

## Thermodynamics of rutile- and $\alpha$ -PbO<sub>2</sub>-type solid solutions from quantum-mechanical calculations

V.L. VINOGRAD<sup>1</sup> AND B. WINKLER<sup>2</sup>

<sup>1</sup>Institute of Energy and Climate Research (IEK6),  
Forschungszentrum Jülich, 52425, Germany  
(v.vinograd@fz-juelich.de)

<sup>2</sup>Institute of Geosciences, University of Frankfurt, Frankfurt  
a.M., 60438, Germany

Recent progress in analytical techniques sensitive to ppm-range concentrations attracted the interest of petrologists to geothermobarometry based on trace element partitioning between various minerals [1]. Current approaches for the calibration of such geothermobarometers are purely phenomenological. Indeed, the thermodynamic mixing properties of solid solutions, whose concentration ranges do not exceed 1000 ppm, cannot be easily measured and thus typically are not known. We propose to use atomistic model simulations for the calibration and extrapolation of such geothermobarometers. In this report we will present the results of density functional theory based simulations of TiO<sub>2</sub>-SiO<sub>2</sub> and TiO<sub>2</sub>-ZrO<sub>2</sub> solid solutions with rutile and  $\alpha$ -PbO<sub>2</sub>-type structures obtained using the double-defect method [2]. The results will be discussed in relation to Zr-in-rutile thermometry and Si-in-rutile barometry. The pressure effects of Ti-in-quartz and Ti-in-zircon thermometers have also been modeled.

[1] T. Zack, R. Moraes, A. Kronz (2004) *Contrib. Mineral. Petrol.* **148**, 471–488. [2] V.L. Vinograd, B. Winkler (2010) *Reviews in Mineralogy & Geochemistry* **71**, 451–475.

## Factors affecting the physical phase state of SOA particles from biogenic and anthropogenic precursors

A. VIRTANEN<sup>1\*</sup>, E. SAUKKO<sup>1</sup>, A. LAMBE<sup>2</sup>, P. MASSOLI<sup>3</sup>,  
T. ONASCH<sup>3</sup>, J. WRIGHT<sup>2</sup>, D.R. CROASDALE<sup>2</sup>,  
A. LAAKSONEN<sup>4</sup>, P. DAVIDOVITS<sup>2</sup> AND D. WORSNOP<sup>3</sup>

<sup>1</sup>Tampere University of Technology, Department of Physics,  
P.O.Box 692, 33101 Tampere, Finland  
(\*correspondence: annele.virtanen@tut.fi)

<sup>2</sup>Boston College, Department of Chemistry, 2609 Beacon  
Street, Chesnut Hill, MA 02467-3860, USA

<sup>3</sup>Aerodyne Research, 45 Manning Road, Billerica, MA 08121-  
3976, USA

<sup>4</sup>Finnish Meteorological Institute, P.O. Box 503, 00101  
Helsinki, Finland

SOA formation and properties are widely studied to clarify the role of SOA in radiative forcing and climate. However, very limited information is available on the morphology and phase state of SOA particles. Verifying the physical phase state of SOA particles gives new and important insight into their formation and growth process and essential information on their implications in the atmosphere [1, 2].

According to our recent results [3], pine derived SOA particles in chamber conditions as well as atmospheric SOA particles formed in boreal forest can be amorphous solid in their physical state at least several hours after their formation. However, it is not known yet how general the observation is and what the atmospheric implications are.

In this study we have investigated the physical phase state of SOA particles formed in Boston College flow tube from various precursor VOCs representing both biogenic and anthropogenic sources. In addition, the phase change was investigated as a function of particle oxidation level (O:C) and flow tube SO<sub>2</sub> concentrations.

According to our results the solid phase is the dominating phase state of formed SOA in the case of both biogenic and anthropogenic precursors at least up to relative humidity (RH) values of 55-70%. At higher RH values the humidity induced phase transition takes place and particles liquefy. We find that the O:C ratio of particles as well as chamber SO<sub>2</sub> concentration have an effect on the phase of SOA particles.

[1] Zahardis *et al.* (2007) *Atmos. Chem. Phys.* **7**, 1237-

[2] Zobrist *et al.* (2008) *Atmos. Chem. Phys.* **8**, 5221-

[3] Virtanen *et al.* (2010) *Nature*, **467**, 467.