

## Interrelation between biotic and abiotic Mn(II) oxidation

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Intensive Mn redox cycling has been reported from many redox stratified environments and microbial Mn(II) oxidation is considered to be a vital part of the Mn redox cycling. At circumneutral pH, homogenous oxidation of Mn(II) is a relatively slow process so that microbial oxidation can be expected to be the prevailing pathway for Mn oxidation in the absence of other catalysts. However, with progressing microbial formation of Mn oxides, the surface catalysed abiotic Mn oxidation could become increasingly dominated. In this study the interplay between microbial and abiotic Mn oxidation was studied in batch experiments with the Mn oxidizing organism *Pseudomonas putida*. In order to manipulate the relevance of either the abiotic or biotic pathway, the pH was varied between 7.0 and 8.5, whereas higher pH is expected to favor abiotic Mn oxidation. Special emphasis was put on identifying the Mn oxides formed in the different stages of the experiments, because abiotic and microbial Mn oxidation are expected to lead to the formation of different Mn oxides. Hence, the composition of the Mn oxides can be used as an indicator for the dominating pathway.

Initially, microbial and abiotic Mn oxidation were studied under conditions at which Mn oxidation can be exclusively attributed to either pathway. In these experiments the rates of Mn(II)<sub>aq</sub> consumption by both, the biotic and abiotic process, can be described with models proposed in the literature and X-ray absorption spectroscopy revealed that Mn(II)<sub>aq</sub> consumption was caused by Mn oxidation. Analysis of EXAFS spectra indicated the formation of hausmannite and birnessite in the abiotic and microbial experiments, respectively, which is in agreement with results from other studies. Based on the results from the experiments on the isolated pathways we anticipated a transition from microbially to abiotically mediated Mn oxidation in the course of the reaction at pH 8.5 in the presence of bacteria. However, it turned out that removal of Mn(II) from solution under these conditions was not caused by Mn oxidation but due to sorption / uptake by the bacteria. Additionally, abiotic Mn(II) oxidation seemed to be inhibited in these experiments. The reason for the inhibition and the underlying Mn(II) binding mechanism by the bacteria will be discussed.

## Back-arc melting: Fluid or source induced?

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Back-arc melting regimes provide the unique opportunity to enhance our knowledge of the influence of mantle heterogeneity on mantle melting, i.e. of the extent of arc-related, fluid-induced melting, vs. decompressional melting. However, few U-Th-Ra disequilibria have been analysed in back-arc lavas so far.

Manus back-arc basin lavas range in composition from N-MORB/transitional MORB to back-arc basin basalts (BABB) and some extremely enriched BABBs (XBABB). We have analysed U-Th-Ra disequilibria 100-400 km off the active New Britain trench. While most display (<sup>230</sup>Th/<sup>238</sup>U) ratios of 0.77-0.95 a few lavas both closer and more distant to the trench have small Th-excesses with (<sup>230</sup>Th/<sup>238</sup>U) <1.06. (<sup>226</sup>Ra/<sup>230</sup>Th) ratios are generally >1 implying that the lavas are <8 ka old and that no post-eruptive age correction needs to be applied to U-Th. While (<sup>230</sup>Th/<sup>238</sup>U) >1 are generally associated with decompressional melting, (<sup>230</sup>Th/<sup>238</sup>U) <0.95 have generally been attributed to the presence of arc-related fluids or unusual melting phases (e.g. apatite, however, we do not find evidence for apatite in these rocks). The Sr-Nd-Pb isotopes imply variable input of an enriched component, i.e. they range from 'MORB'-like depleted signature to more enriched signatures. There is no evidence for a correlation of arc-related melting signatures and long-term source heterogeneity. Instead the U-Th disequilibria are consistent with fluid-induced melting some 200-400 km distant from the active trench. This U-excess requires a) unusual phases during melting or b) storage of fluids in the mantle and re-melting (e.g. amphibole, however, this would lead to Th-rather than U-excess). We thus favour a much quicker/further transport of the arc-related fluid through the mantle wedge (with or without intermediate storage) inducing melting much further away from the active trench then suggested by dehydration of the subducted slab.