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The characterization, mobility, and persistence of roaster-derived arsenic in soils at Giant Mine, NWT

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ABSTRACT

Approximately 20,000 tonnes of arsenic (As)-bearing emissions from roasting gold (Au)-bearing arsenopyrite ore were aerially released from 1949 to 1999 at Giant Mine, near Yellowknife, Canada. Soil samples collected within 4 km of the former roaster from sites undisturbed by mining or other human activity contain up to 7700 mg/kg total As. Total As concentrations are highest within a few cm of the surface, and particularly enriched in soil pockets on rock outcrops. Scanning electron microscopy and synchrotron microanalysis show that roaster-derived arsenic trioxide (As_2O_3) has persisted in shallow soils in the area. Roaster-generated maghemite and hematite are also present. These anthropogenic forms of As are much more common in near-surface soils than natural As-bearing minerals. Comparison of the proportions of As, Sb, and Au concentrations in outcrop soil samples and historic As_2O_3-rich dust captured by emission controls suggest most of the roaster-derived As in soils at Giant was likely deposited before 1964. Topographic restriction by rock outcrops and a dry, cold climate likely contribute to the persistence of As_2O_3 in outcrop soils.

Limited post-depositional mobility of roaster-generated As is evident from textural relationships in thin section, the presence of As in weathering products, the variation of As:Sb with depth, and the elevated As concentrations in soil pore waters sampled by suction lysimeters. Synthetic gastric and lung fluids extracted an average of 34% and 18% of the total As in three adjacent soil samples. Given that As_2O_3 is one of the most toxic and bioaccessible forms of As, the persistence of roaster-generated As in shallow soils may be a human health risk at this site.

1. Introduction

1.1. Site background

The quartz-carbonate vein- and brittle-ductile shear zone-hosted gold (Au) deposit at Giant Mine is located in the Kam Group of the Archaean-age Yellowknife Greenstone Belt (Canam, 2006). Most Au in the Giant deposit is considered refractory, mainly hosted within the crystal structure of arsenopyrite (FeAsS) and to a lesser degree arsenian pyrite (FeS_2). Roasting of iron (Fe)-sulfide-rich floatation concentrate at approximately 500 °C oxidized the Fe-sulfides to nanocrystalline, micro-porous Fe-oxides, principally maghemite and hematite. The porosity of these roaster-derived Fe-oxides exposed refractory Au to subsequent cyanide leaching (Fawcett and Jamieson, 2011; INAC, 2007; Jamiesion, 2014; Walker et al., 2005, 2015; Wrye, 2008). Roasting of arsenopyrite also produces SO_2 emissions and As-rich vapors that precipitate as arsenic trioxide (As_2O_3)-rich dust from the oxidation of As(-I) to As(III):

$$2FeAsS + 5O_2 = Fe_2O_3 + As_2O_3 + 2SO_2 \quad (1)$$

After three years of uncontrolled roaster emissions at Giant (1949–1951), concerns for worker health and the accidental poisoning deaths of several local children spurred the development of As emissions controls and later efficiency increases (Hutchinson et al., 1982; Sandlos and Keeling, 2012; Sinclair, 1951; Walker et al., 2005). The first generation of As_2O_3 capturing technology, an electrostatic precipitator (ESP), was implemented in 1952 (Walker et al., 2015). Other technological advances in roaster efficiency and emissions capturing technology, including the installation of a baghouse, resulted in a dramatic drop in emissions after 1958 (approximately 85% of emissions were released pre-1958); however, As_2O_3-rich dusts were emitted over the area surrounding

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Giant Mine until the roaster ceased operation in 1999 (Jamieson, 2014; Walker et al., 2005; Wrye, 2008).

This study aims to understand the spatial extent, nature, mobility and age of roaster-derived As contamination in soils on the Giant Mine property. These questions were investigated through geochemical and micro-analytical analysis of soil samples from locations isolated from surface mine activities, mostly focusing on outcrop soil pockets. Co-existing soil pore water sampling was also completed at a subset of locations, and gastric and lung bioaccessibility testing, done in partnership with the United States Geological Survey (USGS), was completed at one outcrop soil location.

1.2. Arsenic trioxide in soils

Although arsenolite and claudetite, the two polymorphs of As_2O_3, have been reported both as rare weathering products of arsenic-bearing sulfide minerals and from hot springs and fumaroles, their presence in soils is most commonly due to the impact of waste from mining and mineral processing, and the application of arsenical pesticides and herbicides (Foster and Kim, 2014; Majzlan et al., 2014, and references therein; Morin and Calais, 2006). Majzlan et al. (2014) describe the most common form of anthropogenic arsenic soil contamination in mining environments as the release of arsenolite through ore roasting, and this typically results in high concentrations in near-surface soils. However, in most cases reported, arsenic trioxide has altered rapidly to As-bearing Fe-oxyhydroxides, hydrated ferric arsenates, or sorbed species on clay minerals (Morin et al., 2002; Cancès et al., 2005, 2008; Arai et al., 2006; Drahota et al., 2009; Haffert and Craw, 2009).

1.3. Arsenic in soils near Giant Mine

A previous study of a suite of soil samples from the Yellowknife area beyond the mine property reported that concentrations of As in mineral soils, humus, and leaf litter vary from up to 30 mg/kg near unmineralized bedrock, to 300 mg/kg over mineralized bedrock (Kerr, 2006), whereas average As content in soils for all of Canada is 6.6 mg/kg (Reimann et al., 2009). Naturally occurring As in the Yellowknife Greenstone Belt is derived from arsenopyrite-bearing bedrock and its weathering products (Kerr, 2006; Wrye, 2008). The presence of roaster-derived As_2O_3 and roaster Fe-oxides in soils on the Giant mine property was originally confirmed by Wrye (2008).

Roaster dust captured during the emissions process and stored underground is the closest proxy available for estimating the composition of roaster emissions at Giant Mine. The dust contains 60 wt.% As on average (INAC, 2007). After As_2O_3, which makes up approximately 80% of the dust, the most common As-bearing compounds are roaster-generated Fe-oxides (INAC, 2007; SRK, 2002a). Fawcett and Jamieson (2011) found 88% of As in one dust sample occurring as As(III), with the rest as As(V), generally consistent with a mixture of arsenic trioxide and roaster Fe-oxides. Antimony (Sb) occurs in minor amounts as an impurity in As_2O_3 and as $(As,Sb)_2O_3$ (SRK, 2002b). Gold can also be present in the dust within roaster Fe-oxides, with concentrations ranging from 2 to 76 mg/kg documented in ESP and baghouse dust (SRK, 2002b). Several changes in processing efficiency, emission controls, and ore quality over mine life (SRK, 2002a) correspond with distinct chemical changes in overall roaster dust composition (Table 1) (Canam, 2006). The most notable change in bulk roaster dust chemistry occurs in dust produced pre- and post-1964, when the last and most efficient emissions control was installed (see Table 1). Generally, older dust (pre-1964) had slightly less As and an order of magnitude more Au than newer (post-1964) dust (Table 1).

Arsenic trioxide contains 76 wt. % As, and reagent grade As_2O_3 solubility measures approximately 10 g/L –16 g/L As under standard state conditions (Pokrovski et al., 1996), while arsenopyrite solubility is less than 0.00999 g/L at 25 °C (Craw et al., 2003). However, As_2O_3 dust at Giant is less soluble than reagent-grade As_2O_3. Experimental As_2O_3 solubility measurements on select historic roaster dust samples at Giant range from 8.3 g/L to 10.8 g/L, with one outlier of older dust at 15 g/L at 25 °C (SRK, 2002b). The solubility difference between As_2O_3 at Giant and reagent grade As_2O_3 may be due to Sb content in some Giant As_2O_3 (Riveros et al., 2000).

Roaster-generated Fe-oxides in tailings at Giant have been documented containing from <1 wt% up to 7 wt.% As (Walker et al., 2005) as both As(III) and As(V). Most roaster Fe-oxides are composed of concentrically zoned, nanocrystalline maghemite (Fawcett and Jamieson, 2011). While maghemite is normally metastable relative to hematite at the Earth's surface (Majzlan et al., 2003), evidence shows roaster Fe-oxides produced by the roaster at Giant are stable under surface oxidizing conditions, as the relative proportions of As(III) and As(V) in roaster Fe-oxides exposed for over 50 years in a historic subaerial tailings deposit are similar to those in day-old calcine (Walker et al., 2005). Kinetic barriers, grain size, changes in free energy due to chemical composition (Majzlan et al., 2003), and nanocrystallinity (effecting phase stability and reaction kinetics) might prolong its stability (Fawcett and Jamieson, 2011).

Rock outcrop constitutes up to 70% of the surface cover in the Yellowknife area (Kerr and Wilson, 2000) and covers 30% of the Giant Mine site (Wrye, 2008). Outcrop depressions trap water and promote evaporation during runoff after rainfall and freshet at Giant (Spence and Woo, 2002). Our previous work showed that elevated (up to 3280 mg/kg) concentrations of As were found in soils within depressions in rock outcrops (Wrye, 2008). Thus, large outcrops were optimal sample locations for the purposes of this research.

2. Methods

2.1. Field methods

2.1.1. Soil and water samples

Forty outcrop soils within the dominant wind directions from the roaster were sampled in summer 2010 via grab sampling, mostly targeting soils likely to be high in As based on previous work (Wrye, 2008) and undisturbed by mining activities and infrastructure. Nine soil sample locations were also sampled for coexisting pore water. Six additional soil samples were taken via soil core sampling; however, only one core sample was taken in an outcrop soil pocket. See Fig. 1 for sample locations relative to the roaster, and dominant wind directions.

Specific outcrop soil hollows were chosen based on topography, usually favoring those with few or no visible drainage points. Samples were collected by hand with a trowel and plastic zipper-seal freezer bags, cleaning the trowel with deionized water and paper towels between samples. Large pieces of leaf and organic debris were removed before collection, but due to immaturity outcrop soils tend to be quite heterogeneous, so removing smaller debris was impractical. Moreover, given the historic impact of aerial emissions of soils, it was thought that removal of surface material may remove evidence of that impact. The soil core samples were collected with 5 cm diameter hollow aluminum tubes attached to a drivehead, hammered into the ground with a sledgehammer, cut to appropriate lengths with a pipe cutter, and sealed on the ends with duct tape. At the end of each day soil samples were placed in a freezer.