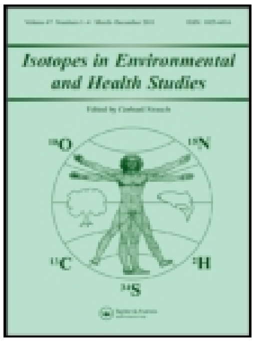

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# SOURCES AND CIRCULATION OF WATER AND ARSENIC IN THE GIANT MINE, YELLOWKNIFE, NWT, CANADA

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Dedicated to Prof. Dr. Dr. h. c. Peter Fritz on his retirement

Recovery of gold from arsenopyrite-hosted ore in the Giant Mine camp, Yellowknife, NWT, Canada, has left a legacy of arsenic contamination that poses challenges for mine closure planning. Seepage from underground chambers storing some 237,000 tonnes of arsenic trioxide dust, has As concentrations exceeding 4000 ppm. Other potential sources and sinks of As also exist. Sources and movement of water and arsenic are traced using the isotopes of water and sulphate. Mine waters (16 ppm As; $\mathrm{As^V/As^{III}} \approx 150$) are a mixture of two principal water sources – locally recharged, low As groundwaters (0.5 ppm As) and Great Slave Lake (GSL; 0.004 ppm As) water, formerly used in ore processing and discharged to the northwest tailings impoundment (NWTP). Mass balance with $\delta^{18}O$ shows that recirculation of NWTP water to the underground through faults and unsealed drillholes contributes about 60% of the mine water.

Sulphate serves to trace direct infiltration to the $As_2O_3$ chambers. Sulphate in local, low As groundwaters (0.3–0.6 ppm As; $\delta^{34}S_{SO_4} \sim 4$ ‰ and $\delta^{18}O_{SO_4} \sim -10$ ‰) originates from low-temperature aqueous oxidation of sulphide-rich waste rock. The high As waters gain a component of $^{18}O$-enriched sulphate derived from roaster gases ($\delta^{18}O_{SO_4} = +3.5$ ‰), consistent with their arsenic source from the $As_2O_3$ chambers. High arsenic in NWTP water ($\sim 8$ ppm As; $\delta^{18}O_{SO_4} = -2$ ‰) derived from mine water, is attenuated to close to 1 ppm during infiltration back to the underground, probably by oxidation and sorption by ferrihydrite.

*Keywords*: Arsenic; Arsenic trioxide; Giant mine; Groundwater; Hydrogen 2; Oxygen 18; Sulphate; Sulphur 34

## INTRODUCTION

Since gold mining operations began in 1947 at the Giant Mine, Yellowknife, NT, some 237,000 tonnes of arsenic trioxide dust has been recovered from the roasting ovens and stored in old stopes and specially designed chambers in the shallow underground. Arsenic concentrations in some mine waters exceeding 4 g/L suggests that seepage from these chambers now occurs. Mine water discharged to the northwest tailings pond (NWTP) carries some 16 ppm As. However, leakage of high-As water from surface tailings impoundments to the mine, and infiltration of meteoric waters through contaminated soils in the

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mining camp occur. This complicates the identification of arsenic sources and pathways required for mine decommissioning.

The objectives of this study were to define groundwater recharge and circulation within the mine, as a basis for determining As sources and transport. The study undertook to characterize the geochemical and isotopic signature of the different water types and solutes and to then identify the sources and pathways for arsenic transport in the subsurface.

## GEOLOGY AND ORE PROCESSING

The Giant Mine is situated within the Archean Slave geological province of the Canadian Shield (Fig. 1). Surface relief is less than 75 m in the district, which has an elevation of about 200 m above sea level. The site is within the zone of discontinuous permafrost. Seasonal temperatures vary between about 17 and −28°C, with the order of 260 mm precipitation annually.

The mine is dug in faulted, steeply dipping metabasalts of the Yellowknife Bay Formation of the Kam Group, bounded by granitic terrain to the west and pelitic schists to the east [1]. Gold is associated with arsenopyrite in cross-cutting schist zones. During the Phanerozoic, the region around Great Slave Lake (GSL) experienced inundation during the relatively widespread late Ordovician to Devonian marine incursion. Evaporated seawater likely infiltrated during this period, present now as Ca-Cl brines [2]. The district experienced extensive Quaternary glaciation, and was covered by the Laurentide ice sheet up to ~10 ka [3], after which glacial Lake McConnell extended eastward over the area until ca. 9 ka [4].

Mining began in 1948 with shallow underground workings, followed by open pit mining in 1974. Underground workings have, since, been developed to a depth of 2000 feet. Waste rock produced during mining of the ore was used as backfill in mined out areas and in construction of the tailings dams and road surfacing. Mineralogical studies of waste-rock samples [5] show that they are dominantly quartz–dolomite assemblages with minor pyrite and arsenopyrite.

Gold-bearing arsenopyrite in Giant Mine ore was separated from the matrix by froth flotation. Barren flotation tailings were mixed with roaster tailings and transferred to the surface tailings containment areas (north, central, south and NWTP), as well as to back fill mined-out stopes underground. A mineralogical study [5] shows them to be largely composed of quartz, Fe–dolomite and calcite, with minor, unweathered sulphide minerals and zoned iron oxides from the roaster.

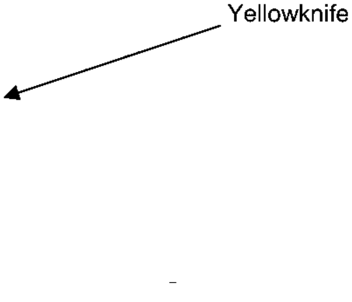

FIGURE 1 Map of Canada with location of Yellowknife, NT, where the Giant Mine is situated.

The concentrated sulphides from the flotation step were dewatered and sprayed into a two-stage fluid bed roaster to release gold from refractory arsenopyrite ore. This process drove off $SO_2$ and arsenite gas. Arsenic trioxide dust, $As_2O_3$, was condensed and removed from the gas stream by a dry dust collector system of electrostatic precipitators and baghouse, then pneumatically piped into shallow stopes and storage chambers in the underground. A chemical analysis of the baghouse dust is given in Table I.

TABLE I Analysis of baghouse dust (composite sample, September 1997) from two independent laboratories (Lakefield and Maxxam) (Royal Oak Mines Report '$As_2O_3$ Management', March 1998).

| | | *Lakefield (%)* | *Maxxam (%)* |
|---|---|---|---|
| Arsenic | $As_2O_3$ | 68.50 | 58.10 |
| Iron | $Fe_3O_3$ | 1.50 | 1.61 |
| Antimony | SbO | 1.16 | 1.39 |
| Aluminium | $Al_2O_3$ | 0.55 | 0.25 |
| Calcium | CaO | 0.39 | 0.35 |
| Magnesium | MgO | 0.26 | 0.23 |
| Potassium | $K_2O$ | 0.16 | 0.02 |
| Sodium | $Na_2O$ | 0.04 | 0.02 |

Arsenic has the highest concentration in this dust, with an average concentration of $As_2O_3$ close to 70% and a concentration of As of about 60% [6]. Sulphur was not analysed but likely present as sulphates within the dust.

The gold-bearing calcine from the roaster, following removal of As and S, is dominantly hematite ($Fe_2O_3$) and magnetite ($Fe_3O_4$). It was thickened and made alkaline with calcium hydroxide ($Ca(OH)_2$) to pH 11. Gold was leached from the slurry by complexing with $CN^-$ and plated onto zinc. Gold-free $CN^-$ solution was reprocessed, with a portion bled to the NWTP (from 1989 to 1999) to reduce impurity build up. Mill effluent was discharged to the NWTP between 1989 and 1999. Tailings water was managed by treatment in an effluent treatment plant, settling pond and polishing pond prior to discharge to GSL via Baker

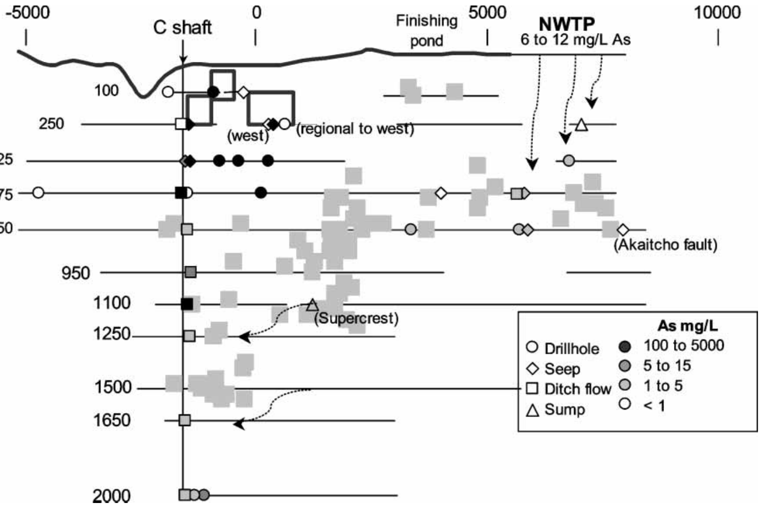

FIGURE 2 Mine section showing concentrations of dissolved As in mine waters. Vertical depth of drifts and northing (horizontal axis) in feet (according to mine protocol), relative to ground at C shaft. The arsenic trioxide chambers (clusters), stopes backfilled with tailings (squares), and infiltration from the NWTP are also shown.

Creek, although the NWTP lost a considerable amount of water by infiltration directly into the local subsurface through faults and open drill holes (arrows in Fig. 2).

## SAMPLING AND ANALYSIS

The sampling program was restricted to water flows within the mine setting. Sampling of arsenic trioxide dust for isotope measurements was not possible as the chambers are sealed for health and safety reasons. Sample sites included flowing drill holes and fractures as well as ditch flows on each drift that carry drainage to the central shaft for pumping to surface.

Groundwater flow in the mine is dominated by old mine workings, drill holes, sub-vertical faults and associated splays. The regional east–west stress pattern favours permeability in the faults with this orientation. Considerable inflow also occurs from fault planes and drill holes in the northern 'Supercrest' mine region underlying the NWTP. Similarities in geochemistry clearly indicate these high-inflow sites. Samples were collected from 42 sites during three campaigns in 2000. These periods were selected to maximize contrasts in seasonal inflows to the subsurface. *In-situ* measurements of temperature, pH, salinity, redox and DO were taken, and samples were collected for geochemical and isotopic measurements. Sample sites (and label designations) include SW – surface waters, BH – flowing boreholes, SP – seeps from fault zones in bedrock, DF – mine drainage from ditch flow, SU – mine waters in sumps and RB – rock bolt holes.

The geochemical analytical program (Taiga Laboratory, Yellowknife) included major cations and anions by inductively coupled plasma–atomic emission spectroscopy (ICP–AES) and liquid chromatography. Trace elements and arsenic speciation were determined by inductively coupled plasma–mass spectrometry (ICP–MS). Environmental isotope analyses were carried out in the Environmental Isotope Laboratory at the University of Waterloo. All results were compiled by Clark [7]. Waters were analysed for $^{18}$O ($CO_2$ equilibration; analytical uncertainty $\pm 0.15‰$) and $^{2}$H (reduction on zinc; analytical uncertainty $\pm 1.5‰$) and referenced to Vienna standard mean ocean water (VSMOW). Tritium, $^{3}$H was measured by electrolytic enrichment ($\pm 0.8$ TU) and by beta-counting ($\pm 8$ TU). The $^{34}$S and $^{18}$O content of sulphate were analysed by precipitation as $BaSO_4$ followed by combustion continuous flow–isotope ratio mass spectrometry (CF–IRMS) (expressed relative to CDT), and by conversion to $CO_2$ with graphite (expressed relative to VSMOW), respectively. Both have an analytical uncertainty of 0.2‰.

## DISCUSSION OF GEOCHEMICAL AND ISOTOPIC DATA IN MINE WATERS

### Current Distribution of As in Mine Waters

Concentrations of As in flowing drillholes and seeps in the vicinity of the arsenic trioxide chambers range from 100 ppm to greater than 4 g/L (Fig. 2). At greater depths in this central mine location, samples have elevated As concentrations with values up to 190 ppm in ditch flow on the 1100 foot level and 14.4 ppm in borehole discharge on the 2000 foot level (Fig. 2). As demonstrated below, this distribution indicates movement of seepage from the chambers through fractures and faults to all levels in the mine.

Northwest tailing pond waters sampled from the surface impoundment have arsenic concentrations between 6 and 12 ppm. However, NWTP water sampled in the underground directly below has arsenic concentrations in the range of only 0.1–5 ppm (Fig. 2). Some dilution with low-As groundwaters in the subsurface may be in part responsible for this attenuation of As, although $^{18}O$ mass balance shows that such dilution must be very minor. More likely is the uptake of $As^{V}$ on ferrihydrite in the tailings sediments. The lowest concentrations ($<1$ ppm) are found in shallow groundwaters beyond the chamber influence, and in inflows from peripheral areas (regional groundwaters). Until 1999, the NWTP water received ore-process water from the mill, which originates from GSL.

Oxidation of tailings in backfilled stopes represents a potential As source. However, the distribution of these tailings with respect to concentrations of As in mine waters provides no indication that they are a significant source of As in mine waters (Fig. 2).

## Origin of Mine Waters – $\delta^{18}O$ and $\delta^{2}H$

The $\delta^{18}O$ and $\delta^{2}H$ composition of mine water is diagnostic of water movement within the mine. Figure 3 shows the isotopic composition of different water sources in the mining area. The local meteoric water line is derived from a five-year period of precipitation monitoring at Yellowknife [8]. All mine waters are enriched in both $^{18}O$ and $^{2}H$ relative to the average of annual precipitation ($-21.8/-168$‰), indicating dominantly summer recharge. Snowmelt is clearly precluded from recharging the subsurface due to seasonal frost.

Great Slave Lake supply water is used on the mine site for drilling and surface utilities. In 2000, GSL water was used for some limited drilling underground and was added to mine water on surface due to pumping system overcapacity. This has a characteristic evaporative enrichment signature gained during regional summer drainage in this dry continental climate. This is reflected in the mine waters, which show a clear mixing trend between GSL water and local low-As groundwaters. These latter include flowing drillholes and seeps in the central mining area with As concentrations $<0.5$ ppm. The local mining camp is essentially free of

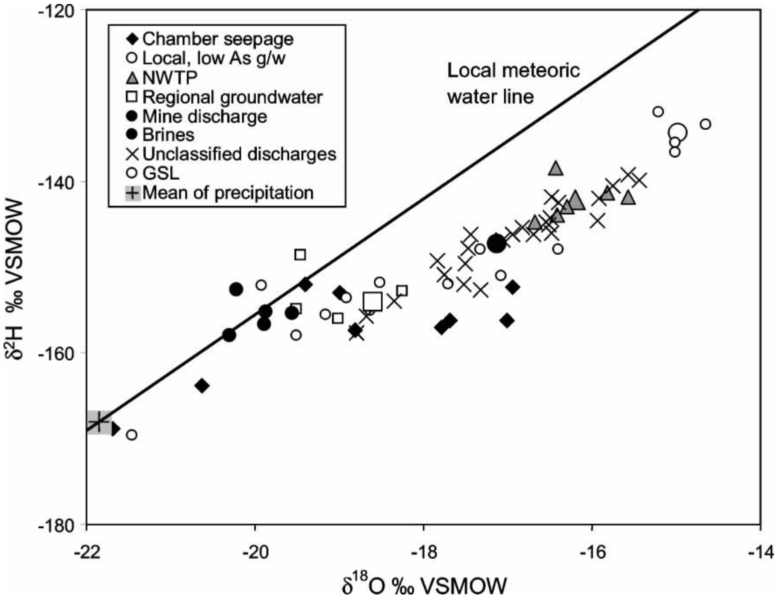

FIGURE 3 Stable isotope composition of different water types. Mean values of water types shown as larger symbols. Chamber waters are characterized by As concentrations $>1$ g/L. Local low-As groundwaters are from shallow sites within the mine camp where recharge can be attributed to direct infiltration alone. The NWTP waters include surface waters from this site and two subsurface sampling sites situated directly below the pond, and where a high rate of inflow of tailings water has been consistently observed.

vegetation, and is characterized by waste rock piles and abandoned open pit mines, through which recharge is enhanced. Although, GSL water has been used in the underground for drilling, it does not seem to contribute significantly to mine waters pumped to the NWTP. For example, no GSL water has been observed in samples from shallow depths in the central mine area. Regional groundwaters are sampled from a fault intersected by a borehole in the extreme northern end of the underground and beyond the influence of surface mining activities.

Mine discharge represents the weighted mean of mine water pumped from the underground and discharged to the NWTP. The NWTP waters are a mixture of surface utility water from the mill, which is derived from GSL, and mine discharge. This water is treated through a treatment plant, settling and polishing ponds before discharge to surface waters. A simple mass balance with $\delta^{18}O$ shows that NWTP water is roughly a 50:50 mix of mine discharge water and mill water. Accounting for the mix of water in the mine underground, this becomes a mixture of $\frac{1}{3}$ locally recharged groundwater and $\frac{2}{3}$ GSL water from the mill. However, heavy losses of NWTP water to the underground in the Supercrest are results in recirculation of the mine discharge water, producing a 50 : 50 mixture between GSL water from the mill and local low-As infiltration.

Chamber waters show an enhanced enrichment in $\delta^{18}O$ (Fig. 3). This trend could be produced by evaporation under low humidity conditions [9–11]. In the chambers, this may occur as vapour diffusion from infiltrating groundwater into the low-humidity dust. An isotopically variable source, such as observed with the local, low As groundwaters, will also contribute to the observed $\delta^{18}O$ enrichment.

The isotopic distinction between GSL water ($\delta^{18}O = -15.0 \pm 0.2‰$), NWTP water ($\delta^{18}O = -16.2 \pm 0.4‰$) and direct infiltration illustrates mixing of these two sources in water through the mine (Fig. 4). The integration of the groundwater and GSL signals is clear. Sites sampled on the northern mine (NWTP) side are fed by infiltration from the NWTP, which is largely influenced by mine process water from GSL. Sites from the central and southern end of the mine, including those beneath the chambers, fall in the range for local rainfall. This is also the range for local low-As groundwaters. Monitoring on the 1100 and 1250 foot levels shows an integration of the local groundwater and GSL signals.

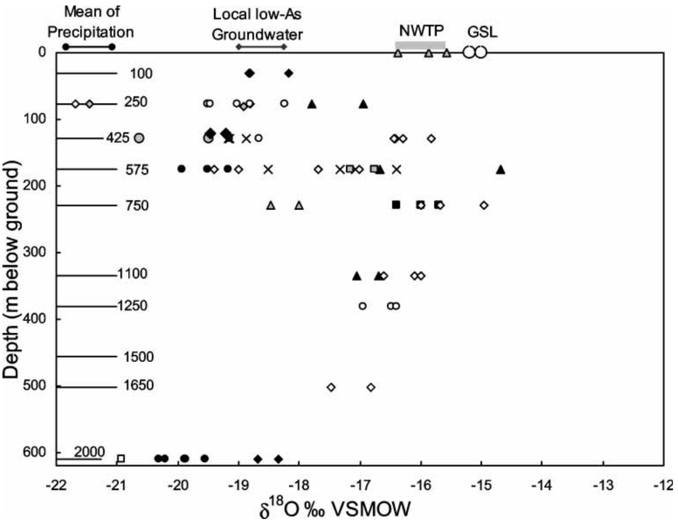

FIGURE 4 Variation in $\delta^{18}O$ of waters with depth. Note that duplicate symbols on a given mine level are repeat samples of the same borehole or seep. The anomalously enriched samples on the 575 and 750 level experienced significant evaporation in the NWTP.

Water sampled from the drillholes on the 2000 foot level is dominated by local recharge, with no evidence of GSL water from the NWTP.

## Geochemical Facies and Redox Conditions

Most Giant Mine groundwaters are dominated by a Ca-$SO_4$ facies with a minor to major Mg component (Tab. II). A minor Na-Cl component is present at most mine levels (Tab. II), and a saline Ca-Cl water is present on the deepest mine level. In the Ca-$SO_4$ waters, gypsum saturation is approached through the complementary reactions of aqueous oxidation of sulphide and weathering of carbonate and silicate minerals. Both calcite and dolomite are saturated in all groundwaters except those dominated by chamber seepage (Tab. II). However, the poor correlation for Ca and Mg with dissolved inorganic carbon (inset diagram in Fig. 5) indicates that Ca and Mg must also be derived from silicate weathering.

The origin of sulphate includes low-temperature aqueous oxidation of sulphides (weathering) and a high temperature oxidation (combustion) of sulphides in the roaster. Minor sulphate of geogenic (brine) origin is also identified. Gypsum is moderately undersaturated in the three principal water types, and thus does not represent a solubility control for sulphate.

Arsenic solubility controls depend to a large degree on its oxidation state. $As^{III}$ (arsenite), occurs as a neutral hydroxide $[H_3AsO_3^0]$ up to pH $>9$, above which the ionized $H_2AsO_3^-$

TABLE II Geochemical and isotopic values of representative principal water types. Concentrations in mg/L.

| | *Type* | | | | | |
|---|---|---|---|---|---|---|
| | *Chamber* | | *Local low As* | | *NWTP 000-SW2** | *Mine Discharge* |
| *Location* | *250-SP1** | *575-DH2** | *250-SP2** | *575-DH1** | | |
| pH-field | 6.37 | 6.43 | 7.42 | 7.67 | 7.98 | 7.68 |
| Temp | 4.5 | 4.3 | 3.9 | 1.7 | 5.8 | 6 |
| TDS | 7560 | 10300 | 1810 | 1280 | 1090 | 2600 |
| Eh (mV) | 150 | −20 | 310 | 100 | 235 | 110 |
| DIC (mg C/L) | 7.4 | 106 | 26.8 | 33.4 | 15.8 | 36 |
| Ca | 241 | 216 | 316 | 181 | 196 | 420 |
| Mg | 186 | 612 | 101 | 77 | 37 | 88 |
| Na | 98.6 | 109 | 53.1 | 113 | 103 | 280 |
| K | 14.9 | 29.9 | 13.3 | 7.41 | 6.77 | 17 |
| Cl | 150 | 60 | 83 | 91 | 240 | 620 |
| $SO_4$ | 1213 | 3610 | 1566 | 563 | 282 | 874 |
| $SiO_2$ | nm | 27.9 | nm | 8.38 | 26.9 | na |
| $\delta^{34}S_{SO_4}$ | 5.8 | 4.5 | 3.2 | 4.9 | 5.5 | 5.3 |
| $\delta^{18}O_{SO_4}$ | −2.7 | 3.8 | −13.3 | −6.2 | −2.1 | −3.5 |
| $NH_3 - N$ | 3.98 | 2.81 | 0.084 | <0.005 | 2.09 | 3.9 |
| $NO_3 + NO_2 - N$ | <0.008 | <0.008 | 0.476 | 0.239 | 8.79 | 17.4 |
| As-diss. | 4210 | 3460 | 0.357 | 0.642 | 7.95 | 16 |
| $As^V/As^{III}$ | 0.1 | 0.8 | 36 | 17 | 120 | 150 |
| Fe-diss. | 0.48 | 0.73 | <0.03 | <0.03 | <0.03 | 0.02 |
| $\delta^{18}O_{H_2O}$ | −17.0 | −17.7 | −18.9 | −17.3 | −15.9 | −17.1 |
| $\delta^2H_{H_2O}$ | −152 | −156 | −153 | −148 | −141 | −147 |
| $^3H_{H_2O}$ (TU) | Ld | 16 | 22 | 25 | 17 | 20 |
| $SI_{calcite}$ | −0.17 | −1.4 | −0.07 | 0.49 | 0.22 | 0.50 |
| $SI_{dolomite}$ | −0.44 | −1.8 | −0.64 | 0.62 | −0.27 | 0.35 |
| $SI_{gypsum}$ | −0.59 | −0.33 | −0.19 | −0.65 | −0.88 | −0.32 |
| $SI_{Ca_3AsO_4 \cdot 4w}$ | −2.79 | −4.8 | −9.1 | −7.5 | −5.04 | −4.8 |
| $SI_{FeAsO_4 \cdot 2w}$ | −2.9 | −6.7 | — | — | — | −6.4 |
| $SI_{As_2O_3}$ | −16.5 | −9.9 | −21.1 | −21.1 | −55.4 | −14.8 |

*Note*: Mineral saturation indices (SI) calculated by the program WATEQ4F [12]. Concentrations in mg/L.
*Location.

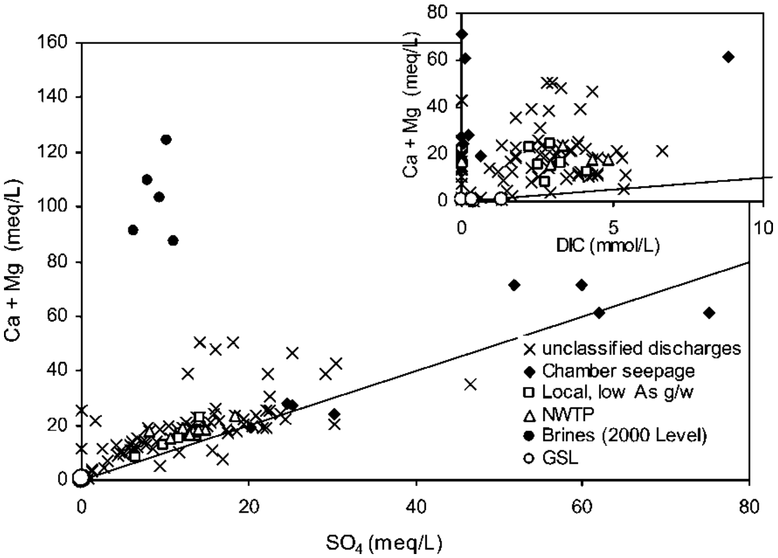

FIGURE 5 Ca and Mg-$SO_4$ geochemical facies. Inset diagram shows correlation of Ca and Mg with DIC.

dominates. In circum-neutral pH waters with elevated salinity, the solubility of arsenite exceeds 10 g/l. Arsenate, $As^V$, forms either $H_2AsO_4^-$ (below pH 6.8) or $HAsO_4^{2-}$ (pH 6.8–11.5). Calcium arsenate salts, $[Ca_3(AsO_4)_2{\cdot}4H_2O]$ and $[Ca_4(OH)_2(AsO_4)_2{\cdot}4H_2O]$, can control $As^V$ concentrations at a few g/l [13] but cannot be important in controlling the chamber seepage, which is dominantly $As^{III}$.

Scorodite $[FeAsO_4{\cdot}6H_2O]$ is relatively insoluble, but requires very high ferric iron activity for stability. It competes with ferrihydrite $[Fe(OH)_3]$ for attenuation of As in neutral pH waters [14]. Arsenate forms a strong surface complex with fresh ferrihydrite precipitate, and is an effective treatment process for As contaminated water. However, Davis et al. [15] show co-precipitation with Fe oxyhydroxides to be of greater importance than sorption on ferrihydrite in attenuating arsenate concentrations. The large reservoir of ferric iron oxide and hydroxide from weathering and roasting of sulphides represents a sink for As within the Giant Mine camp. Orpiment $[As_2S_3]$ is the only significant mineralogical control for $As^{III}$, and is produced under reducing conditions with excess dissolved sulphide. However, redox conditions in mine waters are buffered at a pe higher than that of sulphate reduction (Fig. 6).

Potential arsenic phases are undersaturated and in most cases highly undersaturated in these waters (Tab. II). Arsenic concentrations in the local, low-As groundwaters are likely controlled by release rates during sulphide oxidation at surface. Arsenic concentrations in the chamber waters are due to dissolution of arsenic trioxide dust.

The low pH of the chamber waters (pH 5.8–6.7) reflects the acidity generated by oxidation of arsenic trioxide to arsenate, by reaction with either $Fe(OH)_3$ or $O_2$ as an electron acceptor. Dissolution of $H_2SO_4$, shown below to be gained by infiltration through the chambers, may also contribute. The oxidation of $As^{III}$ in $As_2O_3$ dust to $As^V$, as observed by their ratio in mine waters (Tab. II), is an acid-producing reaction following from dissolution of solid arsenic trioxide:

$$As_2O_3 + 3H_2O \longrightarrow 2H_3AsO_3^0$$

$$H_3AsO_3^0 + H_2O \longrightarrow H_2AsO_4^- + 2e^- + 3H^+.$$

Redox potential measurements (Fig. 6) show that for chamber seepage and much of the ditch flow drainage Eh is buffered by arsenic oxidation. In most natural and contaminated waters, As is generally present at too low a concentration to play an important role on redox potential. As the $As^V/As^{III}$ redox boundary occurs at a lower Eh (pe) than that of $Fe^{3+}/Fe^{2+}$, it is likely that ferric iron oxide is supporting the oxidation of $As^{III}$. This would account for the elevated levels of dissolved iron, which are the range of 0.3–0.7 ppm.

Locally recharged (low As) groundwaters have relatively oxidising conditions, consistent with their short flow path through fractures and faults, and contact with air in the local mining area. The origin of sulphate in these waters (below) is from the low temperature aqueous oxidation of sulphides, likely in locally backfilled deposits of waste rock. Accordingly, these are among the most oxidising waters measured in this study (Fig. 6). The elevated $As^V/As^{III}$ ratio reflects the high oxidation potential of this weathering environment.

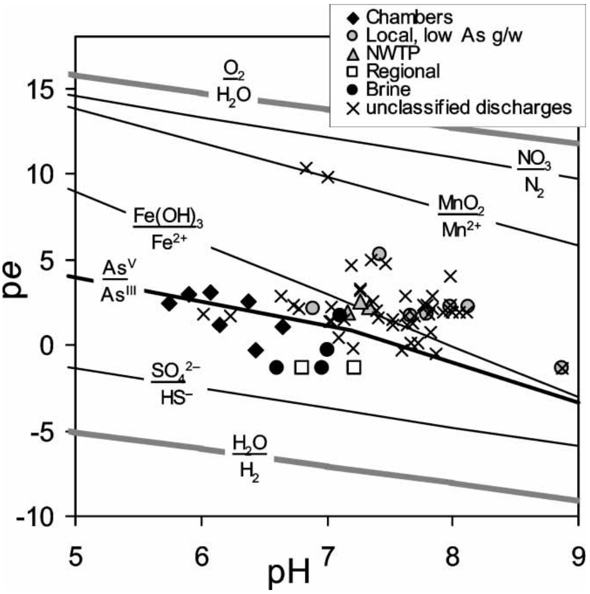

FIGURE 6 Redox potential of $As^V/As^{III}$ in comparison with other dominant redox pairs (calculated from thermodynamic data compiled by Drever [16]). Note that $As^V$ is the stable species under oxidising conditions. Redox conditions are measured *in-situ* with an ORP probe as Eh (V or mV). This is converted to pe or electron activity for thermodynamic calculations (Eh (V) = 0.059 pe).

The elevated As concentrations in the NWTP waters (2–12 ppm and average 8.1 ± 2.3 ppm As) have a very high $As^V/As^{III}$ ratio. Their redox potential indicates that NWTP water is dominated by the $Fe^{3+}/Fe^{2+}$ redox pair, which may be responsible for the oxidation of $As^{III}$. The roaster tailings have abundant ferric iron ($Fe^{3+}$) in the hematite produced by oxidation of sulphide minerals. Northwest tailings pond water sampled in the subsurface in the Supercrest area, however, have substantially lower As concentrations (1.5 ± 1.2 ppm, Fig. 2). Losses can be attributed to sorption of arsenate, $As^V$, onto ferric hydroxide during infiltration to the subsurface.

## Sulphate Systematics

The potential sources and pathways for arsenic in the subsurface are coupled with sulphate. They have a common origin in arsenopyrite [FeAsS], and both are released through aqueous oxidation or during ore roasting. The geochemical and isotopic behaviour of sulphate may then provide a useful tracer for arsenic in mine waters. Three sources are identified, including sulphate from high-temperature oxidation of sulphide (roaster gases), low-temperature aqueous oxidation of sulphides (in waste rock and old tailings) and sulphate from Shield brine unrelated to mining activities.

A plot of sulphate *vs.* total arsenic shows that the highest concentrations of sulphate are associated with the high As chamber drainage waters. Some of the chamber drainage waters have sulphate concentrations in excess of 2500 ppm suggesting a significant source exists in the arsenic trioxide dust. However, there are additional sources of sulphate in the subsurface, as most samples have high sulphate (Fig. 7).

The $\delta^{34}$S ranges for sulphate sources are shown in Figure 8, including the Con mine brine sulphate, sulphate from oxidation of sulphide minerals (pyrite and/or arsenopyrite) and the range observed for shallow groundwaters at the Con mine. Sulphate from sulphide has a fairly well constrained range of 3–7‰, and is the same as observed in tailings sulphate at the Con Mine [17]. The brines have a unique geogenic $\delta^{34}$S signature, unrelated to the oxidation of sulphide minerals.

The $\delta^{18}O_{SO_4}$ measurement offers a constraint on the origin of the sulphate derived from sulphide oxidation. The $\delta^{18}$O value for sulphate from the low-temperature aqueous oxidation of sulphide minerals is low, due to the incorporation of depleted oxygen from local water [18]. Equilibration with groundwater is unlikely given that there is no geochemical evidence for sulphate reduction [19] or low pH conditions [20] that favour such exchange. Further, equilibrium exchange values for $\delta^{18}O_{SO_4} > 10$‰ are not observed. From Figures 9 and 10, the local, low-As groundwaters show such an origin, having $\delta^{18}O_{SO_4}$ values in the range of about −5 to −13‰. This is consistent with their $\delta^{18}$O-$\delta^{2}$H signature that indicates local summer precipitation (Fig. 3). Accordingly, such weathering is carried out within the mining camp.

The $\delta^{18}$O composition of sulphate derived from $SO_2$ produced in the roaster will be enriched (>0‰ VSMOW; [21]) due to the incorporation of atmospheric $O_2$ ($\delta^{18}O_{O_2} = 23$‰) during the combustion of sulphides. Sulphate from chamber seepage

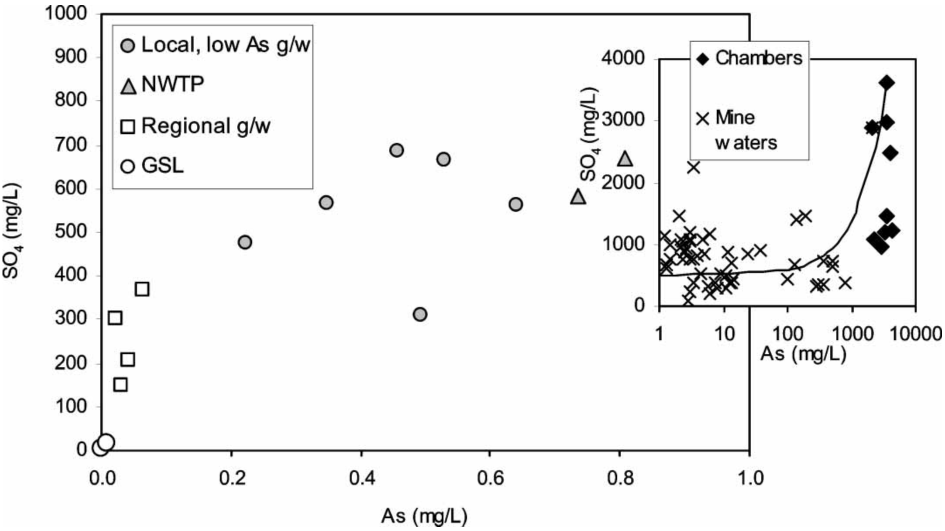

FIGURE 7 Cross-plot of dissolved sulphate and arsenic in all mine waters. Note that Ditch/Sump samples include unclassified discrete samples.

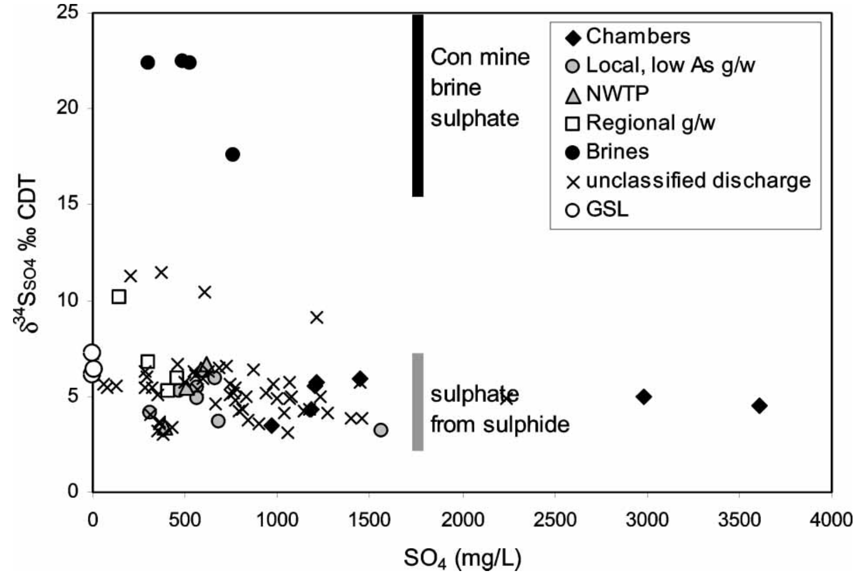

FIGURE 8 Sulphate concentration and $\delta^{34}S$ for different water types. Note that 'Ditch and Sump waters' includes unclassified samples from discrete sample sites.

shows a mixture of low-temperature sulphate from weathering and high-temperature sulphate from the arsenic trioxide dust (Fig. 9). This trend is demonstrated by the curve in Figure 9, which is calculated by successive additions of 500 mg aliquots of sulphate with $\delta^{18}O = 6‰$.

The NWTP waters have also derived much of their sulphate from high temperature combustion of sulphides, likely accompanying the discharge of roaster residues with high

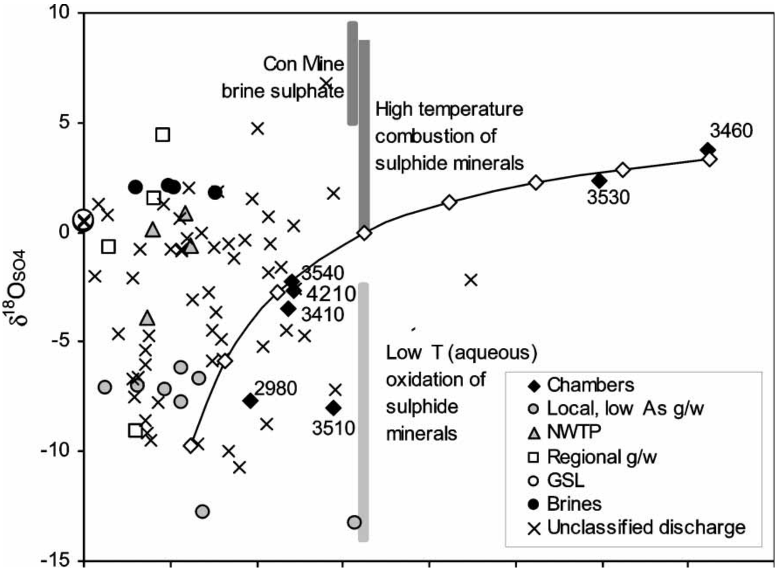

FIGURE 9 Sulphate concentration and $\delta^{18}O$ of sulphate for different water types. Black line shows evolution of sulphate by successive 500 mg additions of high temperature sulphate with $\delta^{18}O = 3.5‰$ (open diamonds), leached from $As_2O_3$ dust in the chambers. The As concentrations are noted for the Chamber waters. Con Mine brine range from Douglas *et al.* [17].

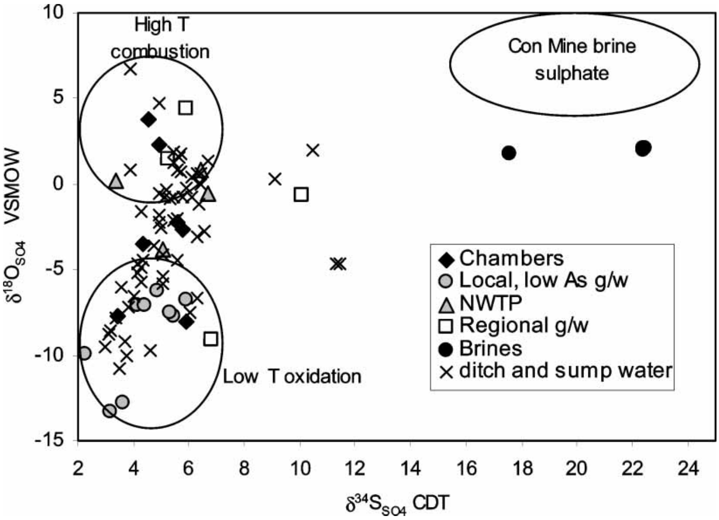

FIGURE 10 Scatter plot of $\delta^{34}$S *vs.* $\delta^{18}$O in sulphate, showing the approximate ranges for the principal sulphate sources.

sulphate in the tailings pond. The NWTP sample with $\delta^{18}O_{SO_4} = -3.9‰$ was collected after the time when mill process water was no longer discharged to the NWTP. Regional groundwaters gain up to 450 ppm sulphate with an enriched $\delta^{18}$O signal indicating an origin as fallout from smelter emissions.

## SUMMARY AND CONCLUSIONS

The origin and movements of mine water at the Giant Mine can be traced with $\delta^{18}$O, which clearly defines two discrete water sources – locally infiltrated meteoric waters and GSL water. Mine water is discharged to the NWTP, which until late 1999 also received mill process water supplied from GSL. Leakage from the NWTP recirculates a significant proportion of mine water back to the underground. Very minor additions to mine waters include a shield-type brine found at the deepest mine level only, and seepage of regional groundwater from faults in the extremities of the mine. Mass balance with $\delta^{18}$O shows that the NWTP water contributed about 60% of the mine water, and is itself a 50:50 mixture between GSL water from the mill and water pumped from the mine. As the mill is now shut down, seepage from the NWTP should reduce to about 30% of mine discharge.

Exclusively, summertime precipitation with an evaporated $\delta^{18}O - \delta^{2}H$ signature recharges local, low-As groundwaters. Seasonal frost precludes contributions from spring snowmelt. Low values for $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ indicate an origin from low-temperature aqueous oxidation of waste rock and old mine tailings disposed of on surface coupled with aggressive weathering of silicate and dolomite ($SI_{dol} > 0$). These waters are not a significant contribution of arsenic (0.3–0.6 ppm) to the ~16 ppm As found in mine discharge.

Chamber seepage waters are generated by the infiltration of the local, low-As groundwaters into the arsenic trioxide storage chambers, where dissolution of $As_2O_3$ provides As concentrations in excess of 4 g/L. Their very high As concentrations make them the principal source of As in mine waters, and has reached all levels in the mine through mine workings, drillholes and fracture flow. The $\delta^{18}$O value of sulphate shows a mixture between a low-temperature sulphide-oxidation source (from the local, low-As groundwaters) and a high-temperature combustion source (sulphide roaster) gained from the arsenic trioxide dust.

The integrated mine drainage water, collected and pumped to the NWTP, is a mixture of local, low As infiltration, chamber seepage and NWTP water that has infiltrated to the subsurface. It has a $\delta^{18}$O signature that indicates about a 60:40 mixture of local, low-As groundwater and NWTP seepage. This mixture carries an average of 16 ppm As derived mainly from the leaking underground $As_2O_3$ storage chambers.

Mine drainage waters are discharged to the NWTP, and so the NWTP water has an integrated geochemical and isotopic signal. While NWTP water clearly contributes to mine waters through infiltration in the Supercrest area, it is not a source of As, and may indeed be a sink. Arsenic concentrations average 8 ppm in surface NWTP water. The $\delta^{18}O_{SO_4}$ in NWTP water is more enriched than the mine discharge ($-3.5‰$), indicating a significant roaster source of sulphate. However, mill effluent did not contribute significant As, as the 8 ppm measured in NWTP water can be attributed to the 50:50 dilution of mine water (16 ppm) with low-As water from the mill (GSL water). Moreover, infiltration of NWTP water into the subsurface is accompanied by a reduction of As to less than 2 ppm, likely through sorption of arsenate onto ferrihydroxide.

Arsenic in mine discharge and tailings pond water is ultimately derived from leakage of the arsenic trioxide chambers, with only very minor contributions from the oxidation of sulphides in the mining camp. Circulation through the mine to all levels is facilitated by fracture permeability. Recirculation through the NWTP and this reservoir of ferric oxyhydroxide precipitates facilitates oxidation of As to arsenate and attenuation by sorption.

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