Chemistry of grain boundaries in mantle rocks

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INTRODUCTION

In polycrystalline materials, segregation of elements to grain boundaries commonly affects the physical and mechanical properties of an aggregate with significant implications for geological processes. Grain boundaries can store significant amounts of trace elements otherwise essentially insoluble in the aggregate, consequently influencing the chemistry of rocks. Grain boundary diffusion, sliding, fracture, and migration are markedly influenced by such segregation, which thereby impacts rheological behavior. For example, Gribb and Cooper (1998) attributed the anomalously high activation energy that they observed for Coble creep of an olivine aggregate to segregation of Ca to the grain boundaries.

Grain boundaries in most mantle rocks are narrow and do not contain secondary phase material such as an amorphous film commonly observed in sintered ceramics (Hiraga et al. 2002). The concentrations of elements such as Ca, Al, and Sr at grain boundaries have been determined for some mantle rocks (e.g., Fraser et al. 1984; Suzuki 1987; Wirth 1996). However, the origin of chemical enrichment of some elements (i.e., chemical segregation) at grain boundaries in rocks is not well understood. Geological phenomena such as partial melting, metasomatism, segregation during cooling, and weathering may all lead to enhanced concentrations of impurities at grain boundaries. The question remains “does grain boundary segregation occur in Earth’s mantle?” Here, we demonstrate that a common set of elements segregates to olivine grain boundaries in both natural and synthetic olivine aggregates. The commonality of the behavior suggests that such segregation is energetically favorable and indicates that such segregation likely occurs in the Earth’s mantle.

EXPERIMENTAL PROCEDURES

STEM/EDX spectrum profiles were acquired from olivine-olivine grain boundaries using a Philips CM200FEG TEM/STEM equipped with a Schottky field emission gun (FEG), an Oxford EDX detector with atmospheric thin window and XP3 pulse processor, and an EMiSPEC (ES) Vision integrated acquisition system. The microscope was operated at an accelerating voltage of 200 kV, and the lens excitations and beam-defining apertures were chosen to achieve an incident probe of ~1.4 nm full width at half maximum (FWHM) and 1.5 nA beam current. To minimize the effects of beam damage, the STEM was set up to raster the beam parallel to the analyzed boundary in a rapid manner (~15 ms line time) so as to prevent prolonged exposure to any point on the sample. The ES Vision system was operated independently such that a single raster of the electron beam contributed to a single 250 ms per pixel of the spectrum profile. A sequence of 10 profiles was acquired from each boundary, which were then summed to yield a single, integrated profile with 2.5 s total acquisition time per pixel. Additional profiles (beyond about 10) from the same boundary exhibited beam damage, rendering ineffectual the improved statistics of more prolonged data acquisition. These methods are described in more detail elsewhere (Hiraga et al. 2002). Net counts above background were determined using the multiple linear least squares (MLLSQ) fitting procedure in Desktop Spectrum Analyzer (DTSA) (Fiori et al. 1992). This method requires the use of spectral references, which show the distribution of intensity among a family of characteristic X-ray lines for a given element, e.g., FeK. For the major elements (Mg, Si, and Fe), the references were the best-fit superposition of gaussian peaks generated by applying the simplex fitting procedure within DTSA to a spectrum from the olivine matrix. For the minor and trace elements segregated to the boundary, spectral references were simulated with the spectral generation function of DTSA, using the best-fit parameters (e.g., spectral calibration and detector resolution) identified from the fit of the major elements. In the absence of spectral intensity