CHARACTERIZATION OF ARSENIC AND ANTIMONY MINERALS IN YELLOWKNIFE BAY SEDIMENTS

by

Katrina Paudyn

A thesis submitted to the Graduate Program in Environmental Studies in conformity with the requirements for the

Degree of Master of Environmental Studies

Queen's University

Kingston, Ontario, Canada

(January, 2021)

Copyright © Katrina Paudyn, 2021

Abstract

Yellowknife Bay, Northwest Territories, Canada, is a waterbody valued by surrounding communities for its subsistence, recreational, and cultural use. Located adjacent to the former Giant and Con Mines, Yellowknife Bay has received inputs from mine waste streams enriched in arsenic (As), antimony (Sb), and metals since the late 1930s. Lake sediments in Yellowknife Bay provided a record of metal(loid) contamination from aerially deposited roaster stack emissions, mine effluent, and direct disposal of Giant Mine tailings. A sediment sampling program was conducted in Yellowknife Bay to characterize both As and Sb mineralogy by scanning electron microscopymineral liberation analysis (SEM-MLA). Results from nine sediment cores collected in summer (August 2018, July 2019) and winter (March 2019) confirmed that As was mobile relative to layers of enrichment associated with peak mining emissions both downwards, where it precipitated as authigenic sulfides (interpreted to be realgar), and upwards where it was attenuated by Feoxyhydroxides and possibly roaster-generated Fe-oxides near the sediment water interface. Antimony minerals appeared to be stable in Yellowknife Bay sediments with no distinct evidence of postdepositional mobility identified. The observed prevalence of arsenic trioxide (As₂O₃) in near surface sediments proximal to Giant Mine suggested that As and Sb contamination is ongoing, likely from terrestrial weathering of contaminated soils and shoreline outcrops. Arsenic bearing oxide minerals were prevalent in near-surface sediments and may become unstable should redox conditions in the hypolimnion change; prolonged anoxia would destabilize the As phases and release As to bottom waters. Therefore, continual monitoring of hypolimnion conditions in Yellowknife Bay is necessary.

Co-Authorship

The manuscript chapter of this thesis (Chapter 2) titled "Characterization of arsenic and antimony minerals in Yellowknife Bay sediments" is intended for journal publication. The co-authors are Heather Jamieson, joint-appointed between the School of Environmental Studies and the Department of Geological Sciences and Geological Engineering at Queen's University, John Chételat from Environment and Climate Change Canada and Carleton University, and Michael Palmer from the Aurora Research Institute and Carleton University. Heather Jamieson supervised all aspects of the research. John Chételat and Michael Palmer provided technical and editorial guidance, and were instrumental in facilitating the field work component of the research. All co-authors provided guidance and encouragement throughout the planning and execution of this thesis.

Acknowledgements

First and foremost, I would like to express my sincerest gratitude and appreciation to my supervisor Dr. Heather Jamieson. The completion of this thesis would not have been possible without your enthusiasm, expert guidance, and patience. Thank you for the incredible opportunities you provided over the past two years. It has been a privilege to learn for you.

I am also indebted to many others for their support. To John Chételat and Michael Palmer, thank you for your essential contributions and feedback at every stage of this project, as well as for your extensive help with the field work component of this thesis. To the Jamieson Lab Group past and present (Anezka, Chris, Clare, Sean, Amy, Brent, Diana, Allie, et al.), thank you for the comradery and all of the fun memories (from group editing sessions to sessions at the climbing gym and The Grad Club). Thank you to Nicholas Pelletier and Maureen Freemark who assisted in the field, and kept sediment extrusion fun. Thank you to QFIR staff (Agatha Dobosz, Don Lougheed, Brian Joy) for spending many hours running samples and patiently helping me (especially during quarantine).

Thank you to the occupants of 141 York St. (past and present, actual and honoree), for all the laughter and overall enrichment of my graduate experience. I am very thankful for the good friends and family who supported me throughout my graduate studies.

Abstract	ii
Co-Authorship	iii
Acknowledgements	iv
List of Figures	vii
List of Tables	ix
List of Abbreviations	x
Chapter 1 Introduction	1
1.1 Research context and objectives	1
1.2 Background information	3
1.2.1 Physiography	3
1.2.2 Geological setting	4
1.2.3 Study area	5
1.2.4 Environmental considerations of arsenic and antimony	6
1.2.5 History of mining in the Yellowknife region	8
1.2.6 Processing history at Giant and Con Mines	10
1.2.7 Waste streams produced at Giant Mine	12
1.2.8 Sources of arsenic and antimony to Yellowknife Bay	13
1.2.9 Transport pathways to Yellowknife Bay	14
1.2.10 Post-depositional mobility of arsenic and antimony	15
Chapter 2 Characterization of arsenic and antimony minerals in Yellowknife Bay sediments	18
2.1 Abstract	18
2.2 Introduction	19
2.3 Materials and Methods	21
2.3.1 Study site	21
2.3.2 Sediment cores	23
2.3.3 Elemental analysis	24
2.3.4 Automated mineralogy	24
2.3.5 Solid-phase arsenic and antimony calculations	25
2.3.6 Electron microprobe analysis	26
2.4 Results	28
2.4.1 Solid-phase arsenic and antimony concentrations	28

Table of Contents

2.4.2 Characterization of arsenic and antimony phases	31
2.4.3 Arsenic and antimony phases in near surface sediment	34
2.4.4 Arsenic and antimony phases in profile	35
2.5 Discussion	
2.5.1 Sources of arsenic and antimony and their pathways to Yellowknife Bay	
2.5.1.1 Baker Creek and terrestrial weathering of contaminated soils	
2.5.1.2 Foreshore Tailings Area	40
2.5.2 Post-depositional mobility of arsenic and antimony	42
2.5.3 Implications for future stability of arsenic	46
2.6 Conclusions	48
Chapter 3 Conclusion	50
3.1 Summary	50
3.2 Future research	53
3.3 Sustainability and gold mining	55
3.4 Relationship to sustainability	57
3.4.1 Social impacts	57
3.4.2 Economic impacts	60
References	63
Appendix A: Sample site locations	76
Appendix B: Photographs of sample sites, field sampling, and sample preparation	77
Appendix C: Supplementary Data to Chapter 2	80
Appendix D: Roaster oxide textures	81

List of Figures

Figure 1: (a) Location map of the Yellowknife region with the study area and Giant and Con Mine lease boundaries overlayed; (b) location of the study area with respect to Canada (Shelton et al. Figure 2: Location of Yellowknife Bay relative to Giant and Con Mine properties, Yellowknife, and the community of Ndilo. Bathymetry of Yellowknife Bay (Golder Associates, 2005), sample locations, and pathways for As and Sb contamination (Baker Creek Outfall, Foreshore Tailings Area) are superimposed. The location of the study area with respect to Canada is shown in the top right Figure 3: Concentration profiles of As (red), Sb (orange), Pb (dark green), Zn (light green), and Fe (brown) at each coring location within Yellowknife Bay. Near field sites were within 2 km of the Giant Mine roaster and far field sites were beyond 2 km; locations shown within bay (left). Sample locations increase in distance from Giant Mine from left to right. Note the x-axis (metal(loid) concentrations, $\mu g g^{-1}$) is not consistent in all samples, a result of the high variability between near field and far field concentrations. Additional elemental concentrations are provided in Appendix C. Figure 4: BSE images of selected As-hosting solid phases from Yellowknife Bay. Authigenic phases: (a) cluster of As_2O_3 grains, (b) discrete As_2O_3 grain with dissolution texture, (c) Sb_2O_3 , (d)I roaster oxides with concentric textures. Authigenic or geogenic phases: (f) arsenopyrite, (g) pyrite with oxidation rim, (h) Sb sulfosalt. Authigenic phases: (i) Fe-(oxy)hydroxides, (j) realgar, and (k) Figure 5: Spatial concentration of As (left, red) and Sb (right, orange) in near surface sediments from subsamples collected in this study, Golder Associates (2005), Stantec (2014a), Chételat et al. (2018), Chételat et al. (unpublished data). The relative distribution of As and Sb hosting minerals are plotted Figure 6: Pie charts (labeled by dept from the SWI in cm) of relative contributions of each mineral host to As (top) and Sb (bottom) concentrations by mass, as calculated by equation 1. Sample locations increase in distance from Giant Mine from left to right and increase in from top to bottom Figure 7: Conceptual diagram of the historical and ongoing sources of As (red) and Sb (orange) minerals to Yellowknife Bay from Giant and Con Mines, and processes governing speciation in the

vii

post-deposition environment under current (oxic and circumneutral) conditions. Anthropogenic	
phases: arsenic trioxide (As ₂ O ₃), antimony trioxide (Sb ₂ O ₃), roaster oxides (y-Fe ₂ O ₃); geogenic	
phases: arsenopyrite (FeAsS), stibnite (Sb ₂ S ₃), Sb sulfosalts; authigenic phases: Fe-oxyhydroxides	
(FeO(OH), realgar (α-As ₄ S ₄).	42

List of Tables

Table 1: Arsenic and Sb waste streams produce at Giant, modified from Walker (2006)	to include Sb
results from Fawcett et al. (2011).	13
Table 2: Anthropogenic, authigenic, and geogenic phases of As and Sb bearing mineral	ls observed in
Yellowknife Bay sediments.	14

List of Abbreviations

- As Arsenic
- As₂O₃ Arsenic trioxide
- B-Billion
- BSE Backscatter electron
- CAD Canadian dollars
- CCME Canadian Council of Ministers of the Environment
- CMMP Canadian Minerals and Metals Plan
- CSR Corporate social responsibility
- Cu-Copper
- DO Dissolved oxygen
- EDS Energy-dispersive X-ray spectroscopy
- ESIA Environmental and social impact assessment
- EMPA Electron microprobe analysis
- ESG Environmental social governance
- FeAsS Arsenopyrite
- $FeS_2 Pyrite$
- FTA Foreshore Tailings Area
- ICP-MS Inductively coupled plasma mass spectrometry
- ISQGs Interim sediment quality guidelines
- M-Million
- MAC Maximum allowable concentration
- NWT Northwest Territories
- OM Organic matter
- opt ounce per tonne
- Pb-Lead
- PELs Probable effects levels
- Sb Antimony
- SEM Scanning electron microscopy
- SIA Social impact assessment
- SLO Social license to operate

SPL – Sparse phase liberation

SWI - Sediment water interface

t – tonne

YKDFN - Yellowknives Dene First Nation

Zn - Zinc

Chapter 1

Introduction

1.1 Research context and objectives

In Canada's North, orphaned and abandoned mines represent a substantial social, environmental, and economic liability to neighbouring communities, and responsibility for their remediation has largely been assumed by initiatives established by the federal government. Mines developed in northern Canada in the mid 20th century operated during a time of few environmental regulations, and often adopted short-sighted approaches to waste management that yielded concentrated releases of mineral processing by-products, some of which had direct or indirect adverse environmental and human health effects. Poor emission controls and low standards for waste management practices during the early years of operation at former gold mines, Giant Mine and to a lesser extent, Con Mine, located near Yellowknife, NWT, Canada, resulted in a complex legacy of contamination (Jamieson 2014). The dispersion of mine-derived arsenic (As) and antimony (Sb) contaminants to the surrounding environment has stimulated studies of regional sediments (e.g., Galloway et al. 2015, 2018; Schuh et al. 2018, 2019; Van Den Berghe et al. 2018; Chenney et al. 2020), soils (e.g., Bromstad et al. 2017; Jamieson et al. 2017; Palmer et al. in review), and waters (e.g., Palmer et al. 2015; Houben et al. 2016). Sediments in Yellowknife Bay, a water body valued by the communities it supports and adjacent to the former Giant and Con Mines, represented a unique media for study as they acted as natural archives for accumulated inputs from natural and anthropogenic sources. Additionally, due to the close proximity of the former mine sites to Yellowknife Bay, and the complex history of ore processing and waste management, the sediments recorded influences from multiple waste streams produced

1

during the long operational periods of Giant and Con Mines (e.g., Andrade et al. 2010; Fawcett et al. 2015; Walker et al. 2015; Bailey 2017). Previous research indicated that As contained in Yellowknife Bay sediments was not being effectively buried over time and was mobile in the post-depositional environment (Andrade et al. 2010; Chételat et al. 2018). The post-depositional mobility of Sb remained uncertain and was worthy of investigation because of some shared geochemical and toxicity properties with As (Wilson et al. 2004, 2010; Fawcett et al. 2015; Radková et al. in press). Although dissolved concentrations of As, Sb, and metals in Yellowknife Bay waters have recovered to levels acceptable for protection of human and environmental health (Canada North Environmental Services 2018), the high concentration of As and Sb hosted in sediments represent a potential leaky reservoir to overlaying waters (Andrade et al. 2010; Chételat et al. 2018). In the context of growing visibility surrounding climate change impacts in northern environments, there is concern for how changing environmental conditions may impact the long-term fate of As and Sb in Yellowknife Bay. Shorter periods of ice-cover (e.g., Magnuson et al. 2000; Weckström et al. 2014), increased permafrost degradation (e.g., Schuur et al. 2015; Wauthy and Rautio 2020), enhanced winter stream flow (e.g., Spence et al. 2015), and changes in precipitation patterns (e.g., Screen and Simmonds 2012) are being observed in northern latitudes. At the lake scale these changes manifest by altering geochemical baselines and redox conditions which influence redox-sensitive metal(loid) efflux from mine-impacted sediments (Macdonald et al. 2005; Miller et al. 2019, 2020; Palmer et al. 2020).

Mineral speciation greatly influences the bioaccessibility, mobility, and long-term fate of As and Sb hosts. The purpose of this study was to characterize As and Sb mineralogy in Yellowknife Bay. The main research objectives can be summarized as follows:

- Determine the distribution of As and Sb within Yellowknife Bay.
- Determine what minerals host the As and Sb.
- Determine whether the distribution of mineral hosts change from winter to summer.

These objectives were achieved through the geochemical and mineralogical analysis of sediment cores collected during winter and summer field seasons. Results from the study represent a component of the knowledge base required to establish predictions for how sediments will respond to changing environmental conditions. Findings have implications for the environmental management of Yellowknife Bay and the development of any mitigation required. They also contribute to literature on the cumulative impacts of anthropogenic activities and natural processes on mine-impacted sediments.

1.2 Background information

1.2.1 Physiography

The study region is characterized by exposed bedrock outcrop interspersed with shallow (less than 10 to 30 cm depth to relief) surficial sediments which have accumulated around outcrops and in topographic depressions (Kerr 2006). The landscape contains many small elongated pocket lakes (approximately one-third of the surface area) and glacial till is the most common surficial sediment, the result of the last period of deglaciation which occurred between 8,000 to 12,000 years ago (Kerr 2006; Wolfe et al. 2014). Yellowknife is south of the treeline, located within the Taiga Shield High Boreal Ecoregion (Great Slave Lowland), which is distinguished by open pine-spruce growth in wooded areas, and drought-tolerant lichen, mosses, grasses, and small shrub growth in areas with shallow soil cover (Ecosystem Classification Group 2008). Permafrost is laterally discontinuous (50-90%), mainly occurring under more insulated areas such as peatland or areas of thicker soil cover

(Wolfe et al. 2014). The region experiences dry cool winters and relatively mild summers. Average precipitation is low, 289 mm annually, and average temperatures range from -26°C to -1.7°C in the winter season (October to April) and 4.6 °C to 17°C in the summer season (May to September) (Environment Canada 2015). Lakes in the region are ice-covered for most of the year, with freeze-up typically occurring in late October and break-up occurring in early June (Stantec 2014a).

Climate warming is expected to significantly impact temperature and precipitation regimes in Canada, and with greater significance in northern geographies such as Yellowknife. In northern Canada mean temperature increased by 2.3°C between 1948 and 2016, approximately three times the global warming rate. It is almost certain that this trend will continue regardless of emission scenario, though magnitude of projected increase depends on future green house gas emissions. Averaged within Canada the projected increase in temperature for a 'low emission' scenario is 1.8°C by 2050, and more than 6°C by the late 21st century for a 'high emission' scenario (Vincent et al. 2018; Zhang et al. 2019). Conditions in Yellowknife Bay are expected to change due to projected increases in the duration of the ice-free season, organic matter loading, and permafrost thaw, as well as shifts in the overall dynamics of northern hydrological regimes (Screen and Simmonds 2012; Weckström et al. 2014; Spence et al. 2015; Griffiths et al. 2017; Miller et al. 2020; Wauthy and Rautio 2020).

1.2.2 Geological setting

Yellowknife's regional bedrock geology is comprised of steeply dipping metavolcanic rocks of the Archean-aged Yellowknife Greenstone Belt (YGB) which transects the study region north-south (Shelton et al. 2004). To the east of the YGB are younger volcanic-derived metasedimentary rocks and to the west of the YGB is a multiphase granodioritic complex which intruded the metasedimentary rocks (Shelton et al. 2004; Canam 2006; Siddorn et al. 2006). Both the Giant and Con deposits are contained within the YGB. The Giant deposit is thought to be an upward extension of the Con deposit (specifically the Con zone), offset by the prominent West Bay Fault which strikes north-northwest and underlies Yellowknife Bay (Siddorn and Cruden 2001; Siddorn et al. 2006). Mineralization at the Giant and Con deposits occurred mostly as disseminated sulfides hosted in silicified zones and quartz-carbonate veins (Coleman, 1957; Canam 2006; Hasuer et al. 2006). Ore shoots typically contained less than 10% sulfides, predominantly comprised of arsenopyrite and pyrite (95%) (Jamieson 2014 and references therein). Other minerals associated with ore mineralization, albeit to a lesser extent, are sphalerite, chalcopyrite, stibnite, Sb-bearing sulfosalts and pyrrhotite. Arsenic was present as arsenopyrite and pyrite; Sb was present as stibnite and Sb sulfosalts (i.e., berthierite, bournonite, jamesonite, and tetrahedrite) (Coleman, 1957; Hasuer et al. 2006).

1.2.3 Study area

Yellowknife Bay, the study area (Figure 1), is on the north shore of Great Slave Lake and is bordered by Yellowknife, and the Willildeh Yellowknives Dene First Nation (YKDFN) communities of Ndilo and Dettah. The study area falls within Akaitcho Territory, the traditional lands of the YKDFN (YKDFN 2020). Yellowknife Bay has a surface area of approximately 20 km² with a maximum basin depth of 15 m in the north area and 30 m near the south area. The onshore wind direction, from the east most of the year and from the south June through August (Pinard et al. 2008; Environment Canada 2015), drives wave action in Yellowknife Bay resulting in irregular water current circulation patterns (Stantec 2014b). Inflow is supplied by Baker Creek, a tributary which runs through the Giant Mine property, and the Yellowknife River (Figure 1).



Figure 1: (a) Location map of the Yellowknife region with the study area and Giant and Con Mine lease boundaries overlayed; (b) location of the study area with respect to Canada (Shelton et al. 2004); (c) regional geology of the Yellowknife Greenstone Belt (Shelton et al. 2004).

1.2.4 Environmental considerations of arsenic and antimony

Arsenic and Sb are both metalloids that share some geochemical properties such as similar valence electron configurations, same grouping on the periodic table, same type of oxidation states in environmental systems (-III, 0, +III, +V), and common co-occurrence in

ore bodies (Wilson et al. 2010; Fawcett et al. 2015; Radková et al. in press). Due to their frequent co-occurrence in ore bodies, As and Sb often co-occur in mining waste, and As is usually the main element of environmental concern in the management of waste produced from hardrock mines (Bowell and Craw 2014). Arsenic and Sb also share some toxicological properties, though considerably less is known about the toxicology of Sb (Gebel 1997; Wilson et al. 2010; Herath et al. 2017; Radková et al. in press). It is well known that As is acutely toxic and chronically hazardous to humans and other animals, being a carcinogen that targets vascularized tissues, and organs such as the liver and kidneys (e.g., Caussy 2003; Health Canada 2006; Abdul et al. 2015). In Canada antimony trioxide (Sb_2O_3) is classified as a possible carcinogen (group 2B) via inhalation (Health Canada 2020). In relative terms, As and Sb in the aqueous phase are considered more bioaccessible than in the solid-phase as determined by *in vitro* methods (Basta and Juhasz 2014). Within aqueous phases, As in the +III oxidation state is considered to be more toxic and bioaccessible than As in the +Voxidation state (Bissen and Frimmel 2003; Peters et al. 2008; Tokalioğlu et al. 2020). Similar to As, Sb(III) is often cited to be more bioaccessible, bioavailable, or toxic than Sb(V). However, this is paradigmatic as data to support a clear difference in Sb toxicity based on speciation has not been published in a peer reviewed journal (Filella et al. 2009; Herath et al. 2017; National Toxicology Program 2018). Relative to As, Sb is a new area of study; the study of Sb health effects gained traction in the 1990s when connections between Sb used as flame retardants in PVC mattress covers and sudden infant death syndrome were studied (Filella, et al. 2009). The solid-phase bioaccessibility of As follows the general order of (from increasing to decreasing): arsenic trioxide (As₂O₃), As-bearing Fe-oxyhydroxides, Asbearing pyrite and As sulfides (e.g., realgar), arsenopyrite and scorodite (Plumlee and Morman 2011). Antimony is expected to follow a similar order as antimony trioxide (Sb_2O_3)

was proven to be more bioaccessible than Sb sulfides (National Toxicology Program 2018 and references therein).

National standards developed by Health Canada and the Canadian Council of Ministers of the Environment (CCME) exist to moderate the extent to which humans and other animals are exposed to various substances, including As and Sb, given their adverse (As) or likely adverse (Sb) effects. In drinking water, the maximum allowable concentration (MAC) of As is 10 μ g L⁻¹ and the MAC of Sb is 6 μ g L⁻¹ (Health Canada 2006). In freshwater the recommended MAC of As for protection of aquatic life is 5 μ g L⁻¹ and there is no guideline for Sb (CCME 1999a). The recommendations for As in sediment are 5.9 μ g g⁻¹ for interim sediment quality (ISQGs) and 17 μ g g⁻¹ for probable effects levels (PELs) (CCME 1999b). There is no defined sediment quality guideline or interim guideline for Sb.

1.2.5 History of mining in the Yellowknife region

The Willideh YKDFN and their ancestors have lived in the Yellowknife region for over 7,000 years (O'Reilly 2015). Their oral history describes a connection to small scalemining; the name Dene comes from their use of native copper in crafting tools (Paci and Villebrun 2005; O'Reilly 2015). The YKDFN also have a long history of supporting subsistence lifestyles by living off the land. Prior to the onset of mining, Yellowknife Bay and the surrounding area were productive regions for fish, berries, medicinal plants, and game (caribou, moose, muskrat, beaver) (O'Reilly 2015; Sandlos and Keeling 2016; Degray 2020). Indications that Yellowknife was a prospective area for mineral exploration were reported in the late 19th century but prospectors didn't stake the Giant and Con Mine claims until 1935, after which transportation to the area by bush aircraft had become more affordable (Moir et al. 2006). Production commenced at Con and Giant Mines in 1938 and 1948, and operation continued for over six decades at Con Mine and five decades at Giant

8

Mine with few interruptions. Giant Mine closed in 1999, at which point the existing operator (Royal Oak Mines Inc.) went into receivership and the mine became the responsibility of the federal government (Silke 2013). Giant Mine's assets were sold to Miramar Mining Corp., the owner and operator of Con Mine, under the agreement that they were indemnified from any existing environmental liability. This was the first and only instance where Giant and Con Mine were consolidated into one operation, and stockpiled ore from Giant Mine was processed at Con Mine's facilities until 2004, with active mining at Con Mine ceasing in 2003. Following the termination of the interim agreement with Miramar, the ongoing care and maintenance of the Giant Mine property was contracted to various engineering consulting firms. At the time of writing site remediation at Con Mine was considered completed, while remediation at Giant Mine was in its very early stages. The Giant Mine Remediation Project (GMRP) was recently approved a water license in September 2020, which allows active remediation to commence. In 2021 to 2022 remediation objectives include constructing a landfill and freeze pads, underground and dam stabilization, and excavating the highly contaminated soils surrounding the roaster, along with other tasks (INAC 2020).

It was estimated that the life of mine production was 7.1 M recovered ounces at Giant Mine, and 5.8 M recovered ounces at Con Mine (Moir et al. 2006). Despite the difference in production, revenues from both mines were estimated to be relatively equal (approximately \$3.7 B CAD at Giant Mine and \$3.4 B CAD at Con Mine in present-day dollars) attributed to production at Giant Mine peaking while gold prices were low and production Con Mine peaking during a period of higher gold prices. It was estimated that Con Mine received \$640 per ounce of gold produced while Giant Mine received only \$310 per ounce produced (Bullen et al. 2006; Bank of Canada 2020). An estimate for the remediation cost of Giant Mine was completed in 2012 and was indicated to be on the order of one billion dollars (AANDC 2012; Jamieson 2014).

1.2.6 Processing history at Giant and Con Mines

The processing history and production of mine waste streams have been described in detail previously (e.g., Walker et al. 2005, 2015; Fawcett et al. 2015; Palmer et al. 2015; Van Den Berghe et al. 2018; Schuh et al. 2018; Schuh 2019). They are briefly summarized here as the processing history has implications for the waste streams deposited to the study area.

At most gold mines ore processing and refining is completed on site. Similar to any gold deposit the nature of mineralization at Giant and Con Mines dictated the choice of processing method, and therefore the type of waste produced (Jamieson 2014). Both Giant and Con Mines contained refractory and free milling gold; at Giant Mine most of the ore was refractory whereas at Con Mine refractory ore was restricted to the upper zones (Con zone and Campbell zone) and was mined during the earlier years of operation. Processing of free milling ore did not require treatment for the gold to be amenable to cyanide leach whereas refractory ore required pre-oxidative treatment to liberate the gold so it could be extracted during leach. At the time of Giant and Con Mines' opening roasting was considered the only pre-oxidative treatment option for refractory ore. The ore was roasted in two stages at 500°C, volatizing the As in arsenopyrite to potentially more soluble and bioaccessible oxide phases (Jamieson 2014). Arsenic and sulfur were oxidized during roasting and the gold-bearing arsenopyrite was converted to gold-bearing Fe-oxides from which gold was more easily extracted (Walker et al. 2005, 2015). These porous Fe-oxides are commonly referred to as roaster oxides in the literature (Walker et al. 2005, 2015; Andrade et al. 2010; Fawcett and Jamieson 2011; Bromstad et al. 2017; Jamieson et al. 2017; Schuh et al. 2018, 2019). Roasting also produced sulfur dioxide and As vapour as off gases which were aerially

10

dispersed to the surrounding environment via the roaster stacks at each site. As the As vapour cooled and condensed it formed arsenic trioxide (As₂O₃), an industrial product with the same chemical formula as natural arsenolite.

A few key differences in the processing and management of roaster waste affected the amount of As₂O₃ emissions released at each site. For example, in the early years of roasting at Con Mine when refractory ore was still being processed, emissions were curbed by the installation of a wet scrubber in 1949 (Bright et al. 1994). Similarly, a baghouse dust collector was installed in 1958 at Giant Mine; albeit prior to its installation a substantial amount of As_2O_3 had already been released to the environment (Hocking et al. 1978; Bromstad et al. 2017). It was estimated that 86% of total As₂O₃ aerial emissions over Giant Mine's life of mine was released by the time Giant Mine refined its emission control process in 1963 (Jamieson 2014). As a result, from 1948 to 1974, aerial emissions of As_2O_3 were seven times greater from the Giant Mine roaster than the Con Mine roaster (Hocking et al.1978). Furthermore, Con Mine sold most of their stockpiled As_2O_3 in the 1980s for use in other industrial applications (Walker 2006). Rather than refining and selling produced As₂O₃, Giant Mine stored the waste in underground chambers. As emission controls increased throughout production, the amount of As₂O₃ released to the environment from Giant Mine decreased, being effectively captured in the baghouse and stored underground. In total an estimated 20,000 t were released to the environment and an additional 237,000 t were stored underground in chambers. The underground store of As₂O₃ dust at Giant Mine represents one of the largest in the world, and developing long-term strategies to deal with the waste is a top priority for remediation of the site (INAC 2018).

1.2.7 Waste streams produced at Giant Mine

Arsenic and Sb contamination from Giant Mine was complicated by the production of multiple mine waste streams, and therefore several studies have aimed to characterize the different components of waste (e.g., Walker et al. 2005, 2015; Fawcett et al. 2015; Bailey 2017). Processing of refractory ore at Giant Mine generated three geochemically distinct waste streams: flotation tailings, calcine, and Electrostatic Precipitator (ESP) dust. Flotation tailings were high volume with relatively low As and Sb content, whereas calcine and ESP dust were low volume with relatively high As and Sb content. Flotation tailings were composed of residual crushed rock separated from the sulfide-rich mill feed prior to roasting, and therefore did not contain oxide phases such as roaster oxides, As₂O₃, or Sb₂O₃. The Sb content of the ore increased over time (Sb content increased with depth and from south to north) (Canam 2006). However, in general it was expected that the Sb content of the roaster feed was monitored to avoid inefficiencies and thus the Sb content in flotation tailings was variable and relatively high (Silke 2013). Walker et al. (2015) suggested that any As₂O₃ found in tailings storage ponds was from co-deposition of flotation tailings with the other waste streams, and the same can be applied to Sb₂O₃. Calcine was the oxidized material that remained in the roaster bed post cyanidation, and contained predominantly As-bearing roaster oxides. ESP dust (the lowest volume waste stream) was residual particulate matter from the discharge of roaster off gases and contained high amounts of As₂O₃ and Sb₂O₃. The As and Sb concentrations and discharge rates of each waste stream are summarized below:

Waste Stream at Giant Mine	Year	Approximate Discharge (tpd)	As Conc. (wt.%)	As Loading (tpd)	Sb Conc. (wt.%)	Sb Loading (tpd)
Flotation	1999	1,000	0.09	0.9	N/A	N/A
Tailings	1963	794	0.28	2.2	N/A	N/A
Calcine	1999	170	1.8	3.4	0.6	1.02
	1963	122	1.2	1.5	N/A	N/A
ESP Dust	1999	9	4.4	0.4	N/A	N/A
	1963	9	6.2	0.6	N/A	N/A

Table 1: Arsenic and Sb waste streams produce at Giant Mine, modified from Walker (2006) to include Sb results from Fawcett et al. (2011).

1.2.8 Sources of arsenic and antimony to Yellowknife Bay

The solid-phase speciation of As and Sb contained in Yellowknife Bay sediment was a factor of the source (which varied over the mines' operation), the source's pathway, and any incurred changes post-deposition as a result of biogeochemical cycling and physical processes. The sources of As and Sb to Yellowknife Bay sediments was a combination of natural (geogenic) and anthropogenic phases (Table 2). Geogenic phases were those which occurred as a result of geological processes, i.e., the gold ore (arsenopyrite, pyrite) and gangue Sb minerals (stibnite, Sb sulfosalts) associated with the Giant and Con deposits. Geogenic phases were concentrated during mineral extraction when they were unearthed and brought to surface. Anthropogenic phases of As and Sb were phases created during gold processing, consisting of either reacted or non-reacted mineralogical and metallurgical products. Anthropogenic phases (arsenic trioxide (As₂O₃), antimony trioxide (Sb₂O₃), roaster oxides) were generated by the processing of ore and gangue minerals. Authigenic phases (e.g., Fe-oxyhydroxides, realgar) in Yellowknife Bay sediments refer to minerals formed *in situ* in the natural environment from precipitation or sorption of dissolved As or Sb from geogenic and anthropogenic sources.

 Table 2: Anthropogenic, authigenic, and geogenic phases of As and Sb bearing minerals observed in Yellowknife Bay sediments.

			Documented range o	
Classification	Mineral or	Mineral or chemical	average	
Classification	chemical	formula	As Conc.	Sb Conc.
			(%)	(%)
Anthropogenic	Arsenic trioxide	As_2O_3	41-76 ^b	0-38 ^b
	Antimony trioxide	Sb_2O_3	3.5-25 ^b	56-80 ^b
	Posstar oxidas		<0.5-7.6 ^c	
	(maghemite	maghemite, $\sqrt{-Fe_2O_3}$, α -Fe_2O_3 hematite)	$(y-Fe_2O_3)$	0.2-1.2 ^b
	(inagine inite,		2°	
	nematite)		$(\alpha - Fe_2O_3)$	
	Arsenopyrite	FeAsS	-	-
	Pyrite	FeS_2	0-3.2 ^b	0-0.4 ^b
Geogenic	Stibnite	Sb_2S_3	-	-
	Sulfosalts			
	(Berthierite,	FeSb ₂ S ₄ , PbCuSbS ₃ ,		
	Bournonite,	(Cu,Fe) ₁₂ (Sb,As) ₄ S ₁₃ ,	-	-
	Tetrahedrite,	Pb ₄ FeSb ₆ S ₁₄		
	Jamesonite)			
Authigenic	Fe-	FeO(OH)	0 5 15 ^b	0 0 1 ^b
	oxyhydroxide		0.3-13	0-0.1
	Realgar	α-As ₄ S ₄	42-70 ^b	$0-2.6^{b}$

^a Stoichiometric value (MSA 2018).

^b Determined by microprobe analysis of Yellowknife Bay sediments (Schuh 2019).

^c Determined by microprobe analysis of Giant Mine calcine residue and Yellowknife Bay Foreshore Tailings (Walker et al. 2005).

^d Determined by microprobe analysis of sediments in two lakes in the Yellowknife region (Long Lake and Martin Lake) (Schuh et al. 2018).

1.2.9 Transport pathways to Yellowknife Bay

There are several possible pathways by which mine waste streams entered

Yellowknife Bay: erosion of submerged tailings deposited at the Foreshore Tailings Area

(FTA), unintentional release or intentional decanting of tailings and mine effluent via Baker

Creek, terrestrial runoff of contaminated soils, and atmospheric dispersion of roaster stack

emissions. Tailings from Giant Mine were deposited directly onto the shore of Yellowknife

Bay (Figure 1) during the first three years of operation (1948-1951), coinciding with

maximum stack emissions from the Giant Mine roaster. It was estimated that 300,000 t of

tailings were deposited via pipeline, and aerial photos show that erosion and wave action have remobilized and dispersed submerged tailings throughout Yellowknife Bay. Approximately a third of the tailings remain near the beach while the rest have been remobilized (mostly contained to Back Bay and along the north western shore of Yellowknife Bay) (INAC 2010). Tailings are estimated to cover 50,000 m³ and range in thickness from 0.5 to 1.7 m (Golder Associates 2005). After 1951, tailings were no longer dumped into the water and were co-deposited with calcine in small pocket lakes on the property which eventually became tailings ponds. In 1958, ESP dust was discharged and also co-deposited into the same ponds (Walker 2006). Through events such as high rainfall, spring freshet, unintentional spills, or intentional decanting, runoff from ponds would pass through Baker Creek and into Yellowknife Bay. In 1981, a water treatment plant was installed to treat mine water before it was discharged to Baker Creek, significantly reducing the load of As and Sb to Yellowknife Bay.

1.2.10 Post-depositional mobility of arsenic and antimony

In lake bottom waters the mobility of aqueous As and Sb species (As(III), As(V), Sb(III), Sb(V)) is controlled by the natural cycling of ferric iron (Fe) and sulfur (S). In oxic waters As(V) is the predominant dissolved species while under reducing conditions As(III) dominates (Smedley and Kinniburgh 2002; Palmer et al. 2020). Aqueous As and Sb species sorb and coprecipitate with Fe-oxides and Fe-oxyhydroxides which are relatively insoluble under oxic conditions, removing As and Sb from waters, and binding them to sediment. Both As(V) and As(III) can sorb to these minerals; however, bonding affinity is affected by pH whereby As(V) sorption decreases with increasing alkalinity (Dixit and Hering 2003; Peters et al. 2008). Additionally, As species have a tendency to outcompete Sb species for sorption sites, preferentially leaving Sb in the dissolved phase (Arsic et al. 2018). In theory this would

be an effective mechanism to remove As from Yellowknife Bay waters; however, Feoxyhydroxide and Fe-oxides are not stable with burial and may be affected by seasonal changes. The main mechanisms to initiate the release of As once bound in the solid-phase are a change in the pH or oxygen conditions of the immediate environment (Smedley and Kinniburgh 2002; Peters et al. 2008). The pH of Yellowknife Bay surface waters and porewaters are expected to be circumneutral based on previous sampling (Golder Associates 2012; Stantec 2014a; Fawcett et al. 2015); however, dissolved oxygen levels are not constant. In sediment dissolved oxygen levels decrease with increasing distance from the SWI and near the SWI reductions in levels may occur seasonally as a result of ice-cover or through the microbially mediated breakdown of organic matter (during which microorganisms consume oxygen). As sediments are buried during diagenesis and oxygen levels decrease, mineralbound As and Sb hosted in an oxide phase are increasingly vulnerable to dissolution. Dissolution releases As(III) to porewaters by reduction of surface bound As(V) and/or releases As(III) and As(V) by complete dissolution of the oxide host (Smedley and Kinniburgh 2002). The mobility of dissolved As species in porewaters is controlled by Fick's first law of diffusion whereby dissolved species flow from areas of high concentration to low concentration. Thus, As(III) diffusion from isolated layers of enriched sediment can occur both upwards and downwards. Where As(III) diffuses upwards it may be recaptured by Feoxides and Fe-oxyhydroxides or released to overlying waters. Where it diffuses downwards, it may precipitate as authigenic As-sulphides (such as realgar, orpiment, mackinawite, and framboidal pyrite) (O'Day et al. 2004; Lowers et al. 2007). Previous analysis of Yellowknife Bay porewater by Andrade et al. (2010) shows elevated concentrations of As coinciding with low amounts of Sb, Pb (lead), Cu (copper), and Zn (zinc), suggesting a labile As source exists and is dissolving to porewaters, while Sb and metals remain in their solid phase. Identifying

the solid-phase forms of As and Sb and their relative abundance will assist in predicting their long-term stability. It is unclear how changing environmental conditions will impact the long-term stability of legacy contaminants in Yellowknife Bay, and other subarctic regions which have been exposed to contaminants derived from mining operations (Miller et al. 2019). As subarctic regions experience the effects of changing environmental conditions such as projected increases in temperature, organic matter (OM) loading, and frequency of erratic rainfall events, the impact on the fate of As and Sb mobility in sediment is significant to the environmental management of Yellowknife Bay.

1.3 Thesis organization

This thesis is organized into three chapters. Chapter 1 outlines the objectives of the project and background information to provide context for the research. Chapter 2 presents the research, in manuscript form, co-authored by Heather Jamieson, John Chételat and Mike Palmer. It addresses the objectives outlined in section 1.1 and is organized by methods, results, and discussion. Chapter 3 summarizes the research, provides recommendations for future work, and discusses the works' relationship to sustainability.

Chapter 2

Characterization of arsenic and antimony minerals in Yellowknife Bay sediments

2.1 Abstract

Yellowknife Bay, Northwest Territories, Canada, is a waterbody valued by surrounding communities for its subsistence, recreational, and cultural use. Located adjacent to the former Giant and Con Mines, Yellowknife Bay has received inputs from mine waste streams enriched in arsenic (As), antimony (Sb), and metals since the late 1930s. Lake sediments in Yellowknife Bay provided a record of metal(loid) contamination from aerially deposited roaster stack emissions, mine effluent, and direct disposal of Giant Mine tailings. A sediment sampling program was conducted in Yellowknife Bay to characterize both As and Sb mineralogy by scanning electron microscopy-mineral liberation analysis (SEM-MLA). Results from nine sediment cores collected in summer and winter confirmed that As was mobile relative to layers of enrichment associated with peak mining emissions both downwards, where it precipitated as authigenic sulfides (interpreted to be realgar), and upwards where it was attenuated by Fe-oxyhydroxides and possibly roaster-generated Feoxides near the sediment water interface. Antimony minerals appeared to be stable in Yellowknife Bay sediments with no distinct evidence of post-depositional mobility identified. The observed prevalence of arsenic trioxide (As_2O_3) in near surface sediments proximal to Giant Mine suggested that As and Sb contamination is ongoing, likely from terrestrial weathering of contaminated soils and shoreline outcrops. Arsenic bearing oxide minerals were prevalent in near-surface sediments and may become unstable should redox conditions in the hypolimnion change; prolonged anoxia would destabilize the As phases and

release As to bottom waters. Therefore, continual monitoring of hypolimnion conditions in Yellowknife Bay is necessary.

2.2 Introduction

Lacustrine sediments act as natural repositories for metal(loid) contaminants from their surrounding environment. During sedimentation contaminants are buried over time, effectively removing them from overlying waters and reducing risk of their exposure. However, if a metal(loid) of concern is redox sensitive (sensitive to changes in dissolved oxygen levels), the shift to reducing conditions with burial or changes in dissolved oxygen levels in the hypolimnion can cause them to become less, or more stable. Sediments containing such contaminants are a source to overlying water when conditions change and induce instability (Martin and Pedersen, 2002; Toevs, et al. 2006; Andrade et al. 2010; Schuh et al. 2019; Miller et al. 2019; Palmer et al. 2020).

In subarctic Canada, multiple sources of mine waste from regional processing of arsenical ore at two former gold mines (Giant Mine and Con Mine) have contributed to a legacy of arsenic (As), antimony (Sb), and heavy metal loading in lake waters and sediments of the Yellowknife area, including Yellowknife Bay (Great Slave Lake, Northwest Territories, Canada) (Andrade et al. 2010; Palmer et al. 2015; Chételat et al. 2018; Van Den Berghe et al. 2018; Schuh et al. 2018, 2019; Pelletier et al. 2020). Two decades after the closure of Giant Mine (1948-1999) and Con Mine (1938-2003), dissolved concentrations of As, Sb, and metals in Yellowknife Bay waters are considered acceptable for protection of human and environmental health (Canada North Environmental Services 2018); however, Yellowknife Bay sediments host high concentrations of solid-phase As and Sb, and represent a potential source to overlying water (Andrade et al. 2010; Chételat et al. 2018). Previous studies of Yellowknife Bay have focused on analyzing concentrations of As and Sb in sediments, porewaters, and surface waters, and have found concentrations significantly elevated relative to estimates of background (Andrade et al. 2010; Chételat et al. 2018). Andrade et al. (2010) demonstrated that As contained in enriched sediment layers associated with peak mining activity was not being buried effectively over time, and was mobile in the post-depositional environment. Results also indicated that As was diffusing from sediments to overlying water, albeit with limited spatial coverage. Chételat et al. (2018) greatly increased the spatial coverage of sediment and porewater sampling in Yellowknife Bay, and included analysis of concentrations in surface waters with a focus on both As and Sb, and other metal contamination. Ongoing work by Chételat et al. continues to investigate As and Sb flux from sediments to waters (Chételat et al. 2020). This work inspired mineralogical analysis of sediments, as the long-term fate (i.e., the response to changing environmental conditions) of these elements is dictated by their solid-phase mineral speciation.

The purpose of this study was to characterize As and Sb mineralogy in Yellowknife Bay to further investigate the sources, stability, and fate of As and Sb contamination in Yellowknife Bay. Mineralogical analysis will also assist in predicting the future stability of As and Sb under changing environmental conditions, and consequently the future risk they pose to public health and the environment. This study aims to contribute to the understanding of As and Sb speciation in mine-impacted subarctic lacustrine sediments.

2.3 Materials and Methods

2.3.1 Study site

The water body investigated, Yellowknife Bay, is on the north shore of Great Slave Lake (Figure 2). Yellowknife Bay is surrounded by the City of Yellowknife, and the Yellowknives Dene (YKDFN) communities of Ndilo and Dettah. Yellowknife Bay has a surface area of approximately 20 km² and a maximum basin depth of 15 m in the north area and 30 m near the south area. Inflows are from Yellowknife River, the largest source of incoming water, and Baker Creek (a tributary which runs through the Giant Mine property) (Environment Canada 2019). Water current circulation patterns are wind driven and irregular; the on-shore wind direction is from the east most of the year and from the south June through August (Pinard et al. 2008; Stantec 2014b; Environment Canada 2015). A mid-bay counterclockwise vortex is also observed (Stantec 2014b). For the majority of the year (late October to late May) Yellowknife Bay is ice-covered (Menard et al. 2002; Golder Associates 2012; Stantec 2014b). Currently, dissolved oxygen levels in waters are highest during the winter and lowest during the summer, albeit contained within the oxic range throughout the year (Golder Associates 2012; Stantec 2014a). Further detailed information on baseline environmental conditions in Yellowknife Bay is available in Stantec's Yellowknife Bay aquatic baseline study (Stantec 2014a).



Figure 2: Location of Yellowknife Bay relative to Giant and Con Mine properties, Yellowknife, and the community of Ndilo. Bathymetry of Yellowknife Bay (Golder Associates, 2005), sample locations, and pathways for As and Sb contamination (Baker Creek Outfall, Foreshore Tailings Area) are superimposed. The location of the study area with respect to Canada is shown in the top right corner.

2.3.2 Sediment cores

The sediment sampling program involved the collection of nine unconsolidated sediment cores over three sampling seasons (August 2018, March 2019, and July 2019) (Figure 2, Appendix A). The program was designed to contain a higher sampling density in the northwestern area of Yellowknife Bay, near historical conduits for mine waste (Baker Creek outfall, Foreshore Tailings Area). Two locations (C1, C2) were sampled to investigate As and Sb concentrations in sediment near Con Mine. Proximal to Ndilo, both a summer and winter core (SC3, WC3) were collected to elucidate whether a hypothesized seasonal effect could be observed from winter to summer. The remaining locations (C4, C6, C9, D1, and BCS) were chosen for their proximity to contaminant sources. Site C9 was closest to the output of Baker Creek, D1 was closest to the Foreshore Tailings Area, and C4, C6, and BCS were distributed with increasing distance from these point sources. Sample sites were located in the field with a portable Global Positioning System (GPS) and were collected using a UWITEC gravity corer with an internal diameter of 8.6 cm, via boat during open water and snowmobile during ice-cover which also required the use of an electric ice auger. The penetration depth of the gravity corer was an average 23 cm, with minimum and maximum core depth collected being 20 cm and 26 cm. Water depth at each sample location ranged from 8 to 15 m. After extraction cores were transported to a lab, stored in a fridge, and extruded within 48 hours of collection. Extrusion involved mounting each sediment core onto a push rod and pushing the core sleeve down until the SWI is at the top of the tube. The sediment in the cores were then subsampled into sections by progressively pushing the core tube down in 0.5 cm intervals from the SWI for the top 10 cm and 1 cm intervals thereafter, slicing the sediment with a core slicer at each increment. The extrusion process was completed in an oxygen-free environment achieved by filling sealed glove bags with a

constant flow of nitrogen gas from a compressed cylinder to ensure preservation of As and Sb hosting mineral phases. All material was then moved to a glove box, which was then filled with nitrogen atmosphere, where each section was homogenized and further subsampled (Appendix B). All samples were stored and frozen in Whirl-PakTM bags until transported, and kept frozen during transport.

2.3.3 Elemental analysis

Samples were freeze dried and homogenised prior to analysis at Bureau Veritas Mineral Laboratories in Vancouver, British Columbia, for analysis of 37 elements by inductively coupled plasma-spectrometry (ICP-MS) following aqua regia digestion. Every 0.5 cm or 1 cm slice of the nine cores (n=299) were analyzed for element concentrations to obtain detailed profiles. Duplicate samples were measured (n=1 per core) and standard deviations were < 10% for As and < 1% for Sb. Measured concentrations of As and Sb in procedural blanks were < 0.3 μ g g⁻¹ and < 0.1 μ g g⁻¹. Recoveries of As and Sb represented (n= 10) 99 ± 5% and 54 ± 5% of the total As and Sb in the certified reference materials. Results were used to inform sample selection for mineralogical analysis. Arsenic and Sb concentration data in near surface sediment collected in this study, Golder Associates (2005), Stantec (2014a), Chételat et al. (2018), and Chételat et al. (unpublished data) were interpolated using ordinary kriging (a linear geostatistical interpolation technique) in ArcGIS 10.6.

2.3.4 Automated mineralogy

For mineralogical analysis, 28 sediment subsamples were selected from the nine sediment cores to be made into thin sections. Three or four subsamples were selected per core based on criteria for As and Sb concentration in combination with their position in profile. Subsamples were chosen at depths where As concentrations were at localized maxima typically coinciding with a near surface peak, a mid-core enrichment peak, and a peak at depth. Selected samples were thawed and dried under nitrogen atmosphere in a pyramid glove bag, and thin sections (with one duplicate per sample) were created at Vancouver Petrographics with minimal use of water and heat. The thin sections were carbon-coated prior to analysis to obtain an electrically conducting surface in preparation for automated mineralogy (Sandmann and Gutzmer 2013). In this study automated mineralogy was analyzed using a FEI Quanta 650 FEG ESEM operating under high vacuum housed in the Queen's Facility for Isotope Research lab. Each scan took between 4 to 12 hours per thin section. Sparse phase liberation (SPL) mode was used to identify As and Sb bearing minerals (identifiable as the brightest grains) due to their relative rarity in sample. SPL selectively targets and defines As and Sb minerals based on user-defined BSE grey-scale. After scanning, each sample was analyzed using a reference library and user-defined EDS spectra.

2.3.5 Solid-phase arsenic and antimony calculations

The relative contribution of each As and Sb hosting phase measured in thin section by automated mineralogy relative to total mass As and Sb in subsample measured by elemental analysis was calculated using the following equation (Van Den Berghe et al. 2018):

$$As_{\%}^{h_{x}}, Sb_{\%}^{h_{x}} = \frac{A^{h_{x}}t^{h_{x}}\delta^{h_{x}}C_{As,Sb}^{h_{x}}}{\Sigma_{h=1}^{n}m_{As,Sb}^{h}} * 100$$
(1)

where $As_{\%}^{h_x}$, $Sb_{\%}^{h_x}$ is the relative contribution of a particular host phase (h_x) to the total As or Sb in a sample (by mass), A^{h_x} is the surface area of a host phase in μm^2 , t^{h_x} is an assumed sample thickness of 1 μ m, δ^{h_x} is the density of the As-hosting or Sb-hosting phase, $C_{As,Sb}^{h_x}$ is the concentration of As or Sb contained in the host mineral phase, and $\sum_{h=1}^{n} m_{As,Sb}^{h}$ is the total mass of As or Sb in all identified As or Sb host mineral phases. The assumed thickness
of 1 μ m accounts for automated mineralogy being a two-dimensional analysis (Schuh et al. 2018). Mineral densities (δ^{h_x}) were obtained from the Mineralogical Society of America (2018) (MSA 2018). Densities for arsenolite and goethite (α -FeOOH) were used to approximate densities for As₂O₃ and Fe-oxyhydroxide (Schuh et al. 2018). Parameters for wt.% As and wt.% Sb for Fe-oxyhydroxides and roaster oxides were based on averages of EMPA results from Schuh et al. (2018) and Schuh (2019).

2.3.6 Electron microprobe analysis

Electron microprobe analysis (EMPA) was conducted on select grains identified by automated mineralogy to be As_2O_3 , Sb_2O_3 , and $(As_3Sb_2O_3)$ (a phase that contained mixed EDS spectra with large peaks for both As and Sb). The objective of this analysis was to determine the Sb content contained within As_2O_3 , previously documented to contain up to 38 wt.% Sb (Schuh 2019), and to delineate the As and Sb concentrations within the intermediary phase, and the rarely observed Sb₂O₃ phase. Thirteen target grains were selected from seven thin sections based on grain diameter. The largest grains for each mineral species were selected to minimize interference from surrounding minerals; however relatively large grains of As₂O₃ were more common than the other species. Due to their rarity and small size, only one Sb_2O_3 grain (approximate widths 15-50 μ m) and three (As,Sb)₂O₃ grains (approximate widths 4-14 μ m) were viable for EMPA, with the remaining being As₂O₃ (approximate width 13 μ m). Targets were analyzed using a JEOL JXA-8230 electron microprobe (EMP) with wavelength dispersive spectrometry (WDS) to quantify the As and Sb content in wt.%. Operating conditions included a beam current of 10 nA, accelerating potential of 15 kV, and a beam diameter of 5 µm where possible. The standards used for As and Sb analysis were synthetic loellingite and natural stibnite.

2.4 Results

2.4.1 Solid-phase arsenic and antimony concentrations

Arsenic and Sb were enriched in Yellowknife Bay sediments. Maximum As concentrations in each core ranged from $325 \ \mu g \ g^{-1}$ (C1) to $8656 \ \mu g \ g^{-1}$ (C9), and maximum Sb concentrations ranged from $3 \ \mu g \ g^{-1}$ (C1) to $1345 \ \mu g \ g^{-1}$ (C9). These values were elevated significantly relative to background concentrations of As and Sb, estimated to be $25\pm10 \ \mu g \ g^{-1}$ for As and $0.7\pm0.1 \ \mu g \ g^{-1}$ for Sb (Chételat et al. 2018). The highest As and Sb concentrations occurred at near field sites, defined as sampling locations within 2 km of the recently decommissioned Giant Mine roaster (C9, C6, D1, BCS, C4). In comparison, As and Sb concentrations were lower at far field sites, defined as sampling locations beyond 2 km of the roaster (SC3, WC3, C2, C1) (Figure 2).

Concentrations of As and Sb varied spatially in sediment profiles with distance from the SWI. In all cores, a minimum of two As peaks were discernable, one near surface and one at depth; a singular Sb peak was visible, coincident with peaks of lead (Pb) and zinc (Zn) at depth. There was general congruence with maxima of Pb, Zn, and Sb, but not with As, which was more closely linked with peak concentrations of iron (Fe). Within the sediment profile, the highest As concentrations in most cores occurred within the shallow As peak, located within the top 5 cm of sediment. The exception was C9, located near the mouth of Baker Creek, which had a substantial As peak at depth containing the highest concentration of As measured in this study ($8656 \mu g g^{-1}$). Some variation between profiles was observed between near field and far field sites. Most significantly, the shallow As peaks in far field sites were consistently located at 4.5-5 cm depth, whereas in near field sites the depth of the shallow As peak was more variable. In all cores As profiles were shaped similar to Sb profiles, albeit the

As peak was displaced either above, below, or both relative to Sb. In far field sites the deep As peak was consistently displaced 1-2 cm deeper than the Sb peak. In near field sites the position of the As peak was not consistently displaced; in some near field cores there were As peaks both shallower and deeper relative to the Sb peak. This was particularly visible in D1 where the prominent Sb peak was positioned at 10-11 cm and was surrounded by As peaks both above at 8-9 cm and below at 12-13 cm (Figure 3). Below the As and Sb peaks at depth in each core, concentrations decreased to lower levels.

Spatial trends were also observed laterally with distance from contaminant point sources. Elemental analysis of near surface sediments indicated that maximum As concentrations increased with proximity to Giant Mine and its corresponding contaminant point sources (Baker Creek, Foreshore Tailings Area) (Figure 3). In near surface sediments the highest range of As concentrations (1000-2500 μ g g⁻¹) and the highest value measured in near surface sediment (2250 μ g g⁻¹) were near the outfall of Baker Creek. The highest range of Sb concentrations (50-100 μ g g⁻¹) were found at both the outfall of Baker Creek and the Foreshore Tailings Area, with the highest Sb concentration documented (226 μ g g⁻¹) located within the Foreshore Tailings Area. Antimony in near surface sediments decreased at a greater rate than As concentrations with distance from the main sources of contamination. Concentrations of Sb in the south end of Back Bay and near Ndilo were less than 10 μ g g⁻¹.



Figure 3: Concentration profiles of As (red), Sb (orange), Pb (dark green), Zn (light green), and Fe (brown) at each coring location within Yellowknife Bay. Near field sites were within 2 km of the Giant Mine roaster and far field sites were beyond 2 km; locations shown within bay (left). Sample locations increase in distance from Giant Mine from left to right. Note the x-axis (metal(loid) concentrations, $\mu g g^{-1}$) is not consistent in all samples, a result of the high variability between near field and far field concentrations. Additional elemental concentrations are provided in Appendix C.

2.4.2 Characterization of arsenic and antimony phases

Arsenic and Sb in Yellowknife Bay sediments were hosted in both sulfide and oxide phases from anthropogenic and geogenic sources, and authigenic phases altered from these sources formed *in situ* in the post-depositional environment. Authigenic phases were differentiated from their detrital counterparts by chemical composition identified in automated mineralogy analysis, and textures identified in BSE images (Figure 4, Appendix D). Oxide phases included arsenic trioxide (As₂O₃), antimony trioxide (Sb₂O₃), As-bearing Fe-oxides (inferred to be roaster oxides), authigenic Fe-oxyhydroxides, and an intermediate phase, (As,Sb)₂O₃, that contained elemental signatures of both As and Sb. Although As₂O₃ in Yellowknife Bay had been previously documented to contain up to 38 wt.% Sb (Schuh 2019), in this study EMPA revealed only trace amounts of Sb within these grains (0-6 wt.% Sb). Analysis of As₂O₃ (nine grains, n=23) found these grains contained 70-76 wt.% As. EMPA of three $(As,Sb)_2O_3$ grains (n=5) indicated that these grains contained a much higher proportion of Sb (23-37 wt.% Sb) relative to As (2-5 wt.% As), albeit totals for these values were low due to the small size (4-14 μ m) of the grain. Antimony trioxide (1 grain, n=1; low sampling capacity due to small grain size and rarity in sample) contained mostly Sb (67 wt.%) with trace amounts As (5 wt.%). These values corresponded well with previous analysis by Schuh (2019), (3 grains, n=5) which also contained more Sb than As. The As₂O₃ grains identified mostly occurred as small discrete or clumped grains (< 10 μ m in diameter), with a few discrete and anomalously large grains (40-50 µm) detected (Figure 4). All grains of Sb₂O₃ and (As,Sb)₂O₃ were $< 15 \mu m$ in diameter, and most commonly occurred as very small and isolated grains $< 5 \mu m$ in diameter.

Arsenic and Sb hosting Fe-oxides were identified in all samples, ranging in abundance from 1.4 to 99.8% by mass, and were the most abundant host of As and Sb. Feoxides containing As and Sb were inferred to be roaster oxides based on large peaks of Fe and oxygen (O) visible in EDS spectra, combined with the absence of distinct carbon (C), aluminum (Al), phosphorous (P), sulfur (S), and calcium (Ca) spectra signatures. Furthermore, roaster oxides were identified by texture: grains classified as roaster oxides had spongey/porous or concentric textures formed from volatized arsenopyrite during roasting (Figure 4, Appendix D) (Walker et al. 2015). Authigenic Fe-oxyhydroxides either occurred as amorphous grains with poorly defined boundaries intergrown with surrounding grains, or as weathering rims on sulfide grains of arsenopyrite, and to a lesser extent pyrite (Figure 4). Sulfide phases identified included arsenopyrite, pyrite, realgar, stibnite, and Sb sulfosalts, easily identified by their elemental signatures.



Figure 4: BSE images of selected As-hosting solid phases from Yellowknife Bay. Authigenic phases: (a) cluster of As_2O_3 grains, (b) discrete As_2O_3 grain with dissolution texture, (c) Sb_2O_3 , (d)I roaster oxides with concentric textures. Authigenic or geogenic phases: (f) arsenopyrite, (g) pyrite with oxidation rim, (h) Sb sulfosalt. Authigenic phases: (i) Fe-(oxy)hydroxides, (j) realgar, and (k) framboidal pyrite.

2.4.3 Arsenic and antimony phases in near surface sediment

Arsenic and Sb hosting minerals in near surface sediment represent the phases most vulnerable to changing redox conditions in the hypolimnion. Arsenic and Sb in near surface sediments were hosted in both oxide and sulfide phases as identified by automated mineralogy (Figure 5). The dominant host of both As and Sb was roaster oxides, accounting for 57% of As and 93% of Sb by mass. Roaster oxides were a more prominent host of As in far field sites relative to near field sites. In far field sites roaster oxides accounted for 77-93% As (median = 83%), whereas in near field sites they accounted for 23-44% As (median = 38%). This was not indicative of fewer roaster oxides near Giant Mine, but rather the abundance of additional hosts of As and Sb in near field sites. For example, at C9 (closest in distance to Giant Mine) n=1668 grains of roaster oxides were detected in thin section and at C1 (furthest from Giant Mine) n=181 grains of roaster oxides were detected in thin section. Other significant hosts of As in near field sites were arsenopyrite and Fe-oxyhydroxides. At sites C9 and C4 the majority of As (81% and 53%) was hosted in Fe-oxyhydroxides, while at sites C6 and BCS the majority of As (59% and 67%) was hosted in arsenopyrite. Arsenic trioxide was present in near surface sediments at all near field sites with the exception of BCS, accounting for 0.3-9.8% As. Arsenic trioxide was not observed in far field shallow sediment samples. Another host of Sb in near surface sediment was Sb-sulfides (stibnite) and Sb sulfosalts. Stibnite was observed at the three sites closest to the FTA (C6, D1, C4) accounting for 3-15% Sb, and Sb sulfosalts were detectable at C9, C6, and D1 accounting for 0.2-8% Sb. Antimony trioxide and (As,Sb)₂O₃ rarely occurred in near surface sediments. Antimony trioxide was detected at C6 accounting for 0.12% As and 5.6% Sb and (As,Sb)₂O₃ was detected at C4 accounting for 0.46% As and 0.14% Sb.



Figure 5: Spatial concentration of As (left, red) and Sb (right, orange) in near surface sediments from subsamples collected in this study, Golder Associates (2005), Stantec (2014a), Chételat et al. (2018), Chételat et al. (unpublished data). The relative distribution of As and Sb hosting minerals are plotted in pie charts for the nearest surface subsample available at each site.

2.4.4 Arsenic and antimony phases in profile

While roaster oxides were the dominant host of As and Sb in near surface sediments, the distribution of mineral hosts was more variable at depth. The other common mineral hosts included arsenopyrite, As₂O₃, realgar, and Fe-oxyhydroxides (Figure 5). At the two closest sites to Giant Mine (C9 and C6) arsenopyrite was the most significant As host. Near the outfall of Baker Creek (C9), the enriched layer at depth (13-14 cm) contained the highest concentrations of As measured in this study (8656 μ g g⁻¹), and was comprised of: arsenopyrite (77%), Fe-oxyhydroxide (18%), roaster oxides (3%), and As₂O₃ (2%).

Arsenopyrite was a less significant host with increasing distance from Giant Mine with the exception of the site closest to Con Mine (C1) where arsenopyrite comprised 85% of As at depth (10-11 cm). Arsenic trioxide was identified in 19 of the total 27 thin sections analyzed and was a prominent As host at mid core and deep core enrichments. Arsenic trioxide was an especially significant host down core in far field sites C2, SC3, WC3, where it was responsible for > 60% of As in the deepest sediment sampled, 15-16 cm 20-21 cm, and 16-17 cm. In sediments at depth at the furthest field site (C1-10-11), located next to Con Mine, As₂O₃ was a much less significant host, containing 4% of the total As (Figure 6). Roaster oxides were detected at all 27 subsamples. In far field samples they are the most significant As hosts in surface sediment and mid-core sediment layers, accounting for >65% of As in all in these samples. In near field sediment their abundance was more variable but they are abundant hosts in D1 and BCS. Similar to roaster oxides, Fe-oxyhydroxides are detectable in all 27 subsamples although their abundance was variable, ranging from 0.1 to 94%. They are particularly important host in C4, where they account for > 50% As at all depths. Realgar was not seen in near surface or mid-core enrichment layers; however, it occurred in deep sediments at D1 (27%, 86%), BCS (46%), WC3 (11%), SC3 (5%).

In addition to roaster oxides, the main Sb hosts were As_2O_3 , Sb sulfosalts, and stibnite. Roaster oxides account for > 50% Sb in 22 samples and > 90% in 13 samples. Sb sulfosalts were much more common in near field sites relative to far field occurrences (Figure 6). Arsenic trioxide was a significant host at depth, especially at far field sites. Sb sulfosalts and stibnite commonly occurred in near field sites, with Sb sulfosalts accounting for > 50% of Sb in C9-10-11, C9-13-14, and C4-10-11, and 15-30% Sb in C6 mid-core and deep core sediments. In most occurrences of Sb sulfosalts, stibnite was also present ranging from 3-

27%.



Figure 6: Pie charts (labeled by dept from the SWI in cm) of relative contributions of each mineral host to As (top) and Sb (bottom) concentrations by mass, as calculated by equation 1. Sample locations increase in distance from Giant Mine from left to right and increase in from top to bottom (not to scale). Detailed concentration and mineralogy profiles for each core are available in Appendix C, SEM-MLA Processed Results.

2.5 Discussion

2.5.1 Sources of arsenic and antimony and their pathways to Yellowknife Bay

Mineralogical analysis indicated that As and Sb in Yellowknife Bay sediments were

complicated by multiple contaminant streams and their transport pathways to Yellowknife

Bay. Furthermore, surface sediments recorded ongoing contamination from Giant Mine waste

streams. Elemental analysis in combination with mineralogical analysis suggested the

combined anthropogenic and geogenic inputs via Baker Creek, and anthropogenic inputs from the redistribution of Foreshore Tailings were the most significant inputs of metalloid contamination, and were independently and collectively more significant than inputs from Con Mine. This was evidenced by the higher concentrations of As and Sb measured in proximity to Giant Mine contaminant sources (Figure 3, Figure 5) and the decrease in variation of anthropogenic As hosts with distance from Giant Mine (Figure 5, Figure 6).

2.5.1.1 Baker Creek and terrestrial weathering of contaminated soils

Sediments at near field sites recorded significant influence from Giant Mine waste streams. Near field deep sediments contained As₂O₃, with high proportion at sites C6 and D1 (Figure 6). Arsenic trioxide could have occurred in deep sediments as a result of direct input during peak production, or terrestrial weathering of As₂O₃ bearing soils during this time, or both. The presence of As_2O_3 in near surface sediments, however, required more explanation, considering Giant and Con Mines are no longer actively producing waste. Giant Mine is slated for remediation in 2021 while remediation at Con Mine is considered complete (INAC 2020). It was reasonable to assume that As_2O_3 could be from a historical waste source at Giant Mine that has an accessible pathway to Yellowknife Bay. Bailey (2017) analyzed the fine-grained component in surface samples of Giant Mine tailings which historically were codeposited with calcine and ESP dust (both of which contain high amounts of As_2O_3). However, results from these analyses found little As₂O₃ was present in near surface tailings, suggesting that it was a negligible component of tailings near the end of production at Giant Mine. Therefore, it was deemed unlikely that windblown dust from tailings (which was confirmed to contain no As_2O_3) (Bailey 2017), or terrestrial weathering of tailings entering Yellowknife Bay via Baker Creek was the source of As₂O₃ to near field near surface sediments in Yellowknife Bay. A more likely source of As₂O₃ was weathering of

contaminated soils on and around the Giant Mine site. Bromstad et al. (2017) determined that As_2O_3 was the most abundant host of As in associated soils, and that As_2O_3 more commonly occurred in topographic depressions, indicating that it was vulnerable to remobilization by physical processes. Arsenic measured in outcrop soil samples averaged 1550 µg g⁻¹, and some of the highest values measured were on shoreline outcrops. Therefore, contaminated soils from the Giant Mine site represented a potential and significant source of As to Yellowknife Bay.

It was likely that Baker Creek acted as a primary conduit for As₂O₃ from weathering of contaminated soils. Arsenic trioxide was detected in all near field shallow sediments, with the exception of BCS, which was located south of Baker Creek. Currents run counterclockwise in Yellowknife Bay, which would allow As₂O₃ to be dispersed northward and eastward from the outfall. The absence of As_2O_3 in BCS near surface sediment suggested that physical processes which affect redistribution of sediment, such as wave action, currents, and particle focusing in deeper areas, played an important role in the lateral distribution of As and Sb hosting minerals. The absence of As_2O_3 in near surface sediments at far field sites suggested that the redistribution of As₂O₃ was limited to near field sites and that terrestrial weathering of potentially As₂O₃ bearing soils at Con Mine was a less significant source relative to Giant Mine soils. Interpolation of near surface sediment As concentrations (Figure 5) illustrated that As was most concentrated (1000 to 2500 μ g g⁻¹) within 1 km of Baker Creek. Furthermore, sediments contained concentrations ranging from 500 to 1000 μ g g⁻¹ upwards of 2 km away from Baker Creek. Overall, Baker Creek represented the most significant pathway by which As was transported to Yellowknife Bay sediments and contained mineralogical evidence for all waste streams produced at Giant Mine (stack emissions, tailings, calcine, and ESP dust). The high percentage of arsenopyrite measured in

mid core and deep core sediments at C9 (but not in the surface sediments) showed that tailings (rich in arsenopyrite, stibnite, and Sb sulfosalts) were a significant source in the early years of operation, when poor waste management practices were in place. This agreed with historical records that indicate Baker Creek was susceptible to sediment laden overflow from tailings during freeze-thaw, spring freshet, and during spills from faulty tailings pipes (Fawcett et al. 2015).

Roaster oxides were also likely sourced from terrestrial weathering of Giant Mine soils, observed to contain roaster oxides as the second most abundant As host (Bromstad et al. 2017). Collectively, anthropogenic As hosts are much more common in near surface Giant Mine soils than geogenic hosts (Bromstad et al. 2017).

2.5.1.2 Foreshore Tailings Area

Roaster oxides were identified to be the most prevalent As and Sb host in near surface sediments. Along with roster oxides being contributed by terrestrial weathering of soils, the Foreshore Tailings Area (FTA) was another likely contributor. Sediments proximal to the FTA contained high concentrations of As and Sb (Figure 5). Minerals associated with tailings included roaster oxides, arsenopyrite, and non-reacted Sb minerals such as Sb sulfosalts and stibnite. Although no sediment cores were collected within the known remobilized tailing plume from the FTA, samples most proximal to the FTA contained roaster oxides, arsenopyrite, and Sb sulfosalts in near surface sediments, and suggested weathering and remobilization sourced from FTA tailings was ongoing. Interpolation of near surface Sb concentrations in sediments showed the extent of the remobilization of the FTA tailings within Yellowknife Bay (Figure 5). The redistribution of tailings was further supported by historical aerial photos of Yellowknife Bay which showed significant dispersion of tailings (up to 1 km) northwards from the FTA (Golder Associates 2005). The pervasiveness of roaster oxides in near surface sediments can partly be attributed to the co-deposition of calcine with tailings in both tailing impoundments and the FTA. Calcine was stockpiled during the early years of operation and was discharged to the FTA when stockpile capacity issues were encountered in winter months (Walker 2006).

The larger influence of roaster oxides sourced from Giant Mine relative to Con Mine was likely due to differences in waste management practices. Giant Mine deposited its tailings waste directly into Yellowknife Bay from 1948-1951, and indirectly via Baker Creek, whereas Con Mine's tailings were deposited to inland lakes west of the mine (and west of Yellowknife Bay) (Falk et al. 1973; Bright et al. 1994; Golder Associates 2005). Inland lakes directly affected by Con Mine contamination include Pud Lake, Kam Lake, and the Meg, Peg, Keg Lake drainage system. Sediment As concentration in these lakes have been measured to contain values similar to those measured in this and other studies of Yellowknife Bay. Peg Lake contained concentrations > 3000 μ g g⁻¹, while Meg and Keg Lake contained concentrations > 1000 μ g g⁻¹ (Falk et al.1973). This system drains into southwest Yellowknife Bay, beyond the boundaries of sediments measured this study, and may explain why impacts from Con Mine were not as well observed in the study area. The output of the Meg-Peg-Keg drainage system outflows where Yellowknife Bay opens to Great Slave Lake; therefore, Con Mine wastes may have been diluted by entry to the larger body of Great Slave Lake. Although terrestrial weathering of contaminated soils was hypothesized as a possible pathway, direct inputs to Yellowknife Bay from Con Mine soils appeared to be minimal. Sources of historical and ongoing As and Sb loading to Yellowknife Bay, along with a conceptual representation of the processes governing their post-depositional mobility are summarized in Figure 7.

41





2.5.2 Post-depositional mobility of arsenic and antimony

Arsenic and Sb are both redox sensitive chalcophile metalloids, and are thought to share some environmental behaviours due to similarities in geochemical properties such as similar valence electron configurations, same grouping on the periodic table, and common co-occurrence in ore bodies (Wilson et al. 2004; Fawcett et al. 2015; Radková et al. in press). Sediment profiles (Figure 3) indicated that solid-phase metal(loid) concentrations peaked during the early years of operations at Giant Mine. While mineralogical evidence supported the mobility of As up and down core from this layer of enrichment, there was less indication of Sb mobility in the post-depositional environment. Mineralogical evidence for Sb mobility in mine-impacted sediments is mainly demonstrated by their shared ability with As to sorb or co-precipitate with authigenic Fe-oxyhydroxides in oxic environments. Though not widely or conclusively observed, Sb(III) in porewater (presumably from a labile source at depth such as Sb-bearing As₂O₃ or Sb₂O₃) could precipitate as authigenic Sb sulfides under Sb-rich reducing conditions (Fawcett et al. 2015; Radková et al. in press). Arsenic trioxide was measured by EMPA to contain up to 6 wt.% Sb in this study and 38 wt.% Sb in Schuh (2019), however no authigenic Sb sulfide minerals were observed in deep anoxic sediments in Yellowknife Bay. Limited Sb mobility in Yellowknife Bay sediments was supported by low concentrations of Sb measured in porewater (near or below detection limit, $2 \mu g L^{-1}$) at almost all sampling sites in Yellowknife Bay (Andrade 2006). Elevated Sb in near surface porewater was detected at sites near the outfall of Baker Creek and within the Baker Creek channel (Andrade 2006; Fawcett et al. 2015). However, the presence of stibnite and Sb sulfosalts determined by automated mineralogy in this study suggested elevated Sb in near surface porewater was more likely a result of oxidative dissolution of Sb sulfides contained near surface, rather than dissolution of a labile source at depth (Schuh 2019). The relative stability of antimony in the post-depositional environment was further evidenced by the coincidence of Sb peaks with peaks of trace metals associated with mining waste and with demonstrated limited redox capacity, such as lead (Pb) and zinc (Zn) (Figure 3). The different depths at which Sb peaks occurred in profile (Figure 3) was interpreted to be a result of different sedimentation rates. Yellowknife Bay sedimentation rates increase with distance from Giant Mine towards Great Slave Lake, resulting in deeper peaks of Sb and Pb in sediments (Pelletier et al. 2020). Additionally, the depths at which the combined Sb, Pb, and Zn peaks occur are interpreted to align with the period of maximum emissions released to the environment, as indicated by previous dating of sediment cores within Yellowknife Bay in

other studies. Sediment cores collected in 2013 by Chételat et al. (2018) and dated using lead-210, cesium-137, and radium-226 methods showed Sb concentrations occurred between 9 and 20 cm in sediments dated to be from 1948-1965, the period of maximum emissions from Giant Mine (Chételat et al. 2018). This depth aligned with the depth of solid-phase Sb maxima measured in this study. Sb contained in stibnite and Sb sulfosalts in near surface sediment are expected to undergo slow oxidative dissolution, releasing aqueous Sb to sediment porewater, and eventually bottom waters (Figure 7). The absence of distinct near-surface Sb peaks in solid-phase concentration profiles (Figure 3) suggested either limited release of Sb from oxidative dissolution of Sb sulfides, or limited availability of sorption sites on Fe-oxyhydroxides due to competition from high As concentrations (Ashley et al. 2003; Casiot et al. 2007). EMPA results of near surface Fe-oxyhydroxides in Yellowknife Bay and other regional lakes contain only trace amounts of Sb (Schuh et al. 2018; Schuh 2019).

Arsenic concentration profiles displayed double concentration peaks. The As peak at depth was consistently displaced 1-2 cm deeper than the solid-phase Sb, Pb, and Zn maxima in far field sites. In near field sites the lower peak displacement was less consistent. Mineralogical analysis attributes the downward displacement of the deep As peak to downward mobility of dissolved As that precipitates as authigenic realgar, a process previously observed in smaller lakes in the Yellowknife region (Schuh et al. 2018; Van Den Berghe et al. 2018). Realgar was detected in the deepest far field samples analyzed (SC3-16-17 and WC3 20-21). At a depth of 16-17 cm realgar comprised 5% of total As, and at 20-21 cm it comprised 11% of total As in these cores. Additionally, at C3-20-21 grains of As₂O₃ cooccur in proximity with grains of realgar, and display partial dissolution textures (Figure 4), indicating the potential dissolution of As₂O₃ to realgar. In near field sites, realgar was also detected at D1-8.5-9, D1-14-15, and BCS-11-12. Complete or partial dissolution of As₂O₃ and roaster oxides provides a labile source of aqueous As that can also diffuse upwards (Figure 7). The near surface As maxima, which occurs at 4-5 cm in far field cores and within the top few cm of near field cores closely corresponds with Fe maxima. Coupled with mineralogical analysis, this suggested that upwardly diffusing As was recaptured by Feoxyhydroxides and Fe-oxides, which form naturally at the oxic-anoxic boundary in sediments (Figure 7). At oxic-anoxic boundaries the first solids formed are poorly crystalline with high specific surface area, but overtime they transform to more crystalline forms. Both forms can coexist at this interface, albeit it was expected that crystalline forms are 2 to > 10 times more abundant (Dixit and Hering 2003). Upwardly diffusing As likely sorbs to these existing solids, or co-precipitates during their formation. Arsenic attenuation by this mechanism is cyclical in that over time Fe-oxide and Fe-oxyhydroxide solids will release As during burial as sediment conditions become less oxygenated (Figure 7). As Yellowknife Bay waters have largely recovered since the closure of regional gold mining operations (Chételat et al. 2018), it was reasonable to attribute Fe-oxides and Fe-oxyhydroxides as an effective mechanism of attenuation for upwardly diffusing As. However, depending on availability of sorption sites, it is possible that As efflux from sediment is occurring and being diluted by dispersion to Great Slave Lake. Previous flux modeling (two single time point measurements) of Yellowknife Bay sediments indicates more attenuation of As near the SWI than release (Andrade et al. 2010). The high concentrations of As contained in sediments, combined with its demonstrated post-depositional mobility was consistent with others studies that highlight the importance of maintaining oxic conditions in Yellowknife Bay bottom waters and near surface sediment (Andrade et al. 2010). Mineralogical analysis suggests that most solid-phase As in near surface sediment was hosted in oxide phases (87-99% at far field sites and 33-98% at near field sites) which are vulnerable to dissolution should prolonged anoxia occur at this

interface (Figure 5). At sites where sulfide phases are the primary As hosts in near surface sediment, the long-term stability of these hosts may favour changing conditions. For example, at C6 and BCS, As in near surface sediments was primarily hosted in arsenopyrite, 59% and 67%. Under existing oxic and neutral conditions arsenopyrite undergoes slow oxidative dissolution, releasing As to water (Walker et al. 2006; Corkhill and Vaughan 2009). Anoxic conditions at the SWI, similar to oxygen conditions in deep sediments, would promote the stability of these As sequestering phases. The prevalence of As₂O₃ in near surface sediment under current oxic neutral conditions given the relatively high solubility of natural arsenolite (0.207 \pm 0.002 mol As L⁻¹ at ambient temperature in pure water; Nordstrom et al. 2014) is poorly understood but not inconsistent with observations in other studies (e.g., Van Den Berghe et al. 2018; Schuh et al. 2018, 2019; Schuh 2019).

2.5.3 Implications for future stability of arsenic

Characterizing the mineral speciation of As and Sb hosts in Yellowknife Bay sediments is an important component of the knowledge base required to predict metalloid efflux from sediments in the 21st century. The circumpolar north is more vulnerable to climate change, with rates of warming occurring faster than the global average, mainly attributed to positive feedback mechanisms related to cryospheric processes, such as ice albedo effects (Holland and Bitz 2003; Macdonald et al. 2005; Hartmann et al. 2013; Stjern et al. 2019). Climate warming in the subarctic has resulted in shorter periods of ice-cover (e.g., Magnuson et al. 2000; Weckström et al. 2014), increased permafrost degradation (e.g., Schuur et al. 2015; Wauthy and Rautio 2020), enhanced winter stream flow (e.g., Spence et al. 2015), and changes to precipitation patterns (e.g., Spence, et al. 2011; Screen and Simmonds 2012). Within subarctic lakes these factors contribute to changes in geochemical baselines and redox conditions which influence metalloid efflux from mine-impacted

46

sediments (Miller et al. 2019; Palmer et al. 2020). A recent study, using late-Holocene warming as an analog for 21st century warming, has linked increasing temperatures with OM loading, which leads to increased As efflux by way of dissolution of As hosts in subarctic lake sediments (Miller et al. 2020).

Currently, Yellowknife Bay waters are typically well oxygenated and circumneutral in both winter and summer months (Stantec 2014a). Sediment cores collected at the same offshore location in March 2018 (WC3) and July 2019 (SC3) demonstrated little variability in metalloid concentration profiles and As and Sb mineralogical hosts (Figure 3, Figure 6). These results were consistent with previous comparative analysis of under ice and open water cores collected 15 years ago in Yellowknife Bay which showed no seasonal variation (Andrade et al. 2010; Schuh 2019). On a seasonal basis, As speciation and concentration in large deep subarctic lakes are less likely to be affected relative to small shallow (<4 m depth) subarctic lakes which experience anoxia mid-winter during prolonged ice-cover (Palmer et al. 2019). Shallow lakes have a larger sediment surface to water volume ratio which increases impacts of benthic processes and physical processes such as cryoconcentration (solute exclusion during ice formation) during ice-cover and evapoconcentration during the open water season (Palmer et al. 2019). Furthermore, Palmer et al. (2020) recently showed that small lakes in the Yellowknife region are more likely to develop anoxia when hydrologically disconnected from an upstream supply of dissolved oxygen during ice-cover, and that during anoxic periods sediments supplied overlying waters with large increases in As(III) and Fe associated with reductive dissolution of Fe-oxyhydroxides (Palmer et al. 2020). Though the authors have stipulated it is difficult to generalize results across the Yellowknife region due to variation in lake biophysical properties, findings from these studies provide insight on the effects of seasonal processes in subarctic lakes. Yellowknife Bay, being larger, deeper, and

hydrologically connected by upstream sources of dissolved oxygen via the Yellowknife River and Baker Creek and the larger body of Great Slave Lake year-round is less likely to see changes in redox conditions at the SWI, and thus less likely to see interannual variations in As concentration and mineralogy. Therefore, it is suggested seasonal variations are not an immediate concern for the environmental management of Yellowknife Bay. However, most of the As and Sb in Yellowknife Bay near surface sediment was hosted in oxide phases vulnerable to dissolution (Figure 5). Should larger scale climate-driven changes occur that induce anoxic conditions in Yellowknife Bay, As minerals have the potential be a long-term source to overlaying waters, and with greater significance as the subarctic environment changes. Another finding of this study was the prevalence of As₂O₃ and roaster oxides in near surface sediment. These As and Sb oxide hosts are inferred to be from continued loading via weathering of Giant Mine soils entering Yellowknife Bay directly from near shore outcrop weathering and via Baker Creek. Increases in weathering as a result of increased precipitation and winter streamflow may represent a significant challenge in decreasing As and Sb loading to Yellowknife Bay.

2.6 Conclusions

Lake sediments in Yellowknife Bay recorded As and Sb contamination and reflected multiple waste streams and pathways. Solid-phase concentration profiles at 0.5-1 cm resolution suggested that under existing conditions As was mobile in the post-depositional environment, while Sb was less mobile and was likely being sequestered with burial. Mineralogical analysis indicated that As₂O₃ and roaster oxides at depth provided a labile source of As. Where As diffuses upwards it was recaptured near the SWI during sorption and co-precipitation with Fe-oxyhydroxides, and possibly sorption to roaster oxides in near surface sediments. Where As diffuses downwards it precipitated as authigenic realgar in anoxic sediments, promoting As sequestration. Three findings from this study have implications for future management of Yellowknife Bay and remediation at Giant Mine:

- Arsenic trioxide (As₂O₃) and roaster oxides, anthropogenic sources of As from former mining operations, were ubiquitously distributed throughout Yellowknife Bay and are detectable at all sampling locations, even at the farthest sampling site more than 8 km from Giant Mine.
- (2) Arsenic trioxide (As₂O₃) and roaster oxides persist in near surface sediments proximal to Giant Mine, and were likely sourced from ongoing terrestrial weathering of contaminated soils on site via Baker Creek or from weathering of shoreline outcrops, such as near the foreshore tailings. Lateral redistribution of roaster oxides within the bay was another likely source to near surface sediments.
- (3) The majority of As hosts in near surface sediment was attributed to oxide phases which are vulnerable to dissolution, and may be of concern under changing environmental conditions.

Given its prevalence in near surface sediments, the solubility of As₂O₃ in mineimpacted sediments and mechanisms controlling its dissolution requires further research. The ongoing deposition of As₂O₃ to sediments in Yellowknife Bay inferred to be from weathering of contaminated soils at Giant Mine, poses a challenge for site remediation. Continued monitoring of As and Sb levels in Yellowknife Bay waters as well as environmental conditions that affect the stability of As and Sb bearing minerals is recommended.

Chapter 3

Conclusion

3.1 Summary

The results presented in this thesis successfully met objectives to provide detailed information on the identity, source, and distribution of As and Sb hosts in Yellowknife Bay. The summarized results are as follows:

Objective 1: Determine the distribution of As and Sb within Yellowknife Bay.

Trends in the lateral and vertical distributions of As and Sb were congruent with those described in previous studies (Andrade et al. (2010); Chételat et al. (2018)). The increased sampling density provided by nine additional sampling sites reinforced previous conclusions based on element concentrations. The area adjacent to Con Mine had not been previously sampled at depth, therefore sites C1 and C2 increased spatial coverage of sampling.

The highest concentrations of As were found in cores closest to Giant Mine, and concentrations decreased with distance from the site. Concentrations measured in this study were combined with others (Golder Associates (2005); Stantec (2014a); Chételat et al. (2018); Chételat et al. (unpublished data)) to create a heat map of As and Sb concentrations in the top layer of sediment (Figure 5). Results indicated the concentration of As was highest near the Baker Creek outfall and the Giant Mine property. Concentrations of Sb were highest near Baker Creek, Giant Mine, and the Foreshore Tailings Area.

The highest concentrations of As and Sb measured in this study, 8656 μ g g⁻¹ and 1345 μ g g⁻¹, were measured in the same sample. The sample was located at a depth interpreted to be the layer of enrichment associated with maximum emissions and at site C9, the site closest to the outfall of Baker Creek. Overall, maximum As concentrations in each core ranged from

325 μ g g⁻¹ (C1) to 8656 μ g g⁻¹ (C9), and maximum Sb concentrations ranged from 3 μ g g⁻¹ (C1) to 1345 μ g g⁻¹ (C9). The study objectives did not include any assessment of risk, however to provide some reference for the concentration values, they greatly exceed the estimated pre-mining As and Sb levels in Yellowknife Bay (25±10 μ g g⁻¹, 0.7±0.1 μ g g⁻¹) and the 5.9 μ g g⁻¹ ISQGs and the 17 μ g g⁻¹ PELs As guidelines established for the protection of human health and aquatic life (CCME 1999b; Chételat et al. 2018). Arsenic and Sb concentration profiles were integral in the selection of samples for automated mineralogy, as well as interpretations of the mineralogical results.

Objective 2: Determine what minerals primarily host the As and Sb.

Arsenic and Sb phases in Yellowknife Bay sediments were characterized in great detail using automated mineralogy. The main hosts of As were determined to be roaster oxides, arsenopyrite, arsenic trioxide (As₂O₃), realgar, and Fe-oxyhydroxides. The main hosts of Sb were determined to be roaster oxides, Sb sulfosalts, stibnite, and a As₂O₃-Sb₂O₃ solid solution. Characterizing As and Sb mineralogy provided valuable information on probable sources (waste streams) of contamination, transport processes, and post-depositional processes occurring within sediments. The most significant mineralogical findings were:

- Arsenic trioxide (As₂O₃) and roaster oxides, anthropogenic sources of As from former ore roasting operations, were ubiquitously distributed throughout Yellowknife Bay and were detectable at all sampling locations, even at the furthest sampling site from Giant Mine more than 8 km away from the former roaster.
- Near surface sediments contained anthropogenic As hosting minerals. Arsenic trioxide and roaster oxides were present in recent, near-surface sediments proximal to Giant Mine. It was proposed these were likely sourced from ongoing terrestrial

weathering of contaminated soils on site via Baker Creek or from weathering of soils containing As₂O₃ that are present on shoreline outcrops (Bromstad et al. 2017).

- At depth, As₂O₃ and roaster oxides were susceptible to dissolution and represented a labile source of As to porewater. The dissolution of buried As₂O₃ was strongly suggested by the presence of secondary As sulfide, interpreted to be realgar, an authigenic As sulfide not present in the ore at Giant or Con Mines which could form in the presence of dissolved arsenic and reduced sulfur. Realgar provided evidence for the downward mobility of As from layers of enrichment associated with peak mining activity (Figure 3, Figure 6). Evidence for the upward mobility of As was suggested by the presence of As-bearing Fe-oxyhydroxides near the SWI deposited after operations at Giant and Con Mines ceased.
- Antimony appeared to be less mobile in the post-depositional environment relative to As and remained effectively contained in sediments. Antimony peaks were co-incident with lead (Pb) and zinc (Zn), metals associated with mine waste that have limited redox capacity.
- The widespread occurrence of As-bearing oxide minerals in near-surface sediments (Figure 5) may affect water quality should sediment oxygen conditions deteriorate in the future, which would destabilize As-bearing oxide mineral hosts.

Objective 3: Determine whether the distribution of mineral hosts change from winter to summer.

The concentration of As and Sb, and relative distribution of As and Sb mineral hosts did not drastically change between winter and summer at an offshore mid-bay sample site. Any subtle differences cannot be reasonably attributed to a seasonal effect as it cannot be guaranteed the cores were taken from the exact location. The results were consistent with previous comparative analysis of under ice and open water cores collected 15 year ago in Yellowknife Bay which showed no seasonal variation (Andrade et al. 2010; Schuh 2019). A recent study suggests that on a seasonal basis, As speciation and concentration in large deep subarctic lakes were less likely to be affected relative to small shallow (<4 m depth) subarctic lakes which experienced anoxia mid-winter during prolonged ice-cover (Palmer et al. 2019).

3.2 Future research

Several opportunities for future research were identified based on the results of this study. Further research is required to (i) quantify contributions of As and Sb from each contaminant source, and (ii) apply results from this work to models of future As and Sb flux from sediments under changing environmental conditions.

Some ambiguities need to be resolved in order to quantify the contributions of As and Sb from each contaminant source. The conclusion that roaster oxides were a significant host of As and Sb in near surface sediments at all locations within Yellowknife Bay inspired further questions about the sources and pathways of waste streams. Several possible explanations were explored such as internal recycling of submerged Foreshore tailings, continued weathering of contaminated soils from nearshore outcrops, and sediment loading via Baker Creek; however, quantifying the contributions from each of these possible sources was outside the scope of this thesis. Is it possible for roaster oxides from each source to be distinguished based on trace elemental signatures or by another method? Delineating the exact sources and pathways of roaster oxides would be helpful in mitigating their continued loading to near surface sediments. Similarly, the conclusion that As₂O₃ was present both in near surface sediments and deep sediments provokes further questions. It is proposed that As₂O₃ and roaster oxides were likely sourced from contaminated soils on site and/or waste streams co-deposited with the Foreshore tailings. Further work to confirm and quantify the loading from these point sources is recommended. Additionally, natural arsenolite is supposedly highly soluble (Nordstrom et al.

2014), yet As_2O_3 persists in near surface and deep sediments. The persistence of As_2O_3 was previously documented in soils and sediments surrounding Giant Mine (e.g., Bromstad et al. 2017; Jamieson et al. 2017; Schuh et al. 2018; Van Den Berghe et al. 2018; Schuh et al. 2019). It was proposed that the solubility of As_2O_3 is limited by the incorporation of Sb into its structure (Riveros et al. 2000; Schuh et al. 2018; Schuh et al. 2019). Given the significance of As_2O_3 as a labile source of As at depth, and its continued loading to near surface sediment, the results from this study further affirm the need for study on the solubility and mechanisms controlling the dissolution of As_2O_3 .

This study characterized the relative contribution of solid-phase mineral hosts in both near surface and deep sediments. Quantifying the current rates of As and Sb sediment efflux to Yellowknife Bay waters would complement the results of this thesis and is currently being investigated by Chételat et al. (2020). Preliminary results from field and lab incubations of Yellowknife Bay sediments indicated that sediment released more arsenic to overlying water when dissolved oxygen was experimentally removed. Additionally, the mass of As diffusing from sediment was estimated to be a similar magnitude to the mass of As added to Yellowknife Bay via Baker Creek. Next steps for this work include developing a model to forecast combined As and Sb loading from sediments and contaminant sources under the influence of changing environmental conditions (Chételat et al. 2020).

Finally, future work on Yellowknife Bay could address some of the limitations of this study. A potential limitation of this work was that it relied on results from previous sampling of Yellowknife Bay to provide context for the ages of the sediment; the cores in this study were not dated using geochronology methods. Results highlighted the complexity of the contamination in Yellowknife Bay with cumulative influences from multiple waste streams, physical sediment processes, and post-depositional geochemical processes. There was inter-bay variability between concentration and mineralogy trends in the nearfield cores, attributed to their proximity to both

54

Baker Creek and the Foreshore tailings. Combining the methods from this study with others may help delineate some of the ambiguities related to the sources of these contaminants. Another potential limitation was the number of thin sections measured per core; additional mineralogical analysis would provide more information on delineating mineralogical processes at near field sites. This was exemplified in D1 where the addition of another thin section sample was helpful in elucidating relationships between realgar and As₂O₃. Specifically, it would be interesting to complete mineralogical analysis at, above, and below the Sb maxima in each core to robustly determine Sb behaviour in deep sediment.

3.3 Sustainability and gold mining

It is generally accepted that sustainability is composed of three intersecting pillars; a social, economic, and environmental framework in which each component functions uncompromised by the others. Together they are the foundation of sustainable development, defined as a system of development that "meets the needs of the present without compromising the ability of future generations to meet their own needs," (Brundtland 1987). The introduction of sustainability concepts by the Brundtland Commission (1987) marked a departure from previous thinking that economic growth and environmental and social values were mutually exclusive (Laurence 2011). The "growth-can-be-good" approach gained traction in government and industry sectors, inclusive of the mining industry (Laurence 2011). Applying sustainability to mining may seem paradoxical in that mining generates returns from the extraction of finite resources; however, sustainability encompasses more than longevity and some mine products can be considered critical for meeting the present needs of society and the projected needs of a low-carbon future (e.g., Heffron 2020; Sovacool et al. 2020). There is no global definition for critical minerals and metals, however in Canada they include materials such as rare earth elements, cobalt, nickel, graphite, lithium, and potash (NRCAN 2019). In the context of critical mineral and

metal mining, the integration of responsible mining practices which aim to incorporate social and environmental considerations into mine development decisions (i.e., corporate social responsibility (CSR), social license to operate (SLO), environmental social governance (ESG), environmental and social impact assessment (ESIA)), could result in mines that yield net positive sustainability gains. Net positive sustainability gains would require that mine products are essential needs of society, and adverse environmental or social impacts are not justified by over compensation in economic benefits (i.e., no significant environmental and/or social impacts rationalized by the offset of impact benefit agreements or variations thereof) (Gibson 2006).

Problematically responsible mining practices have been and continue to be applied to non-critical minerals and metals under the guise of sustainability. A quick web search of the top global gold producers reveals 'Sustainability' as a key header on their homepages, but gold demand is hardly driven by society's basic needs. Gold behaves more like a monetary asset than a conventional commodity with nearly half of 2019 demand driven by jewelry and nearly a third driven by investment (WGC 2020). Only 7.5% of 2019 demand was for use in technology applications (WGC 2020). Therefore, gold's value to society is almost solely driven by its economic and decorative contributions, and any social or economic benefits are arguably conciliatory. Currently the industry is struggling to replace ounces mined, which likely means more energy intensive development; deeper mines coming into production and lower head grade at existing operations being mined to meet demand (Schodde 2019). The slimmer the economic margins, the more likelihood for social or environmental trade-offs. Directives labeled as sustainability initiatives should be under scrutiny to hold gold mine owners and operators accountable for the outcomes of their activities. The gold industry is highly competitive, driven by cyclical price fluctuations, and notoriously lacks transparency; features that limit opportunities for building interactional trust and lasting partnerships with governments, communities, and other industry partners. The complex social, economic, and environmental impacts from former gold

mining operations in the Yellowknife region is an example of the consequences of the shortsighted approach historically adopted by the gold mining industry: the pursuit of near-term value with little consideration of long-term outcomes.

3.4 Relationship to sustainability

The research presented in this thesis represented a component of the study required to understand the existing and long-term environmental impacts from mining in the Yellowknife region. The results characterized both past and present mining-derived contamination in Yellowknife Bay and connections were drawn to future environmental implications. There was a direct connection to the preservation of the environment in discussion of the implications of As and Sb flux to Yellowknife Bay waters. The other two dimensions of sustainability, social equity and economic growth, were not explicitly addressed in this thesis. Given the importance of sustainability to environmental study, connections between the results of this thesis and the social and economic pillars of sustainability are addressed here.

3.4.1 Social impacts

Social components of sustainability in the mining industry are generally discussed in terms of social license to operate (SLO) and social impact assessment (SIA). Obtaining social license is a relatively new concept (introduced in the 1990s), defined as moving beyond full legal compliance to gain the acceptance of local communities and/or civil society (de-Miguel-Molina et al. 2018). Social license exists when a mining project has the broad and ongoing approval to conduct its activities; it is distinct from regulatory approval (which may or may not align with community interests and may or may not require an SIA) (de-Miguel-Molina et al. 2018; Prno and Slocombe 2012, 2014). The most concerning negative social effects of mining are land-use related impacts and environmental impacts which affect human health and human rights (Mancini and Sala 2018).

The connection between the social component of sustainability and this research lies in the traditional and ongoing sustenance, cultural, and recreational use of Yellowknife Bay. Current concerns for the preservation of Yellowknife Bay waters are shared by both the City of Yellowknife and the Yellowknives Dene First Nations (YKDFN) communities; however, because of their close connection with and traditional use of the land, social impacts (both immediate and chronic) were disproportionally experienced by the YKDFN (YKDFNLEC 2005; Sandlos and Keeling 2016). Land management is embedded in Dene culture and prior to the onset of mining activity, the YKDFN engaged in traditional land-use practices throughout the Yellowknife Bay (Willicheh) area such as hunting, trapping, gathering foodstuffs, and collecting drinking water (Degray 2020). Testimony from elders describe the land as a productive area for berries and medicinal plants, game, and an essential gathering area for ceremony (O'Reilly, 2015; Sandlos and Keeling, 2016). Furthermore, the outfall of Baker Creek recognized in this study and others (Andrade et al. 2010; Chételat et al. 2018) to be the most contaminated area within Yellowknife Bay represents a past productive fishing site (Sandlos and Keeling 2016). Mining activity brought settler populations, construction of new infrastructure, and increased land and air traffic, all of which contributed to disruption of caribou and moose migration routes and other land-use fragmentations (Sandlos and Keeling, 2012; Degray 2020). The contaminated environment no longer supported the YKDFN's traditional way of life, and lack of control over environmental degradation marginalized and alienated the communities. Lands and waters that had sustained the YKDFN lifestyle and culture for thousands of years became a source of danger and uncertainty (Sandlos and Keeling 2016). In 1998 at a presentation by the YKDFN to the NWT Water Board, Dene Elder Fred Sangris said, "our people know about the gold and it was a Dene woman who showed the prospectors where to locate it; it was of no value to us. What was important was the water, the fish, and game (moose, beaver, and muskrat)," (YKDFNLEC 2005). This sentiment has been echoed elsewhere; in 2011 at a perpetual care workshop hosted by Alternatives North,

Dene Elder Michelle Papers related, "people love the land, but mining has changed the land and made it dangerous," (Sandlos and Keeling 2012).

Giant Mine represented a case where mine development considerations were solely economic. Nothing resembling a social impact assessment or community consultation occurred during early operation, and the surrounding environment was manipulated to store mine waste as a result of settler economic interests. A recent study investigating the perceived risks and lived experiences of the YKDFN quoted that the most prominent community concern is water security (Degray 2020). Traditional water sources have been contaminated by mining and related settler activity, resulting in requirements for YKDFN communities to depend on trucked water delivery (City of Yellowknife 2019). The YKDFN have already adjusted their land-use activities to avoid areas of known contamination. The potential for As and Sb to be remobilized from sediment to waters creates further uncertainties on water security in communities. Residents of the City of Yellowknife also share concerns regarding water quality. The city sources all of its water from Yellowknife River, upstream of Giant Mine, via an eight-kilometre submerged pipeline, which has passed its design life and is vulnerable to leaking (AECOM 2011, 2017). The replacement of the pipe is expected to be approximately \$35M CAD. The alternative, drawing drinking water directly from Yellowknife Bay and adapting the existing water treatment facility, is the more cost-efficient solution (\$ 9M CAD) and was recommended by an external consultant (AECOM 2011, 2017). However, this option is likely to be rejected due to community anxiety surrounding As contamination; both the YKDFN and the North Slave Métis Alliance have indicated that sourcing drinking water from Yellowknife Bay is not acceptable (City of Yellowknife 2019). Listening to community concern regardless of economic considerations represents an opportunity to build interactional trust. At the time of writing, decisions

regarding the pipeline replacement have not been finalized; however, to abate financial constraints the federal government recently contributed \$25.8M CAD from its Disaster Mitigation and Adaptation Fund to the construction of the new submerged pipeline (City of Yellowknife 2019; Williams 2019).

3.4.2 Economic impacts

Mine reclamation is government mandated in most countries and is usually financially assured by some form of reclamation bond as a requirement for obtaining a mining permit. In Canada mining companies are legally required to reclaim all lands disturbed by mining since 1969, although as in the case of Giant Mine, legislation exists to financially assure reclamation in the event the mine owner is unable to comply (Cheng and Skousen 2014). Government funding for water treatment (discussed in Section 3.4.1) is small relative to the overall costs required for remediation at Giant Mine and the ongoing costs of perpetual care which are greater than \$1B CAD. Further connections between this research and the economic component of sustainability exists in the consideration of cumulative costs of addressing past environmental contamination and future costs of perpetual care, inclusive of potentially addressing sediment contamination in Yellowknife Bay.

Following the bankruptcy of Giant Mine's last owner, the liability of the 237,000 tonnes of As₂O₃ stored underground was transferred to the government. Although up to 50 remediation strategies were considered, *in situ* freezing (frozen block method) was selected to contain the As₂O₃ underground (Indian and Northern Affairs Canada, 2010). In post-closure consultation, the YKDFN expressed that remediation should not only isolate and manage As₂O₃ but remove it entirely to return the land to its pre-mining state, albeit this was resolutely considered not technically feasible by the remediation team (Sandlos and Keeling

2016). The estimated capital expenditure for the frozen block method was indicated to be on the order of \$1B CAD, with an additional \$2M CAD per year required indefinitely (AANDC 2012; Jamieson 2014). The frozen block method is increasingly being viewed as an interim solution, specifically with the Mackenzie Review Board recommending it be redesigned as reversible and for a maximum of 100 years (O'Reilly 2011). Suggesting the frozen block method be temporary eschews responsibility by passing remediation onto future generations to either develop and install technology as a permanent solution or to continue to financially maintain interim solutions. Shifting the onus to future generations to develop solutions also assumes that there will be sufficient technological advancements available to permanently address the complexity of mine waste at Giant Mine, or that communities will have the means and support to maintain the upkeep costs of the site. The perpetual nature of the remediation proposal selected is unlikely to gain full acceptance of community members and future generations will be burdened with the ongoing care and maintenance of the stored As₂O₃, an economically draining liability. In this way, past mining development has directly economically impeded current and future generations.

The YKDFN have requested compensation to account for social impacts, a role in the remediation of site, and a formal apology from the government. The government has responded that it likely will not grant the YKDFN a sole-source remediation contract but there is support for an apology and the government has been working with the YKDFN for the past three years to develop a recognition of rights table (Blake 2020). Reconciliation for past impacts is important in building community-government-industry partnerships and interactional trust. Yellowknife is likely to experience future mine development pressures, as the region remains prospective for exploration investment. For example, in September 2020 Gold Terra Resources announced an exploration agreement with gold major Newmont on

61
land adjacent to the former Con Mine, quoting "the achievement of this Agreement reflects the shared vision of two companies with the same goal, 'find more gold'," (Gold Terra 2020). Additionally, the 2019 Canadian Minerals and Metals Plan (CMMP) envisions Canada as the world leading mining nation and strongly emphasizes the economic opportunity for resource development north of the sixtieth parallel (Natural Resources Canada 2019). With increasing interest in the development of Canada's northern resources, it is imperative to assess the long-term social and environmental impacts of mine development, especially in the context of communities that have been previously exploited by the industry (Gibson and Klinck 2005; Sandlos and Keeling 2016). Although the YKDFN's memory is long, corporate memory in the mining industry is not. Any future development needs to be heavily scrutinized to prevent further negative social impacts and environmental degradation.

References

Abdul, K.S.M., Jayasinghe, S.S., Chandana, E.P.S., Mangala, P., Jayasumana, C., and De Silva, M.C.S. (2015). Arsenic and human health effects: A review. Environmental Toxicology and Pharmacology, 40(3), 826-846. https://doi.org/10.1016/j.etap.2015.09.016.

Aboriginal Affairs and Northern Development Canada (AANDC). (2012). Value for Money Audit of the Giant Mine Remediation Project (Archived). Accessed September 2020. Retrieved from https://www.rcaanc-cirnac.gc.ca/eng/1366814305245/1537466632982.

AECOM. (2011). Yellowknife Water Treatment Plant Information Session. May 10, 2011. Yellowknife.

AECOM. (2017). City of Yellowknife Potable Water Source Selection Study. Project No. 60541637. Yellowknife.

Andrade, C.F. (2006). Arsenic cycling and speciation in mining-impacted sediments and pore-waters from Yellowknife Bay, Great Slave Lake, NWT. MSc Thesis. Department of Geological Sciences and Geological Engineering. Queen's University.

Andrade, C.F., Jamieson, H.E., Kyser, T.K., Praharaj, T., and Fortin, D. (2010). Biogeochemical redox cycling of arsenic in mine-impacted lake sediments and co-existing pore waters near Giant Mine, Yellowknife Bay, Canada. Applied Geochemistry, 25(2), 199-211. https://doi.org/10.1016/j.apgeochem.2009.11.005.

Arsic, M., Teasdale, P.R., Welsh, D.T., Johnston, S.G., Burton, E.D., Hockmann, K. and Bennett, W.W. (2018). Diffusive gradients in thin films reveals differences in antimony and arsenic mobility in a contaminated wetland sediment during an oxic-anoxic transition. Environmental science & technology, 52(3), pp.1118-1127. https://doi-org /10.1021/acs.est.7b03882.

Ashley, P.M., Craw, D., Graham, B.P., and Chappell, D.A. (2003). Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. Journal of Geochemical Exploration, 77(1), 1-14. https://doi-org /10.1016/S0375-6742(02)00251-0.

Bailey, A. (2017). Characterization of Arsenic-Hosting Solid Phases in Giant Mine Tailings and Dust. MSc Thesis. Department of Geological Sciences and Geological Engineering. Queen's University.

Bank of Canada. (2020). Inflation Calculator. Accessed November 2020. Retrieved from https://www.bankofcanada.ca/rates/related/inflation-calculator/.

Basta, N. and Juhasz, A. (2014). Using in vivo bioavailability and/or in vitro gastrointestinal bioaccessibility testing to adjust human exposure to arsenic from soil ingestion. Reviews in Mineralogy and geochemistry, 79(1), 451-472. https://doi.org/10.2138/rmg.2014.79.9.

Blake, E. (2020, December 2). "Our land is spoiled.' YKDFN again calls for Giant Mine apology." Accessed December 2020. Retrieved from https://cabinradio.ca/50773/news/yellowknife/our-land-is-spoiled-ykdfn-again-calls-for-giant-mine-apology/.

Bright, D.A., Coedy, B., Dushenko, W.T., and Reimer, K.J. (1994). Arsenic transport in a watershed receiving gold mine effluent near Yellowknife, Northwest Territories, Canada. The Science of the Total Environment, 155(3), 237-252. https://doi.org/10.1016/0048-9697(94)90503-7.

Bromstad, M.J. (2011). The Characterization, Persistence, and Bioaccessibility of Roaster-Derived Arsenic in Surface Soils at Giant Mine, Yellowknife, NT. MSc Thesis. Department of Geological Sciences and Geological Engineering. Queen's University.

Bromstad, M.J., Wyre, L.A., and Jamieson, H.E. (2017). The characterization, mobility, and persistence of roaster-derived arsenic in soils at Giant Mine, NWT. Applied Geochemistry, 82, 102-118. https://doi.org/10.1016/j.apgeochem.2017.04.004.

Brundtland, G. (1987). Report of the World Commission on Environment and Development: Our Common Future. United Nations General Assembly document A/42/427.

Bowell, R. and Craw, D. (2014). The management of arsenic in the mining industry. In Bowell, R., Alpers, C., Jamieson, H., Nordstrom, K., and Majzlan, J. (Eds.), Reviews in Mineralogy and Geochemistry, 79(1), 507-532. https://doi.org/10.2138/rmg.2014.79.11.

Bullen, W., Robb, M., Anglin, C., Falck, H., Wright, D., and Ambrose, E. (2006). Economic contribution of gold mining in the Yellowknife mining district, in Gold in the Yellowknife Greenstone Belt, Northwest Territories. In Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J., (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results from the EXTECH III Multidisciplinary Research Project (pp.38-48).

Canada North Environmental Services. (2018). Giant Mine Human Health and Ecological Risk Assessment. Yellowknife: Public Services and Procurement Canada.

Canadian Council of Ministers of the Environment (CCME). (1999a). Canadian Water Quality Guidelines for the Protection of Aquatic Life: Arsenic.

Canadian Council of Ministers of the Environment (CCME). (1999b). Canadian Sediment Quality Guidelines for the Protection of Aquatic Life: Arsenic.

Canam, T.W. (2006). Discovery, Mine Production, and Geology of the Giant Mine. In Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J., (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results from the EXTECH III Multidisciplinary Research Project (pp.188-196).

Casiot, C., Ujevic, M.M., Seidel, J., and Elbaz-Poulichet, F. (2007). Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France). Applied Geochemistry, 22(4), 788-798. https://doi.org/10.1016/j.apgeochem.2006.11.007.

Caussy, D. (2003). Case studies of the impact of understanding bioavailability: arsenic. Ecotoxicology and Environmental Safety, 56(1), 164-173. https://doi.org/10.1016/S0147-6513(03)00059-9.

Cheng, L. and J.G. Skousen. 2014. "Comparison of international mine reclamation bonding systems with recommendations for China." International Journal of Coal Science & Technology 4 (2): 67-79. https://doi.org/10.1007/s40789-017-0164-3.

Chenney, C.L., Eccles, K.M., Kimpe, L.E., Thienpont, J.R., Korosi, J.B., and Blais, J.M. (2020). Determining the effects of past gold mining using a sediment using a paleotoxicology model. Science of the Total Environment, 718, 137308. https://doi.org/10.1016/j.scitotenv.2020.137308.

Chételat, J., Amyot, M., Muir, D., Black, J., Richardson, M., Evans, M., and Palmer, M.J. (2018). Arsenic, antimony, and metal concentrations in water and sediment of Yellowknife Bay; Northwest Territories Geological Survey, NWT. Open File 2017-05.

Chételat, J., Palmer, M.J., Astles, B., Amyot, M., Paudyn, K.A., Jamieson, H.E., and Lines, W. (2020). Remobilization of Legacy Arsenic Contamination in Yellowknife Bay Sediments: Field and laboratory measurements of arsenic fluxes. 2020 NWT & Nunavut Geoscience Symposium.

City of Yellowknife. (2019). Claim for Water Compensation (Water Pipeline). Yellowknife: Mackenzie Valley Land and Water Board.

Coleman, L.C. (1957). Mineralogy of the Giant Yellowknife Gold Mine. Economic Geology, 52, 400-425. https://doi.org/10.2113/gsecongeo.52.4.400.

Corkhill, C., and Vaughan, D. (2009). Arsenopyrite oxidation – A review. Applied Geochemistry, 24(12), 2342-2361. https://doi.org/10.1016/j.apgeochem.2009.09.008.

de-Miguel-Molina, B., Chirivella-González, V. and García-Ortega, B. (2019). CEO letters: Social license to operate and community involvement in the mining industry. Business Ethics: A European Review, 28(1), 36-55. https://doi.org./10.1111/beer.12205. Degray, A. (2020). Indigenous risk perceptions and land-use in Yellowknife, NT. MA Thesis. Department of Geography/Faculty of Humanities and Social Sciences Memorial University of Newfoundland.

Dixit, S. and Hering, J.G. (2003). Comparison of Arsenic(V) and Arsenic (III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility. Environmental Science and Technology, 37(18), 4182-4189. https://doi.org/10.1021/es030309t.

Ecosystem Classification Group. (2008). Ecological Regions of the Northwest Territories – Taiga Shield. Department of Environment and Natural Resources, Government of the Northwest Territories.

Environment Canada. (2015). Canadian Climate Normals. Accessed September 2020. Retrieved from https://climate.weather.gc.ca/climate_normals/index_e.html.

Environment Canada. (2019). Real-Time Hydrometric Data. Accessed December 2020. Retrieved from https://wateroffice.ec.gc.ca/mainmenu/real time data index e.html.

Falk, M.R., Miller, M.D., and Kostiuk, S.M. (1973). Biological Effects of Mining Waste in the Northwest Territories. Yellowknife: Department of the Environment Fisheries and Marine Service.

Fawcett, S.E. and Jamieson, H.E. (2011). The distinction between ore processing and postdepositional transformation on the speciation of arsenic and antimony in mine waste and sediment. Chemical Geology, 283, 109-118. https://doi.org/10.1016/j.chemgeo.2010.02.019

Fawcett, S., Jamieson, H.E., Nordstrom, D.K., and McCleskey, R.B. (2015). Arsenic and antimony geochemistry of mine wastes, associated waters, associated waters and sediments at the Giant Mine, Yellowknife, Northwest Territories, Canada. Applied Geochemistry, 62, 3-17. https://doi.org/10.1016/j.apgeochem.2014.12.012.

Filella, M., Williams, P., and Belzile, N. (2009). Antimony in the environment: knowns and unknowns. Environmental Chemistry, 6(2), 95-105. https://doi.org/10.1071/EN09007.

Galloway, J.M., Palmer, M.J., Jamieson, H E., Patterson, R.T., Nasser, N., Falck, H., Lemay, D. (2015). Geochemistry of lakes across ecozones in the Northwest Territories and implications for the distribution of arsenic in the Yellowknife region. Part 1: Sediments. Geological Survey of Canada. Natural Resources Canada.

Galloway, J.M., Swindles, G.T., Jamieson, H.E., Palmer, M.J., Parsons, M., Sanei, H., Falck, H. (2018). Organic matter control on the distribution of arsenic in lake sediments impacted by ~ 65 years of gold ore processing in subarctic Canada. Science of the Total Environment, 622–623, 1668-1679. https://doi.org/10.1016/j.scitotenv.2017.10.048.

Gebel, T. (1997). Arsenic and antimony: comparative approach on mechanistic toxicology. Chemical-Biological Interactions, 107(3), 131-144. https://doi.org/10.1016/S0009-2797(97)00087-2.

Gibson, R.B. (2006). Sustainability assessment: basic components of a practical approach. Impact Assessment and Project Appraisal, 24(3), 170-182. https://doi.org/10.3152/147154606781765147

Gold Terra. (2020, September 8). Press Release: Gold Terra to Earn up to a 60% Interest on Adjacent Mining Claims to the Former Con Mine Owned by Newmont. Accessed September 2020. Retrieved from https://goldterracorp.com/news/gold-terra-to-earn-up-to-a-60-interest-on-adjacen-1809/

Golder Associates. (2005). Investigation of the Distribution Historic Tailings in Yellowknife Bay. Giant Mine Remediation Project Team. Project No. 04-1328-015.

Golder Associates. (2012). Baseline data collection for snow depth, ice thickness and water quality for hydrodynamic modeling of Yellowknife Bay, Great Slave Lake, NWT. Project No. 09-1427-0006-4000-4100.

Griffiths, K., Michelutti, N., Sugar, M., Douglas, M., and Smol, J. (2017). Ice-cover is the principal driver of ecological change in High Arctic lakes and ponds. PLoS One, 12(3). https://doi.org/10.1371/journal.pone.0172989.

Hartmann, D.L., Tank, A.M., Rusticucci, M., Alexander, L.V., Brönnimann, S., and Charabi, Y.A. (2013). Observations: Atmosphere and surface. In Climate change 2013: The physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (pp. 159-254). Cambridge University Press. https://doi.org/10.1017/CBO9781107415324.008.

Hauser, R.L., McDonald, D.W., and Siddorn, J.P. 2006. Geology of the Miramar Con Mine. In Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J., (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results from the EXTECH III Multidisciplinary Research Project (pp. 173-187).

Health Canada. (2006). Guidelines for Canadian Drinking Water Quality: Arsenic. Guideline Technical Document.

Health Canada. (2020). Screening Assessment: Antimony-containing substances. Environment and Climate Change Canada.

Heffron, R. (2020). The role of justice in developing critical minerals. The Extractive Industries and Society, 7(3), 855-863. https://doi.org/10.1016/j.exis.2020.06.018.

Herath, I., Vithanage, M., and Bundschuh, J. (2017). Antimony as a global dilemma: geochemistry, mobility, fate and transport. Environmental pollution, 223, 545-559. https://doi.org/10.1016/j.envpol.2017.01.057.

Hocking, D., Kuchar, P., Plambeck, J.A., and Smith, R.A. (1978). The Impact of Gold Smelter Emissions on Vegetation and Soils of a Sub-Arctic Forest-Tundra Transition Ecosystem. Journal of the Air Pollution Control Association, 28(2), 133-137. https://doi.org/10.1080/00022470.1978.10470580.

Holland, M.M., and Bitz, C.M. (2003). Polar amplification of climate change in coupled models. Climate Dynamics, 21(3-4), 221-232. http://doi.org/10.1007/s00382-003-0332-6.

Houben, A.J., D'Onofrio, R., Kokelj, S., and Blais, J.M. (2016). Factors Affecting Elevated Arsenic and Methyl Mercury Concentrations in Small Shield Lakes Surrounding Gold Mines near the Yellowknife, NT, (Canada) Region. PLoS ONE, 11(4). https://doi.org/10.1371/journal.pone.0150960.

Indian and Northern Affairs Canada (INAC). (2010). Giant Mine Remediation Project Developer's Assessment Report. Submitted by INAC and the Government of the Northwest Territories. EA0809-001.

Indian and Northern Affairs Canada (INAC). (2018). Arsenic trioxide and underground issues at Giant Mine. Accessed October 2020. Retrieved from https://www.aadnc-aandc.gc.ca/eng/1100100027413/1100100027417.

Indian and Northern Affairs Canada (INAC). (2020). Giant Mine Remediation Project. Accessed December 2020. Retrieved from https://www.aadnc-aandc.gc.ca/eng/1100100027364/1100100027365.

Jamieson, H.E. (2014). The Legacy of Arsenic Contamination from Mining and Processing Refractory Gold Ore at Giant Mine, Yellowknife, Northwest Territories, Canada. In Bowell, R., Alpers, C., Jamieson, H., Nordstrom, K., and Majzlan, J. (Eds.), Reviews in Mineralogy and Geochemistry, 79(1), 533-551. https://doi.org/10.2138/rmg.2014.79.12.

Jamieson, H.E., Maitland, K.M., Oliver, J.T., and Palmer, M.J. (2017). Regional distribution of arsenic in near-surface soils in the Yellowknife area; Northwest Territories Geological Survey. NWT Open File 2017-03.

Kerr, D. (2006). Surficial geology and exploration geochemistry, Yellowknife area. Gold in the Yellowknife Greenstone Belt, Northwest Territories. In Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J., (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results from the EXTECH III Multidisciplinary Research Project (pp.301-324).

Laurence, D. (2011). Establishing a sustainable mining operation: an overview. Journal of Cleaner Production, 19(2-3), 278-284. https://doi.org/10.1016/j.jclepro.2010.08.019.

Lowers, H.A., Breit, G.N., Foster, A.L., Whitney, J., Yount, J., Nehal Uddin, M., and Atual Muneem, A. (2007). Arsenic incorporation into authigenic pyrite, Bengal Basin sediment, Bangladesh. Geochimica et Cosmochimica Acta, 71(11), 2699–2717. https://doi.org/10.1016/j.gca.2007.03.022.

Macdonald, R.W., Harner, T., and Fyfe, J. (2005). Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data. Science of the Total Environment, 5-86. https://doi.org/10.1016/j.scitotenv.2004.12.059.

Magnuson, J.J., Robertson, D.M., Benson, B.J., Wynne, R.J., Livingstone, D.M., Arai, T., Vuglinski, V.S. (2000). Historical Trends in Lake and River Ice Cover in the Northern Hemisphere. Science, 289(5485), 1743-1746. http://doi.org/10.1126/science.289.5485.1743.

Mancini, L., and S. Sala. 2018. "Social impact assessment in the mining sector: Review and comparison of indicators frameworks." Resources Policy 57: 98-111. https://doi.org/10.1016/j.resourpol.2018.02.002.

Martin, A.J., and Pedersen, T.F. (2002). Seasonal and Interannual Mobility of Arsenic in a Lake Impacted by Metal Mining. Environmental Science and Technology, 36(7), 1516-1523. https://doi.org/10.1021/es0108537.

Menard, P., Duguay, C.R., Flato, G.M., and Rouse, W.R. (2002). Simulation of ice phenology on Great Slave Lake, Northwest Territories, Canada. Hydrological Processes, 16(8), 3691-3706. https://doi.org/10.1002/hyp.1230.

Miller, C.B., Parsons, M.B., Jamieson, H.E., Swindles, G.T., Nasser, N.A., and Galloway, J.M. (2019). Lake-specific controls on the long-term stability of mining-related, legacy arsenic contamination and geochemical baselines in a changing northern environment, Tundra Mine, Northwest Territories, Canada. Applied Geochemistry, 107(3), 131-144. https://doi.org/10.1016/S0009-2797(97)00087-2.

Miller, C.B., Parsons, M.B., Jamieson, H.E., Ardakani, O.H., Gregory, B.R.B., and Galloway, J.M. (2020). Influence of late-Holocene climate change on the solid-phase speciation and long-term stability of arsenic in sub-Arctic lake sediments. Science of the Total Environment, 709, 136115. https://doi.org/10.1016/j.scitotenv.2019.136115.

Moir, I., Falck, H., Hauser, B., and Robb, M. (2006). The History of Mining and its impact on the Development of Yellowknife. In Gold in the Yellowknife Greenstone Belt, Northwest Territories. In Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J., (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results from the EXTECH III Multidisciplinary Research Project (pp.11-28). Mineralogical Society of America (MSA). (2018). Handbook of Mineralogy. Mineralogical Society of America.

Mudroch, A., Joshi, S.R., Sutherland, D., Mudrich, P., and Dickson, K.M. (1989). Geochemistry of sediments in the Back Bay and Yellowknife Bay of Great Slave Lake. Environmental Geology, 14, 35-42. https://doi.org/10.1007/BF01740583.

National Toxicology Program. (2018). Report on Carcinogens: Monograph on Antimony Trioxide. U.S. Department of Health and Human Services.

Nordstrom, D., Majzlan, J., and Königsberger, E. (2014). Thermodynamic properties for arsenic minerals and aqueous species. In Bowell, R., Alpers, C., Jamieson, H., Nordstrom, K., and Majzlan, J. (Eds.), Reviews in Mineralogy and Geochemistry, 79 (1), 217-255. https://doi.org/10.2138/rmg.2014.79.4.

Natural Resources Canada (NRCAN). (2019). Critical Minerals in Canada: Securing North American and Global Supply Chains. Saskatoon: Pacific NorthWest Economic Region Annual Summit 2019.

O'Reilly, K. (2013). Reviewing the review board: Was the Giant Mine environmental assessment a success? Yellowknife: Northern Public Affairs.

O'Reilly, K. (2015). Liability, Legacy, and Perpetual Care: Government Ownership and Management of the Giant Mine, 1999–2015. In J. Sandlos, & A. Keeling (Eds.), Mining and Communities in Northern Canada (pp. 341-376). Calgary: University of Calgary Press.

O'Day, P.A., Vlassopoulos, D., Root, R., and Rivera, N. (2004). The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. Proceedings of the National Academy of Sciences, 101(38), 13703-13708. https://doi.org/10.1073/pnas.0402775101.

Paci, C. and Villebrun, N. (2005). Mining Denendeh: A Dene Nation Perspective on Community Health Impacts of Mining. Pimatisiwin: A Journal of Aboriginal and Indigenous Community Health, 3(1), 71-86.

Palmer, M.J., Galloway, J.M., Jamieson, H.E., Patterson, R.T., Falck, H., and Kokelj, S.V. (2015). The Concentration of Arsenic in lake waters of the Yellowknife Area. Northwest Territories Geological Survey. Government of Northwest Territories. https://doi.org/10.13140/RG.2.1.2582.5041.

Palmer, M.J., Chételat, J., Richardson, M., Jamieson, H.E., and Galloway, J.M. (2019). Seasonal variation of arsenic and antimony in surface waters of small subarctic lakes impacted by legacy mining pollution near Yellowknife, NT, Canada. Science of the Total Environment, 684, 326-339. https://doi.org/10.1016/j.scitotenv.2019.05.258.

Palmer, M.J., Chételat, J., Jamieson, H.E., Richardson, M., and Amyot, M. (2020). Hydrologic control on winter dissolved oxygen mediates arsenic cycling in a small subarctic lake. (P. J.

Hernes, S. Tank, and R. N. Glud, Eds.) Association for the Sciences of Limnology and Oceanography (Special Issue: Biogeochemistry and Ecology across Arctic Aquatic Ecosystems in the Face of Change.), 1-17. https://doi.org/10.1002/lno.11556.

Pelletier, N., Chételat, J., Cousens, B., Zhang, S., Stepner, D., Muir, D., and Vermaire, J. (2020). Lead contamination from gold mining in Yellowknife Bay (Northwest Territories), reconstructed using stable lead isotopes. Environmental Pollution, 259, 113888. https://doi.org/10.1016/j.envpol.2019.113888.

Peters, G., McCurdy, R., & Hindmarsh, J. (2008). Environmental Aspects of Arsenic Toxicity. Critical Reviews in Clinical Laboratory Sciences, 33(6), 457-493. https://doi.org/10.3109/10408369609080055.

Pinard, J.P., Maisson, J., & Seccombe-Hett, P. (2008). Yellowknife Wind Energy Prefeasibility Report. Prepared for Aurora Research Institute.

Plumlee, G. and Morman, S. (2011). Mine wastes and human health. Elements, 7(6), 399-404. https://doi.org/10.2113/gselements.7.6.399.

Prno, J. and S. Slocombe. 2014. "A systems-based conceptual framework for assessing the determinants of a social license to operate in the mining industry." Environmental management 53 (3): 672-689. https://doi.org/10.1007/s00267-013-0221-7.

Prno, J. and S. Slocombe. 2012. "Exploring the origins of 'social license to operate' in the mining sector: Perspectives from governance and sustainability theories." Resources Policy 37 (3): 346-357. https://doi.org/10.1016/j.resourpol.2012.04.002.

Radková, A.B., Jamieson, H.E., Campbell, K.M., and Hudson-Edwards, K.A. (in press). Antimony in Mine Wastes: Geochemistry, Mineralogy, Microbiology. Economic Geology.

Sandlos, J. and Keeling, A. (2012). Giant Mine: Historical Summary. St. John's: Memorial University. Abandoned Mines in Northern Canada Project.

Sandlos, J. and Keeling, A. (2016). Toxic Legacies, Slow Violence, and Environmental Injustice at Giant Mine, NWT. The Northern Review, 47, 7-21. https://doi.org/10.22584/nr42.2016.002. Sandmann, D. and Gutzmer, J. (2013). Use of Mineral Liberation Analysis (MLA) in the Characterization of Lithium-Bearing Micas. Journal of Minerals and Materials Characterization and Engineering, 1(6), 258-292. http://dx.doi.org/10.4236/jmmce.2013.16043.

Sovacool, B., Ali, S., Bazilian, M., Radley, B., Nemery, B., Okatz, J., and Mulvaney, D. (2020). Sustainable minerals and metals for a low-carbon future. Science, 367(6473), 30-33. https://doi.org/10.1126/science.aaz6003.

Schodde, R. (2019). "Long term trends in gold exploration." NewGenGold Conference. Perth: MinEx Consulting Pty Ltd. 1-29.

Schuh, C., Jamieson, H.E., Palmer, M.J., and Martin, A.J. (2018). 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. Applied Geochemistry, 91 208-220. https://doi.org/10.1016/j.apgeochem.2017.10.025.

Schuh, C., Jamieson, H.E., Palmer, M.J., Martin, A., and Blais, J. (2019). Controls governing the spatial distribution of sediment arsenic concentrations and solid-phase speciation in a lake impacted by legacy mining pollution. Science of the Total Environment, 654, 563–575. https://doi.org/10.1016/j.scitotenv.2018.11.065:ISSN 0048-9697

Schuh, C. (2019). Geochemical and Mineralogical Characterization of Arsenic in Lake Sediments Impacted by Legacy Gold Mining in the Yellowknife Region. PhD Thesis. Department of Geological Sciences and Geological Engineering. Queen's University.

Schuur, E., McGuire, A., Schädel, C., Grosse, G., Harden, J., Hayes, D., Natali, S. (2015). Climate change and the permafrost carbon feedback. Nature, 520(7546), 171-179. https://doi.org/10.1038/nature14338.

Screen, J.A., and Simmonds, I. (2012). Declining summer snowfall in the Arctic: causes, impacts and feedbacks. Climate dynamics, 38(11-12), 2243-2256. http://doi.org/10.1007/s00382-011-1105-2.

Shelton, K., McMenamy, T., Hees, E., and Falck, H. (2004). Deciphering the complex fluid history of a greenstone-hosted gold deposit: fluid inclusion and stable isotope studies of the Giant mine, Yellowknife, Northwest Territories, Canada. Economic Geology, 99(8), 1643-1663. https://doi.org/10.2113/gsecongeo.99.8.1643.

Siddorn, J.P., Cruden, A.P., Hauser, R.L., Armstrong, J.P., and Kirkham, G. (2006). The Giant-Con Deposits: Preliminary Integrated Structural and Mineralization History. In Anglin, C.D., Falck, H., Wright, D.F., Ambrose, E.J., (Eds.), Gold in the Yellowknife Greenstone Belt, Northwest Territories: Results from the EXTECH III Multidisciplinary Research Project (pp. 213-231).

Silke, R. (2013). Giant Mine Milling and Roasting Process, Yellowknife, NWT: A Historical Summary.

Smedley, P.L., and Kinniburgh, D.G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17(5), 517-568. https://doi.org/10.1016/S0883-2927(02)00018-5.

Sovacool, B., Ali, S., Bazilian, M., Radley, B., Nemery, B., Okatz, J., & Mulvaney, D. (2020). Sustainable minerals and metals for a low-carbon future. Science, 367(6473), 30-33. https://doi.org/10.1126/science.aaz6003.

Spence, C., Kokelj, S.V., and Ehsanzadeh, E. (2011). Precipitation trends contribute to streamflow regime shifts in northern Canada. In D. Yang, P. Marsh, & A. Gelfan (Ed.). Wallingford: IAHS Publication.

Spence, C., Kokelj, S.V., Kokelj, S.A., and Hedstrom, N. (2015). Evidence of a change in water chemistry in Canada's subarctic associated with enhanced winter streamflow. Journal of Geophysical Research: Biogeosciences, 120(1), 113–127. https://doi.org/10.1002/2014JG002809.

Stantec. (2014a). Technical Data Report for Yellowknife Bay Baseline Studies Volume 1: Aquatics Final Report. Public Works and Government Services Canada.

Stantec. (2014b). Technical Data Report for the Yellowknife Bay Baseline Studies Volume 2: Hydrodynamics Final Report. Public Works and Government Services Canada.

Stjern, C.W., Lund, M.T., Samset, B.H., Myhre, G., Forster, P.M., Andrews, T., Boucher, O., Faluvegi, G., Fläschner, D., Iversen, T. and Kasoar, M. (2019). Arctic amplification
Response to Individual Climate Drivers. Journal of Geophysical Research: Atmospheres, 124, 6698–6717. https://doi.org/10.1029/2018JD029726.

Toevs, G., Morra, M., Polizzotto, M., Strawn, D., Bostick, B., and Fendorf, S. (2006). Metal(loid) diagenesis in mine-impacted sediments of Lake Coeur d'Alene, Idaho. Environmental science & technology, 40(8), 2537-2543. https://doi.org/10.1021/es051781c.

Tokalıoğlu, Ş., Clough, R., Foulkes, M., and Worsfold, P. (2020). Stability of Arsenic Species During Bioaccessibility Assessment Using the In Vitro UBM and HPLC-ICP-MS Detection. Biological Trace Element Research, 1-7. https://doi.org/10.1007/s12011-020-02066-2.

Van Den Berghe, M.D., Jamieson, H.E., and Palmer, M.J. (2018). Arsenic mobility and characterization in lakes impacted by gold ore roasting, Yellowknife, NWT, Canada. Environmental Pollution, 234, 630-641. https://doi.org/10.1016/j.envpol.2017.11.062.

Vincent, L., Zhang, X., Mekis, É., Wan, H., and Bush, E. (2018). Changes in Canada's Climate: Trends in Indices Based on Daily Temperature and Precipitation Data. Atmosphere-Ocean, 56(5), 332-349. https://doi.org/10.1080/07055900.2018.1514579.

Walker, S.R. (2006). The Solid-Phase Speciation of Arsenic in Roasted and Weathered Sulfides at Giant Mine, NWT. MSc Thesis. Department of Geological Sciences and Geological Engineering. Queen's University.

Walker, S.R., Jamieson, H.E., Lanzirotti, A., Hall, G.M., and Peterson, R.C. (2015). The effect of ore roasting on arsenic oxidation state and solid phase speciation in gold mine tailings. Geochemistry: Exploration, Environment, Analysis, 15(4), 273–291. https://doi.org/10.1144/geochem2013-238.

Walker, S.R. and Jamieson, H.E. (2005). The speciation of arsenic in iron oxides in mine wastes from the Giant Gold Mine N.W.T.: Application of Synchrotron Micro-XRD and Micro-XANES at the grain scale. The Canadian Mineralogist, 43(4), 1205–1224. https://doi.org/10.2113/gscanmin.43.4.1205

Wauthy, M., and Rautio, M. (2020). Permafrost thaw stimulates primary producers but has a moderate effect on primary consumers in subarctic ponds. Ecosphere, 11(6), 1-16. https://doi.org/10.1002/ecs2.3099.

Weckström, J., Hanhijärvi, S., Forsström, L., Kuusisto, E., and Korhola, A. (2014). Reconstructing lake ice cover in subarctic lakes using a diatom-based inference model. Geophysical Research Letters, 41(6) 2026-2032. https://doi.org/10.1002/2014GL059474.

Williams, O. (2019, March 13). Citing possible disaster, YK gets \$26M for new water pipe. Accessed December 2020. Retrieved from Cabin Radio: https://cabinradio.ca/13879/news/yellowknife.

Wilson, N.J., Craw, D., and Hunter, K. (2004). Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand. Environmental Pollution, 129(2), 257-266.

Wilson, S., Lockwood, P., Ashley, P., and Tighe, M. (2010). The chemistry and behaviour of antimony in the soil environment: A critical review. Environmental Pollution, 158(5), 1169-1181. https://doi.org/10.1016/j.envpol.2009.10.045.

Wolfe, S., Stevens, C., Gaanderse, A., and Oldenborger, G. (2014). Lithalsa distribution, morphology and landscape associations in the Great Slave Lowland, Northwest Territories, Canada. Geomorphology, 204, 302-313. https://doi.org/10.1016/j.geomorph.2013.08.014.

World Gold Council (WGC). (2020, January 30). Research Library. Accessed December 2002. Retrieved from Gold Demand Trends, Full year and Q4 2019: www.gold.org.

Yellowknives Dene First Nations (YKDFN). (2020). About our land. Accessed November 2020. Retrieved from https://ykdene.com/.

Yellowknives Dene First Nations Land and Environment Committee (YKDFNLEC). (2005). The Giant Gold Mine – Our Story: Impact of the Yellowknife Giant Gold Mine on the Yellowknives Dene – A Traditional Knowledge Report. Yellowknife: Department of Indian and Northern Affairs.

Zhang, X., Flato, G., Kirchmeier-Young, M., Vincent, L., Wan, H., Wang, X., Kharin, V. (2019). Changes in Temperature and Precipitation Across Canada; Chapter 4. In E. Bush and D. Lemmen (Eds.), Canada's Changing Climate Report (pp. 112-193). Ottawa: Government of Canada.

Appendix A: Sample site locations

Site Name	Latitude	Longitude	Distance from Giant Mine (km)	Approx. Water Depth (m)	Core Depth (cm)	Season Collected	Thin Sections Selected
BCS	62.48181	114.3546	2.1	12	25	July 2019	BCS-0- 0.5, BCS- 1-1.5, BCS-11- 12
C1	62.42667	114.3273	8.3	12	24	July 2019	C1-0.5-1, C1-4-4.5, C1-10-11
C2	62.45361	114.3359	5.3	12	25	July 2019	C2-0-0.5, C2-3.5-4, C2-14-15
WC3	62.47443	114.3309	3.2	15	26	March 2019	WC3-1.5- 2, WC3- 4-4.5, WC3-20- 21
SC3	62.47443	114.3309	3.2	15	25	July 2019	SC3-0- 0.5, SC3- 4.5-5, SC3-16- 17
C4	62.48308	114.3375	2.2	12	20	August 2018	C4-1-1.5, C4-5-5.5, C4-10-11
C6	62.48647	114.3514	1.5	10	21	March 2019	C6-2-2.5, C6-4-4.5, C6-14-15
С9	62.48778	114.3579	1.3	8	20	August 2018	C9-1-1.5, C9-10- 11, C9- 13-14
D1	62.48933	114.3463	1.3	9	25	July 2019	D1-0-0.5, D1-2-2.5, D1-8.5-9, D1-14-15

The following table lists the details for core samples collected in this study.



Appendix B: Photographs of sample sites, field sampling, and sample preparation

Figure 1: (a) Back Bay sampling area (b) Winter sampling equipment set up at site C6 (c) City of Yellowknife water treatment plant (d) Baker Creek at Giant Mine (e) Giant Mine underground As_2O_3 dust chamber storage.



Figure 2: (a) Summer gravity core retrieval by boat (b) Plugging core sleeve during winter sampling (c) Gravity corer (d) Removing core sleeve (e) Sediment cores prior to extrusion (f) Transport of cores and equipment by snowmobile.



Figure 3: Sediment extrusion equipment set up with glove bag seal and nitrogen supply to create an oxygen-free environment.

Appendix C: Supplementary Data to Chapter 2

The data contained in the Excel files listed below provide supplementary material associated with Chapter 2.

Elemental Analysis:

• ICP-MS Results and Sediment Profiles

Mineralogical Analysis:

- SEM-MLA Output Results
- SEM-MLA Processed Results
- EMPA Results

Appendix D: Roaster oxide textures



Figure 1: BSE images of observed roaster oxide textures (sponge and concentric).