# Probing the role of $MgSiO_3$ polymorphs in deep mantle processes

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This PhD thesis presents a first-principles theoretical study, based on state-of-the-art hybrid DFT calculations, on the thermodynamics and phase stability of magnesium silicates that play a relevant role in determining the mineralogical composition and physico-chemical properties of the Earth's mantle: the polymorphs of $MgSiO_3$, in particular the $MgSiO_3$ pyroxenes. Such minerals display a large stability field that spans the shallower portions of the Earth's mantle, down to the mantle transition zone. In fact, pyroxenes make up as much as 30 vol% of the Earth's upper mantle (Irifune & Tsuchiya, 2007; Frost, 2008) (Fig. 1) and are involved in several geochemical and geophyisical processes that take place in the interior of our planet, such as partial melting and mineralogical phase transitions determining global seismic discontinuities in the mantle. Despite the geochemical, geophysical, and petrological importance of pyroxenes in terrestrial and extraterrestrial bodies, their thermodynamic and thermophysical properties are still affected by large uncertainties, which are poorly defined or even completely lacking, particularly for the high-pressure and high-temperature polymorphs. This hinders the possibility not only to obtain a clearer picture of their phase stability, but also to fully understand their rheological behaviour at mantle conditions, preventing the interpretation of global-scale processes in the Earth.

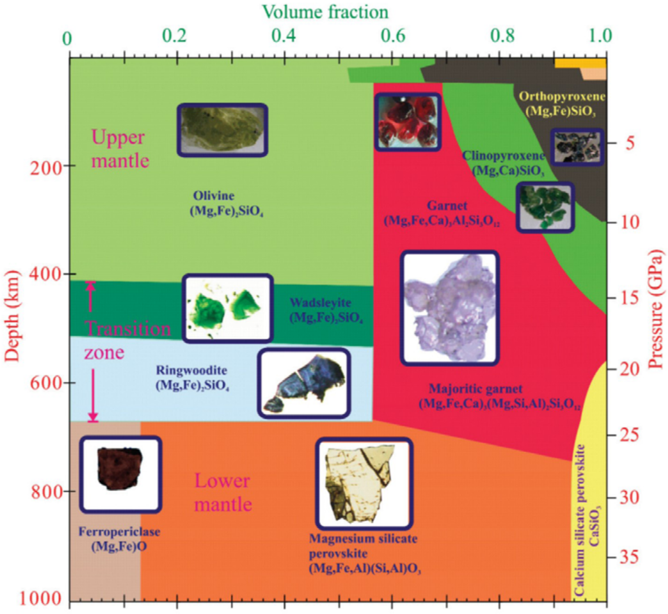

*Figure 1 Mineral volume fractions for the top 1000 km of a pyrolitic mantle. Stability fields of pyroxene phases (ortho- and clino-pyroxene) are represented in dark and light green on the top right of this diagram (after Ringwood, 1991; figure taken from Frost, 2008).*

The thermodynamic stability of the different pyroxene polymorphs depends upon pressure (*P*), temperature (*T*), and chemical composition (*X*). Pyroxenes with $MgSiO_3$ composition are known to exist in at least five different structures and undergo structural phase transitions with increasing *P*-*T* conditions (Fig. 2).

At low *T* and *P*, monoclinic low-clinoenstatite with space group $P2_1/c$ is the stable phase. A displacive phase transition occurs at high pressure (*i.e.*, P > 6-7 GPa), resulting in high-pressure clinoenstatite with space group *C2/c* (Angel et al., 1992). Orthoenstatite (*Pbca*) occurs at high *T* and pressures up to about 7 GPa, whereas protoenstatite (*Pbcn*) and high-*T* clinoenstatite (*C2/c*) have small stability fields at high *T* and low *P* according to current phase diagrams in the literature (*e.g.*, Gasparik, 2014). The polymorphism and stability relations of magnesium pyroxene phases are thus a masterpiece of complexity. This is further complicated by the fact that several additional pyroxene phases have been suggested to exist in the Earth's mantle (Thompson & Downs, 2003), some of which may be preserved as metastable phases.

Moreover, stable and metastable pyroxenes are strongly involved in the dynamics of subducting slabs. In fact, the presence of metastable pyroxenes in subducting slabs directly affects the density of the downgoing plate, modifying its buoyancy and favouring slab stagnation at the mantle transition zone (van Mierlo et al., 2013; Agrusta et al., 2014).

This study focused on the theoretical simulation of thermodynamic and thermoelastic properties of $MgSiO_3$ pyroxenes [namely, low-pressure clinoenstatite (LP-

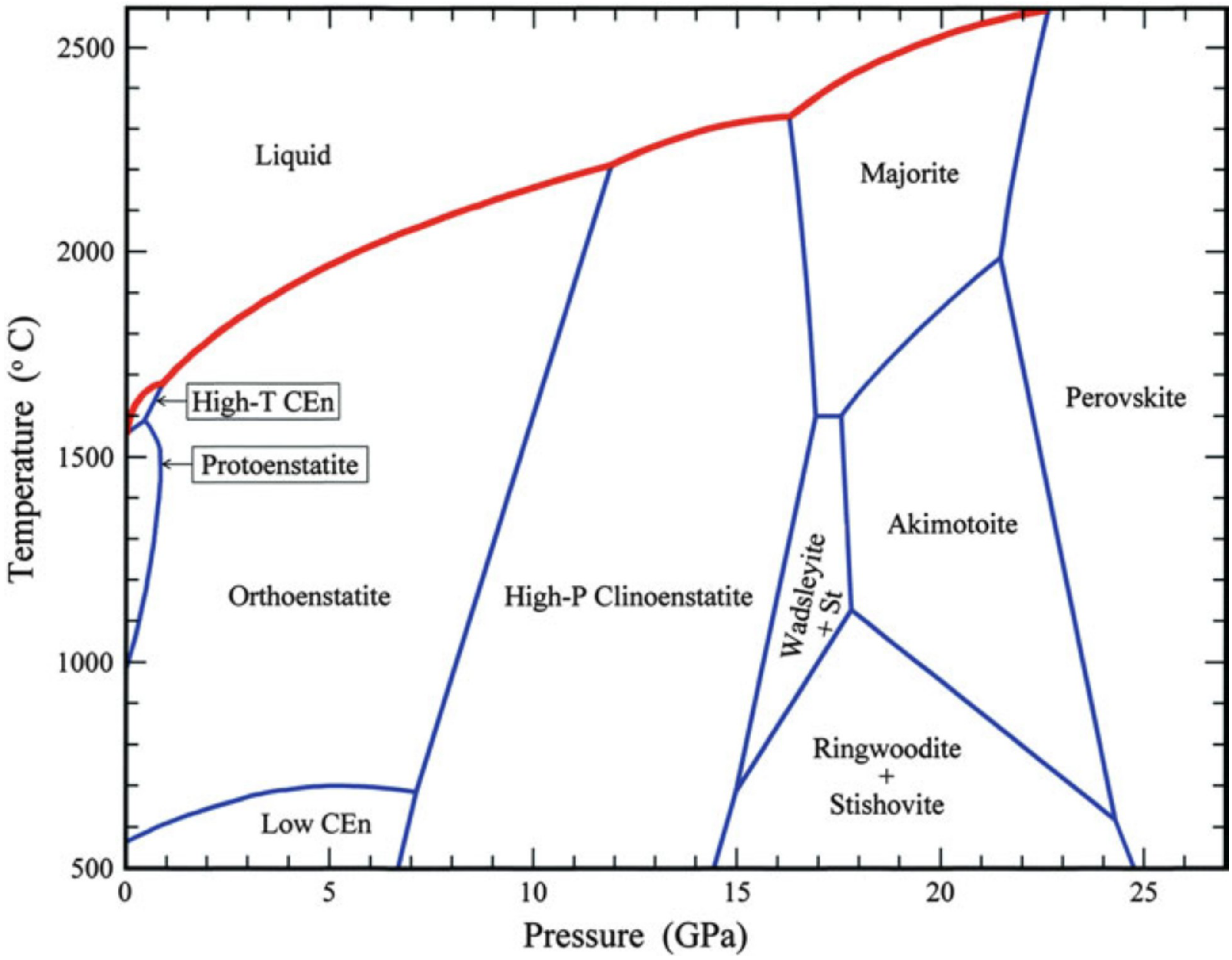

***Figure 2*** *Temperature – pressure phase diagram for the $MgSiO_3$ system (according to Gasparik, 2014).*

CEn), orthoenstatite (OEn), protoenstatite (PEn), high-temperature clinoenstatite (HT-CEn), high-pressure clinoenstatite (HP-CEn)], performed by *ab initio* DFT calculations up to conditions compatible with their stability in the deep mantle. The *ab initio* thermodynamic data computed in this work represent the first attempt to build up a complete dataset of both physically- and internally-consistent properties for $MgSiO_3$ pyroxenes in a broad range a *P-T* conditions. This first-principles dataset includes all the main thermodynamic properties necessary for the calculation of the Gibbs free energy at high-pressure and high-temperature (*i.e.*, enthalpy, entropy, heat capacity, volume thermal expansion, bulk modulus and its pressure and temperature derivatives elastic moduli and seismic properties), hence to investigate phase stability relations of pyroxenes from subsolidus to liquidus conditions. Gibbs free energy minimisation then provides information on the relative stability of $MgSiO_3$ pyroxenes, allowing the calculation of *P-T-X* phase diagrams. Moreover, thermoelastic properties such as the thermal equation of state and volume thermal expansion are fundamental to predict volume and density changes at mantle conditions, which in turn allows to constrain the rheological role of pyroxenes in mantle processes. Computed data also include the elastic and seismic properties (*i.e.*, the full elastic constant tensor and longitudinal and transverse wave velocities, $V_P$ and $V_S$), that can be used to infer seismic velocity jumps and seismic impedance contrasts (*i.e.*, $\Delta\rho V_{P,S}$), allowing for a direct comparison with seismological observations on mid-mantle global seismic discontinuities and providing thermodynamic constraints on their origin. In particular, the origin of the so-called X-discontinuity in the mantle, between 270 and 330 km depths, has been tentatively interpreted in the literature as closely related to mineralogical phase transitions that include the OEn to HP-CEn phase transformation as a viable candidate (Woodland, 1998).

The main results, implications and open issues extracted from this Thesis are briefly summarized and described here.

*Ab initio* hybrid DFT-QHA calculations at the B3LYP level of theory improve the accuracy of the thermodynamic properties of high-pressure magnesium silicates with respect to less sophisticated LDA and GGA

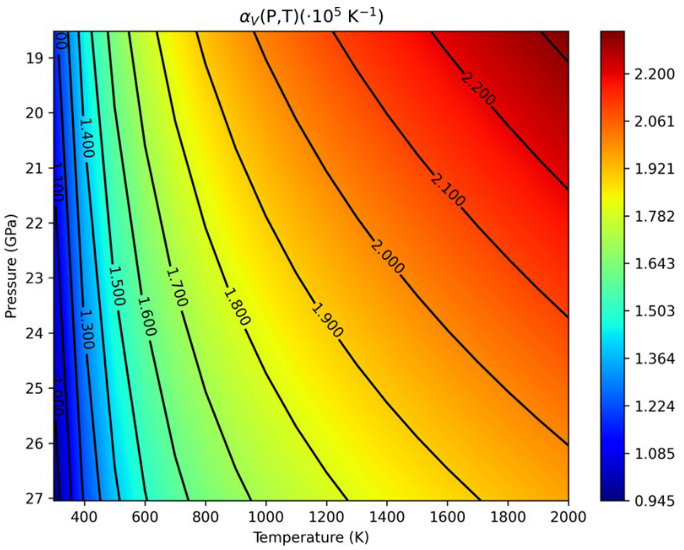

***Figure 3*** *Contour plot of ab initio volume thermal expansivity of $Mg_2SiO_4$ ringwoodite at mantle transition zone conditions.*

density functionals. In order to test the performance of B3LYP, a first stage in the development of this PhD project has been dedicated to the theoretical simulation of thermodynamic and thermoelastic properties of $\gamma$-$Mg_2SiO_4$ ringwoodite, using this mineral as a sort of beta test for calculations on more complex crystal structures. The obtained results not only show that *ab initio* B3LYP calculations are able to accurately predict thermodynamic and thermoelastic properties of this fundamental mineral phase up to lowermost mantle transition zone conditions, but clearly demonstrate that empirical extrapolation of thermoelastic data to deep mantle conditions should be taken with care to avoid inaccurate or spurious predictions in phase equilibrium modelling (*cf.*, Belmonte et al., 2022). The most relevant result that came out from this research is represented by the definition of a single (and quite simple) polynomial function that accurately predicts the values of ringwoodite volume thermal expansivity directly at simultaneous high-pressure and high-temperature conditions compatible with the Earth's mantle transition zone (Fig. 3).

*Ab initio* B3LYP thermodynamic properties of all the pyroxene polymorphs of $MgSiO_3$ (*i.e.*, PEn, OEn, LP-CEn, HP-CEn and HT-CEn) allow to obtain the full phase diagram of $MgSiO_3$, hence providing original insights on the thermodynamic behaviour of such phases at *P-T* conditions compatible with their stability in the Earth's mantle. Despite the lack of experimental results, B3LYP calculations compare favourably with the few experiments available in the literature. *Ab initio* calculations performed in this work help thus to fill the gap in terms of thermodynamic information about some of these unquenchable phases, such as HT-CEn, HP-CEn and PEn. In fact the thermodynamic properties of most of the investigated phases have been determined for the very first time. For instance, the first comprehensive ab initio thermodynamic dataset for high-temperature clinoenstatite (HT-CEn) has been defined in this work, considering that no experimental data exist on this phase and the only information currently available comes from thermodynamic assessments. Thermoelastic properties of protoenstatite (PEn), like volume thermal expansivity and thermal equation of state parameters, were previously almost unknown due to experimental difficulties in the synthesis and characterization of this phase. As a relevant example of the performances of *ab initio* calculations performed in this work, the theoretical isobaric heat capacity of PEn is reported as compared with the only calorimetric data available (Thieblot et al., 1999) and with the polynomial function assessed by Berman (1988) (Fig. 4).

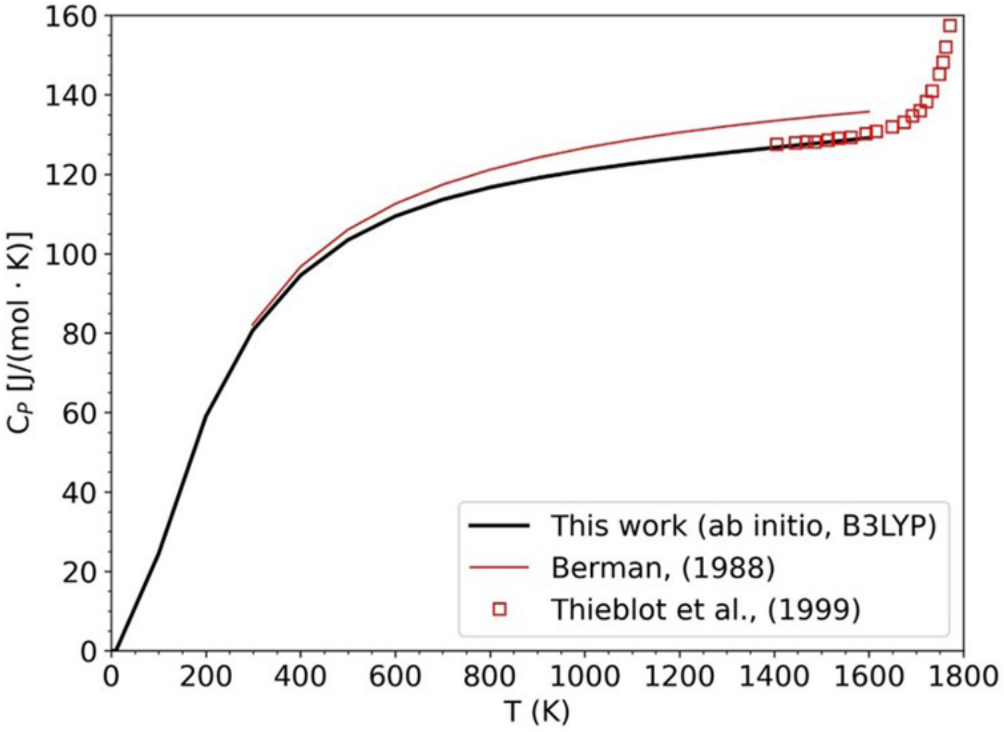

***Figure 4*** *Ab initio isobaric heat capacity ($C_P$) for PEn as compared with experimental results and thermodynamic assessment.*

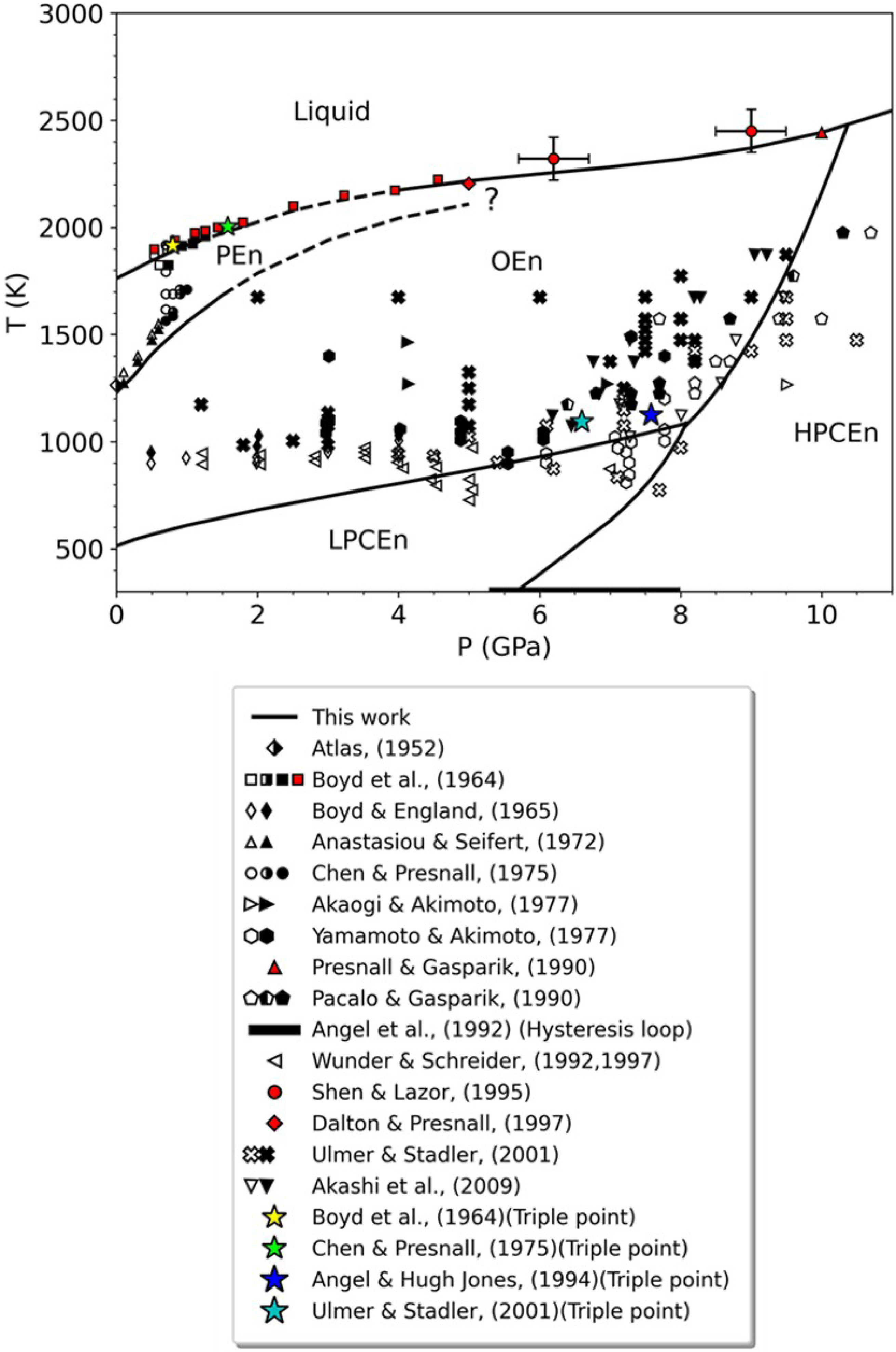

***Figure 5*** *Ab initio phase diagram for the* $MgSiO_3$ *system, as compared with literature data. White markers = PEn/LPCEn/HPCEn, black markers = OEn, red markers = liquid.*

All the pyroxene phase transitions occurring in the $MgSiO_3$ system have been investigated and calculated by employing the first-principles thermodynamic dataset obtained in this work. The following univariant equilibria have been determined: $MgSiO_3$ (low-pressure clinoenstatite) = $MgSiO_3$ (orthoenstatite), $MgSiO_3$ (orthoenstatite) = $MgSiO_3$ (protoenstatite), $MgSiO_3$ (protoenstatite) = $MgSiO_3$ (high-temperature clinoenstatite), $MgSiO_3$ (orthoenstatite) = $MgSiO_3$ (high-pressure clinoenstatite), $MgSiO_3$ (low-pressure clinoenstatite) = $MgSiO_3$ (high-pressure clinoenstatite). The investigation of these phase equilibria allowed the obtaining of novel information on the stability of pyroxenes at mantle conditions (Fig. 5).

Moreover, *ab initio* Clapeyron slopes and density contrasts calculated at high temperature and pressure conditions provide physical constraints to numerical modelling of subduction processes. The computational study shows how some of the phase equilibria involving pyroxenes are extremely sensitive to small variations in the Gibbs free energy, thus difficult to reproduce even employing modern DFT-QHA calculations. In particular, some uncertainties still remain in some portions of the $MgSiO_3$ phase diagram, such as the location of the LP-CEn - OEn phase transition boundary at ambient pressure and that of the triple point between PEn, OEn and liquid. These uncertainties seem to be related to a limitation of the DFT-QHA theory in accurately predicting

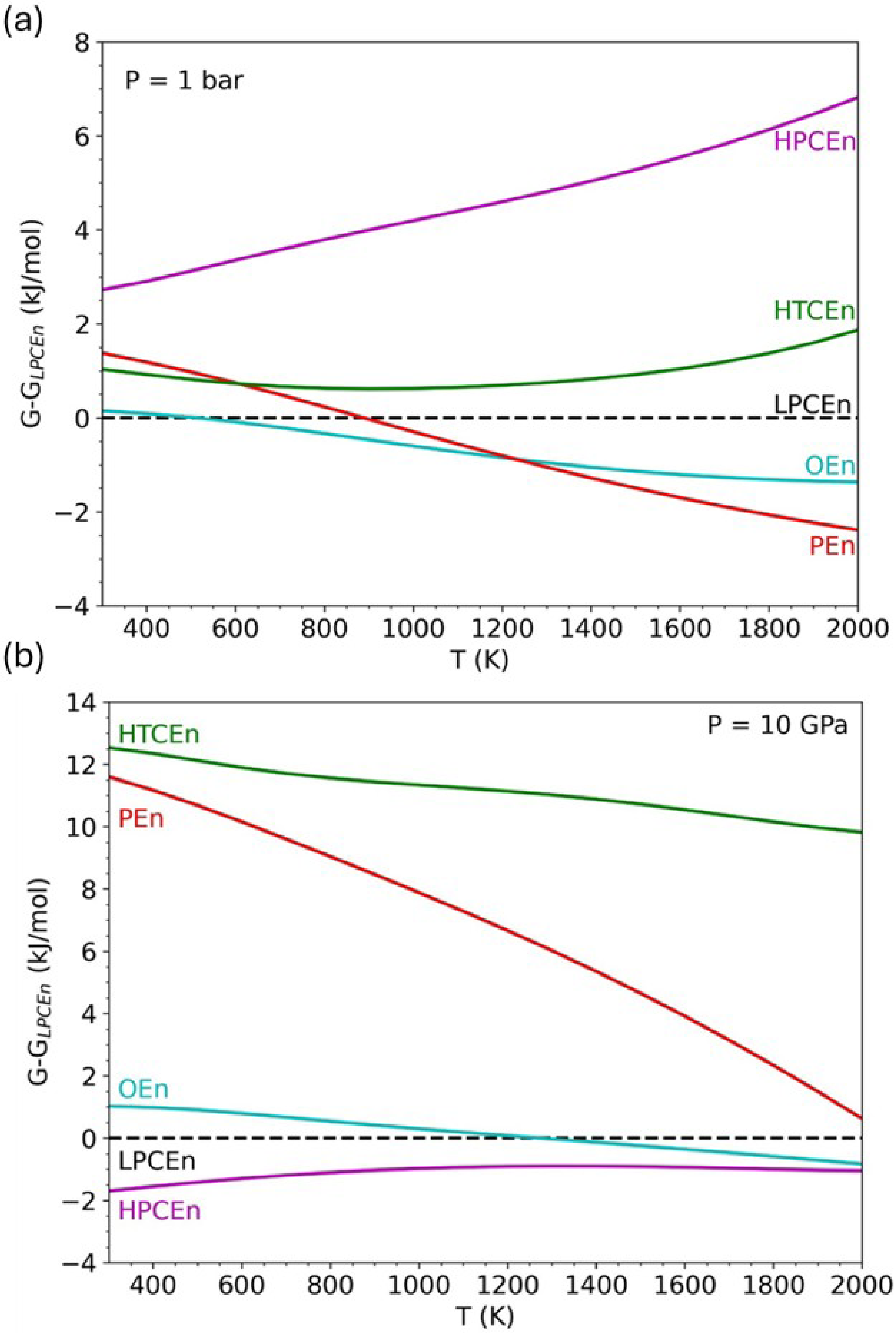

***Figure 6 a)*** *Ab initio Gibbs free energy vs. temperature curves for* $MgSiO_3$ *pyroxenes at 1 bar and* ***b)*** *10 GPa. HPCEn = high-pressure clinoenstatite, HTCEn = high-temperature clinoenstatite, LPCEn = low-pressure clinoenstatite, OEn = orthoenstatite, PEn = protoenstatite. The Gibbs free energy of all polymorphs is normalised to that of the low-pressure clinoenstatite (i.e., the stable polymorph at T = 0 K and P = 0).*

the thermodynamic properties of orthoenstatite (OEn), which can be explained by the presence of relevant anharmonic effects in this phase (Zucker & Shim, 2009).

High-temperature clinoenstatite (HT-CEn) turns out to be unstable in the whole *T*(-*P*) range according to our investigation (Fig. 6). This result strongly questions the role of this mineral as a stable phase on the liquidus of the $MgSiO_3$ system at low pressures, as claimed by some Authors in the literature on the basis of unphysical thermodynamic data (*e.g.*, Shi et al., 1996; Gasparik, 2014).

The predicted melting curve of the $MgSiO_3$ system, as determined by assessing thermodynamic properties for the liquid phase with a polymeric model that is thermodynamically-consistent with ab initio data for the solid phases, is in excellent agreement with experimental results in the pressure range 0 -10 GPa (Boyd et al., 1964; Presnall & Gasparik, 1990; Dalton & Presnall, 1997). Subsolidus and melting phase relations of pyroxenes in the theoretical phase diagram of $MgSiO_3$ are thus fully consistent with each other.

Finally, predicted *P-T* stability fields of orthoenstatite and high-pressure clinoenstatite in the $MgSiO_3$ phase diagram are compatible with the observed depth range of the seismic X-discontinuity in the mantle (*i.e.*, 250-350 km depths). Nevertheless, the theoretical seismic velocity jumps and impedance contrasts calculated for OEn and HP-CEn at mantle conditions turn out to be much higher than those inferred by global seismological studies, thus disregarding the OEn to HP-CEn phase transition as the only responsible for the origin of the X-discontinuity.

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