Osmium and oxygen isotopes in Etendeka picrites and their olivines: mantle melts and crustal interaction

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The existence of basal picrites and picritic dykes in the Etendeka large igneous province (LIP) provides the opportunity to study high-degree, relatively unfractionated melt products from a hot plume head and hence gain the best insight into the source composition. Moreover, highly magnesian olivine phenocrysts (occasionally up to Fo 93.3), which reflect crystallisation from melts with up to 24 wt% MgO [1], provide particularly primitive isotopic information. Such high MgO melts require mantle potential temperatures up to 1700°C [1], amongst the highest known for the Phanerozoic. At the same time, the eruption of the picrites through continental crust allows the role of assimilation, in imparting an isotopic signature, to be investigated.

Here we present major and trace elements and Sr, Nd, Pb and Os isotopes for whole rocks, and combine these with major elements and osmium and oxygen isotopes for olivine phenocrysts. Highly siderophile element abundances are also presented.

The Pb isotopic compositions of whole rocks covary with Pb content and are clearly controlled by a local crustal sedimentary input, and give little information on the source. Strontium and Nd isotopes in the Horingbaai dykes covary negatively, indicating variable contributions from depleted and slightly enriched endmembers, the latter likely local crust.

The $^{187}Os/^{188}Os$ compositions of the primitive Horingbaai and more evolved Spitzkoppe picrites (0.128-0.131) are in the same range as some other high-T plume melts (e.g. North Atlantic Igneous Province picrites: 0.127-0.134 [2]). The least radiogenic values support a predominantly mildly-depleted peridotite source for the highest temperature volcanism in the region, which is also consistent with MORB-like REE patterns. The Os data exclude the possibility of a long-term strongly Re-depleted source input, such as old lithosphere. The more radiogenic values could reflect a contribution from an isotopically enriched mantle component. Olivines from the Horingbaai and Spitzkoppe picrites, however, have similar or slightly lower isotopic compositions than their respective whole rocks, suggesting that, at least in part, the more radiogenic Os isotope values are a result of crustal assimilation after olivine crystallisation, even in these Os-rich picritic melts.

Oxygen isotope compositions in olivines ($\delta^{18}O$ up to 6.5‰) extend higher than typical mantle, and are associated with more radiogenic $^{187}Os/^{188}Os$. Although it is difficult to rule out a mantle eclogite component as a source of coupled O-Os enrichment, a crustal input is the likely cause of this effect, and is supported by the combined isotopic and elemental data.

[1] Thompson & Gibson (2000) *Nature* **407**, 502-506.
[2] Dale et al. (2009) *EPSL* **278**, 267-277.

Fe(III) reduction by the Gram-positive bacterium *Desulfotomaculum reducens*

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Microbial Fe(III) reduction, specifically that of solid phase Fe(III), presents a challenge to bacteria as electrons must be transported to an extracellular electron acceptor. This process has been studied extensively for Gram-negative bacteria such as *Shewanella oneidensis* and *Geobacter sulfurreducens*. Several strategies have been documented in these microbes: (a) the secretion of endogenous redox mediators that are reduced by cells following oxidation by Fe(III); (b) direct contact of outer-membrane multi-heme cytochromes with the solid-phase substrate or (c) the extension of micron-long electroconductive pili that can transport electrons away from the cell. The transfer of electrons in the latter two cases was dependent on several multi-heme cytochromes located in the cytoplasmic and outer membranes as well as in the periplasmic space.

In the case of Gram-positive bacteria, there is evidence either for the involvement of redox mediators [1] or the requirement for direct contact with the electron-receiving surface [2]. In both cases, the mechanism remains unknown. In this study, we probe the reduction of soluble Fe(III) [as Fe(III)-citrate] and of solid-phase Fe(III) [as hydrous ferric oxide, HFO] by the Gram-positive bacterium *Desulfotomaculum reducens*. The best growth was obtained with pyruvate due to fermentation but some growth was detected with lactate as an electron donor. In the presence of HFO, pyruvate was rapidly (~3 days) converted to acetate and Fe(III) slowly reduced over 25 days. Tests with spent medium from pyruvate- and HFO-grown cells indicate the presence of an endogenous redox mediator able to reduce anthraquinone disulfonate (AQDS). In contrast, HFO reduction occurred concomitantly with lactate oxidation to acetate and there was no evidence for a redox mediator. Experiments with HFO enclosed in glass beads (and thus only accessible to diffusable redox mediators) confirmed those findings as reduction of Fe(III) was observed in the pyruvate case but not detectable in the lactate case.

The *D. reducens* genome harbors a sole multi-heme *c*-type cytochrome complex (NrfHA) with homology to the nitrite reductase in *Desulfovibrio vulgaris*. Quantitative reverse transcription PCR (qRT-PCR) showed that while *nrf*HA was expressed during fermentation, there is no evidence for expression during Fe(III) reduction. Hence, we conclude that (a) HFO reduction occurs via a redox mediator with pyruvate while it is mediator-independent in the presence of lactate; (b) the sole *c*-type cytochrome complex present in the genome of *D. reducens is* not involved in Fe(III) reduction. Ongoing work focuses on the characterization of the mechanism of lactate-dependent HFO reduction and aims at providing a mechanistic understanding of electron transfer across the Gram-positive cell wall.

[1] Pham et al. (2008) *Appl. Microbiol. Biotechnol.* **77**, 1119-1129.
[2] Wrighton et al. (2011) *Appl. Environ. Microbiol.* **77**, 7633-7639.