

Microbially-mediated isotopic fractionation of selenium : Relevance for biogeochemical processes in the geological record

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The terrestrial and marine evolution and preservation of life are sensitive to changes in redox conditions. Selenium as an redox-sensitive element can provide information about the oxygenation history of the ocean and atmosphere. Microbial reduction of Se-oxyanions causes isotopic fractionation, and stable Se isotope ratios can be used as a novel tool to detect biological Se cycling in the geological record. In addition, Se isotope ratios, in the geological record as well as in modern environments, may fingerprint specific metabolisms. However, our knowledge about microbially-mediated Se isotopic fractionation is limited due to lack of experimental studies under environmentally relevant Se and electron-donor concentrations. Here we determine new pure culture Se isotopic fractionation factors and investigate their dependence on experimental conditions including selenium and electron-donor concentrations. Results are given as magnitudes of isotopic fractionation, ϵ ($\epsilon = 1000 * (\alpha - 1) [‰]$; $\alpha = (^{82}\text{Se}/^{76}\text{Se})_{\text{Reactant}} / (^{82}\text{Se}/^{76}\text{Se})_{\text{Product}}$). We aim to investigate metabolically diverse microorganisms, including *Desulfitobacterium* st. Viet1, *Geobacter sulfurreducens* PCA, *Pseudomonas stutzeri* KC, *Aeromyxobacter dehalogenans* FRCW, and *A. dehalogenans* FRC-R5.

The pure culture of *Desulfitobacterium* Viet1 coupled the reduction of 44 μM Se(VI) with oxidation of lactate under strictly anaerobic conditions. This reduction yielded an ϵ Se(VI) \rightarrow Se(0) = $9.4 \pm 0.3‰$ ($n=2$). This ϵ is higher than those previously reported for *Bacillus selenitireducens*, *Bacillus arsenicoselenatis* and *Sulfurospirillum barnesii* [1] and could be useful in explaining very high $\delta^{82/76}\text{Se}$ values (up to $-12.77‰$) observed in high-selenium carbonaceous shales from Yutangba deposit, China [2]. Further experiments will determine the ϵ 's for microbial Se reduction under electron-donor rich and electron-donor poor conditions. The results of this study will be useful in interpreting the measured Se isotope ratios in the rock record and may reflect the distribution of microorganisms in modern and ancient Earth.

[1] Herbel (2000) *Fractionation of selenium isotopes during bacterial respiratory reduction of selenium oxyanions* **64#**, 3701-3709.

[2] Wen (2007) *Large selenium isotopic variations and its implication in the Yutangba Se deposit, Hubei Province, China* **52#**, 2443-2447.

Geochemistry and thermobarometry of postglacial Llaima tephras

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Llaima is a large active stratovolcano in the Southern Volcanic Zone in Chile. Field work in 2011 revised the postglacial stratigraphy after Naranjo & Moreno (1991) and led to the subdivision into units I to V. Postglacial activity started 13,500 years ago with caldera-forming eruption of two mafic ignimbrites (unit I). These are overlain by a sequence of three basaltic-andesitic to two dacitic lapilli fallout deposits and reworked tuffaceous sediments (unit II). At ~ 8600 cal BC a large Plinian eruption emplaced a compositionally zoned dacitic to andesitic fallout tephra (unit III) that became capped by subsequent andesitic surge deposits (unit IV) when the eruption became unstable. The following unit V represents a time interval of ~ 7000 years during which at least 30 basaltic to andesitic ash and lapilli fallout deposits with intercalated tuffaceous sediments and paleosols were emplaced.

Bulk-rock, mineral and glass chemical analyses constrain the vertical compositional changes of Llaima tephras. Tephra compositions switch between a calc-alkaline differentiation trend (unit I) and a more tholeiitic trend (units II-IV), with samples of unit V varying between both trends, indicating a strong control of $f(\text{O}_2)$ (and $P(\text{H}_2\text{O})$) on the relative timing of Fe-Ti oxide fractionation. Moreover, iron rich fayalites that are in equilibrium with the glass composition occur in units II and III with calculated $T\text{-}f(\text{O}_2)$ close to the FMQ suggesting that late-stage fayalite precipitation involved crossing of the FMQ boundary. The younger unit V tephras and historical compositions define a second differentiation trend relatively enriched in K_2O , Rb, Ba and Zr; this is not the results of changing source conditions but can be explained by a stronger early olivine fractionation in the respective magmas.

Thermobarometric calculations based on amph, cpx-liq, plag-liq, ol-liq and Fe-Ti-oxide compositions constrain changing magma chamber positions over time. Storage depths were 14 - 19 km for unit I andesite and varied between 10 to 17 km for unit II andesites and dacites. The compositionally zoned eruption of units III and IV withdrew dacite magma from ~ 10 km depth but andesite from a deeper level of 13-15 km. Storage depths of unit V andesitic magmas ranged from 6 to 15 km. Based on temporally changing storage depths and differentiation paths, a 4-stage evolution of the postglacial magmatic system of the Llaima volcanic complex is proposed.