Synchrotron determination of metal mobility in carbonates

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BACKGROUND
Effluent from legacy industrial sites often contains elevated levels of ecotoxic metals which are harmful to the environment. Ecotoxic metals, such as As, Cr and V poison and kill plants and invertebrates and undermine the ecosystems they support. Reducing ecotoxic metal concentrations, or removing them entirely, is therefore a key challenge in remediating legacy industrial sites. Tufas are terrestrial carbonate (calcite) deposits which mainly form in high pH streams with high levels of dissolved inorganic carbon (DIC). They can also form due to anthropogenic industrial activity such as dumping of slags (an industrial by-product from metal processing). Slag weathering releases dissolved calcium and hydroxyl groups which raise the water pH, resulting in CO$_2$ dissolution and hydroxylation which promotes calcite precipitation. Breakdown of slag and similar industrial wastes also releases various ecotoxic metals.

PROJECT AIM
Pilot geochemical data suggests that precipitation of tufa in legacy industrial wastewater streams could capture ecotoxic metals. However, the toxicity of metals in such effluent, and its (re-)mobility after initial capture, are not known. These processes may depend on oxidation state, e.g. As(III) vs. As(V); as a result, this PhD project proposes to investigate the locale and oxidation states of the identified metals in field case-study tufas using synchrotron X-ray Fluorescence Microscopy (XFM) and X-ray Absorption Spectroscopy (XAS). Understanding how metals are bound into the tufa structure will inform the effectiveness of inducing tufa formation as a remediation measure to reduce the long-term mobility and bioavailability of ecotoxic metals in legacy industrial effluent.

RESEARCH APPROACH
Fieldwork
Two field sites (Figure 1) in the north of England – Millom and Consett – will be used as case studies. At Millom a tufa has formed at the edge of a marsh as water has drained through a heap of old blast furnace slag. At Consett, a large tufa has formed in the Howden Burn which drains a large steel slag heap. The student will conduct fieldwork at the case study sites, collecting tufa samples.

Sample Characterisation
The student will prepare thin sections of samples for petrographic analysis to provide context to the subsequent synchrotron analysis. Additionally, sample powders will be analysed using X-Ray Diffraction (XRD). Pilot XRD analyses from co-supervisor Cumberland of a natural metal-deficient tufa and an anthropogenic Fe-rich tufa have confirmed the mineralogy in both are predominantly calcite and are indistinguishable. This indicates that synchrotron research is necessary for further investigation.

Synchrotron Analysis
From the pilot data, it is unknown if ecotoxic metals are incorporated as nanoparticles between layers of calcite within the tufa, or if they substitute for Ca within the crystal lattice. This is key in determining potential re-mobility of the ecotoxic metals should the environmental conditions of the tufa change over time. Understanding metal oxidation state is also of high importance due to effects on metal re-mobilisation and toxicity.

The supervisory team have already submitted a proposal for time at STFC’s Diamond Light Source synchrotron, using the I18 beamline. Should this be successful, the student would participate in the analysis. XFM analyses will comprise (1) mapping of the positioning of metals in environmental samples and (2) conduct X-ray absorption of the near edge structure (XANES) and extended X-ray absorption of the fine structure (EXAFS) analyses (As, Fe, Cr, Pb, V) as spots or transects in addition to XAS analyses on bulk powders. In addition to the current pending beamtime application
prepared by the supervisory team, the student would be expected to work with the supervisors to prepare a subsequent application for additional beamtime at Diamond Light Source.

Data Analysis and Synthesis
Data will be processed using specialist software packages with training and guidance from co-supervisor Cumberland. The results are expected to show that the ecotoxic metals are either incorporated into the calcite crystal lattice or absorbed onto calcite surfaces. We postulate that metals sitting within the crystal lattice would be stable and therefore less likely to remobilise than surface adsorbed metals. The results would therefore aid our understanding of the effectiveness and long-term stability of induced tufa precipitation as a potential new method in environmental remediation.

STUDENT BACKGROUND
The student will likely have an environmental or geoscience background with an interest in geochemistry and the environment. Laboratory experience is desirable although not essential but a willingness to learn new techniques in a laboratory environment is vital. Strong ability in scientific writing, evidenced by a substantial piece of independent writing e.g. undergraduate dissertation, is expected.

FIT TO STFC REMIT
This proposal fits STFC’s remit through the use of the STFC facility, Diamond Light Source synchrotron. Additionally, it aligns with STFC’s science area of ‘Environment’.

Application procedure: 3.5 years of funding for this project is available through an award from the Science and Technology Facilities Council to the University of Glasgow. Please apply via the website of the College of Science and Engineering*. The application deadline is 31 May 2019, and the project will start in October 2019.

*https://www.gla.ac.uk/postgraduate/research/earthsciences/#/applyonline