

## Partitioning of elements between olivine grain matrices and grain boundaries in mantle rocks – The importance of grain boundaries for storage of trace elements

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We have demonstrated that the concentration of Ca at olivine grain boundaries follows a simple thermodynamic model for equilibrium grain boundary segregation driven by misfit strain energy in the grain interior. Extension of our model to elements with larger ionic radii and to a variety of common minerals indicates that considerable amounts of elements with ionic radii larger than ~0.11 nm can be stored at grain boundaries in mantle rocks.

The compositions of olivine grain boundaries in olivine, olivine + anorthite, and olivine + diopside aggregates annealed at 1373-1523 K were analyzed using energy dispersive X-ray (EDX) profiling obtained with a scanning transmission electron microscope (STEM). Profiles across grain boundaries reveal a substantial segregation of Ca, Al and Ti at grain boundaries with widths <5 nm. High-resolution electron microscopy (HREM) images reveal that the boundaries do not contain an intergranular film. The number of effective monolayers of Ca segregated to grain boundaries were calculated, assuming that the solute is confined entirely to divalent regular lattice sites at the grain boundary plane. Plots of Ca concentration within olivine grain matrices (GM) versus the concentration in the grain boundaries (GB) reveal that 1) the GB concentration increases with increasing GM concentration, 2) the partition coefficient  $D^{Ca}_{GMGB}$  decreases with decreasing temperature, and 3)  $D^{Ca}_{GMGB}$  increases with increasing GM concentration. A simple thermodynamic model for equilibrium grain boundary segregation predicts all of these features. In addition, the magnitude of  $D^{Ca}_{GMGB}$  is consistent with the misfit strain energy calculated for substitution of Ca for Mg in olivine grains.

Since the misfit strain energy controlling  $D^{i}_{GMGB}$  can be calculated simply from known parameters such as ionic radius and Young's modulus for the crystal, we can predict the value of  $D^{i}_{GMGB}$  for other elements, i, in a variety of minerals such as clinopyroxene and orthopyroxene. Based on this calculation, we conclude that grain boundaries can be primary storage sites in mantle rocks for elements with large ionic radii such as Sr, Ba, K and Rb. This model provides a new framework for interpreting geochemical signatures in mantle rocks.

## Controls on eruptive style for North Arch lavas

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The North Arch Volcanic Field covers some 25,000 km<sup>2</sup>, spanning an area 170-390 km north of Oahu Island on the Hawaiian Arch, as flood lavas on the abyssal plain. There are no large scale topographic features which would mark volcanic edifices or vents, but detailed bathymetric mapping by SeaBeam survey during JAMSTEC cruises in 1999 and 2002 revealed scattered small vents throughout the field in the form of both flat-topped and steep-sided cones. Some extensive lava flows, however, as revealed by side-scan sonar, have no obvious topographic vents and may have initially been emplaced as shallow sills within pelagic sediment that eventually breached the seafloor surface. Previously, only dredged samples were available for geochemical studies of North Arch lavas, so no correlations could be made between lava composition and eruptive style. In the current study of samples collected during JAMSTEC dives, we have found that geochemical variation of lavas correlates with vent and lava morphology.

Two JAMSTEC dives were conducted in 2002. The first dive traversed a flat-topped cratered cone, consisting of dense alkali basalt, and then reached the base of steep cone. The second collected dense alkali basalt from a sheet flow at the western edge of the field. Hyaloclastite between the two cones, as well as vesicular lava from the steep cone's base are identical in composition and are basanitic. Mudstone atop the flat-topped cone also contains very similar basanitic glass fragments, suggesting that pyroclasts from the steep cone travelled >3 km from vent. Glasses from the cones and western sheet flow were analyzed by LA-ICPMS. Trace elements of all samples show similar patterns when normalized to primitive mantle, and are generally similar to other ocean island basalts, except for significantly higher Ba and lower K, Sm, Zr, and Hf. However, basanite lavas clearly have higher concentrations of LILE, HFSE and LREE than the alkali basalts. HREE compositions, on the other hand, are not so variable. These geochemical variations are consistent with the lavas forming from different degrees of partial melting of the same source. These observations suggest that degree of partial melting may control eruptive style, with more alkalic, lower degree partial melts erupting more explosively, probably due to higher initial volatile contents.