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Ab initio thermodynamics and seismic properties of $MgSiO_3$ polymorphs at mantle transition zone conditions: the geodynamic role of non-olivine phases

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$MgSiO_3$ polymorphs with the garnet, pyroxene and ilmenite structure play a key role in controlling phase equilibria and seismic velocity gradients in the mantle transition zone (440-660 km). Despite the relative abundance of structural and thermoelastic informations, thermodynamic data are still poorly constrained and their extrapolation at high pressure and temperature conditions is affected by large uncertainties.

In this work, ab initio calculations of the thermodynamic properties of $MgSiO_3$ polymorphs stable at MTZ conditions (tetragonal majorite, Mj; akimotoite, Ak; HP-clinoenstatite, HPCEn) have been carried out with the hybrid B3LYP density functional method. The static and vibrational features of these minerals (equation of state, elastic constants, seismic velocities and anisotropy, IR and Raman spectra, mode Grüneisen parameters) have been fully characterized in a broad range of P-T conditions. The vibrational density of states (vDOS) have been reproduced in the framework of quasi-harmonic approximation through a full phonon dispersion calculation or, alternatively, a modified Kieffer's model splitting the acoustic and optic modes contribution to the thermodynamic functions.

The calculated heat capacities are in good agreement with the relatively few calorimetric investigations made so far on these minerals in the low- to medium-T range. However, physical unsoundness may affect the high-temperature extrapolation of calorimetric results, so that the use in phase equilibria calculation deserves great care. The calculated Gibbs free energies allow to define phase transition boundaries in the $MgSiO_3$ phase diagram and locate the majorite-akimotite-perovskite triple point at P = 21.09 $\pm$ 0.13 GPa and T = 2247 $\pm$ 31 K. The effect of partial structural disorder in majorite, assessed via an interchange enthalpy (ΔHint = 15 kJ/mol) and configurational entropy [Sconf = 1.9 J/(mol$\times$K)] contribution, must be taken into account to accurately reproduce the Mj-Ak-Pv triple point. The predicted Clapeyron slopes of the phase boundaries Mj-Pv, Mj-Ak, Ak-Pv and HPCEn-Mj turn out to be 2.2, 8.3, -4.0 and -3.6 MPa/K, respectively, in good agreement with experimental observations and thermodynamic optimizations as well. The geophysical implications concerning the role of non-olivine mineral phases in mantle dynamics, deep seismic discontinuities, density change and slab stagnation at 660 km depth are briefly outlined and discussed.