Dissolution Rates of Arsenic Minerals in Natural and Mining Environments, New Zealand

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Abstract

Mineral solubility is widely recognised as a control on environmental release of dissolved arsenic. Thermodynamic modelling indicates that most arsenic minerals are readily soluble when exposed to surface waters. However, field observations and actual measurements demonstrate that in some environments, these thermodynamically predicted solubilities are overestimated. This study compiles empirical observations made on several arsenic minerals across a range of sites in New Zealand. These observations were made on natural settings and at mine sites and cover a range of time scales, from months in the case of kinetic leach tests, decades in historic mine wastes, to millions of years in natural settings.

We have observed widespread arsenopyrite (FeAsS) in oxic settings, despite it being thermodynamically unstable in oxygenated environments. In each case, the arsenopyrite has a coating of As-bearing Fe-oxyhydroxide and/or scorodite ($FeAsO_4.2H_2O$). Further, scorodite is theoretically highly soluble under circumneutral-alkaline conditions, but secondary scorodite, kankite ($FeAsO_4.3.5H_2O$) and bukovskyite ($Fe_2(AsO_4)(SO_4)$ $(OH).7H_2O$) can remain essentially unaffected by rain and surface water runoff, with minor local mobilisation and recrystallization.

Arsenolite (As_2O_3) is generally regarded as highly soluble; solubility studies show that arsenolite dissolution can yield 12 g/L dissolved As. Our empirical observations have seen a maximum of "only" 0.3 mg/L dissolved As in saturated historic mine tailings and arsenolite has remained largely intact for 80 years. In a lab experiment to simulate arsenopyrite dissolution in waste rock with monthly water inundation, dissolved As levels reached 16mg/L and an arsenolite coating formed on the arsenopyrite surface which persisted after subsequent inundations.

We find that the processes and physical parameters that control the dissolution rates of arsenic minerals are complex; and grain size, surface area, secondary mineral armouring and subsequent encapsulation are important factors. Our observations provide some context for further research of dissolution rates of arsenic mineral solubilities.

Keywords: Arsenic, Dissolution rates, Solubility, Arsenopyrite, Scorodite, Arsenolite.

Introduction

Most arsenic minerals are predicted to be readily soluble in surface waters by thermodynamic modelling. However, actual measurements at mine sites suggest that the thermodynamically predicted solubilities overestimate the likely dissolved arsenic levels in associated waters. Dissolution rates of arsenic minerals are limited by exposed surface areas and grain sizes. These dissolution rates are further hindered by development of secondary mineral armouring and associated encapsulation. We have compiled empirical observations on a range of common arsenic minerals occurring in both natural and mine-related settings in New Zealand, and on timescales ranging from months to millions of years, to provide some context for further research and quantification of dissolution rates (Figure 1).

Methods

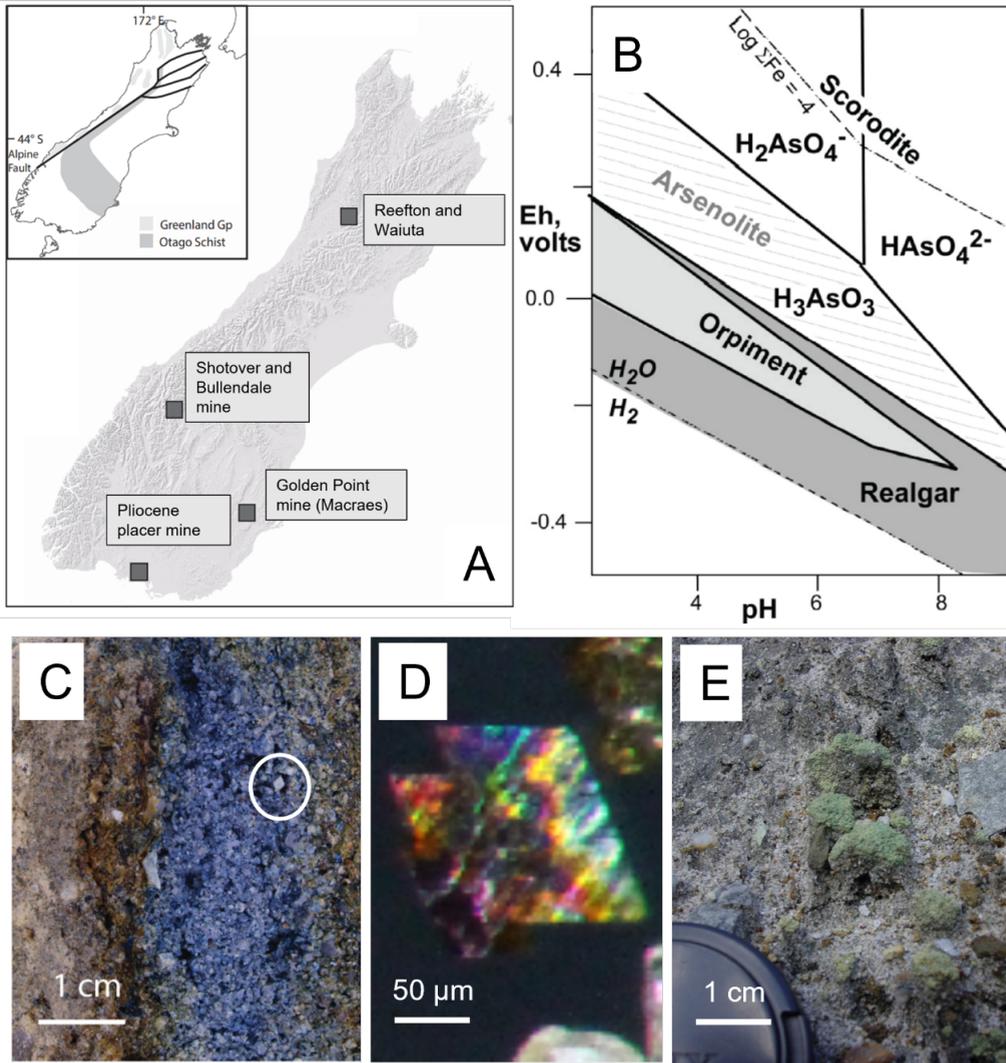Arsenic mineral phases were identified with standard incident and transmitted light

Figure 1 (a) Location of study sites and regional geological setting. (b) Summary Eh-pH diagram (compiled from Geochemists Workbench and Vink 1996; partly modified from Craw and Kerr 2017) showing the predicted relationships of As minerals based on thermodynamic modelling. (c-d) Examples of minimally altered detrital arsenopyrite in oxic conditions. (c) Euhedral arsenopyrite crystal surrounded by scorodite (blue) and Fe oxydroxide (brown) in ca. 80-year-old mine wastes. (d) Tarnished detrital arsenopyrite from Pliocene-age gravels in a placer mine, Southland. (e) Kankite (green, centre) on surface of ca. 100-year-old tailings, pH 8; Bullendale historic gold mine, Shotover.

microscopy and X-ray diffraction (XRD). XRD analysis was performed on a PANalytical X'Pert Pro MPD PW3040/60 diffractometer housed in the Geology Department, University of Otago. High Score Plus and ICDD PDF-4 software packages were used for phase identification. Further detailed characterisation of solid materials utilised a Zeiss Sigma VP (variable pressure) SEM fitted with a HKL INCA Premium Synergy Integrated EDX system at the Otago Centre for Electron Microscopy (OCEM), University of Otago. Samples were mounted into epoxy blocks or on pin stubs and carbon-coated prior to examination. Due to the inhomogeneous nature of the samples, and irregular surfaces, analyses of As is semiquantitative, with a detection limit of ≈ 0.5 wt%.

Laboratory studies of arsenic dissolution rates were conducted using a leach column containing arsenopyrite rich ore collected from a modern mine site near Reefton, West Coast. The leachate was filtered and analysed using ICP-MS at Hill Laboratories, Hamilton to determine dissolved metal concentrations. Encrustations of fine-grained crystalline material developed on the surfaces of the arsenopyrite-rich ore fragments. After 6 months, samples were examined using the SEM. The morphologies and compositions of crystals were determined, and the textures of the original rock fragment surfaces were examined in detail to detect evidence for dissolution.

Arsenopyrite and scorodite

Arsenopyrite (FeAsS) is thermodynamically unstable in any oxygenated environment, but arsenopyrite is widespread in 5–20-million-year-old oxic settings, in supergene oxide zones of orogenic mines, in placer gold deposits, and in historic mine processing wastes (Fig 1c-d, Fig 2; Craw 2017; Kerr *et al* 2018). The arsenopyrite ranges from almost completely oxidised to minimally altered (Fig 1c-d, Fig 2a-b). Minimally altered arsenopyrite is frequently observed to have a coating of As-bearing Fe-oxyhydroxide, scorodite (Fig 2a) or kankite (Fig 2b) which likely has an 'armouring' effect limiting further dissolution.

Scorodite ($FeAsO_4.2H_2O$) is theoretically highly soluble under circumneutral-alkaline conditions, but secondary scorodite coatings and veins in 80–100-year-old mine wastes exposed to the high-rainfall environment of the West Coast remain intact with little discernible dissolved As downstream (Fig 1c, Fig 3; Haffert and Craw 2008). Similarly, at sites in the Otago region, surface kankite ($FeAsO_4.3.5H_2O$) and bukovskyite ($Fe_2(AsO_4)(SO_4)(OH).7H_2O$) appear unaffected by rain and surface water runoff, with only minor local mobilisation and recrystallization despite the neutral to alkaline conditions of the wider environment (Fig 1e, Fig 3a-b, Haffert and Craw 2010; Haffert, Craw & Pope 2010; Kerr & Craw 2021a).

At Waiuta, West Coast, some of that local remobilisation leads to precipitation of realgar and related As sulfides, limiting dissolved As release to the wider environment (Fig 3c-d; Kerr *et al* 2018; Kerr & Craw 2021b). These As sulfides form under reducing conditions (Figure 1b) yet are visible on exposed surfaces (Fig 3c-d). The presence of organic matter, and water saturated conditions, have created reductive microenvironments and facilitated the precipitation of these rare secondary arsenic minerals (Kerr *et al*, 2018). The As sulfides are closely associated with other arsenic phases (Fig 3c) and replacement and/or cycling between the phases may occur as environmental conditions fluctuate.
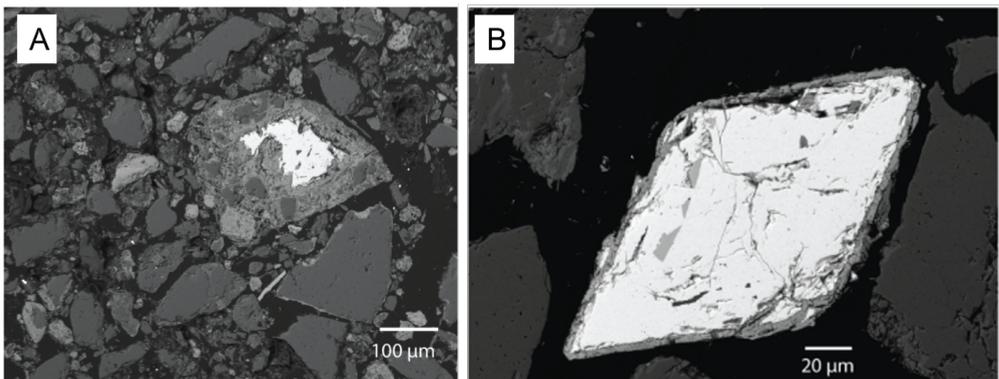

Figure 2 Arsenopyrite in ca. 80 year old mine wastes, West Coast, New Zealand. (a) Partially weathered primary arsenopyrite crystal (bright white) with wide scorodite rim. Lighter grey grains (i.e. centre left) are HFO/hematite with < 2 % As. Dark grey grains are quartz. (b) Well-preserved primary arsenopyrite crystal (white) and ≈ 5 µm kankite rim.
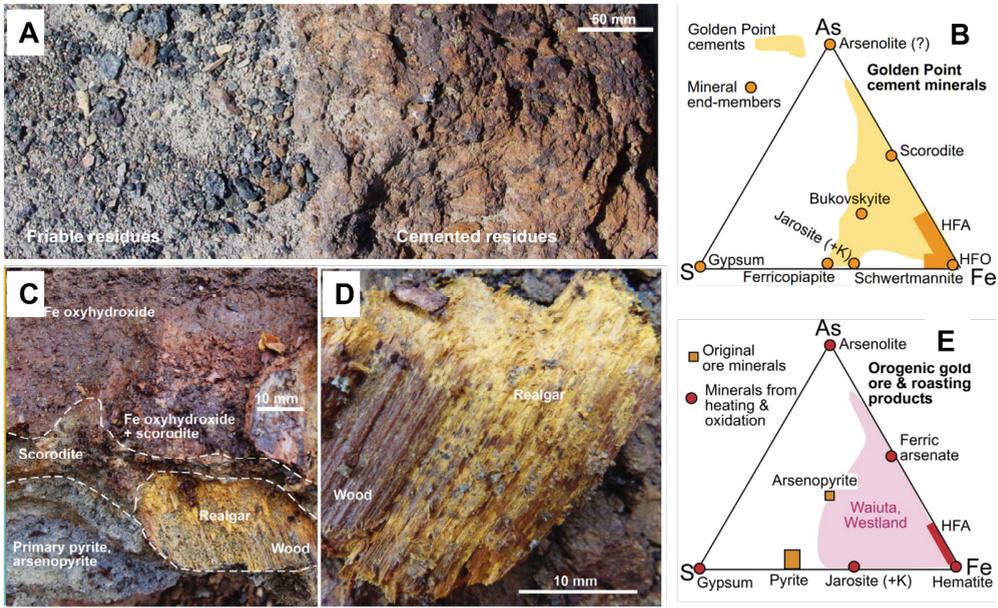
Figure 3 *Arsenic phases observed in historic mine wastes, in Otago and the West Coast. (a) Mine processing residues at Golden Point historic site with cemented bukovskyite/scorodite residues (brown) on the right. (b) As-S-Fe ternary diagram showing the typical mineral phases present in the Golden Point cements. (c) Mine processing residues at Waiuta showing primary sulfides, intermediate scorodite and realgar and the most oxidised material at the top (Fe oxyhydroxides). (d) Close-up view of secondary arsenic sulfide forming on discarded wooden framing. (e) As-S-Fe ternary diagram showing the typical mineral phases present at Waiuta. (Modified from Kerr & Craw 2021a and Kerr & Craw 2021b).*

Arsenolite

The most extreme examples of differences between thermodynamic predictions and empirical observations relates to arsenolite (As_2O_3). Arsenolite is theoretically highly soluble ($\approx$12g/L, Vink 1996), yet at Waiuta arsenolite-bearing mine wastes lying on open ground in a wet climate (>2000mm rain/year) have survived for 80 years with only partial alteration (Fig 4a-c; Kerr and Craw 2021b). At the same site, bulk arsenolite piles, formed during roasting of ore and somewhat sheltered by the historic cyanide tanks, have remained intact (Fig 4d). Arsenic levels in this material are up to 60 wt% and appear to have undergone little remobilisation, apart from surface disturbance by sheltering animals that mistakenly chewed their bedsheets (Fig 4e; Kerr and Craw 2021b).

Laboratory-based leach column studies yielded ~16 mg/L dissolved As (Kerr *et al* 2015) yet empirical observations have seen a maximum of "only" 0.35 mg/L dissolved As

at the Waiuta site (Haffert and Craw 2008). The leach column experiments simulated arsenopyrite dissolution in Reefton ore rock with monthly water inundation. Over six months, arsenolite formed a coating on the arsenopyrite surface (Kerr *et al* 2015; Fig 4f). This 'armouring' effect likely limited further arsenopyrite dissolution and, despite its high solubility, the arsenolite persisted after subsequent inundations. In the field, and over longer timescales, dissolved As is further limited by the formation of iron arsenates and iron oxyhydroxides either by total replacement or as a protective rim or cement (Fig 1e, 2a, 3a,c).

Conclusions

We find that the processes and physical parameters that control the dissolution rates of arsenic minerals are complex; and grain size, surface area, secondary mineral armouring and subsequent encapsulation are important factors. Additionally, highly localised conditions can control As dissolution
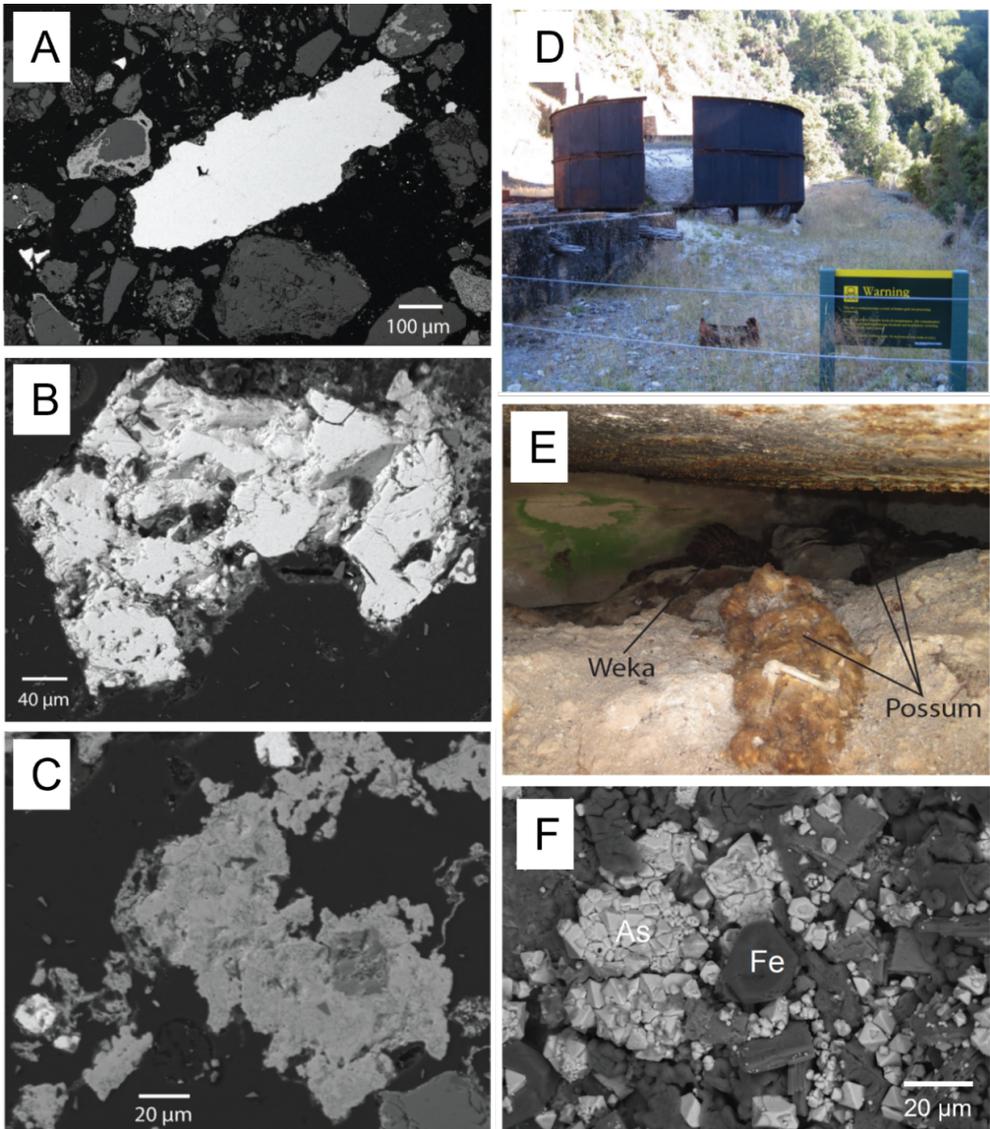
Figure 4 Examples of arsenolite in historic mine waste and leaching experiments. (a-c) Detrital arsenolite crystals at the West Coast site showing varying levels of alteration. (a) Large unaltered arsenolite grain with quartz/scorodite grains (centre left). (b) Arsenolite grain with minor As-Mg-Si-O rim. (c) Altered arsenolite grain (light grey) with smaller arsenolite grains (bright white). (d) Cyanide tank with bulk arsenolite material beneath. (e) Remains of several possums and weka beneath the cyanide tank where highest As levels were recorded on site. (f) Arsenolite (As) and iron sulfates (Fe) obscuring primary arsenopyrite in leaching column experiments.

rates and these microenvironments are not necessarily representative of the wider environmental conditions of a site. Our empirical observations across several sites, which represent a range of environments and timescales, suggest that thermodynamically predicted solubilities are overestimated, and that certain arsenic minerals can persist for far longer than expected. Our observations provide some context for further research of dissolution rates of arsenic mineral solubilities.

Acknowledgements

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