**Effects of pH on arsenic mineralogy and stability in Poldice Valley,
Cornwall, United Kingdom**

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ABSTRACT

Many abandoned mine sites in Cornwall, UK, are characterised by elevated concentrations of arsenic (As), which can cause contamination of surrounding soil and water resources. These sites have important historical value that requires access to be maintained, despite exposure of humans to toxins that may lead to health issues including hyperpigmentation keratosis (including skin cancers) and liver fibrosis. The abandoned mine tailings at Wheal Maid has been assessed for As-bearing mineralogy and stability taking into account the public footpaths made by the local council to areas of potential contamination.

To assess the potential risk associated with these mine sites, the As concentration in waters along the tailings dam and Carnon River have been measured and range up to 3.6 ppm, which is 2 orders of magnitude above the WHO guideline value of 0.01 ppm for drinking water. Samples of water, rocks and soils from the mine tailings ponds and the Carnon River were analysed using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) to determine the concentration of individual elements in each sample followed by mineral identification using X-Ray Diffraction (XRD). Mineralogical evaluation indicated that the majority of mine tailings consist of clay-rich rocks, with few associated As-bearing minerals. Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) is observed in the mine tailings pond and appears critical to the As distribution and storage in this surface environment. Using the analysed water chemistry, a modified version of PHREEQC is used to calculate the saturation index of scorodite as a function of pH conditions. The strong variation of the solubility of this mineral with pH and oxidation state highlights potential risks for using scorodite for As fixation and storage.

1 INTRODUCTION

1.1 Background

Human exposure to high arsenic (As) levels can lead to numerous health issues. These include hyperpigmentation keratosis (including skin cancers) and liver fibrosis (ATSDR, 2013). Arsenic may form toxic dust that can rest on garden soils and footpaths that young children may ingest via hand to mouth (Bowell, et al., 2013). Arsenic is a known toxin (Pascoe et al., 1994 ; Lorenzana et al., 1996; Farago et al., 1997; Kenyon et al., 2008; Pinyayev et al., 2011) and numerous studies have demonstrated higher As uptake in children (Eligali, 1994). A preliminary study of inorganic As and methylated metabolites in urine from adults and children in Cornish mining villages showed elevated urinary As contents (Farmer & Johnson, 1990). High As concentrations are commonly found associated with the desired ore products during the mining process and are typically discarded with the rest of the mine wastes (Craw & Bowell, 2014).

Arsenic concentrations at Earth surface conditions are largely controlled by As-bearing minerals through dissolution, precipitation, incorporation, sorption and desorption (Fendorf et al., 1997; Ford, 2002; Bostick & Fendorf, 2003; Amirbahman et al., 2006; Benzerara et al., 2008; Deditius et al., 2008; Catalano et al., 2011; Li et al., 2011; Zhu et al., 2014; Karimian et al., 2017; Sowers et al., 2017; Catelani et al., 2018). Arsenic is similar to many chalcophile elements in that it is commonly released by sulphide oxidation. Arsenic is modified by various biogeochemical processes, and attenuated by adsorption and co-precipitation with Fe-minerals, clays, and organic matter (Wen, et al., 2020; Schittich, et al., 2018; Bauer & Blodau, 2006; Redman, Macalady, & Ahmann, 2002; Kalbitz & Wennrich, 1998; Wang & Mulligan, 2006; Pallier, Feuillade-Cathalifaud, Serpaud, & Bollinger, 2010; Dobran & Zagury, 2006). It is a non-metal/metalloid and is a member of the Group VB elements (P, As, Sb, Bi) in the periodic table. In natural waters (CCME, 2001), the predominant form of As is arsenate (As^{+5}) and may be also found as arsenite (As^{+3}) in a reduced environment. The common As-bearing compounds can be grouped into arsenate, arsenide, oxide, and sulphide and sulphosalts. The precipitation of the Fe-arsenate scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$, is commonly found in oxidised zones of As-bearing ore deposits (Rieros et al., 2001) and understanding how it transforms over time is key to reduce health risks.

Mining for copper and tin in Cornwall began at least by the early eighteenth century (Hunt & Howard, 1994). Towards the end of the nineteenth century, Cornwall dominated copper, tin and arsenic production globally (Buckley, 2005). Prolonged periods of mining without environmental regulations have had a significant impact to the surroundings (Farago et al., 1997; Camm et al., 2004; Howell et al., 2013). One such mine, the Wheal Maid is located in the Poldice Valley in central Cornwall (Figure 1). This site is of particular interest due to its popularity for outdoor recreation, the lack in reclamation of mine dumps, and its prominence in the production of As. Mine waste and derelict As kilns are still present at the site (Camm et al., 2004). Runoff from the workings flow through tributaries approximately 2 km before entering the Carnon River to the southeast.

The objective this study are to: (1) identify all potentially harmful contaminants and As-bearing minerals present at the site, (2) assess and evaluate the most common As-bearing minerals in an oxygenated mine tailings dam, (3) collect and analyse water, rock and soil samples from Wheal Maid and along the Carnon River, and (4) determine the minerals controlling As mobility and the effects of varying pH conditions. Thermodynamic and crystallographic data collected in (2), combined into an internally consistent thermodynamic database, can help to predict and explain the occurrence and assemblages of arsenates and associated minerals.

1.2 Geology and Conceptualisation

The Wheal Maid mineralization consisted of hydrothermal veins of cassiterite-sulphide-quartz-fluorite-clay within a Devonian aged Mylor Slate Formation. The mineralization is associated with Carboniferous-Permian magmatism that provided the heat source that developed a hydrothermal cell under the area leading to metal leaching from shales and deposition along faults in the Mylor formation (Hill et al., 1990).

Due to the increasing challenges of deep mining 'the Great County Adit' was constructed to remove water starting in 1748 and reaching the Poldice Valley 12 years later (Buckley, 2005). Water from the mines is discharged more than 60 km (40 miles) away into the Carnon River. The estimated depth of the adit beneath the Poldice Mine is 510 meters. An engine (Taylor's engine house) worked in association with gravity in the adit to pump water out of the mine towards to the river mouth. Runoff from the mines caused a decline in biodiversity in the river system (Neal et al., 2005). A conservation management plan was made by the Cornwall County Council in October 2004. The plans involved construction of horse rider paths, footpaths but no mention of removing toxic waste materials. The Camborne mining district has a region of unique geology and mineralisation zones. A considerable array of supergene minerals has been recorded from the Mineral Tramway area including: azurite ($\text{C}_2\text{H}_2\text{Cu}_3\text{O}_8$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6$), chalcopyrite (CuFeS_2), chenevixite ($\text{Cu}_2\text{Fe}^{3+}_2(\text{AsO}_4)_2(\text{OH})_4$), clinoclase ($\text{Cu}_3(\text{AsO}_4)(\text{OH})_3$), goethite ($\text{FeO}(\text{OH})$), lironite ($\text{Cu}_2\text{Al}[(\text{OH})_4|\text{AsO}_4]\cdot 4$), pharmacosiderite ($\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4\cdot(6-7)\text{H}_2\text{O}$), scorodite ($\text{FeAsO}_4\cdot 2\text{H}_2\text{O}$) and torbernite ($\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$) (Bowell, et al., 2013).

A conceptual model for the Wheal Maid mine tailings facility (Figure 2) was developed from a review of previous studies mentioned above and observation of the general topography and the following assumptions are made through discussions regarding the flow of water onsite. The assumptions are as follow:

1. Water falls onto the tailings facility from rainfall;
2. Water from rainfall enters the Carnon River through surface runoff and infiltration of the tailings facility;
3. Water flows downstream moving from tailings pond 1 to tailings pond 3 and enters the Carnon River through a controlled water barrier;
4. Water in the tailings pond infiltrates only a minor amount of water into the deep "Great Adit" groundwater system and mixes with the tailings water leaving the facility at the controlled water barrier; and
5. Surface runoff is neglected in the model as it is not quantified, and the amount is deemed negligible compared to the flows from the tailings ponds and the "Great Adit" system.

2 PREVIOUS STUDIES

In a study focusing on the potential for As contamination on the Mineral Tramway and mining sites in the Gwennap and Camborne mining districts, sediments were found to contain elevated bioavailable metalloids and metals (Buckley, 2005). The source of this material is primarily related to past mining activity but also reflects naturally elevated background levels associated with the mineralisation (Bowell, et al., 2013). A further study (Neal et al., 2005) measured daily water quality in the River Carnon. The measurements were collected over 18 months in November 1992 to March 1994. Two distinct chemical groups of water were distinguished based on their response to environmental factors. One group comprised of B, Cs, Ca, Li, K, Na, SO_4 , Rb and Sr. The concentrations of these elements decreased with increasing groundwater and sewage flow. The second group, comprised of Al, Be, Cd, Ce, Co, Cu, Fe, La, Pb, Pr, Nd, Ni, Si, Sb, U, Y and Zn, exhibited concentrations that was strongly linked to the acidity of the waters. There was little direct relationship between the concentrations of this group of elements and fluid flow. When compared to the WHO drinking water quality guideline values (WHO, Guidelines for drinking-water quality, fourth edition, 2011), water samples contained pH 3.33 to 6.0 and concentrations of Cd, Ni and Pb exceed recommended values.

2.1 Arsenic related minerals and solubilities

The Camborne and Gwennap mining district contains a considerable array of supergene minerals. For the purpose of this study, several As-bearing minerals have been studied on their environmental occurrence and solubility understanding. Known As-bearing minerals in the environment stated in (Bowell, et al., 2013) included scorodite and liroconite. Other As-bearing minerals are described in Supplementary Information A to give a wider perspective of what minerals can be dominant in a mine tailings system which include: arseniosiderite, geminite, haidingerite, pushcharovskite, yukonite and zýkaite.

Scorodite

Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) water interaction is critical to As distribution and storage in surface environments (Zhu, et al., 2019). Scorodite has a low solubility in a low pH environment and is a common secondary As-bearing mineral in acidic Fe(III)-As(V)- H_2O systems, such as As-contaminated soil and mine wastes (Drahota & Filippi, 2009). Understanding of iron arsenates in the natural environment are still ambiguous but past studies have clearly demonstrated the presence of scorodite from mine waters (Bowell, 2018). The low solubility of scorodite has motivated many studies to suggest the precipitation of this mineral as As fixation strategy in the mining industry (Zhu, et al., 2019). A large number of

studies have reported scorodite solubility over the past six decades (Table 2). Reported values of K_{sp} consistent with the reaction

vary by five orders of magnitude ($10^{-20 \pm 0.58}$ and $10^{-25.81 \pm 0.1}$). These inconsistencies were addressed by (Zhu, et al., 2019) and originated from

1. The effect of crystal size on solubility (natural scorodite crystals are mostly nano-sized, but laboratory synthesised crystals can rarely replicate natural scorodite dimensions);
2. The formation of secondary Fe-containing minerals during incongruent dissolution experiments; and
3. Mis-interpretation of certain solution chemistry effects.

These factors were taken into consideration by Zhu, et al. (2019) who synthesised scorodite crystal ranging in sizes from 10 to 30 μm as measured using scanning electron microphotography. This size range is similar to those found in nature. Scorodite dissolution was investigated at pH 1.15 over the temperature range of 50 – 90°C and measurement were extrapolated to 25°C to obtain thermodynamic properties at room temperature. The estimated scorodite solubility of $10^{-25.81 \pm 0.1}$ specified by Zhu, et al. (2019) agreed with past literature data at low pH conditions but is one to two orders of magnitude smaller than previous values measured as pH > 4.0 – 4.5 as shown in curve A in Figure 3. When ferrihydrite is allowed to precipitate at pH > 4.0 consistent with incongruent dissolution (curve B), however, the match between calculated and measured solubilities are significantly improved, suggesting that previous studies may have provoked incongruent dissolution through iron phase precipitation. Depending on the product precipitated, if goethite precipitated instead of ferrihydrite (curve C), the predicted arsenic release is overestimated at pH > 2.5 but closely matches measured As concentrations collected from acid mining drainage waters at pH 3 stated in Zhu, et al. (2019). Additional data points showing acid mining drainage (AMD) solutions were measured by Zhu, et al. (2019) and closely matches curve C. This is taken into account in this study with a modified PHREEQC database which is explained further in section 3.5.

Liroconite

Variability in the chemical composition and crystal chemical properties of secondary copper minerals lends them for the understanding of the formation and evolution of oxidation zones of ore deposits (Magalhães et al., 1988, Williams, 1990). Among others, copper arsenates are also common and widely distributed minerals in such oxidation zones (e.g. Števkó et al., 2017; Southwood et al., 2020) where they form through weathering of sulfidic minerals in low pH environments. Copper arsenates are capable of taking up and releasing not only copper and

arsenic but also other elements such as lead, zinc, and selenium (e.g. Ingwersen, 1990). Liroconite was named by Wilhelm Karl von Haidinger in 1825 (Mohs and Haidinger, 1825), and before this it was known as octahedral arsenate of copper (de Bournon, 1801). One of the first descriptions of the crystal structure of liroconite was in 1962 as $\text{Cu}_2\text{Al}[\text{((AsP)O}_4\text{)(OH}_4\text{)}].4\text{H}_2\text{O}$ by Giuseppetti et al. (1962).

Natural liroconite is found in the type locality Wheal Gorland at St. Day, Cornwall, UK (Plumhoff et al., 2020). The mine Wheal Gorland is part of the Camborne-Redruth mining district which is situated in Cornwall, the south-western part of Great Britain, approximately 90 km west of Plymouth. The study used a tabular liroconite crystal of 0.080 mm by 0.065 mm by 0.045 mm for the acid-solution calorimetry and relaxation calorimetry, giving a solubility $\log K_{\text{sp}}$ of -4.92 from reaction [2].

3 METHODOLOGY

3.1 World Health Organisation Guideline

Water samples representative of the mine tailings and the Carnon River were collected, and characterised following guidelines (Table 1) where available of the World Health Organization's Guidelines for Drinking-water Quality (WHO, Guidelines for drinking-water quality, fourth edition, 2011). Many national authorities have followed the WHO guideline value of 0.01 mg/L (10 ug/L) for As; only one out of 104 countries set a value below this value (WHO, 2018). The guideline values adapted from WHO's "A global overview of national regulations and standards for drinking water quality" for As, B, Ba, Cd, Cr, Cu, Ni and Pb are deemed appropriate for this study because these values have been obtained and validated against other members of the WHO International Network of Drinking-water Regulators (RegNet).

3.2 Field Methods

Water sampling

Water samples were collected in June 2018 at each of the three tailings ponds and 400 metres along the Carnon River (Figure 1). A summary of the quantity of water samples collected is shown in Table 3. Sampling teflon vials were prepared in the lab using ultra-pure deionised and distilled water (to 18.2 MΩ cm resistivity at +25°C) produced by the VWR Ultrapure water system (VWR, 2019), P series, to prevent contamination from bacterial growth. Each vial was filled with ultra-pure water that were removed and dried thoroughly 12 hours before sampling. At each sampling location, water were extracted using a 0.2 µm Whatman syringe filter and two drops of 2% aqueous nitric acid (HNO₃) were added (dwi, 2005). The pH was measured on site while collecting each sample using a Mettler Toledo 5-easy plus pH probe. The pH probe was calibrated on-site using three buffer solutions, pH 4.0, pH 7.0 and pH 9.21. Detection limit was not applicable. Duplicate samples were collected at each of the tailings ponds.

Rock/Soil sampling

Rocks and soils were sampled in June 2018 at five sites from high to low topography to determine the leachability of material from these solids (the locations are shown in Figure 4). Table 3 summarises the quantity of samples collected and analysed in the study. The top 10 to 20 cm of the surface material was removed prior to collecting these samples. This method was adopted to avoid solids that may have been affected by surface chemical weathering. Samples were then retrieved and stored in separately labelled transparent sample bags (dimensions: 76 x 83 mm). Sampled sediments greater than 0.5 cm in size were considered as rocks, and those less than 0.5 cm as soil. Preliminary elemental analysis was completed using a portable X-Ray Florescent (p-XRF) analyser (Figure 5). The instrument used was the

Olympus Delta XRF Analyser. Calibration was completed using three certified reference materials which include a blank SiO₂, NIST2710a and NIST2711a reference materials given by the provider. A map showing the locations of the p-XRF samples can be found in Supplementary Information B.

3.3 Sample Analysis

Water sample analysis

The collected water samples were stored in a refrigerator prior to analysis. 18 samples were analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES) and the inductively coupled plasma mass spectroscopy (ICP-MS) for the major and minor elements respectively. The analysis was completed on a Varian 720 ICP-OES (axial configuration) equipped with autosampler and a Bruker M90 ICP-MS equipped with autosampler. 3 duplicates and 5 blank samples were analysed simultaneously to assess the reproducibility. The detection limits specified in Table 5 have been removed from the subsequent calculations. Certified reference material TMDA-70 (fortified lake water) was used during the analysis. The duplicate and blank samples together with the TMDA-70 were used to calculate the uncertainties of each analysis and check accuracy and reproducibility. The uncertainty of all elemental analyses were found to be less than +/- 10% when evaluated with TMDA-70. Detailed data processing method can be found in Supplementary Information C.

X-ray diffraction

Samples for diffraction analysis were prepared by side-filling the powder, against a ground-glass surface, into a 1.5 mm wide sample holder and consolidating it by gentle tapping. X-ray powder diffraction data were then collected with Cobalt (Co) Potassium (K) alpha (α) radiation, using a PANalytical X'Pert Pro diffractometer, with Bragg-Brentano para-focusing reflection geometry. The X-ray peaks produced are evaluated using the database provided by the PANalytical HighScore Plus software with the ICDD (International Centre for Diffraction Data) database. The minimum tip width for the searched peaks is 0.01, which corresponded to a relative error of 1%, the counting statistical error. A more detailed methodology can be found in Supplementary Information D.

3.4 Geochemical Calculations

Thermodynamic calculations in this study were computed with PHREEQC (version 3.5.0.14000) together with a modified version of the WATEQ4F.v4 database (Parkhurst & Appelo, 2013). This database was selected for this study because it includes the all of elements considered for this study of water quality in a mine tailings environment. The solubility constant of scorodite in the database was updated from $10^{-20.25}$ to $10^{-24.5}$. This scorodite solubility constant value concurs with the value from that published in literature (Zhu,

et al., 2019), as pure scorodite does not occur in the natural environment. As discussed in section 2, a solubility constant of $10^{-24.5}$ closely matches with measured As concentrations collected from acid mining drainage waters in low acidic pH waters. Thus, the modified value for the scorodite + goethite system is more fitting for an acid mine drainage environment.

The pH of the mine drainage waters was measured in-situ but the temperature and pe at the site were not. Samples were taken during June, hence, calculations were performed assuming an average temperature of 25°C. The pe was assumed to be in equilibrium (SOEST, 2008) with the atmosphere such that:

- $pe = -pH + 20.85$

The objective of the geochemical calculations is to verify site observations with the analysed data and to validate the thermodynamic data available in the literature, as detailed above.

3.5 Additions to PHREEQC database

Nordstrom et al., 2014 described the PHREEQC thermodynamic database as an over-determined network in a theoretical sense, but also contains large uncertainties. This inconsistency led to the idea of evaluating previous literature on how solubility measurements were made, in return to limit the use of solubility products measured where large impurities were present. Wagman et al., 1982 pointed out that typically two methods have been used to evaluate thermodynamic data, the sequential method, and the simultaneous fit method. In this study, a mixture of both techniques have been used and the solubility product values added to the PHREEQC WATEQ4F.v4 database are shown in Table 4. The details on how the updated thermodynamics of the As-bearing minerals are found in section 2.1 and in Supplementary Information A.

4 RESULTS

4.1 Mineralogy of the Mine Site

Mineralogical samples collected from the Wheal Maid (Figure 4) were found to be similar in composition confirming a similar style of mineralisation. Whole-sample XRD demonstrated that the predominant mineralogy for sand, silt and clay fractions are quartz, muscovite and chlorite. The XRD patterns produced are presented in Supplementary Information E. Cassiterite, dickite, lizardite ($\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$), tourmaline are also present. These occurrences depend on local geology and weathering of nearby outcrops. Of the samples taken, the products identified by XRD include jarosite, goethite and pyrite (FeS_2). Table 6 summarises the major and minor minerals. The major and minor minerals are characterised by the abundance of clusters in which the XRD identifies. Minor rutile (TiO_2), arsenopyrite (FeAsS), arsenian pyrite ($\text{Fe}(\text{As},\text{S})\text{S}$), löllingite (FeAs_2), tennantite-tetrahedrite ($\text{Cu}_{10}(\text{Zn},\text{Ag},\text{Fe})_2(\text{As},\text{Sb})_4\text{S}_{13}$) have previously been reported at these sites, but were not observed in this study (Bowell, et al., 2013).

4.2 Bulk Geochemistry

Geochemistry of rocks and soils

The arsenic concentrations in the soil samples range from 0.001 pp, to 1 ppm as measured using the p-XRF (Figure 5). The results of the other metal concentrations such as Al, Fe and K can be found in Supplementary Information F. The concentration of all these parameters tend to increase with decreasing elevation. The highest concentrations of As and K were found at the lowest elevation (sites 23 to 25). This is an indication the metals are being leached. Some data-points lack measurements which are most likely due to concentrations lower than the detection limit.

Hydrogeochemistry in the vicinity of the mine site

To assess background levels of As in surface water, three tailings ponds and five river water samples were collected and analysed using ICP-OES and ICP-MS. The concentrations are compared with the WHO drinking water guideline values. Figure 6 delineates the As chemistry in each of the monitoring points. The accumulation of metals in the tailings ponds results in highly acidic waters (pH 2-3) with As concentrations 2 orders of magnitude above the WHO drinking water guideline value (0.01 mg/L). Other elements with concentrations exceeding the WHO drinking water guideline values are Cd, Cr, Cu, Ni and Pb. In the Carnon River, arsenic concentrations were 1 – 2 orders of magnitude above the 0.01 ppm WHO water quality limits despite the pH being circum-neutral (pH 6-7). The pH of the waters were made near to neutral pH by the dilution of tailings pond waters with groundwater.

345 Several elements including Cr, Cu and Ni had concentrations below the WHO limits in the river
346 water, but Cd and Pb concentrations remained to be above the drinking water guidelines.

5 DISCUSSION

5.1 Mass balance calculation

Taking account of the conceptual model in Section 1.2, water flows downstream from the tailings pond and enters the Carnon River through a controlled water barrier. The dilution of tailings pond water with subsurface water was a strategy created by previous land remediation efforts. The flow rate of the waters from the tailings pond and the underground source were not measure, hence, the mixing ratio of these waters was estimated through onsite observation of the quantity of water flowing from each source entering the river. The estimated mixing ratio of water entering the Carnon River comprises of 15% tailings pond water and 85% subsurface underground adit-water. This mixing ratio is understood to be representative as the majority of water entering the main river was observed to be from the underground source.

5.2 Geochemical Calculations

The water chemistry at the monitoring points delineated in section 4.2 was used as inputs (Table 7) to the PHREEQC geochemical model and the saturation index (SI) of minerals was calculated. The SI of a mineral indicates the “tendency” of the water to want to precipitate the mineral, if the SI is at or above 0 (the solubility equilibrium, it indicates that the water wants to precipitate the mineral. The SI of the mine runoff waters before and after dilution with respect to scorodite is shown in Figure 7A which indicates that the SI ranges from -2.75 to +2.5. Scorodite is supersaturated in the second tailings pond water and in the marshland of the river which suggests that precipitation of the mineral is likely and can be a factor controlling As mobility in the waters.

Using the provided mixing ratios described in section 5.1, the water chemistry at the monitoring points were mass balanced and used as inputs to the PHREEQC geochemical model to produce the SI of scorodite downstream of the mixing zone (Figure 7B). The four orange bars represents the four monitoring points where predictions are made. Three out of four predictions are noticeably similar to the site measurement. The constrains placed on the water calculations involved changing pH (+/- 2 s.u. from pH 7) shown in Figure 7C. The bar chart suggests that changing pH alters the saturation index of scorodite significantly in the waters. With an increase of pH units (more alkaline), the water becomes heavily under-saturated in terms of the As-bearing mineral. However, in a more acidic environment (lower pH) the solubility of As is little affected.

The result of the mass balance indicate that an increase of pH leads to the waters becoming increasingly undersaturated with respect to scorodite. The SI of other As minerals have been studied but all minerals are shown to be heavily undersaturated in the waters, hence, scorodite is the most likely mineral to be controlling As concentration in the water. Thus, it may be

expected that increasing the pH could lead to the enhanced concentration and mobility of As in the water. Due to the decades of infiltration of mine tailing water into the groundwater system, the dilution mechanism used previously does not prove to be effective as the water chemistry from the groundwater outlet is very similar to those found in pond C of the mine tailings delineated in Figure 6.

5.3 Environmental Consequences

Sampling of surface soil and water at Wheal Maid identified the presence of elevated As content related to the mining activities and re-distribution of that As in response to chemical weathering and surface runoff. This is shown from the leaching of metals to the lower elevations delineated in Figure 5. The mining activity and formation of the tailings dam in the nineteenth century led to faster weathering rates of the clay-rich shale and hornfels country rock through the disturbance of the natural geology. The high abundance of clay minerals found in the sampled rocks (Table 6) may be a contributing factor in the increased As after the weathering processes.

Elevated As concentration was found in the soil and water samples of the Wheal Maid. This is similar to the high As concentrations found in the overburden at other mines such as Higher Condurrow and Wheal Fortune (Bowell, et al., 2013). In such systems, oxidized iron can form secondary As(+V) mineral phases or minerals that absorb As. This is observed in the SI values of the PHREEQC output using site measured chemistry. The mass calculation concludes that scorodite may be a controlling factor of the high As in the water, as the SI values of scorodite through the monitoring points lie very close to the equilibrium line (Figure 7). Therefore, slight changes in the saturation index of scorodite could result in major changes in the concentration of As in the water. Efforts were made to find other common As-bearing minerals in a mining environment such as: arseniosiderite, geminite, and others, but all the SI values were extremely negative, hence, were not investigated further.

6 CONCLUSIONS

Wheal Maid mine tailings is integrated along a wider mining network known as 'the Great County Adit' that contains elevated concentrations of numerous potentially toxic metal(loid)s. The source of these metal(loid)s is related to past mine waste and disturbance of clay-rich country rocks leading to faster weathering rates from placing waste products in mine tailings sites. Arsenic concentrations in waters along the tailings dam and Carnon River range up to 3.6 mg/L which is more than 2 orders of magnitude above the WHO guideline value of 0.01 mg/L for drinking water.

This study indicated that the soil and water of mine tailings at Wheal Maid has the potential of releasing As and precipitating As-bearing minerals. The sampling programme captures information for the site during a relatively the summer period but could be improved by monthly sampling to monitor seasonal fluctuations in one year. The SI of scorodite was near to equilibrium indicating precipitation of the mineral is likely, however, it doesn't conclude that it is the sole mineral controlling As concentrations. This study highlights the need to better understand As-bearing minerals and slight environmental changes such as increase alkalinity in waters may cause serious consequences in an industrial setting.

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653 **TABLE CAPTIONS**

654 Table 1: WHO Drinking Water Quality Guideline Values (WHO, 2011)

655 Table 2: Summary of scorodite solubility data available in the literature

656 Table 3: Summary of the quantities, location and purpose of samples taken

657 Table 4: Solubility data added to the PHREEQC database

658 Table 5: Water quality analysis limit of detection

659 Table 6: Summary of rock mineralogical composition from XRD analysis (chemical formula)

660 Table 7: Water Chemistry Inputs into PHREEQC

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TABLES

Table 1: WHO Drinking Water Quality Guideline Values (WHO, 2011)

Element	WHO Drinking Water Quality Guideline Values (ppm)
As	0.01
B	2.4
Ba	0.7
Cd	0.003
Cr	0.05
Cu	2
Ni	0.07
Pb	0.01

689 *Table 2 : Summary of scorodite solubility data available in the literature*

Reference	Medium used	Temperature (°C)	pH Initial Average	pH Final Average	pH Range	Logarithm of the Solubility Constant
Chukhlantsev 1956	Sulfuric Acid (H ₂ SO ₄)	20	N/A	2.31	1.9 – 2.95	-20 ± 0.58
Nishimura & Tozawa 1978	Nitric Acid (HNO ₃)					
	Sulfuric Acid (H ₂ SO ₄)	25	N/A	2.45	1 – 4	-21.1
Robins 1987	Perchloric Acid (HClO ₄)	25	N/A	1.47	0 – 2	-22.3
	Sulfuric Acid (H ₂ SO ₄)					
	Nitric Acid (HNO ₃)					
(Dove & Rimstidt, 1985)	Hydrochloric Acid (HCl)	25	5.57	6.02	5.53 – 6.36	-21.7 ± 0.5
	Sodium Hydroxide (NaOH)					
(Krause & Ettel, 1988)	Sulfuric Acid (H ₂ SO ₄)	23	1.58	1.84	0.97 – 2.00	
(Krause & Ettel, 1988) using Incongruent dissolution	Sodium Hydroxide (NaOH)	23	From 3.45 to 12.36	From 2.55 to 7.92	3.45 – 7.92	Overall average -24.41 ± 0.15
	Sulfuric Acid (H ₂ SO ₄)					
(Zhu, et al., 2019)	Hydrochloric Acid (HCl)	50-90 (extrapolated to 25)	1.5			-25.81

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695 *Table 3: Summary of the quantities, location and purpose of samples taken*

Type of Sample	Quantities	Location Description
Water	18	In the three mine tailings ponds and 400 m along the Carnon River. Duplicate samples were made in each of the three mine tailings ponds.
Solid (p-XRF)	25	Throughout the mine and in regular intervals along the Carnon River
Solid (XRD)	5	Sampled from the highest to the lowest elevation points
Soil	5	Sampled from the highest to the lowest elevation points

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699 *Table 4 : Solubility data added to the PHREEQC database*

Additional Phases	Log K	Reference papers
Arseniosiderite	-21.6	Paktunc et al., 2015
Pushcharovskite	-17.2	Plumhoff et al., 2020
Geminite	-15.9	Plumhoff et al., 2020
Liroconite	-4.92	Plumhoff et al., 2020
Zýkaite	-77.0	Majzlan et al., 2015
Haidingerite	-4.79	Bothe and Brown (1999b)
Scorodite	-24.5	Zhu, et al., 2019

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712 *Table 5 : Water quality analysis limit of detection*

Limit of Detection Table		
Parameters	Units	Concentration
Ag	mg/L	1.9E-06
Al	mg/L	0.06
As	mg/L	2.9E-04
B	mg/L	0.07
Ba	mg/L	0.02
Be	mg/L	0.004
Ca	mg/L	0.06
Cd	mg/L	0.04
Co	mg/L	0.01
Cr	mg/L	0.01
Cu	mg/L	0.02
Fe	mg/L	0.002
K	mg/L	0.002
Li	mg/L	5.0E-06
Mg	mg/L	0.001
Mn	mg/L	1.2E-04
Mo	mg/L	0.04
Na	mg/L	4.3E-06
Ni	mg/L	0.01
Pb	mg/L	0.30
V	mg/L	0.001
Zn	mg/L	0.03

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716 *Table 6: Summary of rock mineralogical composition from XRD analysis (chemical formula)*

Rock Sample Location	Major Composition	Accessory Minerals
1	Quartz (SiO ₂) Chlorite ((Mg,Fe,Li) ₆ AlSi ₃ O ₁₀ (OH) ₈) Muscovite (KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂)	
2	Quartz (SiO ₂) Chlorite ((Mg,Fe,Li) ₆ AlSi ₃ O ₁₀ (OH) ₈) Muscovite (KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂)	Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)
3	Quartz (SiO ₂) Chlorite ((Mg,Fe,Li) ₆ AlSi ₃ O ₁₀ (OH) ₈) Muscovite (KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂)	Pyrite Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)
4	Quartz (SiO ₂) Muscovite (KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂)	Dickite (Al ₂ Si ₂ O ₅ (OH) ₄) Jarosite (KFe ³⁺ ₃ (OH) ₆ (SO ₄) ₂) Tourmaline (Na(Fe ²⁺ ₃)Al ₆ (Si ₆ O ₁₈)(BO ₃) ₃ (OH) ₃ (OH))
5	Quartz (SiO ₂) Chlorite ((Mg,Fe,Li) ₆ AlSi ₃ O ₁₀ (OH) ₈) Muscovite (KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂)	Jarosite (KFe ³⁺ ₃ (OH) ₆ (SO ₄) ₂) Goethite (FeO(OH)) Schorl (Na(Fe ²⁺ ₃)Al ₆ (Si ₆ O ₁₈)(BO ₃) ₃ (OH) ₃ (OH)) Cassiterite (SnO ₂)

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720 *Table 7: Water Chemistry Inputs into PHREEQC*

Parameters	Units	Locations								
		Pond A	Pond B	Pond C	Mixing Zone 1	Mixing Zone 2	Mixing Zone 3	River 1	River 2	River 3
pH	s.u.	7.84	2.56	2.57	2.71	8	6.67	6.8	7.16	7.28
Ag	mg/L	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Al	mg/L	0.02	0.33	7.83	12.2	0.05	0.27	0.42	0.92	0.51
As	mg/L	0.002	0.268	0.001	0.008	0.004	0.002	0.003	0.035	0.002
B	mg/L	0.026	0.070	0.150	0.120	0.021	0.029	0.029	0.040	0.026
Ba	mg/L	0.0003	0.0001	0.0004	0.0002	0.0002	0.0003	0.0007	0.0005	0.0004
Be	mg/L	0.0001	0.0002	0.0013	0.0010	0.0001	0.0001	0.0000	0.0001	0.0001
Ca	mg/L	4.49	20.0	5.35	3.02	11.3	12.4	11.9	18.1	12.4
Cd	mg/L	0.0003	0.083	0.066	0.076	0.0002	0.0001	0.0003	0.0053	0.0007
Cl	mg/L	13.4	13.7	17.2	16.2	20.7	21.6	21.5	18.5	21.8
Co	mg/L	0.0003	0.103	0.184	0.197	0.003	0.004	0.006	0.004	0.005
Cr	mg/L	0.0012	0.03	0.03	0.04	0.0009	0.0006	0.0014	0.0013	0.0014
Cu	mg/L	0.03	9.62	9.88	10.0	0.15	0.10	0.17	0.20	0.19
Fe	mg/L	0.043	0	1.73	1.71	0.21	0.18	0.53	0	0.62
K	mg/L	1.72	0.64	1.16	0.60	4.04	4.18	4.13	0.69	4.18
Li	mg/L	0.0025	0.2062	0.4686	0.4902	0.0033	0.0052	0.0063	0.0051	0.0065
Mg	mg/L	1.99	11.4	15.4	3.17	3.43	3.76	3.72	4.47	3.85
Mn	mg/L	0.05	3.02	7.97	7.66	0.04	0.08	0.09	0.56	0.12
Mo	mg/L	0.003	0.003	0.003	0.002	0.003	0.001	0.003	0.003	0.003
Na	mg/L	8.70	8.87	11.2	10.5	13.4	14.0	14.0	12.0	14.1
Ni	mg/L	0.006	0.198	0.324	0.332	0.004	0.002	0.009	0.009	0.005
Pb	mg/L	0.002	0.066	0.019	0.022	0.002	0.014	0.005	0.005	0.004
Ru	mg/L	8.93E-06	6.30E-06	3.08E-06	3.10E-06	0	3.30E-06	2.60E-06	3.10E-06	2.10E-06
S(6) as CaCO ₃	mg/L	38.5	77.0	77.0	38.5	38.5	38.5	38.5	38.5	38.5
V	mg/L	1.01E-05	2.08E-04	3.94E-05	6.47E-05	1.00E-05	9.20E-06	3.03E-05	2.54E-05	1.06E-04
Zn	mg/L	0.048	0.273	0.530	0.505	0.098	0.331	0.411	0.059	0.444

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728 **FIGURE CAPTIONS**

729 Figure 1: Map of St Day, Cornwall, South-west England and the location of Wheal Maid,
730 Poldice Valley with annotated water sampling localities including the mine tailings pond 1 – 3
731 and along the Carnon River

732 Figure 2: Conceptual model for the flow of water through the tailings to the Carnon River.
733 Numberings delineate chemical input parameters used in mass balance calculation:

- 734 1. *Water leaving tailings pile*
735 2. *Water from underground adit prior to mixing*
736 3. *Water in Carnon River after mixing*

737 Figure 3: Arsenic concentrations in equilibrium with scorodite at 25°C calculated assuming its
738 A) congruent dissolution B) incongruent dissolution due to ferrihydrite precipitation at local
739 equilibrium and C) incongruent dissolution calculation due to goethite precipitation at local
740 equilibrium. Calculated curves can be compared to reported experimental data as indicated
741 by the symbols.

742 Figure 4: Localities of rock and soil sampling and the elevation difference created using
743 ArcGIS

744 Figure 5: Arsenic concentration in the soil in mg/L measured on p-XRF

745 Figure 6: Arsenic concentration in the water compared to WHO guidelines (WHO, 2011). The
746 location names are as follow: (A) Tailings Pond A; (B) Tailings Pond B; (C) Tailings Pond C;
747 (D) Carnon River.

748 Figure 7: Saturation index (SI) of scorodite along the mine drainage pathway. (A) SI using
749 measured chemistry; (B) SI comparison of measured (blue) and mass balanced (orange); (C)
750 SI change varying pH +/- 2 from natural conditions

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752 **FIGURES**

753 *Figure 1: Map of St Day, Cornwall, South-west England and the location of Wheal Maid,*
754 *Poldice Valley with annotated water sampling localities including the mine tailings pond 1 – 3*
755 *and along the Carnon River*

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760 Figure 2: Conceptual model for the flow of water through the tailings to the Carnon River.

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Figure 3: Arsenic concentrations in equilibrium with scorodite at 25°C calculated assuming its
A) congruent dissolution B) incongruent dissolution due to ferrihydrite precipitation at local
equilibrium and C) incongruent dissolution calculation due to goethite precipitation at local
equilibrium. Calculated curves can be compared to reported experimental data as indicated
by the symbols. (taken from Zhu et al., 2019)

769 Figure 4: Localities of rock and soil sampling and the elevation difference created using
770 ArcGIS

771 *Figure 5: Arsenic concentration in the soil in mg/L measured on p-XRF*

773 *Figure 6: Arsenic concentration in the water compared to WHO guidelines (WHO, 2011). The*
774 *location names are as follow: (A) Tailings Pond A; (B) Tailings Pond B; (C) Tailings Pond C;*
775 *(D) Carnon River.*

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777

778 *Figure 7: Saturation index of Scorodite along mine*
 779 *(A) Measured water quality data*
 780 *(B) Comparison of measured (blue) and mass balanced (orange)*
 781 *(C) SI change varying pH +/- 2 from natural conditions of mass balanced values*

A)

B)

C)

SUPPLEMENTARY INFORMATION

Supplementary Information A - Other As-bearing minerals – natural occurrences and thermodynamic properties

Supplementary Information B – Map and elevation (metres above sea level) of p-XRF sampling localities

Supplementary Information C – Data Analysis Methodology

Supplementary Information D – XRD Analysis Methodology

Supplementary Information E – XRD Results of Rocks 1 to 5

Supplementary Information F – Soil chemistry from p-XRP

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797 **Supplementary Information A**

798 Other As-bearing minerals

799 Ca-Fe arsenates such as yukonite and arseniosiderite are important constituents of mine
800 wastes resulting from the processing of some gold and base metal ores and neutralisation of
801 acidic effluents (Paktunc et al., 2015). Both of them minerals occur as secondary alteration
802 products in relation to the oxidation of arsenopyrite and arsenian pyrite and as discrete grains
803 in mine tailings and contaminated soils. Although the understanding of the conditions
804 promoting their formation and dissolution is limited, the study by Paktunc et al., 2015 found
805 both minerals readily form from solutions with highly variable compositions at a wide pH range
806 from slightly acidic to alkaline conditions. A mixture of synthesis and calorimetric experiments
807 were carried out to form arseniosiderite and yukonite. It was found that the formation of
808 arseniosiderite is kinetically controlled with faster development of crystallinity at neutral to
809 slightly acidic pH and slower kinetics under alkaline conditions. The resultant log K_{sp} values
810 for arseniosiderite and yukonite are -21.6 and 6.88 respectively.

811 Geminite and pushcharovskite are Cu arsenates and are commonly distributed minerals in
812 oxidised ore deposits. Geminite was reported as a new species by Sarp and Perroud (1990)
813 on material from Cap Garonne (Var, France) as $\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O})$. Pushcharovskite was
814 described later by Sarp and Sanz-Gysler (1997) on material from the same site with the same
815 ideal chemical composition and space group $P-1$. They concluded that pushcharovskite is a
816 polymorph of geminite and structurally related to yvonite $(\text{Cu}.\text{AsO}_3\text{OH})(\text{H}_2\text{O}).\text{H}_2\text{O}$ (Plumhoff et
817 al., 2020). Their thermodynamic properties were determined by a combination of acid-solution
818 calorimetry and relaxation calorimetry, resulting in Gibbs free energies of formation ($\Delta_f G^\circ$, all
819 values in kilojoules per mole) of -1036.4 +/- 3.8 (pushcharovskite, $\text{C}(\text{Cu}.\text{AsO}_3\text{OH})(\text{H}_2\text{O}).\text{H}_2\text{O}$
820 and -926.7 +/- 3.2 (geminite, $\text{Cu}(\text{AsO}_3\text{OH})(\text{H}_2\text{O})$). The resultant log K_{sp} values for geminite and
821 pushcharovskite are -15.88 and -17.21 respectively.

822 Zýkaite nominally $\text{Fe}_4(\text{AsO}_4)_3(\text{SO}_4)(\text{OH}).15\text{H}_2\text{O}$, is a common ferric arsenate in damp, moist
823 environments, especially in underground spaces where the humidity does not decline during
824 the year and the temperature fluctuations are minimal. The natural sample used in this study
825 had chemical composition $\text{Fe}_{1.23}(\text{AsO}_4)_{0.93}(\text{PO}_4)_{0.07}(\text{SO}_4)_{0.31}(\text{OH})_{0.07}.5.89\text{H}_2\text{O}$ and typical
826 poor crystallinity. In order to construct phase diagrams for the system $\text{Fe}_2\text{O}_3\text{--As}_2\text{O}_5\text{--SO}_3\text{--}$
827 H_2O , without constraining the activity of phosphate and considering the ferric phosphates, we
828 have re-interpreted the solubility data and calculated an equilibrium constant of log $K_{sp} = -$
829 76.98 for the reaction:

Supplementary Information B

Map and elevation (metres above sea level) of p-XRF sampling localities

Supplementary Information C

Water data analysis

Results were produced in an Excel Spreadsheet format. For determination of reproducibility, the limit of detections (LODs) was calculated using the blank and the standard solution data. Comparison of the LODs with the field sample data-set found a majority of values were above the LOD. The average LOD from the ICP-AES and ICP-MS were under 0.1 ug/L, indicating high precision measurements were made for most elements. In addition, the ICP-MS data produced and adapted in this study were found to have differences of lower than 15% compared against the certified water reference material (TMDA 70). The resulting data were plotted in respect of the distance from the mine tailings pond and along the Carnon River

Reference source not found..

Supplementary Information D

XRD Analysis Methodology

Samples were prepared by side-filling the powder, against a ground-glass surface, into a rectangular sample holder 1.5 mm deep and consolidating it by gentle tapping. X-ray powder diffraction data were then collected with Cobalt (Co) Potassium (K) alpha (α) radiation, using a PANalytical X'Pert Pro diffractometer, with Bragg-Brentano para-focusing reflection geometry. This instrument is equipped with a Ge(1 1 1) Johansson geometry focusing monochromator, producing a CoK α 1 incident beam. The X-ray tube was operated at 40 kV and 30 mA. Variable-width divergence and anti-scatter slits were used in the incident-beam and diffracted-beam optics, together with a 15 mm wide beam mask in the incident beam, so as to illuminate a constant 12 x 15 mm area of the sample; 0.04 radian Soller slits were present in both the incident and diffracted beams to reduce the axial divergences. The X-ray detector was an "X'Celerator" position-sensitive detector; this device covers an angular range in 2θ of ± 1.061 degrees, with an effective fixed step size of 0.0167 degrees. The minimum tip width for the searched peaks is 0.01, which corresponded to a relative error of 1%, the counting statistical error. The PANalytical HighScore Plus software was then used to convert the data to fixed-divergence slit geometry, determine the peak positions and intensities and determine the phases present in the sample by comparison with the ICDD (International Centre for Diffraction Data) database.

884 **Supplementary Information E**
Site

Pattern List			
Compound Name	Scale Fac.	Chem. Formula	Colour
Quartz	0.997	SiO ₂	Red
Muscovite	0.163	KAl ₂ (AlSi ₃ O ₁₀)(FOH) ₂	Blue
Clinocllore	0.127	Mg ₅ Al(AlSi ₃ O ₁₀)(OH) ₈	Green

Site 2

Pattern List			
Compound Name	Scale Fac.	Chem. Formula	Colour
Quartz	0.922	SiO ₂	Red
Chamosite	0.147	(Fe ²⁺ ,Mg,Al,Fe ³⁺)6(Si,Al) ₄ O ₁₀ (OH,O) ₈	Green
Muscovite	0.120	KAl ₂ (AlSi ₃ O ₁₀)(FOH) ₂	Blue
Muscovite	0.102	KAl ₂ (AlSi ₃ O ₁₀)(FOH) ₂	Black
Kaolinite	0.045	Al ₂ (Si ₂ O ₅)OH ₄	Olive Green

Site 3

Pattern List			
Compound Name	Scale Fac.	Chem. Formula	Colour
Quartz	0.993	SiO ₂	Red
Chamosite	0.377	Mg _{5.036} Fe _{4.964}	Green
Muscovite	0.311	K _(0.82) Na _(0.18)	Blue
Pyrite	0.018	FeS ₂	Olive Green
Jarosite	0.040	(K,H ₃ O)Fe ₃	Brown

Site 4

Pattern List			
Compound Name	Scale Fac.	Chem. Formula	Colour
Quartz	0.987	SiO ₂	Red
Muscovite	0.128	KAl ₃ Si ₃ O ₁₀	Blue
Potassium sodium tecto-alumosilicate	0.056	K _{0.94} Na _{0.06} Al	Green
Dickite	0.032	Al ₂ Si ₂ O ₅ (OH) ₄	Olive Green
Jarosite	0.019	K(Fe ₃ (SO ₄) ₂)	Brown
Schorl	0.016	NaFe ₃ Al ₆ (BO ₃)	Sky blue

Site 5

Pattern List			
Compound Name	Scale Fac.	Chem. Formula	Colour
Quartz	0.990	SiO ₂	Red
Muscovite	0.119	(K _{0.727} Na _{0.170} C)	Blue
Chamosite	0.133	(Mg _{5.036} Fe _{4.964})	Green
Jarosite	0.038	K(Fe ₃ (SO ₄) ₂)	Brown
Goethite	0.043	FeO(OH)	Lavender
Schorl	0.031	NaFe ₃ Al ₆ (BO ₃)	Sky Blue
Cassiterite	0.417	Sn _{0.912} O ₂	Grey

Site 1 – Claudetite

Pattern List		
Compound Name	Chem. Formula	Colour
Quartz	SiO ₂	Red
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(FOH) ₂	Blue
Clinocllore	Mg ₅ Al(AlSi ₃ O ₁₀)(OH) ₈	Green
Claudetite	As ₂ O ₃	Black

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