

AB INITIO THERMODYNAMICS OF DEEP MANTLE MINERALS: THE SYSTEM MgO-SiO₂

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ABSTRACT

First principles theory plays a key role in the prediction and modelling of thermodynamic properties of Earth's materials at high pressure and temperature conditions (Wentzcovitch & Stixrude, 2010). *Ab initio* thermodynamics, allowing the computation of the free energy and thermodynamic potentials of crystalline phases by means of a combined approach of quantum- and statistical mechanics, provide an alternative and self-consistent way to check the confidence of experimental phase boundaries, calorimetric measurements and thermodynamic optimizations.

In this work, *ab initio* modelling of the thermodynamic and thermoelastic properties of deep mantle minerals in the MgO-SiO₂ system have been carried out with the hybrid B3LYP density functional method (Becke, 1993) as implemented in the CRYSTAL quantum-mechanical code (Dovesi *et al.*, 2009). The minerals investigated in this study are periclase (MgO), stishovite (SiO₂), the Mg₂SiO₄ polymorphs (forsterite, Mg-wadsleyite and Mg-ringwoodite), phase anhydrous B (Mg₁₄Si₅O₂₄) and the high-pressure polymorphs of MgSiO₃ (*C2/c* clinoenstatite, Mg-akimotoite with the ilmenite structure, tetragonal majorite, perovskite and post-perovskite). The vibrational density of state (vDOS) of these minerals has been reproduced in the framework of quasi-harmonic approximation through full phonon dispersion calculations or, alternatively, a modified Kieffer's model (Kieffer, 1979) splitting the acoustic and optic modes contribution to the thermodynamic functions (Ottonello *et al.*, 2010a). Both methods seem to reproduce well the vDOS, allowing an accurate determination of the equation of state parameters and thermodynamic properties as well (Ottonello *et al.*, 2010a, 2010b; Belmonte *et al.*, 2013). The calculated values show a good agreement with experimental results and concur to define an internally-consistent thermodynamic dataset suited for the computation of phase equilibria between pure phases at very high pressures and temperatures. The results obtained for phase equilibria of geophysical interest are discussed, along with some possible petrological implications concerning phase relations and seismic discontinuities in the Earth's mantle.

VIBRATIONAL SPECTRA AT AMBIENT AND NON-AMBIENT CONDITIONS: MAJORITE AS AN EXAMPLE

The experimental characterization of the vibrational properties of deep Earth's minerals is still challenging, mainly due to technical problems affecting their high-pressure synthesis in the laboratory. Mg-majorite is a masterpiece of complexity as to this regard. Pervasive merohedral or pseudomerohedral twinning is always present in the tetragonal end-member of the majorite-pyrope series (Mg₄Si₄O₁₂ or, for simplicity, MgSiO₃), as outlined by TEM studies (Angel *et al.*, 1989; Hatch & Ghose, 1989; Wang *et al.*, 1993). The finding of single-crystals for structural refinement is thus prevented and the IR- and Raman-spectra currently available for this phase were obtained exclusively on polycrystalline samples (McMillan *et al.*, 1989; Rauch *et al.*, 1996; Manghnani *et al.*, 1998). Moreover, the relative mode assignment in the vibrational spectra is not trivial owing to the lowering of symmetry with respect to cubic garnets (*Ia-3d* → *I4_{1/a}* space group). Finally, structural disorder may further affect and complicate the vibrational features. *Ab initio* calculations thus represent a formidable tool to get new insights into the vibrational properties and the ensuing thermodynamics of majorite. This ability is further supported by the fact that hybrid functionals like B3LYP proved to provide excellent results (often more accurate than those of pure LDA or GGA functionals) as concerning the

reproduction of the vibrational spectra of condensed phases at ambient and non-ambient conditions (see for instance Demichelis *et al.*, 2010; Töbrens & Kahlenberg, 2011). The *ab initio* IR spectrum of MgSiO₃ majorite, compared to that of pyrope garnet, is shown in Fig. 1; as far as I know, this is the first single-crystal IR spectrum produced so far on this Mg end-member phase.

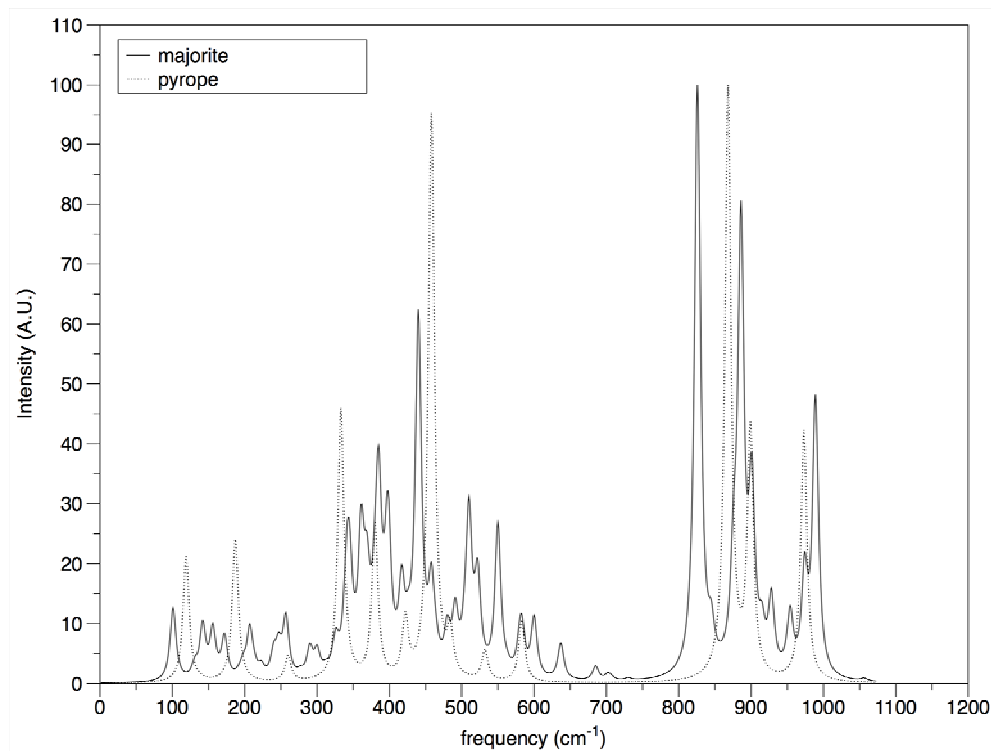


Fig. 1 - *Ab initio* IR spectra of MgSiO₃ majorite (solid line) and Mg₃Al₂Si₃O₁₂ pyrope (dotted line), calculated at B3LYP level of theory.

P-V-T THERMAL EQUATION OF STATE: MIE-GRÜNEISEN APPROACH

A central problem which has to be tackled by thermodynamic modelling of the Earth's deep interiors is the definition of the thermal equation of state of minerals, namely a formalism providing a reliable description of their P-V-T relations.

It turns out that the most widespread isothermal equations of state (like the ones derived from finite strain theory, viz. the Murnaghan and the Birch-Murnaghan EoS) can lead to physical unsoundness in material properties (negative thermal expansivity, hence entropy increase with pressure) if they are extended to a polythermal regime without a proper parameterization of thermal effects (Jacobs & Oonk, 2000; Helffrich & Connolly, 2009).

First principles theory overcomes this problem adopting a Mie-Grüneisen approach to split the static and vibrational contributions to pressure, then calculating the former by structure-energy properties and the latter from lattice vibrations.

Fig. 2 shows the results obtained for the thermal equation of state of periclase (MgO) at very HP-HT conditions: by comparing first principles calculations with shock-wave compressions, it turns out that a Mie-Grüneisen equation of state is able to reproduce shock-wave data well within their experimental uncertainty (note from the pressure scale represented on the x axis of Fig. 2 that we are in the Mbar pressure regime, namely at pressures greater than 100 GPa and temperatures between 3000 K and 4000 K).

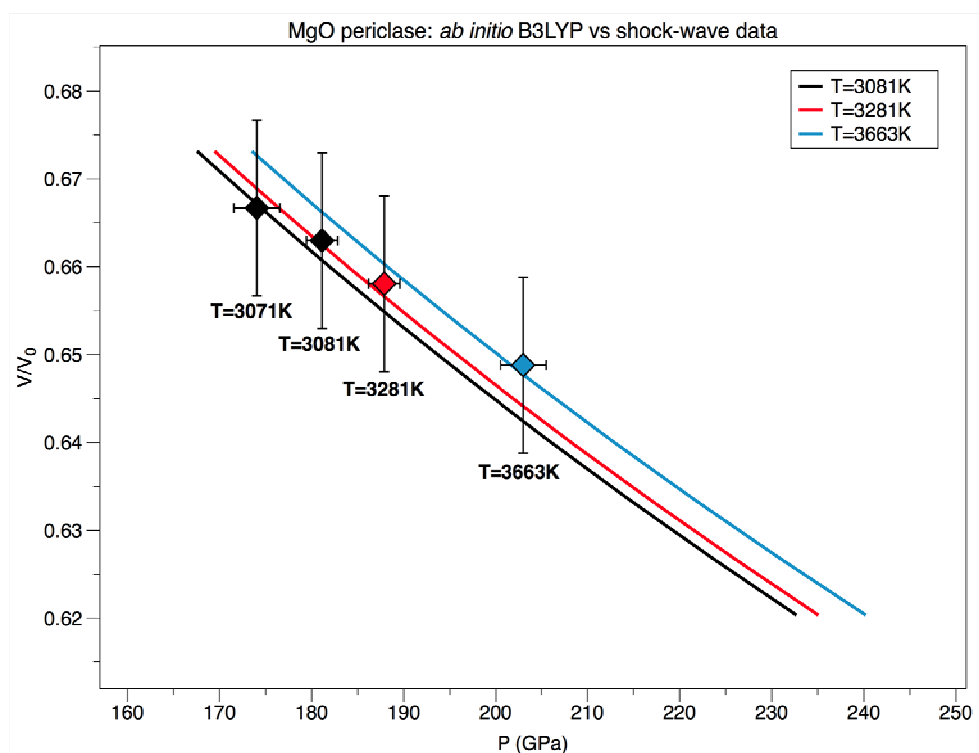


Fig. 2 - *Ab initio* B3LYP relative compression (V/V_0) of MgO periclase, calculated at three selected HT conditions (*i.e.*, $T = 3081$ K, 3281 K and 3663 K) and $P > 170$ GPa (black, red and blue curves in the diagram, respectively). The results of this work are compared with shock-wave data obtained at the same conditions (black, red and blue diamonds) by Svendsen & Ahrens (1987).

THERMODYNAMIC PROPERTIES AND PHASE EQUILIBRIA CALCULATION AT HIGH PRESSURE AND TEMPERATURE CONDITIONS

The thermodynamic data calculated *ab initio* for dense magnesium silicates and oxides have been collected in a first principles internally-consistent dataset which allows the calculation of univariant phase equilibria among fixed-composition phases at HP-HT conditions (Table 1). The dataset lists the fundamental thermodynamic ingredients for a Gibbs free energy minimization [namely standard state molar volume, V_{298}^0 ; standard state entropy, S_{298}^0 ; enthalpy of formation from the elements at standard state, $H_{f,298}^0$; isothermal bulk modulus, K_0 , along with its pressure and temperature derivatives, $K'_0 = (dK/dP)_T$ and $(dK/dT)_P$; the polynomial coefficients of the volume thermal expansion ($\alpha_V = \alpha_0 T + \alpha_1 + \alpha_2 T^{-1} + \alpha_3 T^{-2} + \alpha_4 T^{-3}$) and isobaric heat capacity ($C_P = a + b \times T + c \times T^{-2} + d \times T^2 + e \times T^{-1/2}$)].

The *ab initio* thermodynamic and thermophysical characterization of MgSiO_3 majorite deserves great attention since experimental data are still poor and affected by large uncertainties and evident shortcomings at high pressure and temperature conditions. The heat capacity calculated for majorite in this work is in good agreement (within 1-2%) with the only calorimetric determination made so far on this end-member phase in the low- to medium-T range (Yusa *et al.*, 1993). However, the HT extrapolation of calorimetric results suffers from inaccuracy and definitively lacks of physical consistency. It turns out that the empirical polynomial function obtained by fitting the calorimetric results up to HT (adopted by the most popular thermodynamic databases; *e.g.*, Fabrichnaya *et al.*, 2004) violates the Dulong-Petit limit for C_P already at $T = 1000$ K and cannot be used with confidence in phase equilibria calculations. *Ab initio* values show a more reasonable trend up to HT attaining the Dulong-Petit limit, being so physically-consistent, besides internally-consistent. The inconsistency

of the heat capacity values of majorite at HT seems to be related to a poor definition of its thermal expansion, which turns out to be severely underestimated at those conditions. The main reason for this anomalous thermal expansion may be related to the reproduction of phase boundaries in the MgSiO_3 phase diagram: lowering the assessed thermal expansivity of majorite by 25% at high-T might allow to get the triple point majorite-perovskite-akimotoite correct in the phase diagram. Conversely, the *ab initio* thermoelastic properties calculated for majorite in this work allow a thermodynamically-consistent reproduction of the MgSiO_3 phase diagram with a reliable thermal expansion adopted for this phase. So first principles calculations could be useful to reveal possible physical inconsistencies in the thermodynamic data of minerals at HP-HT conditions.

Table 1 - *Ab initio* B3LYP thermodynamic dataset for HP-oxides and silicates in the system MgO-SiO_2 .

	Periclase MgO	Stishovite SiO_2	Forsterite $\text{Mg}_2\text{SiO}_4\text{-}\alpha$	Wadsleyite $\text{Mg}_2\text{SiO}_4\text{-}\beta$	Ringwoodite $\text{Mg}_2\text{SiO}_4\text{-}\gamma$	AnhB $\text{Mg}_{14}\text{Si}_2\text{O}_{24}$	Majorite MgSiO_3	Akimotoite MgSiO_3	HP-CEn MgSiO_3
V_{298}° (cc/mol)	11.406	14.355	44.794	41.530	40.026	258.220	29.286	27.061	31.707
S_{298}° (J/mol K)	26.0	27.8	94.1	87.3	81.7	561.2	66.606*	54.013	66.089
$\Delta_f H_{298}^\circ$ (kJ/mol)	-604.2	-841.3	-2173.0	-2140.6	-2128.2	-13195.4	-1486.1*	-1479.0	-1526.6
K_0 (GPa)	167.01	255.12	130.8	161.8	196.4	155.0	153.03	199.39	104.22
K'_0	3.95	6.588	4.001	4.415	4.322	4.14	4.82	4.54	5.86
$(dK/dT)_P$ (bar/K)	-308.0	-345.0	-174.6	-118.0	-104.1	-189.0	-237.0	-279.0	-184.0
$\alpha_0 \times 10^7$	0.2608	0.059040	0.10031	0.0	0.0	0.08628	0.1375	0.10997	0.1596
$\alpha_1 \times 10^7$	-104.7795	167.77	269.31	464.00	323.00	230.86	0.136136	82.9564	67.7796
$\alpha_2 \times 10^3$	42.9578	2.2872	5.6082	-13.8005	-7.3084	8.313	24.23995	17.9906	18.899
α_3	-17.04307	-2.1518	-2.6162	3.6196	1.3745	-4.3445	23.5629	-8.0792	-6.9718
α_4	2122.59	237.0245	243.828	-395.094	-150.406	528.465	-10.0127	1019.1	818.75
$a \times 10^{-2}$	0.44072	0.67136	1.5513	1.6139	1.5346	9.7527	1.8370	1.1254	1.0925
$b \times 10^2$	0.39563	0.89306	2.1307	2.2270	2.1405	11.177	-1.7173	1.2291	0.95260
$c \times 10^{-6}$	-1.2871	-2.2585	-4.4060	-4.1112	-4.7490	-27.102	-0.91451	-3.6255	-3.8474
$d \times 10^5$	0.12154	-0.12004	-0.07918	-0.24731	-0.30796	-0.39865	0.46114	-0.035901	0.053650
$e \times 10^{-2}$	0.92500	-0.34437	0.87536	-0.86514	1.2708	3.5226	-15.073	0.59560	1.7989

* Note: data for MgSiO_3 majorite refer to a perfectly ordered phase. Structural disorder effects on thermodynamic properties must be considered in phase equilibria calculation at HP-HT conditions, through configurational and interchange contributions to entropy and enthalpy, respectively: $\Delta S_{\text{conf}} = 1.9 \text{ J}/(\text{mol} \times \text{K})$, $\Delta H_{\text{int}} = 15 \text{ kJ}/\text{mol}$ (corresponding to a degree of cation disorder $x = 0.17$ at $T = 2093 \text{ K}$).

The *ab initio* dataset of this work has been used to calculate some of the most relevant phase diagrams for the physics of the Earth's deep interiors, like the Mg_2SiO_4 and MgSiO_3 phase diagrams. The phase transitions of MgSiO_3 and the triple point majorite-akimotoite-perovskite calculated at B3LYP level of theory are shown in Fig. 3. *Ab initio* calculations show the best agreement with the experimental results of Chudinovskikh & Boehler (2004) obtained by *in situ* XRD in LH-DAC. The calculated ΔV_0 , ΔS_0 and ΔH_0 of the reactions $\text{Mj} = \text{Pv}$, $\text{Ak} = \text{Pv}$ and $\text{Mj} = \text{Ak}$ match the calorimetric results and the thermodynamic assessments as well. B3LYP calculations locate the Mj-Ak-Pv triple point at $P = 21.09 \pm 0.13 \text{ GPa}$ and $T = 2247 \pm 31 \text{ K}$, in excellent agreement with previous experimental determinations ($P \cong 21.5 \text{ GPa}$ and $T \cong 2255 \text{ K}$ according to Gasparik, 2003; $P \cong 21 \text{ GPa}$ and $T \cong 2300 \text{ K}$ according to Chudinovskikh & Boehler, 2004). B3LYP seems to reproduce better the experimental phase boundaries than GGA (which underestimate the temperature of the triple point), whereas LDA results are severely underestimated as concerning the pressure (Yu *et al.*, 2011; Fig. 3). However, the B3LYP Clapeyron slopes are substantially equal to those calculated by LDA and GGA. Despite the outstanding

agreement between experiments and B3LYP calculations, the first results obtained for the MgSiO_3 phase diagram considering a perfectly ordered majorite were not so accurate: the temperature of the triple point was severely underestimated (by ~ 1000 K), although the pressure of the triple point and the Clapeyron slopes of the phase transitions displayed an overall agreement with the experiments. To reproduce accurately the triple point, the effect of partial structural disorder of cations among the octahedral sites of MgSiO_3 tetragonal majorite must be considered through an interchange enthalpy ($\Delta H_{\text{int}} \cong 15$ kJ/mol) and configurational entropy [$S_{\text{conf}} \cong 1.9$ J/(mol \times K)] contribution to the thermodynamic properties of a fully ordered end-member majorite. This contribution can be modelled by taking into account an interchange reaction of Mg and Si atoms among the octahedral sites of the structure and defining the equilibrium constant of this reaction process by means of the degree of disorder. According to this new calculation, it turns out that a degree of disorder of 17% at $T = 2073$ K is enough to get the Mj-Ak-Pv triple point correct, assuming that the effect of pressure on the Mg-Si disorder in garnet is negligible. This amount of structural disorder is consistent with the few experimental results available (Angel *et al.*, 1989; Phillips *et al.*, 1992). The conclusion is that the Mg-majorite actually stable at mantle transition zone conditions is a partially disordered phase, of formula $^{\text{VIII}}\text{Mg}_3^{\text{VI}}(\text{Mg}_{1-x}\text{Si}_x)^{\text{VI}}(\text{Si}_{1-x}\text{Mg}_x)^{\text{IV}}\text{Si}_3\text{O}_{12}$ with $x = 0.17$, and the effects of structural disorder on thermodynamic properties is crucial to accurately locate the Mj-Ak-Pv triple point in the MgSiO_3 phase diagram.

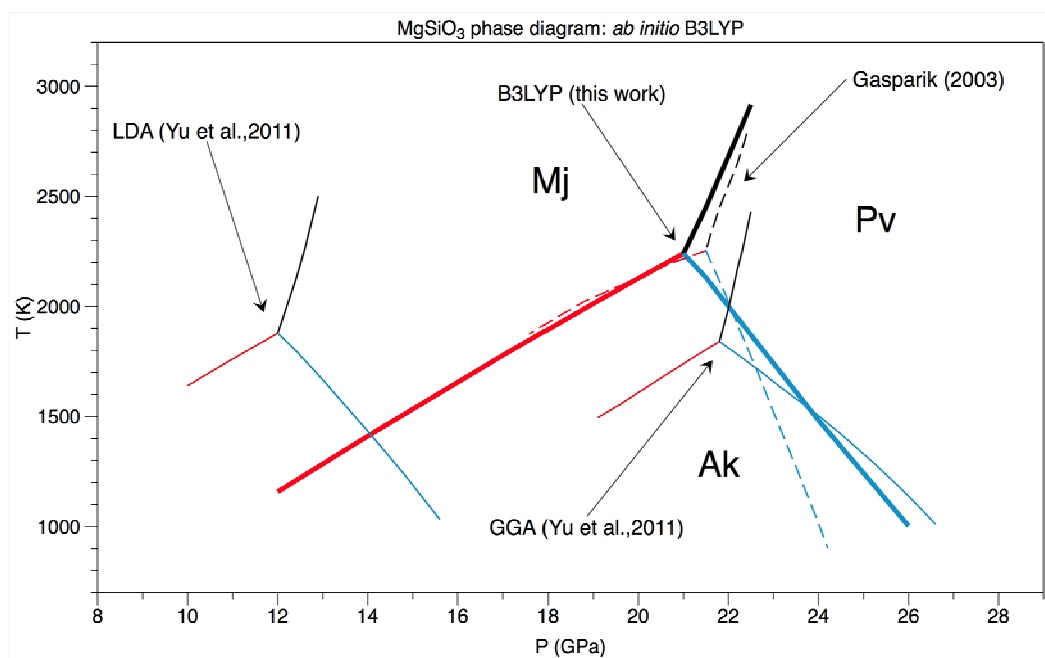


Fig. 3 - *Ab initio* B3LYP calculated phase boundaries for MgSiO_3 majorite (Mj) - akimotoite (Ak) - perovskite (Pv) transitions (black, red and blue bold lines in the figure), compared with the results of other *ab initio* theoretical simulations at LDA and GGA level of theory (Yu *et al.*, 2011; black, red and blue thin lines). In the phase diagram calculation a *partially disordered* MgSiO_3 majorite has been considered (see text). The experimental results of Gasparik (2003) are shown for comparison (black, red and blue dashed lines in the figure).

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