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A systematic study of the effects of volatile species on the structure and physical properties of amorphous SiO_2

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1. Introduction

Significant amounts of OH, F, and Cl have been found on the surfaces of Earth, the Moon, and Mars, respectively.[1,2] Volatiles such as these lower the solidus and facilitate melting in Earth, the Moon, and Mars. Measuring the elastic and structural properties of amorphous silicates is required to understand the origin and distribution of volatiles in these terrestrial bodies. We aim to understand the atomistic mechanisms that control the volumetric and elastic properties of amorphous silicates, which include melts and glasses, their frozen counterparts. To do this, we use resonant ultrasonic spectroscopy and gigahertz ultrasonic interferometry to measure the elastic moduli and acoustic wave speeds of glasses containing OH, F, and Cl (as melt analogues). We also perform shockless ramp compression experiments on pure and 1000 ppm OH silica samples from 0 to ~9 GPa and compare these results with the 1-atm measurements. We also performed Raman spectroscopy and molecular dynamics simulations to interpret the differences in elastic behavior between these volatile-doped silica. Taken together, the 1-atm and high-pressure elastic experiments indicate that dry and hydrated silicas exhibit similar trends in behavior through 9 GPa, and the differences in ambient acoustic wave speeds persist through 8 GPa.

References & acknowledgments

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2. Motivation

We want to understand origin and distribution of melts in terrestrial planets. The presence of volatiles in planetary interiors facilitates melting by lowering the solidus of rock. We determine the effects of three volatile species which may facilitate melting on the Earth (OH), the Moon (F), and Mars (Cl).

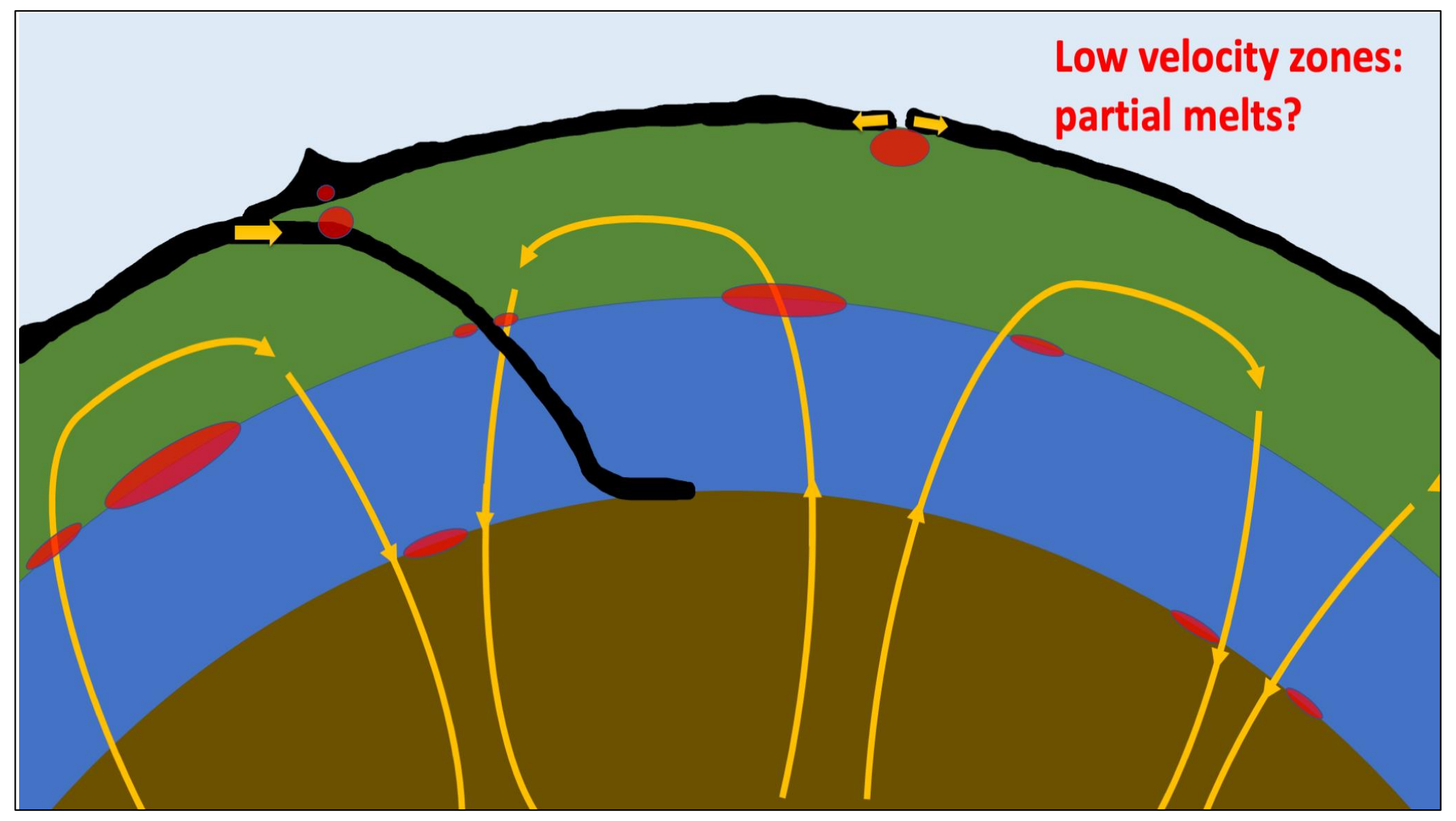
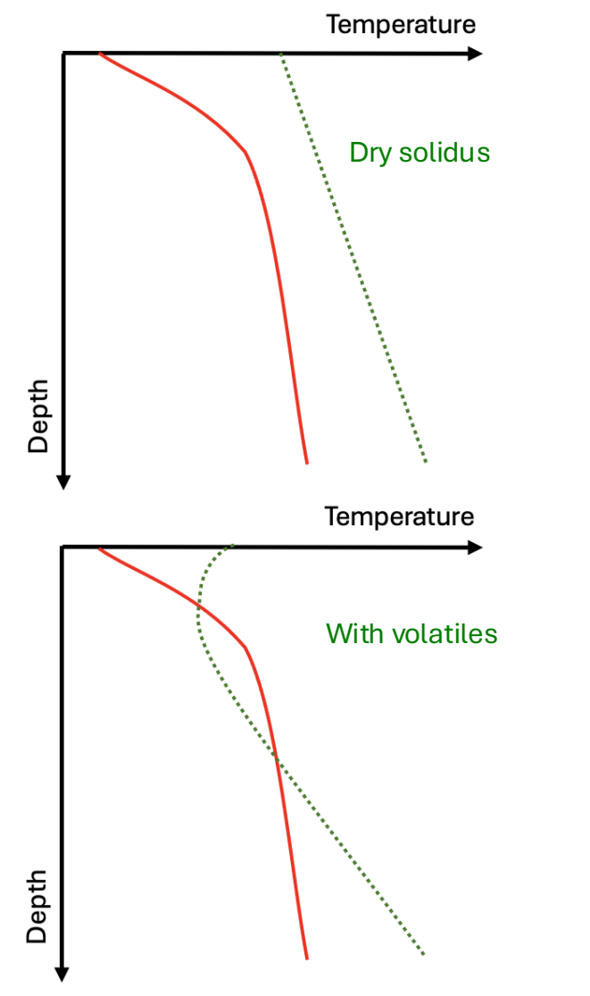


Fig. 1. A schematic of Earth's mantle with yellow arrows indicating the convective motion of material, and low velocity zones (red) at subduction zones and just above and below the mantle transition zone (MTZ). The upper mantle, green, the MTZ, dark blue, and the lower mantle, brown. (After refs. 3-5)



Inside Earth, the solidus is hotter than the geotherm, so the production of melt requires the reduction of solidus temperatures. This can be facilitated with volatiles, such as water (OH), fluorine, or chlorine, among others.

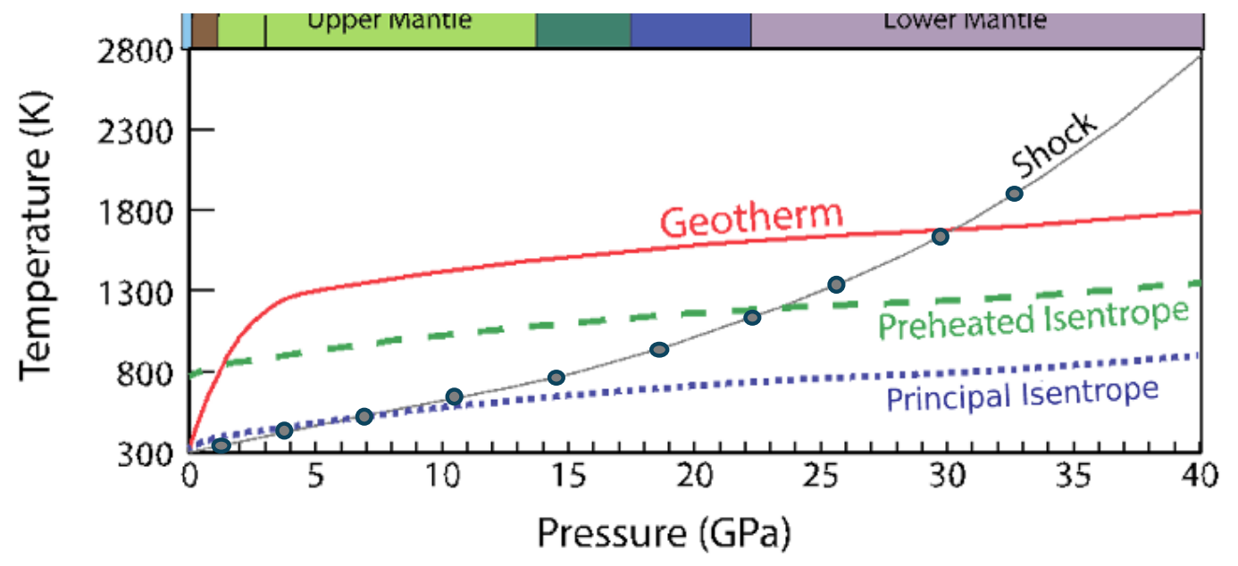
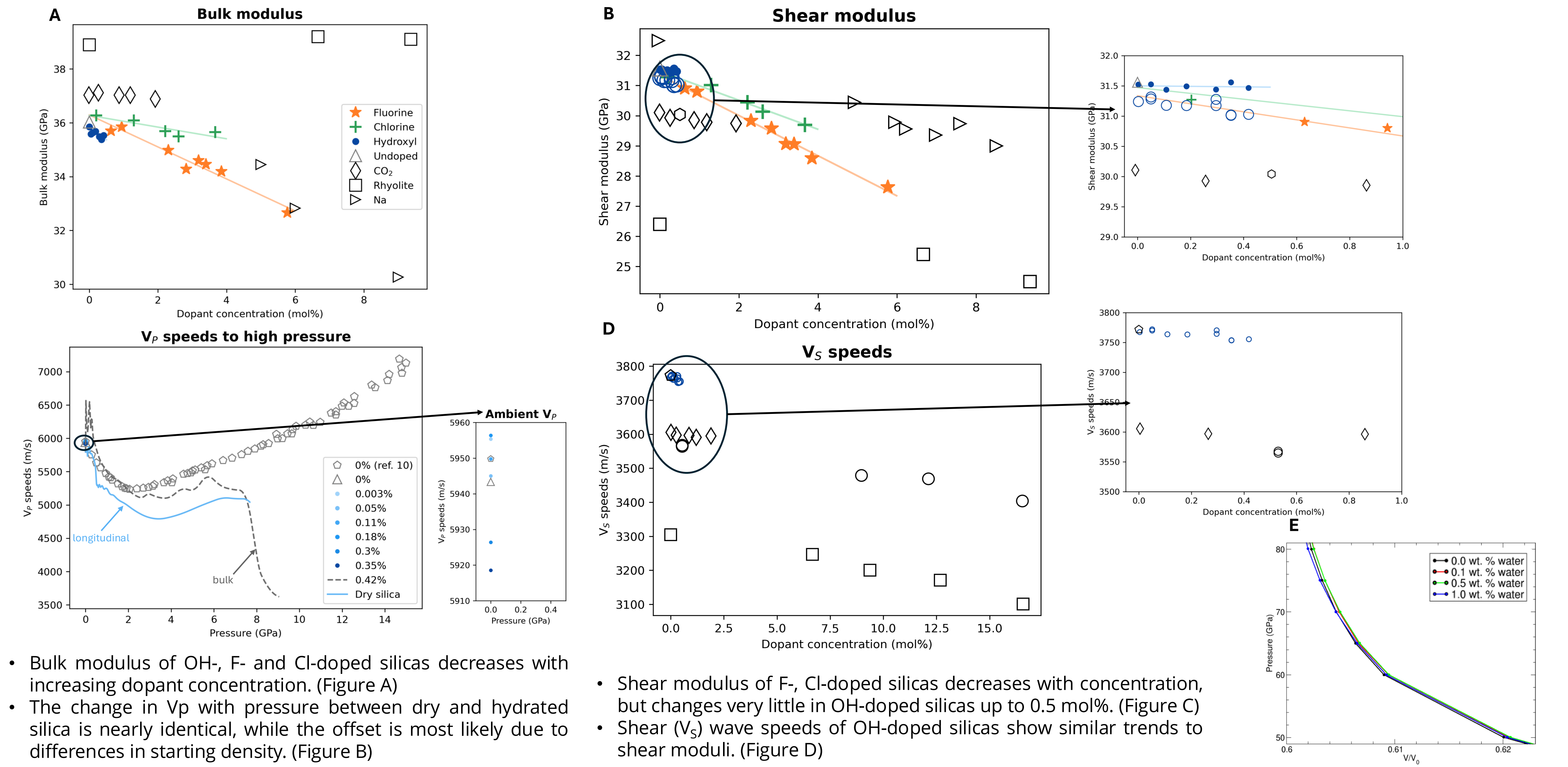


Fig. 2. Above left: two plots demonstrating the effect of volatiles on the solidus curve vis-à-vis Earth's geotherm. (image credit: Wikimedia commons) Fig. 3. Above right: Graph showing different experimental P-T paths with the geotherm for comparison.

We compare our 1-atm results to high-pressure shockless ramp compression experiments performed on the Thor pulsed power accelerator at the Dynamic Integrated Compression Experimental Facility at Sandia National Laboratories. These experiments follow a quasi-isentropic curve, which mimics the adiabatic mantle geotherm.

3. Insights from 1-atm elastic and structural studies



- Bulk modulus of OH-, F- and Cl-doped silicas decreases with increasing dopant concentration. (Figure A)
- The change in Vp with pressure between dry and hydrated silica is nearly identical, while the offset is most likely due to differences in starting density. (Figure B)

- Shear modulus of F-, Cl-doped silicas decreases with concentration, but changes very little in OH-doped silicas up to 0.5 mol%. (Figure C)
- Shear (V_S) wave speeds of OH-doped silicas show similar trends to shear moduli. (Figure D)

Fig. 4. A) Bulk modulus of several doped silicas. B) Shear modulus, with inset plot to the right showing a closer look at shear moduli for OH-doped silicas at lower concentrations. Shear moduli measured from GHz interferometry is represented by hollow blue circles. C) V_P (longitudinal) wave speeds. D) V_S (shear) wave speeds. E) Compression curve of several OH-containing silicas.[6] Other data: Squares – OH-containing rhyolite from Liu et al. (2023) (7); Diamonds – CO_2-doped silica from Seifert et al. (2011) (8); Circles – OH-containing haplogranite glass from Malfait et al. (2011) (9); Pentagons – silica glass from Weigel et al. (2019) (10); Sideways triangles – Na-doped silica from Jabraoui et al. (2016) (11)

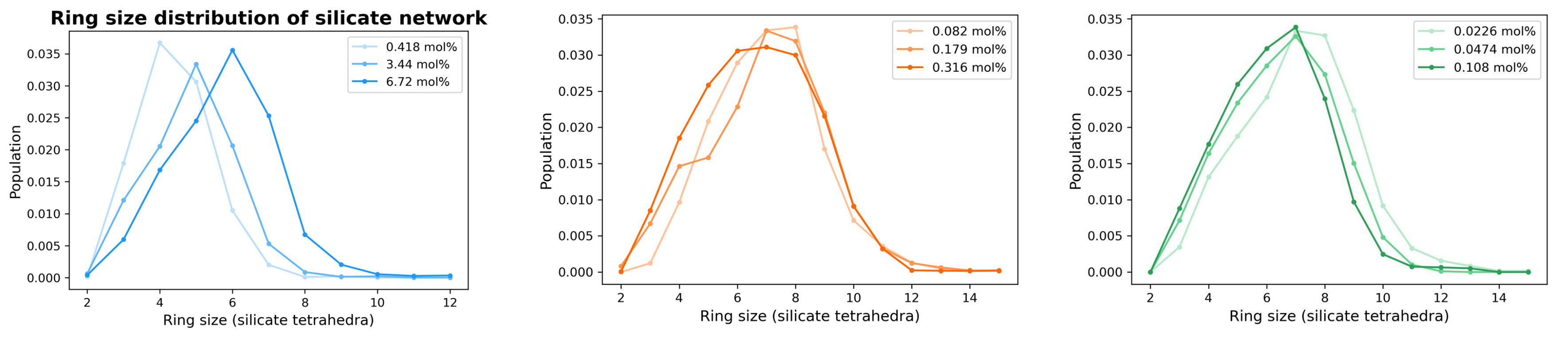


Fig. 5. Silicate tetrahedra ring size distribution across doped silicas. Left: OH-doped silicas; Center: F-doped silicas; Right: Cl-doped silicas.

Molecular dynamics simulations

- With increasing concentration, OH-doped silicas show increases in larger ring populations, whereas F- and Cl-doped silicas show increases in smaller ring populations.

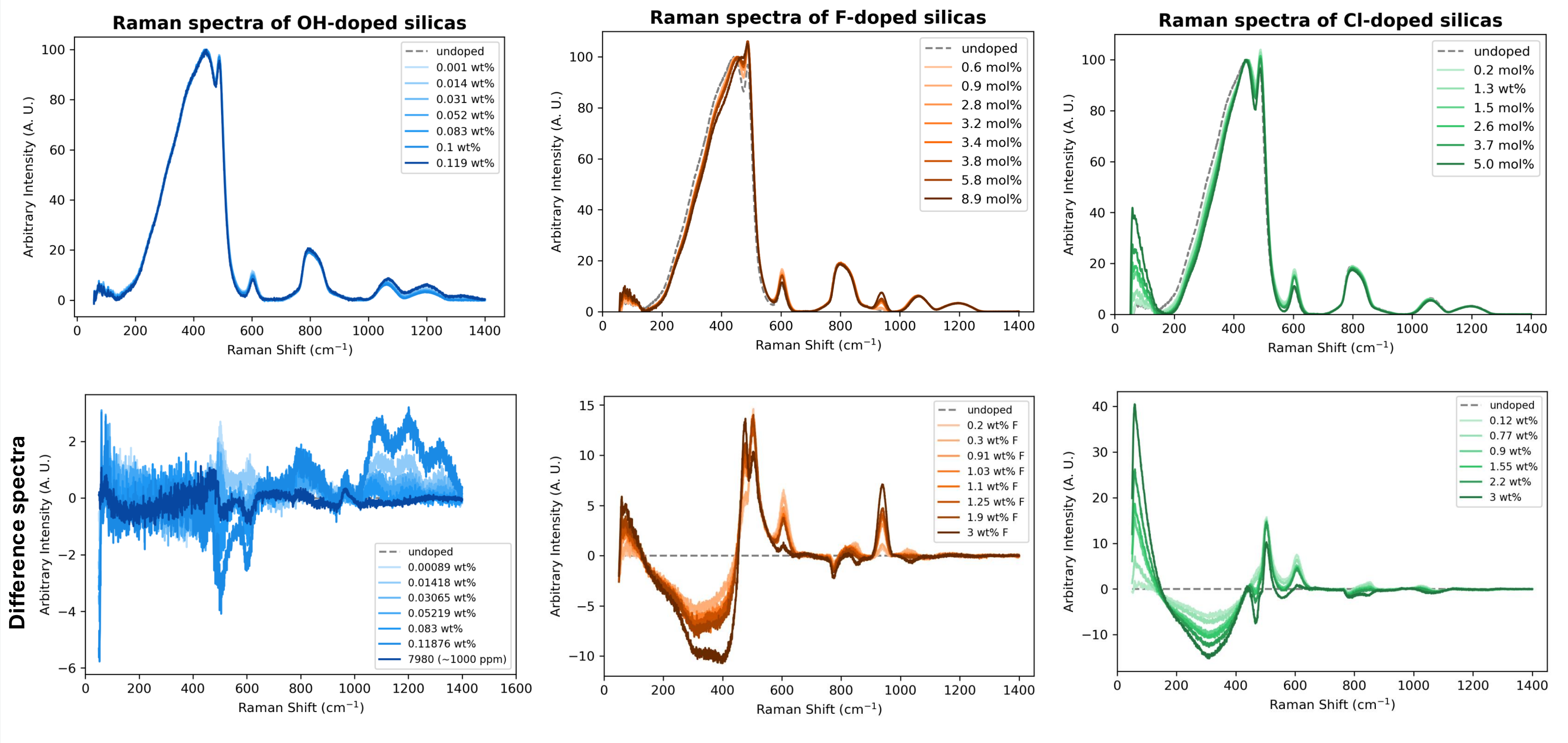


Fig. 6. Raman difference spectra plots of several doped silicas: Left: OH-doped silicas; Center: F-doped silicas; Right: Cl-doped silicas. The saturation of the hue indicates its relative concentration; lightest colors indicate smaller volatile concentrations, and darker colors indicate larger volatile concentration. Dotted line indicates the difference spectra of undoped (pure) silica.

Raman spectra

- Hydroxyl (blue) shows little change between 200-600 cm^{-1}, which includes peaks that correspond to 5+, 4, and 3-membered rings.
- Fluorine (orange) shows decreasing intensity in peaks attributed to larger (5+) membered rings, as does chlorine (green).
- This difference in structural response to increasing dopant concentration is consistent with MD simulations (above). Together, they indicate that F and Cl stabilize more smaller rings and fewer larger rings, but OH has the opposite effect, stabilizing more larger rings.

4. Conclusions

Key takeaways

- Between OH-, F-, and Cl-doped silicas, compressive wave speeds and bulk modulus show decreases in bulk modulus with respect to increasing dopant concentration and pressure, with smaller ions (OH, F) causing larger decreases and larger ions (Cl) having diminished effects on the bulk modulus.
- Shear modulus and shear wave speeds show little to no dependence on OH content up to 0.42 mol%. However, F- and Cl-doped silicas show stronger dependence on volatile content that can be attributed to their incorporation and effects on the silicate network; addition of F and Cl cause decreases in larger ring sizes (5+) and increases in smaller ring sizes (3-4 members).
- Stiffness increases as ring sizes increase in amorphous silicates with stiffness at high pressures. Although we see the same anomalous softening behavior from 0-2.5 GPa in both pure and 1000 ppm OH silica up through 9 GPa, we hypothesize that the opening of ring structures by OH incorporation allows networks to stiffen following irreversible densification. Conversely, we hypothesize that F- and Cl-doped silicas will not exhibit the same stiffening behavior as OH-doped silicas with increasing pressure.

Future directions

- Since F and Cl have different effects on the silicate network from OH, it would be interesting to perform shockless ramp compression experiments to investigate high-pressure behavior.
- To better understand the effect of Cl on the silicate network, we will perform magic-angle spinning nuclear magnetic resonance spectroscopy on Cl-containing silicas.