

## Hydrous components in the nominally anhydrous minerals

GEORGE R. ROSSMAN

Division of Geological and Planetary Sciences, California  
Institute of Technology, Pasadena, CA 91125-2500, USA  
(grr@gps.caltech.edu)

Hydrous components in the nominally anhydrous minerals were first of significance for their impact on the mechanical strength of minerals and on the dielectric properties of synthetic materials. They are now known to influence a large number of chemical and physical properties of the host mineral and are thought to be an important contribution to the Earth's water cycle.

Detection, and concentration determination is now most conveniently achieved by infrared spectroscopy, but requires independent calibration for accurate analyses. IR spectra distinguish between OH and H<sub>2</sub>O and can also establish if the water is present in fluid inclusions or alteration products. NMR spectroscopy, likewise, can often determine the specific species in the mineral, but requires larger amounts of pure sample and cannot deal well with commonly encountered concentrations of paramagnetic ions. Nuclear profile analysis with N-15 ions has required a long development period, but has proven to be a highly useful absolute analytical method. Raman spectroscopy can detect OH, but, in our experience, has not proven reliable for absolute concentration determinations.

Minor amounts of OH are found in most common mantle phases and numerous crustal phases including many common silicates and oxides. Concentrations range from <10 ppm in pyrope garnets to percents in grossular garnets. Useful calibrations of the IR spectra now exist for olivine, certain garnets, pyroxenes, kyanite, zircon, and some oxides. Generic calibrations also have improved, but do not remove the need for mineral-specific calibrations for accurate work.

H<sub>2</sub>O is typically found at concentrations reaching 2% in ring silicates and minerals with large channels. In feldspars and feldspathoids concentrations range from near zero to nearly 0.2%.

Studies of synthetic minerals have shown that significantly larger concentrations can be incorporated in silicates under high PT conditions and have led to the current discussion of the importance of OH in the deep mantle and the question of how many oceans of water exist at depth.

Recent work has also shown that water resides in some phases as nano-inclusions and may be an exsolution product in phases that formerly contained higher concentrations of OH in the deep earth.

## Hydrogen in the Al<sub>2</sub>SiO<sub>5</sub> polymorphs

J.B. BURT, N.L. ROSS, G.V. GIBBS AND D.L. COX

Department of Geosciences, Virginia Polytechnic and State  
University, Blacksburg, VA 24060, USA (jaburt@vt.edu)

It has been shown that water can be incorporated within the structures of nominally anhydrous silicates and oxides [1]. This study examines incorporation of hydrogen within the aluminosilicate polymorphs, kyanite, andalusite and sillimanite. Potential hydrogen bonding sites within the aluminosilicate polymorphs were determined based on an analysis of the Laplacian of the electron density distribution, following the method of Ross et al. [2]. The CRYSTAL98 program [3] was used to generate analytical electron density distributions for kyanite, andalusite and sillimanite, and TOPOND [4] was used to locate the (3,-3) critical points. The location of the (3,-3) critical points indicate that the potential sites are large enough to accommodate hydrogen and also indicate that the O-H bonds in andalusite and sillimanite are highly directional. In andalusite, the O-H vectors lie within (001) and are approximately parallel to [-1 1 0] and [110]. In sillimanite, the O-H vectors also lie within (001) but are oriented closer to [010]. The location of potential sites for hydrogen in kyanite is less clear.

In addition, hydrogen was introduced in the structures using the Vienna Ab-initio Simulation Package (VASP) [5]. The results from these calculations not only determine the location of the hydrogen within the structure, but also provide binding energies for hydrogen in different sites of the structures. VASP calculations indicate H bonding near OA within the (001) plane of andalusite and in multiple locations in sillimanite and kyanite. Locations of hydrogen in the structures will be compared with polarized infrared spectroscopy.

### References

- [1] Bell D.R. and Rossman G.R. (1992) *Science*, 255, 1391-1397.
- [2] Ross N.L., Gibbs, G.V., and Rosso, K.M. (2003) *Am. Mineral.*, 88, 1452-1459.
- [3] Saunders V.R., Dovesi R., Roetti C., Causa M., Harrison N. M., Orlando R., and Zicovich-Wilson C. M. (1998) *CRYSTAL98 User's Manual*. Univ. of Torino.
- [4] Gatti C. (1997) *TOPOND96 User's Manual*, CNR-CSRSC.
- [5] Kresse, G., and Furthmuller, J., 1996, *Computational Materials Science*, v. 6, p. 15-50.

## Magmatic water contents recorded by hydroxyl concentrations in plagioclase phenocrysts from Mount St. Helens, 1980-1981

E.A. JOHNSON

Department of Earth and Space Sciences, University of  
California, Los Angeles, CA 90095 (johnsoel@ucla.edu)

Magmatic water contents could potentially be determined by measurement of OH concentrations in nominally anhydrous phenocrysts, assuming an equilibrium partitioning of water between the phenocrysts and melt. In this study, the OH concentrations of plagioclase phenocrysts from nine eruptions of Mount St. Helens between May 18, 1980 and April 1981 were measured using infrared spectroscopy, in order to evaluate this method of determining magmatic water content. The eruption temperature, oxygen fugacity, and bulk chemical composition were all fairly constant through the eruption sequence from 1980-1981 at Mount St. Helens. The water content of melts from successive eruptions decreased from 4.6 wt% H<sub>2</sub>O for the Plinian eruption on May 18, 1980 (Rutherford et al. 1985, JGR 90, 2929-2947), to less than 1 wt% H<sub>2</sub>O for the latest dome-forming dacites. There is a linear relationship between the water content of melt inclusions (Melson, 1983, Science, 221, 1387-1391) and the average OH concentration of plagioclase from each eruption, with the OH concentration of plagioclase ranging from 200 ppm H<sub>2</sub>O for the May 18, 1980, eruption, down to 20 ppm for the April 1981 dome-building eruption. The partition coefficient of hydrogen between plagioclase and melt was determined to be 0.004 for this system, and is similar to other estimates of partition coefficients of water between anhydrous minerals and melt (Dobson et al., 1995, Contrib Min Pet, 118, 414-419). Homogeneous distribution of OH in feldspar grains >100 micrometers is observed even for those grains with pronounced major element zoning. The estimated diffusion rate of hydrogen at 930°C is  $1.1 \times 10^{-13}$  m<sup>2</sup>/sec (Johnson, 2003, Caltech thesis), and estimates of magma ascent rates from 8 km depth are on the order of days to weeks (Rutherford and Hill, JGR, 98, 19667-19685). On these time scales, OH in feldspars had time to reequilibrate with the magma during ascent, whether or not it was temporarily stored at shallow (<4.5 km) depths (Cashman, 1992, Contrib Min Pet, 109, 431-449). These data show that, in the absence of large changes in oxygen fugacity or eruption temperature, the water contents of silicic melts immediately prior to eruption are recorded in the OH concentration of volcanic plagioclase.

## Water, decompression, and mantle melting at Galunggung, Indonesia

KATHERINE A. KELLEY<sup>1</sup>, ERIK H. HAURI<sup>1</sup>  
AND THOMAS W. SISSON<sup>2</sup>

<sup>1</sup>Department of Terrestrial Magnetism, Carnegie Institution of  
Washington, 5241 Broad Branch Rd. NW, Washington  
DC 20015, USA (kelley@dtm.ciw.edu,  
huri@dtm.ciw.edu)

<sup>2</sup>USGS, Menlo Park, CA, USA (tssisson@usgs.gov)

Galunggung, western Java, is one of the few arc-front volcanoes where decompression melting has been indentified as an important magma-generating process. Here, we present new SIMS measurements of volatile and trace elements in olivine-hosted melt inclusions (n=60) from two high-Mg basalt bombs from its 1982-83 eruption. The inclusions are <100 μm in diameter and each consists of naturally clear, brown glass with a single vapor bubble. A prior melt inclusion study using these bombs revealed H<sub>2</sub>O-poor basaltic melts atypical of many arc-front volcanoes (Sisson & Bronto, 1998), but the new data resolve three distinct populations of magmatic volatile compositions. Most abundant are nearly dry (0.3-0.5 wt.% H<sub>2</sub>O) melts similar to those of Sisson & Bronto (1998), with trace element signatures indicative of some involvement of slab-derived material into the magma source (e.g. Th/La=0.15-0.16) despite low H<sub>2</sub>O. The new SIMS data also reveal two smaller populations of melt inclusions, one that is ultra-dry, similar to MORB in both H<sub>2</sub>O content and trace elements (0.08-0.3 wt.% H<sub>2</sub>O; Th/La=0.12-0.16), and one that is wetter (1.4-2.5 wt.% H<sub>2</sub>O), with trace element characteristics similar to the whole rock lava (Th/La=0.16-0.20). Water-fluxed and decompression melting are thus both significant melting processes beneath Galunggung. The distinct juxtaposition of low H<sub>2</sub>O and slab-derived signatures, however, further suggests that the mantle experiencing decompression melting beneath Galunggung may also be infiltrated by H<sub>2</sub>O-poor brines (H<sub>2</sub>O/Cl=0.7-3.9) that impart slab-derived signatures without dominating the melting process or adding significant H<sub>2</sub>O to the melt. The volcanic arc in western Java consists of northern (rear-arc) and southern (arc-front) volcanic groups separated by the Bandung depression, which is probably an axial graben. The two volcanic groups converge eastward and join near Galunggung. This intra-arc extension may allow such a broad spectrum of primitive melts, generated by distinct processes, to reach shallow levels within a single arc magmatic system.

## A new reflectance IR spectroscopy method for analyzing H<sub>2</sub>O in rhyolitic to basaltic glasses

P.L. KING, K.D. DALBY, D.K. LUI AND T. GRIFFIN

Dept. Earth Sciences, Univ. Western Ontario, London ON  
N6A 5B7, Canada (penny.king@uwo.ca)

To model volatile processes in magma chamber processes and apply 'geospeedometers' it is necessary to measure volatile species in glasses. Fourier Transform infrared (IR) spectroscopy provides information on the volatile species in glasses such as OH<sup>-</sup> and molecular H<sub>2</sub>O. Transmission IR (T-IR) is used; however it is difficult to prepare the thin samples required for melt inclusion analysis. Also, to obtain quantitative data with T-IR it is necessary to use extinction coefficients that have large errors; likely due to the fact that glasses used in calibrations were prepared at different pressures and temperatures. Standard reflectance IR (R-IR) has large uncertainties associated with the baseline position and no calibrations are available for H<sub>2</sub>O in basalt.

We have calibrated a new method for R-IR using the Kramers-Kronig (KK) algorithm. The raw R-IR data (5400 - 650 cm<sup>-1</sup>) was smoothed to a ~40.5 cm<sup>-1</sup> window before calculating a KK-absorbance (KK-Abs.) spectrum that corrects for optical dispersion effects due to a specular component. The KK-Abs. was measured from a linear baseline ( $1\sigma < 5\%$  for 3-4 replicates on samples with  $> 1$  wt. % total H<sub>2</sub>O), and the ~3550 cm<sup>-1</sup> band KK-Abs. = 0.045 units for total H<sub>2</sub>O wt.% = 6.7 wt.%. The total H<sub>2</sub>O wt.% =  $m * (3550 \text{ cm}^{-1} \text{ band KK-Abs.})$ , where  $m$  changes as a function of composition. The following are compositions/ $m/r^2$  of the fit: rhyolite/204/0.99; Mascota andesite/156/0.99; Mt. Hood andesite/154/0.93; and basalt/125±15/0.92. Samples with compositions slightly different from our calibration standards will only have a small error in H<sub>2</sub>O<sub>total</sub> wt.%, but errors increase in glasses with total H<sub>2</sub>O  $< \sim 1$  wt.% ( $1\sigma < 20\%$ ), suggesting a minimum detection limit. For andesite glasses we found the following relation: molecular H<sub>2</sub>O =  $417 * (1635 \text{ cm}^{-1} \text{ KK-Abs.})$ ,  $r^2 = 0.88$ .

We are investigating depth of penetration issues with R-IR because doubly-polished andesite glasses  $< \sim 100 \mu\text{m}$  thick produce mixed reflectance-transmission spectra.

In addition to variations in the bands associated with H-O species, the Si-O band widths vary as a function of H<sub>2</sub>O content due to modification of the Si-O network and these variations may influence estimates of glass composition with remote sensing data.

## Experimental determination of hydrogen partitioning between melts and nominally anhydrous minerals: Consequences for melting and H storage capacity in the upper mantle

CYRIL AUBAUD, MARC M. HIRSCHMANN AND ANTHONY C. WITHERS<sup>1</sup>

Dept. of Geol. & Geophys., Univ. of Minnesota, Minneapolis, MN 55455, USA (aubau001@umn.edu)

The small amounts of H dissolved in nominally anhydrous mantle minerals (NAMMs) have significant influence on the melting behavior of the mantle. Unfortunately, direct experiments determining the effect of H in NAMMs on the peridotite solidus temperature are intractable and thermodynamic calculations are impeded by a lack of available calibration data. However, mineral/melt partition coefficients can be used to model the effect of H on the peridotite solidus using a cryoscopic approximation. Recent determinations of H partitioning between NAMMs and silicate melt by newly developed low blank SIMS techniques (Koga et al., 2003; Aubaud et al., 2004) yield a bulk  $D^{\text{peridotite/melt}}$  of 0.009, consistent with estimates based on analogies to LREE in oceanic basalts (e.g., Michael, 1988). Tests of the cryoscopic approximation in simple systems (forsterite-H<sub>2</sub>O, enstatite-H<sub>2</sub>O, diopside-H<sub>2</sub>O) reproduce melting behavior for modest amounts of H<sub>2</sub>O ( $< 10$  wt.%) in the liquid. Applied to peridotite, this approach indicates that 50–200 ppm H<sub>2</sub>O causes melting beneath ridges 5–20 km deeper than intersection with the dry peridotite solidus. Beneath plumes, where the H<sub>2</sub>O content may be 500–1000 ppm, the predicted increase is 60–100 km.

The H storage capacity is the maximum H that can be stored in solid peridotite at a given  $T$  and  $P$  without stabilization of a hydrous fluid or melt. Solubility measurements of individual NAMMs provide some evidence of peridotite storage capacities, but a critical additional constraint is equilibrium partitioning of H between coexisting peridotitic minerals. Experiments indicate values of  $D^{\text{pyx/ol}}$  of  $\sim 10 \pm 1$  ( $n=6$ ) at modest pressure (1–2 GPa). Combined with solubility measurements of H in olivine (Kohlstedt et al. 1996; increased by 3 X: Bell et al., 2003, Koga et al., 2003), this suggests that the storage capacity of H<sub>2</sub>O in the upper mantle is at least 0.4 wt.% at 410 km. This challenges the view that the storage capacity of the upper mantle is small and that hydrous material advected from the transition zone will likely melt.

## Water contents in anhydrous minerals from the upper-mantle (peridotites and eclogites)

A.H. PESLIER<sup>1</sup> AND J.F. LUHR<sup>2</sup>

<sup>1</sup>Texas Center for Superconductivity and Advanced Materials (TCSAM), University of Houston, Houston, TX 77204, USA (apeslier@mail.uh.edu)

<sup>2</sup>Department of Mineral Sciences, NHB-119, Smithsonian Institution, Washington, DC 20560, USA (jluhr@volcano.si.edu)

Water has a strong influence on the chemical and physical properties of silicate minerals, fluids, and melts in the lithosphere. The reactions occurring during the dehydration of a down-going slab, the quantity of water being kept by the slab and that expelled to the overlying mantle wedge, how water is stored in these various components, and in what form it can be released, are important factors in understanding the water budget of the mantle. Nominally anhydrous minerals may represent an important site for storing water (or more exactly hydrogen) in subducted slabs and in the mantle above slabs at depths where hydrous minerals may not be stable. This study attempts to estimate the water content of various parts of the upper mantle focusing on its primary phases, olivine, pyroxene and garnet. Here, samples from subducted basalts and mantle xenoliths are examined.

The water contents in pyroxenes and olivines from spinel peridotite xenoliths from Mexico and Simcoe (Washington State, USA) are negatively correlated with oxygen fugacity measured on the spinels. This can be related to the inferred mechanism of hydrogen incorporation in most nominally anhydrous minerals, which is thought to be based on the ferrous-ferric equilibrium. As subduction zones appear to be characterized by high oxygen fugacities, the low water content of mantle-wedge pyroxenes was interpreted as being the result of oxidation of the mantle above subduction zones by slab-derived metasomatic fluids or melts.

Preliminary results on eclogites from high-pressure terranes of the Alps yield contents of the structurally-bond water in clinopyroxenes (omphacites) and garnets of 200-425 ppm and 0-40 ppm respectively. No relation has been found yet with pressure or temperature of equilibration (range of 2.6 to 4 GPa and 700-900°C). This study will include an evaluation of the influence of decompression and cooling metamorphism on water content of nominally anhydrous minerals.

## Hydrogen isotope geochemistry of nominally anhydrous minerals

JULIE A. O'LEARY, JOHN M. EILER AND  
GEORGE R. ROSSMAN

<sup>1</sup>California Institute of Technology, MC 100-23, Pasadena, CA 91125, USA (oleary@gps.caltech.edu)

Mantle derived materials span a range of ~100 ‰ in hydrogen isotopic composition. Nominally anhydrous minerals from mantle xenoliths are the most deuterium depleted of all mantle materials, with  $\delta D$  values 50 ‰ lower than average mid ocean ridge basalt. These variations suggest large hydrogen fractionations within the mantle but available data are limited to large, high quality samples needed for conventional measurement techniques. We have recently developed a continuous-flow technique for measuring hydrogen isotopic composition in small (5-50 mg) samples of mantle pyroxenes, making it possible to analyze many more mantle samples.

Pyroxenes from a lherzolite xenolith from the continental interior have  $\delta D$  values of  $-113\text{‰} \pm 3$  (cpx) and  $-127\text{‰} \pm 10$  (opx), in agreement with prior measurements of the same samples, supporting the conclusion that nominally anhydrous minerals in the upper mantle are a reservoir of low  $\delta D$  hydrogen.

Our initial measurements are of a lherzolite from the Central American arc. The hydrogen isotopic composition of clinopyroxene is  $-92 \pm 6$  ‰, and orthopyroxene is  $-65$  ‰. This xenolith is deuterium enriched by 30-50‰ relative to xenoliths from the continental interior and is similar to mid-ocean ridge basalts. These are the first measurements of nominally anhydrous mantle minerals from an arc environment.

Models of hydrogen fractionation during mantle processes create a framework for interpreting isotopic results and will be used to guide further sampling. In subduction zones the  $\delta D$  of subducting material can be calculated using experimental and predicted fractionation factors. Altered oceanic basalt with an initial  $\delta D$  of  $-40$  ‰ has hydrogen remaining in nominally anhydrous minerals with a  $\delta D$  of  $-110$  ‰ following dehydration. Though the number of samples analyzed is very small, our data show there is hydrogen isotopic variation in nominally anhydrous minerals and potential for using hydrogen isotopes to describe the mantle water cycle.

## FTIR spectrum of OH in olivine: A new tool in diamond exploration

S. MATVEEV AND T. STACHEL

Earth and Atmospheric Sciences, U of A, Edmonton, Canada  
(smatveev@ualberta.ca; tstachel@ualberta.ca)

FTIR spectroscopy revealed anomalously high hydroxyl concentrations in kimberlitic olivines from South Africa and Siberia. The purpose of our current study is to test whether this finding merely represents an anomaly or whether kimberlitic olivines from other cratonic areas, including Canada, are also high in hydroxyl content. In the latter case such a distinct FTIR signature could be used to discriminate between kimberlitic and non-kimberlitic olivines in exploration till samples collected in the Canadian Arctic.

We measured FTIR spectra and chemical compositions of olivines from seven Canadian kimberlites. Single-grain FTIR measurements were performed in transmittance mode on double polished, ~300 micron thick sections of individual olivines and rock slabs. For application in diamond exploration the method was also tested on unpolished samples.

The majority of olivines exhibit strong OH-related IR absorption bands in the wavenumber range from 3670 to 3230 cm<sup>-1</sup>. A large proportion of olivines predominantly absorb at higher frequencies in the wavenumber range from 3670 to 3440 cm<sup>-1</sup> (Group 1 OH bands). Noteworthy are high frequency IR peaks at wavenumbers >3570 cm<sup>-1</sup>, that are common for olivines originating at high pressures but that are not observed in spectra of basaltic phenocrysts. Some olivines also show absorption at lower frequencies between 3240 and 3340 cm<sup>-1</sup> (Group 2 OH bands). Group 2 OH bands indicate equilibrium with orthopyroxene and thus may reflect a peridotitic origin of olivine macrocrysts in kimberlites. Hydroxyl concentrations vary from grain to grain but typically remain constant across individual grains. So far, we have observed no correlation between the frequency or intensity of absorption bands and the trace element composition of olivines. A significant proportion of the studied kimberlitic olivines show OH concentrations that are not only much higher than those reported for olivines crystallized at lower water fugacities (mantle xenoliths) but also than those of olivines formed under hydrous conditions but at shallower depth (e.g. phenocrysts from boninites; Matveev et al., 2005). Spectra measured on unpolished grains exhibit broader absorption bands and higher spectral noise, but otherwise are sufficiently similar to spectra of polished samples to suggest that FTIR spectroscopy can be used to identify kimberlitic olivines even with unpolished grains.

## Hydration of olivine and the Earth's deep water cycle

JOSEPH R. SMYTH<sup>1,2</sup>, DANIEL J. FROST<sup>2</sup> AND  
FABRIZIO NESTOLA<sup>2</sup>

<sup>1</sup>Department of Geological Sciences, University of Colorado,  
Boulder, CO 80309 USA (smyth@colorado.edu)

<sup>2</sup>Bayerisches Geoinstitut, Universität Bayreuth, 95440  
Bayreuth, Germany (dan.frost@uni-bayreuth.de)

Although natural olivine of upper mantle origin generally contains less than 300 ppm H<sub>2</sub>O by weight, olivine synthesized at temperature and pressure conditions near the 410 km discontinuity, can contain up to 20 times this amount of H, enough to affect elastic properties, crystal structures, and unit cell volumes. Hydrous olivines have been synthesized at 12 GPa and several temperatures and bulk compositions to examine the effects of silica activity, and temperature on H contents of the olivine. Mineral phases were identified by Raman spectroscopy and analyzed for H content by FTIR spectroscopy of oriented, faceted grains.

Forsterite olivines synthesized at 1250°C have been observed with up to 5000 ppm H<sub>2</sub>O coexisting with clinoenstatite and up to 8000 ppm H<sub>2</sub>O coexisting with clinohumite. Pure-Mg forsterites synthesized at 1250° have been observed with up to 8000 ppm H<sub>2</sub>O coexisting with clinoenstatite and 8500 ppm H<sub>2</sub>O coexisting with clinohumite.

Crystal structure refinements indicate that the hydration mechanisms are different in the two different conditions. The silica-excess sample appears to contain M2 cation vacancies, whereas the magnesia-excess sample shows tetrahedral site vacancies up to two percent, consistent with 5000 ppm by weight H<sub>2</sub>O. Further, the partially vacant coordination polyhedra are significantly larger than their fully occupied counterparts. Cell parameter refinements indicate expansion of the unit cell by up to 0.3 percent with hydration in both samples, with tetrahedral vacancies causing an increase in both *b* and *c* axes and contraction of *a* relative to the crystal showing octahedral vacancies. Static compression measurements by single crystal X-ray diffraction to 8GPa indicate a decrease in the bulk modulus from about 129GPa for anhydrous forsterite to 120 GPa for a sample containing 8000 ppm H<sub>2</sub>O.

These results indicate that olivine can be a major host for H at depths greater than 200 km in the mantle. If olivine can contain these relatively high H contents, it is unlikely that major melting would occur at 410 km in a mantle containing a two thousand ppm H<sub>2</sub>O in a region of ascending convection.

## Water solubility in octahedrally-coordinated silicates

WENDY R. PANERO<sup>1</sup>, LARS P. STIXRUDE<sup>2</sup> AND  
SOFIA AKBER-KNUTSON<sup>3</sup>

<sup>1</sup>Dept Geological Sciences, Ohio State University, Columbus,  
OH 43120, USA (panero.1@osu.edu)

<sup>2</sup>Dept Geological Sciences, University of Michigan, Ann  
Arbor, MI 48109, USA (stixrude@umich.edu)

<sup>3</sup>Division of Geological and Planetary Sciences, Caltech,  
Pasadena, CA 91125, USA (sofia@gps.caltech.edu)

The incorporation of water in nominally anhydrous silicates is associated with mechanical weakening, lowered melting points, and can serve as a significant volatile reservoir in the planet. We have performed first-principles calculations addressing the substitution mechanism of H<sub>2</sub>O in octahedrally coordinated silicates. The solubility of H<sub>2</sub>O in these silicates results from combining static calculations with a statistical-mechanical model for the entropy of solution. We address the H<sub>2</sub>O solubility in three silicates: stishovite (SiO<sub>2</sub>), Mg- and Ca- perovskite, with H solution mechanisms constrained by charge balance in the structure. In the CMASH system, the only stable solution mechanisms are Al+H = Si or 2H=Ca or Mg.

The OH bond in octahedrally coordinated silicates varies between 1.02Å and 1.2Å, with only the OH bond in stishovite lengthening with increasing pressure. The incorporation of 3.1 mol% H<sub>2</sub>O in each mineral accounts for minimal density decrease (<1%) and a 4.1%, 2.2% and 1.5% decrease of the bulk modulus (K<sub>0</sub>) for stishovite, MgSiO<sub>3</sub> and CaSiO<sub>3</sub>, respectively. The decrease of K<sub>0</sub> is comparable to the effects of vacancy-compensated aluminum incorporation.

In all cases, the solution enthalpy is positive, such that solubility of H<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> is an entropy-driven process. In MgSiO<sub>3</sub>, we find a total solubility of aluminum of about 15-20 mol % at 25 GPa and 2000 K. The solubility of water in stishovite exceeds 0.3 wt% H<sub>2</sub>O at 25 GPa and 1500 K, increasing with increasing pressure and temperature. This accounts for the transport of water equivalent to the mass of the oceans over the age of the Earth. The solubility of H<sub>2</sub>O in both Mg- and Ca-perovskite is significantly lower, with solubilities less than 100 ppm H<sub>2</sub>O at pressures and temperatures equivalent to the top of the lower mantle, accounting for a mass of water equivalent to about 1% of the Earth's oceans.

### Reference

Panero W. P., Stixrude L. P. (2004) *Earth Planet Sci Lett*, **241**, 421-431.