

Bacterial cell walls – Promoters and inhibitors of mineral nucleation

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Formation of minerals at the Earth's surface can often be directly or indirectly assigned to the activity of microorganisms. Regarding a direct effect, several examples of microbially controlled, extracellular precipitation of minerals have been reported, which typically involve the enrichment of metal ions at the bacterial surface.

However, sorption of metal ions to microbial cell walls might also inhibit mineral formation. Here, we present two examples in which interactions between metal ions and bacterial cell walls interfere with the formation of mineral although a promoting effect could be anticipated: the formation of UO₂ as a consequence of microbial U reduction and the formation of Mn oxides in the presence of a Mn oxidizing organism.

Microbial reduction of U(VI) to U(IV) is expected to result in the precipitation of solid UO₂ at neutral pH. However, EXAFS analyses of samples from incubation experiments with the organism *Shewanella putrefaciens* revealed that enzymatic reduction of U(VI) did not instantaneously lead to the formation of an UO₂ precipitate but that U(IV) was monomerically associated with the bacterial cells. Indications were obtained that U(IV) in this form is very susceptible for reoxidation.

The kinetics of Mn(II) oxidation with and without the organism *Pseudomonas putida* were studied at pH 7.5 and 8.5. The rates of Mn²⁺(aq) consumption in the presence of bacteria were similar at both pH values although the rates of abiotic Mn oxidation, determined in the absence of bacteria, were higher at pH 8.5. XANES analyses showed that the removal of Mn(II) from solution by the bacteria at pH 8.5 was, in contrast to pH 7.5, not caused by Mn oxidation. Consequently, not only enzymatic Mn(II) oxidation but also the abiotic oxidation were inhibited at pH 8.5 in the presence of bacteria. Possible mechanisms for the removal of dissolved Mn(II) by the bacteria and the inhibition of the abiotic oxidation at pH 8.5 will be discussed.

U-Th-Ra disequilibria along the EPR: Evidence for off-axis melting?

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Lavas erupted along Mid-Ocean Ridges provide important information on melt formation and movement beneath the oceanic lithosphere. Despite the fact that the majority of lavas are erupted along the spreading axis itself, there is increasing evidence that lavas along certain ridge sections are erupted off-axis at distances >5km.

The East Pacific Rise has a fast (5.5 cm/yr) half spreading rate and hence the age of lavas sample off-axis are well-constrained if erupted on-axis. We present U-Th-Ra disequilibria from three traverses long the East Pacific Rise (9°30', 10°30', 11°20') extending to a maximum distance of ~45 km East and ~30 km West of the ridge axis.

Our analyses show greater U-Th disequilibria than predicted solely by decay of the ridge axis signal. Relative to a calculated decay curve assuming an initial (²³⁰Th/²³⁸U) of 1.23, lavas from 9°30'N have Th excess of 2-4%, lavas from 10°30' have Th excesses of 0.5-3.6% and the most extreme U and Th excesses are observed at 11°20'N (<40% and <50% , respectively). (²²⁶Ra/²³⁰Th) excesses up to ~2 have been observed at 10°30' and 11°20', whereas all three traverses also display ²²⁶Ra deficits with (²²⁶Ra/²³⁰Th) down to 0.63. We observe a systematic variation with increasing distance from the ridge axis. Lavas closer to the ridge axis (12-20 km) exhibit Th excess followed by U excess (20-28km) and mostly ²³⁰Th/²³⁸U equilibrium at >30km.

If formed at the ridge axis the observed Th excesses require anomalously high initial (²³⁰Th/²³⁸U) ratios of ≥2. However, reasonable dynamic melting parameters (e.g. upwelling rate = 0.5cm/a; 10-20% melting degree) produce initial ²³⁰Th/²³⁸U ratios of ≤1.4 that are too low to explain the off-axis disequilibria. (²²⁶Ra/²³⁰Th) ratios of ≥1 require melting within the last 8,000 years, whereas Ra deficits require D_{Ra}>D_{Th}, which could reflect the presence of hydrous phases such as amphibole or phlogopite in the melting regime.

The combined occurrence of both, Th and Ra excesses some 5-45 km distant from the ridge axis may be consistent with off-axis melting <8,000 years ago, largely independent from ridge axis melting. The systematic shift from Th to U excess implies a continuous re-melting of previously depleted peridotite over timescales <<75,000 years.