Supplementary Information

Comparison of water behavior between hydrous silicate melts and bulk water at Earth's mantle conditions

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Supplementary text 1. Hard sphere-based equation of state

In the hard sphere (HS) model, the liquid is considered as a mixture of deformable spheres corresponding to different oxide components of silicate melts which are MgO, FeO, SiO_2 and H_2O (Jing and Karato, 2011) The equation of state is expressed as

$$P = \frac{RT}{V}\left[(1-\xi)\Phi - \Phi_0\left(\frac{V_0}{V}\right)^{1/3} + \xi\Phi_0\left(\frac{V_{m0}}{V_m}\right)^{5/3}\right]$$

Here Φ represents the excluded volume effect and is expressed as

$$\Phi = \frac{1+f+f^2}{(1-f)^3}$$

with packing fraction $f = V_m/V$ relating the molar volume of liquid (V) to the volume occupied by a mole of spheres ($V_m = \pi\sigma^3 N_A/6$). Our hard-sphere model adopts average sphere diameter σ and deformability factor ξ.

The sphere diameter is considered to be temperature and volume dependent.

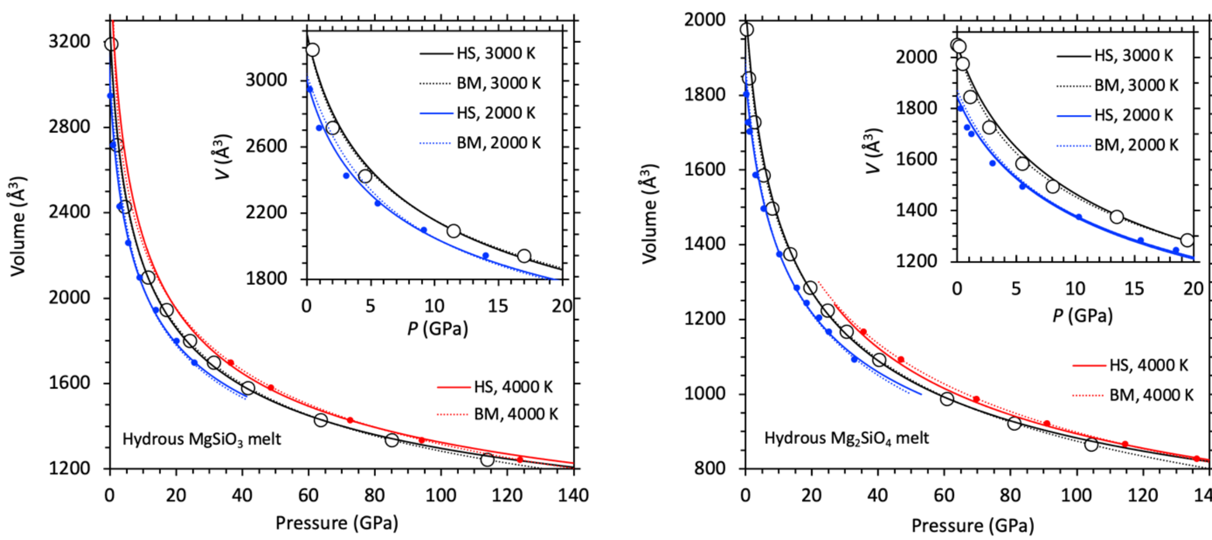
$$\sigma = \sigma_0\left(\frac{T}{T_0}\right)^{\eta} \exp[\alpha_0\xi(T-T_0)/3]\left(\frac{V}{V_0}\right)^{\xi/3}$$

The factor ξ represents the deformability of spheres. Its value is 0 for hard sphere liquid. If ξ = 1, liquid behaves as a solid because spheres and liquid are equally compressible. Our fitting shows that the model requires smaller and more deformable spheres for hydrous melts compared to dry melts because H_2O corresponds to the smallest sphere among all oxide components. For each melt, the sphere diameter tends to decrease somewhat with temperature, but it decreases considerably with pressure because of non-zero values of ξ in the range 0.42 and 0.54. The hard-sphere equation of parameters are given in table below.

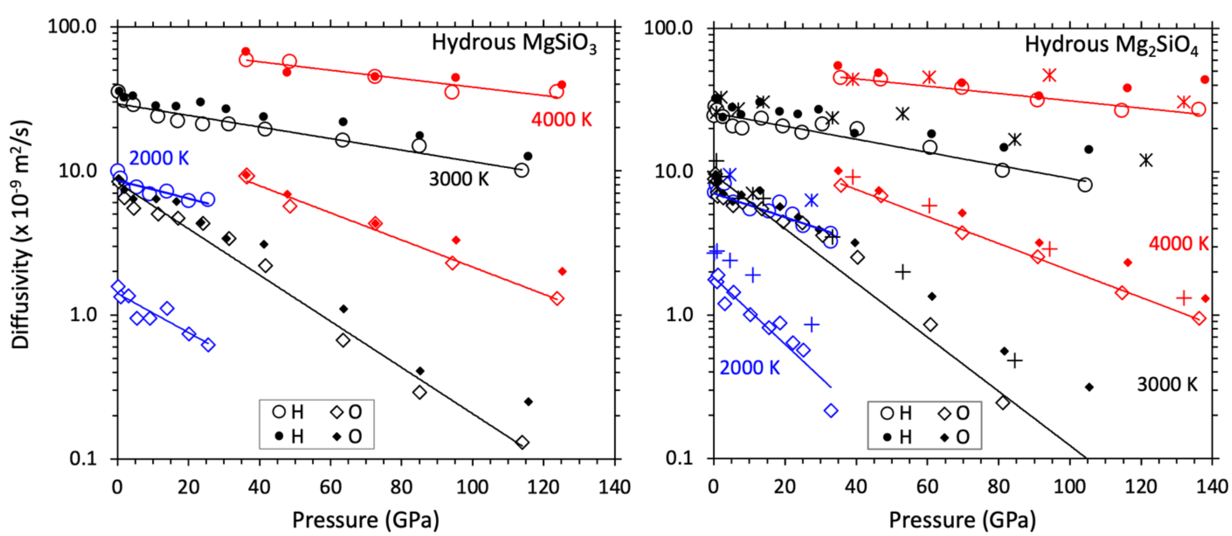
	$32MgSiO_3$	$32MgSiO_3+16H_2O$	$16Mg_2SiO_4$	$16Mg_2SiO_4+8H_2O$
V_0 (Å^3)	2415	3280	1670	2050
σ (Å)	3.152	2.396	3.104	2.410
η	-0.05	-0.05	-0.05	-0.05
ξ	0.52	0.42	0.54	0.49
α (x10^{-5} 1/K)	5.6	8.8	7.8	10.0

Jing, Z. and Karato, S. A new approach to the equation of state of silicate melts: an application of the theory of hard sphere mixtures. *Geochim. Cosmochim. Acta* **75**, 6780–6802 (2011)

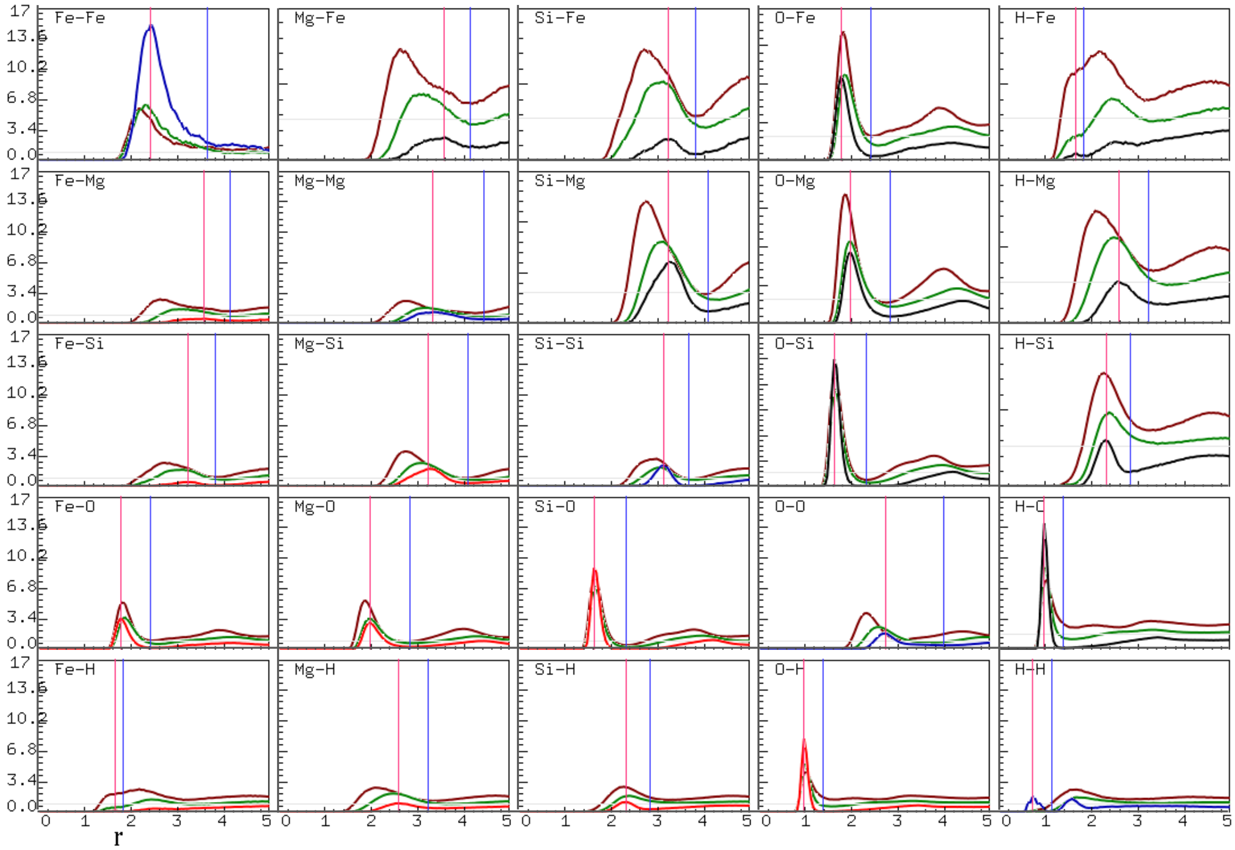
Supplementary figure S1. Comparison between the hard sphere (HS) and Birch-Murnaghan (BM) equation of state fits to the calculated pressure-volume results of hydrous enstatite (left) and forsterite (right) melts at 2000, 3000 and 4000 K. The open circles represent the calculated results at 3000 K and small filled circles represent the calculated results at 2000 and 4000 K.



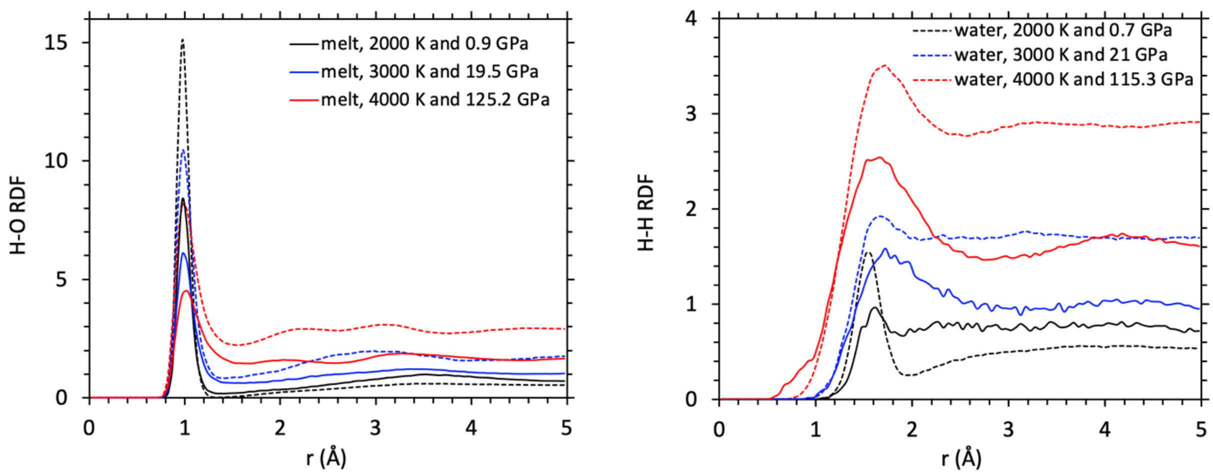
Supplementary figure S2. Diffusivity of hydrogen (open circles) and oxygen (open diamonds) in hydrous $MgSiO_3$ (8.2 wt% water) and Mg_2SiO_4 (6.0 wt% water) melts as a function of pressure at 2000, 3000, and 4000 K. The results for the corresponding iron-bearing phases are shown by small solid symbols. Also shown are the diffusivity results for Mg_2SiO_4 +11.4 wt% water, H: asterisks and O: pluses. The straight lines represent the Arrhenius trends for iron-free cases.



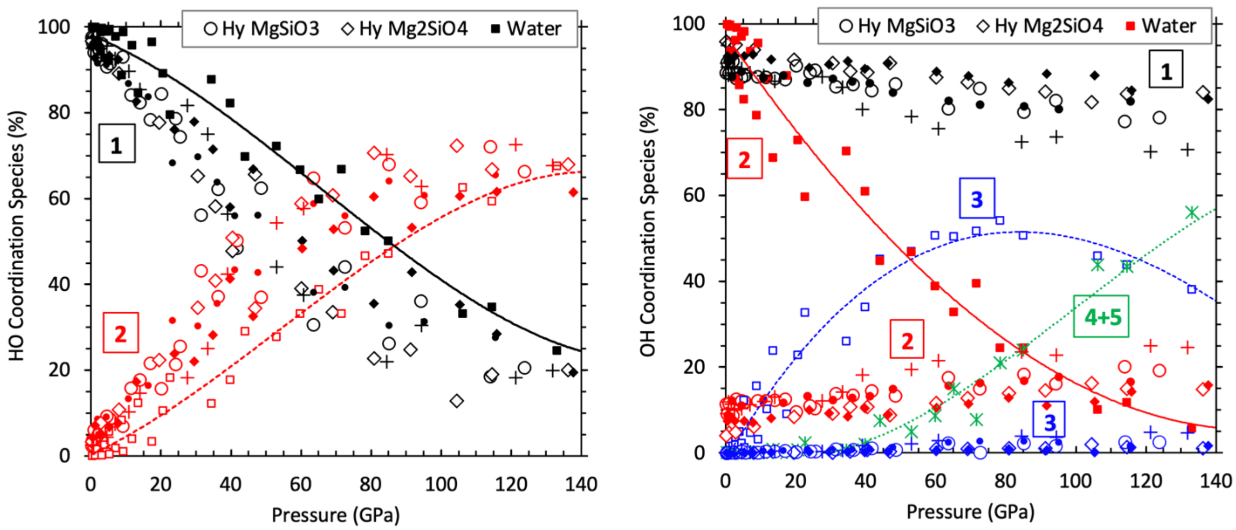
Supplementary figure S3. RDF matrix (symmetric) plot showing all radial distribution functions (like and unlike atom pairs) of hydrous $Mg_{0.75}Fe_{0.25}SiO_3$ melt at three different conditions: 0 GPa and 2000 K (black, blue and red curves), 23.5 GPa and 3000 K (green curves), and 125.2 GPa and 4000 K (brown curves). The vertical lines mark the first peak and the minimum after the first peak. The H-Fe RDF shows a shoulder around 1.6 Å with its amplitude increasing with compression. This feature represents a direct bonding between hydrogen and iron. A peak appears around 0.7 Å in the H-H RDF (corresponding to molecular hydrogen) at zero pressure but it almost disappears at higher pressures.



Supplementary figure S4. The H-O and H-H radial distribution functions of hydrous $MgSiO_3$ melt (solid curves) compared with those of pure water (dashed curves) at three pressure-temperature conditions. The H-O RDF shows a clear first peak at all conditions, thus signifying direct bonding between oxygen and hydrogen in both silicate melt and water. The peak position is almost the same between water and melt, also being insensitive to pressure. The right side of the peak slightly extends to large distance and the minimum after the peak becomes non-zero (more so for water) with compression. This indicates the absence of a clear first coordination shell in water, consistent with the pressure-induced dissociation of water molecules. A weak shoulder (peak) in the H-H function around 0.7 Å detected in some simulation runs of hydrous melt implies presence of metastable H_2 molecule. At low pressure, liquid water shows a clear peak at distance ~1.5 Å corresponding to the H-H distance within H_2O molecule. The peak becomes boarder with further compression.



Supplementary figure S5. The H-O and O-H coordination distributions of hydrous $MgSiO_3$ (8.2 wt% water) and Mg_2SiO_4 (6.0 wt% water) melts compared to those of water (squares and asterisks) as a function of pressure at 2000, 3000 and 4000 K. The results for the corresponding iron-bearing melts are shown by small solid symbols. The numbers in boxes denote the coordination states (1: one-fold, 2: two-fold, 3: three-fold, 4: four-fold, and 5: five-fold). Also shown are the results for hydrous Mg_2SiO_4 with 11.4 wt% water (pluses).



Supplementary figure S6. Hydrogen-induced electrical conductivity (σ) of hydrous $MgSiO_3$ (20 mol% water) and Mg_2SiO_4 (14.3 mol% water) melts as a function of pressure at different temperatures. Small solid symbols represent the results for the corresponding iron-bearing melts at 3000 and 4000 K. The averages taken between the iron-free and iron-bearing compositions are also shown (lines).