

NEW RAMAN SPECTROSCOPIC OBSERVATIONS OF HYDRATED TRANSITION ZONE SPINEL/SPINELLOID PHASES

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Wadsleyite [β -(Mg,Fe)₂SiO₄, spinelloid III] and ringwoodite [γ -(Mg,Fe)₂SiO₄, spinel], the nominally anhydrous high pressure polymorphs of olivine are thought to be the most abundant minerals in the Earth's mantle transition zone between 410 and 660 km depth. They can incorporate respectively up to 3.3 and 2.5 wt% H₂O in form of OH into their crystal structure. While the Fe-content of wadsleyite and ringwoodite with an assumed natural amount of ~11% Fe influences transition zone properties (e.g., elasticity) globally the OH content may be more important within and adjacent to cool subducting slabs. Wadsleyite II (spinelloid IV) is a hydrous, Fe-bearing silicate phase that might occur between the stability regions of wadsleyite and ringwoodite.

We present Raman spectra from ~50 to 4000 cm⁻¹ of high-quality single-crystals of hydrous Mg-endmember and hydrous Fe-bearing wadsleyite, wadsleyite II, and ringwoodite. The transition zone phases were synthesized in a multi-anvil apparatus at the Bayerische Geoinstitut, Germany and high-pressure Raman spectra were obtained up to 60 GPa using a diamond-anvil cell and solid helium as pressure-transmitting medium.

The Raman spectra of wadsleyite and wadsleyite II are similar as would be expected from their closely related structures. In the OH stretching region the spectrum of wadsleyite II appears more complex than the spectrum of wadsleyite consisting of at least 6 modes. The most interesting observation of the high-pressure study of wadsleyite II is the appearance of Raman bands (not detectable/resolvable at 1 bar) in the region 450-650 cm⁻¹ above ~35 GPa. For ringwoodite, the Raman spectrum of Fo₁₀₀ composition shows all five characteristic spinel modes whereas the hydrous Fo₈₉ composition exhibits additional modes in the range 709-939 and 100-250 cm⁻¹. In both phases the SiO₄ stretching modes shift continuously up to 60 GPa; additional bands emerge in the region 550-580 cm⁻¹ near 40 GPa in the Fo₈₉ sample. Comparisons of Raman spectra of hydrated transition zone phases with varying iron content reveal that pure protonation has only a minor effect on the lattice dynamics while coupled iron and proton substitution leads to additional levels of transformation complexity reflected in reversible, pressure-induced modifications in the Raman spectra of hydrous Fo₈₉ ringwoodite and wadsleyite II. The present observations could provide additional insight into the existence of new protonated, iron-bearing, unquenchable phases in cool, wet regions near subducted material.