Microbially mediated mobilisation of redox-sensitive metals in relict hydrothermal sulphide deposits

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The diagenetic re-mineralisation of Fe, Mn, Cu, Zn, Cd, Mo and S and the role of microbes in the metal-exchange processes were investigated in metalliferous sediments from a relict hydrothermal zone in the TAG area. The TAG hydrothermal field is located within a 40km long, slow-spreading ridge segment of the Mid-Atlantic Ridge (MAR) at 26°08'N. The field comprises the active TAG mound, situated 2.4 km east of the neovolcanic zone, two areas (Mir and Alvin) of former high-temperature venting to the north of the active mound, and an area of low-temperature Mn-oxide deposits to the east [1]. The core investigated here is from the 'Alvin' zone, which is a 2km long, N-S trending area of discontinuous, highly altered sulphide deposits. Radiometric dating suggests that the Alvin zone deposits formed over a period of at least 100,000 years, and the last hydrothermal event maybe as recent as 6000 years ago [2]. Mass gravitational processes, submarine weathering and re-crystallisation of the original mineral assemblage has led to intensive reworking, modification and alteration of the primary sulphide textures. Since cessation of the active venting, the deposits have been covered by a substantial layer of pelagic sediments.

Downcore measurements of the solid phase metals, and the concomitant pore water metal-contents, were made in a 230 cm-long gravity core collected from the central part of the Alvin zone. These detailed measurements were compared with observations from a suite of five cores collected across the Alvin zone. The altered sulphidic sediments are capped with a ~30cm thick layer of carbonate-rich (~80% $CaCO_3$), Fe stained sediments. Two distinct sulphide layers (50–65 cm and 170–230 cm) interbedded with Fe-oxysilicates and overlain by a thin layer of Fe/Mn oxyhydroxides were found in this core. Scanning electron microscopy (SEM) and solid phase data suggest that the dominant mineral-phase in both sulphide layers is FeS, with small amounts of covellite, sphalerite and chalcopyrite (S: 8 mmol/g, Fe: 7 mmol/g, Cu: 0.8 mmol/g, Zn: 50 μmol/g in the top layer). The presence of sulphides within hydrothermal sediments has been attributed to mass wasting of active sulphide deposits [3].

The pore-water profiles demonstrates that Mn is released at depth and the upward diffusing Mn^{2+} is re-oxidised at the redox-boundary (~30cm), as indicated by a sharp peak in the solid phase Mn. This is well matched by specific activity of Mn reducing bacteria, which are low at the surface but markedly increased below 70 cm, where pore water Mn increases (3.5 μmol/l) [4].

Solid phase data indicate re-mobilisation of Zn from primary sulphides within the sulphide layers and re-precipitation directly above and below. SEM analysis has shown that where mobilisation occurs, the sphalerite is marginally corroded, whereas in the zone where it is re-precipitated, grains are rather angular. Sharp peaks of dissolved Cu (12 μmol/l) and Cd (1 μmol/l) within the sulphide layer, and Zn (15 μmol/l) and Mo (80 nmol/l) below 70 cm demonstrate remobilisation of these metals. Pore water Fe^{2+} is elevated below 65cm (30–90 μmol/l), but is low within the sulphide layer (0.5–8 μmol/l), indicating upward migration and precipitation as FeS. EDS-SEM mapping of individual sulphide grains shows marked zonation of Zn, Cd and Cu across the minerals. This, together with the pore water data, suggests that these metals are sequentially released from the primary sulphides and replaced by Fe.

In summary, post-depositional processes leading to re-mineralisation in these metal-rich sediments include oxic diagenesis, driven by penetration of overlying oxygenated seawater, microbially mediated mineralisation, and percolation of reactive pore-fluids through the porous sediments, causing dissolution and re-precipitation. The majority of sulphide textures appear to be secondary, which suggests that diagenetic mineralisation makes a significant contribution not only to the alteration, but also to the growth of these sulphide layers. A possible mechanism for this process is the microbial reduction of seawater-derived sulphate, as indicated by elevated activity of sulphate reducing bacteria directly above the sulphide layer [4]. The reduced sulphur species would then readily react with the Fe^{2+} mobilised further below, and precipitate as FeS. Identification of the involvement of microbial processes in metal transformation in hydrothermal systems, and quantification of the rates of these processes is required in any evaluation of fluxes between the crust and the ocean.

References

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