

## The effect of water on the solubilities of metals and accessory phases in granitic melts

ROBERT L. LINNEN

Department of Earth Sciences, University of Waterloo,  
Waterloo, ON, Canada, rlinnen@uwaterloo.ca

The solubilities of manganocolumbite, manganotantalite, wolframite (hübnerite), rutile, zircon and hafnon were determined as a function of the water content in a peralkaline (ASI=0.6) and a subaluminous (ASI=1.0) granite melt. All experiments were conducted at 1035°C and 2 kbar in TZM rapid quench autoclaves and the water contents of the melts ranged from nominally dry to approximately 6 wt% H<sub>2</sub>O. Accessory phase solubilities are not affected by the water content of the peralkaline melt. By contrast, solubilities are affected by the water content of the subaluminous melt. There is a decrease in the solubilities of all the accessory phases at less than ~1 wt% H<sub>2</sub>O, but at water contents higher than this value, solubilities are nearly constant. It can be concluded that water is not an important control of accessory phase solubility, although the water content will affect diffusivities of components in the melt, and thus whether or not accessory phases will be present as restite material. The solubility behaviour in the subaluminous melt supports previous spectroscopic studies, which have observed changes in coordination of high field strength elements only in subaluminous melt compositions, and only in nominally dry melts.

Wolframite solubility has an additional complexity because tungsten is potentially 4<sup>+</sup>, 5<sup>+</sup> or 6<sup>+</sup> in granitic melts. The experiments were conducted at constant hydrogen fugacity, thus the oxygen fugacities of the melts are progressively lower with progressively lower water contents. If wolframite dissolves as W<sup>5+</sup>, e.g.,  $\text{MnWO}_4^{\text{crystal}} = \text{MnO}^{\text{melt}} + 0.5 \text{W}_2\text{O}_5^{\text{melt}} + 0.25 \text{O}_2^{\text{melt}}$  then wolframite solubility should decrease with increasing the water content of the melt. The decrease of solubility with increasing water content will be even greater if tungsten is quadrivalent. However, wolframite solubility increases with increasing water content in the subaluminous composition suggesting that tungsten dissolved as a hexavalent species.

## Water solubility in the lower mantle minerals

K.D. LITASOV AND E. OHTANI

Inst. Mineralogy, Petrology and Economic Geology, Tohoku University, Sendai, Japan (klitasov@ganko.tohoku.ac.jp)

Water storage capacity of the lower mantle becomes a matter of debate. Meade et al. (1994) reported 60-70 ppm H<sub>2</sub>O in MgSiO<sub>3</sub>-perovskite. However, Bolfan-Casanova et al. (2000) showed absence of water (<1 ppm H<sub>2</sub>O) in MgSiO<sub>3</sub>-perovskite. Murakami et al. (2002) reported 0.1-0.4 wt% H<sub>2</sub>O in Al-Fe-Mg-perovskite, 0.3-0.4 wt% H<sub>2</sub>O in Ca-perovskite and 0.2 wt% H<sub>2</sub>O in ferropericlae measured by SIMS and FTIR. Bolfan-Casanova et al. (2002) reported less than 20 ppm H<sub>2</sub>O in ferropericlae at 25 GPa. Here we report new data on water solubility in Mg-perovskites, Ca-perovskite, and ferropericlae in Al-Fe-bearing systems. Using the measured water content we estimate water storage capacity in the Earth's lower mantle.

The phase relations were determined at 25-26 GPa and the temperature range from 1000 to 1800°C. We used several starting materials corresponding to perovskite and ferropericlae. The hydrous composition was prepared by adding Mg(OH)<sub>2</sub> or Ca(OH)<sub>2</sub> adjusting the proportion of MgO and CaO. The furnace assemblies and experimental details are described by Litasov and Ohtani (2002). Water contents were measured by FTIR (Litasov et al., 2003).

IR spectra of pure MgSiO<sub>3</sub> perovskite synthesized at 1300°C show bands at 3397, 3423, 3448, and 3482 cm<sup>-1</sup>. Calculated water content corresponds to about 100 ppm H<sub>2</sub>O. Al-Mg-perovskite containing 4-7 wt% of Al<sub>2</sub>O<sub>3</sub> shows broad IR spectra with bands at 3404, 3448, and 3565 cm<sup>-1</sup>. Calculated water content is 1100-1400 ppm. IR spectra of MORB-related Mg-perovskite (Mg#=58-61, Al<sub>2</sub>O<sub>3</sub>=13-17 wt%) synthesized at 1000-1200°C show major bands at 3397 cm<sup>-1</sup>. The H<sub>2</sub>O content in MORB-related Mg-perovskites is 90-110 ppm. IR spectra of peridotite-related Mg-perovskite (Mg#=88-90, Al<sub>2</sub>O<sub>3</sub>=5-6 wt%), synthesized at 1400-1600°C, also show major bands at 3397 cm<sup>-1</sup>. The H<sub>2</sub>O content in Mg-perovskite related to peridotite is 1400-1800 ppm.

IR spectra of aluminous Ca-perovskite (2.0 wt% Al<sub>2</sub>O<sub>3</sub>) synthesized at 1900°C composed of two major bands at 3343 and 3607 cm<sup>-1</sup>. Preliminary H<sub>2</sub>O content in Ca-perovskite is near 5100 ppm.

IR spectra of periclae show weak bands at 3299, 3308, and 3404 cm<sup>-1</sup>. Ferropericlae (Mg#=88) has major bands at 3299 and 3474 cm<sup>-1</sup>. Calculated H<sub>2</sub>O content in periclae is 11 ppm at 1400°C (Al<sub>2</sub>O<sub>3</sub> in periclae is 1.2 wt%) and 20-25 ppm at 1600-1800°C (Al<sub>2</sub>O<sub>3</sub>=0.9 wt%). The H<sub>2</sub>O content in ferropericlae is 14 ppm at 1400°C (Al<sub>2</sub>O<sub>3</sub>=0.9 wt%) and 80 ppm at 1800°C (Al<sub>2</sub>O<sub>3</sub>=2.4 wt%).

The present results indicate that Ca-perovskite has highest water solubility among the lower mantle minerals following by Mg-perovskite and ferropericlae. The maximum amount of water potentially stored in the lower mantle is estimated as 3.42x10<sup>21</sup> kg. This is 2.5 times of the present ocean mass and comparable with the amount of water potentially concentrated in the transition zone.