

EXPERIMENTAL STUDY OF AMPHIBOLITE AND ECLOGITE STABILITY

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The amphibolite-eclogite transition is often observed in metamorphic rocks and may be expected to occur in the lower crust or upper mantle if $P_{H_2O} \approx P_S$. Many simple amphiboles become unstable at high water pressures due to backbending of dehydration reactions or to solid-solid transitions involving sheet silicates. Contrary to YODER and TILLEY (1962), eclogite is expected to be stable relative to amphibolite at sufficiently high water pressures because of the formation of dense garnet and the high compressibility of water vapor. Experiments in progress on several basaltic compositions have produced eclogite at the expense of amphibolite at high water pressures. Seeding has been found to be important as hornblende crystallizing from glass will persist at least

4 kb above its stability field defined by reversals with garnet-pyroxene-amphibole mixtures. In reconnaissance experiments on a quartz tholeiite and an alkali olivine basalt, hornblende disappears at high water pressures between 15-25 kb and 700-900 °C. Biotite appears to be stable in the alkali olivine basalt to at least 40 kb at these temperatures.

Basaltic amphibolites do not appear to be stable very far into the low-velocity zone even at $P_{H_2O} = P_S$ confirming LAMBERT and WYLLIE's (1968) earlier experiments. Biotite however seems to be stable deeper in the mantle (at least for potassic basalts) than previously considered possible if $P_{H_2O} \approx P_S$ and may be a source of water for magmas when partially melted.

1. Introduction

Eclogite and amphibolite relationships have long been of interest to the petrologist as both rocks are closely associated in metamorphic terranes. The classical petrological studies of HEZNER (1903), BRIERE (1920), ESKOLA (1921) and TILLEY (1936, 1937) showed that early-formed eclogites have often become partially hydrated to amphibolites. ESKOLA (1939) originally placed the eclogite facies at the highest pressures and temperatures, but it is now recognized that eclogites may form at relatively low pressures as well. If eclogites form at relatively low temperature and low P_{H_2O}/P_T^* then increase of water pressure could hydrate the eclogites to amphibolites (or glaucophane schists) as suggested by SAHLSTEIN (1936), BEARTH (1959), GREEN and RINGWOOD (1967) and others. For $P_{H_2O} \ll P_T$, either other gases must be very abundant to keep $P_F \approx P_T$, or there can be no vapour phase as in the water-deficient region (YODER, 1955). A third possibility is that the thermodynamic properties of intergranular films of impure water are markedly different from those of pure water. Most eclogites (except for rare scapolite-

bearing varieties) show little evidence of abundant gases other than water, though of course they need not be evident in the preserved solid phases. One may also question the possibility of crystallizing a coarse-grained eclogite from an initial olivine-pyroxene-feldspar rock in the absence of a vapour phase without leaving traces of the original basaltic minerals, though BEARTH (1959, 1965) has observed all steps of the basalt-eclogite transition for some unusual eclogites. The possibility that the partial pressure of impure water is considerably lower "in solution" along grain boundaries than pure water vapour at the same $P-T$ cannot be properly evaluated at present. To avoid the apparent difficulties in these explanations ESSENE and FYFE (1967) postulated that eclogites are stabilized relative to amphibolites at high water pressures and showed that density data alone confirm this prediction. Similarly, GREEN and RINGWOOD (1967, p. 805-6) showed that amphiboles including the simple end member tremolite, will break down to anhydrous products and water vapour at sufficiently high P_{H_2O} and argued that this would considerably restrict the stability of amphibole in the upper mantle. Experiments are clearly needed to resolve the role of water pressures in the formation of eclogites.

* The notation used is $P_T = P_{Total}$, $P_F = P_{Fluid}$, $P_S = P_{Solid}$.

2. Previous experiments

YODER and TILLEY (1962) showed that the stable subsolidus assemblage for many basaltic rocks is amphibolite for $P_T = P_{H_2O} > 2$ kb, < 10 kb, $T > 600$ °C, and concluded that eclogite is unstable in the presence of water for *all* water pressures. However the beginning of melting could develop a positive slope and the disappearance of amphibole a negative slope at high water pressures due to the formation of garnet and the high compressibility of water. The combination of these two effects leads to the stabilization of eclogite relative to amphibolite at sufficiently high water pressures (fig. 1).

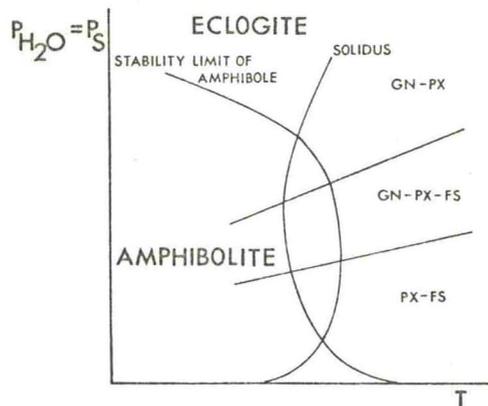


Fig. 1. A possible geometry for the beginning of melting and the stability of amphibole in basaltic rocks. The solid-solid transformation of feldspar to garnet and the high compressibility of water combine to stabilize eclogite at high water pressures. Fs = Feldspars, Px = Pyroxenes, gn = garnet.

This geometry has been confirmed in preliminary synthesis experiments on hornblende stability under its own composition and in a gabbro by LAMBERT and WYLLIE (1968). HENSEN and GREEN (unpublished) established the synthesis limit of hornblende in an alkali olivine basalt* with similar results also for $P_{H_2O} \approx P_T$ (fig. 2). These experiments show that eclogite is stable at high water pressures but represent syntheses mostly in the supersolidus region.

3. Thermodynamic calculations

Many simple amphiboles can be shown to be unstable at high water pressures by thermodynamic cal-

* The composition of this alkali-olivine basalt as well as the albite-rich quartz tholeiite used in following experiments is listed in GREEN and RINGWOOD (1967).

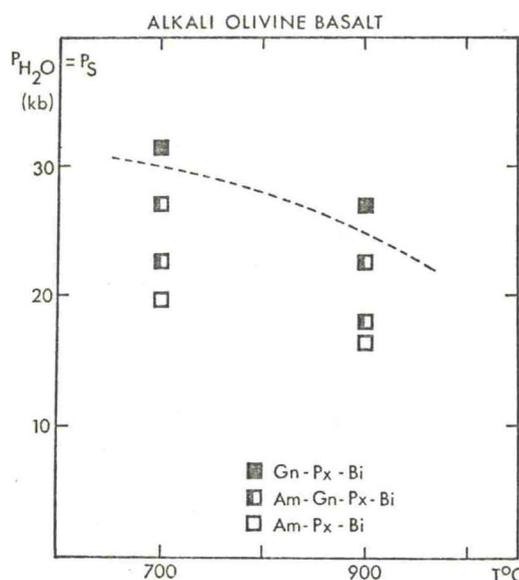


Fig. 2. Stability of amphibole for an alkali olivine basalt as determined by syntheses in cold-sealed gold capsules. The restriction of garnet to relatively high pressures is probably a reflection of the lack of initial garnet nuclei. This stability of amphibole compares well with the hot-sealed synthesis runs of fig. 3, showing that water pressures were not significantly lowered by chance leaks during the run. Am = Amphibole, Bi = Biotite, Px = Pyroxenes.

culations which permit extension of experimental data to higher water pressures (see Appendix 1 for thermodynamic data and procedures)*. The simple dehydration of tremolite (BOYD, 1959) will develop a negative slope at high water pressures due only to the rapid compressibility of water vapor, as predicted by GREEN and RINGWOOD (1967). At high enough water pressures the tremolite = diopside + enstatite + quartz + water curve will cross the talc = enstatite + quartz + water curve and a solid-solid decomposition of tremolite = talc + diopside is found instead (fig. 3). A similar solid-solid transformation predicted for anthophyllite by GREENWOOD (1963) is also shown in fig. 3, though calculations using ROBIE *et al.*'s (1967) volume data would move this curve to at least 50 k̄. Glaucophane might similarly be expected to break down to talc + jadeite at high pressures (shown schematically in fig. 3), and the curve could be located more exactly if dependable experiments were available for the stability of glaucophane. Amphiboles may also break down at

* These calculations ignore the possibility of partial melting at high water pressures.

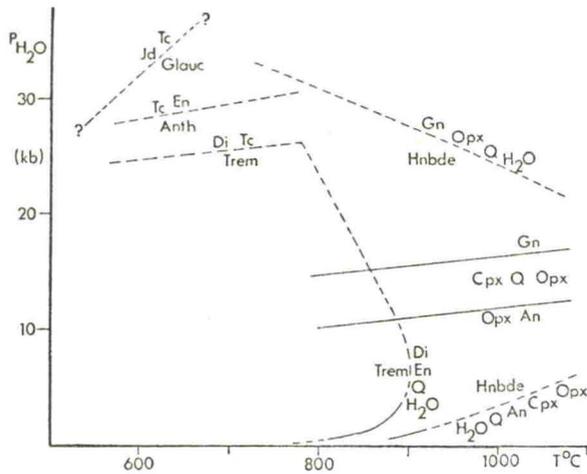
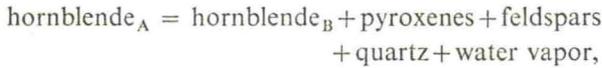


Fig. 3. Stability of various amphiboles estimated at high water pressures. Trem = Tremolite, Di = Diopside, En = Enstatite, Q = Quartz, Hnbde = "Hornblende", Gn = Garnet, Opx = Orthopyroxene, Cpx = Clinopyroxene, An = Anorthite, Anth = Anthophyllite, Tc = Talc, Jd = Jadeite, Gl = Glaucophane.

high water pressures because the products themselves react to form denser phases, as shown in fig. 3 for a "hornblende" - $\text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$. The initial point for the curve "hornblende" = anorthite + diopside + enstatite + water is taken at 900 °C and 1 kb* and when the feldspar reacts with pyroxenes to yield garnet the stability of this amphibole is sharply back-bent (fig. 3). While the true stability of this "hornblende" may be represented instead by some reaction as



the effect of high water pressures when garnet is produced may be qualitatively represented as in fig. 3**.

The instability of these amphiboles at high water pressures disagrees markedly with similar estimates by O'HARA (1967), who extended the stability of amphiboles vertically regardless of reactions among the products giving garnet at the expense of feldspars. O'Hara's schematic amphibole stability curves are unrealistic and

* This is an estimate taken from BOYD'S (1959) experiments. When Boyd attempted to determine the stability of pargasite + quartz the pargasite broke down to form an amphibole close to $\text{Ca}_2\text{Mg}_4\text{Al}_2\text{Si}_7\text{O}_{22}(\text{OH})_2$ stable to ~900 °C, 1 kb.

** Following preparation of this manuscript, GILBERT'S (1969) note on the experimental stability of end-member amphiboles appeared in the Ann. Rept. Geophys. Lab. Carnegie Inst. Wash. Gilbert's preliminary experiments on tremolite and "hornblende" are generally consistent with the calculations shown in fig. 3.

should be disregarded. Extrapolation of simple amphibole stabilities to high water pressures demonstrates that they may decompose by increasing water pressure but bear little on the stability of complex amphiboles which may first react with other phases in natural basaltic compositions.

4. Present experiments

The writers attempted to establish the upper stability limit of amphibole in an alkali olivine basalt and a quartz tholeiite for $P_{\text{H}_2\text{O}} = P_S$ by sealing glassy and crystalline samples with water and holding them in a piston cylinder apparatus at P and T for >24 hours (see appendix II for details of experimental procedure). Amphibole disappeared rather sharply within a 2 kb interval (figs. 4, 5) and in the case of the alkali olivine basalt, compared rather well with earlier experiments with cold-sealed capsules (fig. 3). When the crystallized mixtures of the earlier runs (amphibolite and eclogite) were rerun, amphibole was found to be unstable in the region where it had previously been synthesized, and it did not perceptibly grow at the expense of the garnet and pyroxene until the pressure had been lowered 5-10 kb below the original synthesis limit. While the reversal limits are rather wide in these preliminary experiments, they illustrate the danger of accepting short-time synthesis experiments as representing equilibrium at these relatively low temperatures, even if the syn-

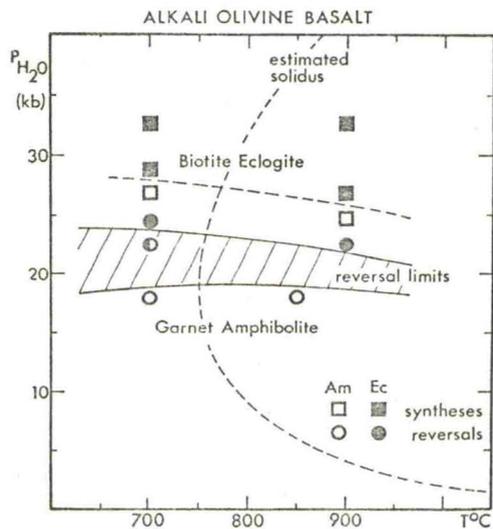


Fig. 4. Stability limit of amphibole in an alkali olivine basalt, comparing synthesis runs with reversals. Am = Amphibolite, Ec = Eclogite.

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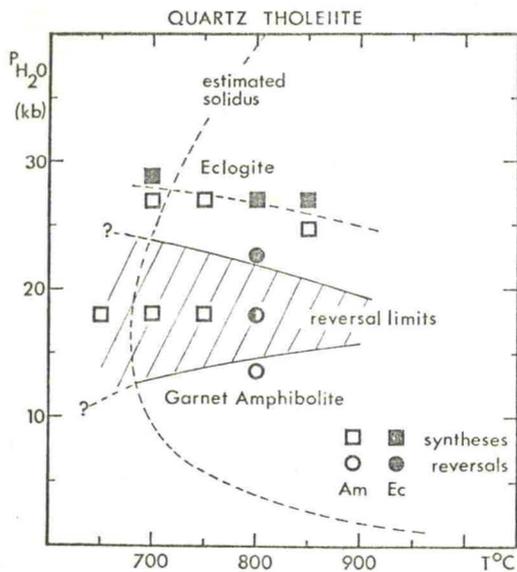


Fig. 5. Stability limit of amphibole in an albite-rich quartz tholeiite, comparing synthesis runs with reversals.

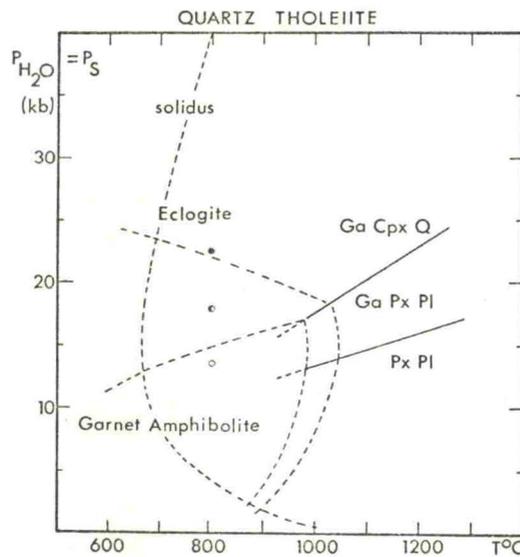


Fig. 6. Combination of present data for the alkali olivine basalt with that of GREEN and RINGWOOD (1967). Sa = Sanidine, Ga = Garnet, Pxs = Pyroxenes, Pl = Plagioclase, Ol = Olivine.

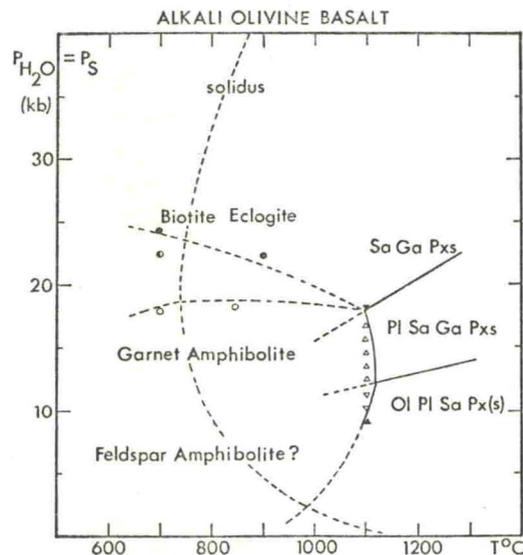


Fig. 7. Combination of the present data for the quartz tholeiite with that of GREEN and RINGWOOD (1967) and data for the amphibole stability from the Silberbach eclogite as determined by YODER and TILLEY (1962).

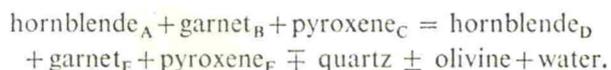
thesis boundary appears to be rather sharp and reproducible.

The solidus was difficult to locate for these basaltic compositions due to the formation of quench amphibole and the formation of only a small amount of glass near the solidus. It was estimated from the runs plotted in figs. 4 and 5 and by comparison with YODER and TILLEY's (1962) and LAMBERT and WYLLIE's (1968) data. The solidus for the alkali olivine basalt with 26% normative olivine is thought to be 50-75° higher than that for the quartz-normative tholeiite.

The upper stability of amphibole in supersolidus runs will involve reaction with melt as well as vapor, but these data have been included to place gross limits on the possible slopes for the supersolidus curves. GREEN and RINGWOOD (1967) found amphibole between 10.1 and 16.8 kb at 1100 °C with $P_{H_2O} < P_T$ in the alkali olivine basalt and this is used in fig. 6 to tentatively fix the amphibole stability. Yoder and Tilley's data on the stability of amphibole in various basalts have been consulted to estimate the amphibole stability in the quartz tholeiite (fig. 7).

The subsolidus reaction of amphibolite to eclogite is not likely to be a sharp transition but a gradual reaction among amphibole, garnet and pyroxenes (and feldspars?). It is best thought of as a sliding reaction with a number of substitutions in each phase and may be

generalized as:



The hornblende etc. on each side of the reaction will form a solid solution shifting with $\Delta P, T$ to any of a

large number of end members. The area over which this sliding reaction will occur has not been determined experimentally and much longer run times (≈ 1 month) may be needed to establish this zone.

5. Interpretation

The present data suggest that eclogite will form at the expense of amphibolite when pressures are somewhere in the region of 10–30 kb at medium temperatures for basaltic rocks at high water pressures. This generally confirms LAMBERT and WYLLIE's (1968) experiments, but the difference between syntheses and reversals found here suggests that their synthesis experiments may be in error and should not be used for any specific argument as to magma generation in the upper mantle. Stability of one amphibole in a basaltic rock or under its own composition is no guide to the behavior of another amphibole in an ultramafic rock. Certainly their incoming of garnet at $P > 18$ kb (LAMBERT and WYLLIE, 1970) is open to doubt as no garnet nuclei were available in the starting mix. Tighter reversals are needed before evaluating the possibility that crustal eclogites form at high water pressures.

Garnet amphibolites lacking feldspar are expected to have higher densities ($3.2\text{--}3.4\text{ g/cm}^3$) and higher estimated seismic velocities ($V_p = 7.6\text{--}8.0\text{ km/s}$) than previously thought possible for hydrated basic rocks, and may be important in the lower crust or upper mantle ($< 70\text{ km}$), if water pressures are high. Garnet amphibolites lacking feldspar have been found in high-pressure crustal rocks (ESSENE, 1967) and may be widespread in the lower crust.

The apparent stability of biotite in the potassic alkali olivine basalt suggests that trioctahedral mica may be an important hydrous phase in the upper mantle. The decomposition of several amphiboles at high water pressures (fig. 3) apparently involves formation of another sheet silicate (talc) at high water pressures. SCLAR (1970) has synthesized a 10 \AA micaceous phase in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$ at $P > 30\text{ kb}$ and $T < 500\text{ }^\circ\text{C}$ but has not yet shown whether this phase is stable by reversals nor reported its relation to other phases of $\approx 10\text{ \AA}$ – as attapulgite. KUSHIRO *et al.* (1967) have examined phlogopite at high pressures and claim it is stable to at least 100 kb, but they have located a solidus in the system outside their stability field for phlogopite, whereas LUTH (1967) has shown that phlogopite breakdown

curve intersects the solidus at only 2 kb water pressure. This suggests that KUSHIRO *et al.* may have had $P_{\text{H}_2\text{O}} \ll P_T$ in their runs; they may have also had trouble with quench phlogopite. In a later series of experiments, YODER and KUSHIRO (1969) confirmed Luth's data and showed that phlogopite remains stable up to $1200\text{ }^\circ\text{C}$ and 40 kb.

Appendix I

The thermodynamic calculations in fig. 3 were all based on experimental data, and extended to higher pressures and temperatures with the well-known relations

$$\left(\frac{\delta\Delta G}{\delta T}\right)_P = -\Delta S, \quad \left(\frac{\delta\Delta G}{\delta P}\right)_T = \Delta V.$$

The free energy data for water were taken from BURNHAM *et al.* (1968) below 10 kb, and above 10 kb from SHARP (1962). Measured high-temperature entropies ($S_T - S_{298}$) are not available for talc, tremolite or "hornblende" and were estimated by summing the high-temperature entropies of other silicates:

$$\begin{aligned} \text{talc} &= 2 \text{ serpentine} - 3 \text{ brucite}^*, \\ \text{tremolite} &= \text{talc} + 2 \text{ diopside}^{**}, \end{aligned}$$

and the entropy of "hornblende" was assumed equal to tremolite. From these estimates, the high-temperature entropies of talc and tremolite were fitted to the quadratic equation of the form

$$S_T - S_{298} = a \ln T + b10^{-3}T + c10^5T^{-2} + d,$$

where the values of a , b , c , d are given in table 1.

TABLE I

| | a | b | c | d |
|-----------|---------|--------|--------|----------|
| Talc | +126.26 | -5.06 | +24.89 | -745.82 |
| Tremolite | +232.00 | +10.02 | +38.63 | -1365.52 |

The molar volumes (V^0) of the silicates were taken from ROBIE *et al.* (1967) and the standard entropies (S_{298}^0) from ROBIE (1966); these data are not available for "hornblende" and were estimated: $V^0 = 270.5\text{ cm}^3$, $S_{298}^0 = 131.6\text{ e.u.}$ In making the calculations the com-

* Entropy data for serpentine and brucite are from KING *et al.* (1967).

** High-temperature entropy data for diopside are from KELLY (1960).

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TABLE 2

| | amphibole | garnet | pyroxene | biotite | rutile | opaque | quartz |
|-----------------------|-----------|--------|----------|---------|--------|--------|--------|
| Alkali olivine basalt | | | | | | | |
| amphibolite | ×× | × | × | × | tr | tr | — |
| eclogite | tr | ×× | ×× | × | tr | — | — |
| Quartz tholeiite | | | | | | | |
| amphibolite | ×× | × | × | — | — | tr | — |
| eclogite | tr | ×× | ×× | — | tr | — | tr |

×× = major component; × = minor component; tr = trace.

compressibility of the solids was neglected, i.e. $\Delta V_{\text{solids}} =$ constant.

Because of the approximations involved in the estimation of volumes and entropies at high pressures and temperatures, the slopes and locations of the solid-solid reactions can only be regarded as approximate. Negative slopes for these curves cannot be ruled out at present.

Appendix II: Details of experimental procedure

The starting material for the synthesis runs were glasses of the appropriate composition prepared as described by GREEN and RINGWOOD (1967). Weighed amounts of glass (10–40 mg) were sealed in Au, Pt or Ag–Pd capsules with 5–10 wt% water added with a microburette. The capsules were sealed with a carbon arc-welder and reweighed to ensure against loss of the water. For reversals, products of earlier runs containing amphibolite and eclogite were mixed, weighed with additional water and rerun. The capsules were enclosed with a talc assembly which fitted into the standard graphite furnace and external talc sheath of the Boyd piston-cylinder apparatus. Pt-(Pt+10% Rh) or chromel–alumel thermocouples were used to measure and control temperatures to ± 10 °C. Pressure (10–40 kb) was first applied then the cell was brought to temperature (600–900 °C) with the piston remaining on the compression stroke; a –10% pressure correction was applied to all runs. Synthesis run times were generally 12–24 hours, but successful reversals required at least 2–3 days. At temperatures > 800 °C large pressure and/or temperature drops often occurred due to talc dehydration, and boron nitride was substituted for the talc internal to the graphite furnace. After the run was quenched in ≈ 30 s by cutting the power input, the capsule was removed, cleaned and reweighed. It was then punctured and examined for excess water, usually

seen only when > 2 mg water had initially been added. Runs were then heated to ≈ 120 °C for at least 1 hour and reweighed to measure the water loss insuring that excess water had been present during the run. The sample was then optically examined and powder photographs taken. Iron loss to the Pt capsule at these relatively low temperatures was probably restricted to a narrow 2–5 μ bleached zone observed at the edge of the sample after a run. Reducing conditions of an uncontrolled nature were guaranteed by the presence of the graphite furnace external to the sample.

Appendix III: Phases observed in the experimental runs

The phases observed in the alkali olivine basalt and the quartz tholeiite are listed in table 2. Feldspar was not positively identified in low pressure runs though small amounts of glass are difficult to distinguish from these phases. In synthesis runs on the quartz tholeiite at 27 kb and 700 °C, large weakly birefringent crystals with a low refractive index were tentatively identified as quartz. When amphibole is a major constituent, other minor phases (except for biotite) are difficult to distinguish with powder photographs because of the overlap with amphibole lines, and an optical identification is necessary. Small amounts of pyroxene can be distinguished from amphibole by their equant habit, and garnet by its characteristic shape, refringence and lack of birefringence. The trace amounts of amphibole in the eclogite may be quench material. For the alkali olivine basalt, some of the pyroxene may be orthopyroxene though much has probably reacted with the K-feldspar component to give biotite. The eclogitic pyroxene of the quartz tholeiite has $\approx 20\%$ Jd and that of the alkali olivine basalt $\approx 10\%$ Jd, as determined by the $\bar{2}21$ *d*-spacing (see ESSENE and FYFE, 1967).

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