

## 3.5.22

### Modelling of P-V-T properties of water by a Peng-Robinson-SAFT equation of state

E. PERFETTI<sup>1</sup> J. DUBESSY<sup>1</sup>, R. THIERY<sup>2</sup>

<sup>1</sup>G2R, Nancy, France (jean.dubessy@g2r.uhp-nancy.fr)

<sup>2</sup>LMV, Clermont-Ferrand, France (R.Thiery@opgc.univ-bpclermont.fr)

Equations of state (EOS) for geological fluids are a prerequisite to model fluid mineral equilibria, fluid mixing, fluid unmixing. As water and salts are ubiquitous components of crustal fluids, classical equations of state based on simple cubic EOS are not suitable to model the macroscopic properties resulting from hydrogen bonding, solvation, charge-charge and charge-dipole interactions.

Additional contribution must be included in the model to take into account these interactions, considering that the Helmholtz energy is made of several contributions: a reference fluid, described by a Peng-Robinson equation of state [1], and an association term described by the Statistical Association Fluid Theory [2] which takes into account hydrogen bonding between water molecule.

In this paper, from the formulation of Wu and Prausnitz [3], we optimize the parameter to model the P-V-T properties of pure water along the saturation curve, in the single phase field above and below the critical temperature.

#### References

- [1] Peng D.Y. and Robinson (1976) *Ind. Eng. Chem. Fundam.*, **15**, 59-64.
- [2] Chapman W.G., Gubbins K.E., Jackson G., Radosz M. (1990). *Ind. Eng. Chem. Res.*, **29**, 1709-1721.
- [3] Wu J., and Prausnitz J. M. (1998). *Ind. Eng. Chem. Res.*, **37**, 1634-1643.

## 3.5.23

### Carbon solubility in major mantle minerals

S.S. SHCHEKA<sup>1</sup>, M. WIEDENBECK<sup>2</sup>, D.J.FROST<sup>3</sup> AND H.KEPPLER<sup>1</sup>

<sup>1</sup>Institut für Geowissenschaften, Universität Tübingen, 72074, Tübingen, Germany (svyatoslav.shcheka@uni-tuebingen.de; hans.keppler@uni-tuebingen.de)

<sup>2</sup>GeoForschungsZentrum Potsdam, 14473 Potsdam, Germany (michawi@gfz-potsdam.de)

<sup>3</sup>Bayerisches Geoinstitut, Universität Bayreuth, 95440, Bayreuth, Germany (dan.frost@uni-bayreuth.de)

According to numerous estimates the Earth's mantle hosts approximately  $5 \times 10^{23}$  g of carbon. The solubility of carbon in ordinary mantle minerals is a critical but poorly known parameter in the global carbon cycle. A few hundred p.p.m. of carbon in mantle silicates or spinel would be fully adequate to incorporate all mantle C, thereby making other carbon-rich phases unstable and dramatically reducing the mobility of mantle carbon.

We synthesized C-saturated forsterite, enstatite, diopside, garnet, spinel (upper mantle), wadsleyite, ringwoodite, MgSiO<sub>3</sub>-ilmenite (transition zone) and MgSiO<sub>3</sub>-perovskite (lower mantle) by growth from a carbonatite melt, which was isotopically enriched to contain more than 99 % of the isotope <sup>13</sup>C. This method eliminates the main problems of previous studies – a) contamination with C of normal isotopic composition, and b) low diffusion rates of C in pre-existing crystals. Experiments were performed in a piston-cylinder apparatus (T=900-1200°C, P=1.5 – 3.5 GPa), and a multi-anvil press (T=1200-1400°C, P=6-26GPa). Carbonates recovered from the capsule were removed by etching with hydrochloric acid or water (for high pressure phases); carbon contents of synthesized minerals were measured with a Cameca ims 6 f ion probe extensively modified in order to suppress C background. Measured carbon was dominated by the <sup>12</sup>C isotope, but synthesized crystals yielded a stable, elevated ratio of <sup>13</sup>C/<sup>12</sup>C. Data for olivine were quantified using synthetic forsterite, ion-implanted with a known dose of <sup>13</sup>C. Carbon contents of other upper mantle minerals were calibrated against synthetic tholeite glasses doped with <sup>13</sup>C and should be considered as preliminary results because secondary ion yields are matrix dependent.

The data obtained indicate that carbon solubility in the upper mantle silicates is extremely low, of the order of 0.1-1 µg/g. No C was detected in spinel. This implies that separate carbon-rich phases (fluid, carbonates) are responsible for the storage of most upper mantle carbon. Measurement of carbon in high-pressure phases are in progress and will be reported at the conference.