Cytochromes and iron reduction

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The key innovation that enables cells to respire on metals like ferric iron or manganese is the development of a respiratory chain to the cell surface. Most of the known bacterial ferric iron reducers are proteobacteria. These cells all have in common the canonical blueprint of a Gram-negative cell with cytoplasm, cytoplasmic membrane, periplasm and outer membrane as separated reaction compartments. We study the electron transport chain to the cell surface using *Shewanella oneidensis* MR-1 as a model organism. *C*-type cytochromes are the dominant electron transferring proteins in *Shewanella*. They establish a conductive connection to the cell surface and catalyze the final reduction step onto a metallic electron acceptor. Interestingly, *S. oneidensis* as well as other dissimilatory iron reducers produces a multitude of different cytochromes while growing under dissimilatory ferric iron reducing conditions. Our work aims at elucidating as to why expression of this high number of cytochromes might result in a selective advantage. We can show that periplasmic cytochromes build a dynamic electron-transferring network. We can furthermore show that these cytochromes can catalyze ferric iron reduction. Hence, so called outer membrane cytochromes that are localized to the cell surface simply allow for contact between respiratory electrons and the electron acceptor. Although these surface localized cytochromes are crucial for wild type cells to respire on ferric iron or manganese, we could surprisingly establish that they are not necessary. Two simple point mutations can enable a *Shewanella* mutant to find a way around this necessity for outer membrane cytochromes. We currently complete our studies concerning these point mutations but will already provide evidence for the possible functions of the genetic exchanges.

The relase of Hf isotopes during weathering

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Studies of river and ocean waters suggest that Hf isotopes are released incongruently during weathering of the continental crust. The governing processes in soils are poorly understood because the release of Hf isotopes from soils during weathering has thus far hardly been explored. Such an understanding is crucial to the eventual use of Hf isotopes for the reconstruction of past weathering conditions. Here we explore Hf isotope behaviour in a soil chronosequence from Scotland, spanning an age-range of 0.1-13ka.

Bulk soil Hf isotopes digested in a pressure bomb span a relativley small range between εHf = -22.1 and -19.7. Hot plate digests, which exclude most Hf from zircons, are more radiogenic and also show a larger isotopic range (εHf = -20.1 to -16.0). The isotopic compositions of both digestion procedures are well correlated, which indicates that zircons attenuate the variabilty that is imparted by weathering of the zircon-free portion and seem largely inert on the time scales of the chronosequence. Although all soil profiles consistently show a depletion of radiogenic Hf in their upper horizons, documenting the removal of radiogenic Hf, the evolution of the soils with time is not very systematic. In particular the 10 ka profile is less radiogenic throughout, which is likely to indicate heterogenity in the parent material of the chronosequence.

Currently, it is diffult to asses the proportion of removed Hf from the soils and derive an estimate of the corresponding Hf isotopic composition released to the hydrosphere. Hf/Zr ratios in the bulk soils (bomb digestions) are relatively homogenous and a calculation of the depletion of Hf from these geochemical twins seems inappropriate. A correlation of Hf/Zr with Hf isotopes which would support such an approach is not observed.

In summary the data shows that Hf isotopes removed from soils is more radiogenic than the bulk. This preferential removal of radiogenic Hf mainly relates to the zircon free portion of the soil, in which weathering imparts a variablity of 4 εHf. These findings will be consolidated by establishing the Hf budget of the rocks (zircon free crustal Hf vs bulk Hf) and the measurement of Hf isotopes in the draining rivers.