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The Study of Intergranular Segregation and Elemental Partitioning in Partially Molten Olivine-bearing Geological Composites by STEM-EDX

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Understanding the deformation behavior of composite ceramic materials at high temperature and applied stress is a common goal of geologists and the developers of ceramic materials for high-temperature structural applications. For example, the nature of grain boundaries at the "operating" temperature of the composite has significance to the creep behavior of both silicon nitride ceramics used in advanced automotive engines and for olivine-rich partially molten rocks that comprise the Earth's upper mantle. The presence of nanometer-scale glassy intergranular phases at the grain boundaries can provide fast diffusion paths and promote grain boundary sliding as a significant creep mechanism [1]. Scanning transmission electron microscopy (STEM) in conjunction with energy-dispersive X-ray (EDX) or electron energy-loss (EELS) spectroscopies is a powerful method for characterizing the grain boundary phases and segregants at nanometer resolution. However, the STEM-EDX analysis of such composites can be compromised by changes in chemistry, including sublimation, elemental redistribution, and bond-breaking, that may occur under the intense irradiation of the focused electron beam. The goal of the present study is to characterize by STEM-EDX techniques the elemental distributions and intergranular segregation in partially molten olivine-bearing geological composites, to better understand the rheological behavior of these materials in the Earth's upper mantle. The technical challenges encountered in the characterization of these materials suggest strategies for such characterization of beam-sensitive materials in general.

The data were acquired with a Philips CM200FEG, equipped with an Oxford EDX detector with super atmospheric thin-window and XP3 pulse processor, and an EMiSPEC (ES) Vision integrated acquisition system. The electron optical conditions were adjusted to obtain a ~1.4 nm probe (FWHM) with 1 nA of beam current. A modified data acquisition procedure was used, as it became immediately evident that no dwell time was sufficiently short to avoid beam damage during the collection of a spectrum profile. With this procedure, the beam was rasterred to accomplish numerous (>10) scans parallel to the boundary during the acquisition of each spectrum of ~250 ms duration, while ES Vision was operated in spectrum imaging mode to acquire a time series of spectrum profiles with 100 spectra per profile. In this way, the instantaneous duration of the intense probe on any part of the specimen was minimized. With this procedure, approximately ten spectrum profiles could be acquired from boundaries between the olivine grains before a visible change in the elemental distributions (a broadening of the profiles) could be detected; the ten equivalent spectra were summed to yield a 100-pixel spectrum profile with ~2.5 s total acquisition time per pixel. Elemental intensities were determined using the multiple linear-least squares (MLLSQ) fitting routine of DTSA [2]; concentrations were determined using the olivine matrix $[(Mg_{0.9}Fe_{0.1})_2SiO_4]$ as a standard and interpolating the k-factors of Al, Ca and Ti.

Concentration profiles are shown in Fig. 1 for two different olivine-rich composites: (a) olivine + 12vol% basalt and (b) partially molten lherzolite, which were deformed at 300 MPa confining pressure, 36 MPa uniaxial stress, and ~1423K and ~1523K, respectively, for 5 h. Details are given elsewhere [3]. The presence of Ca and Ti is clearly evident at the boundaries for both specimens. In contrast, appreciable Al segregation is evident only in the partially molten lherzolite. The robust extraction of the Al intensity is complicated by the Al K X-ray peak being situated between those of Mg and Si (major elements in the olivine matrix) and at a place in the spectrum where the background is variable. The absence of appreciable Al, a major component of the basalt second phase, in the grain boundaries of the olivine + basalt specimen suggests that the glass phase does not extend from the triple junctions into the grain boundaries. High-resolution imaging confirms that a nm-scale glassy film, such as is found in silicon nitride ceramics, is not present at the grain boundaries of either geological composite. The Ca and Ti at the grain boundaries are therefore interfacial segregants.

Comparable spectrum profile time series at the olivine-basalt phase boundary at the triple junctions of the composites clearly indicate the beam sensitivity of these materials. Elemental redistribution rapidly developed in the glass phase to produce concentration oscillations of the elements comprising the glass with a spatial frequency of a few nanometers. Such material beam sensitivity demands stringent control of the electron beam during initial examination and analysis for robust characterization. Strategies could include blanking the beam except when data are being acquired (including during the “fly-back,” when the position of the beam is returned to the beginning of the raster at the beginning of each line scan), and a quantitative accounting of the electron dose and dose-rate to the specimen, so that appropriate extrapolations to zero dose could be performed [4].

References
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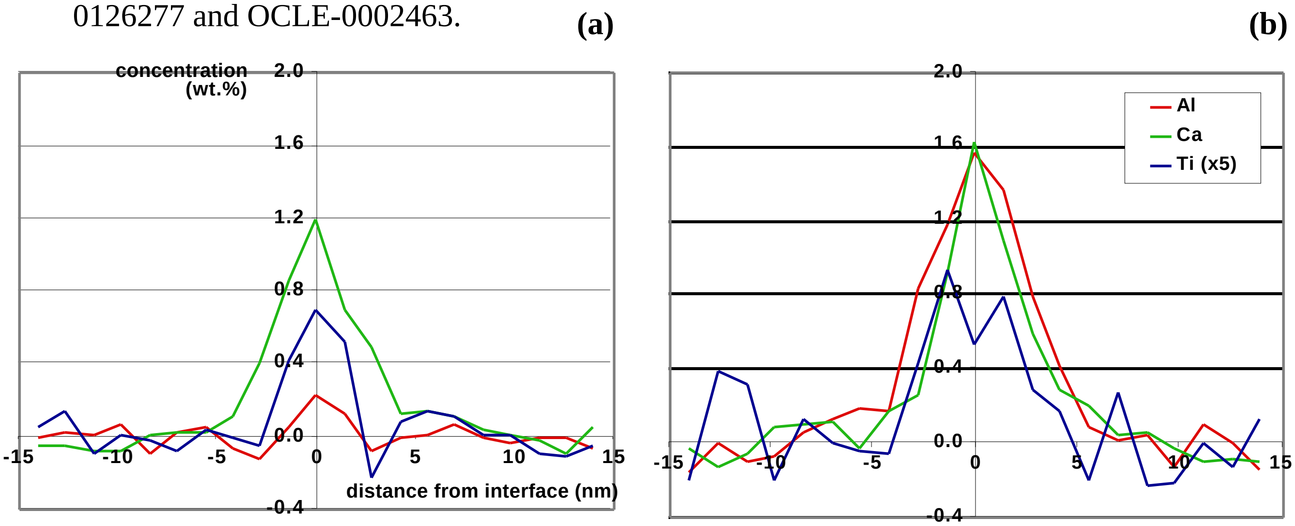

FIG. 1. Characteristic X-ray intensity profiles indicating interfacial segregation at olivine grain boundaries in (a) olivine + basalt and (b) partially molten lherzolite composites.