Water in MgSiO$_3$-majorite at high temperatures and pressures: Incorporation mechanisms and elastic properties

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Water cycle is widely distributed from the surface to the interior of the Earth. At relatively shallow depths, a large amount of water is transported into the mantle through hydrous silicate minerals in the subducting slabs (Fig. 1). At higher temperatures these hydrous silicate minerals become increasingly unstable, then water is expected to be mainly transported as hydrous defects (hydroxyl point defects) in nominally anhydrous minerals (NAMs). As the major component of garnet, the second most abundant phase in the Earth's transition zone (Fig. 2), $MgSiO_3$-majorite (Mgmj) may be an important reservoir of water.
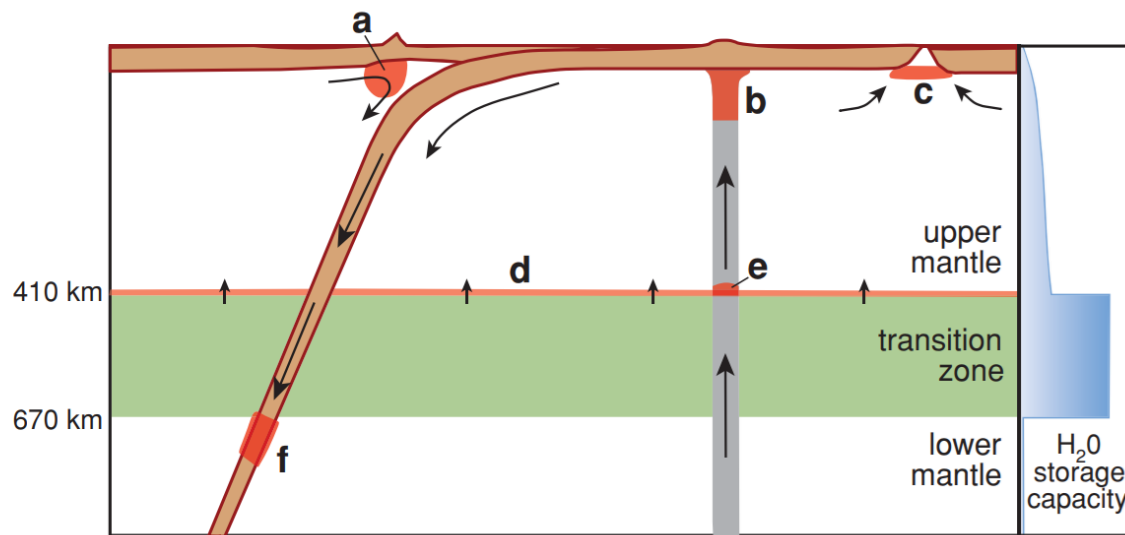

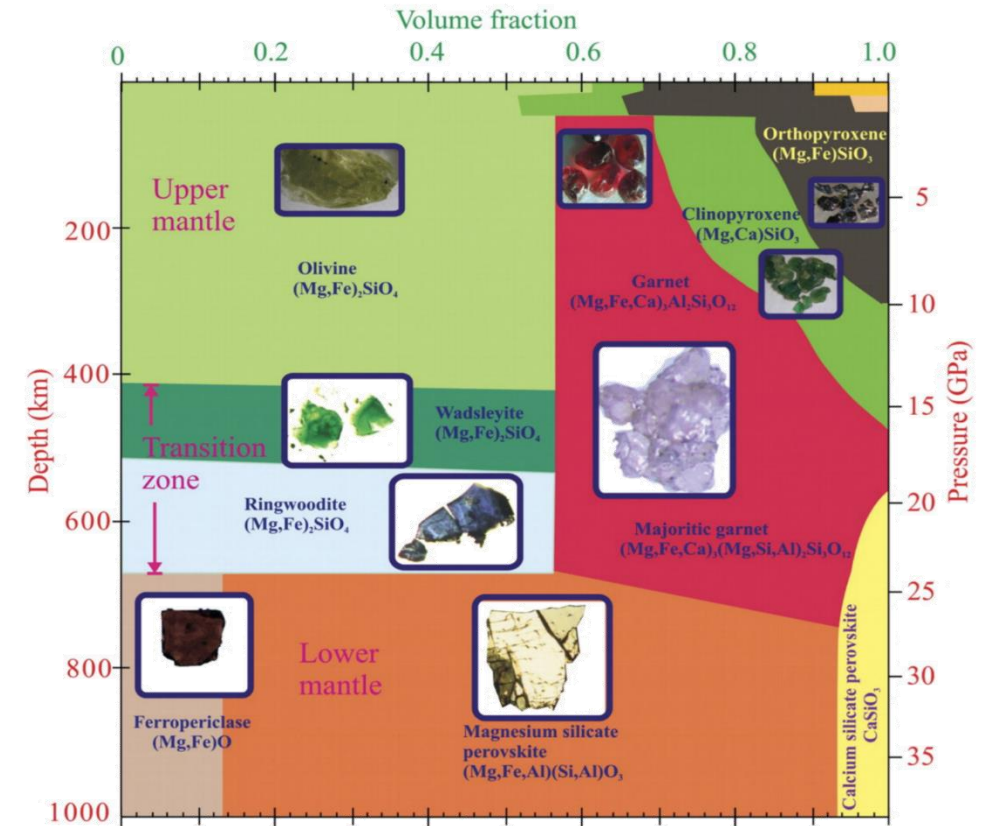Fig. 1. Water cycle in the mantle (Hirschmann, 2006).

Fig. 2. The phase proportion of minerals in pyrolite (Frost, 2008).

Frost, D.J. (2008). The upper mantle and transition zone. *Elements, 4*(3), 171-176. doi:10.2113/Gselements.4.3.171

Hirschmann, M.M. (2006). Water, melting, and the deep Earth H_2O cycle. *Annu. Rev. Earth Planet. Sci., 34*, 629-653.
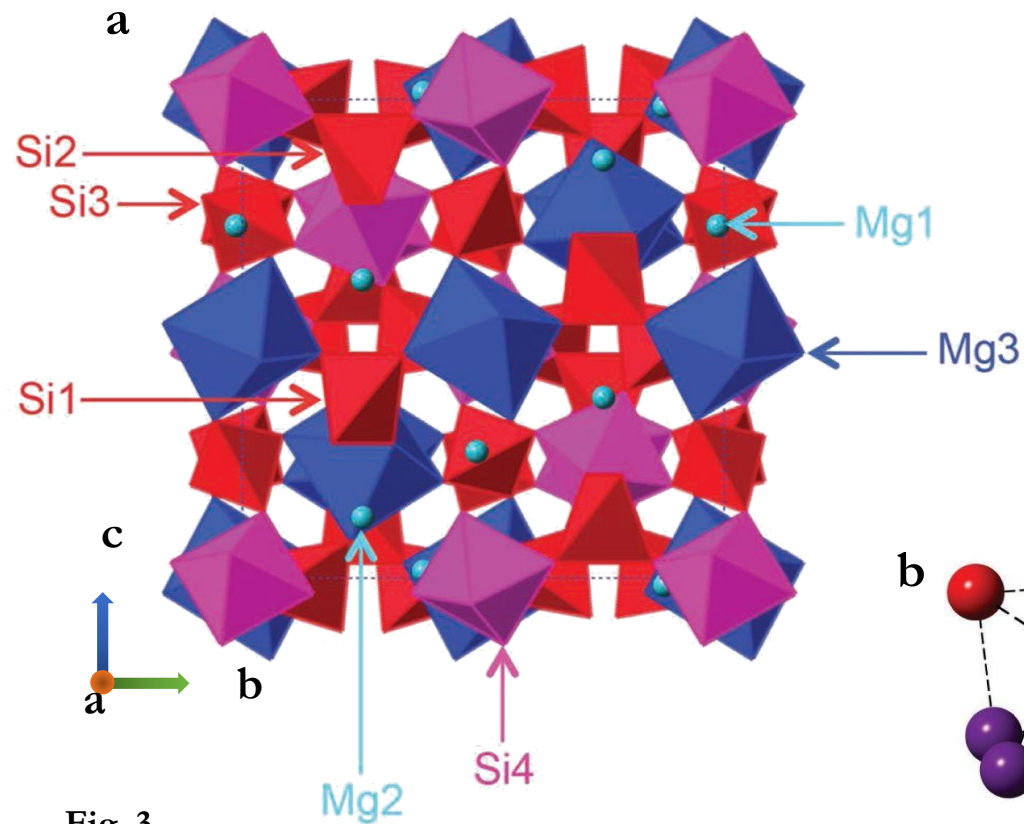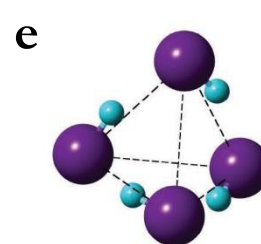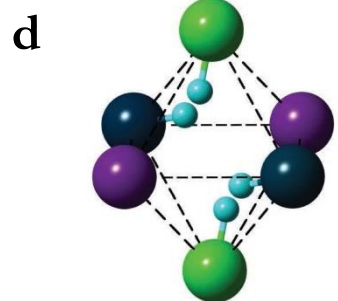
2. Crystal Structure

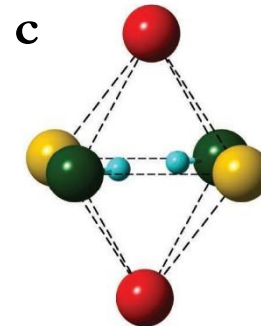MgSiO$_3$-majorite, which belongs to the tetragonal system (space group: I4$_1$/a), has a similar structure with other cubic garnet end-members (such as pyrope). Its structural chemical formula is Mg$_3$(Mg,Si)[SiO$_4$]$_3$ which makes it has 8 structural formula units in a 160-atom unit cell (Fig. 3). The main structural parts in Mgmj are three types of oxygen polyhedra (tetrahedron, octahedron, and dodecahedron). Due to the differences of environment and neighboring cations, these can be divided into 7 kind of unique polyhedral sites: Mg1 and Mg2 are dodecahedral sites, the main difference is that Mg1 dodecahedron is more distorted than Mg2;

Mg3 and Si4 are octahedral sites; Si1, Si2 and Si3 are tetrahedral sites, Si1 tetrahedra are bonded to four magnesia octahedra, Si2 are bonded to four silica octahedra and Si3 are bonded to two magnesia octahedra and two silica octahedra.

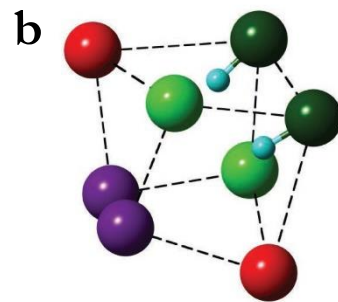**Fig. 3.**
a: the unit cell of Mamj and 7 polyhedra;
b: OH in the Mg2 vacancy ([☐$_{Mg2}$+2OH$^-$]) ;
c: OH in the Mg3 vacancy ([☐$_{Mg3}$+2OH$^-$]);
d: OH in the Si4 vacancy ([☐$_{Si4}$+4OH$^-$]);
e: OH in the Si2 vacancy ([☐$_{Si2}$+4OH$^-$]).
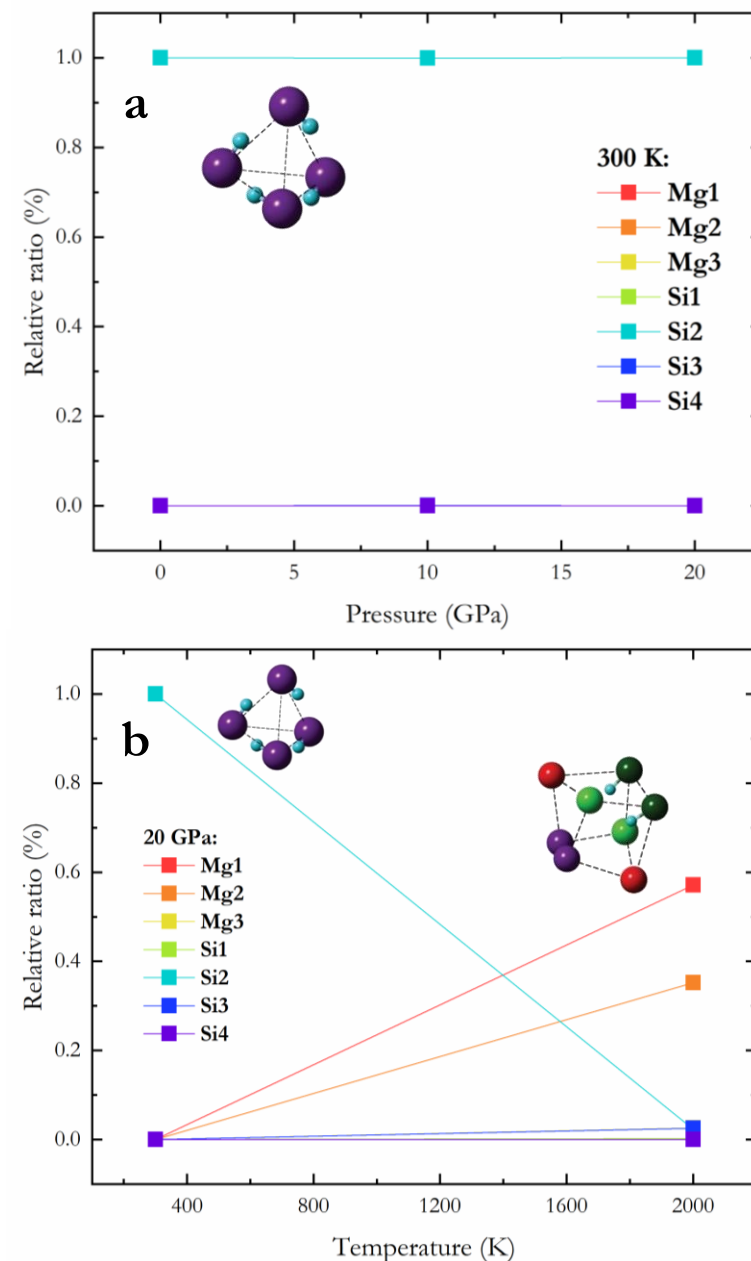In b-e, large balls represent different type of O^{2-}, small balls represent H$^+$. (Pigott et al., 2015)

Pigott, J. S., Wright, K., Gale, J. D., & Panero, W. R. (2015). Calculation of the energetics of water incorporation in majorite garnet. American Mineralogist, 100(5-6), 1065-1075. doi:10.2138/am-2015-5063

3. Incorporation Mechanisms

We systematically considered all possible incorporation mechanisms in the seven polyhedral sites. By extensive first principles simulations and solving the equations for the equilibrium constants of the substitution reactions, we obtained the ratios of various polyhedral substitutions and their temperature and pressure dependences.

In Fig. 4, our results show the occupations of water (H^+) in Mgmj change mainly with temperature and are generally pressure-independent. Almost all hydrogen prefer to occupy Si2 sites (tetrahedra) at 300 K (Fig. 4a), which agrees with previous static calculations (Pigott et al., 2015). But the amount of water occupying the dodecahedral vacancies (Mg1 and Mg2 sites) increases substantially with temperature (Fig. 4b). At 2000 K and 20 GPa, the dodecahedral occupations would account for more than half of the possible incorporation sites.

The significant temperature effects on the incorporation mechanisms of water in NAMs find their root from the remarkably larger configurational entropies when the hydrogen is intended to enter the Mg-vacancies. These effects should also be found in other NAMs as well, such as forsterite (Qin, et al., 2018), which would highlight the importance of in-situ measurements and calculations at high temperature and pressure.

Pigott, J. S., Wright, K., Gale, J. D., & Panero, W. R. (2015). Calculation of the energetics of water incorporation in majorite garnet. American Mineralogist, 100(5-6), 1065-1075. doi:10.2138/am-2015-5063

Qin, T., Wentzcovitch, R. M., Umemoto, K., Hirschmann, M. M., & Kohlstedt, D. L. (2018). Ab initio study of water speciation in forsterite: Importance of the entropic effect. American Mineralogist, 103(5), 692-699. doi:10.2138/am-2018-6262

Fig. 4. The relative ratios of seven sites along (a) pressure at 300 K and (b) temperature at 20 GPa.

4. Elastic properties

Different incorporation mechanisms of water in Mgmj should have important effects on its elastic properties. We calculated the elastic velocities and anisotropies of hydrous Mgmj with both Mg1 and Si2 substitutions.

Our results show that ~1 wt% water in Si2 vacancy would decrease wave velocities of Mgmj by ~3% in both V_P and V_S, while the same amount of water in Mg1 vacancy would more effectively decrease the velocities by ~6% (Fig. 5).

In Fig. 6, we find that water in Mg1 vacancy would improve the seismic anisotropy of Mgmj, while those in Si2 vacancy essentially show no effects.

Kawai, K., & Tsuchiya, T. (2015). Elasticity and phase stability of pyrope garnet from ab initio computation. Physics of the Earth Planetary Interiors, 240, 125-131.

Kiefer, B., Stixrude, L., & Wentzcovitch, R. M. (1997). Calculated elastic constants and anisotropy of Mg2SiO4 spinel at high pressure. Geophysical Research Letters, 24(22), 2841-2844.

Mainprice, D. (2015). 2.20—Seismic anisotropy of the deep earth from a mineral and rock physics perspective. Treatise on Geophysics . Elsevier, Oxford, 487-538.

Mao, Z., Jacobsen, S. D., Jiang, F., Smyth, J. R., Holl, C. M., & Duffy, T. S. (2008). Elasticity of hydrous wadsleyite to 12 GPa: Implications for Earth's transition zone. Geophysical Research Letters, 35(21). doi:10.1029/2008gl035618

Zha, C.-s., Duffy, T. S., Mao, H.-k., Downs, R. T., Hemley, R. J., & Weidner, D. J. (1997). Single-crystal elasticity of β-Mg2SiO4 to the pressure of the 410 km seismic discontinuity in the earth's mantle. Earth Planetary Science Letters, 147(1-4), E9-E15.
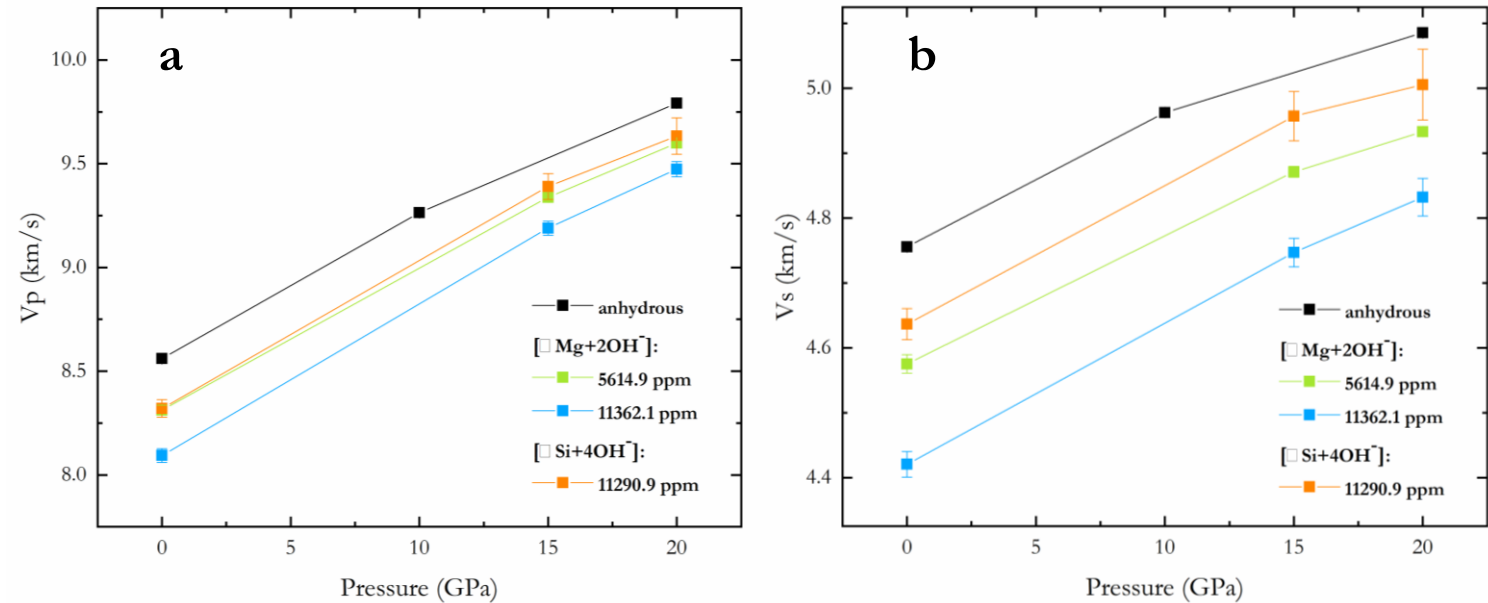
Fig. 5. (a) V_P and (b) V_S of Mgmj with OH in Mg1 and Si2 vacancies at static conditions.
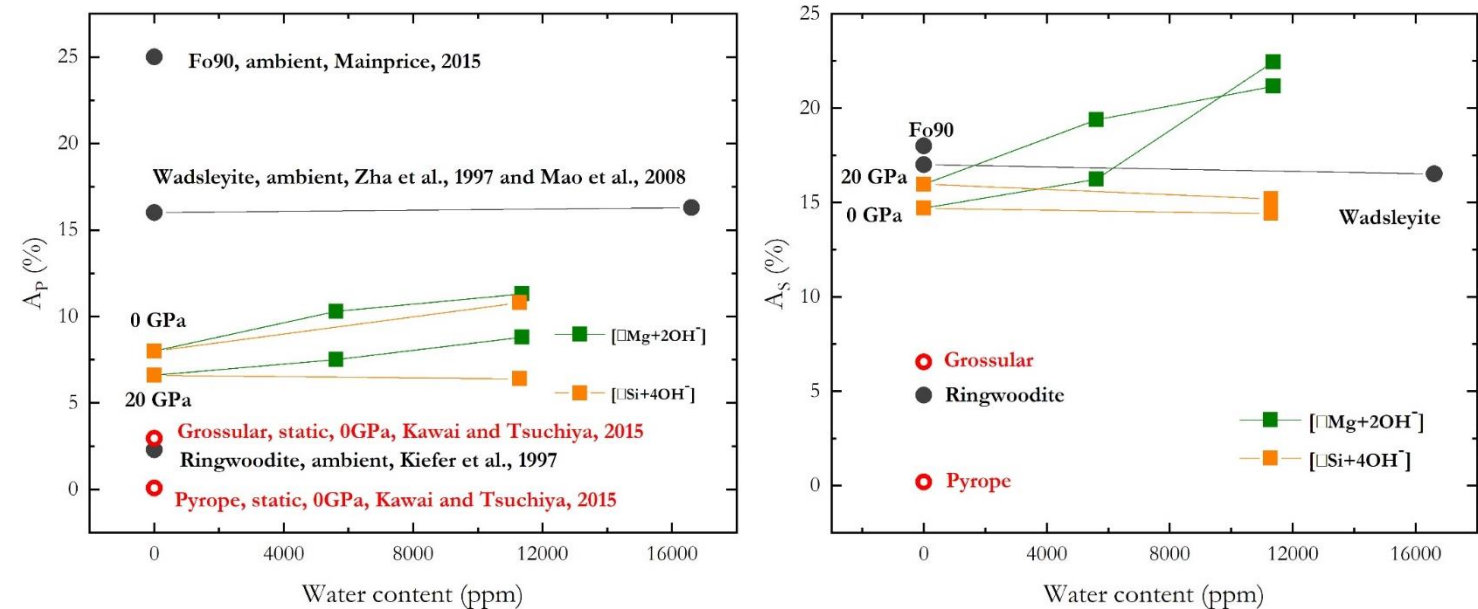

Fig. 6. (a) A_P and (b) A_S of Mgmj with OH in Mg1 and Si2 vacancies at static conditions.

Thanks for your attentions!

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