, S.R., Andrade, C.F., Wrye, L.A., Rasmussen, P.E., Lanzirotti, A., Parsons, M.B., 2011. Identification and characterization of arsenic and metal compounds in contaminated soil, mine tailings, and house dust using synchrotron-based microanalysis. Hum. Ecol. Risk Assess. 17 (6), 1292–1309.
- Jamieson, H.E., Bromstad, M.J., Nordstrom, D.K., 2013. Extremely arsenic-rich, pHneutral waters from the Giant mine, Canada. Mine Water Solut. 2013, 1–10.
- Jamieson, H.E., 2014. The legacy of arsenic contamination from mining and processing refractory gold ore at Giant Mine, Yellowknife, Northwest Territories, Canada. Rev. Mineral. Geochem 79, 533–551.

Jones, P.R., 1976. Cominco's Con Mine. Paper presented at Session 5 of the Canadian Institute of Mining and Metallurgy's Metal Mining Division, 1976 Underground Operators Conference.

Lowers, H.A., Breit, G.N., Foster, A.L., Whitney, J., Yount, J., Uddin, Md N., Muneem, Ad A., 2007. Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. Geochim. Cosmochim. Acta 71 (11), 2699–2717.

- Mackay, E.B., Jones, I.D., Folkard, A.M., Barker, P., 2012. Contribution of sediment focussing to heterogeneity of organic carbon and phosphorus burial in small lakes. Freshw. Biol. 57, 290–304.
- Martin, A.J., Pedersen, T.F., 2002. Seasonal and interannual mobility of arsenic in a lake impacted by metal mining. Environ. Sci. Technol. 36, 1516–1523.
- Martin, S.L., Soranno, P.A., 2006. Lake landscape position: relationships to hydrologic connectivity and landscape features. Limnol. Oceanogr. 51 (2), 801–814.
- Mineralogical Society of America, 2016. Handbook of Mineralogy.

Mitchell, V.L., 2014. Health risks associated with chronic exposures to arsenic in the environment. Rev. Mineral. Geochem 79, 435–449.

- Moir, I., Falck, H., Hauser, R.L., Robb, M., 2006. The history of mining and its impact on the development of Yellowknife. In: Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J. (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results of the EXTECH III Multidisciplinary Research Project. Geological Association of Canada, Mineral Deposits Division, Special Publication No. 3.
- Moore, J.N., Ficklin, W.H., Johns, C., 1988. Partitioning of arsenic and metals in reducing sulfidic sediments. Environ. Sci. Technol. 22, 432–437.
- Nordstrom, D.K., Alpers, C.N., 1999. Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. Proc. Natl. Acad. Sci. U. S. A. 96 (7), 3455–3462.
- Nordstrom, D.K., Majzlan, J., Königsberger, E., 2014. Thermodynamic properties for arsenic minerals and aqueous species. Rev. Mineral. Geochem 79, 217–255.
- O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. P. Natl. Acad. Sci. U. S. A. 101 (38), 13703–13708.
- Palmer, M.J., Galloway, J.M., Jamieson, H.E., Patterson, R.T., Falck, H., Kokelj, S.V., 2015. The concentration of arsenic in lake waters of the Yellowknife area. Northwest Territories Geological Survey, NWT. Open File 2015–06, 25.
- Pinard, J.P., Maisson, J.F., Seccombe-Hett, P., 2008. Yellowknife Wind Energy Pre-feasibility Report.

Pirrie, D., Rollinson, G.K., 2011. Unlocking the applications of automated mineral analysis. Geol. Today 27 (6), 226–235.

Plumlee, G.S., Morman, S.A., 2011. Mine wastes and human health. Elements 7, 399–404. Pokrovski, G., Gout, R., Schott, J., Zotov, A., Harrichoury, J.C., 1996. Thermodynamic properties and stoichiometry of As(III) hydroxide complexes at hydrothermal conditions. Geochim. Cosmochim. Acta 60 (5), 737–749.

- Prescher, C., Prakapenka, V.B., 2015. Dioptas: a program for reduction of two-dimensional X- ray diffraction data and data exploration. High. Press. Res. 35 (3), 223–230.
- Riveros, P.A., Dutrizac, J.E., Chen, T.T., 2000. Recovery of marketable arsenic trioxide from arsenic-rich roaster dust. Environ. Improv. Mineral Process. Extr. Metall. II, 135–149.
- Savage, K.S., Tingle, T.N., O'Day, P.A., Waychunas, G.A., Bird, D.K., 2000. Arsenic speciation in pyrite and secondary weathering phases, mother lode gold district, tuolumne county, California. Appl. Geochem 15, 1219–1244.
- Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem 17, 517–568.
- Tighe, M., Lockwood, P., Wilson, S., Lisle, L., 2004. Comparison of digestion methods for ICP-OES analysis of a wide range of analytes in heavy metal contaminated soil samples with specific reference to arsenic and antimony. Commun. Soil Sci. Plant Anal. 35, 1369–1385.
- Van Den Berghe, M.D., Jamieson, H.E., Palmer, M.J., 2017. Arsenic mobility and characterization in lakes impacted by gold ore roasting, Yellowknife, NWT, Canada. Environ. Pollut (accepted with revisions).
- Walker, S.R., 2006. The Solid-phase Speciation of Arsenic in Roasted and Weathered Sulphides at the Giant Gold Mine, Yellowknife, NWT: Application of Synchrotron MicroXANES and MicroXRD at the Grain Scale. Ph.D. Thesis. Queen's University.
- Walker, S.R., Jamieson, H.E., Lanzirotti, A., Hall, G.E.M., Peterson, R.C., 2015. The effect of ore roasting on arsenic oxidation state and solid phase speciation in gold mine tailings. Geochem. Explor. Environ. Anal. 15 (4), 273–291.
- Waychunas, G.A., Rea, B.A., Fuller, C.C., Davis, J.A., 1993. Surface-chemistry of ferrihydrite. 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. Geochim. Cosmochim. Acta 57, 2251–2269.
- Wright, J., 1992. Nerco Con Mines Autoclave Project: Final Project Report.
- Wright, D.F., Irwin, D., Pierce, K., Buckle, J., 2006. 2-D digital geoscience database of the EXTECH III study area. In: Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J. (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results of the EXTECH III Multidisciplinary Research Project. Geological Association of Canada, Mineral Deposits Division, Special Publication No. 3, accompanying DVD.
- Wrye, L.A., 2008. Distinguishing between Natural and Anthropogenic Sources of Arsenic in Soils from the Giant Mine, Northwest Territories, and the North Brookfield Mine, Nova Scotia. M.Sc. Thesis. Queen's University.
- Yue, Z., Donahoe, R.J., 2009. Experimental simulation of soil contamination by arsenolite. Appl. Geochem 24, 650–656.