Terceira lavas isotopic signatures and multi-scale mantle heterogeneity at the Azores Archipelago

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Terceira Island mafic lavas (< 30 ka), erupted from two main active volcanic systems, were analysed in this study: Fissural zone (F), interpreted as the sub aerial expression of the Terceira Rift, and Sta Bárbara central volcano (SB), which dominates the western topography of the island. These mafic lavas present a significant elemental range, with SB (Mg# <50) being generally more evolved than F (typically Mg# >50). However, if fractional crystallization explains the intra-system variability, it cannot be considered responsible for some chemical differences between those 2 volcanic systems. This is clearly demonstrated by distinct Ba/Th (200 vs. 80), Ce/Th (35 vs. 25) and ^{206}Pb/^{204}Pb ratios (19.93 – 19.99 vs. 19.34 -19.85), which clearly point to a heterogeneous mantle source. Terceira magmas formed from sources characterized by time-integrated depletion (εNd: 5.4 to 6.4; εHf: 7.7 to 10.7) significantly more marked than the observed for coeval lavas outcropping in the neighbouring islands of Pico and S. Miguel, the later also formed in relation with the Terceira Rift. In opposition Terceira is characterized by more radiogenic Pb isotopic ratios indicating a stronger HIMU presence at its source. From elemental reasoning, SB magmas were generated by lower % of partial melting being also characterized by higher ^{206}Pb/^{204}Pb ratios. This indicates that the HIMU domains of mantle source were preferentially sampled during the lower degree melting events. Considering the positioning of Terceira samples below the NHRL and the negative correlation between Nb/U and ^{206}Pb/^{204}Pb, the development of HIMU signatures is a relatively recent event. Our data strengthen the heterogeneous character of the sub-Azores mantle, which is evident even when mantle is sampled along the same structure (Terceira Rift) and, also, at the scale of an individual island.

Functional characterization of c-type cytochromes from Iron-respiring bacteria

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Cytochromes c have been shown to facilitate microbial Fe(III)-reduction in neutrophilic and acidophilic Fe(III)-respiring bacteria, and this study focuses on the functional characterization of several c-type cytochromes produced by the acidophile *Acidiphilium cryptum* and the neutrophile *Geobacter sulfurreducens*. UV-VIS spectropscopy was used to determine heme coordination and redox spectra. Cyclic voltammetry was conducted to determine mid-point potentials and reactivity towards metals. Optical waveguide lightmode spectroscopy (OWLS) was used to examine adsorption kinetics of protein-surface interactions. Spectral analysis of periplasmic cytochromes ApcA and ApcB from *A. cryptum* indicate that both reduced cytochromes can be reoxidized by Fe(III) and Cr(VI) at pH 3.0 as well as pH 7.0. Mid-point potentials (pH 7.0) are 258mV for ApcB and 233mV for ApcA (vs. SHE). Protein sorption studies suggest that small periplasmic cytochromes such as *G. sulfurreducens* PpcA are compact, and adsorb and desorb more slowly to surfaces than outer membrane (OM) cytochromes (such as OmcB) that are less dense and contain much more solvent. Homology modelling of these proteins supports the conclusion that compared to dense and compact periplasmic proteins, OM cytochromes have discrete domains and a greater potential for conformational flexibility and interaction with mineral surfaces. Taken together, these data show that these proteins are specifically tailored for electron transfer in different cellular and extracellular locations, by virtue of their electrochemical and structural properties.