Thermodynamic phase relations of the MgO-FeO-SiO$_2$ system in the lower mantle

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The perovskite (Pv) to post-perovskite (PPv) phase transition at pressures near the Earth's core-mantle boundary (CMB) is currently the favored candidate for explaining most, if not all, of the peculiarities of the D'' layer (~200 km region above core) [1, 2]. The intense interest in this layer is motivated by its role in determining the boundary condition on the bottom of the convecting mantle, thereby greatly affecting mantle dynamics. The post-perovskite phase boundary in pure MgSiO$_3$ is fairly well known, but the experimental and calculated results on the partitioning of Fe among the stable coexisting phases and its influence on the transition pressure are currently contradictory [3-5].

To gain a better understanding of this region, it is useful to develop a complete thermodynamic understanding of a simplified system, before the complex behavior of the actual phase assemblage is addressed. Using density functional theory (DFT), we investigate the MgO-FeO-SiO$_2$ ternary system over the temperatures and pressures relevant to the core-mantle boundary. The regions of stability for the phases present under these conditions, Pv, PPv, (Mg, Fe)O magnesiowustite, and SiO2 stishovite, are determined as a function of iron compositions. We first use DFT to calculate the energies of the oxide and silicate phases for a number of Fe compositions along the Mg-Fe binary. We then carry out DFT perturbation calculations to obtain vibrational heat capacities, and parameterize the effect of Fe using a Vinet equation of state with a Grüneisen thermal correction. These equations of state are then used to explore the predicted phase relations for this simplified lower mantle chemistry. The results of this investigation are a complete thermodynamic description of the stable phases for this simplified chemistry and a theoretical prediction for iron partioning in the lower mantle. This work is also useful in the planning of future experiments, indicating what studies are most crucial to constraining the phase relations near the transition region.

[1] Murakami *et al.* (2004) *Science* **304**, 855-858. [2] Oganov & Ono (2004) *Nature* **430**, 445-448. [3] Caracas & Cohen (2005) *GRL* **32**, L16310. [4] Kobayashi *et al.* (2005) *GRL* **32**, L19301. [5] Auzende *et al.* (2007) *Goldschmidt Abstract.*

Release of hexavalent Chromium by ash and soils in wildfire impacted areas

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The highly oxidizing environment of a wildfire has the potential to convert any chromium present in the soil or in residential or industrial debris to its more toxic form, hexavalent chromium, a known carcinogen. In addition, the highly basic conditions resulting from the combustion of wood and wood products could result in the stabilization of any aqueous hexavalent chromium formed.

Samples were collected from the October 2007 wildfires in Southern California and subjected to an array of test procedures to evaluate the potential impact of fire-impacted soils and ashes on human and environmental health (Plumlee *et al.*, http://pubs.usgs.gov/of/2007/1407/). Soil and ash samples were leached using de-ionized water to simulate conditions resulting from rainfall on fire-impacted areas (Hageman *et al.*, 2007, http://pubs.usgs.gov/tm/2007/05D03/). The resulting leachates were of high pH (10-13) and many, particularly those of ash from burned residential areas, contained elevated total chromium up to 33 µg/L. Samples were also leached using a near-neutral pH simulated lung fluid (Plumlee *et al.,* 2006, Rev. Min. Geoch., v. 64, ch. 2) to model potential chemical interactions of inhaled particles with fluids lining the respiratory tract.

High Performance Liquid Chromatography coupled to Inductively Coupled Plasma Mass Spectrometry (Wolf, *et al.*, J. Anal. At. Spectrom., 2007, 22, 1051–1060) was used to separate and detect individual species (e.g., Cr^{+3}, Cr^{+6}, As^{+3}, As^{+5}, Se^{+4}, and Se^{+6}). These procedures were utilized to determine the form of the chromium present in the de-ionized water and simulated lung fluid leachates.

The results show that in the de-ionized water leachate, all of the chromium present is in the form of Cr^{+6}, and the resulting high pH tends to stabilize Cr^{+6} from reduction to Cr^{+3}. Analysis of the simulated lung fluid leachates indicates that the predominant form of chromium present in the near-neutral pH of lung fluid would be Cr^{6+}, which is of concern due to the high possibility of inhalation of the small ash and soil particulates, particularly by fire or restoration crews.