GEOPHYSICAL RESEARCH LETTERS, VOL. 11, NO. 10, PAGES 955-958, OCTOBER 1984

THE ECLOGITE TO GARNETITE TRANSITION -- EXPERIMENTAL AND THERMODYNAMIC CONSTRAINTS

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Abstract. We have found that the forms of the experimentally determined phase diagrams for pyroxene-garnet transformations require the volume changes for these reactions to be much smaller at 130 kbar (400 km) than at 1 atm. Using these volume data we calculated the width of the eclogite-garnetite transition in natural quartz tholeiite and alkali olivine basalt compositions taking account of mixing in multicomponent pyroxene and garnet phases. We find that the eclogite-garnetite transition does not exhibit any discontinuity in bulk sound velocity in the pressure range 110 to 230 kbar. In addition, this velocity, when plotted as a function of pressure, possesses a curvature which is in the opposite sense to that given by the Preliminary Reference Earth Model (PREM). This phase transition, therefore, does not appear to be a satisfactory model for the 400 km seismic discontinuity.

Introduction

The eclogite-garnetite transition has been proposed as a possible model for the 400 km seismic discontinuity [Anderson, 1982, 1984]. This proposition was based, in part, on the experimental study of Akaogi and Akimoto (1977) who found, in synthesis experiments, that pyroxene components dissolve substantially into the garnet structure in the pressure range of interest. We have taken the eclogite-garnetite hypothesis one step further by determining whether the experimental data actually require a seismic discontinuity to be produced by the transformation of pyroxene to garnet structure in natural eclogitic compositions. By making use of available thermodynamic data for low pressure mineral phases [Wood and Holloway, 1982, 1984], we derived thermodynamic parameters for high pressure majorites (pyroxene in garnet structure) from the experimental phase equilibrium data in the manner discussed below. We then used these data to compute stable phase assemblages and their properties as functions of pressure, temperature, and bulk composition by the technique of free energy minimization.

Data Base

The eclogite-garnetite transition, if it occurs in the earth, takes place by progressive dissolution of $M_4Si_4O_{12}$ pyroxene (M = Mg, Fe and Ca) in $M_3Al_2Si_3O_{12}$ garnet with increasing pressure. This gives rise to an $M_3Al_2Si_3O_{12}$-$M_4Si_4O_{12}$ garnet-majorite solid solution. High pressure phase equilibrium data are available for the joins $Mg_3Al_2Si_3O_{12}$-$Mg_4Si_4O_{12}$, $Fe_3Al_2Si_3O_{12}$-$Fe_4Si_4O_{12}$ [Akaogi and Akimoto, 1977], and $Ca_{1.5}Mg_{1.5}Al_2Si_3O_{12}$-$Ca_2Mg_2Si_4O_{12}$ [M. Akaogi, personal communication, 1983]. These authors obtained, in synthesis experiments, the approximate limits of majorite solution for garnet coexisting with pyroxene over the pressure-temperature range of 40 to 200 kbar and 850 to 1450°C.

The coexistence of pyroxene and garnet may be considered in terms of equilibria such as:

$$\underset{\text{pyroxene}}{M_4Si_4O_{12}} = \underset{\text{garnet}}{M_4Si_4O_{12}} \qquad (1)$$

for which we have at equilibrium:

$$\Delta G^o_{P,T} = -RT \ln K \qquad (2)$$

where $\Delta G^o_{P,T}$ is the standard state free energy change at the pressure and temperature of interest and K is the equilibrium constant. Expressing K in terms of activity and referring $\Delta G^o_{P,T}$ to 1 atmosphere measurements, we have

$$\Delta G^o_{P,T} = \Delta H^o_{1,T} - T\Delta S^o_T + \int_1^P \Delta V^o_T dP = -RT \ln \frac{a_j^{gt}}{a_j^{px}} \qquad (3)$$

where H, S and V refer to enthalpy, entropy and volume, respectively, and a_j^i is the activity of j (= $M_4Si_4O_{12}$) component in the i phase. The entropies of the majorite components were calculated from known values for the aluminosilicate garnets which were adjusted for the removal of Al^{VI} and the addition of M^{VI} and Si^{VI} (Table 1). Heat capacities were estimated in the same manner as the entropies. The activities of $M_4Si_4O_{12}$ components were calculated by assuming ideal disordered (M-Si-Al) solution for the Mg- and Fe-majorites and by applying the non-ideality relations of Haselton and Newton (1980) for the CaMg-majorite. Thus, from equation (3), the shape of the pyroxene-majorite equilibrium curve (i.e., the pyroxene-garnet miscibility gap) on an isothermal pressure-composition diagram (Figure 1A) is completely determined by the integral of the volume change of reaction over the pressure interval of interest. The end-member (pure $M_4Si_4O_{12}$ in garnet structure) intercept pressure of the curve is determined by the standard enthalpy change of reaction.

To determine the functional form of ΔV^o_T versus P, we have used the thermal expansion data of Kieffer (1980), zero-pressure volumes from Akaogi and Akimoto (1977) and the review paper of Jeanloz and Thompson (1983), and bulk modulus data from Jeanloz (1981), Jeanloz and Thompson (1983), and Levien et al. (1979). Gruneisen ratios and Anderson-Gruneisen parameters were obtained from Jeanloz and Thompson (1983) and Anderson et al. (1968). (See Table 1.) The pressure dependence

Paper number 4L6300.
0094-8276/84/004L-6300$03.00

TABLE 1. Adjusted data base consistent with phase equilibria

	$Mg_2Si_2O_6$	$Fe_2Si_2O_6$	$CaMgSi_2O_6$	$Mg_4Si_4O_{12}$	$Fe_4Si_4O_{12}$	$Ca_2Mg_2Si_4O_{12}$
phase	px	px	px	gt	gt	gt
S^o_{1000K} (cal)	94.17	109.94	96.0	189.13	224.26	~~221.68~~ 193.8
$\alpha_0 \times 10^6$ (K^{-1})	22.031	29.3	21.013	15.439	10.303	14.67
$\left(\frac{d\alpha}{dT}\right)_P \times 10^6$ (K^{-2})	0.010	0.013	0.010	0.014	0.019	0.013
$V_{0,298}$ (cm^3)	62.58	65.96	66.1	114.20	117.06	122.17
K_{0S} (GPa) raw	104.-112.	84.-112.	107.-113.	212.-229.	217.-239.	unknown
K_{0S} (GPa) adj.	106.	104.	113.	225.	227.	215.
$\left(\frac{dK_{0S}}{dP}\right)_T$ raw	4.5-9.5	4.5-9.5	4.5-9.5	3.5-5.5	3.5-5.5	unknown
$\left(\frac{dK_{0S}}{dP}\right)_T$ adj.	4.5	4.5	4.5	4.5	4.5	4.5
γ	1.1	1.1	1.1	1.1	1.1	1.1
δ_S	6.0	6.0	6.0	6.3	6.3	6.3
H^o_{1000K} (cal)	-15215.	-6500.	-35320.	-40.	27458.	-33797.

Phases are pyroxene (px) and majorite (gt). S^o_{1000K} is entropy at 1000 K, α_0 thermal expansion extrapolated to 0 K, $V_{0,298}$ zero-pressure volume at 298 K, K_{0S} zero-pressure adiabatic bulk modulus at 300 K, γ Gruneisen ratio, δ_S Anderson-Gruneisen parameter, H^o_{1000K} enthalpy of formation from oxides at 1000 K and 1 bar. Observed ranges (raw) and best-fit values (adj.) are given for bulk moduli and their pressure derivatives. See text for references.

of the volume was calculated using the second-order Birch-Murnaghan equation of state. Adoption of average values of these parameters leads to a very poor fit to the phase equilibrium data (Figure 1A). However, by adjusting the bulk moduli and their pressure derivatives (and, to a lesser extent, the zero-pressure volumes) of the garnets and pyroxenes within their experimental uncertainties, we are able to obtain a functional form of the volume change of reaction which produces an excellent fit to the experimental data (Figure 1A). These best-fit values fall within the scatter of reported values (Table 1) and were obtained by interdependent perturbation of the mean reported values. Since the derived pyroxene and majorite properties are interdependent, we do not claim that our values are the most accurate; they simply yield volumes which are consistent with the phase equilibrium data. We find that the phase equilibrium data require a volume change of reaction which is significantly smaller at high pressures (approximately 50% smaller at 100 kbar) than the zero-pressure volume change (Figure 1B); this is the case for all three of the compositional joins studied. Utilizing a volume change which does not decrease significantly with pressure produces a curve whose slope is much shallower than any curve consistent with the experimental data (Figure 1A,B). If we were to assume non-ideal mixing behavior or short range ordering of M (= Mg in this case), Si, and Al in the majorite-garnet solutions, the calculated curve would be even flatter than that obtained from the ideal assumption. (In general, coupled substitutions of the type under consideration lead to positive excess enthalpies and short range order [e.g., Wood et al., 1980]; it can readily be shown that this leads to a shallower slope.) Thus, the experimental data constrain the volume changes to be very small at high pressures (Figure 1A,B).

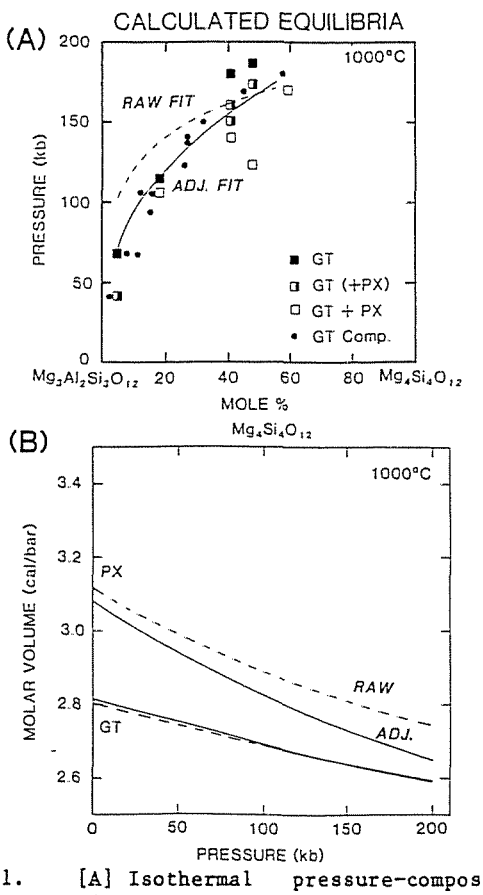

Fig. 1. [A] Isothermal pressure-composition diagram showing experimental data of Akaogi and Akimoto (1977) and pyroxene-garnet miscibility gap fit to initial (RAW) and adjusted (ADJ.) data base. [B] Isothermal volume-pressure diagram showing volume change of pyroxene-majorite (PX-GT) reaction as a function of pressure for initial (RAW) and adjusted (ADJ.) data base.

Results

Having arrived at a consistent form for $\Delta V_T^o(P)$, we then solved equation (3) for a best fit value of ΔH^o_{1000K} to the equilibrium data in a least squares sense. This gave us a complete set of thermodynamic data for the pyroxene-majorite transition consistent with phase equilibrium experiments (Table 1). We calculated the stable phase assemblages and mineral compositions as functions of temperature and pressure for two natural eclogitic compositions from Green and Ringwood (1967): a silica-oversaturated quartz tholeiite "A" and a silica-undersaturated alkali olivine basalt. We used thermodynamic data for the pyroxene and aluminosilicate garnet components from Wood and Holloway (1982, 1984) and the majorite data discussed above. The free energy of the system was minimized utilizing the steepest descent algorithm of Storey and Van Zeggeren (1964). From our volume and compressibility data we were able to determine the density and the volume-averaged bulk modulus, and hence the bulk sound velocity $\phi^{\frac{1}{2}}$, of each stable assemblage. Along 1600 K and 2000 K isotherms, the bulk sound velocity as a function of pressure for the quartz tholeiite (Figure 2A) exhibits a sharp discontinuity at 100-110 kbar due to the coesite-stishovite transition [silica polymorph data from Holm et al., 1967 and Jeanloz and Thompson, 1983] but no discontinuity due to the eclogite-garnetite transition. This is seen more clearly in the silica-undersaturated alkali olivine basalt (Figure 2B) which exhibits no discontinuity at all within the 50 to 230 kbar pressure range. The eclogite-garnetite transition takes place gradually and smoothly, and much of the transition takes place at pressures lower than those corresponding to 400 km (i.e., approximately 130 kbar). Note also that the sense of the curvature (i.e., increasing or decreasing slope) of $\phi^{\frac{1}{2}}$ versus P for the transition is opposite that of the Preliminary Reference Earth Model [Dziewonski and Anderson, 1981], although the magnitudes of the velocities do not differ greatly.

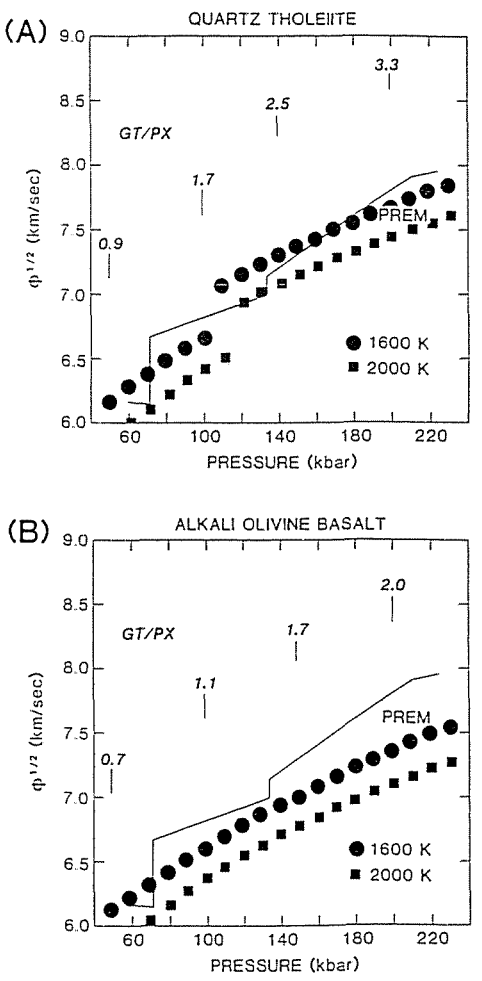

Fig. 2. Bulk sound velocity ($\phi^{\frac{1}{2}}$) as a function of pressure along 1600 K and 2000 K isotherms for natural eclogite compositions and comparison with Preliminary Reference Earth Model (PREM--solid line). [A] Quartz Tholeiite "A". [B] Alkali Olivine Basalt. Vertical lines labeled 0.9, 1.7, etc. give calculated volume ratio of garnet to pyroxene.

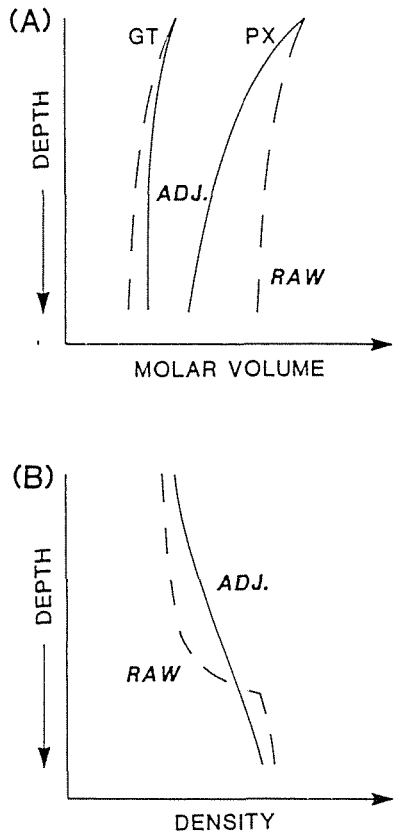

Fig. 3. Schematic representation of: [A] volume change for pyroxene-garnet transition as a function of depth for initial (RAW) and adjusted (ADJ.) data base, [B] density as a function of depth across the eclogite-garnetite transition for initial (RAW) and adjusted (ADJ.) data base.

Conclusions

We conclude that phase equilibrium data provide a strong constraint upon the volume change of reaction as a function of pressure for the eclogite-garnetite transition. The available data require the volume change to be substantially smaller at high pressures than at zero pressure (Figure 3A). Whereas a less pressure-

dependent volume change of reaction would permit the occurrence of a sharp pyroxene-garnet transition, this form of the volume change requires a smooth transition from pyroxene to majorite (Figure 3B), exhibiting no discontinuity in bulk sound velocity over the pressure range 110 to 230 kbar and producing a curvature of $\phi^{\frac{1}{2}}$ versus P which is in the opposite sense to that of PREM. It seems probable, therefore, that the eclogite-garnetite transition is not a satisfactory model for the 400 km seismic discontinuity. We would be able to assert this conclusion more strongly if the experimental data had convincingly demonstrated equilibrium by "reversibility" [Fyfe, 1960] of the pyroxene-garnet miscibility gap.

Acknowledgements. We would like to thank Masaki Akaogi for kindly providing us with experimental data on the $Ca_{1.5}Mg_{1.5}Al_2Si_3O_{12}$-$Ca_2Mg_2Si_4O_{12}$ join from his thesis and Seth Stein for helpful discussions of the seismological data. This material is based upon work supported under a National Science Foundation Graduate Fellowship (C.R.B.).

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(Received July 20, 1984;
accepted August 15, 1984.)