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Redox-Linked Coordination Change in OMCA: Implications for Dissimilatory Fe(III) Reduction

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Differentiation of high-K calcalkaline magmas at Mount Bidkhan volcano (Central Iranian Volcanic Belt)

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Mount Bidkhan is an Oligo-Miocene stratovolcano, with a caldera, located in the southeastern part of the Central Iranian Volcanic Belt (CIVB). A detailed stratigraphically-controlled sampling of deposits was performed in the proximal, medial and distal sectors of the volcanic edifice. Eight kinds of products have been recognized: 1) pyroclastic flows 2) fall-out levels; 3) lahars; 4) surges 5) lava flows; 6) brecciated lavas and lava breccias; 7) dacitic domes/plugs; 8) ring and radial dykes. Major and trace element compositions of whole rocks were obtained on selected volcanics by means of WD-XRF and ICP-MS. Analyses on mineral phases were carried out by SEM-EDS; plagioclase and clinopyroxene were analyzed in detail along core-rim profiles and through X-ray mapping for major elements. Products exhibit high-K calcalkaline affinity and can be classified as andesites and dacites. The mineral assemblage is chiefly composed of plagioclase and, subordinately, clinopyroxene, orthopyroxene, amphibole, biotite and magnetite. Quartz phenocrysts and abundant K-feldspar in the groundmass make the dacitic products peculiar. Accessory minerals are apatite, zircon and sphene. Core-rim compositional profiles in plagioclase and clinopyroxene evidence that almost all of the crystals are complexly zoned. Specifically, plagioclase and clinopyroxene commonly exhibit small-scale oscillatory zoning, which sometimes turns into significant An mol% and Mg# changes respectively. The integrated analysis of petrochemical data allows the preliminary hypothesis that the geochemical evolution of magmas might be chiefly ruled by AFC processes at shallow depth, to which repeated episodes of mixing due to inputs of less evolved magmas are superimposed. In particular, micro-analytical data highlight that the most significant magma recharging episodes are recorded at the phenocryst rims, slightly prior to the eruption. Future research will be focused on possible relations between inputs of less differentiated magmas into the feeding system and the onset of violent strombolian to plinian eruptions.

Redox-linked coordination change in OmcA: Implications for dissimilatory Fe(III) reduction

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OmcA is a bis-his ligated decaheme *c* type cytochrome with an unknown crystal structure expressed in the outer-membrane of the metal reducing bacteria *Shewanella oneidensis* in response to reducing conditions. Although metal reducing bacteria play an important role in bioremediating toxic and heavy metals, their mechanism of electron transfer to solids is not yet completely understood. We hypothesized that the sorption behavior of OmcA is redox dependent due to its purported role in electron transfer to metal-oxides. Fe K-XANES and EXAFS data for the reduced and oxidized OmcA in solution, oxidized OmcA dissolved in 6 M GdnHCl (Guanidinium-HCl) and oxidized OmcA sorbed to SnO₂ surfaces were collected and analyzed. Our previous work with a monoheme equine cytochrome *c* showed based on Fe K-XANES spectroscopy that sorption and denaturant induced changes in the heme Fe coordination were similar.

Fe K-XANES and EXAFS spectra for oxidized OmcA showed evidence for a sorption induced change in the coordination environment of heme Fe. Similar to our results for the equine cytochrome *c*, the heme Fe coordination of sorbed OmcA was similar to the denatured OmcA. Denatured oxidized OmcA however, disintegrated, based on its XANES and EXAFS spectral similarities to Fe metal foil. OmcA behavior was markedly different from the behavior of the monoheme equine cytochrome *c* which, on denaturation changed from its native his-met ligation to a bis-his ligation. Based on XANES and EXAFS spectral similarities of sorbed oxidized OmcA with denatured OmcA, our results indicate that oxidized OmcA is not designed to interact with metal-oxide minerals. If OmcA is indeed the electron shuttle to metal-oxide surfaces, we expect reduced OmcA to sorb readily in order to transfer electrons; similarly, the oxidized OmcA should be designed to desorb. Fe K-XANES and EXAFS spectra for dissolved OmcA showed redox linked changes, suggesting that the sorption behavior of reduced and oxidized OmcA would differ consistent with the demands of its role in dissimilatory Fe(III) reduction.