

Oxygen and silicon partitioning between molten iron and silicate melts up to 70 GPa and 4000 K

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The Earth's core is mainly composed of a Fe-Ni alloy. The core density compared to that of pure iron highlights a deficit that calls for the presence of light elements in addition to Fe and Ni to be explained. Si and O are among the likely candidates. Core formation is speculated to occur in a deep magma ocean in which the molten metal equilibrates with the silicate melt. The depth of this magma ocean, constrained by siderophile element partitioning, appears larger than previously thought. Thus, the experimental studies carried so far that have focused on Si and O partitioning between molten metal and silicates only up to 25 GPa, or at higher pressure, between metal and (Mg, Fe)O to interpret the behavior of oxygen in iron melts, have to be extrapolated to be relevant for the conditions of Earth's core formation.

In this study, we investigated directly the partitioning of oxygen and silicon between molten iron and silicate melts from 40 to 70 GPa using the laser-heated diamond anvil cell. We loaded the DAC with samples of olivine surrounding pure iron metal. Three olivine compositions, from 0 to 8 wt% FeO, were loaded with iron at 50 GPa to study the effect of oxygen fugacity on partitioning. Recovered samples were milled with the Focused Ion Beam technique and analyzed with electron microprobe and Transmission Electron Microscopes to obtain compositions of quench metal and silicate. The partition coefficients of oxygen and silicon between metal and silicate were determined as a function of pressure and oxygen fugacity. Quenched analyzed samples clearly show an oxidation of the silicate during the experiments. We report large amounts of oxygen (6-12 wt%) and silicon (2-10 wt%) in the metal at fO_2 around IW-1. The obtained results are used with literature lower-pressure data to thermodynamically parameterize the partitioning of oxygen and silicon. Oxygen and silicon solubility trends at high pressure are different than what expected on the basis of the extrapolation of lower pressure data.

A comparison of the reactivity at the solid-solution interface of nano- and micro-crystalline TiO₂ phases

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The acid-base surface reactivity of rutile (α -TiO₂), with the (110) crystal face predominant, has been studied extensively. Specifically, theoretical simulations, X-ray techniques and potentiometric titration studies have provided molecular-scale and macroscopic details on the ion adsorption behaviour of rutile. Results of the collective studies have been integrated into the multisite complexation (MUSIC) model. Similar detailed studies examining the surface charging properties of nano-crystalline anatase samples are now being conducted.

Primary surface charging curves of rutile in LiCl, NaCl, KCl, and RbCl electrolyte media are compared with similar titration data for nanoparticle anatase samples. The effect of electrolyte media and ionic strength on the primary charging behaviour of anatase was studied as a function of nanoparticle size (3–40 nm diameter). The primary charging curves of rutile and all nano-anatase samples are generally analogous, when normalized to their respective pH_{zpc} values. At low ionic strength (0.03 m) the development of negative surface charge was similar for all electrolyte cations. However, with increasing ionic strength negative surface charge development was enhanced as the bare crystallographic radii of the cations decreased. Subtle differences in the macroscopic charging behaviour of the 3 nm diameter anatase sample were noted, particularly below the pH_{zpc} value were Cl⁻ counterions screen the surface from bulk solution.

For rutile, X-ray data and MD simulations show that electrolyte cations are adsorbed as inner-sphere complexes, principally in tetradentate geometry. Similarly, DFT-MD simulations show inner-sphere sorption of monovalent cations onto anatase; however, bidentate sorption predominates. For both anatase and rutile, a CD-MUSIC model, coupled with a Basic Stern layer description of the electric double (EDL), successfully integrates all microscopic information with the macroscopic experimental results. Though for the smallest anatase particles, it is necessary to account for some curvature of the EDL.