# How Much Do We Know About Mantle Thermochemistry?

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Although mankind has set foot on the moon, a journey to the center of the Earth remains fictional and technologically unattainable. Information about the interior of our planet comes from four main sources: (i) seismology, which is remote sensing primarily through the tracking of sound waves passing through the Earth; (ii) geodynamics, which seeks to construct global models of rheology and mass transfer; (iii) geochemistry, which infers possible compositional constraints for the Earth's interior from knowledge of elemental abundances in the solar system, meteorites, and rocks; and (iv) mineral physics—laboratory and computational simulations of matter under high pressure and temperature. Thermodynamics plays a major role in these mineral physics studies, both in the definition of the equation of state (the volume as a function of pressure and temperature) and in the understanding of phase changes (reorganization of the crystal structures of minerals) with increasing depth. It is important to make clear what we know and do not know about the thermochemistry of the mantle.

Discontinuities, or ranges of depth in which properties change sharply over a few kilometers, separate atmosphere from surface, crust from upper mantle (the Mohorovicic discontinuity or Moho), upper mantle from transition zone, transition zone from lower mantle, lower mantle from outer core, and outer core from inner core. The major discontinuities in the mantle have been long associated with phase transitions (*1*). The 400-km discontinuity is probably related to the transformation of the ferromagnesian silicate olivine to the spinel structure, with an intervening intermediate spinelloid or beta phase. The 660-km discontinuity is probably dominated by the transformation of a $(Mg,Fe)_2SiO_4$ spinel phase to a $(Mg,Fe)SiO_3$ perovskite phase (with much less iron than the spinel) with minor amounts of an iron rich (Mg,Fe)O phase having the rocksalt structure and possibly some $SiO_2$ stishovite having the rutile structure. Both the silicate perovskite and stishovite contain silicon in octahedral coordination, in contrast to the $SiO_4$ tetrahedra found in most silicates at lower pressure. Magnesium silicate perovskite in the lower mantle may constitute over 50% of the mass of our planet.

| Phase | Enthalpy | Entropy | Volume | |
|---|---|---|---|---|
| | | | Ambient | (*P*, *T*) |
| | | *End-members* | | |
| Mg olivine | A | A | A | A- |
| Mg beta | A | A- | A | B |
| Mg spinel | A | A- | A | B |
| Fe olivine | A- | A- | A | A- |
| Fe beta | B- | B- | B- | C |
| Fe spinel | A | A- | A | B- |
| Mg pyroxene | A | A | A | B- |
| Mg garnet | A | B | A | C |
| Mg ilmenite | A | B | A | C |
| Mg perovskite | A | B | A | C |
| Fe pyroxene | A | B | A | B- |
| Fe garnet | C | C | B- | C |
| Fe ilmenite | C | C | C | C |
| Fe perovskite | C | C | C | C |
| Ca perovskite | C | C | B | C |
| Hydrous Mg silicates | C | C | B- | C |
| | | *Solid solutions* | | |
| Fe,Mg olivine | A | B | A | A- |
| Fe,Mg beta | C | C | B | C |
| Fe,Mg spinel | A | B | A | B |
| Fe,Mg pyroxene | A | B | A | B |
| Fe,Mg garnet | C | C | C | C |
| Fe,Mg ilmenite | C | C | C | C |
| Fe,Mg perovskite | C | C | C | C |
| Al substituted in garnet | B | B | A | C |
| Al substituted in ilmenite | C | C | C | C |
| Ca substituted in garnet | C | C | C | C |
| Ca substituted in perovskite | C | C | C | C |

**Geophysical report card.** Important thermochemical parameters (enthalpy, entropy, volume at ambient pressure and temperature, and volume as a function of pressure and temperature) for mantle phases are ranked by the author as (A) well known, (B) moderately known, or (C) poorly known. The table is divided into end-member phases (that is, the indicated element is fully substituted) or solid solutions (mixtures of the substituted elements). Sources of data are (*1–4, 8, 9, 11, 14, 15*).

From a thermodynamic perspective, to tell whether the above phase transitions adequately describe mantle mineralogy requires answers to the following questions: What are the enthalpy, entropy, and volume changes for the major phase transitions? What is the equation of state of each likely mantle phase? What are the mixing properties of Fe-Mg substitutional solid solutions? Are the elastic properties of mantle phases at high pressure and temperature consistent with observed seismic velocities?

Phase equilibrium studies at high pressure and temperature done with diamond cell and multi-anvil presses provide thermodynamic data. Another approach to thermochemistry is through solution calorimetry of quenched high-pressure phases to obtain enthalpies of formation and through heat-capacity measurements and vibrational modeling to obtain entropies. These two independent approaches have provided quite consistent results for phase equilibria in the system $MgO-SiO_2$, and an internally consistent set of thermochemical data describe phase equilibria involving olivine, beta, spinel, garnet, ilmenite, and perovskite phases (*2*). For iron-substituted phases, the data set is much sparser (see table), especially because $\beta$-$Fe_2SiO_4$, $FeSiO_3$ ilmenite, and $FeSiO_3$ perovskite do not exist and their properties must be extrapolated from a limited range of solid solutions (*3, 4*). Why Fe-Mg substitution is complete and energetically facile in low-pressure minerals but appears increasingly limited and energetically costly in high-pressure silicates is interesting in terms of crystal chemistry (*5*).

The 660-km discontinuity is quite sharp, at most a few kilometers wide. Binary phase loops between coexisting (Fe,Mg) solid solutions are often broad, in pressure, but the reaction

$$(Mg,Fe)SiO_4 \text{ (spinel)} \rightleftharpoons (Mg,Fe)O \text{ (rock salt)} + (Mg,Fe)SiO_3 \text{ (perovskite)} \quad (1)$$

appears to occur at almost a single pressure, despite very different Mg/Fe ratios in the three phases (*4*). The thermodynamic and crystal chemical reasons for such a sharp transition need further study.

The static picture of a concentrically layered Earth must be modified extensively in light of new geophysical evidence and as a consequence of the dynamic processes implied by plate tectonics (*10*). The mantle couples the energy generated in the rotating liquid outer core and the processes in the crust. The immediate region 50 km above the core-mantle boundary, the so-called D" layer, is probably a swirling, convecting chemical reactor among metal and silicate phases (*1*). Especially energetic localized regions there may generate disturbances that propagate up through the mantle, perhaps even being the source of mantle "plumes," which may trigger large-scale volcanic and tectonic events (*6*).

The mantle itself is plastic, and though solid, has a viscosity that permits convection on a geologic time scale (*7*). Slabs of cold oceanic lithosphere originating in regions of downward-moving matter in subduction

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zones probably sink as far as the 660-km discontinuity. They may maintain temperatures several hundred degrees lower than the surrounding mantle for millions of years. Whether such slabs penetrate the 660-km discontinuity into the lower mantle, thus allowing whole mantle convection, or spread out on top of this discontinuity, leading to a stratified mantle, is a very important unsolved question (*1*, *8*).

One factor that may influence this behavior is the slope, $dP/dT$, of the transition

$$Mg_2SiO_4 \text{ (spinel)} \rightleftharpoons MgSiO_3 \text{ (perovskite)} + MgO \text{ (rock salt)} \qquad (2)$$

It is slightly negative, as confirmed by both phase equilibria and calorimetry; the denser perovskite phase has the higher vibrational entropy because of the weaker bonding resulting from the change in silicon coordination from tetrahedral to octahedral (*9*). It has recently been suggested that this weakly negative slope is just on the borderline of precluding whole mantle convection and that the boundary layer between transition zone and lower mantle may have been catastrophically breached only a few times in Earth's history (*10*). This is a prime example of processes on the molecular scale influencing process on the global scale.

Another unanswered question concerns the role of volatiles. How much water and carbon dioxide reside in the mantle, and in what phases? How do they affect mineralogy, melting relations, and physical properties? Subducting slabs may bring with them sedimentary and metamorphic rocks containing volatiles. How fast do they heat up and release their load of water and carbon dioxide? A new class of hydrous magnesium silicates containing both octahedral and tetrahedral silicon has been discovered to be stable to pressures over 15 GPa, though at temperatures cooler than normal mantle geotherms (*11*). Can these minerals carry water in the interiors of cooler subducting slabs? Nominally anhydrous phases such as olivine contain 1 to 100 parts per million of hydrogen as hydroxyl (*12*). The large mass of these major phases would enable them to store several oceans' worth of water homogeneously distributed thoughout the mantle. How rapidly does such water cycle through the mantle or exchange between mantle and core, mantle and crust? Does it play a role in fixing the oxidation state of iron and other elements? Does it influence reaction rates, elastic properties, and rheology? The thermodynamic data are very sparse.

$MgSiO_3$ perovskite quenched to ambient conditions is orthorhombic (*13*). Could this perovskite become cubic under lower mantle conditions? Pressure may be expected to increase the distortion, temperature to decrease it, and the limited experimental studies are somewhat in conflict (*14*). Furthermore, at temperatures near 2000 K, it is doubtful that $(Mg,Fe)SiO_3$ perovskite (or any other phase) is strictly stoichiometric, either in terms of $(Mg + Fe)/Si$ or in terms of oxygen content. But the details of nonstoichiometry, the nature of the defect chemistry, and the effect on physical and transport properties are essentially unknown.

$CaSiO_3$ perovskite is known as a separate phase with incomplete solid solution in $MgSiO_3$ perovskite (*15*). The role of aluminum in silicate perovskite and other high-pressure phases is only sketchily known.

Future work will emphasize accurate control of $P$, $T$ conditions, well-characterized materials, in situ measurements, and relation of thermodynamic and geophysical parameters to obtain a better picture of mantle processes.

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