

# *EUG XI*



Symposium MS05

Water in the Earth's Mantle

Convenors

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# MS05 Water in the Earth's Mantle

## Tuesday PM Session

### MS05 : TUpm25 : F6 Hydrogen Content in Spinel Lherzolite Xenoliths Coming from Different Depths (Kilbourne Hole, NM)

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In order to estimate the concentration level of hydrogen stored in the upper mantle we need to collect data on hydrogen content of mantle xenoliths, their conditions of equilibrium and the partition coefficients of hydrogen between different nominally anhydrous minerals (Ingrin and Skogby, 2000). Quantitative hydrogen content in mantle xenoliths has been estimated by infrared analysis performed on individual grains and then summed in order to record an averaged infrared spectrum representative of each mineral phase present in the xenolith. Calibrations proposed by Bell et al., (1995) and Libowitzky and Rossman, (1997) were used to transform OH absorption values into hydrogen concentration in wt. ppm H<sub>2</sub>O. We report results from analyses performed on 3 xenoliths from Kilbourne Hole (New Mexico) coming from around 30, 50 and 85 km depth (1.1 GPa; 1.7 GPa; 2.8 GPa; Glücklich, 1992). Infrared profiles realised within single crystals and across grain boundaries show no hydrogen concentration gradient, at least at a scale of 10 microns. In these conditions, the hydrogen content of each mineral phase can be assumed homogeneous and each phase is in equilibrium with the others. More than 100 analyses were recorded and averaged from each xenolith, allowing to measure the hydrogen content in olivine, enstatite and diopside:

Colivine = 1 ppm H<sub>2</sub>O ; 1.1 ppm H<sub>2</sub>O ; 1 ppm H<sub>2</sub>O  
Cpx = 175 ppm H<sub>2</sub>O ; 174 ppm H<sub>2</sub>O ; 212 ppm H<sub>2</sub>O  
Cpx = 410 ppm H<sub>2</sub>O ; 388 ppm H<sub>2</sub>O ; 492 ppm H<sub>2</sub>O,

respectively for increasing depths. Within the uncertainty of the analysis the amount of hydrogen stored in these xenoliths is almost independent of the depth of origin, with an average of 100 ppm H<sub>2</sub>O. The partition coefficients between each phase are:  $F_{\text{cpx/cpx}} = 0.44 \pm 0.10$ ,  $F_{\text{ol/ol}} = 0.0025 \pm 0.0015$  and  $F_{\text{en/en}} = 0.006 \pm 0.003$ . The constant H concentration measured within xenoliths coming from different depth may be interpreted in two ways in term of H content, the equilibrium with a basalt of homogeneous H concentration or/and the homogeneity of the lithospheric mantle below Kilbourne Hole. This study was financially supported by the EU through the Human Potential Program HPRN-CT-2000-00056.

Bell DR, Ihinger PD & Rossman GR, *Amer. Mineral.*, **80**, 465-474, (1995).

Glücklich M. *Thesis Univ. Paris 7*, pp270, (1992).  
Ingrin J & Skogby H, *Eur. J. Mineral.*, **12**, 543-570, (2000).  
Libowitzky E & Rossman GR, *Amer. Mineral.*, **82**, 1111-1115, (1997).

### MS05 : TUpm26 : F6 Comparison of FTIR and NMR Data on OH in Diopside: Towards a Site-Specific Calibration of FTIR Spectra

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Infrared spectroscopy is frequently used to determine hydrogen concentrations in nominally anhydrous minerals (NAMs), and may distinguish hydroxyl ions in different structural environments. Since the method is not self-calibrating the calculation of hydrogen concentrations rely on molar extinction coefficients that are normally obtained by comparisons with bulk hydrogen analysis methods. However, the IR spectra of many NAMs are complex and the molar extinction coefficient are known to vary strongly with band frequency. A calibration method with a similar site-specific capability would hence be preferable. The possibility of using <sup>1</sup>H MAS NMR for such a calibration has been explored in this study.

The sample investigated consists of flux grown diopside single crystals that were synthesised under reducing conditions in a CO<sub>2</sub>-H<sub>2</sub> gas mixing furnace. Polarised FTIR spectra were measured in the  $\alpha$ ,  $\beta$  and  $\gamma$  directions on oriented single crystals. <sup>1</sup>H MAS NMR spectra were obtained on about 200 mg of hand-picked crystals which were lightly crushed before measurements, using recycle delays up to 204 min. Both FTIR and NMR spectra contain three well-resolved peaks, and some weaker features (shoulders). These spectra could be accurately fitted by using a minimum of five or six peaks respectively. By aid of the well-known correlations between the strength of the hydrogen bonding and both IR band frequency (e.g. Libowitzky, 1999) and NMR chemical shift (Eckert et al. 1988), the individual peaks were then matched together for the two methods.

Comparisons of the peak area ratios obtained by the two methods for the matched bands result in extinction coefficients for the FTIR peaks that generally increase with decreasing band frequency, in agreement with previous studies (Paterson, 1982; Libowitzky and Rossman, 1997). However, the accuracy of the derived extinction coefficients is limited by the rather wide range of possible fits to the spectra.

Eckert H, Yesinowski JP, Silver LA & Stolper EM, *J. Phys. Chem.*, **92**, 2055-2064, (1988).

Paterson M, *Bull. Min.*, **105**, 20-29, (1982).

Libowitzky E, *Mh. Chem.*, **130**, 1047-1059, (1999).

Libowitzky E & Rossman GR, *Am. Min.*, **82**, 1111-1115, (1997).

### MS05 : TUpm27 : F6 Single-Crystal IR Spectroscopic Measurements on Transition Metal Bearing Pyrope: The Incorporation of Hydroxide in Upper Mantle Garnets

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Pyrope single crystals doped with transition-metal ions (Co, Cr, Ni, Ti and V) were synthesised in a piston-cylinder device and studied by single-crystal IR spectroscopy in order to determine their OH- concentrations and site substitutions. Stoichiometric oxide mixtures were used as starting materials and distilled water was used as a fluid flux. Crystals up to 2 mm in size were grown. Microprobe analysis and optical absorption spectroscopy were used to determine on which positions and in which oxidation states the transition-metal ions are incorporated in the pyrope structure. Cr<sup>3+</sup> and Ti<sup>3+</sup>-ions occupy the octahedral site and Co<sup>2+</sup> and Ni<sup>2+</sup> the dodecahedral site.

IR spectra in the OH- stretching region between 4000 and 3000 cm<sup>-1</sup> obtained on pyrope single-crystals that contain divalent and trivalent transition-metal ions like Ni<sup>2+</sup>, Co<sup>2+</sup>, and Cr<sup>3+</sup> are similar to that normally shown by end-member pyrope (Geiger et al., 1991). At room temperature the spectra show a single band at ~3630 cm<sup>-1</sup> that splits at ~79 K into two bands of smaller FWHM's at ~3618 cm<sup>-1</sup> and 3636 cm<sup>-1</sup>. These bands are assigned to OH- stretching modes resulting from the hydrogen substitution. The spectra of Ti<sup>4+</sup>-bearing pyrope measured at 298 K show four OH- stretching bands at approximately 3686, 3630, 3567 and 3527 cm<sup>-1</sup>. At ~79 K the band at 3630 cm<sup>-1</sup> splits into two narrow bands at 3636 cm<sup>-1</sup> and 3614 cm<sup>-1</sup>. This suggests that additional OH- substitutional mechanisms occur in Ti-containing garnets. In the IR spectrum of a V<sup>4+</sup>-bearing pyrope the same number of OH- stretching bands is observed, suggesting that higher charged cations cause additional OH- substitutions and increased OH- concentrations in garnet. The IR spectra of most natural pyrope-rich garnets appear to be different from those of the synthetics, which suggests that they are not characterised by the hydrogen substitution. They also contain less OH- than synthetics synthesised under H<sub>2</sub>O saturated conditions. However, the OH- substitution mechanism and concentrations in garnets from grosspyrite or similar parageneses are similar to those of the synthetics, which may reflect their formation in water-rich environments.

Geiger CA et al., *Am. Min.*, **76**, 49-59, (1991).

### MS05 : TUpm28 : F6 Location and Quantitative Analysis of OH in Coesite

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The incorporation of hydrogen (deuterium) into the coesite structure was investigated in multi-anvil experiments performed at 3.1 to 7.5 GPa and 700 to 1100 °C. Hydrogen enters the coesite structure at high pressure (> 5.0 GPa) and high temperature (1100 °C) only. The hydrogen isotopes and trace elements incorporated in the synthetic coesites have been determined by ion probe analyses (e.g., 1335 ±16 H/10<sup>6</sup>Si and 57 ±5 Al/10<sup>6</sup>Si at 7.5 GPa). No correlation between the amount of trace elements and the hydrogen content could be observed. The FTIR spectra show three relatively intense bands at 3575, 3516 and 3459 cm<sup>-1</sup> ( $\nu_1$ ,  $\nu_2$ , respectively) and two very weak bands at 3296 and 3210 cm<sup>-1</sup> ( $\nu_4$  and  $\nu_5$ , respectively). The band at 3516 cm<sup>-1</sup> is strongly asymmetric and can be resolved into two bands 3528 ( $\nu_{2a}$ ) and 3508 ( $\nu_{2b}$ ) cm<sup>-1</sup> with nearly identical areas. Polarized infrared absorption spectra of single-crystal slabs parallel to (010) and (100) were performed to calibrate the IR spectroscopy for quantitative analysis of "water" in coesite ( $\epsilon_{\text{H}_2\text{O}} = 190000 \pm 30000 \text{ l mol}^{-1} \text{ cm}^{-2}$ ) and to locate the OH dipoles in the structure. The polarized spectra reveal a strong pleochroism of the OH-bands. High-pressure FTIR spectra at pressures up to 8.0 GPa were performed in DAC to get further insight into the incorporation mechanism of OH in coesite. The peak positions of the  $\nu_1$  to  $\nu_3$  bands decrease linearly with pressure. The mode Grüneisen parameter for  $\nu_1$  to  $\nu_3$  are -0.074, -0.144 and -0.398, respectively. There is a linear increase of the pressure derivatives with band position which follows the trend proposed by Hofmeister et al. (1999). The FWHM's of the  $\nu_1$  to  $\nu_3$  bands increase from 35, 21 and 28 cm<sup>-1</sup> in the spectra at ambient conditions to 71, 68 and 105 in the 8 GPa spectra. On the basis of these results a model for the incorporation of hydrogen in coesite has been developed: the OH-defects are introduced into the structure by the substitution  $\text{Si}^{4+} + 4\text{O}^{2-} = \text{H} + 4\text{OH}^-$  which gives rise to the  $\nu_1$  to  $\nu_3$  vibrations. Since the OH(D)-bearing samples do contain traces of Al, the bands  $\nu_4$  and  $\nu_5$  may be coupled to Al substitution - but a clear correlation could not be detected.

Hofmeister AM, Cynn H, Burnley PC & Meade C, *Am. Mineral.*, **84**, 454-464, (1999).

### MS05 : TUpm29 : F6 New Raman Observations of Hydrous Phases at High Pressures

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Hydrogen storage in dense hydrous magnesium silicates (DHMS) and nominally anhydrous minerals (NAM) is likely to play an important role in the global hydrogen cycle. Phase E, one of the DHMS, is a potential carrier of water in cold subducted oceanic lithosphere between 350 and 500 km. It may be an important link in a chain of hydrous phases that could result in hydration of the mantle transition zone. Hydration of ringwoodite, the highest pressure polymorph of olivine and most abundant mineral between 520 and 660 km depth, would significantly influence physical and chemical properties of the lower part of the mantle transition zone. Consequently stability and hydration mechanism of hydrous ringwoodite and phase E have been the focus of many recent experimental and theoretical investigations. In general, the nature of the proton sites remains poorly understood. We report Raman spectra (from 80 to 4000 cm<sup>-1</sup>) on high-quality single-crystals of hydrous ringwoodite (Fo<sub>90</sub> with ~1.6 wt% H<sub>2</sub>O) and phase E (synthesized at the Bayerische Geoinstitut by J. Smyth and N. Ross respectively) measured in a diamond-anvil cell (DAC) at room temperature with solid helium as pressure-transmitting medium. Spectra of ringwoodite measured to 60 GPa contain a larger number of framework bands than expected from group theoretical predictions for the ideal cubic (Fd3 m) spinel structure, with the main vibrations of

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the SiO<sub>4</sub> tetrahedra at 796 cm<sup>-1</sup> and 840 cm<sup>-1</sup>. There is no evidence for any discontinuous behaviour in the pressure dependence of the observed modes to the maximum pressure, but new modes appear near 40 GPa. Unusually, OH stretching vibrations expected near 3150 to 3200 cm<sup>-1</sup> (inferred from IR absorbance measurements on the same sample) were not observed. Raman spectra of phase E contain several broad features between 80 and 1200 cm<sup>-1</sup> reflecting known long-range disorder in its crystal structure. The framework frequencies show a positive pressure dependence and no indication for a major change in the underlying crystal structure to at least 10 GPa. Broad OH stretching vibrations observed around 3400 and 3600 cm<sup>-1</sup> show only minor frequency shifts with pressure up to 10 GPa indicating weak or the possible absence of hydrogen bonding.

### MS05 : TUpm30 : F6 Hydrous Silicate Olivines and Spinelloids and the Hydration State of the Mantle

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The H content of the Earth is one of the most poorly constrained compositional variables for the planet. The nominally anhydrous olivine and spinelloid phases thought to compose the bulk of the upper mantle and transition zone may contain many times the amount of H and O that reside in the hydrosphere. Exploratory synthesis experiments were carried out in order to better define the stability fields of the various hydrous spinelloid phases and to better constrain the effect of H incorporation into these phases on their physical properties. Specific objectives were to explore the olivine-wadsleyite and wadsleyite-ringwoodite transitions and synthesize single crystals of sufficient size for physical property measurements. Two different compositions were formulated: the first to approach a natural Fo<sub>90</sub> hydrous olivine and the second richer in trace elements and silica to approximate a natural peridotite. Hydrogen is ten to twenty times more soluble in wadsleyite than in olivine, so it is possible that the olivine to wadsleyite transition may be displaced to lower pressures by the presence of water.

Three synthesis experiments were conducted on the hydrous Fo<sub>90</sub> olivine composition at 12 GPa and 1100/4C, 1300/4C and 1700/4C with the objective of producing hydrous olivine crystals for further study. Crystals were analyzed by single-crystal X-ray diffraction. The run at 1100/4C produced coexisting crystals of olivine and wadsleyite, whereas the two runs at higher temperature produced olivine only. Although further study will be required to quantify the effect, these results suggest that the olivine to wadsleyite transition may be displaced to lower pressures by the presence of water. All runs produced single crystals of sufficient size for X-ray diffraction study.

Three synthesis experiments were also conducted on the hydrous peridotite composition at 1400/4C and at three different pressures of 15, 17.5 and 20 GPa. The objectives were to produce crystals for elastic property measurements and to see if other spinelloid phases might occur in this region. The experiment at 20 GPa produced single crystals of hydrous ringwoodite up to 500 μm in size, whereas the two runs at lower pressure produced crystals of wadsleyite of similar size. The wadsleyite II phase which is similar to spinelloid IV observed in anhydrous nickel-aluminosilicate systems was not observed. All of the run products have been characterized by single-crystal X-ray diffraction.

### MS05 : TUpm33 : F6 Ordering of Hydroxyl Defects in Hydrous Wadsleyite

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Samples of wadsleyite containing 2.0 and 0.5 wt% dissolved water were synthesised at 1300°C and 15 GPa in the 5000 T multi-anvil press in the Bayerisches Geoinstitut. The samples were studied using <sup>1</sup>H MAS NMR and FTIR to determine the ordering of OH within the structure. As the <sup>1</sup>H NMR chemical shift and O-H stretching frequency are both known to be correlated with the O-H...O distances in silicate materials, the spectroscopic data were compared with O...O distances calculated from the crystal structure of Kudoh et al. (1996).

Three principal observations were made: i) An OH environment with strong hydrogen bonding is present. This site was not observed in any previous studies. ii) For low water concentrations the hydroxyl is well ordered, with four environments being much more abundant than all the others. Of these, three involve protonation of O1 in agreement with most previous suggestions (e.g. Smyth, 1994; Kudoh et al., 1996); in addition the site between O2 oxygens is occupied by H, in agreement with the theoretical prediction of Downs (1989). The presence of O2-H...O2 hydroxyl has not been considered by most recent workers. iii) The hydroxyl in wadsleyite containing 2.0 wt% H<sub>2</sub>O is highly disordered, with nearly all possible O-H...O environments being occupied.

The observation that many different sites are protonated, means that the solubility of water may not be limited to 3.3 wt%, as this value was predicted using the assumption that only O1 is protonated. Furthermore, the hydroxyl disorder observed here has far reaching implications for the mantle transition zone. The P/T stability field, density and elastic properties could all be affected, and the seismic constraints on the maximum water content of the transition zone (Wood, 1995) would be relaxed.

Downs JW, *Am. Min.*, **74**, 1124-1129, (1989).

Kudoh Y, Inoue T & Arashi H, *Phys. Chem. Minerals*, **23**, 461-469, (1996).

Smyth JR, *Am. Min.*, **79**, 1021-1024, (1994).

Wood BJ, *Science*, **268**, 74-76, (1995).

### MS05 : TUpm34 : F6 Iron and the Incorporation of OH<sup>-</sup> in Nominally Anhydrous Mantle Phases

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The possibility that significant amounts of water might be incorporated in nominally anhydrous phases within the transition zone has motivated a number of high-pressure studies, yet few have addressed the role of iron. We have therefore conducted a systematic study of both nominally dry and hydrous phases of the dominant minerals within the transition zone using a number of different analytical methods that focus on the role of iron in stabilising OH<sup>-</sup> in these phases.

Single crystals of hydrous wadsleyite were synthesised using a multi-anvil press from a mixture of natural olivine and orthopyroxene mixed with synthetic oxides and brucite in a Pt capsule lined with Re foil. The run product contained 1.5 wt% water and showed relative ferric iron contents of approximately 4%, which are slightly higher than for a nominally dry wadsleyite. Similar experiments to synthesise single crystal hydrous ringwoodite gave a run

product that contained 2.2 wt% water and showed a relative ferric iron content of approximately 10%, which is higher than for a nominally dry ringwoodite. These results suggest a relationship between iron oxidation state and incorporation of OH<sup>-</sup> in the crystal structure.

In a different set of experiments single crystals of monoclinic wadsleyite and wadsleyite II were synthesised using a multi-anvil press from starting mixtures of Mg-free KLB-1 peridotite gel, brucite and FeO in an Au-Pd capsule. The run products contained 2-3 wt% water and a high relative proportion of ferric iron (46% and 95%). Single crystals of majorite were synthesised in the same high-pressure runs as the monoclinic wadsleyite and wadsleyite II, but were essentially dry, containing a maximum of approximately 20 ppm water. Nearly all iron was trivalent. The high proportion of ferric iron is not related solely to the incorporation of OH<sup>-</sup> in the structure, therefore, but might have arisen from a high oxygen fugacity due to dissolution of water and subsequent hydrogen loss through the walls of the Au-Pd capsule.

The preliminary picture suggests that while iron is not required to stabilise OH<sup>-</sup> in the crystal structure of these minerals, its presence does play a role in the mechanism by which OH<sup>-</sup> is incorporated. On the other hand, oxygen fugacity is also an important influence. Analysis is underway of the results from single crystal refinements, Mössbauer and electron energy loss spectroscopy, and powder X-ray diffraction to construct models for the relationship between iron and OH<sup>-</sup> in nominally anhydrous minerals of the transition zone.

### MS05 : TUpm35 : F6 Hydrogen Bonding at High Pressures: A Comparison of Brucite and Superhydrous B

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One of the challenges for more than a decade to our understanding of the earth's deep interior has been the experimental finding that phases with structurally bound water may be stable throughout the Earth's upper mantle and possibly even at greater depth, especially in comparatively cold environments such as subduction zones. The presence of dense hydrous magnesian silicates (DHMS) in the earth's mantle can have profound influences on its physical characteristics. It is therefore important to understand the nature of the hydrogen bond in great detail to derive quantitative models for the distribution of water deep within the earth.

To address these issues we performed first principle calculations for brucite and superhydrous B, structures with very different structural building blocks. This can serve to illuminate the range and richness of the physics that may be relevant to understand hydrogen bonding. In superhydrous B, hydrogen bonds are surrounded by cages formed by comparatively incompressible Si and Mg coordination polyhedra. In contrast, in brucite, the OH-bonds are not protected and come into contact with the opposing octahedral sheet at low pressure. This correlates with a phase transition in brucite at low pressures as observed in Raman spectra. Our preliminary results for brucite show that the OH-bonding mode becomes unstable suggesting that the phase transition is due to increased O-H...O bonding between sheets. The calculated vibrational spectra of Brucite can be used to investigate directly correlations between OH-bond geometry and OH stretching frequencies. Experiments find that OH-stretching frequencies decrease with increasing pressure. Our findings reproduce this trend and suggest that this is due to increased O-H...O bonding between sheets. In contrast we find that the OH bond length in superhydrous B is nearly independent of pressure, it decreases by less than 0.5% between 0 and 25 GPa.

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### MS05 : TUpm36 : F6 H<sub>2</sub>O Distribution in the Upper Mantle: Constraints from Experimental Measurement of Compressional Wave Velocity in Talc at High Temperature and Pressure

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The combination of high-pressure, high-temperature measurements of elastic properties of hydrous phases with the results of seismic tomography allows better understanding of H<sub>2</sub>O distribution in the mantle wedge above subduction zones. Talc is likely to be an important hydrous phase at depths between 30 and 60 km, i.e. from the top of the mantle down to its pressure stability limit. At temperatures between about 620 and 680°C and pressures lower than 2 GPa, talc will be the primary hydrous phase in subduction zone peridotites. Therefore, compressional wave velocity,  $V_p$ , in talc has been measured as a function of temperature at 0.5 GPa by a time of flight ultrasonic method in an internally heated gas pressure vessel. At this pressure,  $V_p$  decreases from  $5.27 \pm 0.23 \text{ km s}^{-1}$  at 25°C to  $4.35 \pm 0.15 \text{ km s}^{-1}$  at 800°C. Combining the results for talc with a previously published bulk modulus  $K$  and  $\delta K/\delta P$  (Pawley et al., 1995), gives a Poisson's ratio,  $\nu$ , of 0.268 and a shear modulus,  $G$ , of 22.6 GPa under atmospheric conditions. Assuming  $\nu$  is independent of temperature gives a  $\delta K/\delta T$  value of  $-19.3 \pm 0.64 \text{ MPa K}^{-1}$  at 0.5 GPa. These experimental data, in combination with published data, have been used to calculate the Voigt, Reuss, and Hashin-Shtrikman-Walpole bounds, and the Voigt-Reuss-Hill average of the elastic moduli of a peridotite hydrated with talc, just above a cold subducting lithosphere, and seismic velocities derived from those. A talc-bearing assemblage containing only 0.9 weight% H<sub>2</sub>O has elastic wave velocities (calculated from the Voigt-Reuss-Hill average) slower than the anhydrous peridotite by an average of 7.6% for  $V_p$ , and 9.7% for shear waves  $V_s$  at 700°C, between 0.5 and 4 GPa. These results can be examined in connection with seismic observations of converted elastic wave phase behavior near the surface of cold subducting slabs, e.g., in the northern Pacific. A layer of silica enriched peridotite, just above the subducting slab, hydrated by talc could explain these observations at depths shallower than 155 km (where talc is replaced by the 10 Å phase). This silica could come from mechanical incorporation of subducting sediments.

Pawley AR, Redfern SAT & Wood BJ, *Contrib. Mineral. Petrol.*, **122**, 301-307, (1995).

### MS05 : TUpm37 : F6 Dehydration Processes within a Subducting Slab: An Experimental and TEM-Study on the Polysomatism of Antigorite

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The serpentine-variety antigorite is proposed to be the predominant phase for carrying large amounts of water into the upper mantle during subduction of hydrated ultrabasic rocks. Water-induced processes within subduction zones, like triggering of partial melting, metasomatic alteration or even intermediate depth seismicity (80-150 km), seem to be strongly associated with the decomposition of antigorite. Antigorite forms a series of discrete compositions, which can be expressed by the general formula  $M_3 m-3T_2 mO_3 m(OH)_4 m-6$  ( $T$  = tetrahedral cations like Si, Al;  $M$  = octahedral cations like Fe<sup>2+</sup>, Mg;  $m$  = number of tetrahedra in a single chain defined by the wavelength  $a$ ). According to Mellini et al. (1987), typical compositions of natural antigorites are in a narrow range and the  $m$ -value seems to decrease with increasing metamorphic grade. The aim of this experimental study was to investigate the P,T-dependence of the antigorite polysomatism and to test if antigorite can be used as a possible geothermobarometer. As starting materials brucite and talc were mixed in the stoichiometric proportions of antigorite with  $m=17$  plus 20 wt.% additional water. Piston-cylinder and hydrothermal experiments were performed over a wide P,T-range (350-710°C, 0.2-5.0 GPa) in the pure system MgO-SiO<sub>2</sub>-H<sub>2</sub>O. Run products were characterized by X-ray diffraction and by using TEM. For the determination of the  $a$ -lattice modulation (and corresponding  $m$ -values) of antigorite, lattice fringe spacings were deduced from diffraction patterns of selected (010) sections in the lattice fringe image. Our study indicated that increasing tempera-

ture and decreasing pressure of antigorite formation is correlated with a smaller  $m$ -value. For the P,T-conditions investigated, the compositional  $m$ -range of antigorite is rather narrow (14-18). The change in the crystal structure of antigorite from high to low  $m$ -values is combined with a gradual partial dehydration process. Therefore, during an ongoing subduction of serpentine-bearing lithosphere a successively partial dehydration of antigorite might occur. Fluids set free by this process might influence the rheological properties of surrounding rocks: Fluid migration into pores or along interfaces, thus changing the adhesion of the grains, might reduce the effective confining pressure. As a consequence, for a better understanding of rheological processes like e.g. dehydration embrittlement, which is thought to be a possible reason for seismicity within subduction zones, the proceeding dehydration process of antigorite has to be considered. Additionally, for any formulation of reactions (e.g. within internally consistent thermodynamic datasets) under the participation of antigorite, the variation of its chemical composition with pressure and temperature has to be considered.

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### MS05 : TUpm38 : F6 Hydrous Phases in Pyrolite-H<sub>2</sub>O System up to 25 GPa and Water Storage Capacity of the Earth's Mantle

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We provided series of melting experiments on hydrous primitive mantle compositions to evaluate the possible influence of water on stability field of hydrous phases under high pressure. Phase relations and melt compositions in pyrolite with 2% of water have been determined at 10-25 GPa and temperature range between 800 and 1400°C. Starting composition was anhydrous primitive mantle composition after Jagoutz et al. (1979) simplified to the system CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and 2 wt.% of H<sub>2</sub>O was added as Mg(OH)<sub>2</sub> adjusting the proportion of MgO. We have found that phase A is stable at 10 GPa and temperature below 1000°C and olivine was absent according to the reaction of Ol+H<sub>2</sub>O=A+Opx. Phase E is stable at 12 GPa and temperature below 1000°C and coexist with olivine. No hydrous phases instead of wadsleyite are stable in pyrolite at 14 GPa and 1000°C. Superhydrous phase B is stable in pyrolite at temperature below 1100°C and 18.5 GPa pressure and below 1300°C at 25 GPa. The phase assembly at 18.5 GPa and 1000°C was Superhydrous B + Rw + Gt + AlOOH (+Cpx). The phase assembly at 25 GPa and 1000°C was MgPv + CaPv + MgO + Superhydrous B + AlOOH. Superhydrous phase B was also detected at 25 GPa and 1200°C, where total phase assembly was MgPv + CaPv + Superhydrous B + Gt + another Al-rich phase (similar with those reported for MORB composition at 27 GPa (Irifune and Ringwood, 1993). Minor diaspore or  $\delta$ -AlOOH (new Al-rich phase, Suzuki et al., 2001) with phase transition near 17 GPa at 1000°C is present trough over the pressure range from 10 to 25 GPa and temperature of 1000°C as probably metastable phase usually rimmed by garnet. As well as for water-saturated experiments (Kanzaki, 1991; Gasparik, 1993) we found same sequence of dense hydrous phases at lower temperature with the increasing of pressure: phase A at 10-14 GPa, phase E at 12-14 GPa, superhydrous phase B at 18-25 GPa. Our data suggest that dense hydrous phases (A, E, super B, and probably phase G (in the water-saturated system (Ohtani et al., 2000) could exist in pyrolitic composition only under the conditions of subducting slabs descending into the lower mantle. Any exotic dense hydrous phases can not exist along the normal mantle geotherm. At the normal mantle and hot plume conditions wadsleyite ( $\beta$ -Mg<sub>2</sub>SiO<sub>4</sub>) or ringwoodite ( $\gamma$ -Mg<sub>2</sub>SiO<sub>4</sub>) are major H<sub>2</sub>O-bearing phases. Thus, transition zone, where these phases are stable, can be considered as a major water reservoir in the Earth's mantle, whereas distribution of water to upper mantle and lower mantle is restricted along the normal mantle geotherm.

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## MS05 Water in the Earth's Mantle

### Tuesday PO Session

#### MS05 : TUp01 : PO

##### Effect of Pressure on the Hydrogen Solubility in (Mg,Fe)O up to 25 GPa

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Magnesiowüstite is the second most abundant phase in the lower mantle of the Earth, accounting for about 15% by volume. Based on results of a previous study, water partitions more strongly into periclase in comparison with MgSiO<sub>3</sub> perovskite (Bolfan-Casanova et al., 2000). Therefore, (Mg,Fe)O could play an important role in storing water in the deep silicate Earth. Such water could have important effects on the physical and chemical properties of the lower mantle, such as melting, rheology and electrical conductivity.

Single crystals of Mg<sub>99.99</sub>Fe<sub>0.01</sub>O were imbedded in an oxide mixture of the same composition but containing water, added as Mg(OH)<sub>2</sub> and H<sub>2</sub>O. The hydrothermal annealing experiments were performed at 1200°C and pressures ranging between 1.2 and 25 GPa using a multi-anvil apparatus. The sample container consisted of an inner rhenium capsule to avoid iron loss from the sample, and an outer platinum capsule that was sealed by welding. Rhenium oxide was added to the sample charge and, by reaction with the Re metal, maintains a high oxygen fugacity, between Ni-NiO and hematite-magnetite (Pownceby and O'Neill, 1994). The compositions of the recovered samples were analysed by electron microprobe and the results show very homogeneous Fe contents, which, for the different samples, are almost identical. The infrared spectra of the magnesiowüstite single crystals were recorded using a Fourier transform infrared spectrometer.

The FTIR spectra exhibit multiple OH stretching bands with intensities that show different dependencies on the pressure of hydrothermal annealing. The main bands are located at ~3700, 3480, 3400 and 3320 cm<sup>-1</sup>. It is possible to unambiguously attribute the bands at 3320 and 3480 cm<sup>-1</sup> to H structurally bound in magnesiowüstite, based on their uniform intensities throughout the samples, as well as their steady increase in intensity with pressure. On the other hand, the intensity of the 3400 cm<sup>-1</sup> band seems to decrease with pressure. The nature of the bands at ~3700 cm<sup>-1</sup> remains unclear because their intensities are strongly correlated with the presence of inclusions.

Because magnesiowüstite exists dominantly in the Earth's lower mantle, only the bands that are present in the spectra of the very high-pressure samples, namely those at 3480 and 3320 cm<sup>-1</sup>, are relevant for estimating H solubility in magnesiowüstite. The amount of water incorporated in magnesiowüstite at 25 GPa and 1200°C under water saturated conditions is ~100 H/10<sup>6</sup>Si (~20 ppm wt H<sub>2</sub>O), based on the bands at 3480 and 3320 cm<sup>-1</sup>. When integrated over the mass of the entire lower mantle, this amounts to ~7.3 x 10<sup>18</sup> kg H<sub>2</sub>O, i.e. 0.5% of the total mass of the oceans.

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#### MS05 : TUp02 : PO

##### The Effect of Oxygen Fugacity on the Solubility of Water in Wadsleyite

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We have conducted multianvil experiments in order to understand the relationship between OH<sup>-</sup> and Fe<sup>3+</sup> contents of the high pressure (Mg,Fe)<sub>2</sub>SiO<sub>4</sub> polymorph wadsleyite. Oxygen thermobarometry measurements performed on mantle xenoliths indicate that the Earth's upper mantle is relatively oxidising (FMQ +0.5 to -1.5). This is, in part, a

consequence of Fe<sup>3+</sup> being partitioned strongly into spinel and clinopyroxene, which are modally relatively minor phases in the upper mantle. The Fe<sup>3+</sup> component activities in these minerals are, therefore, high, which leads to a relatively high oxygen fugacity. The dominant C-O-H fluid species at such conditions will be H<sub>2</sub>O and CO<sub>2</sub>. In the Earth's transition zone, however, the modally dominant phase wadsleyite can partitioning quite significant quantities of Fe<sup>3+</sup>. As Fe<sup>3+</sup> will then be relatively dilute in wadsleyite this will result in a lowering of the oxygen fugacity to values that are perhaps close to the iron-wüstite oxygen buffer. Under these conditions fluids are quite likely to be CH<sub>4</sub> and H<sub>2</sub>-rich. Several studies have shown that wadsleyite can accommodate significant amounts of OH<sup>-</sup> within its structure, with maximum estimates equivalent to 3.3 weight% H<sub>2</sub>O. However, realistic mantle Fe<sup>3+</sup> contents may result in lower OH<sup>-</sup> solubility due to a lowering of the H<sub>2</sub>O partial pressure.

We are performing experiments in order to understand the solubility of OH<sup>-</sup> in wadsleyite and the stability field of hydrous wadsleyite with respect to pressure and FO<sub>2</sub>. A double capsule technique is employed where an inner 0.6 mm diameter capsule filled with an olivine-orthopyroxene composition is placed inside an outer 3 mm diameter capsule containing a redox buffer (Re-ReO<sub>2</sub>, Mo-MoO<sub>2</sub>, and W-WO<sub>2</sub>). Outer capsules are of platinum but inner capsules of iron, platinum, rhenium and molybdenum are used. Water is added as brucite to the inner capsule and as H<sub>2</sub>O in the outer. Experimental run products are analysed for H<sub>2</sub>O using infra red spectroscopy and for Fe<sup>3+</sup> using Mössbauer spectroscopy. Experiments performed between 11 and 14 GPa at 1200°C employing the Re-ReO<sub>2</sub> buffer produced wadsleyite and an MgO-rich silicate melt. These preliminary results indicate that the stability field of wadsleyite may be expanded to lower pressure under these relatively wet oxidising conditions.

#### MS05 : TUp03 : PO

##### H<sub>2</sub>O Activity in H<sub>2</sub>O-N<sub>2</sub> Fluids at 10 Kbar and 15 Kbar Measured by the Brucite-Periclase Equilibrium

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Nitrogen is commonly found in mineral fluid inclusions from various metamorphic settings. It also represents a major impurity in natural diamonds, which indicates its importance in the mantle-derived fluids. Thermodynamic mixing properties of N<sub>2</sub> in the aqueous fluids have, nonetheless, been poorly constrained by the experiments at high pressure. Here we present first experimental results constraining activity of H<sub>2</sub>O, a(H<sub>2</sub>O), in the H<sub>2</sub>O-N<sub>2</sub> binary fluid mixtures at P=10 kbar and 15 kbar, in the temperature and compositional ranges corresponding to 650-900°C, X(N<sub>2</sub>) from 0.05-0.5. Simple dehydration reaction: Mg(OH)<sub>2</sub> = MgO + H<sub>2</sub>O (1) was used as a monitor of H<sub>2</sub>O activity in the binary mixtures. Temperature depression of reaction (1) in the binary mixtures relative to its equilibrium position in pure H<sub>2</sub>O, very well known from previous study (Aranovich and Newton, 1996), gives a direct measure of H<sub>2</sub>O activity in the fluid. Experiments were done in a conventional piston-cylinder apparatus with NaCl pressure medium. Starting solids were synthetic coarsely crystalline brucite and periclase mixed in a stoichiometric proportion. The H<sub>2</sub>O and N<sub>2</sub> (latter as AgN<sub>3</sub> according to a method described by Keppler, 1989) were carefully weighed in to produce a desired starting X(N<sub>2</sub>) composition of the fluid phase. Reaction progress was detected primarily by a weight loss method, supported by the optical and X-ray observations on the solid run products. Tightly converging brackets of the final fluid composition in equilibrium with the two-phase solid assemblage were obtained in the 250° temperature range. The resulting a(H<sub>2</sub>O) values depart significantly from those predicted by the Raoult law. Nonideality in the binary system should be taken into account in the speciation calculations for the system H-O-N at high pressures.

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#### MS05 : TUp04 : PO Water Diffusion in Mantle Olivine

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Knowledge of water or OH content of nominally anhydrous minerals is important in order to understand processes in subducting plates, mantle rheology and the physical and chemical behaviour of Earth's interior. Experimental studies of olivine, the major upper mantle mineral, indicate that significant amounts of OH can dissolve within olivine as point defects (Bell and Rossman, 1992; Kohlstedt et al., 1996). At low temperatures or short times, OH incorporation occurs by redox exchange of protons with polarons (essentially the excess charge on ferric iron in octahedral cation site). At higher temperatures and/or longer times, additional OH is incorporated as defect associates involving both protons and intrinsic defects, such as cation vacancies (Kohlstedt and Mackwell, 1998). The present study, which is based on piston-cylinder experiments and FTIR analyses, aims to constrain more fully the speciation of the mobile OH defects in olivine and rates of diffusion at a variety of pressure and temperature conditions.

Diffusion of OH defects in single crystals of olivine is being investigated for diffusion parallel to the [100], [010] and [001] crystallographic axes during both dehydration and hydrogenation. We use xenolithic crystals from San Carlos, Arizona, that have no cracks or inclusions. The dehydration experiments are performed in a room-pressure furnace at temperatures between 900° and 1200°C, with the oxygen fugacity controlled using mixed CO and CO<sub>2</sub> gases. The hydrogenation experiments are performed in a piston-cylinder apparatus at a pressure of 1 GPa and temperatures between 1000° and 1200°C. We place the samples inside platinum-rhodium capsules along with 10 mg of water and a mix of olivine (90%) and orthopyroxene powder (10%). In order to control the oxygen fugacity during the experiments, NiO powder and Ni foil are also included in the capsule prior to welding.

The hydroxyl distributions within our samples are analyzed using polarized FTIR spectroscopy. Diffusion profiles for the OH defect species are measured parallel to [100], [010] and [001] for each sample. The defect diffusivity is obtained by fitting a solution of a theoretical diffusion law to the OH concentrations, which are determined by integration of the infrared bands between 3650 and 3400 cm<sup>-1</sup>. Our current results indicate that incorporation of OH species into olivine is a 2-step process with an initial stage of proton-polaron exchange, followed by slower diffusion of OH species, probably as defect associates of protons and octahedral cation vacancies. Only after this latter stage is complete can the samples attain equilibrium with the imposed hydrous environment.

This study is supported financially by the EU through the Human Potential Programme HPRN-CT-2000-00056.

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#### MS05 : TUp05 : PO

##### Hydrogen Mobility in Pyrope: Preliminary Results

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The quantification of the hydrogen mobility in major nominally anhydrous mantle minerals is an important parameter for the modelisation of the hydrogen cycle in the Earth interior (Ingrin and Skogby, 2000). In clinopyroxenes, it has been established that the kinetic of dehydrogenation depends on the iron content (Hercule and Ingrin, 1999; Woods et al., 2000). Recently, Wang et al. (1996) performed dehydrogenation experiments on natural pyrope megacrysts (Py<sub>68-70</sub>) leading to the diffusion-out law:

$$\log D_{\text{out}} (\text{m}^2/\text{s}) = 0.247 - 110.4 (\text{kJ/mol}) / RT.$$

However, we do not know yet if this law corresponds to the rate of hydrogen diffusion and if the kinetic of dehydrogenation in pyrope is also sensitive to the iron content. The

## MS05 Water in the Earth's Mantle

aim of this study is to measure the diffusion rate of hydrogen and the kinetic of dehydrogenation in pyrope rich garnets in order to identify the mechanisms of hydrogen mobility.

In this way, we investigated by IRTF the kinetic of hydrogen-deuterium exchange in a pyrope from Dora Maira, western Alps (Py<sub>80</sub>). The fit of infrared data (mean OH concentrations), collected after each annealing, gives a rate of hydrogen exchange of  $2.5 \times 10^{-14}$  m<sup>2</sup>/s at 700°C. This value is close to the results of Wang et al. (1996), suggesting that, for their mineral composition and their temperature range, the kinetic of dehydrogenation is controlled by hydrogen diffusion. We also performed dehydrogenation experiments at 800°C on the same crystal. The extraction rate obtained is equal to  $5 \times 10^{-14}$  m<sup>2</sup>/s which is one order of magnitude lower than Wang's data. These preliminary results suggest that the extraction-incorporation of hydrogen in pyrope is probably dependent on the iron content, at least in this restricted range of iron concentration.

This study was financially supported by the EU through the Human Potential Program HPRN-CT-2000-00056.

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### MS05 : TUp06 : PO High Pressure Behaviour of Serpentine Minerals: An In Situ Raman Spectroscopic Study of Lizardite, Chrysotile, Antigorite and Polygonal Serpentine

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Serpentine minerals are hydrous phyllosilicates resulting from the hydration of ultrabasic rocks; they contain approximately 13 wt% of structurally bounded water. Among the population of serpentine minerals, antigorite has been recently highlighted as the stable variety under high pressure conditions [1, 2]. Thus, antigorite probably plays a key role in recycling water in the mantle along subduction zones. It is therefore of prime importance to understand the structural justifications for the high pressure stability of antigorite. To answer the question, the behaviour of the four main serpentine varieties (lizardite, chrysotile, antigorite, and polygonal serpentine) has been investigated *in situ* by Raman spectroscopy as a function of pressure. Well-characterised samples (chemistry, MET) were loaded in a diamond anvil cell and subsequently characterised by Raman spectroscopy upon compression up to 15 GPa and during decompression at room temperature. The evolution of the Raman modes of each varieties indicates that all serpentine minerals have quite a similar behaviour at high pressure. They display a quasi linear shift towards high frequencies with a mean slope of about 7 cm<sup>-1</sup>.GPa<sup>-1</sup>. No phase transition could be observed within the investigated pressure range, indicating that the low pressure varieties do not transform into antigorite when metastably compressed, as it might have been expected. The Raman spectra acquired during pressure release also indicate that all pressure-induced changes are fully reversible. This study also provides new insights into the still debated assignment of OH vibrational modes in serpentine minerals. Serpentine minerals are trioctahedral phyllosilicates of 1:1 type and display two kinds of OH groups. While the inner hydroxyl groups lie at the center of each 6-fold ring at the same z-level as the apical oxygen of the tetrahedra, the outer OH groups form bonds with the basal oxygens of the tetrahedra, linking two successive sheets. It is usually assumed that Raman modes in the 3645-3660 cm<sup>-1</sup> range correspond to vibrations of the inner OH groups

whereas those in the 3680-3700 cm<sup>-1</sup> arise from vibrations of the OH groups. Our HP observations show that at least one of the low frequency OH Raman mode shift much faster (12 cm<sup>-1</sup>.GPa<sup>-1</sup>) as a function of pressure than the high frequency group (2.5 cm<sup>-1</sup>.GPa<sup>-1</sup>). Although these results are in contradiction with the classical interpretation aforementioned, they agree well with recent crystallographic data obtained on lizardite by neutron diffraction [3]. Hence, this leads us to propose a new assignment for OH vibrational modes in serpentine minerals.

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### MS05 : TUp07 : PO Elastic Properties of Lawsonite and its Variation with Temperature

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The transport of hydrous minerals to depth via the subduction of oceanic lithosphere seems to be a fundamental mechanism in which water is recycled into the Earth's mantle. To constrain the variation of the elastic properties with temperature Brillouin spectroscopy on single crystal lawsonite samples were carried out. Up to 1 wt.% H<sub>2</sub>O might be transported within lawsonite in an altered oceanic crust to depth greater than 200 km. Thus the elastic properties are of great importance for the simulation of subduction processes and for the interpretation of geophysical observations and for thermodynamic modeling. Lawsonite is an orthorhombic sorosilicate with a total water content of 11.5 wt.%. Besides the water molecules it is chemically identical to anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). Notwithstanding its close chemical similarities with anorthite, lawsonite has a higher density - 3.09 g/cm<sup>3</sup> for lawsonite versus 2.77 g/cm<sup>3</sup> for anorthite - which is related to an octahedral Al coordination in lawsonite instead of the tetrahedral Al coordination in anorthite. Previous measurements of the bulk modulus at STP show a large range of values, between 96 (±2) to 192 (±5) GPa. Our Brillouin spectroscopic experiments at ambient conditions resolve these discrepancies, and yield an independent value of the bulk modulus of KS = 125 GPa (Voigt-Reuss-Hill average; Sinogeikin et al., 2000). Lawsonite displays a large degree of shear anisotropy, with the minimum shear velocity ca. 2.3 times lower than the maximum. Lawsonite also shows extremely high V<sub>p</sub> to V<sub>s</sub> ratio (V<sub>p</sub>/V<sub>s</sub> = 1.94), and Poisson's ratio (σ = 0.318). Daniel et al. (1999) suggested a non-linear temperature dependence of the bulk modulus with a minimum at 500 K. However, our results show that the bulk modulus slightly and steadily decreases with increasing temperature, without any minimum. On the other hand, the shear modulus increases with increasing temperature, which result in a decrease of Poisson's ratio. The unusual temperature behavior of the elastic properties will be discussed in terms of structural changes of lawsonite with increasing temperature.

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### MS05 : TUp08 : PO Inclusions of DHMS in Olivines from Mantle Nodules: 10Å-phase and Hydrous Olivine

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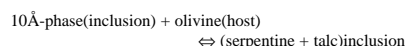
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DHMS-phases (dense hydrous magnesium silicates) such as phase A, phase B, superhydrous phase B, phase D, phase E, 10Å-phase, humite-group minerals and 3.65Å-phase (see ref. in Prewitt and Downs, 1999) were synthesized at high pressures and high temperatures. The DHMS are

possible phases in the upper mantle (Thompson, 1992). However, except for the humite-group minerals, no other DHMS phases were found in natural rocks till now. Our first observations of the 10Å-phase as nanometer-sized inclusions in mantle olivine (Wirth and Khisina, 1998) give evidence that natural DHMS can occur in a mode of small inclusions in olivines. Here we report on nanometer-sized inclusions in olivines from mantle nodules, which contain 10Å-phase Mg<sub>5</sub>Si<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>nH<sub>2</sub>O and hydrous olivine Mg<sub>2-x</sub>v<sub>x</sub>Si<sub>2</sub>O<sub>7</sub>H<sub>2x</sub>. FTIR as well as TEM methods including AEM, EELS, SAED and HRTEM were applied. The 10Å-phase was observed in octagonal and hexagonal-like inclusions of several hundred nm in size always intergrown with talc and serpentine. Absorption bands of the 10Å-phase together with absorption bands of serpentine and talc were observed in IR spectra of the olivine samples. From the TEM data, the 10Å-phase is considered to be a primary crystalline phase of inclusions while serpentine and talc are considered to be secondary phases, which replaced the 10Å-phase, by the reaction:



Hydrous olivine Mg<sub>2-x</sub>v<sub>x</sub>Si<sub>2</sub>O<sub>7</sub>H<sub>2x</sub> as a new phase among DHMS phases is suggested to occur in both the lamellar defects of several ten nm in width, and in small inclusions of hexagonal-like shape up to several ten nm in size. Data suggest hydrous olivine to be an OH-bearing olivine with ordered Mg-vacancies; several kinds of ordered superstructures, corresponding to different concentrations of Mg-vacancies, were observed. We assume that during cooling and decompression of the rock, the hydrous olivine was exsolved from the olivine matrix, which was saturated by OH-bearing point defects. The 10Å-phase and hydrous olivine found as nanometer-sized inclusions in olivines from mantle nodules show that water in the mantle can be incorporated as precipitated phases in nominally anhydrous minerals.

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### MS05 : TUp09 : PO H Isotope Compositions and Oxidation State of Mantle-Derived Hydrous Minerals

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H isotope compositions of mantle fluids have been studied most extensively by analysing mantle-derived hydrous minerals (micas and amphiboles). The presently published data base shows large scatter in H isotope composition that has been interpreted to be the result of primary mantle inhomogeneity, source contamination by subduction processes, crustal contamination, and near-surface processes such as degassing, late-stage isotope exchange, alteration, and weathering. The interpretation is further complicated by the uncertainties in the knowledge of mineral-water H isotope fractionations. Important information on these processes may be provided by the Fe(III)/Fe(II) content of hydrous minerals. However, the available Fe(III)/Fe(II) data set is even more limited and also shows a large scatter in this ratio. The present study deals with alkali basic complexes in two well known areas: the Canary Islands and the Pannonian Basin. The minerals studied are phlogopite, biotite and amphibole from alkali basalts, basanites, nephelinites and lamprophyres whose ages range from Cretaceous to Pleistocene. The oxygen isotope compositions of the studied samples range from 4.6 to 6.2 ‰ with an average of 5.3 ‰, suggestive of unaltered compositions.

Amphibole megacrysts from the Pliocene-Pleistocene alkali basalts of the Pannonian Basin have very high (up - 19 ‰) to very low (to -107 ‰) δD values correlating well with their H<sub>2</sub>O and Fe(III) contents. The correlations clearly indicate the effect of degassing and allow us to estimate the amphibole-water H isotope fractionation to be

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about -80 ‰. The very high  $\delta D$  value can be interpreted as a result of mantle metasomatism by fluids released from subducted ocean crust. Amphiboles and phlogopites from Mesozoic alkali basalts and lamprophyres of the Pannonian Basin have significantly lower H isotope compositions (-85 to -39 ‰). These, together with the primary compositions of the Pliocene-Pleistocene megacrysts show a positive trend between Fe(III) and  $\delta D$  that may be related to the metasomatic influence of subduction-related fluids. Comparing the data set with the H isotope compositions and Fe(III)-contents of hydrous minerals from Canary Island rocks, a common component with about  $\delta D = -85$  ‰ and  $100^{*}Fe(III)/Fe(tot) = 12$  in the hydrous minerals is indicated.

### MS05 : TUp010 : PO Anomously High $\delta D$ Values and Micro-Scale Hydrogen Isotope Heterogeneities in the Mantle: Ion Microprobe Analysis of Amphiboles from Peridotite Xenoliths at Nushan, Eastern China

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Hydrogen isotopic compositions of amphibole grains from three different lherzolite xenoliths found in Cenozoic basanites of the Nushan province, eastern China (Chen & Peng 1988), have been analyzed by ion microprobe.  $\delta D$  values of all analyzed points range from -94 to +46, some of them are much higher than the highest  $\delta D$  value (+8) reported previously for mantle materials. Heterogeneities of D/H ratios have been observed within single grains, with variations of  $\delta D$  values up to 80 delta units on the scale of less than 400  $\mu m$ . No correlation between hydrogen isotopic ratios and hydrogen contents can be found, implying that the scatter of the  $\delta D$  values couldn't result from a late shallow processes such as hydrogen loss or hydrothermal alterations and should be considered as inherited from the source at depth. Chemical compositions of Nushan amphiboles are very homogeneous, excluding that the scatter observed on the  $\delta D$  values could arise from variable fractionation factors between a single fluid source and minerals. Therefore, metasomatic fluids responsible for the formation of Nushan amphiboles should be heterogeneous, or variable through time and result in the observed large variable and anomalously high  $\delta D$  values of amphiboles. We suggested that the variation of the H isotopic composition of the metasomatic fluids could be related to magma degassing in the mantle source and to the isotopic fractionation between the metasomatic fluid and the released gas. Based on the D-H diffusion data and the scale of hydrogen isotope heterogeneities, it was inferred that the mantle metasomatism took place soon before the eruption of host magma.

Chen DG, Peng ZC, *Acta Petrologica Sinica*, **31**, 3-12, (1988).

### MS05 : TUp011 : PO Dynamic Model of Joint Lherzolitic Column and Basaltic Melts Evolution beneath Vitim Plateau

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Composition of plum basaltic melts and lherzolites in mantle columns demonstrate rapid (Ashchepkov et al, 1999, 2000) and correlated evolution during the 5 stages (18, 12-14, 7-9, 5-2, 0,8 Ma) of the lava plateau creation coinciding with the appearance of the alkaline melts with abundant mantle inclusions. The 1 pre- rifting stage and the last scoria cone post- erosion stage are characterized by hydrous melts percolation in mantle found as the intergranular glasses in xenolith and visible in abundant pyroxenites and metasomatic peridotites with Amph and Phl as megacrysts (Phl for stage V) and phenocrysts in lavas. Main basaltic chambers were located close to 110 km for

first and to 85 km for the last stage. In 2-3 stage- (bottom and top of lava plateau) upper concentrating levels was near 50-60 km and near 70 km in stage 4 (valley basalts). Fluctuations of the intermediate magma concentrating levels are pronounced in Fe-Ti peaks for minerals in thermal sections. In 1-5 stages the amount of melts in intermediate conduits quickly reduces upward while in 2-4 stages it sufficient enough in multilevel chambers to produce wide reactions. Geochemistry of mantle xenoliths in lherzolitic column also rapidly changes. Nearly primitive TRE patterns (Ga-Sp abundance dependent) sometimes with the infiltrated hydrous melts in 1 stage changes to the increase of siderophile elements and some of HFSE due to direct melt percolation in stage 2-3. Motley compositions with depleted and enriched patterns high variations in LILE and HFSE and their ratios - Zr/Hf, Ta/Nb etc. are characterized for the 4 stages with the individual behavior in each level. These means pulsing type of percolation or presence of individual melts/ fluids in each stage levels during the lava plateau creation. But TRE and ratios characteristics do not coincide completely with that of hosting lavas what suppose high scale reaction. Splitting of geochemical characteristics rises upward. This is due to independent additional melt differentiation in each level. The model for the basaltic melt evolution suppose preceding metasomatism and then dissolution of pyroxenites and Amph- Phl- bearing rocks regulating mainly HFSE, LILE concentration that are higher for 1 stage. But more deep metasomatic sources serving as the melt conductors may be also suggested. Thus plum basalts geochemistry is highly dependent from the dynamics of melt movement and interaction with the mantle column but not only from the deep source. Though due to relatively low concentration of Sr, Pb in peridotites the isotopic changes not so drastically. Supported by RBRF grant 99-05-65688.

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Ashchepkov, Andre, Malkovets et al, *J. Conf. Abs.*, **4(3)**, 364, (1999).

### MS05 : TUp012 : PO The Study of Lakes of Antarctic Oases for Development of Polluted Hydrological System Strategy

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Now there are not any places on the Earth where the problem of polluted hydrological system is not acute. Should we study similar background regions? The research of water systems, which are started using and polluting by people, is important for scientific aims. Similar research allows to study processes of changing hydrological systems for using this dates for working out of methods of cleaning of the more polluted water bodies. The water bodies of Antarctic oases comprise at present a group of the most clean water bodies on Earth. The generalization of dates and singling out of special feature of hydrological, hydrobiological and hydrochemical regimes of such systems are conducted in according with the project of Russian Foundation of the Basic Research has a title: 'Assessment of stability of Lake Ecosystems in the Antarctic oases and diagnostics of their development under climatic changes and anthropogenic impact'. The following results were obtained from the project implementation: · The structure of the database on lakes and epishelf water bodies of the oases of Antarctica was created. Information on the water bodies of the Bunger, Shirmacher, Untersee and Dry Valley oases was entered to the database. The total number of the fields for each water body is up to 45, including the characteristics of the hydrological, hydrochemical and hydrobiological regimes. The database works in the modern environment. · Filtration of available date was performed resulted in subdividing the water bodies of the oases into types corresponding to state and stability classes · The subject maps, diagrams and graphs were created; the main features of regime of the water bodies and features of the time - space scale distribution of the regime parameters were distinguished. Observations have been conducted by different countries in the oases area, with building of scientific stations and changing of all natures features of the oases and water bodies (for example using water for drinking and managing necessities) of course. · So if conditions of the development of 'live water' of Antarctic oases are known, will be possible to establish the evaluation of ecological risk when using the stations and will provide ability to forecast changes of water body's regimes and strategy of saving such unique objects will be important for mankind.

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