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Cyanobacterial mineralisation of posnjakite ($Cu_4(SO_4)(OH)_6{\cdot}H_2O$) in Cu-rich acid mine drainage at Yanqul, northern Oman

Bernhard Pracejus[a,*], Aliya Al-Ansari[b], Huda Al-Battashi[b]

[a] Department of Earth Science, P.O. Box 36, 123 Al-Khoud, Muscat, Oman
[b] Department of Biology, Sultan Qaboos University, P.O. Box 36, 123 Al-Khoud, Muscat, Oman

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ABSTRACT

This is the first detailed account of the copper sulfate posnjakite ($Cu_4(SO_4)(OH)_6{\cdot}H_2O$) coating cm-long filaments of a microbial consortium of four cyanobacteria and *Herminiimonas arsenicoxydans*. It was first observed on immersed plant leaves and stalks in a quarry sump of the abandoned Yanqul gold mine in the northern region of Oman; rock surfaces in the immediate vicinity show no immediate evidence of posnjakite. However, a thin unstructured layer without filaments but also containing the brightly coloured turquoise posnjakite covers ferruginous muds in the sump. Although copper is a potent bactericide, the microbes seem to survive even at the extreme heavy metal concentrations that commonly develop in the sump during the dry season ($Cu^{2+} \approx 2300$ ppm; $Zn^{2+} = 750$ ppm; $Fe^{2+} \approx 120$ ppm; $Ni^{2+} = 37$ ppm; $Cr_{total} = 2.5$ ppm; $Cl^- = 8250$ ppm; and $SO_4{}^{2-} = 12{,}250$ ppm; pH ~2.6), thus leading to the precipitation of posnjakite over a large range of physicochemical conditions. Upon exposure to the prevailing arid climate, dehydration and carbonation quickly replace posnjakite with brochantite ($Cu_4(SO_4)(OH)_6$) and malachite ($Cu_2(CO_3)(OH)_2$). To characterise and understand the geochemical conditions in which posnjakite precipitates from undersaturated fluids (according to our thermodynamic modelling of the dominant elements), waters from rainy and dry periods were analysed together with various precipitates and compared with the observed field occurrences. The findings imply that posnjakite should not form in the examined environment through purely inorganic mechanisms and its origin must, therefore, be linked to the encountered microbial activities.

1. Introduction

Situated in the Samail ophiolite (obducted continental crust) of northern Oman, the abandoned Yanqul gold mine (23°40′40.79″N; 56°32′27.35″E) was established in a belt of mafic rocks (basalts) that contain numerous Cyprus-type copper-rich volcanogenic massive sulfide (VMS) deposits (Fig. 1; Hannington, 1993; Galley et al., 2007). Once the gold and copper production at the Yanqul deposit ceased, the open pits collected occasional rain and ground waters that had reacted with the relict metal sulfides of the surrounding rocks. Onsetting ore mineral oxidation resulted in a strong acidification of the waters through the formation of sulfuric acid (e.g., Chavéz, 2000; Essalhi et al., 2011), thus intensifying further oxidation and dissolution processes (industrially induced enhanced gossan development in the open quarry) and mobilising significant quantities of base metals. Drainage focused these acidic and metal-laden fluids in the quarry sumps (lowest part of the mine), where various mineralisation and/or dissolution processes occur continuously, depending on strongly changing water availability during dry and "rainy" seasons and large ambient temperature fluctuations, respectively.

During a sampling campaign collecting waters and secondary copper minerals, conspicuously coloured precipitates enveloping centimeter-long microbial filaments were observed on the edge of one of the mining sumps; we later identified these mineralised coatings as posnjakite ($Cu_4(SO_4)(OH)_6{\cdot}H_2O$). Similar turquoise precipitates had previously been noted by the first author in inaccessible places of the same sump and in a Zambian copper mine (Fitwaola mine) but had not been sampled. The detailed genetic identification of the microbial consortium is subject of a separate paper by Al-Ansari et al. (in preparation), but we report here that up to 4 different cyanobacterial species plus *Herminiimonas arsenicoxydans* seem to be present.

Although the role of microbes in mineralisation and mobilisation processes has been investigated for some time in the context of almost any conceivable element (Walter et al., 1972; Pan-Hou and Imura, 1981; Kretzschmar, 1982; Vuorinen et al., 1983; Wood and Wang, 1983; Zierenberg and Schiffman, 1990; Anderson and Lovley,

* Corresponding author.
E-mail address: pracejus@squ.edu.om (B. Pracejus).

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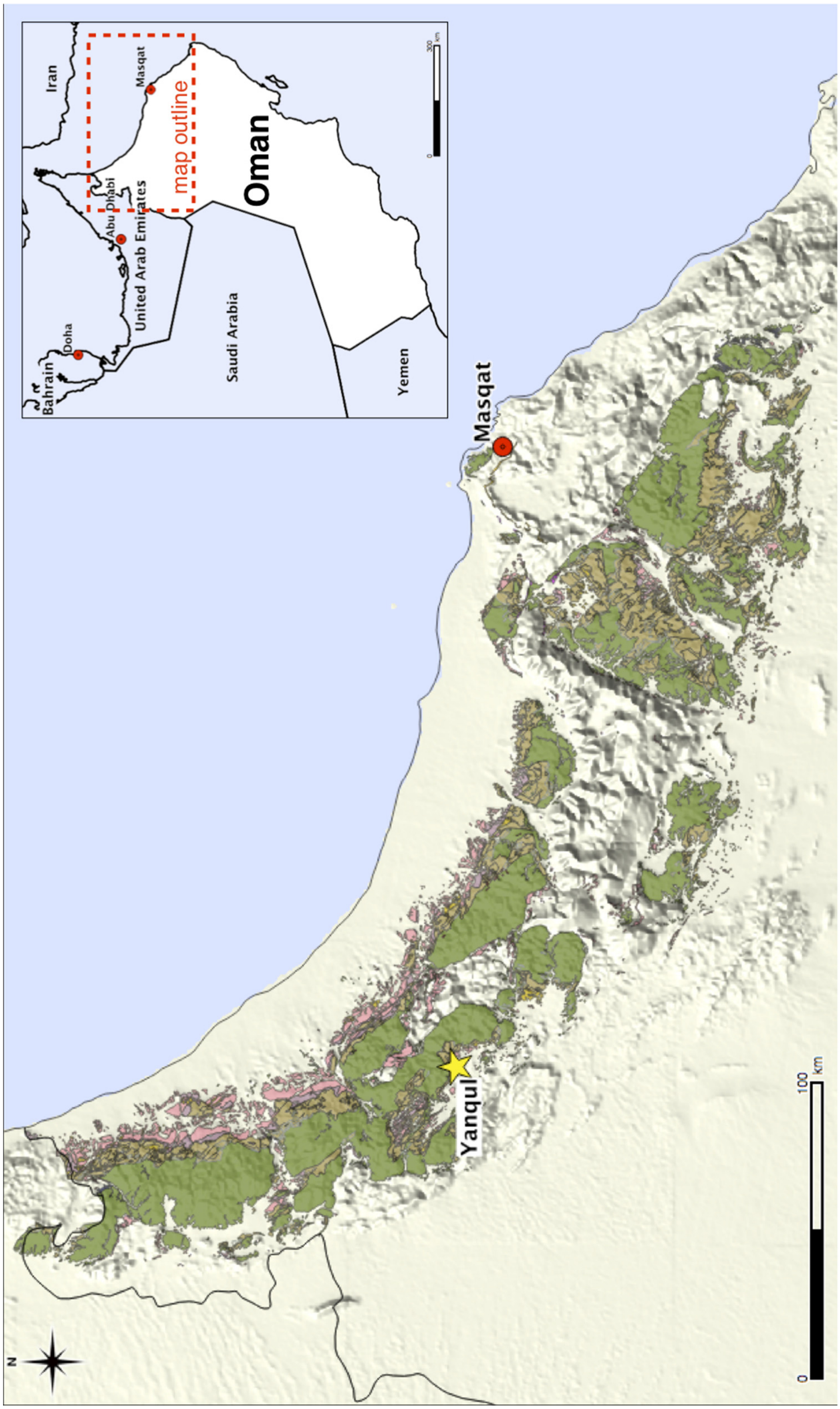

Fig. 1. Northern Oman with its coastal mountain chain is the host of an ophiolite system containing numerous volcanogenic massive sulfide (VMS) deposits within mafic rocks; the Yanqul gold mine (asterisk; 23°40′40.79″N; 56°32′27.35″E) belongs to these deposits. The green/olive-coloured regions reflect the distribution of mantle (ultramafic) rocks, while the pink areas illustrate the spread of crustal (mafic) rocks. The map was produced with SimpleDEMViewer for Mac (version 4.4.9), ASTER GDEM data (product of METI and NASA), QGIS (version 2.0.1-Dufour) under GNU General Public License, and the geological map of Oman (Béchennec et al., 1993).