



## Occurrence and mobility of thiolated arsenic in legacy mine tailings

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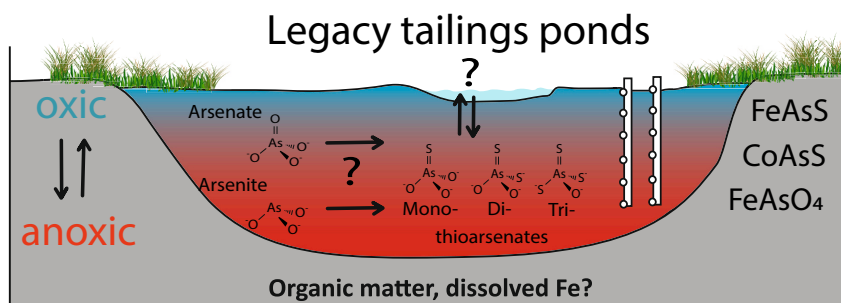
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### HIGHLIGHTS

- Analysis of As speciation in >35 tailings samples from 5 legacy mine tailings.
- Thiolated As comprised up to 17 % of total dissolved As in reducing environments.
- The majority of thiolated As was observed in sub-oxic, low Fe porewater samples.
- Abundance of thiolated As was higher in tailings when As was mainly hosted in sulfides.

### GRAPHICAL ABSTRACT



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### ABSTRACT

We studied the occurrence of dissolved thiolated Arsenic (As) in legacy tailings systems in Ontario and Nova Scotia, Canada, and used aqueous and mineralogical speciation analyses to assess its governing geochemical controls. Surface-accessible and inundated tailings in Cobalt, Ontario, contained ~1 wt-% As mainly hosted in secondary arsenate minerals (erythrite, yukonite, and others) and traces of primary sulfide minerals (cobaltite, gersdorffite and others). Significant fractions of thiolated As (up to 5.9 % of total dissolved As) were detected in aqueous porewater and surface water samples from these sites, comprising mostly monothioarsenate, and smaller amounts of di- and tri-thioarsenates as well as methylated thioarsenates. Tailings at the Goldenville and Montague sites in Nova Scotia contained less (<0.5 wt-%) As, hosted mostly in arsenopyrite and As-bearing pyrite, than the Cobalt sites, but exhibited higher proportions of dissolved thiolated As (up to 17.3 % of total dissolved As, mostly mono- and di-thioarsenate and traces of tri-thioarsenate). Dissolved thiolated As was most abundant in sub-oxic porewaters and inundated tailings samples across the studied sites, and its concentrations were strongly related to the prevailing redox conditions and porewater hydrochemistry, and to a lesser extent, the As-bearing mineralogy. Our novel results demonstrate that thiolated As species play an important role in the cycling of As in mine waste systems and surrounding environments, and should be considered in mine waste management strategies for high-As sites.

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## 1. Introduction

Gigatons of mine wastes (waste rock, tailings) are produced annually by the global mining industry, and mismanagement of these materials can generate wastewater with high levels of toxic metal(loid)s and other contaminants that may negatively impact downstream environments (Jamieson, 2011; Blowes et al., 2014; Lindsay et al., 2015; Lèbre et al., 2017; Vriens et al., 2020). Arsenic is a widely known, redox-sensitive, solute of concern in mine waste systems across the world, due to its toxicity and elevated mobility under both acidic and neutral ambient conditions (Andrade et al., 2010; DeSisto, 2014; Filippi et al., 2015; Hiller et al., 2012; Larios et al., 2012; Vriens et al., 2019). Mobilization of As in mine wastes is caused by weathering of As-bearing minerals, commonly sulfide and oxide minerals, but As can also be sequestered through precipitation of secondary As-bearing minerals or adsorption of As to other secondary oxide minerals (Ahn et al., 2005; Andrade et al., 2010; Azcue and Nriagu, 1995; Dradrach et al., 2020; Foster et al., 1998; Kim et al., 2003; Langmuir et al., 1999; Meunier et al., 2010; You et al., 2024). The rates of these As-mineral dissolution-precipitation and their combined controls on leachate quality are highly site-specific and dependent on the prevailing modal mineralogy and geochemical conditions (Andrade et al., 2010; Craw and Bowell, 2014; Drahotka et al., 2016; Gault et al., 2005; Jamieson, 2011; Jamieson et al., 2015); predicting the mobility of As in mine waste systems on timescales of several decades and longer remains a persistent technical challenge (Blowes et al., 2014; St-Arnault et al., 2019; Vriens et al., 2020). To improve our understanding of the fate of As in mine wastes and assess its potential downstream environmental impacts, it is necessary to quantitatively and mechanistically understand the geochemical and mineralogical controls on As mobilization, especially at high-As sites.

Previous work on As in mine tailings and mining-impacted environments has shown that dissolved As occurs predominantly in oxyanionic form, either as fully oxidized arsenate (As[+5]) or reduced arsenite (As[+3]; Andrade et al., 2010; Azcue and Nriagu, 1995; Miller et al., 2019). Although arsenite tends to be more mobile than arsenate, both species can be mobilized from As-rich tailings and migrate into receiving downstream environments (Andrade et al., 2010; Bowell et al., 2014; Herrera et al., 2021; Moriarty et al., 2014). Arsenic also has a diverse organic biogeochemistry, including As-bearing metabolites and volatile methylated As species, that may occur in wide variety of mining-affected environments (Zhuang et al., 2023). However, dissolved As compounds other than arsenite and arsenate are not typically considered in assessments of As mobility in tailings and other mine waste systems (Liu et al., 2023). Our recent laboratory experiments have shown that aqueous thiolated As species [thio-As] may be produced from the weathering of As-sulfide minerals in mine waste rock (Ali et al., 2023). Such thiolated As species (arsinothioyl structures; As—S) have been previously found in other sub-oxic and reducing environments, including wetlands and hydrothermal vents (Guo et al., 2017; Herath et al., 2018; Planer-Friedrich et al., 2007; Suess et al., 2011, 2015). Various types of mine tailings and waste rock systems may be expected to harbor the same circumneutral-to-alkaline and sub-oxic conditions that are expected to promote the formation and occurrence of thio-As. Even though thio-As may occur in mine waste environments with lower relative abundances compared to other environmental systems, as evidenced by our previous experimental findings (Ali et al., 2023), thio-As species are important for As mobilization due to their lower propensity to adsorb to, or co-precipitate with, secondary minerals, in comparison to other oxyanionic As species (Herath et al., 2018; Plant et al., 2003; Suess and Planer-Friedrich, 2012). Thus, the occurrence of thio-As could be particularly problematic in high-As mine wastes and contribute significantly to As loads and mobilization into downstream environments.

Many high-As mine waste systems exist globally (e.g., sites in North America (Fawcett et al., 2015; Wang and Mulligan, 2006), Europe (Craw and Bowell, 2014; Camm et al., 2004) and South America (Ng et al.,

2019; Vriens et al., 2019)), but the formation mechanisms and distribution patterns of thio-As in these systems have received little to no attention. Thio-As production and stability appear influenced not only by the prevailing geochemical redox conditions, but also by the type of As-bearing sulfide minerals (e.g., arsenopyrite producing less thio-As than enargite), as well as the presence of other elements that can serve as oxidants (e.g., Fe) and mineral phases that can provide adsorption sites (e.g., Fe-(oxy)hydroxides; Ali et al., 2023). The role of thio-As compounds in governing As cycling in other environmental systems has been investigated (e.g., Guo et al., 2017; Herath et al., 2018; Planer-Friedrich et al., 2007; Wang et al., 2020), but to the best of our knowledge, there are no field studies on the formation and occurrence of thiolated-As in tailings materials. In particular, the source and fate of thiolated-As in the variable mineralogical and geochemical conditions encountered in legacy tailings facilities, especially those containing elevated levels of As and other metal(loid)s, remain to be determined.

To this end, we investigated the aqueous As speciation and mineralogical As hosts at five As-enriched legacy tailings deposits located in Cobalt, Ontario (ON), and Montague and Goldenville, Nova Scotia (NS). These high-As mine tailings sites constitute an ideal opportunity to study the occurrence and behaviour of thio-As across redox gradients in mine waste systems, as further discussed in the next section. We hypothesized that the elevated As contents of the tailings materials, circumneutral to alkaline pH, and ubiquitous reducing conditions in these systems allow for a significant abundance of thio-As. The main objectives of this work are to determine the abundance of inorganic thiolated As, and to assess the sources and mobility of dissolved As and (bio)geochemical conditions that affect the occurrence and mobility of thiolated As in mine waste tailings.

## 2. Study areas

A number of legacy tailings sites with high As and variable mineral As(—S) hosts that have been intensively studied previously were selected for this study (Fig. 1). The sites were located in Cobalt, Ontario (Cobalt Lake, Crosswise Lake, and LaRose pond) and Nova Scotia (Montague and Goldenville), all in Canada. A summary of site characteristics and previously reported geochemical data, including porewater compositions and tailings mineralogy, are provided in Tables S1–S5.

### 2.1. Cobalt, Ontario

The Cobalt-Coleman mining camp, located ~600 km north of Toronto, Canada (Fig. 1), was established in the early 1900s after the discovery of quartz-carbonate veins containing high-grade silver mineralization (Clarke, 2017; Kwong et al., 2007; Petruk et al., 1971; Turcotte, 2022). Two main periods of mining and near-site processing occurred until the 1980s; the generated tailings were disposed of into surrounding water bodies and low-lying land, and stored as submerged and exposed tailings (Turcotte, 2022). These largely un-remediated mine tailings contain environmentally harmful metal(loid)s, including As, Hg, and Co, that have contaminated surrounding water bodies, sediments, and vegetation (Chen et al., 2019; Kelly et al., 2007; Little et al., 2020; Turcotte, 2022). Previous studies conducted on the tailings in the Cobalt region reported bulk As and S concentrations of up to 1 and 3 wt-%, respectively (Table S3). These studies have also reported dissolved As and S concentrations of up to 325 and 2941 ppm, respectively, with a circumneutral-to-alkaline pH range (Table S1), and shown that As is predominantly hosted in erythrite-annabergite, cobaltite-gersdorffite, safflorite-skutterudite, arsenopyrite, and realgar (Table S5; Clarke, 2017; Turcotte, 2022).

In this work, we studied aqueous and solid (sediments, tailings) samples from locations in LaRose Pond (submerged tailings), Crosswise Lake, Cobalt Lake and LaRose tailings (surface-accessible tailings). These locations overlap with previous studies at these sites and were selected to capture the broad range of contrasting mineralogical and

geochemical conditions encountered around Cobalt (Fig. 1). Exact sampling locations (coordinates, dates, types of samples) are detailed in Tables S6, S7.

## 2.2. Montague and Goldenville, Nova Scotia

Historical gold (Au) mining activities in Nova Scotia date as far back as the mid-1800s and have resulted in multiple legacy mine waste sites across the province (DeSisto et al., 2017). Amongst these sites, the Montague and Goldenville tailings are known to contain particularly elevated As concentrations (DeSisto, 2014). Montague is a residential community ~20 km north of Halifax, Canada, and Goldenville is located about 140 km east of Halifax, Canada (Fig. 1). Gold production began in the 1860s and ended in the 1940s in both Montague and Goldenville (Bates, 1987; DeSisto, 2014). Tailings generated at these two sites were typically discharged into surrounding waterways, and led to abandoned sites that have contaminated nearby waters, soils, sediments, and biota (DeSisto, 2014; DeSisto et al., 2011; Parsons et al., 2012). Previous studies recorded bulk As levels up to 0.8 and 1.2 wt-% in Montague and Goldenville, respectively, as well as bulk S concentrations up to 0.7 and 1 wt-% in Montague and Goldenville, respectively (Table S4). Reported dissolved As concentrations in pore waters range up to 58 and 128 ppm in Montague and Goldenville, respectively, whereas dissolved S concentrations vary from up to 157 and 404 ppm in Montague and Goldenville, respectively, with predominantly circumneutral pH (Table S2). Previous studies at these sites have further shown that As is predominantly hosted in arsenopyrite, As-bearing pyrite, and As-bearing Fe (oxy)hydroxide minerals (Table S5; DeSisto, 2014).

As for the samples collected at Cobalt, we here studied aqueous and solid (sediments, tailings) samples from Montague and Goldenville at locations that were similar to those of the abovementioned studies (Fig. 1). Detailed sampling locations (coordinates, dates, sample types) are provided in Tables S6, S7.

## 3. Methods and materials

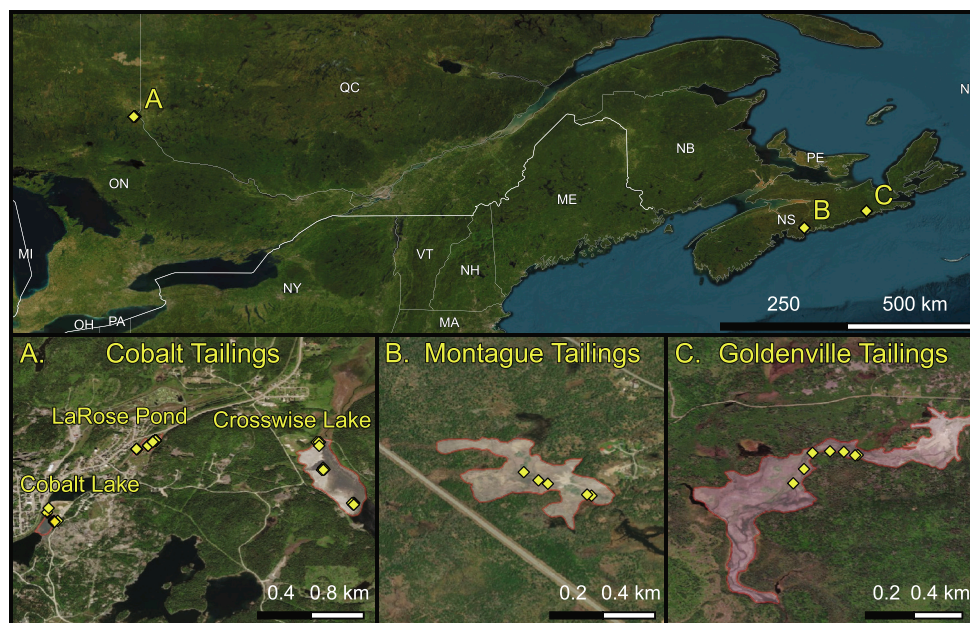
### 3.1. Sampling of tailings, porewaters, and surface waters

Field sampling was conducted in the fall of 2022 in both Cobalt, ON

and Nova Scotia. Sediments, tailings porewaters, and shallow as well as deeper overlying surface waters at the various sites were sampled depending on accessibility.

Surface-accessible tailings were collected at 15 sampling locations in Cobalt Lake, Crosswise Lake, LaRose Pond, Montague and Goldenville (locations detailed in Table S6) using augers and immediately transferred into argon (Ar)-purged Ziploc bags. A sediment core was collected as replicate at each of these sampling areas using a 60-cm length, 8-cm diameter polyvinyl chloride (PVC) push corer, immediately Ar-purged and capped, and stored inside an Ar-purged high-density polyethylene (HDPE) glovebag in the field. Submerged sediment cores were collected at 3 locations in LaRose Pond (Table S6) from a boat, using a submersible 60 cm length, 8 cm diameter Kajak-Brinkhurst gravity corer, and capped immediately. The submerged sediment cores were extruded (at every 10 cm per sediment core) into Ar-purged Ziploc bags within an Ar-purged HDPE glovebag after returning to shore. A replicate core was collected at each of the sampling areas in LaRose Pond, and the head-space filled with Ar, capped and stored in an Ar-purged HDPE glovebag. Before sampling, all coring materials were pre-rinsed with de-ionized (DI) water (18.2 MΩ, MilliPore Sigma). All sediment samples were stored in the dark at <4 °C both in the field and the laboratory until further analysis.

Tailing porewater samples from surface-accessible tailings (25 samples in total; see details in Table S7) were collected using pre-rinsed 1-m length suction lysimeters with a porous ceramic membrane cup (Irrrometer; vacuum at -70 to -80 centibars) at varying depths (0.4–0.95 m). Surrounding and overlying surface waters were collected as grab samples using pre-rinsed (DI water) 50 mL Falcon tubes, whereas overlying water columns (deeper waters) of submerged tailings were obtained using a horizontal acrylic Niskin-type water sampler (horizontal alpha water sampler, Cole-Parmer). Exact locations are detailed in Table S7. Duplicate aqueous samples were collected every third sample. Aliquots of all collected porewater, surface water, and deep-water samples were separated immediately in the field (see below). The following aqueous parameters were recorded on excess sample in the field: pH and conductivity (HANNA HI9813-6 multimeters), redox potential [ORP] (Milwaukee MW500 Portable ORP meters), dissolved oxygen [DO] and temperature (Extech DO-210 Dissolved Oxygen probes); all field probes were calibrated according to manufacturer's



**Fig. 1.** Locations of sampled legacy mine waste sites in Canada (top frame). Three legacy tailings locations were studied in depth: A) Cobalt, Ontario, including tailings at Cobalt Lake, LaRose Pond, and Crosswise Lake; B) Montague and C) Goldenville, Nova Scotia (lower frames), with sampled locations indicated by the diamonds in panels A, B, and C. Figure adopted from Silva et al. (2023b). Detailed sampling coordinates can be found in Table S6.



instructions at each sampling site.

### 3.2. Sample processing

Upon return to the laboratory, each 10 cm-section of the extruded sediments was transferred into 50 mL Falcon tubes inside an anaerobic chamber (Coy Laboratory Products, US) that was kept at <10 ppm oxygen and ~ 2 % H<sub>2</sub>, balance N<sub>2</sub> (AirLiquide, Canada). Sediments were then centrifuged at 8000 rpm for 5 min (Sorvall Legend X1; Thermo Scientific) and transferred back into the anaerobic chamber, in which porewaters from the submerged tailings were separated by decantation.

All aqueous samples were divided into the following three aliquots immediately upon collection in the field (surface, deep waters, and lysimeter-sampled porewater) or after processing in the laboratory (centrifugation of extruded core materials):

- One aliquot (15 mL) was filtered (0.25 µm PTFE membrane syringe filters, VWR, Canada), not acidified, and frozen in a portable freezer (−18 °C) in the field or flash frozen with liquid N<sub>2</sub> in the laboratory for the analysis of aqueous ferrous Fe, dissolved sulfate, carbonate alkalinity, and pH (for extruded porewater samples in the laboratory only), using spectrophotometry (Section 3.3.2);
- One aliquot (15 mL) was filtered as above but acidified to 1 % with concentrated ultrapure nitric acid (HNO<sub>3</sub>; 70 % Suprapur, Anachemia, Canada) for analysis of total dissolved elemental concentrations using inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Section 3.3.2); and,
- One aliquot (>5 mL) was filtered and not acidified and stored in 10 mL gas-tight glass screw-capped vials that were purged with Ar before shut and lined with an inert, PTFE-lined silicone septum (Thermo Scientific). To these samples, >50 µL (dependent on aliquot volume) of 99.5 % ethanol (analytical grade, Sigma Aldrich, Canada) and neutralized (NaOH-buffered) 0.5 M disodium ethylenediamine tetra-acetic acid solution (Na<sub>2</sub>-EDTA; 99.9 %, Sigma Aldrich, Canada), each, were added (protocol modified from Suess et al., 2011, 2015), after which they were subsequently frozen in a portable freezer in the field or flash-frozen in liquid N<sub>2</sub> in the laboratory, for the analysis of aqueous thiolated As species using high performance ion chromatography (HPIC) coupled to (triple-quad)- inductively coupled plasma-mass spectroscopy ((TQ)-ICP-MS) (Section 3.3.3).

All chemicals used were of ultrapure grade, and all vials and tubes were rinsed with ultrapure DI water before use. All vials and tubes used in a) and c) above were Ar-purged and capped after sampling. All aqueous samples were stored in the dark at −18 °C (when frozen or flash-frozen) or < 4 °C until analysis.

### 3.3. Geochemical analyses

#### 3.3.1. Mineralogy and bulk geochemistry

A portion of all tailings sediments were freeze-dried under vacuum for 72 h (−50 °C Freezezone, Labconco). Two grams of every dried tailings sample, each (25 samples, total) were molded into 2 cm epoxy mounts using EpoThin 2 resin and hardener (Buehler, US). Epoxy mounts were carbon-coated on the exposed surface prior to analysis. The bulk modal mineralogy and grain size of the sediment samples, as well as elemental As and S apportionment, were analyzed using a field-emission gun scanning electron microscope (SEM) (FEI, now ThermoFisher, Quanta 650) equipped with the Mineral Liberation Analysis (MLA) software (version 3.1.4.686) to characterize the particles via backscatter electron (BSE) image analysis and energy-dispersive X-ray spectroscopy (EDS). Additional details of these mineralogical analyses are provided in the Supporting Information (Methods S1). Mineral identification was based on the default FEI library, a library for As-phases (Schuh et al., 2018), and a site-specific (Cobalt, ON) library (Turcotte, 2022). Additionally, 5 g of each of the dried sediments were pulverized using a pestle and

mortar, and then dispensed into 2 cm LDPE cups and covered with Kapton tape, for analysis of bulk elemental composition using X-ray fluorescence (XRF) (Handheld XRF Tracer 5, Bruker), which was calibrated to a quantitative scanning mode with a collection time of 90 s and operated according to manufacturer instructions.

#### 3.3.2. Total dissolved concentrations

Total dissolved concentrations of As, S, Fe, and other elements in aqueous samples were measured on an ICP-OES (iCAP Pro XPS, Thermo Scientific). Internal and commercial external certified reference materials (EU-H and NIST1643f), replicates and blanks were measured every  $n = 10$  samples to determine accuracy and reproducibility. The concentrations of dissolved sulfate (SO<sub>4</sub>), ferrous Fe (Fe[+2]), and carbonate alkalinity, as well as pH (for extruded porewater samples in the laboratory) were measured on an automated photospectrometer (Gallery Discrete Analyzer, Thermo Scientific), using supplier reagents and according to manufacturer specifications. Detection limits and recovery of certified reference materials are provided in Table S8.

#### 3.3.3. Aqueous As speciation

Dissolved inorganic and thiolated As species were quantified by HPIC-(TQ)-ICP-MS, according to the methodology described in Ali et al. (2023), modified after Planer-Friedrich et al. (2007). In brief, chromatographic separation of dissolved As species was performed on an IonPac AS-18 anion exchange column using a Dionex Integron HPIC (Thermo Scientific) equipped with a column thermostat, electrolytic suppressor, and automated eluent generator. The HPIC was hyphenated to a (TQ)-ICP-MS, either an Agilent 8800 at the Trent University Water Research Center, or Perkin-Elmer NexION 300D at the Royal Military College of Canada. For this, eluent from the HPIC was routed into a 1/16" PEEK T-split and then led through PEEK tubing towards a 2 mL PFA micro-nebulizer on the TQ-ICP-MS. The ICP-MS was tuned for elements at low (<20 amu) and mid-mass (89–115 amu) using a 1 mM Li and Se solution, as well as for low oxide formation, at the appropriate flow rate when hyphenated. Chromatograms of the standards and samples were processed using OriginPro (OriginLab software) for blank subtraction and peak integration.

Aqueous samples and calibration standards were thawed in an anaerobic chamber (Coy Laboratory Products, US, <10 ppm oxygen and ~ 2 % H<sub>2</sub>, balance N<sub>2</sub> (AirLiquide, Canada)) immediately prior to speciation analysis. Instead of synthesizing methylated thio-As standards (Lee et al., 2018; Yan et al., 2022) because only standards for monomethylated oxyarsenate and dimethylated oxyarsenate are commercially available, methylated thio-As species were identified by comparison of their relative retention factors to those derived by Wall-schläger and London (2008) and Wang et al. (2023), and quantified using inorganic thio-As calibration standards. Detection limits and compound retention factors are provided in Tables S8 and S9, respectively. Total dissolved As concentrations measured by ICP-OES aligned with the sum of concentrations of the individual species measured by HPIC-(TQ)-ICP-MS ( $R^2 = 0.8$ ; Fig. S1). Additional instrumental settings, standard synthesis, and analytical figures of merit are provided in Ali et al. (2023).

## 4. Results and discussion

### 4.1. General tailings mineralogy and geochemistry

The modal mineralogy and bulk elemental compositions of our studied tailings are detailed in Table S11 and S12, respectively; a selection of relevant elements and their bulk composition, and qualitative bulk mineralogy are summarized in Table 1. Bulk As contents ranged between 0.02 and 1.12 wt-% for Cobalt, 0.26–0.45 wt-% for Goldenville, and 0.08–0.48 wt-% for Montague. Bulk S contents were generally higher than those of As across the studied tailings (Cobalt: 0.16–2.36 wt-%; Goldenville: 0.45–1.05 wt-%; Montague: 0.18–0.71 wt-%);

additionally the bulk Fe contents were 2 to 6 times higher than those of both As and S (Table 1).

The main As-S-bearing minerals observed in the Cobalt tailings were broadly classified as Co–Ni arsenosulfides such as cobaltite-gersdorffite [CoAsS–NiAsS], as well as Co–Ni arsenates such as annabergite-erythrite [Co<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O–Ni<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O] and Ca- and Fe-arsenates such as yukonite [Ca<sub>3</sub>Fe(AsO<sub>4</sub>)<sub>2</sub>(OH)<sub>3</sub>·5H<sub>2</sub>O] and scorodite [FeAsO<sub>4</sub>·2H<sub>2</sub>O] (Table S13). In contrast, arsenopyrite [FeAsS] and As-bearing pyrite [As·FeS<sub>2</sub>] were most abundant in the Nova Scotia tailings (Table S14). Non-As-bearing sulfides, including pyrite, chalcopyrite, and pyrrhotite, were also observed in the tailings from both Cobalt and Nova Scotia. The modal mineralogy of the studied tailings showed that carbonate content (Cobalt: 5.5–9.1 wt-%; Nova Scotia: 0.8–1.1 wt-%) was higher than sulfide content (Cobalt: 1.9–2.6 wt-%; Nova Scotia: 0.3–0.4 wt-%), which is consistent with the circumneutral pH observed in the tailings-impacted surface water and porewater samples (see below).

The bulk As and S contents of the tailings were in a similar range to those observed in previous studies at these sites, i.e., differences were not statistically significant between our and previous studies ( $p > 0.3$  for As,  $p > 0.06$  for S); also compare Tables 1 and S12 with data obtained in previous studies in (Tables S3, S4), even though differences in bulk Fe content were statistically significant ( $p < 0.01$ ). The As-bearing mineralogy determined in previous studies (Table S5) is also similar to the mineralogy of our samples (Tables S13, S14), except for arsenopyrite in the Cobalt tailings by Turcotte (2022), and scorodite in the Montague tailings by DeSisto (2014), both of which were not detected in our Cobalt

and Montague tailings samples, respectively.

Total dissolved concentrations of some elements (As, S, and Fe), pH, redox potential (Eh), and other aqueous parameters are summarized in Table 1. Aqueous samples (surface waters, deeper overlying waters, and porewaters) at all sites were circumneutral to alkaline: pH = 6–9 (Cobalt), 6–8 (Montague), and 6–7 (Goldenville) (Table S7). Porewater and deeper overlying waters (5–10 m depth) were relatively sub-oxic with dissolved oxygen (DO; % relative to atmospheric) ranging from 4.1 to 10.9 % and 6.4–12.2 % for Cobalt and Nova Scotia, respectively, in contrast to more oxygenated surface waters with higher DO (14.1–19.8 %). Measured DO in the aqueous samples generally increased with increasing measured redox potential (Fig. S2A), but no trend was observed between pH and alkalinity (Fig. S2B).

The surface, deep, and porewaters across the studied sites in Cobalt and Nova Scotia exhibited variable concentrations of dissolved As, S, and Fe (Table S15). Overall, total dissolved As concentrations were higher in Cobalt (LaRose Pond: 2.3–60.0 mg/L; Cobalt Lake: 0.8–5.5 mg/L; Crosswise Lake: 0.9–94.0 mg/L) than at the Nova Scotia sites (Montague: 0.3–3.2 mg/L; Goldenville: 0.1–17.0 mg/L), across all aqueous sample types, and the same was true for total dissolved S and Fe levels, with higher concentrations at Cobalt (0.4–190 mg/L and 0.004–9.1 mg/L total S and Fe, respectively) compared to the Nova Scotia sites (0.2–4.8 mg/L and 0.1–9 mg/L total S and Fe, respectively). This difference between the Cobalt and Nova Scotia sites is likely explained by the different site mineralogies (see below), and did not appear to relate to particle size: Cobalt tailings generally had slightly coarser grain sizes (30  $\mu\text{m} > d_{50} > 60 \mu\text{m}$ ) than the Nova Scotia tailings

**Table 1**  
Summary of the geochemical and mineralogical composition of tailings measured in this work.

Sampling area	LaRose Pond, Cobalt ON	Cobalt Lake, Cobalt ON	Crosswise Lake, Cobalt, ON	Montague, Nova Scotia	Goldenville, Nova Scotia
<b>Bulk content [wt%]</b>					
As	0.08–1.12	0.11	0.02–0.14	0.08–0.48	0.26–0.45
S	0.16–2.36	0.23	0.19–2.27	0.18–0.71	0.45–1.05
Fe	6.05–9.64	5.21	4.86–7.84	3.36–4.73	2.59–3.54
<b>Mineralogy [wt%]</b>					
Silicates	0.5–44.5	–	3.5–27.8	92.7	90–93.6
Sulfides	1.6–2.3	–	1.8–3.5	5.9	5.3–7.5
Carbonate	3.7–8.4	–	8.6–9.6	0.8	0.0–2.2
Oxides	0.0–1.8	–	1.4–1.6	0.2	0.1–0.6
<b>Aqueous parameters</b>					
pH	6–8	7–8	7–9	6–8	6–7
Eh [V]	–0.1 to 0.5	0.1 to 0.3	0.04 to 0.4	0.1 to 0.2	0.05 to 0.3
DO [%]	4.1–17.6	9.8–17.9	6.9–19.8	6.5–16	6.4–17.0
Alkalinity [mg/L]	61–267	68–191	43–287	78–315	6.0–186
Total As [mg/L]	2.3–60	0.8–5.5	0.9–94	0.3–3.2	0.1–17.0
Total S [mg/L]	0.8–190	0.4–3.3	1.0–7.7	0.8–4.8	0.2–1.8
Total Fe [mg/L]	0.05–9.1	0.05–1.1	0.05–3.1	0.1–9.0	0.3–3.9
<b>Qualitative Bulk Mineralogy<sup>a</sup></b>					
As-bearing minerals	<b><i>Cobaltite-gersdorffite</i></b> , realgar, <b><i>erythrite-annabergite</i></b> , <b><i>yukonite</i></b> , P-bearing Ca–Fe arsenates, Fe–As oxides	N/D <sup>b</sup>	<b><i>Cobaltite-Gersdorffite</i></b> , <b><i>erythrite-annabergite</i></b> , <b><i>yukonite</i></b> , P-bearing Ca–Fe arsenates, Fe–As oxides	<b><i>Arsenopyrite</i></b> , <b><i>As-bearing pyrite</i></b> , realgar, cobaltite-gersdorffite	<b><i>Arsenopyrite</i></b> , <b><i>As-bearing pyrite</i></b> , realgar, Fe–As oxides, cobaltite-gersdorffite
Other minerals (wt > 0.1 %)	Calcite, dolomite, apatite, actinolite, hornblende, tremolite, biotite, clay minerals, epidote, spessartine, plagioclase, titanite, chalcopyrite, pyrite, mixed clay+pyrite	N/D <sup>b</sup>	Calcite, dolomite, apatite, actinolite, tremolite, biotite, chlorite, clay minerals, epidote, spessartine, chalcopyrite, pyrite, mixed clay+pyrite	Ankerite, dolomite, rutile, apatite, orthoclase, hornblende, tremolite, biotite, chlorite, clay minerals, albite, enstatite, quartz, chalcopyrite, pyrite, pyrrhotite, mixed clay+pyrite	Ankerite, calcite, dolomite, ilmenite, apatite, orthoclase, hornblende, tremolite, biotite, chlorite, clay minerals, epidote, albite, enstatite, quartz, chalcopyrite, pyrite, pyrrhotite, mixed clay+pyrite

<sup>a</sup> The complete modal mineralogy and As and S apportionment are provided in Table S11 and Tables S13, S14.

<sup>b</sup> N/D-No data; main As-bearing minerals are bolded and italicized.

( $d_{50} < 25 \mu\text{m}$ ) (Fig. S3). Amongst the Cobalt tailings materials, concentration ranges of total dissolved S and Fe for LaRose Pond were 2 to 10 times higher than those in Cobalt Lake and Crosswise Lake tailings; however, Crosswise Lake tailings exhibited the highest total As ranges. Across the Nova Scotia tailings, the dissolved concentration ranges of As, S, and Fe were reasonably similar. Total dissolved concentrations of As, S, and Fe in all aqueous tailings samples were further similar to those observed in earlier studies at these sites (not significantly different with  $p > 0.1$ ), implying long-term consistency in these tailings' porewater hydrochemistry, as well as minimal adsorption to the deployed lysimeter cups (Wenzel et al., 1997). Although the collected samples thus appear representative for the various sites, the comparatively small number of samples within each tailings site, particularly Cobalt Lake ( $n = 3$ ) and Crosswise Lake ( $n = 5$ ), could be increased to further characterize the potential heterogeneity at these sites.

The relative dissolved concentrations (As, S, and Fe) of the aqueous samples (surface waters, deeper overlying waters, and porewaters) generally did not correlate with their respective bulk elemental abundances; a lack of correspondence was particularly prevalent for Fe (highest element abundance, but lowest total dissolved concentrations; Tables S12 and S15). Geochemical processes, including precipitation into secondary mineral phases or adsorption of these elements (As, S, and Fe), may have contributed to the disconnect between the bulk contents and dissolved concentrations under the variable redox conditions observed (Pal, 2015; Scholz, 2006; Suess et al., 2011). The weathering rates of minerals can also be a determining factor in the

availability of elements in solution; for instance, sulfide minerals (Fe-rich sphalerite and pyrite) under a similar pH range = 6–9, have been observed to have lower oxidative dissolution rates under sub-oxic conditions than under oxic conditions (Silva et al., 2023a). Thus, bulk As content is not the sole factor controlling dissolved As concentrations, which also depends on the prevalent in-situ geochemical and redox conditions in these systems (Andrade et al., 2010; Miller et al., 2019; Vriens et al., 2019).

Overall, the studied legacy tailings deposits in Cobalt were variable in composition and exhibited a wide range of As-bearing minerals and geochemical conditions, with significantly different bulk and dissolved elemental concentrations and mineralogies than those at the Nova Scotia sites. Although elevated tailings As contents are identified as an important source of As to porewaters and receiving waters, additional mineralogical composition and hydrochemical factors (pH, redox, availability of ligands) also affected the occurrence of As at all sites.

#### 4.2. Presence of thiolated As species in aqueous tailings samples

Aqueous As speciation analysis of the tailings porewater and surface/overlying waters showed a wide distribution of dissolved As species (Fig. 2); concentrations and relative abundances of aqueous As species in the tailings samples are detailed in Table S10. Oxyanionic arsenite and arsenate were the dominant As species observed at all sites. However, thiolated As species were also observed, at up to 17 % relative abundance. Monothioarsenate was the most prevalent thio-As species, but

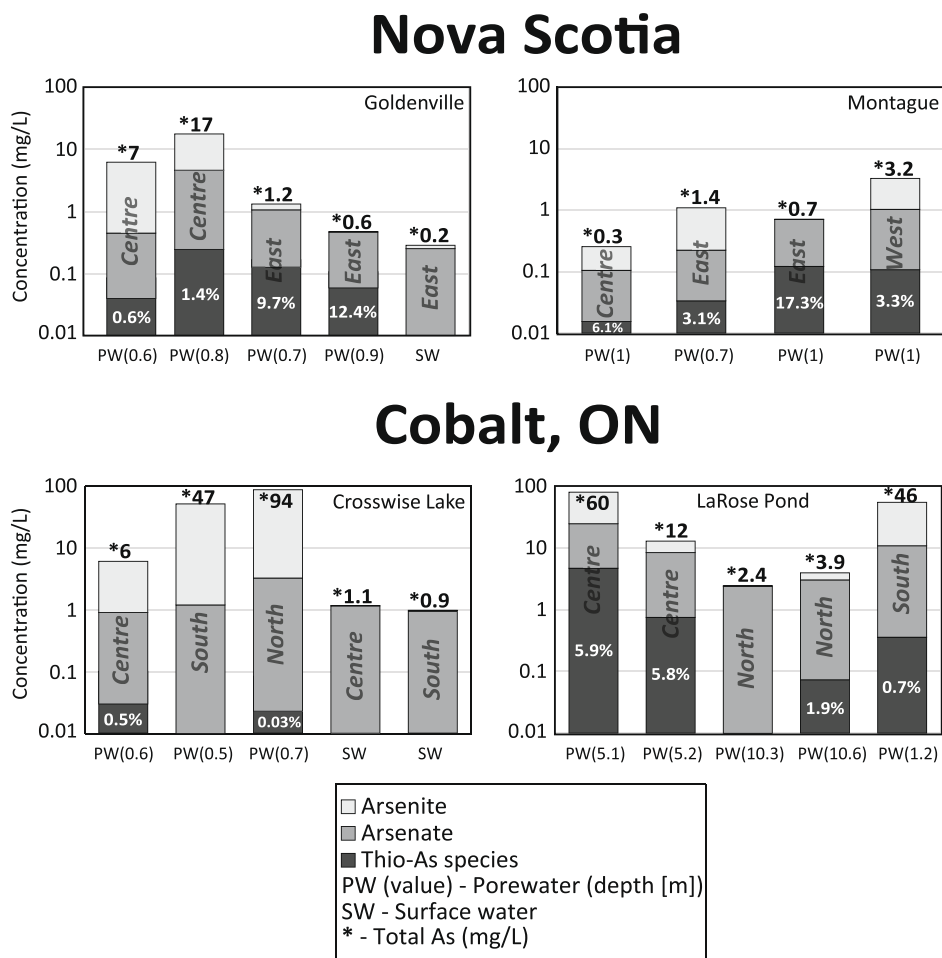


Fig. 2. Concentrations and distributions of dissolved As species measured in select tailings samples from legacy mine sites in Nova Scotia and Cobalt, Canada. The concentrations of different species are stacked in the bar charts on logarithmic y-axes. Some samples had measured thio-As concentrations of  $< 0.01 \text{ mg/L}$ ; see full data in Table S10.

higher degrees of thiolation (i.e., di- and tri-thioarsenate) were observed and their concentration reach up to several ppb in solution for the most As-rich waters analyzed (Table S10). Methylated species (dimethylated dithioarsenate, monomethylated oxyarsenate, and monomethylated dithioarsenate) were identified as well (Fig. S4). All quantifiable thio-As species were more abundant in the (sub-oxic) porewater samples than in the more oxic surface and overlying water column samples. Higher concentrations of thio-As were generally observed in the Cobalt samples (up to 4.7 mg/L) compared to the Nova Scotia samples (up to 0.24 mg/L), as was the case for total dissolved As levels, which were equally higher, on average, at the Cobalt samples (up to 94 mg/L) compared to the Nova Scotia samples (up to 17 mg/L) (Table S15). Interestingly however, the relative abundance of thio-As was generally higher in the Nova Scotia samples (up to 17.3 %; average: 5 %) than in the Cobalt samples (up to 5.9 %, average: 0.6 %) (Fig. S5C), despite those sites having lower total dissolved As.

Thio-As concentrations and relative abundances varied across the different sites at Cobalt: LaRose Pond samples (submerged tailings) showed higher concentrations and relative abundances of thio-As (up to 4.7 mg/L and 5.9 %, respectively) than the Crosswise Lake and Cobalt Lake tailings (exposed tailings; concentration up to 0.03 mg/L and relative abundances <0.5 %). The thio-As concentrations of exposed tailings from Montague and Goldenville in Nova Scotia were up to 0.11 and 0.24 mg/L, respectively, and their relative abundances were up to 17.3 and 12.4 % of total dissolved As, respectively. In Cobalt, samples with higher total dissolved S concentrations generally exhibited higher abundance of thio-As, but this trend was not apparent in the Nova Scotia samples (Fig. S5A and S5B), likely attributable to a narrower range of dissolved S (0.1–4.79 mg/L) in the Nova Scotia samples (Table S15). The bulk dissolved S/As ratios of the studied tailings did not correlate to the overall relative abundance of thio-As (Fig. S5D).

Thio-As abundances observed in the tailings sites (up to 17.3 %) were higher than abundances found in previous laboratory studies with mine waste rock (up to 5 %) (Ali et al., 2023), but lower than other environments, such as hydrothermal vents (up to 83 %) and wetland porewaters (up to 50 %; Herath et al., 2018; Planer-Friedrich et al., 2007; Suess et al., 2011, 2015). The abundance of thio-As in the studied tailings being not as high as in other systems may be explained by the fact that the hydrothermal vents are more alkaline and sulfidic, and just like wetlands with higher organic carbon, are therefore likely more reducing than the (low organic carbon) mine tailings systems studied here. Additionally, mineral mine wastes tend to have higher Fe and can contain pre-oxidized minerals even in their sub-oxic regions arising from the continual deposition of tailings, leading to a lesser abundance of reduced S and/or As to form thio-As species.

Overall, these results show that in the studied tailings systems, thio-As is present at significant concentrations (even above permissible surface water limits in a few instances) as well as with significant relative abundances, but also that its occurrence varies considerably across the prevailing geochemical conditions.

#### 4.3. Controls of geochemical redox conditions on As dynamics

Select correlations between redox potential, total dissolved concentrations of As, Fe, and S, and the abundance of aqueous thio-As species of the tailings sites are provided in Fig. 3; additional plots are provided in Figs. S5 and S6. The total dissolved concentration ratio of As[+5]/As[+3] generally increased with increasing redox potential (Eh) across all the aqueous samples: higher ratios generally corresponded to higher redox potential values, indicating a higher concentration of dissolved arsenate (As[+5]) as compared to arsenite (As[+3]) under oxidizing conditions. As expected, surface water and upper overlying water (<5 m) samples predominantly showed higher As[+5]/As[+3] values and redox potential (higher arsenate concentrations) in comparison to the porewaters and deeper ( $\geq 5$  m) waters, which are more reducing (Fig. S7).

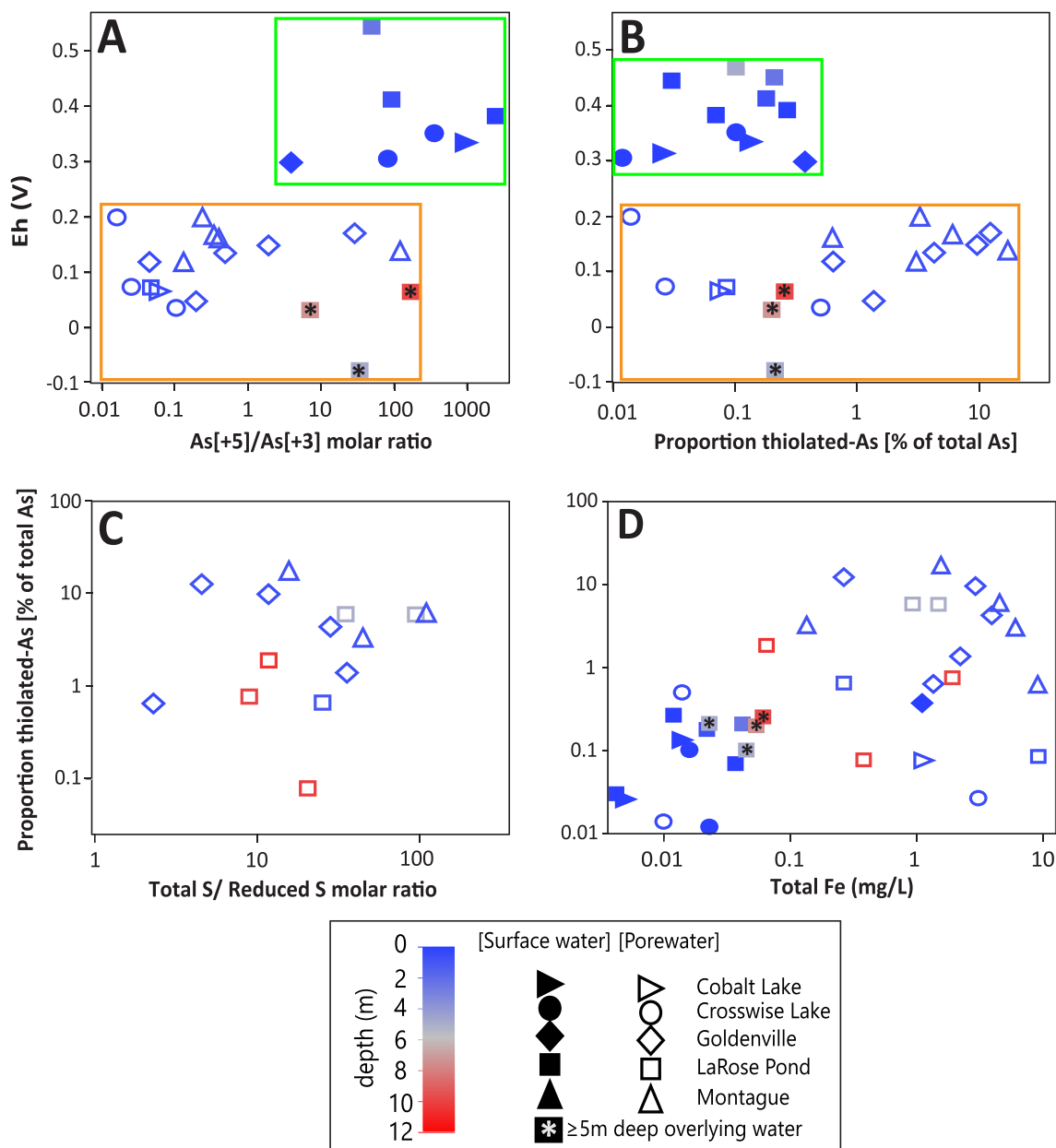
Lower thiolated As abundance was observed with higher redox potential, in that the surface water samples and upper overlying water samples showed higher redox potential (oxidizing conditions) and lower thio-As (Fig. 3B). In contrast, porewater and deeper overlying water samples showed lower redox potential (more reducing conditions), and significantly higher abundance of thio-As species, especially in the sub-oxic porewater samples (Fig. 3B). This indicates that thio-As species are generally more prevalent under sub-oxic to reducing conditions at the studied tailings sites, as has been observed or suggested in other systems (Guo et al., 2017; Herath et al., 2018; Planer-Friedrich et al., 2007; Suess et al., 2015).

Sulfur speciation can influence the occurrence of thio-As species because reduced S species may mediate As thiolation in solution (Herath et al., 2018; Wang et al., 2018). Samples from Silva et al. (2023b) and samples in this study were taken at the same time and location, and intermediate, incompletely oxidized S concentrations were derived from Silva et al. (2023b) by taking the difference between sulfate and the summation of the incompletely oxidized S species sulfite, thiosulfate, and tetrathionate (i.e., the proportion of reduced S within total S). Interestingly, no trend was observed between the relative abundance of thio-As and the proportion of intermediate S (Fig. 3C), not between redox potential and the proportion of intermediate S (Fig. S6A). This lack of correlation may suggest that S speciation data may not be reflective of the in-situ redox conditions in the field, either because of the kinetic stability of intermediate S species (Silva et al., 2023b) or insufficient spatial resolution across the studied redox gradients.

Dissolved Fe can potentially de-thiolate and oxidize thio-As species (Herath et al., 2018; Suess et al., 2011, 2015). However, a comparison between the relative abundance of thio-As and total dissolved Fe shows that porewater samples generally had higher total dissolved Fe compared to surface- and shallow overlying waters (Fig. 3D). A scatterplot of redox potential versus dissolved Fe[+3] concentrations (with no dependency on pH because all studied aqueous samples were within the circumneutral pH range; Fig. S2B) showed that the sub-oxic to reducing porewater samples generally had higher dissolved total Fe and Fe[+3] concentrations than the oxidizing surface- and overlying waters (Fig. S6B), possibly resulting from the precipitation of Fe[+3] under oxidizing conditions (Pal, 2015; Scholz, 2006; Suess et al., 2011). Consequently, no significant anticorrelation between dissolved Fe concentrations and the prevalence of thio-As could be established.

Methylated As species (as well as inorganic As with higher degrees of thiolation) were observed across all the five tailings sites in Cobalt and Nova Scotia (Table S10). These methylated species were observed in all but one sampling point in Nova Scotia, and were higher in abundance in Nova Scotia sites (averaging 2.7 % of total As) compared to Cobalt (averaging 0.1 % of total As) (Table S16). Biofilms were observed on nearby surface waters in Goldenville, as well as ebullition within shallow surface and porewaters in Montague (Table S7). DeSisto (2014) also reported As(–S)-bearing minerals co-existing with organic matter-rich layers within tailings from Montague and Goldenville. The organic-rich layers in LaRose Pond in Cobalt (Turcotte, 2022), exhibited the highest concentrations and abundances of methylated thio-As species, and higher degrees of inorganic As thiolation, in Cobalt. This may indicate that organic matter influences the production and persistence of methylated thio-As in mine waste systems, as has been suggested for aquifer systems (Kumar et al., 2020a, 2020b). Our observations suggest that the presence of organic matter may have influenced the occurrence and stability of methylated and (thio-)As species entirely, consistent with observations in previous work (Chen and Rosen, 2020; Di et al., 2019; Wang et al., 2023).

Ultimately, the occurrence and prevalence of thio-As species, as well as the dynamics of As-speciation in general, appear significantly influenced by the redox potentials and hydrogeochemical conditions prevailing at the investigated mine tailings sites.



**Fig. 3.** a) redox potential versus total dissolved As[+5]/As[+3] ratios and versus b) percentage thiolated As, as well as correlations between the relative abundance of thiolated As species c) total dissolved total S/intermediate S ratios, and versus d) total dissolved Fe concentrations. Scatterplots contain select aqueous tailings samples only (legend at bottom applies to all frames). Additional parameters are provided in Fig. S2 and S6. Green and orange boxes in panels a and b represent surface water and upper overlying water (<5 m), and porewaters and deeper ( $\geq 5$  m) waters, respectively.

#### 4.4. Arsenic mobilization in relation to bulk composition and mineralogy

Bulk elemental compositions and As-apportionments of the studied tailings are detailed in Tables S12-S14. Arsenic deportment across the minerals in Cobalt tailings was generally characterized by As being hosted in arsenate minerals (erythrite-annabergite, Ca-Fe arsenates), yukonite, and, to a lesser extent, in As-bearing sulfide minerals (cobaltite-gersdorffite). Arsenic in the Nova Scotia tailings was predominantly hosted in sulfide minerals such as arsenopyrite or As-bearing pyrite and realgar. Cobaltite-gersdorffite, realgar, and Fe-As oxides were observed in both the Cobalt and Nova Scotia tailings. However, cobaltite-gersdorffite and Fe-As oxides were more abundant in the Cobalt tailings, whereas realgar was more abundant in the Nova Scotia tailings.

Tailings in this study with the most As-bearing sulfide minerals

(Nova Scotia), but not total bulk As levels, had higher percentages of thio-As species. The weathering and dissolution of As-bearing sulfide minerals under reducing conditions and circumneutral to alkaline pH is expected to produce thio-As species more effectively than that of other As mineral groups (Herath et al., 2018; Kumar et al., 2020a, 2020b; Planer-Friedrich et al., 2007, 2020; Suess and Planer-Friedrich, 2012). Amongst As-bearing sulfide minerals, previous studies have shown that thio-As production is higher in arsenosulfide minerals (realgar, orpiment, enargite) than in arsenopyrite or As-bearing pyrite, in part because of the higher relative abundance of As-S bonds in their respective crystal lattices (Ali et al., 2023; Suess and Planer-Friedrich, 2012). Namely, enargite-rich samples with low bulk As levels exhibited higher production of thio-As during leaching in comparison to arsenopyrite-rich samples with high bulk As (Ali et al., 2023). However, our results show that the presence of arsenosulfides does not necessarily



produce larger amounts thio-As than arsenopyrite (i.e., arsenopyrite dominant Nova scotia samples exhibited higher thio-As abundances; Table S10). Circumneutral to alkaline dissolution of arsenopyrite concurrently induces Fe-(oxy)hydroxide precipitation, which provides re-sorption sites for the newly formed thio-As species from arsenopyrite (Herath et al., 2018; Wang et al., 2018). Adsorption experiments with Fe-(oxy)hydroxide mineral phases show that adsorption rates are slower with thio-As species in comparison to arsenite and arsenate (Suess and Planer-Friedrich, 2012), thus providing a mechanism for enhanced thio-As occurrence even in arsenopyrite-rich systems. The exact controls of the individual As(-S) bearing minerals on the production and abundance of thiolated As remain to challenging to constrain, especially in heterogenous mine waste systems such as the tailings studied here, where arsenosulfide minerals and arsenopyrite, as well as other sulfide and As minerals co-exist together. Nevertheless, mineralogical analyses show that the variable mineralogical sources of As amongst the tailings sites in this study contribute to variable yet significant thio-As abundances, and total As concentrations as a whole, in such composite systems.

## 5. Conclusions

We studied the occurrence of aqueous thiolated As species at As-rich legacy mine tailings sites with contrasting mineralogical As(-S) sources in Cobalt, Ontario, and Nova Scotia, both Canada. Our results reveal that dissolved thiolated As is ubiquitous across these legacy tailings systems, present mostly in the form of monothioarsenate, some higher thiolated species (i.e., di- and tri-thioarsenates) as well as thiolated methylated As species. Higher thio-As abundances were observed in the Nova Scotia tailings where As was hosted in As-sulfide minerals (arsenopyrite, As-bearing pyrite, and realgar) than in the Cobalt tailings where As was contained in oxidized arsenate phases such as erythrite-annabergite or yukonite and to a lesser extent in As-sulfide minerals like cobaltite/gersdorffite. Thio-As species were more abundant in sub-oxic porewaters than in overlying water columns and surface waters across the studied sites, and their relative abundance generally decoupled from total As levels, but strongly related to the prevailing redox conditions. These findings largely validate our initial hypotheses and align with our previous laboratory investigations regarding the occurrence of thio-As in mine waste systems (Ali et al., 2023). Further study is required to understand the exact kinetic stability and transformation pathways of individual thio-As species in solution, as a function of geochemical and redox conditions, as well as the controls of microbial activity and organic matter on thio-As species, including in mine waste systems.

Overall, this study demonstrates for the first time that thiolated As (which exhibits a lower propensity to adsorb to, or co-precipitate with, secondary minerals than fully oxidized oxyanionic As) can occur across tailings systems that exhibit widely different mineralogical compositions and geochemical conditions, even at concentrations well-above permissible total-As water quality guidelines. Measurement of thiolated species of As, as well as of other elements that are prone to thiolation (e.g., selenium, antimony, molybdenum, tungsten), should be considered in mine wastewater management and monitoring programs, particularly in high-As environments. On a broader scale, this study contributes to the expanding body of evidence supporting the presence of thio-As species in a wide range of natural and engineered environments.

## CRedit authorship contribution statement

**Jaabir D. Ali:** Writing – original draft, Visualization, Validation, Resources, Methodology, Investigation, Formal analysis, Data curation. **Adriana Guatame-Garcia:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Heather E. Jamieson:** Writing – review & editing, Resources, Methodology. **Michael B. Parsons:** Writing – review & editing, Resources, Methodology, Investigation,

Conceptualization. **Matthew I. Leybourne:** Writing – review & editing, Methodology, Investigation, Data curation. **Iris Koch:** Writing – review & editing, Validation, Investigation, Formal analysis. **Kela P. Weber:** Writing – review & editing, Validation, Investigation, Data curation. **David J. Patch:** Writing – review & editing, Methodology, Investigation. **Anna L. Harrison:** Writing – review & editing, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis. **Bas Vriens:** Writing – original draft, Supervision, Project administration, Investigation, Funding acquisition.

## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Bas Vriens reports financial support was provided by Natural Sciences and Engineering Research Council of Canada. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supporting information (Supporting Methods S1, Figs. S1–S7, and Tables S1–S16) contains additional methodological details and quality assurance data, additional details of the investigated materials, and additional hydrogeochemical and mineralogical results and interpretations. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.172596>.

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