

Surface charge, ion adsorption and molecular dynamics at the α -SnO₂/water interface

J. ROSENQVIST¹, L. VLCEK², E. MAMONTOV¹,
M. L. MACHESKY³, P. T. CUMMINGS²
AND D. J. WESOLOWSKI¹

¹Oak Ridge National Laboratory, Oak Ridge TN 37831, USA
(rosenqvistjk@ornl.gov), (mamontove@ornl.gov),
(wesolowskid@ornl.gov)

²Vanderbilt University, Nashville TN 37235, USA
(lukas.vlcek@vanderbilt.edu),
(peter.cummings@vanderbilt.edu)

³Illinois State Water Survey, Champaign IL 61821, USA
(machesky@uiuc.edu)

Introduction

It has been hypothesized that the bulk dielectric constant (ϵ) of the oxide solid influences the structure of interfacial water as well as the nature of ion sorption at the interface.¹ To investigate this, we have studied cassiterite (α -SnO₂, with $\epsilon=9$) using potentiometric titrations, quasielastic neutron scattering (QENS) and molecular dynamics (MD) simulations; and compare the results to previously obtained results for isostructural rutile (α -TiO₂, with $\epsilon=121$).

Results and discussion

QENS experiments performed on nanosized powders of cassiterite and rutile, predominantly showing the 110 crystal face, indicated considerable differences in the dynamics of water molecules at the interface. Our MD simulation results showed excellent agreement with the measured relaxation times of interfacial water on the 1–100 ps time scale.

Titrations showed that the charging of the cassiterite surface is of the same magnitude as for rutile. However, for cassiterite we obtained virtually identical charging curves in RbCl and NaCl media, whereas charging on rutile is clearly different in the different media. Results from MD simulations indicate that the distribution of Rb⁺/Na⁺ on the two surfaces is quite different, thus providing an explanation for the observed results. Significant differences are also observed for Sr²⁺ adsorption, while Zn²⁺ adsorption is similar on the two mineral surfaces.

Using O-H bond distances obtained in ab initio and MD simulations together with hydrogen bonding schemes obtained from MD, we constructed a surface complexation model based on the MUSIC model² that was able to predict the observed charging and distribution of ions.

References

- [1] Sverjensky D. A. (2001) *Geochim. Cosmochim. Acta* **65**, 3643-3655.
- [2] Venema P., Hiemstra T., Weidler P. G. and van Riemsdijk W. H. (1998) *J. Coll. Int. Sci.* **198**, 282-295.

Phase and melting relations of a residual garnet clinopyroxenite

A. ROSENTHAL¹, G.M. YAXLEY¹, D.H.GREEN¹,
J. HERMANN¹ AND C.S. SPANDLER²

¹Research School of Earth Sciences, Australian National University, Canberra (anja.rosenthal@anu.edu.au)

²Institute of Geological Sciences, University of Bern

Melting behaviour and high pressure phase relations of refertilised mantle comprised of mixed lithologies (e.g. discrete bodies of mafic eclogite or pyroxenites and diverse types of metasomatised, re-fertilised or depleted mantle) are poorly constrained, yet this information is essential for understanding the observed geochemical diversity of primitive magmas on Earth.

Our project is designed to explore the melting behaviour of subducted crust in an inhomogeneous, buoyant, upwelling mantle. We track a sequential process in which melts are redistributed from the (initially) low temperature melting of average oceanic crust, and then from the residues (garnet pyroxenite) until the solidus of the latter equals or exceeds the solidus of refertilised peridotite.

Composition Res-2 is the melting residue of an anhydrous altered MORB composition (GA2 of Spandler *et al.*, submitted) at 5 GPa near the point of coesite out, and hence is a model for recycled eclogite which has lost a siliceous melt component during mantle upwelling. It is therefore depleted in incompatible minor elements, with 2.2 wt% Na₂O and a CaO/Na₂O ratio of 4.9. Res-3 is identical but has higher CaO/Na₂O ratio of 12.1.

The subsolidus phases of Res-2 & 3 are grt and cpx with accessory coesite/quartz. The solidus of Res-2 is at 1275°C at 3 GPa, 1400°C at 4 GPa, 1425°C at 5 GPa, and <1450°C? at 6 GPa. The solidus of Res-3 behaves similarly, but is at slightly higher T than that of Res-2 (1300°C at 3 GPa).

Low-degree melting (<10%) is eutectic-like. Once coesite is melted out, the grt-cpx cotectics control melt compositions and proportions with cpx>grt. However, with increasing degree of melting, cpx/grt ratios decrease until cpx is exhausted, leaving grt as the sole liquidus phase. In contrast, coesite-out for Res-3 remains approximately constant at ~50°C above solidus at all pressures. In residues of Res-3 the proportion of grt increases with P, and always exceeds that of cpx.

Melt compositions vary with increasing degree of melting from dacitic to basaltic for Res-2 at 3 GPa. However, at higher P, melts of Res-2 are generally much less silica rich, varying from andesitic to basaltic. This is similar to Res-3 at all pressures.

For both Res-2 & 3, Ti behaves incompatibly in cpx at all P-T conditions, but D^{Ti}[cpx/melt] decreases toward higher temperature. Na however, is incompatible at 3 GPa, but compatible at higher pressures.

Reference

- Spandler C., Yaxley G., Green D.H. and Rosenthal A. (2007), *J. Petrol.* submitted.