Gabbro-Eclogite Reaction Rate and Its Geophysical Significance

THOMAS J. AHRENS

Seismological Laboratory, California Institute of Technology
Pasadena, California 91109

GERALD SCHUBERT

Department of Planetary and Space Science, University of California
Los Angeles, California 90024

The gabbro–garnet granulite–eclogite transformation may play a significant role in driving the motions of terrestrial lithospheric plates. Whether or not this transformation is in fact important as a driving mechanism for plate tectonics depends on the relationship of the reaction time to geologic time. Solid state diffusion under completely dry conditions is investigated as a possible model for the gabbro-eclogite reaction, with the result that it could not produce the transition in geologically meaningful times at temperatures less than circa 600°–800°C in the earth's upper mantle. Other reaction mechanisms must exist for the geologically rapid occurrence of the phase change at lower temperatures. It is found that one of these mechanisms can be grain interstitial diffusion in a mantle with minute amounts of water. In this model, dissolved ions migrate through water films surrounding mineral grains to sites of reaction. A water-undersaturated mantle contains a small quantity of hydrous phases, such as chlorite, amphibole, or talc, the presence of which implies that interstices within the rock can contain water in equilibrium with these minerals and at a pressure P_{H_2O} which is less than the pressure in the rock. Implicit then is the presence of other gases and/or structural rock integrity. This P_{H_2O} is calculated for serpentine, tremolite, and talc as a function of temperature and rock pressure. Various pertinent cations are sufficiently mobile in aqueous solution that at high temperature and high pressure, diffusion through water will not significantly slow the reaction. Rather, pressure-induced solubility of ions in this water vapor is the important rate-limiting process in the model. Rock pressure and temperature must be such as to generate at least ~ 0.5–1 kbar of P_{H_2O} in the presence of the hydrous phases for geologically short reaction times. Under ambient conditions P_{H_2O} is quite small, the cations are relatively insoluble, and the reaction time is geologically long. Upon subduction of a basaltic upper crust or lithosphere, for example, an increase in P_{H_2O} occurs, and with increasing pressure the mineral solubility in this supercritical water increases dramatically, yielding geologically short reaction times; for example, ~ 20 m.y. for chlorite-containing rocks with $\sim 10^{-5}$-cm film thickness for ion diffusion at depths of ~ 15–30 km and at temperatures of $\sim 150°$–300°C for different heating models of the descending slab. For gabbros in which amphibole (tremolite)–pyroxene equilibria buffer the partial pressure of water, depths of ~ 55–70 km and temperatures of $400°$–550°C are required for rapid eclogitization, again for different slab heating models. Thus contrary to previous suggestions, the gabbro-eclogite transformation, as it probably occurs in the descending or spreading lithosphere, is not simply rate-controlled by temperature but depends heavily on pressure and on the nature of the minor hydrous minerals present.

INTRODUCTION AND BACKGROUND

It has been observed that with increasing pressure at high temperature ($\sim 800°$ to 1200°C) a gabbroic mixture (pyroxene and plagioclase, with or without olivine, quartz, and spinel) with a density of 2.9–3.1 g/cm³ reacts, starting at 10–15 kbar, and forms a garnet granulite (garnet, pyroxene, and plagioclase) with a density between 3.2 and 3.3 g/cm³. At still higher pressure (15–30 kbar), depending on specific composition, an eclogite assemblage (garnet and pyroxene) with a density in the range 3.4–3.5 g/cm³ forms.

There have been numerous speculations regarding the role of this gabbro–garnet granulite–eclogite phase transformation in a number of phenomena in the earth's interior. *Ito and Kennedy* [1971] and *Kennedy and Ito* [1972] on the basis of their claim of fairly sharp increases in density at the onsets of the gabbro–garnet granulite and garnet granulite–eclogite transitions have recently modified the original phase change interpretation of the Mohorovicic discontinuity [*Lovering*, 1958; *Kennedy*, 1959]. They suggest that the discontinuity in seismic P wave velocity from 7.5 to 8.2 km/s found at depths of about 50 km under continental areas which have undergone recent

vertical movement and at depths of about 20 km under certain ocean rises may represent the equilibrium phase boundary between garnet granulite and eclogite [*Ito and Kennedy*, 1970]. Also they propose that the shallower seismic P wave velocity discontinuity of 6.5–7.5 km/s may map a rate process boundary that is an approximate isotherm along which the temperature is sufficiently high ($\sim 400°$C) that recrystallization of metastable gabbro to the stable garnet granulite occurs.

Ringwood and Green [1966] in spite of their objections to a worldwide gabbro-eclogite M discontinuity suggested that in areas of high heat flow and presumably of high temperatures at the base of the crust, as occur in tectonic provinces, the gabbro-eclogite transition could explain the often gradational Moho observed in these regions. They also speculated that piles of basalt and gabbro formed at continental margins in the initial stages of orogeny would subsequently transform to eclogite and sink into the underlying mantle, triggering the orogenic epic and eventually resulting in continental accretion. A second related hypothesis proposed by *Ringwood and Green* [1966] (see also *Schubert and Turcotte* [1972]) is that gabbro in the oceanic crust undergoes thermally activated transformation to eclogite upon descending into the mantle at an island arc subduction zone. The gravitational body force associated with this relatively cool and dense eclogitic layer provides all

or part of the driving mechanism for the mantle flow field associated with plate tectonics. The gabbro-eclogite transformation then takes place in the upper ~300 km of the subduction zone. At greater depths the downward body forces accompanying the lower transition of α-(Mg, Fe)$_2$SiO$_4$ to the β and γ phase have recently been described by Turcotte and Schubert [1971].

Press [1969] has suggested that as the basalts and gabbros which may be produced at depth under midocean ridges move laterally away from the ridge, carried by the horizontal motion of the lithosphere below, transformation to eclogite could occur upon cooling. The resulting gravitationally unstable lithosphere would then readily sink at an island arc subduction zone. This idea calls for the gabbro-eclogite transformation to occur during cooling at relatively constant pressure, whereas the Ringwood and Green [1966] and Schubert and Turcotte [1972] suggestion, although similar in some respects, envisions the phase change taking place upon heating with increasing pressure. A further significant distinction between the Press [1969] and Ringwood and Green [1966] and Schubert and Turcotte [1972] mechanisms is that the former invokes an eclogite suboceanic lithosphere, while the latter refer only to the gabbro-eclogite phase change in the oceanic crust known to be of basaltic composition. We emphasize that the phase change densification of only the subducting oceanic crust, should it occur at sufficiently shallow depth in the mantle, could provide a downward body force in the lithosphere comparable to that of thermal contraction of the entire descending lithosphere or to that associated with the elevation of the olivine-spinel phase boundary [Turcotte and Schubert, 1971].

Proper evaluation of these proposals requires knowledge of the pressure-temperature stability field of the transformation, its rate of reaction, and either the nature of the variations in the geotherm or the heating or cooling rates of material elements. Extensive experimental investigations have delineated the equilibrium stability field of the phase change at relatively high temperatures and pressures [e.g., Boyd and England, 1959; Yoder and Tilley, 1962; Ringwood and Green, 1966; Green and Ringwood, 1967; Cohen et al., 1967; Ito and Kennedy, 1970, 1971; Green and Ringwood, 1972; Kennedy and Ito, 1972], and although extrapolation of the experimental data to lower temperatures and pressures is still a controversial issue [Green and Ringwood, 1972; Kennedy and Ito, 1972], our knowledge of the equilibrium stability field is adequate for evaluation of the role of the reaction in many geophysical processes. However, the same cannot be said of our knowledge of the reaction rate; aside from approximate estimates of the reaction times at two temperatures in a single experiment [Ito and Kennedy, 1971], no data on the reaction rate are available. Unfortunately, our lack of knowledge of reaction rates is the most serious limiting factor in our assessment of the importance of the gabbro-eclogite transformation in many phenomena.

As an example, consider the gabbro-eclogite transformation in the descending crust. According to the pressure-temperature stability diagram of Figure 1 and the shear stress heating curves for crustal elements [Turcotte and Schubert, 1973] (shown in Figure 9, for example), a layer of crustal basalt and gabbro attached to the upper surface of a lithospheric slab descending into the mantle will find itself in the stability field of eclogite at relatively shallow depth (notwithstanding the controversy over the extrapolation of the empirically determined stability fields to low temperature and pressure, this
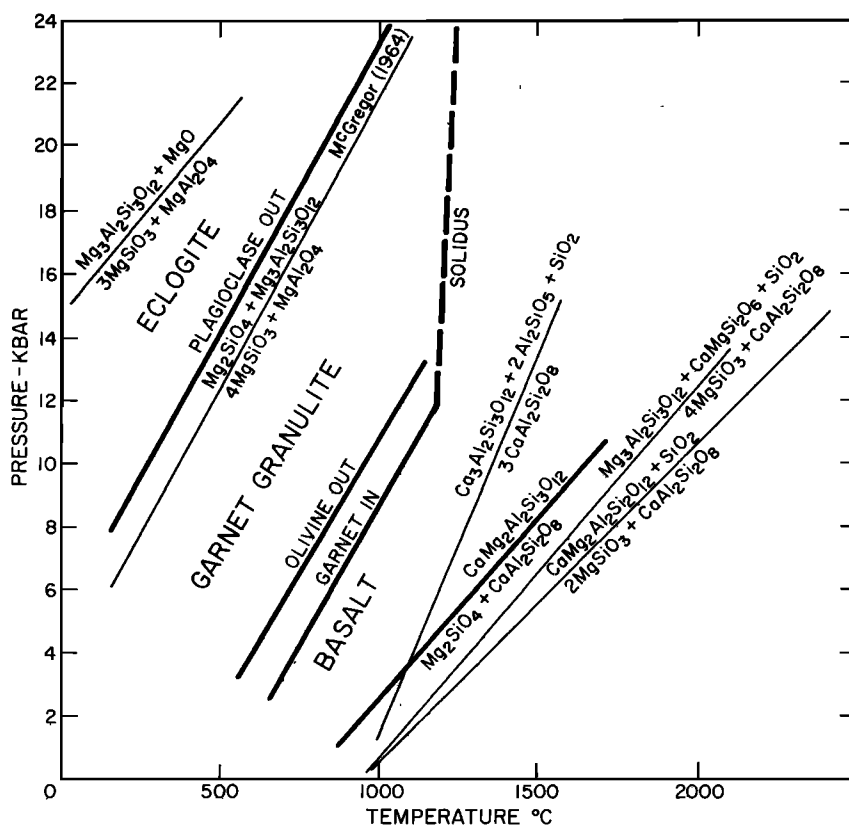

Fig. 1. Theoretical phase lines for garnet-forming reactions in Mg-rich pyroxene and olivine determined from thermochemical data of Robie and Waldbaum [1968] and Ahrens [1973]. Also shown is the experimentally determined phase line of the reaction enstatite + spinel = forsterite + pyrope [McGregor, 1964] together with the approximate range of the gabbro–garnet granulite–eclogite phase change.

depth will certainly be no more than 20–30 km). However, at these shallow depths the temperature of crustal elements will be less than about 200°C [*Turcotte and Schubert*, 1973], and the rate of reaction may be sufficiently slow for the gabbro to be metastable well into the eclogite stability field. The transition from gabbro to eclogite in the relatively cold descending crust is a rate-dominated process. The equilibrium phase diagram tells us only that the reaction may occur in the descending crust; rate processes determine whether or not the reaction will in fact take place.

In the present paper we hope to clarify the importance of the gabbro-eclogite transition to several processes in the earth's interior by better understanding the reaction rate of the transformation. This is accomplished by developing simplified microscopic models of the phase change which permit assessments of reaction times and their dependences on variables such as pressure, temperature, and grain size. Two basic models will be considered, one a solid state diffusion model for the transition under totally dry conditions and the other a model of diffusion through interstitial water vapor. The major conclusion we reach is that the transformation may occur via grain interstitial diffusion of ionic species if the gabbro-eclogite reaction is to occur on a geologically significant time scale at temperatures below $\sim 800°C$. The reaction rate, instead of being controlled by temperature as was commonly believed (recall the *Ringwood and Green* [1966] and *Schubert and Turcotte* [1972] proposal for thermally activated transformation in the descending crust, for example) is governed mainly by the generation of water vapor in equilibrium with hydrous mineral phases and the increase in ion solubility with pressure in the supercritical water.

CASE FOR SOLID STATE DIFFUSION

In examining the possible physical mechanisms which control the gabbro-eclogite transformation under dry conditions, solid state diffusion is a prime candidate since it is known to be experimentally difficult to form garnet granulite, or eclogite, at temperatures lower than about 800°C [*Ito and Kennedy*, 1971]. However, even at these temperatures with $Li_2B_4O_7$ as a fluxing agent, complete transformation in very fine grained starting materials was not achieved on a 1-week time scale. *Ito and Kennedy* [1971] reported that at 1200°C equilibrium was attained in approximately 5 min. From these data and the assumption that the reaction time is proportional to the exponential of the product of a constant and the reciprocal temperature (see (8)), they inferred that in geologic times of $10^6–10^7$ yr, recrystallization of gabbro to garnet granulite, or eclogite, should occur down to temperatures as low as about 400°C. At still lower temperatures, gabbro was inferred to remain metastable in the garnet granulite, or eclogite, fields for extremely long periods.

The solid state diffusion model of the gabbro-eclogite reaction considers the growth of garnet at the interface between crystals of olivine and plagioclase with the rate of reaction controlled by the diffusion of cations through the growing garnet crystal. Geologic examples of solid diffusion limited mineral formation may be provided by certain of the coronas or reaction rims in high-temperature metamorphic rocks. In the formation of certain of these metamorphic textures, coarse-grained anhydrous mineral assemblages in cooling from high temperature undergo reactions at grain boundaries resulting in the growth of new minerals which armor the primary ones and thus slow the diffusion-controlled reactions. A classic multilayered corona which occurs at the junction

of olivine and plagioclase in gabbroic rocks is described by *Spry* [1969] as follows. The successive rims in the compound corona are olivine-hypersthene-hornblende-garnet-plagioclase. The end members olivine and plagioclase apparently reacted under anhydrous metamorphic conditions to produce hypersthene and garnet, which were in part later transformed under hydrous conditions to hornblende. Figure 2 [from *Spry*, 1969] shows the approximate compositions of the successive rims in this complex layered corona. The mineral composition of each rim represents the chemical gradient formed by the migration of Fe^{++} and Mg^{++} outward from olivine and Ca^{++} and Al^{+3} outward from plagioclase. An example of a complex corona texture between olivine and plagioclase is shown in Figure 3 [from *Spry*, 1969].

We shall attempt by considering only one reaction to examine the diffusion processes in systems which realistically represent the more crucial of the 19 or so reactions which *Green and Ringwood* [1967] list as occurring in gabbros of various initial compositions upon transforming to eclogite. The reaction, which is most amenable to a simple analysis, is

$(Mg, Fe)_2SiO_4(olivine) + CaAl_2Si_2O_8(anorthite)$

$$\rightarrow (Mg, Fe)_2CaAl_2Si_4O_{12}(garnet) \quad (1)$$
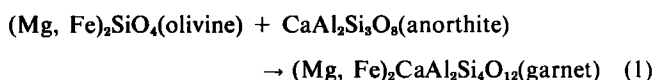
The theoretical phase lines for this reaction (assuming only the Mg end member) and other garnet-forming reactions for Mg-rich pyroxene and olivine together with the approximate range of the gabbro-eclogite phase change are shown in Figure 1. Thermochemical data selected from *Robie and Waldbaum* [1968] and *Ahrens* [1973] were used in the calculations. A point on the theoretical phase equilibrium line was found by iteratively determining values of temperature and pressure at which the free energies of the phases were identical. This point, together with the Clausius-Clapeyron relation, determines the theoretical phase line.

The simplicity of reaction (1) follows from the fact that it involves only three species, each having the same Si/O ratio. We assume that although the SiO_4^- tetrahedra are rearranged in reaction (1), they undergo no net transport. This assumption seems well justified, as recent data for O^- self-diffusion in forsterite [*Heuer et al.*, 1973] demonstrate very low diffusivities ($10^{-15}–10^{-14}$ cm²/s at 1400°–1500°C). Thus we assume that under dry conditions diffusion of such cations as Ca^{++}, Al^{+3},
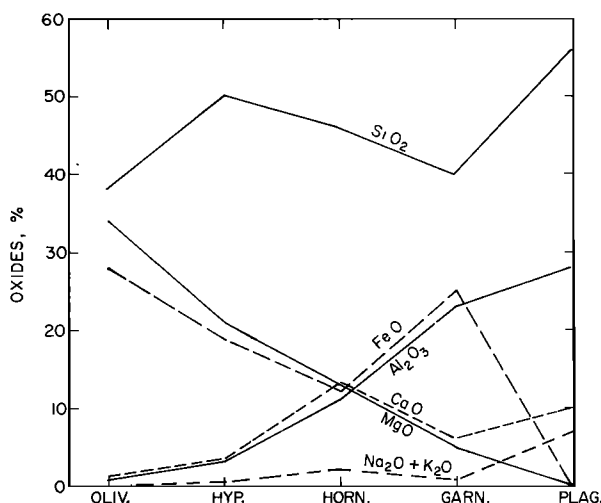

Fig. 2. Variation in composition of minerals in successive layers of a compound corona texture; from inside to outside: olivine, hypersthene, hornblende, garnet, and plagioclase [from *Spry*, 1969].

Fig. 3. Microphotograph of complex corona texture between olivine (center) and plagioclase (outside) of the type depicted in Figure 1 [from *Spry*, 1969].

Mg^{++}, and Fe^{++} will occur as suggested in Figure 4. Note, as in Figure 2, that the garnet forms between the olivine and plagioclase. Similar solid state diffusion-controlled reactions, which occur in the formation of spinels from the oxides, have been treated in detail by *Schmalzreid* [1969]. Other similar diffusion-controlled reactions have been studied for the growth of $SrAl_2O_4$ and $BaAl_2O_4$ (spinels) by *Iseki et al.* [1970], for $BiFeO_3$ (a perovskite) by *Mukherjee and Wang* [1970], for Al_2SiO_5 (mullite) by *Davis and Park* [1972], and for $CaZrO_3$ by *Augers et al.* [1972] all via solid state reaction from the oxides. For reaction (1), charge balance considerations at the interfaces imply that two moles of garnet form at the garnet-anorthite interface for each mole of garnet forming at the forsterite-garnet interface.

To relate diffusion constants to reaction rates, we have assumed that cation diffusion through a growing garnet crystal will limit its growth rate, because, of the three species participating in reaction (1), garnet is the densest and because, since garnet is forming in situ, it is likely to be relatively free from deformation-induced defects (and hence present a high impedance for diffusive transport). If F is the number of reaction-limiting cations diffusing across a growing garnet crystal per unit area per second, i.e., cation flux, then

$$F \propto DC/x \qquad (2)$$

where C is the number concentration of this ion in the species in which it originates, x is the thickness of the growing garnet crystal, and D is the coefficient of diffusion of this ion in garnet. Proportionality (2) assumes that the excess concentration of the reaction-limiting ion is linearly distributed over the garnet phase and that this concentration gradient drives the diffusion process. This assumption cannot be completely valid since
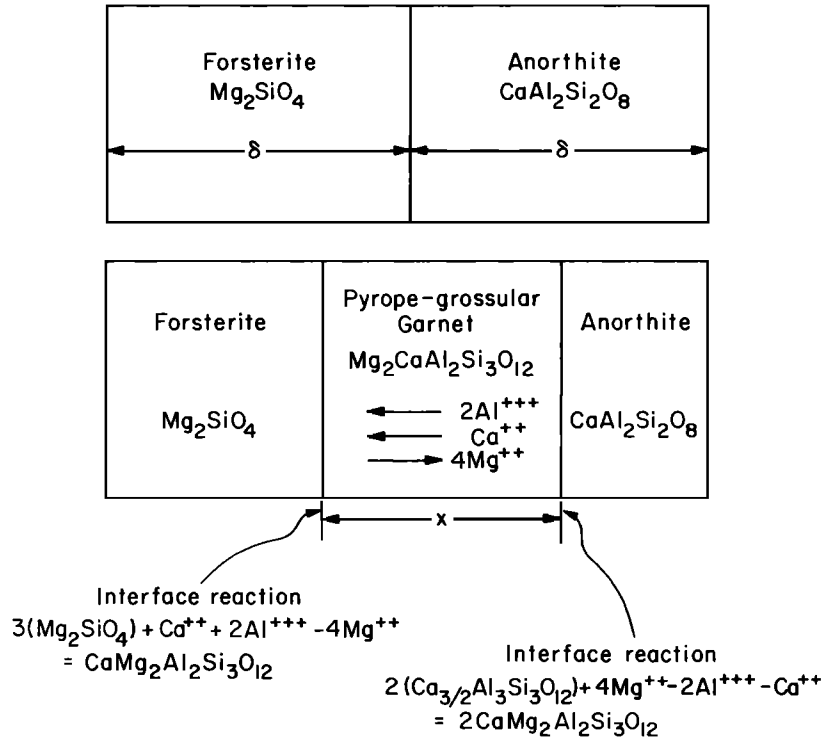
Forsterite
Mg_2SiO_4

Anorthite
$CaAl_2Si_2O_8$

$\longleftarrow$ δ $\longrightarrow$ $\longleftarrow$ δ $\longrightarrow$

Forsterite

Mg_2SiO_4

Pyrope-grossular
Garnet

$Mg_2CaAl_2Si_3O_{12}$

$\longleftarrow$ $2Al^{+++}$
$\longleftarrow$ Ca^{++}
$\longrightarrow$ $4Mg^{++}$

Anorthite

$CaAl_2Si_2O_8$

$\longleftarrow$ x $\longrightarrow$

Interface reaction
$3(Mg_2SiO_4) + Ca^{++} + 2Al^{+++} - 4Mg^{++}$
$= CaMg_2Al_2Si_3O_{12}$

Interface reaction
$2(Ca_{3/2}Al_3Si_3O_{12}) + 4Mg^{++} - 2Al^{+++} - Ca^{++}$
$= 2CaMg_2Al_2Si_3O_{12}$

Fig. 4. Solid state diffusion model for the formation of garnet in the reaction Mg_2SiO_4 (forsterite) + $CaAl_2Si_3O_8$ (anorthite) $\rightarrow$ $Mg_2CaAl_2Si_4O_{12}$ (garnet). The thickness of initial forsterite and anorthite grains is δ, and the thickness of the growing garnet region is x. The diffusion of the cations Al^{+++}, Ca^{++}, and Mg^{++} across the garnet region limits the rate of reaction.

we are also assuming that the reaction is taking place at close to but not precisely at conditions of thermodynamic equilibrium and hence that the free energy of the ions in the garnet is not quite equal to that in the other two species. The cation flux F is also related to the increase in thickness of the garnet region by

$$F \propto C_{ga}\dot{x} \qquad (3)$$

where C_{ga} is the concentration of the reaction-limiting ion in garnet and $\dot{x}$ is the time rate of change of the garnet crystal thickness. Equations (2) and (3) yield

$$x\dot{x} \propto D\frac{C}{C_{ga}} \qquad (4)$$

If δ is the grain size characteristic of the plagioclase and olivine, the volume fraction of garnet formed, Ψ, is

$$\Psi = x/2\delta \qquad (5)$$

Thus using (4) and (5), we find the transformation rate law

$$\Psi\dot{\Psi} \propto \frac{D}{4\delta^2}\frac{C}{C_{ga}} \qquad \Psi\dot{\Psi} = K_0\frac{D}{\delta^2} \qquad (6)$$

where K_0 is a constant taken as 1. If D were constant, integration of (6) would yield a reaction or growth law of the form

$$\Psi^2 \propto t \qquad (7)$$

where t is time. As pointed out by Jost [1960], this parabolic growth law is often experimentally observed in tarnishing and other interface reactions involving solids. This type of time dependence was explicitly observed by Augers et al. [1972] and Davis and Park [1972] upon growth of $CaZrO_3$ and Al_2SiO_5 at interfaces. The characteristic reaction time for the formation of garnet τ is

$$\tau \equiv \frac{\delta^2}{K_0 D} = \frac{\delta^2}{K_0 D_0 e^{-\Delta G/RT}} \equiv \tau_0 e^{A/T} \qquad (8)$$

where T is the temperature in degrees Kelvin, ΔG is the diffusion activation energy, R is the gas constant, A is $\Delta G/R$, D_0 is the diffusion frequency term, and τ_0 is δ^2/K_0D_0.

We now examine the values of τ_0 and A which are required to form garnet (eclogite) in lower crustal and upper mantle environments on time scales of 10^5-10^6 yr and 10^7-10^8 yr. These are of interest as they represent times required to transform gabbro to eclogite on tectonically significant distance scales of ~ 10-100 km and $\sim 10^3$-10^4 km, respectively, in the subducting oceanic crust [Ringwood and Green, 1966; Schubert and Turcotte, 1972] and in the suboceanic lithosphere as the latter moves away from an ocean ridge [Press, 1969; Forsyth and Press, 1971]. Equation (8) determines values of A as a function of τ_0 for which a reaction time τ would be achieved at a temperature T. Figure 5 shows A versus τ_0 for reaction times of 10^5 yr (solid lines) and 10^6 yr (dashed lines) at temperatures between 700° and 1200°K. For example, with $A = 3 \times 10^4$ °K and $\tau_0 = 10^{-2}$ s, the reaction time would be 10^5 yr at 900°K. The distance interval listed with each temperature is an approximate measure of the distance along the slip zone of a subducting slab at which that temperature is reached as a result of frictional heating [Turcotte and Schubert, 1973]. In addition, Figure 5 shows A versus τ_0 for a reaction time of 10^8 yr and temperatures of 700° and 800°K, appropriate to the movement of suboceanic lithosphere laterally away from a rise.

By comparing the plots of A versus τ_0 with values of these parameters inferred from the limited self-diffusion and binary diffusion data available for related materials and summarized in Table 1 (no explicit diffusion data exist for garnet), we can assess whether solid state diffusion is a mechanism capable of

TABLE 1. Solid State Diffusion Data

Diffusing Species	Host	Temperature Range of Data, °C	D_0, cm²/s	ΔG, kCal/mol	Source
Ca⁺⁺	α'-Ca₂SiO₄	1165–1514	0.036	65	Fyfe and Verhoogen [1958]
	α-Ca₂SiO₄	1165–1514	0.02	55	Fyfe and Verhoogen [1958]
	α-CaSiO₃	...	70,000	112	Fyfe and Verhoogen [1958]
	β-CaSiO₃	...	0.2	78	Lindner [1955]
	CaSi₂O₇	...	0.01	73	Lindner [1955]
	CaFe₂O₄	...	30.	86	Fyfe and Verhoogen [1958]
	CaO	...	0.4	81	Lindner [1955]
	CaO	1465–1760	11.75×10^{-5}	64.3	Kumer and Gupta [1969]
Mg⁺⁺-Fe⁺⁺*	(Mg, Fe)₂SiO₄	1000–1100	3.7×10^{-7}	28.8	Buening and Buseck [1973]†
	(Mg, Fe)₂SiO₄	900–1100	3.4×10^{-3}	47	Meisner [1972]‡
Ca⁺⁺	MgO	790–1850	8.9×10^{-4}	63.67	Wuensch and Vasilos [1968]
Mg⁺⁺	MgO	1400–1600	0.249	79.13	Wuensch and Vasilos [1968]
	MgAl₂O₄	...	200.	86.0	Lindner and Akerström [1958]
Fe⁺⁺	MgO	...	8.83×10^{-3}	41.75	Wuensch and Vasilos [1968]
	MgO	...	3.2×10^{-4}	41.99	Wuensch and Vasilos [1968]
Al⁺⁺⁺	Al₂O₃	...	27.54	114	Birchenall [1968]
Na⁺⁺	perthite	550	10^{-11}–10^{-12}§	...	Fyfe and Verhoogen [1958]
Na-K	KAl₂Si₃O₈-NaAl₂Si₃O₈	1020–1088	1.5×10^{19}	167	Fyfe and Verhoogen [1958]

* Interdiffusion of Fe⁺⁺-Mg⁺⁺ in olivine.
† Along C axis, $p(O_2) = 10^{-12}$ atm, 10 wt % Fe.
‡ Along C axis, 5 wt % Mg⁺⁺.
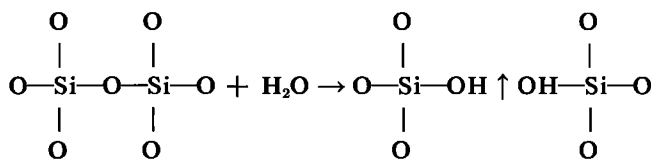§ Values given are the range of diffusion constants.

yielding the gabbro-eclogite transformation at temperatures and on time scales of interest. The values of r_0 and A shown in Figure 5 for various pertinent minerals are calculated for the grain size range which we believe describes oceanic gabbros and accompanying basalts, 0.1–1 cm. We think that the recent binary diffusion data for olivine [Meisner, 1973; Buening and Buseck, 1973] and the previous data for Al⁺⁺⁺ diffusion in Al₂O₃ [Paladino and Kingery, 1962] delineate the range of possibilities for garnet. (For the present purposes, we are neglecting the small decrease of diffusivity with compression.) Although activation energies for multicomponent diffusion in garnet could conceivably be as low as the 29 kcal/mol reported by Buening and Buseck [1973] below 1125°C in olivine, we infer from previous examination of complex diffusion systems [Cooper, 1965; Schmalzreid, 1969; Buckley, 1973] that the effective ternary diffusion constant for reaction (1) is more likely within one order of magnitude of the value of the diffusivities of the slowest moving species, in our case, Al⁺⁺⁺. The examples given by Buckley [1973] further suggest that the activation energy in the case of a binary system is also close to that of the slowest diffusing end member. (Since in ideal solutions the binary diffusion fluxes are, at thermodynamic equilibrium, linear combinations of end member self-diffusion fluxes, for the present purpose we have not differentiated between binary and self-diffusion data.)

The question of whether cation diffusion in a polycrystalline aggregate can be controlled (and presumably occur more rapidly) by surface diffusion processes has been examined by Paladino and Coble [1963] and Mistler and Coble [1971]. They conclude that cation-diffusion is usually independent of grain boundaries in ionic compounds although they point out that some exceptions do occur. In the case of Al₂O₃ they find that apparent self-diffusion coefficients (surface diffusion) for oxygen are greater than those for Al⁺⁺⁺ only in aggregates having crystallites smaller than 20 μ. We conclude that there are insufficient experimental data at present to assess the possible importance of solid state surface diffusion processes as they pertain to the basalt- or gabbro-eclogite reaction rate.

From Figure 5 we infer that if the effective bulk diffusion constant for the gabbro-eclogite transition is similar to that of

Al⁺⁺⁺ in Al₂O₃, solid state diffusion cannot produce the gabbro-eclogite transformation on the required time scale below ~900°C within the oceanic crust during subduction and within the suboceanic lithosphere as spreading from a ridge takes place. However, if diffusion activation energies of ~30 kcal/mol, such as those found for Mg⁺⁺-Fe⁺⁺ diffusion in olivines, are more typical of the diffusion constant associated with solid state growth of garnet (a possibility we believe to be less likely), then minimum gabbro-eclogite transformation temperatures of ~600°C are a possibility. However, the usual occurrence of strongly zoned metamorphic garnets in nature [e.g., Graham and Ahrens, 1973] strongly suggests that diffusion in garnet occurs very slowly at crustal temperatures.

Recent studies of the reactivity and sintering of silicates [Burte and Nicholson, 1972; Cutler, 1969] have demonstrated that recrystallization rates in a parabolic growth (7) can be enhanced by the presence of water vapor at low partial pressures (<1 atm). Although the rates seem to be controlled by bulk diffusion through silicate lattices, it appears that water vapor tends to react with the SiO₄⁻ bonds in the manner

$$\begin{array}{cccc} O & O & O & O \\ | & | & | & | \\ O-Si-O-Si-O + H_2O \to O-Si-OH \uparrow OH-Si-O \\ | & | & | & | \\ O & O & O & O \end{array}$$

and effectively provide a broken bridge (↑) in the lattice. According to Burte and Nicholson [1972], this type of reaction results in an effective O⁻ vacancy production, which in turn will enhance cation bulk diffusion via interstitial sites in the silicate lattice. A detailed model for this effect has not yet been proposed, although a similar mechanism has been discussed by Greenwood [1963] in his study of the synthesis of anthophyllite.

GRAIN INTERSTITIAL DIFFUSION

In the preceding section we have demonstrated that under totally dry conditions in the relatively cool down-going slab or in the spreading suboceanic lithosphere, solid state diffusion processes appear to be too slow to bring about the gabbro-eclogite transformation on the necessary time scale. If
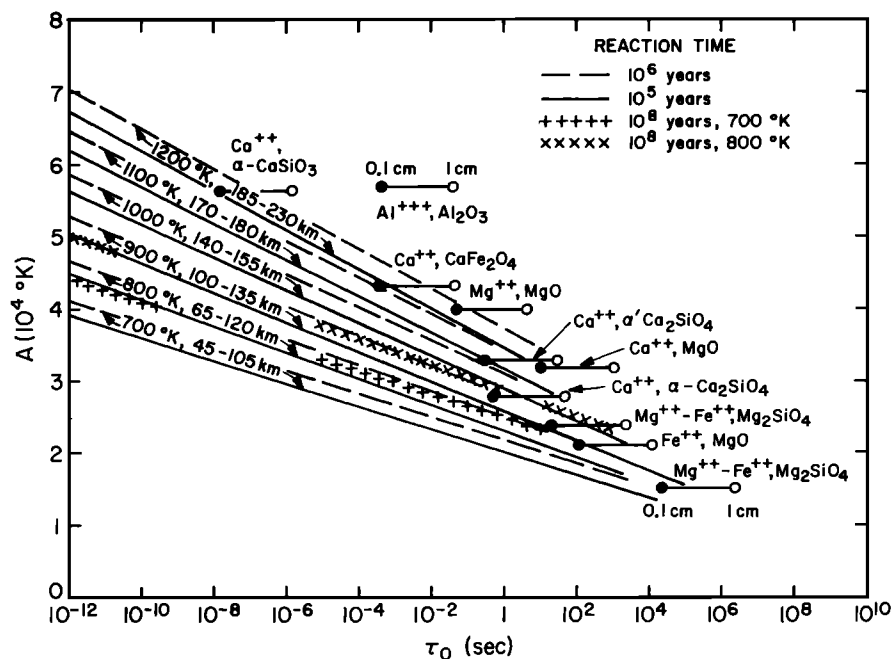
Fig. 5. Solid state diffusion activation energy $A = \Delta G/R$ versus diffusion frequency parameter $\tau_0 = \delta^2/K_0 D_0$ for gabbro-eclogite reaction times of 10^5, 10^6, and 10^8 yr at various temperatures. Distance intervals corresponding to a given temperature indicate the approximate distance along the slip zone of a subducting slab at which that temperature is reached via frictional heating. Also shown are values of A and τ_0 for 0.1- and 1.0-cm grain sizes inferred from measurements of self-diffusion in various minerals (Table 1).

minute amounts of water are present, the rate of reaction may be speeded up via the formation of vacancies as a result of broken Si—O⁻ structural bridges or through a transport mechanism that we refer to as grain interstitial diffusion. In this latter process, ions involved in the gabbro-eclogite transformation migrate through a thin film of interstitial water vapor to sites of garnet formation, as depicted in Figure 6.

It seems generally accepted that water is a minor constituent of the earth's crust [Ronov and Yaroshevsky, 1969; Vinogradov, 1967; Poldervaart, 1955], while studies of mantle-derived ultramafic nodules and rocks show that small amounts of phlogopite and amphibole are to be found in the upper mantle [Wyllie, 1971] and recently, still another water-bearing mineral, titanoclinohumite, has been identified as probably being derived from the mantle [McGetchin et al., 1970]. Very recently, Giardini et al. [1974] have found biotite as a primary inclusion in diamond. The thermal regime calculations by Turcotte and Schubert [1973] demonstrate that the portion of island arc andesitic volcanism over a subduction zone correlates well with the achievement of the solidus temperature ~1100°C in basaltic rocks containing small quantities of water. The work of Essene et al. [1970] on amphibole-containing basalts shows that if the water content is small, the eclogite stability remains similar to that of dry basalts over the range of pressures and temperatures studied in the dry systems. Wyllie [1970] has also noted that the presence of a small amount of water would probably not affect the phase relationships below the solidus. The effect of water vapor, possibly with some dissolved CO_2 or N_2, either in excess or in the undersaturated situation in vapor pressure equilibrium with the minerals serpentine [Kitahara et al., 1966], anthophyllite [Evans and Trommsdorf, 1970], amphiboles [Essene et al., 1970; Oxburgh, 1964; Kushiro et al., 1967], or micas [Allen et al., 1972; Modreski and Boettcher, 1973], which can exist to successively greater depths down to at least 100 km, is explored in the following section.

It is assumed that small quantities of water exist as part of an interstitial fluid, the other components of which may be CO_2 or N_2, and thus the H_2O vapor pressure (P_{H_2O}) may be less than the total pressure P_T. In general, the water will be above the 374°C and 221 bar critical point, at a pressure greater than (if it is in excess) or equal to the pressure of water in equilibrium with the existing minerals. The interstitial water is thus capable of transporting ions in solution. The effect of excess water on the equilibrium for the greenschist-amphibolite-eclogite transformation has been investigated by Essene et al. [1970] and Allen et al. [1972]. If the rocks of the lithosphere are water-saturated (an assumption which the laboratory data from the extreme lowering of melting intervals argue against [Hill and Boettcher, 1970]), the equilibrium transformation of amphibolite to eclogite will occur at considerably higher pressure than in the undersaturated basalt- or gabbro-eclogite system (Figure 7). In the water-saturated situation, transformation rates (schist, amphibolite-eclogite) are quite rapid, as is shown below.

According to the grain interstitial diffusion model, the gabbro-eclogite (or, if saturated, the greenschist, amphibolite-eclogite) transformation rate could be limited either by the ease with which ions can dissolve in the inter-
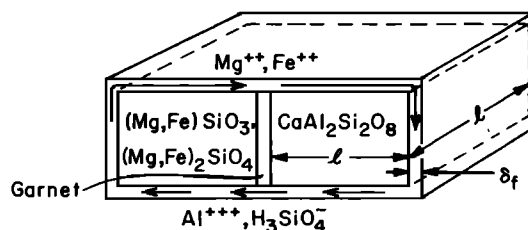

Fig. 6. Schematic of grain interstitial diffusion model for basalt-eclogite reaction. Cations dissolve in water of film thickness δ_f surrounding forsterite and anorthite grains of size l and diffuse to sites of garnet formation.
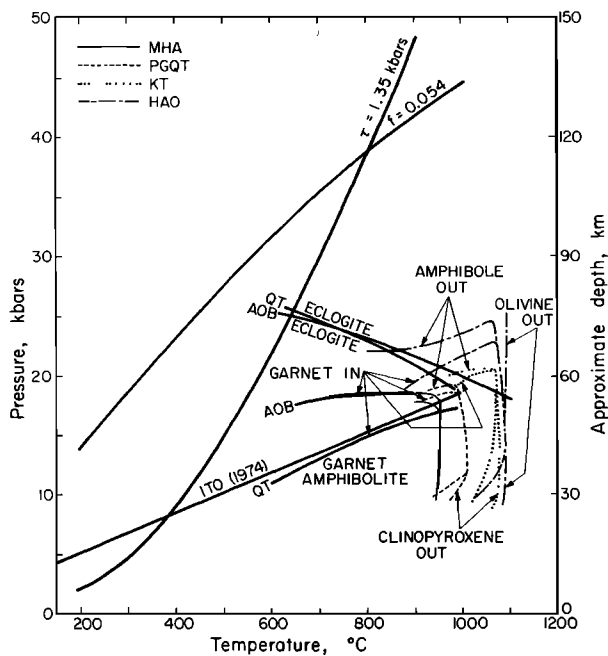
Fig. 7. Stability field of basic rocks containing amphibole, P_{H_2O} = P_T. At high pressures (18 to 25 kbar) various low-temperature (below 950°-1075°C) eclogites are formed. At higher temperatures, partial melting occurs. MHA, PGQT, KT, and HAO indicate Mount Hood andesite, Picture Gorge quartz tholeiite, 1921 Kilauea tholeiite, and Hualalai alkali olivine basalt [Allen et al., 1972], and QT and AOB approximate stability fields for quartz tholeiite and alkali olivine basalt [from Essene et al., 1970].

stitial water film or by their mobility in diffusion through the water. We consider each effect separately, first examining the effective diffusion constants if the pertinent ions needed to crystallize garnets were available in the interstitial fluid solution. Diffusion constants at ambient pressures and temperatures up to ~100°C for cations such as Na^+, K^+, and Ca^{++} are all of rather similar magnitude, varying from ~10^{-5} to 10^{-4} cm²/s [Longworth, 1972]. Walton [1960] has in fact shown that in the crust the molecular components of rocks, including silica, have, in aqueous solution, diffusivities of the order of 10^{-3}–10^{-4} cm²/s under a wide range of temperature and pressure. Were the ions required for the transformation of basalt to eclogite, from a simple picture such as that shown in Figure 6, present in sufficient concentration in a film of fluid surrounding each grain, then straightforward application of (8), with D (conservatively) varying from 10^{-4} to 10^{-5} cm²/s, would yield time constants of only ~3–30 days for 1-cm grains.

Under ordinary near-surface conditions, even when water participates in other silicate equilibrium reactions, the transformation rates are slow because the normal concentration of the necessary ions in the interstitial solution is far too low. An estimate of the concentration of ions participating in typical silicate reactions in a predominantly water interstitial fluid at standard conditions can be obtained by using the Garrels and Christ [1965] estimate of the standard free energy of the ion $H_3SiO_4^-$, in aqueous solution, of -286.8 kcal/mol. Straightforward application of the directly determined thermochemical data [Robie and Waldbaum, 1968] for solution and ionization of $MgSiO_3$, $CaAl_2Si_2O_8$, and Mg_2SiO_4 yields values of the Mg^{++} and Al^{+++} concentrations of ~1 × 10^{-5} mol/l and 2 × 10^{-13} mol/l, respectively. These values were calculated assuming the pH of seawater. For neutral water the above estimates must be increased by factors of ~4 and ~25,

respectively. The above concentration values imply unacceptably long reaction times.

In contrast to near-surface conditions, in a water-saturated system at depth, eclogite forms above 19 ± 7 kbar (Figure 7). At this pressure, Figure 13 demonstrates that ion solubility is sufficiently great that the amphibolite-eclogite transition will occur rapidly.

Since ample evidence exists that some water-bearing minerals are present in virtually all mantle-derived rocks and since melting data for water-saturated basaltic compositions indicate that it is unlikely that the lithospheric rocks are fully water-saturated, it is important to consider the conditions in unsaturated rocks which are required to enhance the reaction rates associated with the gabbro-eclogite transformation. For water vapor to exist inside voids within minerals or along grain boundaries and yet not be in excess requires either that another fluid phase(s) be present, such that the partial pressure of the other phase(s) plus P_{H_2O} is equal to P_T, or that $P_{H_2O} < P_T$ and that the rock be able to support kilobar-level stress differences over a grain size distance scale. Although it has long been believed that the small openings in samples of crustal and mantle rocks are a superficial effect, recent observations of equant pores in crustal rocks [e.g., Brace et al., 1972], in crustal pyroxene in eclogite [Champness et al., 1974], and olivine from diamond pipes [Green, 1972] demonstrate that small openings can in fact exist within deeply buried rocks. From the observations of openings within pyroxenes, Champness et al. [1974] suggest that in the crust, eclogites might crystallize at low temperature as a result of ion transport in a fluid phase. These authors carried out microprobe analyses for a trace of chlorine in these holes (possibly from connate seawater) but found none. They suggested instead that where a melange of ocean floor material, including sediment, is subducted, sufficient quantities of N_2 may be trapped, such that

$$P_{fluid} = P_{N_2} + P_{H_2O} + P_{CO_2} \cdots \simeq P_T$$

In this case even though the partial pressure of water is low, it may be sufficient to provide the high-diffusivity medium needed to produce the gabbro-eclogite transformation at low temperatures within geologically significant time scales.
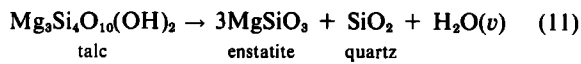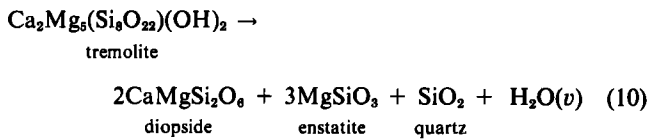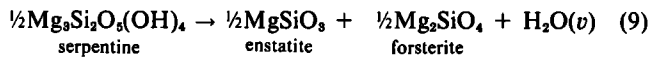
VAPOR PRESSURE OF HYDROUS MINERALS

Of major concern in recent studies of the stability of hydrous minerals such as serpentine, chlorite, tremolite, talc, and phlogopite at high temperatures and pressures has been their dehydration, which can then give rise to partial melting in the upper mantle. Our concern in the present paper is the vapor pressure associated with the suboceanic basaltic lithosphere both below the ocean floor and upon subduction into the mantle. Although it is likely that only a small percentage of hydrous phases are present in most of an undersaturated lithosphere, the presence of these hydrous phases, even if only in trace quantities, will give rise to a nonzero H_2O vapor pressure if either another gaseous phase (e.g., CO_2, N_2) is present or the grains within the rock can support kilobar stress differences over distances comparable to the grain size. Thus within each grain of a hydrous mineral, a low but nonnegligible P_{H_2O} will be present at temperatures below the dehydration temperature by the very existence of the hydrous mineral. (The value of P_{H_2O} will only equal the P_T at the temperature and pressure associated with dehydration, if no other gases are present.) The water vapor pressures associated

TABLE 2. Vapor Pressure in Kilobars for Serpentine, $Mg_3Si_2O_5(OH)_4$

Temper-	Total Pressure, kbar										
ature, °K	1	2.5	5	10	15	20	25	30	35	40	50
400				0.41	4.86	10.11	15.75	21.68			
500	0.14	0.22	0.37	2.89	7.68	12.74	18.54	24.43	30.60	37.01	50.24*
600	0.42	0.48	1.82	6.14	11.05	16.34	21.97	27.87	34.04	40.31*	
700	1.11*	2.11	4.02	8.39	13.32	18.59	24.18	30.01*	36.12*		
800				11.18*							

* Calculated vapor pressure exceeds total pressure, indicating H_2O is stable.

with the presence of serpentine, tremolite, and talc were calculated using the following reactions, which are taken to be typical for the spontaneous breakdown of each mineral below its dehydration temperature:

$$\tfrac{1}{2}Mg_3Si_2O_5(OH)_4 \rightarrow \tfrac{1}{2}MgSiO_3 + \tfrac{1}{2}Mg_2SiO_4 + H_2O(v) \quad (9)$$
serpentine   enstatite   forsterite

$$Ca_2Mg_5(Si_8O_{22})(OH)_2 \rightarrow$$
tremolite

$$2CaMgSi_2O_6 + 3MgSiO_3 + SiO_2 + H_2O(v) \quad (10)$$
diopside   enstatite   quartz

$$Mg_3Si_4O_{10}(OH)_2 \rightarrow 3MgSiO_3 + SiO_2 + H_2O(v) \quad (11)$$
talc   enstatite   quartz

These water vapor pressures are the osmotic equilibrium pressures of water associated with each of these minerals [Greenwood, 1961]. In the actual assemblages involved in the gabbro-eclogite transition, higher values of P_{H_2O} may occur. The vapor pressure P_{H_2O}, which we take to be the minimum value which can be associated with each of the above minerals, was numerically calculated using [Kern and Weisbrod, 1967]

$$\Delta G_T^0 = \int_{1\,bar}^{P_T} \Delta V_T^s \, dP + \int_{1\,bar}^{P_{H_2O}} V_{H_2O} \, dP \quad (12)$$

Here ΔG_T^0 is the difference in molar free energy of the mineral between the pressures P_T and 1 bar at temperature T, ΔV_T^s is the molar volume change of the solid phases between the pressures P and 1 bar at temperature T, and V_{H_2O} is the molar specific volume of water at pressure P and temperature T. Although ΔV_T^s is also a function of pressure, we have assumed the value at standard conditions [Robie and Waldbaum, 1968], largely because the equations of state of the hydrous minerals are so poorly known.

The results given in Tables 2, 3, and 4 and Figures 8–10 were obtained by using the high-temperature free energy data of Robie and Waldbaum [1968] with the exception of serpentine,

for which we used the data of King et al. [1967]. The value of the second integral was obtained from the tabulation of Helgeson and Kirkham [1974] below 10 kbar and by numerical integration using the equation of state tabulation for water given by Kennedy and Holser [1966] above 10 kbar.

It should be noted that in Figures 8–10 each line of constant vapor pressure intersects the dehydration reaction boundary at the point where $P_{H_2O} = P_T$. Similar calculations for the reactions forsterite + talc → enstatite + water and analcite → albite + nepheline + water at low pressures have been carried out by Yoder [1955] and Greenwood [1961]. Greenwood [1961] has derived a series of formulas which give the slope $(\partial P / \partial T)_{P_{H_2O}}$ and the curvature $(\partial^2 P / \partial T^2)_{P_{H_2O}}$ of the lines of constant P_{H_2O} at the point of intersection with the dehydration curve. The calculated dehydration boundary for reaction (9) (Figure 8) is virtually indistinguishable below 20 kbar from that for the reaction

$$Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \rightarrow 2Mg_2SiO_4 + H_2O \quad (13)$$
serpentine   brucite   forsterite
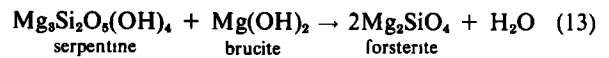
observed by Kitahara et al. [1966] also shown in the figure. Moreover, Evans and Trommsdorf [1972] have demonstrated that the conditions for the hydration of dunites are relatively insensitive to iron content. In the case of tremolite, the calculated dehydration boundary lies at ~100°C higher temperatures but has a shape similar to that computed earlier by Essene et al. [1970] on the basis of estimated thermodynamic properties for tremolite. As can be seen in Figure 10, the calculated stability field of talc plus diopside relative to tremolite is displaced at 6–7 kbar higher pressure (based on the Robie and Waldbaum [1968] compilation) than that obtained by Essene et al. [1970].

It should be noted that at temperatures below the dehydration temperature of serpentine the vapor pressure associated with serpentine (and probably also, because of its structural similarity, chlorite) is considerably greater than that of tremolite (or talc). Comparison of Figures 9 and 10 or Tables 3

TABLE 3. Vapor Pressure in Kilobars for Tremolite, $Ca_2Mg_5[Si_8O_{12}](OH)_2$

Temper-	Total Pressure, kbar											
ature, °K	1	2.5	5	10	15	20	25	30	35	40	50	60
400								0.59	7.57	15.45		
500							0.31	3.85	10.98	18.87	36.40	55.76
600					0.02	0.28	1.03	7.15	14.38	22.33	39.73	59.36
700				0.07	0.26	0.44	3.87	10.22	17.57	25.51	42.85	62.36*
800		0.03	0.11	0.26	0.41	1.74	6.96	13.61	21.07	29.10	46.47	66.26*
900	0.16	0.20	0.27	0.40	1.69	4.54	10.28	17.44	25.13	33.40	51.50*	
1000	0.30	0.33	0.39	0.55	2.79	7.51	13.96	21.39	29.30	37.76	57.41*	
1100	0.40	0.43	0.48	1.74	5.23	10.52	17.54	25.03	33.09	41.58*		

* Calculated vapor pressure exceeds total pressure, indicating H_2O is stable.

TABLE 4. Vapor Pressure in Kilobars for Talc, $Mg_3Si_4O_{10}(OH)_2$

Temper-ature, °K	Total Pressure, kbar											
	1.0	2.5	5	10	15	20	25	30	35	40	50	60
400								0.49	6.01	12.24		
500						0.06	0.40	4.03	9.74	16.00	29.72	44.66
600					0.19	0.39	2.76	7.76	13.63	19.93	33.74	48.59
700		0.02	0.10	0.25	0.40	1.60	6.14	11.57	17.55	23.95	37.73	52.68
800		0.23	0.29	0.41	1.07	4.84	9.75	15.42	21.57	28.07	41.90	57.30
900	0.34	0.38	0.43	0.92	3.84	8.22	13.63	19.59	22.93	32.62	46.94	63.57*
1000	0.46	0.49	0.87	3.03	6.84	11.76	17.59	23.76	30.24	37.13	52.40*	
1100	1.78*	2.41	3.81	7.55	12.49	18.24	24.31	30.72*				

* Calculated vapor pressure exceeds total pressure, indicating H_2O is stable.

and 4 demonstrates that the vapor pressures associated with talc and tremolite are similar. The considerably higher vapor pressure associated with serpentine or chlorite implies, as *Fry and Fyfe* [1969] have pointed out, that if eclogite forms in communication with other minerals, serpentine or chlorite generally would be expected to dehydrate in favor of forming amphibole (tremolite or talc if sufficient Ca exists in the system) at high pressures. Although some tremolite is formed associated with serpentine in the metamorphosed ultramafic rocks of the Alps, studies of the mineral assemblages present [*Evans and Trommsdorf*, 1970] demonstrate that talc and serpentine are not found in the same rocks. Although we are only considering three minerals, we would generally expect that if both olivine and pyroxene are present, a water-deficient system will tend to form amphibole at the expense of serpentine. Upon subduction at relatively low temperature, talc will form at pressures above ~25–30 kbar at the expense of serpen-

tine and probably chlorite. Thus we expect chlorite or serpentine to control the minimum P_{H_2O} only in the case of silica-poor rocks containing little pyroxene.

We conclude this section by estimating the reaction time for the interstitial diffusion mechanism, given the concentration of ionic species in the water containing fluid film. In our model, ionic transport takes place within a thin film of fluid (thickness δ_f) within and around each crystal grain along a length l, as shown in Figure 6. If pore fluid occupies a very small fraction of the rock volume, as is assumed here, the mass fraction of fluid m_f is given by

$$m_f = G \frac{\delta_f}{l} \frac{\rho_f}{\rho_r} \qquad (14)$$

where G is a geometrical factor, equal to 3 in the case of cube-shaped crystals, and ρ_f and ρ_r are the mass densities of the fluid and rock, respectively. Assuming that $G = 3$, $\delta_f = 10^{-5}$–10^{-6} cm, $l = 1$ cm, $\rho_f \sim 1$ g/cm^3, and $\rho_r \sim 3$ g/cm^3, we find $m_f = 10^{-5}$–10^{-6}. This value of m_f is certainly an overestimate, as it is unlikely that continuous fluid films surround every mineral grain. We feel that $\delta_f = 10^{-6}$ cm is probably a lower bound to film thickness, as this is ~100 interatomic spacings, and hence the fluid in any thinner film will no longer have the intrinsic transport properties of the bulk fluid. Thus a grain interstitial diffusion mechanism for the formation of eclogite from basalt or gabbro involves only a very small quantity of water, much less than that required to saturate the system.

The time t required to transport S moles of a solute a distance l through a tube of cross-sectional area q is [*Jost*, 1960]

$$t = Sl/DqC_0 \qquad (15)$$

where C_0 is the concentration of the diffusing species at the dissolving end of the tube and D is the diffusion constant, assumed independent of concentration. We consider (15) as only an approximate relation since the fluid is undoubtedly dissolving ions such as Mg^{++}, Fe^{++}, Al^{+++}, and Ca^{++} with coordinated water molecules everywhere around the crystal. With $q = l\delta_f$, (15) becomes $t = S/(DC_0\delta_f)$. For complete transformation of 1 cm^3 of basalt or gabbro to eclogite, $S = 0.02$ mol ($S \propto l^3$). If some transportation under standard conditions is possible, the time scale t may be calculated from (15) by using $D = 10^{-4}$ cm^2/s, $\delta_f = 10^{-6}$–10^{-5} cm, $C_0 = 10^{-8}$ mol/cm^3, and $S = 0.02$ mol. These values yield about 10^8–10^9 yr, which implies essentially no reaction on a tectonically meaningful time scale in agreement with geological observation. As will be discussed in the following section, the time scale can be markedly reduced, as C_0 is increased many orders of magnitude by increases in both pressure and temperature. We assume that the time required to dissolve the cations and establish the con-
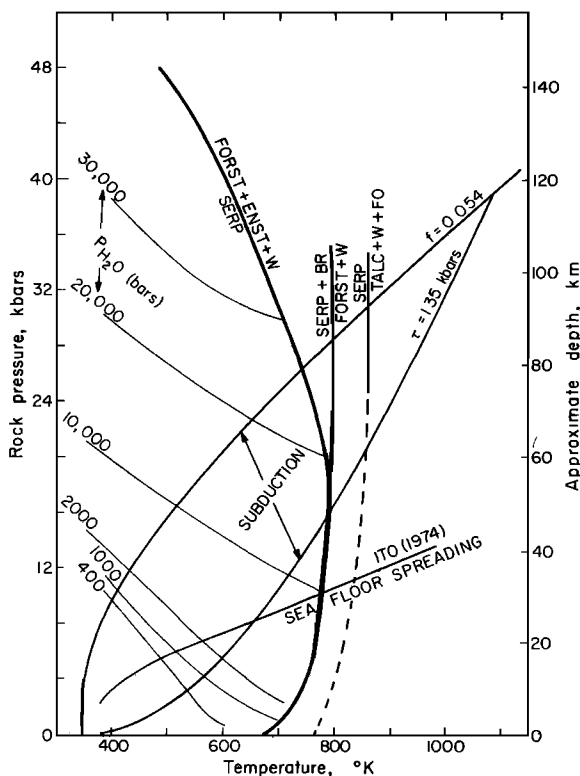

Fig. 8. Vapor pressure of H_2O associated with pure serpentine for spontaneous dehydration, according to reaction (9), as a function of temperature and total pressure. Possible thermodynamic paths for the top of the subducting lithosphere are shown as lines of constant τ and f [*Turcotte and Schubert*, 1973].

centration C_0 in the interstitial fluid is small, i.e., this time is not the rate-limiting step in the gabbro-eclogite reaction.

EFFECT OF PRESSURE AND TEMPERATURE ON SOLUBILITY AND DIFFUSION OF IONS

To estimate the effect of pressure p and temperature T on the diffusion constant D of ions in aqueous solution, we have assumed, following *Jost* [1960] and *Walton* [1960], that D could be inferred from the viscosity of the fluid η using the Stokes-Einstein equation

$$D = \frac{R}{6\pi N_A r_i} \frac{T}{\eta} \qquad (16)$$

where R is the gas constant, N_A is Avogadro's number, and r_i is the effective radius of the diffusing ion. The use of (16) is, of course, necessitated by the lack of direct experimental measurement of D at high pressures and temperatures, whereas data on the viscosity of water are available at pressures up to 1 kbar over a wide range of temperature and even to 10 kbar at temperatures below 100°C. We assume that the concentration of the diffusing ions is sufficiently low not to affect the properties of the fluid.

The dependence of viscosity on temperature and pressure is shown in Figure 11. The solid portions of the curves are based on experimental data, while the dashed parts are extrapolations to higher pressures. Viscosity data for compressed water and superheated steam in the temperature range 0°-700°C and for pressures between 1 and 800 bars are tabulated by *Kestin and Dipippo* [1972]. Measurements of viscosity of water for temperatures up to 900°C and pressures to 1 kbar have been reported by *Nagashima and Tanishita* [1969]. *Dudziak and Franck* [1966] have measured water viscosities for pressures as high as 3.5 kbar and temperatures up to 560°C. Finally, *Bett and Cappi* [1965] presented viscosity values for compressed liquid at temperatures up to 100°C and pressures to 10 kbar. All these data have been included in Figure 11. The compressed liquid viscosities (for $T = 100°$, $200°$, and $300°C$ in Figure 11) were extrapolated to higher pressures by noting that the measured viscosity values for the temperatures of 100°, 200°, and 300°C showed an essentially linear dependence on pressure. This linear dependence was assumed to apply at higher pressure for the viscosity curves at temperatures of 100°, 200°, and 300°C. For supercritical steam (temperatures 400°-900°C in Figure 11), the viscosities were extrapolated to high pressure by assuming the validity of the correlation given by *Kestin and Dipippo* [1972]. This correlation is strictly applicable only for 375°C < T < 700°C and 1 bar < p < 800 bars. Use of the correlation required knowledge of the density of supercritical steam at the relevant pressures and temperatures [*Kennedy*, 1950; *Rice and Walsh*, 1957; *Kennedy and Keeler*, 1972].

Walton [1960] has noted that better agreement with experimental results is obtained if the 6π in (16) is replaced by 4π. With this change, (16) may be rewritten as

$$Dr_i = (1.1 \times 10^{-17} \, \text{erg/°K})T/\eta \qquad (17)$$

Figure 12 shows the product Dr_i obtained from (17) and the data of Figure 11 as a function of pressure with temperature as a parameter. This is a useful intermediate step since the diffusion coefficient for different ions is then readily obtainable. Since r_i is of the order of an angstrom unit, the diffusion coefficients of various cations will vary between about 10^{-3} and 10^{-4} cm²/s over a wide range of geologic conditions, a conclusion already reached by *Walton* [1960]. As can be seen from Figure 12, the diffusion constant characteristic of supercritical water
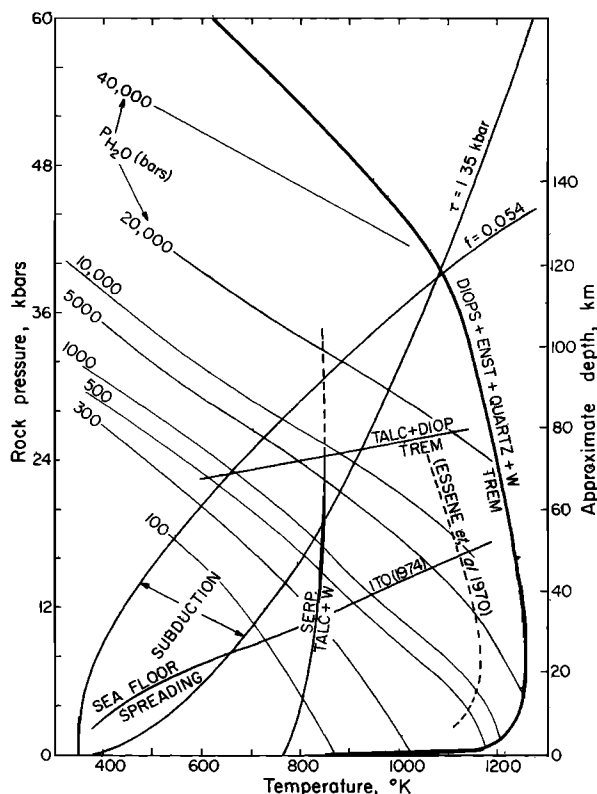
Fig. 9. Vapor pressure of H_2O associated with pure tremolite for spontaneous dehydration, according to reaction (10), as a function of temperature and total pressure. Possible thermodynamic paths for the top of the subducting lithosphere are shown as lines of constant τ and f [*Turcotte and Schubert*, 1973].
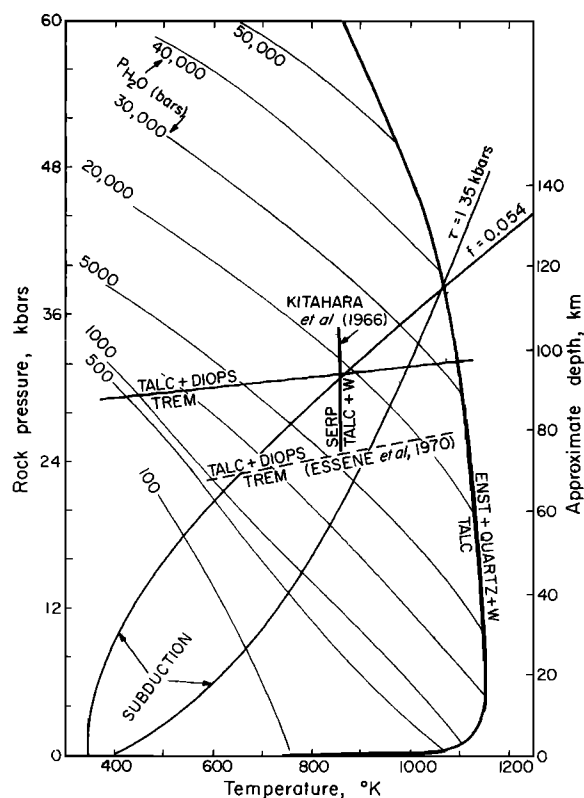
Fig. 10. Vapor pressure of H_2O associated with pure talc for spontaneous dehydration, according to reaction (11), as a function of total pressure. Possible thermodynamic paths for the top of the subducting lithosphere are shown as lines of constant τ and f [*Turcotte and Schubert*, 1973].
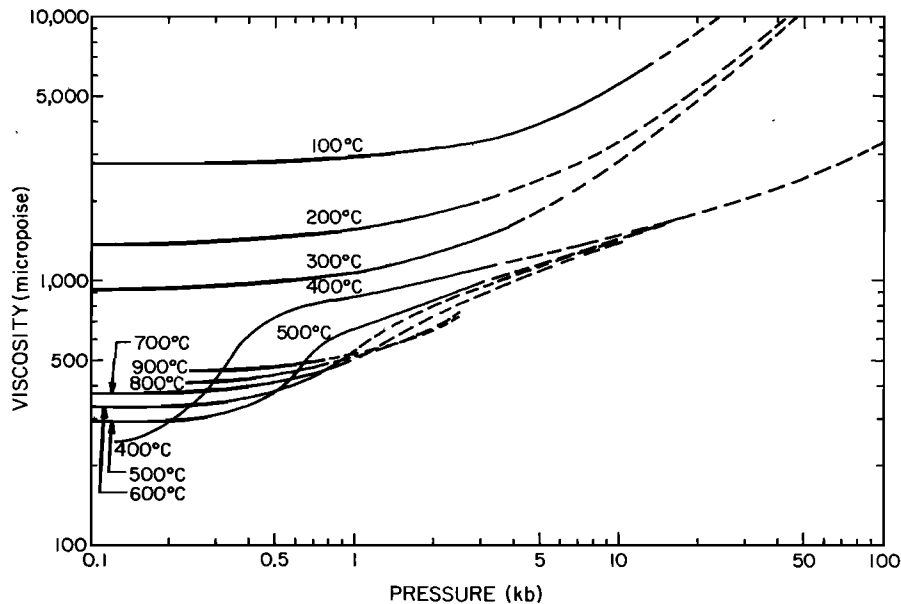
Fig. 11. Experimental viscosity data (solid portions of curves) for compressed liquid and superheated steam as a function of pressure p with temperature T as a parameter. Extrapolations to higher pressures are indicated by dashed parts of the curves. Data were obtained from *Kestin and Dipippo* [1972], *Nagashima and Tanishita* [1969], *Dudziak and Franck* [1966], and *Bett and Cappi* [1965].

above 400°C may vary even less than an order of magnitude, from a depth of perhaps 3 km to several hundred kilometers in the mantle. Effective ionic radii for cations in hydrothermal solution are typically in the range 2 Å for Na^+ to ~4.5 Å for Al^{3+} [*Garrels and Christ*, 1965].

In contrast to the effective diffusion constant, although pertinent data are less abundant, the concentration of the diffusing species in supercritical water is strongly dependent on pressure and to a lesser degree on temperature. This effect, which strongly controls grain interstitial diffusion and hence transformation of gabbro to eclogite in the lower crust and upper mantle, has not been previously recognized. The data of *Morey and Hesselgesser* [1951] and *Kennedy et al.* [1962] for

Fig. 12. The product of diffusion constant D and ionic radius r_i for ions diffusing through compressed liquid and superheated steam as a function of pressure at various temperatures. The dependence of Dr_i on temperature and pressure has been determined from the Stokes-Einstein relation between Dr_i and viscosity and the dependence of viscosity on temperature and pressure (Figure 11).

the amount of the equivalent oxide dissolved in supercritical water are summarized in Figure 13. These data should represent an upper bound to the ion concentration (we have not attempted to calculate the appropriate aqueous dissociation reactions, although in principle it is possible to do so [*Helgeson and Kirkham*, 1974]). It can be seen that silica, either from SiO_2 crystal or from feldspar or pyroxene, is about an order of magnitude more soluble than the other oxides. The single datum for the solubility of Al_2O_3 (corundum) suggests that this oxide is less soluble in pure form than when the source is a feldspar, probably because of the lack of highly ionic readily soluble associated cations. When extrapolated to 1 bar, these data are not inconsistent with the very low solubilities under standard conditions inferred in the previous section. The data of Figure 13 indicate a negligible dependence of solubility on temperature; they also suggest a power law dependence of solubility on pressure. The relation

$$C_0(mol/l) = 2.38 \times 10^{-12}(p(bars))^{2.7} \qquad (18)$$

should be approximately valid for the concentration of ions in equilibrium with feldspars and pyroxenes (and presumably also olivine) in the 1-30 kbar and 300°-1000°C range.

Finally, the gabbro-eclogite reaction time as a function of temperature and pressure, based on the grain interstitial diffusion model, can be calculated from (15), (17), (18), and Figure 11 with $q = l\delta$, $S = 0.02$ mol, $\delta_f = 10^{-5}$ and 10^{-6} cm, and $r_i = 0.5$ Å. Figure 14 shows the resultant partial pressure of water required to achieve transformation as a function of reaction time. The H_2O partial pressures accompanying traces of various hydrous minerals contained in or associated with basalts and gabbros, which were calculated in the preceding section, are applied to the reaction rate problem in a later section.
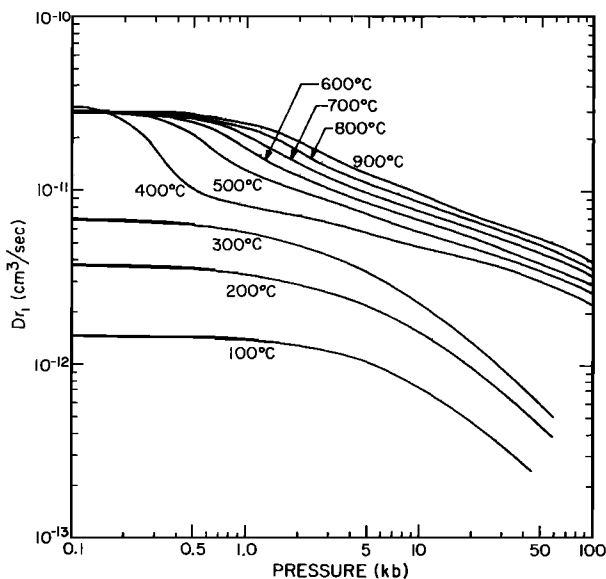
EFFECT OF CO_2 ON SOLUBILITY AND PHASE EQUILIBRIA

In this section we summarize the available data on the solubility of various cations in high pressure and high temperature H_2O-CO_2 mixtures and on the influence of CO_2
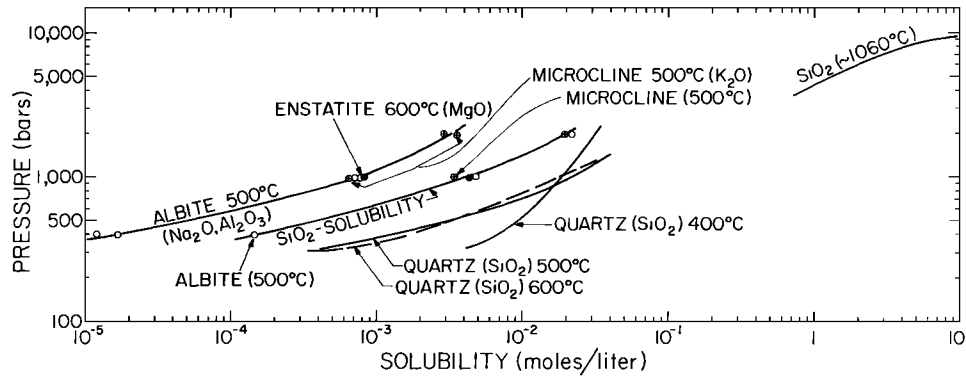
Fig. 13. Measured values of the solubility of a number of minerals in superheated steam at various pressures and temperatures. The solubility is strongly pressure-dependent and relatively insensitive to temperature. Data are from *Morey and Hesselgesser* [1951] and *Kennedy et al.* [1962].

on different mineral system phase equilibria. Table 5, from *Morey* [1957], shows that the addition of a small amount of CO_2 to superheated steam at 500°C and 1 kbar significantly increases the solubility of iron and tin oxides and $CaCO_3$ while it decreases the solubility of quartz. *Burnham* [1967] reported on the effects of 2 and 5 wt % CO_2 solutions on the composition of the aqueous phase in equilibrium with granite at 650°C and 6.0 kbar. The total solute content was considerably reduced below that in distilled water at the same temperature and pressure; the reduction in solute content was proportional to the percentage of CO_2. For the 5% CO_2 mixture the ratio of the concentration of Si to the concentration of Si in the pure aqueous phase was 0.55. A similar concentration reduction ratio for Al was 0.49, for K it was 0.28, and for Na it was 0.25. Calcium content in the 5% CO_2 mixture as compared with that in the pure H_2O phase was reduced even more than the Na content. *Burnham* [1967] pointed out that the effects of CO_2 on the solubilities of the alkalies K and Na as compared with the solubilities of Si and Al were consistent with the element distributions in contact metasomatic aureoles.

Shettel [1973] has published the most complete information on the solubility of quartz in H_2O-CO_2 mixtures at 5 kbar and 500°-900°C. Decreasing the fugacity of H_2O by dilution with

CO_2 exponentially decreases the Si solubility, a result of the value of the hydration number n in the reaction $SiO_2 + nH_2O \rightarrow SiO_2 \cdot nH_2O$. Values of n are 4.9, 4.4, and 4.5 at temperatures of 500°, 700°, and 900°C, respectively. At 700°C the solubility of SiO_2 is 2.35 wt % for pure H_2O, 0.5 wt % for $X_{H_2O} = 0.75$, and 0.1 wt % for $X_{H_2O} = 0.5$ [*Shettel*, 1973].

The compositions of fluid phase solutes in a basalt-water-carbon dioxide system consisting of 50 wt % of 1921 Kilauea basalt, 16% H_2O, and 34% CO_2 have been given by *Holloway* [1971] for temperatures of 800°, 900°, 1000°, and 1100°C. The total solute content was small, ranging from 0.5 to 2 wt %, the solute content tending to be proportional to fluid density and thus tending to decrease with increasing temperature and to increase with increasing pressure. SiO_2, Al_2O_3, and MgO constituted most of the solute, other oxides such as CaO, Na_2O, and TiO_2 also being present.

In addition to the influence of CO_2 on mineral solubility in superheated steam, the effect of CO_2 on the phase equilibria of minerals is clearly an important one for our study of the basalt-eclogite reaction. *Hill and Boettcher* [1970] have determined the solidus curves for basalt-H_2O and basalt-H_2O-CO_2 mixtures at pressures up to 30 kbar (Figure 15). The basalt-H_2O system contained 15% H_2O by weight, while the mixture with CO_2 had 50 mol % each of CO_2 and H_2O. Below 15 kbar the presence of CO_2 raises the solidus temperature as much as 100°C, while above this pressure the influence of CO_2 on solidus temperature is insignificant. *Hill and Boettcher* [1970] also demonstrated that plagioclase is stabilized at high pressure in the presence of CO_2. Above about 10 kbar, amphibole stability is also increased in the presence of CO_2 as a result of the reduction in H_2O activity with the addition of CO_2. *Holloway and Burnham* [1972] have also investigated the solidus and upper stabilities of plagioclase and amphibole in a basalt-H_2O-CO_2 system containing about 36 wt % H_2O and 64 wt % CO_2 in the fluid phase at pressures of 2, 5, and 8 kbar and temperatures between 800° and 1100°C. In comparison with the properties of a basalt-H_2O mixture, it was found that the
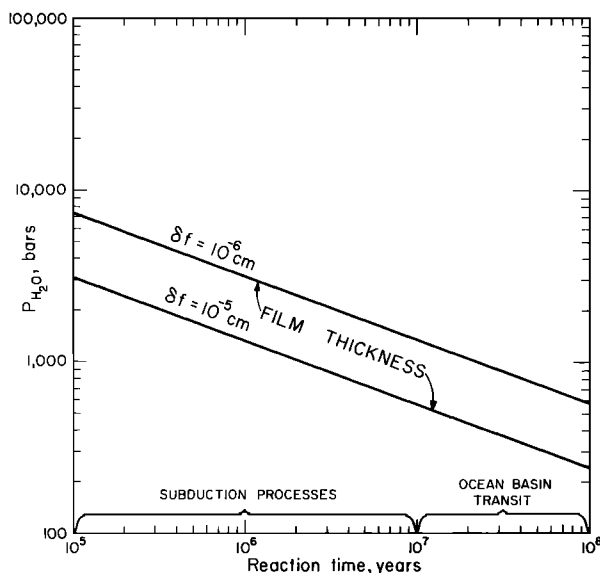

Fig. 14. Time scales for the gabbro-eclogite transition as a function of P_{H_2O} according to the grain interstitial diffusion model. Equation (15), with values of $D = 10^{-4}$ cm²/s, $S = 0.02$ mol, and C_0 given by (18), is used to construct the diagram.

TABLE 5. Solubilities in Parts per Million in Superheated Steam With About 7% CO_2 at 500°C and 1 Kilobar [After *Morey*, 1957]

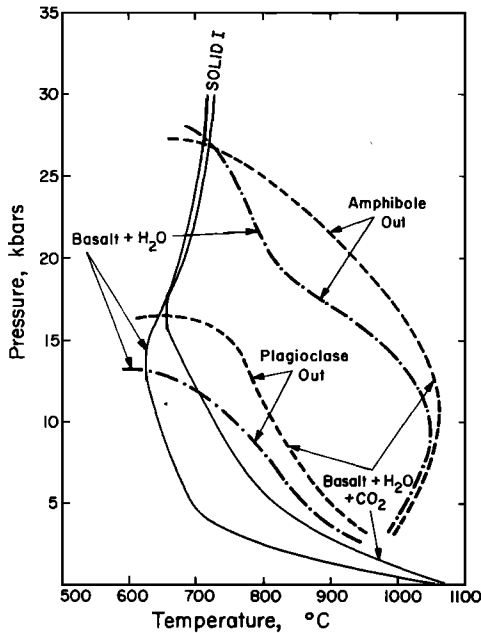|	Without CO_2	With CO_2
$CaCO_3$	120	940
Fe_2O_3	80	230
NiO	20	43
SnO_2	2	50
Quartz	26,000	19,000

Fig. 15. Effect of CO_2 on approximate phase diagram of vapor saturated basalt-water-carbon dioxide compositions [*Hill and Boettcher*, 1970].

solidus temperature and upper stability temperature of plagioclase were increased by about 100°C and the decomposition temperature of amphibole was increased by about 60°C.

For a peridotite (SiO_2 wt % 43.7–45.7, Al_2O_3 wt % 1.6–8.2, CaO wt % 0.7–8.1)–H_2O–CO_2 system, *Mysen and Boettcher* [1973] have studied the stability of amphibole at pressures from 7.5 to 30 kbar and for X_{H_2O} (mole fraction) between 0.25 and 1.0. Amphibole was stable up to temperatures of 1080°, 1100°, 950°, and 760°C at pressures of 7.5, 13, 23.5, and 20 kbar, respectively. Changing X_{H_2O} from 1.0 to 0.25 did not significantly affect the amphibole stability.

We conclude from the foregoing that although the presence of CO_2 modifies the phase diagrams and affects the ion solubility in superheated steam, the major role of CO_2 is to provide an additional fluid partial pressure so that water vapor may be present in undersaturated rock interstices.

APPLICATION OF THE GRAIN INTERSTITIAL DIFFUSION MODEL TO SUBDUCTION

We assume in the following that basaltic composition rocks of the uppermost lithosphere comprising the basement rock of the ocean floor are subducted and are in the process exposed to a thermodynamic path similar to the paths computed by *Turcotte and Schubert* [1973] and *Toksöz et al.* [1971]. The question as to how deep basaltic-type composition rocks extend into the mantle portion of the lithosphere, i.e., depths greater than ~12 km, in the form of granulite, or eclogite, has been the subject of several recent studies [*Forsyth and Press*, 1971; *Ito*, 1974] and remains to be definitively settled. However, there appears to be little doubt that the uppermost igneous rocks are basaltic. If, as we believe is likely, these rocks are undersaturated with respect to H_2O, we can apply the H_2O vapor pressure calculation for serpentine (assuming a similarity to chlorite), tremolite, and talc to give lower bounds on the time scale for the gabbro-eclogite transformation. In general, the presence of other major phases, and possibly extra but not excess water, will only tend to increase the vapor pressure and hence give faster reaction times. By only considering the above

three minerals we are tacitly assuming that the system contains sufficient water to have formed all the possible very low vapor pressure minerals such as phlogopite. We suspect that the breakdown reactions of such minerals as phlogopite and possibly titanoclinohumite will buffer the H_2O partial pressure at temperatures greater than ~1100°C and pressures of ~100 kbar, probably below regions in the subducting slab where both the gabbro-eclogite transition and possibly partial melting [*Turcotte and Schubert*, 1973] are occurring.

For rocks which are predominantly composed of olivine and plagioclase, with some chlorite representing the hydrous phase, Figure 8 demonstrates that upon subduction the minimum H_2O vapor pressure will be quite high. Along the constant shear τ and constant coefficient of friction f curves, vapor pressures of 1000 bars will be induced at depths of only 15 and 30 km, respectively. For 10^{-5}- and 10^{-6}-cm-thick films on the grains, vapor phase assisted diffusion can produce the gabbro-eclogite phase change on a time scale of ~2 and ~20 m.y., respectively. Vapor pressures of 2 kbar corresponding to reaction times of 300,000 yr to 3 m.y. are achieved at depths of ~15 and ~35 km for constant shear stress and constant friction coefficient models, respectively. Hence in a predominantly olivine-rich assemblage containing some water at temperatures below the high-pressure dehydration temperature of serpentine or chlorite, ~450°C (~775°K), the gabbro-eclogite transition, at least as far as the olivine components are concerned, will occur readily. At temperatures above the serpentine dehydration temperature, even more water will be available, and the system may behave like the saturated system (Figure 7) if sufficient pyroxenes are unavailable to form amphiboles. For the more usual pyroxene-rich assemblages, serpentine or chlorite dehydrates in favor of amphibole, and the vapor pressure in the rock will probably be controlled by amphibole (here modeled by tremolite, if sufficient Ca^{++} is present). In this case tremolite, or some similar mineral, controls the minimum vapor pressure until it breaks down in favor of such minerals as talc and diopside. (The vapor pressure in equilibrium with talc is virtually the same as that in equilibrium with tremolite.) In this case, 1000 bars·of water pressure is inferred to occur at depths of about 70 and 50 km, respectively, along the constant friction and constant shear stress paths. We recall that the characteristic reaction times are 2 and 20 m.y., respectively, for films 10^{-5} and 10^{-6} cm thick. Again as in the case of serpentine- or chlorite-controlled P_{H_2O}, these total pressures are well within the stability field of eclogite in a 'dry' system; however, the pressures required are comparable to the 15–20 kbar required to produce eclogite from a garnet amphibolite in a totally saturated system.

Approximate contours of constant reaction time for the upper 200 km of the mantle in the region of a descending slab are shown in Figure 16 for serpentine and tremolite, or talc, buffered H_2O vapor pressures. The temperature distribution given in Figure 16 is based on the calculations of *Turcotte and Schubert* [1973] and *Schubert et al.* [1974] for an angle of dip of 45° and a velocity of the plate approaching the trench equal to 8 cm/yr. Frictional heating on the upper surface of the descending slab raises the temperature along the slip zone until an assumed melt temperature of 1000°C is reached. The shear stress heating occurs under a constant coefficient of friction f = 0.054. The volcanic line is located directly above the point on the slip zone where melting first occurs. Behind the volcanic line beneath the region of anomalously high heat flow the temperature on the slip zone is buffered at the melt
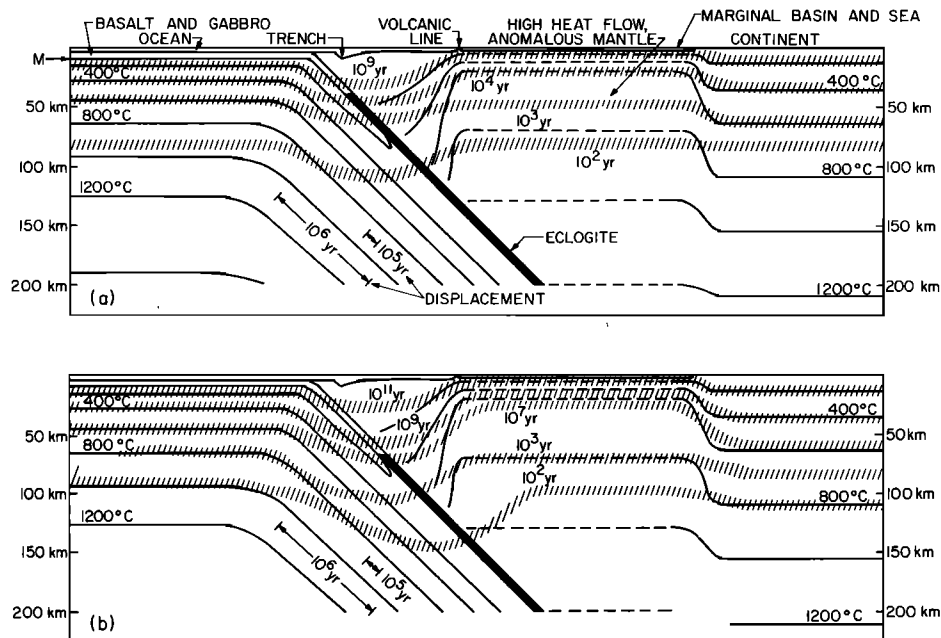
Fig. 16. Approximate contours of constant reaction time for the gabbro-eclogite phase change in a thermal model [*Turcotte and Schubert*, 1973; *Schubert et al.*, 1974] of the downgoing slab and the surrounding mantle with H_2O partial pressure buffered by (a) serpentine and (b) talc or tremolite.

temperature, which increases with pressure. The dashed isotherms above the descending slab in this region are only estimates of the temperature, since processes such as magma transport of heat may significantly influence the thermal structure. The continental geotherm is from *Froidevaux and Schubert* [1975], and the oceanic geotherm is from *Turcotte and Oxburgh* [1969].

Since the temperatures and pressures in the model of Figure 16 are completely known, the H_2O vapor partial pressure at any point in the mantle can be determined from Figure 8 for a serpentine- or chlorite-buffered system and from Figures 9 or 10 for a tremolite- or talc-controlled H_2O vapor pressure. For pressures and temperatures sufficiently high for dehydration of any of these minerals, we assume that $P_{H_2O} = P_{total}$ is the lithostatic pressure. Figure 14, with an assumed film thickness of 10^{-5} cm then yields the reaction times shown approximately by the hatched contours of Figure 16. In the serpentine- or chlorite-buffered situation for a gabbroic oceanic crust the grain interstitial model predicts change to eclogite at depths of around 30 km. In contrast, a depth of about 70 km is required for transformation of the oceanic gabbroic crust to eclogite in the talc- or tremolite-buffered system. If basalt or gabbro exists in the suboceanic lithosphere beneath the crust, it will transform to eclogite at depths indicated by the reaction time contours of Figure 16 according to our diffusion model.

The net gravitational body force on the descending slab is an important part of the driving force for plate motions [*McKenzie*, 1969]. *Schubert and Turcotte* [1971] and *Griggs* [1972] have discussed the downward body forces due to thermal contraction of the slab and the elevation of the olivine-spinel phase boundary; the force due to the olivine-spinel transition was estimated to be about a third of that due to thermal contraction [*Turcotte and Schubert*, 1971]. The gabbro-eclogite transition, even if confined only to the oceanic crust, also contributes importantly to the net downward body force on the slab. The downward body force per unit distance parallel to the trench and per unit depth, associated with the formation of eclogite, is $\Delta\rho \cdot g \cdot (t_c/\sin\theta)$, where $\Delta\rho$ is the density of eclogite minus the

density of the surrounding mantle, t_c is the crustal thickness, and θ is the angle of dip. With $\Delta\rho = 3.5$–3.3 g/cm^3, $t_c = 5$–10 km, and $\theta = 45°$, we find this gabbro-eclogite phase change associated body force per unit depth and trench length is about 0.2 kbar. *Schubert et al.* [1974] find about 0.5 kbar for the body force 'density' associated with thermal contraction. If the oceanic crust transforms to eclogite at a depth of 50 km in the descending slab, then the total downward body force per unit length of trench due to an eclogite crust extending down to 400-km depth is about 0.7×10^{16} dyn/cm. This is to be compared with the total downward body force per unit length of trench of about 10^{16} dyn/cm associated with the elevation of the 400-km olivine-spinel phase change in the descending slab, the downward body force of thermal contraction in the slab to a depth of 400 km of about 2×10^{16} dyn/cm, and the upward body force associated with the hypothetical depression of the 650-km spinel-oxide transition of approximately 0.3×10^{16} dyn/cm [*Schubert et al.*, 1974].

SUMMARY AND CONCLUSIONS

Our major objectives have been to estimate the reaction rate of the gabbro-eclogite phase change and to delineate where the reaction may occur in the basalts and gabbros of the oceanic crust upon subduction beneath island arcs and in any initial gabbroic constituent of the upper ~100 km of the oceanic lithosphere as it moves away from a ridge. In the case of transformation of the basaltic and gabbroic oceanic crust to eclogite upon subduction [*Ringwood and Green*, 1966; *Schubert and Turcotte*, 1972], times of the order of 10^5–10^6 yr are of interest since these correspond to distances along the slab of ~10–100 km for typical subduction rates. For the transformation of a possible gabbroic constituent of the oceanic lithosphere as it spreads from a ridge [*Press*, 1969; *Forsyth and Press*, 1971], the pertinent time scale is 10^7–10^8 yr. The smaller value corresponds to the approximate time required to produce the increase in lithospheric seismic velocity with distance from a spreading ridge, as observed at the ~50 m.y. line in the North Atlantic [*Hart and Press*, 1973]. The 10^8 yr value

is the approximate time required for an ocean basin transit of the moving suboceanic lithosphere.

On the basis of the laboratory diffusion data for oxides and silicates, we have examined the range of possible reaction times for transformation of gabbro to eclogite via the mechanism of solid state volume diffusion of cations such as Al^{+++}, Fe^{++}, Mg^{++}, and Ca^{++}. We conclude that the effective multicomponent diffusion constant is probably within an order of magnitude of the slowest moving species, which within garnet we infer to be Al^{+++}. Our results imply that formation of 0.1–1 cm crystals of garnet by solid state diffusion below 600°C in the upper 100 km of the subducting or spreading oceanic lithosphere is impossible on the time scales of interest. Considerable indirect evidence demonstrating that solid state diffusion disequilibrium in garnets can be maintained under metamorphic conditions for millions of years also stems from the typically gross variation in chemistry observed within a single garnet crystal from these environments [*Dudley*, 1969; *Graham and Ahrens*, 1973].

Upon considering the implications of the presence of interstitial superheated steam in the suboceanic crust and lithosphere, even in a quantity as small as 10^{-6} mass fraction, we conclude that eclogite can form relatively rapidly via the mechanism of interstitial diffusion. Evidence for the existence of water vapor in the suboceanic lithosphere stems from the chlorite- and amphibole-bearing igneous rocks which have been dredged from the ocean floor. Presumably a small fraction of the water is interstitial and probably at a lower pressure than that of the rock, being in vapor equilibrium with the minerals.

In the interstitial diffusion process, we envision ions such as Al^{+++}, Fe^{++}, Ca^{++}, Mn^{++}, Cr^{+++}, Fe^{+++} and $HSiO_4^-$ produced in the interstitial fluid upon solution of such minerals as olivine, pyroxene, plagioclase, and spinel. Upon transport of these ions through a layer of superheated steam, which can probably be as thin as 10^2 Å, deposition at sites of garnet crystallization occurs. We infer that although SiO_2 is more readily soluble in superheated steam than such oxides as Al_2O_3 and MgO, its transport is less important, as garnet will probably form upon minor rearrangement of SiO_4^- tetrahedra at sites of other minerals.

For the interstitial diffusion process, the time constant for complete reaction of gabbro to eclogite will in general depend upon the grain size of the minerals in the rock, the partial pressure of water, the diffusion constant of ions in the fluid, and the concentration of the ions in solution at the point in the fluid where these go into solution. Although we have explicitly taken into account the (relatively minor) variations of viscosity and hence the diffusion constant with pressure and temperature, both the increase of solubility with pressure in superheated steam and the partial pressure of H_2O which is available for ion transport turn out to be the two controlling parameters for interstitial diffusion rates. We infer from the limited pertinent solution data that once the temperature and pressure of the water triple point are achieved, temperature has only a minor effect on silicate solubility. The relatively large increase in the solubility of silicates with pressure could in principle be predicted on the basis of the marked increase with pressure in ionic electrical conductivity in water and D_2O [*Hamann and Linton*, 1966]. These authors have demonstrated that this arises from the large increase in the self-ionization of water with increasing pressure (in essence, the water acts as a strong acid at high pressure).

Turcotte and Schubert [1973] have shown that the frictional heating of the subducting oceanic lithosphere at trenches would produce an increase of temperature ΔT in time Δt for material at the top of the oceanic crust given by

$$\Delta T = 2u(\kappa\Delta t/\pi)^{1/2} \tau/k \qquad (19)$$

where κ is the thermal diffusivity, k is the thermal conductivity, u is the velocity of the subducting plate, and τ is the assumed constant shear stress acting along the top of the subducting crust. This increase of temperature with depth (or pressure) is shown in Figures 8–10 for a subduction angle of 45°, $u = 8$ cm/yr, $\kappa = 1.15 \times 10^{-2}$ cm²/s, $k = 10^{-2}$ cal/cm s °K, and $\tau = 1.35$ kbar. Also shown is the increase in temperature calculated under the assumption that the coefficient of friction along the shear zone is a constant ($f = 0.054$). By assuming that these temperature-pressure paths are typical of those to which oceanic lithosphere containing an uppermost gabbro composition layer is exposed upon subduction, it is possible to estimate the time scale required to complete the gabbro-eclogite transition for olivine- or pyroxene-rich rocks. By applying Figure 14 to infer the time required for transformation, we conclude that for chlorite-rich rocks with 10^{-5}-cm-thick grain boundaries, vapor phase assisted diffusion can occur on a time scale of ~2 m.y. at depths of only ~15 and ~30 km, respectively, for constant shear stress ($\tau = 1.35$ kbar) and constant friction coefficient ($f = 0.054$) models. The temperatures of the reaction are extremely low for these models, only 150° and 300°C, respectively. For rocks which are pyroxene-rich, where the vapor pressure is buffered by the formation of amphibole, with tremolite (or talc) as a model, complete reaction of gabbro to eclogite, the phase diagram for the dry system being assumed, is calculated to occur at depths of 50 and 70 km for the two assumed thermodynamic paths. The reaction time is again ~2 m.y. The temperatures achieved upon complete reaction, 400° and 550°C, although higher than those of chlorite-buffered rocks, are still lower than the temperatures (>600°C) required of the solid state diffusion model. We note however that in the case of a tremolite-buffered H_2O system, the predicted depths for the gabbro-eclogite phase change imply pressures comparable to the considerable range of transformation pressures observed for garnet amphibolite transforming to eclogite in the water-saturated basalts studied by *Essene et al.* [1970] and *Allen et al.* [1972]. The above ranges of temperature (~150°–550°C) are similar to the low crystallization temperatures inferred by *Taylor and Coleman* [1968] for the glaucophane-bearing rocks of the California Franciscan formation, which presumably formed upon subduction of the Mesozoic lithosphere.

Finally, we examine the possible time scales for the transformation of initially hot basalt or gabbro to garnet granulite or eclogite within the oceanic lithosphere. From Figure 14 we infer that H_2O vapor pressures greater than ~600 and ~1500 bars (depending on grain boundary thicknesses) are required to transform gabbro to eclogite on a time scale of ~10 m.y. Using the steady state pressure-temperature profile of *Ito* [1974], which essentially implies horizontal flow streamlines, we conclude from Figure 8 that such vapor pressures are always achieved at greater temperatures than those required for the dehydration of chlorite or serpentine. Hence we infer that the H_2O vapor pressure in the lower 'steady state oceanic' lithosphere (below 33 km) is probably buffered by equilibrium with amphibole. If the minimum vapor pressure associated with tremolite can be used as a measure of the in situ vapor pressure, our results imply that if a basaltic composition was originally crystallized upon cooling during sea floor spreading, garnet granulite and/or eclogite could form via the vapor assisted diffusion mechanism at depths of ~39 ± 3 km at

temperatures of $\sim 675°C$ in $\sim 10^7$ yr. Thus at greater depths the distribution of garnet will be controlled by the equilibrium phase diagram and not appreciably by reaction rates provided there are a small quantity of hydrous phases with vapor pressures similar to those of tremolite or talc. In this connection we note that the velocities of the S_n phase propagating through the oceanic lithosphere are definitely more consistent with a partially water-bearing rock [*Hart and Press*, 1973]. Also, comparison of the *Hart and Press* [1973] results with petrological models of *Forsyth and Press* [1971] shows better agreement of the observed velocities with a wet peridotite-eclogite mix model than with a pure wet peridotite model lithosphere. If an appreciable gabbroic fraction exists in the 100-km-thick cooling lithosphere, we expect that increases in P_n and S_n velocity would reflect the gabbro-eclogite phase change predicted from the equilibrium phase diagram upon lithospheric cooling with distance from a ridge. This idea is, of course, compatible with the observation of *Odegard and Sutton* [1972] and *Hart and Press* [1973] of higher seismic velocities in the older lithosphere.

Both the formation of eclogite from the oceanic crust, which should most certainly occur at relatively shallow depth upon subduction, and the possible presence of substantial eclogite in the upper ~ 100 km of the oceanic lithosphere will produce substantial downward body forces on the slab, possibly controlling the subduction process.

REFERENCES

Ahrens, T. J., Petrologic properties of the upper 670 km of the earth's mantle: Geophysical implications, *Phys. Earth Planet. Interiors, 7,* 167–186, 1973.

Allen, T. C., P. J. Modreski, C. Haggood, and A. L. Boettcher, The role of water in the mantle of the earth, The stability of amphiboles and micas, *Proc. Int. Geol. Congr. 24th, Sect. 2,* 231–240, 1972.

Augers, R., R. Tremblaiz, and A. C. D. Chaklader, Formation of $CaZrO_3$ by solid-state reaction between CaO and ZrO_2, *J. Amer. Ceram. Soc., 55,* 425–426, 1972.

Bett, K. E., and J. B. Cappi, Effect of pressure on the viscosity of water, *Nature, 207,* 620–621, 1965.

Birchenall, C. E., Diffusion in oxides: Assessment of existing data and experimental problems, in *Mass Transport in Oxides,* edited by J. B. Wachtman, Jr., and A. D. Franklin, *Nat. Bur. Stand. Spec. Publ. 296,* 119–127, 1968.

Boyd, F. R., and J. L. England, Pyrope, *Carnegie Inst. Wash. Yearb., 58,* 83–87, 1959.

Brace, W. F., E. Silver, K. Hadley, and C. Goetze, Cracks and pores: A closer look, *Science, 178,* 162–163, 1972.

Buckley, G. R., Prediction of cation diffusion data in simple and complex oxides including silicates, submitted to *Contrib. Mineral. Petrol.,* 1973.

Buening, D. K., and P. R. Buseck, Fe-Mg lattice diffusion in olivine, *J. Geophys. Res., 78,* 6852–6862, 1973.

Burnham, C. W., Hydrothermal fluids at the magmatic stage, in *Geochemistry of Hydrothermal Ore Deposits,* edited by H. L. Barnes, pp. 34–76, Holt, Rinehart, and Winston, New York, 1967.

Burte, A. S., and P. S. Nicholson, Influence of anisotropy and water vapor on the solid-state reaction of CaO and beta quartz, *J. Amer. Ceram. Soc., 55,* 472, 1972.

Champness, P. E., W. S. Fyfe, and G. W. Lorimer, Dislocations and voids in pyroxene from a low temperature eclogite: Mechanism of eclogite formation, *Contrib. Mineral. Petrol., 43,* 91–98, 1974.

Cohen, L. H., K. Ito, and G. C. Kennedy, Melting and phase relations in an anhydrous basalt to 40 kilobars, *Amer. J. Sci., 265,* 475–518, 1967.

Cooper, A. R., Jr., Model for multicomponent diffusion, *Phys. Chem. Glasses, 6,* 55–61, 1965.

Cutler, I. B., Effect of water vapor on the sintering of glass powder compacts, *J. Amer. Ceram. Soc., 52,* 11–13, 1969.

Davis, R. F., and J. A. Park, Diffusion and reaction studies in the system Al_2O_3-SiO_2, *J. Amer. Ceram. Soc., 55,* 525–531, 1972.

Dudley, P. P., Electron microprobe analyses of garnet in glaucophane schists and associated eclogites, *Amer. Mineral., 54,* 1139–1150, 1969.

Dudziak, K. H., and E. V. Franck, Messungen der Viskosität des Wassers bis 560°C and 3500 bar, *Ber. Bunsenges. Phys. Chem., 70,* 1120–1128, 1966.

Essene, E. J., B. J. Hensen, and D. H. Green, Experimental study of amphibolite and eclogite stability, *Phys. Earth Planet. Interiors, 3,* 378–384, 1970.

Evans, B. W., and V. Trommsdorf, Regional metamorphoses of ultramafic rocks in the central Alps: Paragenesis in the system CaO-MgO-SiO_2-H_2O, *Schweiz. Mineral. Petrogr. Mitt., 50,* 481–492, 1970.

Evans, B. W., and V. Trommsdorf, Dereinfluss des Eisens auf die Hydratisierung von Duniten, *Schweiz. Mineral. Petrogr. Mitt., 52,* 251–256, 1972.

Forsyth, D. W., and F. Press, Geophysical tests of petrological models of the spreading lithosphere, *J. Geophys. Res., 76,* 7963–7979, 1971.

Froidevaux, C., and G. Schubert, Plate motion and structure of the continental asthenosphere: A realistic model of the upper mantle, *J. Geophys. Res., 80,* in press, 1975.

Fry, N., and W. S. Fyfe, Eclogites and water pressure, *Contrib. Mineral. Petrol., 24,* 1–6, 1969.

Fyfe, W. S., and J. Verhoogen, Kinetics of metamorphic reactions, in *Metamorphic Reactions and Metamorphic Facies,* edited by W. S. Fyfe, F. J. Turner, and J. Verhoogen, *Geol. Soc. Amer. Mem., 73,* 53–103, 1958.

Garrels, R. M., and C. L. Christ, *Solutions, Minerals, and Equilibria,* pp. 96, 421, 100–106, Harper and Row, New York, 1965.

Giardini, A. A., V. J. Hurst, C. E. Melton, and J. C. Stormer, Jr., Biotite as a primary inclusion in diamond: Its nature and significance, *Amer. Mineral., 59,* 783, 1974.

Graham, E. K., and T. J. Ahrens, Shock compression of iron-silicate garnet, *J. Geophys. Res., 78,* 375–392, 1973

Green, D. H., and A. E. Ringwood, An experimental investigation of the gabbro to eclogite transformation and its petrological applications, *Geochim. Cosmochim. Acta, 31,* 767–834, 1967.

Green, D. H., and A. E. Ringwood, A comparison of recent experimental data on the gabbro-garnet granulite-eclogite transition, *J. Geol., 80,* 277–288, 1972.

Green, H. W., II, A CO_2 charged asthenosphere, *Nature Phys. Sci., 238,* 1–4, 1972.

Greenwood, H. J., The system $NaAlSi_2O_6$-H_2O-argon: Total pressure in metamorphism, *J. Geophys. Res., 66,* 3923–3946, 1961.

Greenwood, H. J., The synthesis and stability of onthophyllite, *J. Petrol., 4,* 317–351, 1963.

Griggs, D. T., The sinking lithosphere and the focal mechanism of deep earthquakes, in *The Nature of the Solid Earth,* edited by E. C. Robertson, pp. 361–384, McGraw-Hill, New York, 1972.

Hamann, S. D., and M. Linton, Electrical conductivity of water in shock compression, *Trans. Faraday Soc., 62,* 2234–2241, 1966.

Hart, R. S., and F. Press, S_n velocities and the composition of the lithosphere in the regionalized Atlantic, *J. Geophys. Res., 78,* 407–411, 1973.

Helgeson, H. C., and D. H. Kirkham, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures, 1, Summary of the thermodynamic-electrostatic properties of the solvent, *Amer. J. Sci., 274*(10), 1089, 1974.

Heuer, A. H., A. R. Cooper, and R. Barnard, Oxygen diffusion in forsterite, paper presented at the Carnegie Conference on Geochemical Transport and Carnegie Inst. Washington, Airlie House, Warrenton, Va., June 4–6, 1973.

Hill, R. E., and A. L. Boettcher, Water in the earth's mantle: Melting curves of basalt-water and basalt-water-carbon dioxide, *Science, 167,* 980–982, 1970.

Holloway, J. R., and C. W. Burnham, Melting relations of basalt with equilibrium water pressure less than total pressure, *J. Petrol., 13,* 1–29, 1972.

Iseki, T., K. Yamaguchi, and A. Tagai, Solid-state reaction between SrO and BaO and single-crystal Al_2O_3, *J. Amer. Ceram. Soc., 53,* 425, 1970.

Ito, K., Petrological models of the oceanic lithosphere: Geophysical and geochemical tests, *Earth Planet. Sci. Lett., 21,* 169–180, 1974.

Ito, K., and G. C. Kennedy, The fine structure of the basalt-eclogite transition, *Mineral. Soc. Amer. Spec. Pap. 3*, 77–83, 1970.

Ito, K., and G. C. Kennedy, An experimental study of the basalt–garnet granulite–eclogite transition, in *The Structure and Physical Properties of the Earth's Crust*, edited by J. G. Heacock, *Geophys. Monogr. Ser.*, vol. 14, pp. 303–314, AGU, Washington, D. C., 1971.

Jost, W., *Diffusion in Solids, Liquids, Gases*, Academic, New York, 1960.

Kennedy, G. C., Pressure-volume-temperature relations in water at elevated temperatures and pressures, *Amer. J. Sci., 248*, 540–564, 1950.

Kennedy, G. C., The origin of continents, mountain ranges, and ocean basins, *Amer. Sci., 47*, 491–504, 1959.

Kennedy, G. C., and W. T. Holser, Pressure-volume-temperature and phase relations of water and carbon dioxide, in *Handbook of Physical Constants*, rev. ed., edited by S. P. Clark, Jr., *Geol. Soc. Amer. Mem., 97*, 371–384, 1966.

Kennedy, G. C., and K. Ito, Comments on 'A comparison of recent experimental data on the gabbro-garnet granulite-eclogite transition,' *J. Geol., 80*, 289–292, 1972.

Kennedy, G. C., and R. N. Keeler, Compressibility, in *American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray, pp. 4-38–4-104, McGraw-Hill, New York, 1972.

Kennedy, G. C., G. J. Wasserburg, H. C. Heard, and R. C. Newton, The upper three-phase region in the system SiO_2-H_2O, *Amer. J. Sci., 260*, 501–521, 1962.

Kern, R., and A. Weisbrod, *Thermodynamics for Geologists*, p. 141, Freeman Cooper, San Francisco, Calif., 1967.

Kestin, J., and R. Dipippo, Viscosity of gases, in *American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray, pp. 2-232–2-248, McGraw-Hill, New York, 1972.

King, E. G., R. Barang, W. W. Weller, and L. B. Paukratz, Thermodynamic properties of forsterite and serpentine, *U.S. Bur. Mines Rep. Invest. 6962*, 1967.

Kitahara, S., S. Takanouchi, and G. C. Kennedy, Phase relations in the system MgO-SiO_2-H_2O at high temperatures and pressures, *Amer. J. Sci., 264*, 223–233, 1966.

Kumer, V., and Y. P. Gupta, Cation self-diffusion in single crystal CaO, *J. Phys. Chem., 30*, 677–685, 1969.

Kushiro, I., Y. Syona, and S. Akimoto, Stability of phlogopite at high pressures and possible presence of phlogopite in earth's upper mantle, *Earth Planet. Sci. Lett., 3*, 197–203, 1967.

Lindner, R., Studies on solid state reactions with radiotracers, *J. Chem. Phys., 23*, 410–411, 1955.

Lindner, R., and A. Akerström, Diffusion von Ni-63 in Nickelspinellen, *Z. Phys. Chem. Neue Folge, 18*, 303–307, 1958.

Longworth, L. G., Diffusion in liquids, in *American Institute of Physics Handbook*, 3rd ed., edited by D. E. Gray, pp. 2-221–2-227, McGraw-Hill, New York, 1972.

Lovering, J. F., The Nature of the Mohorovicic discontinuity, *Eos Trans. AGU, 39*, 947–955, 1958.

McGetchin, T. R., L. T. Silver, and A. A. Chodos, Titanoclinohumite: A possible mineralogical site for water in the upper mantle, *J. Geophys. Res., 75*, 255–259, 1970.

McGregor, I. D., The reaction 4 enstatite + spinel = forsterite + pyrope, *Carnegie Inst. Wash. Yearb., 63*, 157, 1964.

McKenzie, D. P., Speculations on the consequences and causes of plate motions, *Geophys. J. Roy. Astron. Soc., 18*, 1–32, 1969.

Meisner, D. J., Cationic diffusion in olivine to 1400°C and 35 kb, in Geochemical Transport and Kinetics, edited by A. W. Hoffman, B. J. Gillette, H. S. Yoder, Jr., and R. A. Lund, *Carnegie Inst. Washington Publ. 634*, 117–130, 1974.

Mistler, R. E., and R. L. Coble, Rate determining species in diffusion-controlled processes in Al_2O_3, *J. Amer. Ceram. Soc., 54*, 60–61, 1971.

Modreski, P. J., and A. L. Boettcher, Phase relations of phlogopite in the system K_2O-MgO-CaO-Al_2O_3-SiO_2-H_2O to 35 kilobars: A better model for micas in the interior of the earth, *Amer. J. Sci., 273*, 383–414, 1973.

Morey, G. W., The solubility of solids in gases, *Econ. Geol., 52*, 225–251, 1957.

Morey, G. W., and J. M. Hesselgesser, The solubility of some minerals in superheated steam at high pressures, *Econ. Geol., 46*, 821–835, 1951.

Mukherjee, J. L., and F. F. Y. Wang, Kinetics of solid-state reactions of Bi_2O_3 and Fe_2O_3, *J. Amer. Ceram. Soc., 54*, 31–34, 1970.

Mysen, B. O., and A. L. Boettcher, Phase relations in peridotite-H_2O-CO_2 systems with controlled H_2O and f_{O_2}, *Eos Trans. AGU, 54*, 480, 1973.

Nagashima, A., and I. Tanishita, Viscosity measurements of water and steam at high temperatures and high pressures, *Bull. JSME, 12*, 1467–1478, 1969.

Odegard, M. E., and G. H. Sutton, The Cannikin airborne seismic experiment, *Geol. Soc. Amer. Progr. Abstr., 4*, 212, 1972.

Oxburgh, E. R., Petrological evidence for the presence of amphibole in the upper mantle and its petrogenetic and geophysical implications, *Geol. Mag., 101*, 1–19, 1964.

Paladino, A. E., and R. L. Coble, Effect of grain boundaries on diffusion-controlled processes in aluminum oxide, *J. Amer. Ceram. Soc., 46*, 133–136, 1963.

Paladino, A. E., and W. D. Kingery, Aluminum ion diffusion in aluminum oxide, *J. Chem. Phys., 37*, 957–962, 1962.

Poldervaart, A., Chemistry of the earth's crust, *Geol. Soc. Amer. Spec. Pap. 62*, 119–144, 1955.

Press, F., The suboceanic mantle, *Science, 165*, 174–176, 1969.

Rice, M. H., and J. M. Walsh, Equation of state of matter to 250 kilobars, *J. Chem. Phys., 26*, 824–830, 1957.

Ringwood, A. E., and D. H. Green, An experimental investigation of the gabbro-eclogite transformation and some geophysical implications, *Tectonophysics, 3*, 383–427, 1966.

Robie, R. A., and D. R. Waldbaum, Thermodynamic properties of minerals and related substances at 298.15°K (25°C) and one atmosphere (1.013 bars) pressure and at higher temperatures, *U. S. Geol. Surv. Bull., 1259*, 1968.

Ronov, A. B., and A. A. Yaroshevsky, Chemical composition of the earth's crust, in *The Earth's Crust and Upper Mantle*, edited by P. J. Hart, *Geophys. Monogr. Ser.*, vol. 13, pp. 37–57, AGU, Washington, D. C., 1969.

Schmalzreid, H., Chemical reactions between crystalline solids, in *Reactivity of Solids*, edited by J. W. Mitchell, R. C. DeVries, R. W. Roberts, and P. Cannon, pp. 551–566, John Wiley, New York, 1969.

Schubert, G., and D. L. Turcotte, Phase changes and mantle convection, *J. Geophys. Res., 76*, 1424–1432, 1971.

Schubert, G., and D. L. Turcotte, Basalt-eclogite phase transition in the descending crust, *Eos Trans. AGU, 53*, 521, 1972.

Schubert, G., D. A. Yuen, and D. L. Turcotte, Role of phase changes in a dynamic mantle, *Geophys. J. Roy. Astron. Soc.*, in press, 1974.

Shettel, D. L., Jr., Solubility of quartz in H_2O-CO_2 fluids at 5 kb and 500°–900°C, *Eos Trans. AGU, 54*, 480, 1973.

Spry, A., *Metamorphic Textures*, pp. 104–108, 153, Pergamon, New York, 1969.

Taylor, H. P., and R. G. Coleman, O^{18}/O^{16} ratios of coexisting minerals in glaucophane-bearing metamorphic rocks, *Bull. Geol. Soc. Amer., 79*, 1727–1757, 1968.

Toksöz, M. N., J. W. Minear, and B. R. Julian, Temperature field and geophysical effects of a downgoing slab, *J. Geophys. Res., 76*, 1113–1138, 1971.

Turcotte, D. L., and E. R. Oxburgh, Convection in a mantle with variable physical properties, *J. Geophys. Res., 74*, 1458–1474, 1969.

Turcotte, D. L., and G. Schubert, Structure of olivine-spinel phase boundary in the descending lithosphere, *J. Geophys. Res., 76*, 7980–7987, 1971.

Turcotte, D. L., and G. Schubert, Frictional heating of the descending lithosphere, *J. Geophys. Res., 78*, 5876–5886, 1973.

Vinogradov, A. P., The formation of the ocean, *Izv. Akad. Nauk SSSR Ser. Geol., 4*, 3–9, 1967.

Walton, M., Molecular diffusion rates in supercritical H_2O vapor estimated from viscosity data, *Amer. J. Sci., 258*, 385–401, 1960.

Wuensch, B. J., and T. Vasilos, Impurity cation diffusion in magnesium oxide, *Nat. Bur. Stand. Spec. Publ. 296*, 95–112, 1968.

Wyllie, P. J., Ultramafic rocks and the upper mantle, *Mineral. Soc. Amer. Spec. Pap. 3*, 3, 1970.

Wyllie, P. J., *The Dynamic Earth: Textbook in Geosciences*, pp. 63–90, John Wiley, New York, 1971.

Yoder, H. S., Jr., The role of water in metamorphism, The Crust of the Earth, *Geol. Soc. Amer. Spec. Pap. 62*, 505–524, 1955.

Yoder, H. S., Jr., and C. E. Tilley, Origin of basalt magma: An experimental study of natural and synthetic rock systems, *J. Petrol., 3*, 342–352, 1962.