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Phase transition Clapeyron slopes and transition zone seismic discontinuity topography

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Abstract. The depths, widths, and magnitudes of the 410-km and 660-km seismic discontinuities are largely consistent with an isochemical phase change origin, as is the observation that the topography on these discontinuities is negatively correlated and significantly smaller than predicted for chemical changes. While most thermodynamic studies of the relevant phase changes predict greater topography on the 410 than the 660, recent seismic studies suggest greater topography on the 660. The seismic results are consistent with some recent thermochemical studies which suggest that the Clapeyron slopes of the perovskite-forming reactions exceed in magnitude those of the spinel-forming reactions; however, we have reexamined the relevant Clapeyron slopes in light of other, more recent, experimental studies as well as the requirements of internal thermodynamic consistency. We conclude that the bulk of the evidence indicates a greater Clapeyron slope magnitude for the 410 than for the 660. Thus the recent seismic results are unexpected. One explanation might be that lateral temperature variations near 660 km depth exceed those near 410, consistent with a model of the 660 as a thermal boundary layer. An alternate interpretation, which requires neither a thermal boundary nor metastable olivine, is that the 410 does possess greater topography but is simply less visible seismically than the 660. This latter idea, and recent short-period observations of P'410P' seismic phases in conjunction with an elevated 660, is consistent with thermodynamic modeling of subduction zones illustrating the extreme broadening of the olivine $\alpha \rightarrow \beta$ transition in cold slab interiors and, conversely, its sharpening in regions of high temperature.

Introduction

The depths, widths, and magnitudes of the major seismic discontinuities in Earth's mantle, at 410 km and 660 km depth, are consistent with their being primarily due to isochemical phase transformations [*Bernal,* 1936; *Ringwood,* 1969; *Bina and Wood,* 1987; *Wood and Helffrich,* 1990; *Bina,* 1991]. Indeed, the observation that the "topography" or geographic variation in depth of occurrence of these discontinuities [*Shearer,* 1991; *Shearer and Masters,* 1992; *Richards and Wicks,* 1990] is an order of magnitude less than that predicted for chemical contrasts in a convecting mantle [*Christensen and Yuen,* 1984; *Kincaid and Olson,* 1987] virtually requires that they primarily be manifestations of phase changes. Recent seismological studies of mantle structure [*Revenaugh and Jordan,* 1989, 1991] reveal that lateral variations in the depths to these major seismic discontinuities are negatively correlated: the "410" is elevated when the "660" is depressed, and vice versa. This result is consistent with the thermochemical properties of mantle mineral phases.

Upper mantle phase transitions involving the transformation of olivine to β- or γ-spinel possess positive Clapeyron (dP/dT) slopes [*Suito,* 1977; *Kawada,* 1977; *Fukizawa,* 1982; *Ashida et al.,* 1987; *Akimoto,* 1987; *Katsura and Ito,* 1989] so that a rise in temperature results in an increase in the pressure (depth) of the phase change. On the other hand, both the predicted [*Navrotsky,* 1980] and measured [*Ito and Yamada,* 1982; *Ito and Takahashi,* 1989] Clapeyron slopes of lower mantle perovskite-forming phase changes are negative, so that a rise in temperature results in a decrease in the pressure (depth) of the phase change. Thus attribution of the the 410-km discontinuity to the β-spinel-forming reaction and the 660 to a perovskite-forming reaction implies anticorrelation of the 410 and the 660: where

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one is deflected downward, the other should be deflected upward. Furthermore, with a recent exception [*Ito et al.*, 1990], studies of the magnitudes of these Clapeyron slopes indicate a greater magnitude for the β-spinel-forming reaction than for the perovskite-forming reactions. This, in turn, implies greater deflection of the 410-km discontinuity than of the 660 for a given temperature perturbation.

Recent studies of seismic waves interacting with these discontinuities, however, demonstrate just the opposite effect. *Shearer* [1991] found greater variation in the depths to the 660 compared to the 410 recorded in reflections and conversions of long-period body waves from these discontinuities. The depths were estimated from the arrival times of $P \rightarrow S$ and $S \rightarrow P$ conversions and of topside and bottomside reflections. Different methods of analyzing this data set consistently show greater standard errors for 660 depth estimates than for 410 estimates. Moreover, near the northwest Pacific subduction zones where the observations are most abundant, 410 and 660 depths are positively correlated, not negatively correlated as the Clapeyron slopes would predict.

Vidale and Benz [1992] also found greater 660 variability but by different means. They stacked short-period waveforms from deep earthquakes to image the arrivals between P and pP, arrivals which correspond to bottomside reflections and conversions of upgoing P and near-source $S \rightarrow P$ conversions mediated by mantle discontinuities. Discontinuity depths are estimated from the arrival times of these phases. Assuming nominal depths of 410 and 660 km for these discontinuities in "typical" mantle distant from the subduction zones in which the events occurred, the 660 is displaced ~ 25 km downward whereas the 410 is displaced 10 km upward. Though the signs of the displacements are consistent with a phase change origin for both discontinuities, their relative magnitudes are not.

Thus the observed variability in the depth to the 660-km discontinuity exceeds the observed topography on the 410. The authors of these studies cite the consistency of their observations with recent thermochemical studies [*Akaogi et al.*, 1989; *Ito et al.*, 1990], suggesting that the Clapeyron slopes of the perovskite-forming reactions may exceed in magnitude those of the spinel-forming reactions and thus predicting greater vertical deflection of the 660 for a given temperature increment.

Here we reexamine the magnitudes of the relevant Clapeyron slopes, reassessing the available thermochemical data in light of the most recent phase equilibrium studies and the requirements of internal thermodynamic consistency. We find that the magnitude of the Clapeyron slope of the 410-km phase change does indeed appear to exceed that of the 660-km phase change for the Mg-bearing end-members of the Mg-Fe solid solutions. Furthermore, we conclude that the bulk of the experimental evidence points to a greater Clapeyron slope magnitude for the 410 than for the 660 when solid solution effects are included. Thus, rather than being consistent with the known thermochemical properties of the relevant phase transitions, the recent results of *Shearer* [1991] and *Vidale and Benz* [1992] are unexpected. They are telling us something interesting, either about Earth's mantle or about our seismological methods of investigating it. We illustrate that the broadening of the olivine $\alpha \rightarrow \beta$ transition at lower temperatures should cause upward deflection of the 410 to be less visible seismically, leading to underestimation of 410 topography. In addition, the small Clapeyron slope for the 660-km phase transformation found herein should present a weaker barrier to subducting slabs than is commonly assumed, rendering the geodynamical argument for segregated upper and lower mantle reservoirs less compelling.

Seismologically Observed Clapeyron Slopes

What is meant by the Clapeyron slope of a seismologically observed mantle phase transition? In complex systems like the mantle where multicomponent phase transformations such as those involving the olivine polymorphs and perovskite occur, a Clapeyron slope cannot be thermodynamically defined. A useful analogy with phase transformations in single-component systems may rescue the concept, however. In such systems, if a phase boundary is crossed, all of the newly unstable phase is transformed to the newly stable phase, yielding a first-order discontinuity in seismic properties. In multicomponent systems of fixed bulk composition, regions where two or more stable phases coexist commonly appear when a phase boundary is crossed, yielding seismic properties which are some weighted average of those of the individual phases [*Bina and Wood*, 1987]. Suppose that this occurs as one follows a mantle adiabat to higher pressures. Imaged seismically at an appropriate frequency from a distance above the boundary, a radially finite multiphase field resembles a first-order discontinuity at some depth, even though it is really a gradient zone. Referenced to this adiabat, the displacement of this apparent discontinuity from its unperturbed depth by some temperature variation may be quantified and a "seismic" Clapeyron slope defined. Though dependent upon frequency, such a slope otherwise depends only upon thermodynamic properties.

Methods

The primary constraints upon the Clapeyron slopes of mantle phase transitions arise from phase equilibrium experiments which attempt to map the reaction boundaries at high pressures (P) and temperatures (T) [*Katsura and Ito*, 1989; *Ito and Takahashi*, 1989]. However, since a finite overstep of a reaction boundary in either P or T is necessary to generate a driving force for the reaction, such experiments must be "reversed" if they are to completely bound the region in P–T space in which the equilibrium phase boundary must lie [*Fyfe*, 1960]. Additional constraints upon the phase boundary, and hence upon the Clapeyron slope, may be obtained by considering calorimetric measurements of heats of

solution and measured equations of state. In the absence of a complete set of experimental reversals, such additional constraints become even more desirable.

The Clapeyron slope for a phase transition, where the free energy change ΔG between reactants and products is zero at equilibrium, is determined by the entropy change $\Delta S(P,T)$ and volume change $\Delta V(P,T)$ of reaction via the Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta S(P,T)}{\Delta V(P,T)}. \quad (1)$$

Suitable equations of state yield the volume change of reaction $\Delta V(P,T)$. The enthalpy change of reaction $\Delta H(P_0,T_0)$ is obtained by integration of calorimetric measurements of heat capacities $C_P(P_0,T)$ or by direct measurements of heats of solution. This is corrected to the P and T of interest by integration of ΔV and the heat capacity difference ΔC_P:

$$\Delta H(P,T) = \Delta H(P_0,T_0) + \int_{T_0}^{T} \Delta C_P(P_0,\hat{T})d\hat{T} + \int_{P_0}^{P} \Delta V(\hat{P},T) - T\cdot\Delta[\alpha(\hat{P},T)\cdot V(\hat{P},T)]d\hat{P} \quad (2)$$

where α is the volume coefficient of thermal expansion.

Since ΔG of reaction is zero at equilibrium:

$$0 = \Delta G(P,T) \equiv \Delta H(P,T) - T\cdot\Delta S(P,T)\,, \quad (3)$$

we may obtain $\Delta S(P,T)$ from $\Delta H(P,T)$ by selecting a point in $P-T$ space which we believe to lie on the equilibrium boundary (e.g., from a high-pressure experimental reversal bracket) and solving equation (3) for $\Delta S(P,T)$. Hence $\Delta S(P,T)$ and $\Delta V(P,T)$ yield the Clapeyron slope via equation (1). Since we have

$$\Delta S(P,T) = \Delta S(P_0,T_0) + \int_{T_0}^{T} \frac{\Delta C_P(P_0,\hat{T})}{\hat{T}}d\hat{T} - \int_{P_0}^{P} \Delta[\alpha(\hat{P},T)\cdot V(\hat{P},T)]d\hat{P}\,, \quad (4)$$

we have determined the Clapeyron slope by effectively solving for $\Delta S(P_0,T_0)$ as constrained by our selected point on the equilibrium phase boundary. We call this the "fixed-point" method, and it has been applied in several studies [*Akaogi et al.*, 1989; *Ito et al.*, 1990; *Akaogi and Ito*, 1993b].

Here we adopt a modified method which avoids the potential bias associated with the selection of a single $P-T$ point assumed to be representative of equilibrium. Rather than choosing a single point, we simultaneously make use of all N of the experimental data points. Each of these points consists of a pair of pressures, $P_{i,+}^{\text{expt}}$ and $P_{i,-}^{\text{expt}}$, which bracket the equilibrium transition pressure at the temperature T_i^{expt}. For a given value of $\Delta S(P_0,T_0)$, we evaluate the global misfit function $\sum_{i=1}^{N}\Delta P_i^2$, where ΔP_i parameterizes the degree to which the calculated equilibrium pressure violates the constraints imposed by the data. Thus ΔP_i is zero uniformly inside the bracket [*Demarest and Haselton*, 1981] but grows linearly when one of the bounds is exceeded:

$$\Delta P_i = \begin{Bmatrix} P_i - P_{i,+}^{\text{expt}} \\ 0 \\ P_{i,-}^{\text{expt}} - P_i \end{Bmatrix} \text{if} \begin{Bmatrix} P_i > P_{i,+}^{\text{expt}} \\ P_{i,+}^{\text{expt}} \geq P_i \geq P_{i,-}^{\text{expt}} \\ P_i < P_{i,-}^{\text{expt}} \end{Bmatrix}. \quad (5)$$

Here, P_i is the calculated equilibrium pressure determined via equation (3) at the temperature T_i^{expt}, using $\Delta H(P,T)$ determined from equation (2) and equations of state $\Delta V(P,T)$. We use Brent's method of numerical minimization [*Press et al.*, 1986] to find the value of $\Delta S(P_0,T_0)$ which minimizes this global misfit function, and we then use $\Delta S(P,T)$ from equation (4) to determine the Clapeyron slope via equation (1). We call this the "optimization" method. When we quote uncertainties in the derived Clapeyron slopes, these are the uncertainties due solely to the error bars on the $\Delta H(P_0,T_0)$ values.

Results for $\alpha\rightarrow\beta$ at 410 km

Katsura and Ito [1989] performed synthesis experiments to locate the boundary between the stability fields of α-olivine and β-spinel at high P and T and successfully reversed the transition in Mg_2SiO_4 at 1600°C. They estimated the Clapeyron slope for the $\alpha\rightarrow\beta$ reaction in Mg_2SiO_4 to be +2.5 MPa/K (Figure 1), centered in the range of $+2.5\pm1.0$ MPa/K determined in most earlier studies [*Suito*, 1977; *Ashida et al.*, 1987; *Akaogi et al.*, 1989] (although a few studies [*Kawada*, 1977; *Akimoto*, 1987] had reported somewhat larger values).

Akaogi et al. [1989] performed a fixed-point analysis (using $\Delta G = 0$ at 14.4 GPa and 1473 K) for the $\alpha\rightarrow\beta$ transition in Mg_2SiO_4 using measured heats of solution and $\Delta C_P(T)$. They computed $\Delta V(P,T)$ from measured thermoelastic parameters, but they assumed a temperature-independent bulk modulus due to insufficient constraints on equations of state. They obtained a significantly shallower Clapeyron slope of $+1.5\pm0.5$ MPa/K (Figure 1).

Our optimization analysis of the $\alpha\rightarrow\beta$ transition uses the heat of solution measurements of *Akaogi et al.* [1989] but employs the more recent equations of state of *Fei et al.* [1990]. Simultaneously minimizing the misfit to all of the *Katsura and Ito* [1989] data (where the reversal at 1873 K gives $P_{i,+}^{\text{expt}} = P_{i,-}^{\text{expt}}$ in equation (5), thus providing a particularly strong equilibrium constraint), we find the best fitting Clapeyron slope for the $\alpha\rightarrow\beta$ transition in Mg_2SiO_4 to be +2.9 MPa/K at 1673 K, rising to +3.0 MPa/K at 1923 K (Figure 1). These values, substantially larger than that determined in the *Akaogi et al.* [1989] fixed-point analysis, are also consistent with the values of +2.7 to +2.9 MPa/K estimated by *Chopelas* [1991] upon fitting measured high-P Raman spectra to lattice vibrational models.

The thermochemical properties of natural, iron-bearing olivine differ from the end-member Mg_2SiO_4 properties through solid solution effects, where the composition of mantle olivine is approximately $(Mg_{0.9}Fe_{0.1})_2SiO_4$

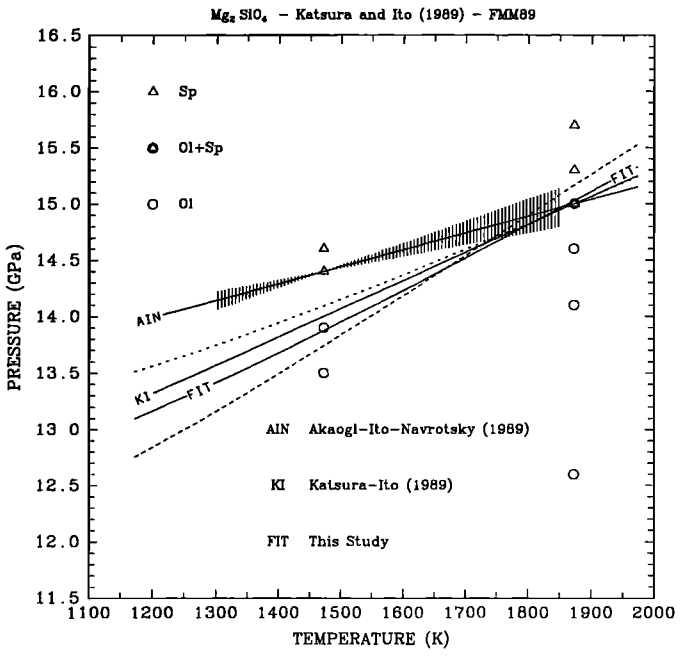

Figure 1. Phase diagram in $P-T$ space for Mg_2SiO_4 showing transition of α-olivine to β-spinel. Points are experimental data of *Katsura and Ito* [1989]. Lines are (KI) boundaries fit by *Katsura and Ito* [1989], (AIN) boundaries calculated by *Akaogi et al.* [1989] with one-σ enthalpy uncertainties (hatchure), (FIT) boundaries calculated in this study with one-σ enthalpy uncertainties (dashed).

[*Ringwood,* 1970]. In this two-component system, the phase transition is no longer "univariant" with a discontinuous change from α to β; it is "divariant", with α transforming to β continuously through a mixed phase region. Clapeyron slopes are not defined for such multivariant systems, since the P and T dependence of the equilibrium phase assemblage is a function not just of ΔS and ΔV but also of the mixing properties (i.e., activity-composition relations) of the coexisting phases. However, we can deduce whether or not the Clapeyron slope in the Fe end-member exceeds that in the Mg end-member to determine whether the natural multicomponent system should exhibit greater topography than expected for Mg_2SiO_4 alone. *Katsura and Ito*'s [1989] experiments demonstrate that the transition in the fictive Fe end-member has a larger Clapeyron slope than the Mg end-member, indicated in part by the flattening of the $\alpha + \beta$ divariant loop with increasing temperature. This is expected since the instability of Fe-rich β-spinel (Fe_2SiO_4 end-member β-spinel does not exist as a stable phase) implies a large entropy decrease for the phase change in the fictive Fe end-member. Furthermore, a larger Clapeyron slope for the Fe end-member is also consistent with the observed stability of Mg-rich β-spinel and the continued instability of Fe-rich β-spinel at high T. This same result can be seen in *Fei et al.*'s [1991] thermodynamic models. Therefore, adding Fe should increase the seismically observed Clapeyron slope at a given bulk composition.

Results for $\gamma \rightarrow pv + mw$ at 660 km

Ito and Takahashi [1989] performed synthesis experiments to locate the boundary between the stability fields of γ-spinel and perovskite + magnesiowüstite under mantle conditions. While they could not reverse their experiments in a strict sense, they did perform several runs with segregated $MgSiO_3$ and Mg_2SiO_4 starting materials which yielded coexisting perovskite and γ-spinel. They assumed these runs indicated equilibrium, which may bias the position of their equilibrium boundary slightly if Mg_2SiO_4 spinel-perovskite transformation rates are significantly slower than $MgSiO_3$ ilmenite-perovskite rates. Nonetheless, they estimated the Clapeyron slope for $Mg_2SiO_4 \rightarrow MgSiO_3 + MgO$ ($\gamma \rightarrow pv + mw$) to be -2.8 MPa/K (Figure 2), close to the estimate of -2 MPa/K derived from earlier work *[Ito and Yamada,* 1982] and with a magnitude well within the range of 2.5 ± 1.0 MPa/K cited above for the 410-km phase change.

Ito et al. [1990] performed a fixed-point analysis (using $\Delta G = 0$ at 24 GPa and 1573 K with a 13-min run duration) for the $\gamma \rightarrow pv + mw$ transition ($Mg_2SiO_4 \rightarrow MgSiO_3 + MgO$), using measured heats of solution and assuming $\Delta C_P(T) = 0$ due to insufficient calorimetric data. They tried two candidate equations of state: a constant ΔV independent of P and T, and a $\Delta V(P,T)$ constructed from measured thermoelastic

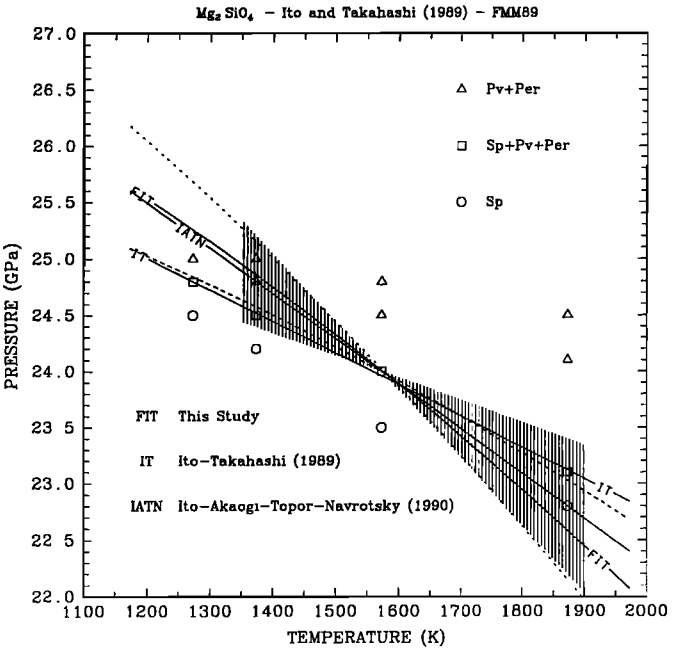

Figure 2. Phase diagram in $P-T$ space for Mg_2SiO_4 showing transition of γ-spinel to perovskite + magnesiowüstite (periclase). Points are experimental data of *Ito and Takahashi* [1989]. Lines are (IT) boundaries fit by *Ito and Takahashi* [1989], (IATN) boundaries calculated by *Ito et al.* [1990] with one-σ enthalpy uncertainties (hatchure), (FIT) boundaries calculated in this study using $\Delta H(T_0)$ of *Ito et al.* [1990] with one-σ enthalpy uncertainties (dashed). Note that *Ito et al.*'s [1990] boundaries are marginally inconsistent with syntheses of $pv + per$ at both low and high temperatures.

parameters (including a small perovskite thermal expansion coefficient). They obtained a Clapeyron slope of -4.0 ± 2.0 MPa/K (Figure 2) which, although significantly steeper, does overlap the 2.5 ± 1.0 MPa/K magnitude range cited above for the 410-km phase change. More importantly, the fact that the steeper portion of this range is inconsistent with the phase diagram upon which it is based (Figure 2) suggests possible problems in either their equations of state, their choice of fixed point, or their perovskite heat of solution which may bias their estimated slope to high magnitude values.

This effect may also be seen in our optimization analysis of the $\gamma \rightarrow pv + mw$ transition using the heat of solution measurements of *Ito et al.* [1990] but employing the recent equations of state of *Fei et al.* [1990] and simultaneously minimizing the misfit to all of the *Ito and Takahashi* [1989] data. The best fitting Clapeyron slope for the $\gamma \rightarrow pv + mw$ transition in Mg_2SiO_4 of -4.5 MPa/K (Figure 2) is even steeper, clearly inconsistent with the experimental data of *Ito and Takahashi* [1989], and it becomes marginally consistent (with a slope of -3.2 MPa/K) only when the $\Delta H(T_0)$ value is decreased by one quoted standard deviation. This suggests that *Akaogi et al.* [1989] may have systematically overestimated $\Delta H(T_0)$ (given that they were able to perform only a single heat of solution measurement for perovskite).

Indeed, *Akaogi and Ito* [1993b] have recently reevaluated $\Delta H(T_0)$ for this reaction, performing multiple heat of solution measurements on perovskite and obtaining a value for $\Delta H(T_0)$ significantly (10.7 kJ/mol) smaller than that of *Ito et al.* [1990]. *Akaogi and Ito* [1993b] then performed a new fixed-point analysis (using $\Delta G = 0$ at 24 GPa and 1573 K) for the $\gamma \rightarrow pv + mw$ transition using their new heat of solution measurements as well as measured $\Delta C_P(T)$ [*Akaogi and Ito,* 1993a]. Their fixed-point analysis yields a significantly shallower Clapeyron slope of -3.2 MPa/K, and their subsequent application of a Kieffer-type model to estimate entropy changes yields an even shallower slope of -2.6 MPa/K (Figure 3).

We have performed an optimization analysis of the $\gamma \rightarrow pv + mw$ transition using the heat of solution measurements of *Akaogi and Ito* [1993b] and employing the equations of state of *Fei et al.* [1990]. Simultaneously minimizing the misfit to all of the *Ito and Takahashi* [1989] data, rather than choosing a single fixed point, we find the best fitting Clapeyron slope for the $\gamma \rightarrow pv + mw$ transition ($Mg_2SiO_4 \rightarrow MgSiO_3 + MgO$) to be -1.9 MPa/K at 1673 K, steepening to -2.1 MPa/K at 1923 K (Figure 3). (Adopting an alternate equation of state for perovskite from *Mao et al.* [1991] results in a slightly steeper slope of -2.0 MPa/K at 1673 K, steepening to -2.7 MPa/K at 1923 K.) These values, substantially shallower than those determined in the *Ito et al.* [1990] or *Akaogi and Ito* [1993b] fixed-point analyses, are also consistent with the bounds of -2.8 to -2.0 MPa/K obtained by A. Chopelas et al. (Thermodynamics of γ-Mg_2SiO_4 from Raman spectroscopy at high pressure: The Mg_2SiO_4 phase diagram, submitted to *Physics and Chemistry of Minerals,* 1993) upon fitting measured high-P Raman spectra to lattice vibrational models.

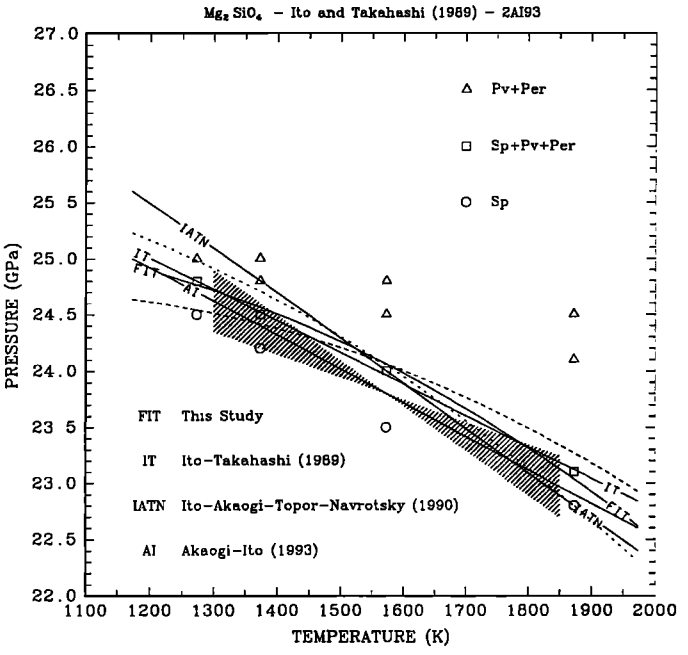

Figure 3. Phase diagram in $P-T$ space for Mg_2SiO_4 showing transition of γ-spinel to perovskite + magnesiowüstite (periclase). Points are experimental data of *Ito and Takahashi* [1989]. Lines are (IT) boundaries fit by *Ito and Takahashi* [1989], (IATN) boundaries calculated by *Ito et al.* [1990], (AI) boundaries calculated by *Akaogi and Ito* [1993] with one-σ enthalpy uncertainties (hatchure), (FIT) boundaries calculated in this study using $\Delta H(T_0)$ of *Akaogi and Ito* [1993b] with one-σ enthalpy uncertainties (dashed).

Iron solid solution effects may also influence the $\gamma \rightarrow pv + mw$ transformation, but the data of *Ito and Takahashi* [1989] provide no evidence for the effect of Fe on the Clapeyron slope within experimental uncertainty. Again, Clapeyron slopes are not strictly defined for the multicomponent system. However, we expect the Clapeyron slope in the Fe end-member to be less negative (i.e., smaller in magnitude) than that in the Mg end-member since the relative instability of Fe-rich perovskite suggests a smaller entropy increase for the phase change in the fictive Fe end-member. On the other hand, *Fei et al.*'s [1991] thermodynamic models predict a larger entropy increase for the Fe end-member, but their thermodynamic parameters for fictive Fe-perovskite and their magnesiowüstite solid solution models are based upon analogue compounds and extrapolations from limited solid solution. Indeed, they acknowledge that their parameters are inconsistent with the experimental data of *Ito and Takahashi* [1989]. Furthermore, their entropy increase is so large as to yield an Fe_2SiO_4 Clapeyron slope for $\gamma \rightarrow pv + mw$ which is substantially more negative than that for $\gamma \rightarrow 2mw + st$, a situation which is inconsistent with the observed instability of Fe-rich perovskite relative to $FeO + SiO_2$ (wüstite + stishovite) at high T.

Discussion and Conclusions

Thus we find that the best fit Clapeyron slope of the 410-km phase change does indeed exceed in magnitude that of the 660-km phase change for the Mg-bearing end-members of the Mg-Fe solid solutions. Furthermore, the effect of Fe in solid solution should yield even greater topography on the $\alpha \rightarrow \beta$ transition but lessen that on the $\gamma \rightarrow pv + mw$ transition.

In view of this analysis, seismological observation of greater deflection of the 660-km discontinuity relative to the 410 is unexpected and surprising. One explanation might be that lateral temperature variations are greater near 660 km depth than they are near 410, a somewhat startling conclusion in view of seismic studies which suggest decreasing lateral heterogeneity in upper mantle velocities with increasing depth [*Grand*, 1987; *LeFevre and Helmberger*, 1989; *Woodward and Masters*, 1991]. However, such an explanation for greater topographic variation of the 660 might be consistent with a scenario in which the 660 constitutes a chemical and thermal boundary layer [*Jeanloz and Thompson*, 1983]. Another explanation for greater 660 variability near subducted slabs [*Vidale and Benz*, 1992] might be that the $\alpha \rightarrow \beta$ transition is kinetically hindered in their cold interiors, resulting in metastable persistence of α-olivine and a consequent decrease in the predicted uplift of the 410-km discontinuity in such regions [*Sung and Burns*, 1976]. The existence of such wedges of metastable olivine, however, is currently a matter of active debate [*Solomon and U*, 1975; *Roecker*, 1985; *Iidaka and Suetsugu*, 1992].

An alternative interpretation, which is valid even in the absence of thermal boundary layers or metastable olivine wedges, is simply that the topographic variations are in fact larger on the 410 than the 660 but that they are less visible seismically and so lead to underestimated topographic variability. Indeed, several studies [*Davis et al.*, 1989; *Paulssen*, 1988a,b; *Nakanishi*, 1986, 1988; *Petersen et al.*, 1993] have noted the greater difficulty in observing boundary-interaction phases from the 410 relative to the 660. Large topographic variations would present a rougher surface to interacting seismic waves so that spatial averaging, scattering, and focusing effects might conspire to conceal discontinuity topography [*Richards*, 1972; *Davis et al.*, 1989]. Even more fundamental, however, is the observation [*Bina and Wood*, 1987; *Katsura and Ito*, 1989] that the $\alpha \rightarrow \beta$ transition becomes sharper at higher temperatures or, conversely, broader at lower temperatures. This low-temperature broadening of the transition, which can be seen (Figure 4) by calculating stable phase assemblages along adiabats via numerical minimization of the free energy [cf. *Bina and Wood*, 1987], should make much 410 topography less visible to such seismic probing. The 660-km transition, on the other hand, appears to remain sharp over a broad range of temperatures [*Ito and Takahashi*, 1989; *Wood*, 1990]. Thus hot mantle should yield a sharp, depressed 410 and a sharp, uplifted 660; cold mantle should yield a diffuse, uplifted 410 and a sharp depressed 660.

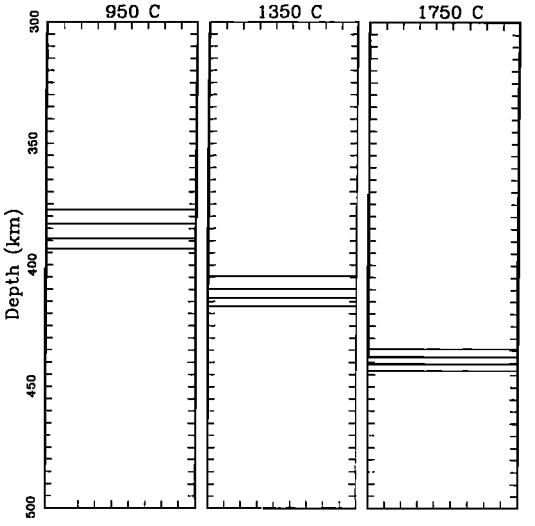

Figure 4. Equilibrium phase proportions of α-olivine in a model mantle of $(Mg_{0.9}Fe_{0.1})_2SiO_4$ composition illustrating low-temperature broadening of the $\alpha \rightarrow \beta$ transition, calculated via free energy minimization using the thermodynamic parameters of *Fei et al.* [1991]. Transition thicknesses are for a cool transition zone region (left, 950°C adiabat), a normal transition zone region (middle, 1350°C adiabat), and a hot transition zone region (right, 1750°C adiabat). Mole fraction of α phase is contoured for values of 0.2, 0.4, 0.6, and 0.8.

Recent observations [*Benz and Vidale*, 1993] of seismic $P'410P'$ phases from a region beneath the Indian Ocean provide some support for this idea in that they require a very sharp (4 km wide) 410-km transition to accompany a sharp 660-km transition which is somewhat elevated (to 650 km). Contrary to the assertion of *Benz and Vidale* [1993], the high-pressure synthesis experiments [*Katsura and Ito*, 1989] place only an upper bound on phase transition thickness, not a lower bound, due to the necessity of finite reaction overstep [*Fyfe*, 1960]. Moreover, the transition width is influenced by the solid solution properties of the participating phases, which are difficult to constrain experimentally [*Wood*, 1990]. These details may contribute to up to 1/3 of the overall transition thickness predicted thermodynamically [*Bina and Wood*, 1987]. Thus it is unrealistic to exclude a phase transition explanation for this discontinuity on the grounds that it overpredicts the width of the observed transition. The observation of *Benz and Vidale*'s [1993] $P'410P'$ precursor phases is consistent with sharpening of the $\alpha \rightarrow \beta$ transition in a region of high temperatures. The corresponding broadening of the transition which should attend regions of low temperature (Figure 4) may render the 410 so diffuse as to preclude the observation of topography via seismic boundary-interaction phases.

Finally, the best fit Clapeyron slopes found herein differ from those in common use for convection modeling [*Peltier and Solheim*, 1992; *Zhao et al.*, 1992; *Honda et al.*, 1993; *Tackley et al.*, 1993; *Weinstein*, 1993]. In particular, the shallow slope found for the 660-km phase transformation may present a weaker barrier to

subducting slabs than has been commonly assumed, rendering the geodynamical argument for largely segregated upper and lower mantle chemical reservoirs less compelling.

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