

## Effect of Iron Absorption by Noble-Metal Capsules on Phase Boundaries in Rock-Melting Experiments at 30 Kilobars

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### Abstract

Andesite-H<sub>2</sub>O and basalt-H<sub>2</sub>O mixtures encapsulated in Pt, Ag<sub>30</sub>Pd<sub>70</sub>, and Ag<sub>75</sub>Pd<sub>25</sub> with high ratios of metal/sample were run in half-inch diameter piston-cylinder apparatus at 30 kbar at temperatures where the mixtures were molten or partly crystallized. For andesite liquid at 1100°C the rate of iron absorption by the capsules is greatest in the first hour, 70 percent of initial FeO being lost with Pt capsules. After 3 hours, percentages of initial FeO lost are 85 percent for Pt, 35 percent for Ag<sub>30</sub>Pd<sub>70</sub>, and 25 percent for Ag<sub>75</sub>Pd<sub>25</sub>. For the phase assemblage garnet(Ga) + clinopyroxene(Cpx) + liquid(L) with 80 percent L at 1100°C in Ag<sub>75</sub>Pd<sub>25</sub> capsules, clinopyroxene and liquid lose about 30 percent FeO in the 4-hour interval between 1 and 5 hour runs, but garnet does not change composition. Distribution coefficients for Fe and Mg between liquid and minerals therefore vary as a function of run duration. At 1000°C and below, iron loss is not a serious problem in Ag<sub>30</sub>Pd<sub>70</sub> for runs of 10 hours duration, but attempts to reverse the Cpx-out phase boundary in andesite-10% H<sub>2</sub>O near 950°C demonstrate kinetic and nucleation problems; the reversal bracket is wide, 890°–975°C. Consistency between one-stage and two-stage low-to-high temperature runs for andesite and basalt with at least 10 percent H<sub>2</sub>O between 1050°C and 1200°C suggests a close approach to equilibrium for garnet and clinopyroxene after 1-hour runs. For runs with basalt-H<sub>2</sub>O in Pt capsules, longer runs cause the recorded positions of the Cpx-out and Ga-out phase boundaries to increase and decrease in temperature, respectively, with discrepancies of 25–50°C between runs of 1 hour and 12 hours. This makes it difficult to demonstrate reversible equilibrium of a high-temperature phase boundary in a rock-H<sub>2</sub>O system; reversibility in a system of changing bulk composition is not necessarily an equilibrium condition.

### Introduction

Gold, platinum, silver, and alloys of silver-palladium are the only satisfactory materials employed so far to encapsulate rock samples with volatile components for high-pressure phase equilibrium studies. In most rock-melting experiments, it is necessary to use platinum or silver-palladium. It is well known that these metals absorb iron from the sample during a run but it appears to be less generally acknowledged that this can have significant effects on the experimental results obtained in piston-cylinder apparatus where the sample is small and the metal/sample ratio is high.

Merrill and Wyllie (1973) reviewed the problem and determined the rate of iron lost to Pt capsules in

piston-cylinder apparatus from a basaltic liquid at 10 kbar, 1250°C. Nehru and Wyllie (1975) investigated the effect of temperature and capsule size on the rate of iron loss from a partly melted peridotite. We now report the rates of iron loss to Pt, Ag<sub>30</sub>Pd<sub>70</sub>, and Ag<sub>75</sub>Pd<sub>25</sub> capsules from andesitic liquid and liquid+crystal mixtures, with varying water contents at 30 kbar, and at several temperatures (Stern, 1973). In addition, we have determined the extent to which the iron loss causes changes in recorded temperatures of phase boundaries.

### Experimental Method

The starting materials are a tonalite from the Sierra Nevada Batholith and a basalt from a sill in Scotland.

Complete chemical analyses and incomplete phase relationships for these samples are given by Lambert and Wyllie (1972,1974) and Stern and Wyllie (1973). The tonalite (andesitic liquid when melted) has Fe<sub>2</sub>O<sub>3</sub>, 2.3 percent; FeO, 3.6 percent; all Fe as FeO, 5.7 percent; and 0.8 percent H<sub>2</sub>O combined in hornblende and biotite. The basalt (gabbro or quartz eclogite when recrystallized, basaltic liquid when melted) has Fe<sub>2</sub>O<sub>3</sub>, 2.3 percent; FeO, 7.7 percent; all Fe as FeO, 9.8 percent; and 1.8 percent H<sub>2</sub>O combined in serpentine.

The crushed rock samples were sealed within noble-metal capsules with known proportions of water, and run in piston-cylinder apparatus (½-inch diameter chamber) using the methods described by Merrill and Wyllie (1973). Nominal pressures using the piston-out procedure are reported. Temperatures measured with Pt/Pt10%Rh thermocouples were not corrected for pressure effects on emf. The furnace assemblage used produces an oxygen fugacity similar to the N-NO buffer (Stern, 1973).

After each run, the sample was removed from its capsule, mounted in epoxy, and polished for microprobe analysis. Samples were analyzed on a 4-spectrometer ARL-EMX microprobe using as standards an augitic pyroxene (for Fe), anorthite (for Si and Ca), diopside with 2 percent Ti (for Mg and Ti), albite (for Na), and sanidine (for K). An automatic scanning beam was used to analyze a 20 micron by 20 micron area, with 10 such areas being analyzed for each sample. Merrill and Wyllie (1973) found nearly uniform distribution of iron across glasses quenched from run charges held in platinum capsules for times of one hour or more. Similarly, according to our uncorrected probe data, the glasses were homogeneous,

and iron content was uniform throughout each sample. Raw data were examined for inconsistencies, corrected for instrumental factors (background, detector dead time, beam current drift) using a program written by I. Steele at the University of Chicago, and for matrix effects (absorption, fluorescence, and atomic number effect) using a program written at the Geophysical Laboratory (Boyd, Finger, and Chayes, 1968; Hadidiacos, Finger, and Boyd, 1970). The accuracy of the microprobe analysis is ± 2 percent relative for each element of greater than 5 percent concentration, and ± 5 percent for elements of less than 5 percent concentration. The detectability level is 0.5 percent for all elements.

### Experimental Results on Iron Loss

#### *Effect of Different Capsule Materials*

Results are shown in Figures 1A and B for the andesitic liquid with 16 ± 2 wt percent dissolved water, sealed in three different capsule materials (Table 1). The samples were held at 30 kbar and 1100°C for various lengths of time. The liquidus temperature for this andesite with 16 ± 2 wt percent dissolved water is 25 ± 20°C below 1100°C, as determined from previous runs (Stern and Wyllie, 1973). The liquids quenched to uniform glasses without quench crystals, and with no evidence for a vapor phase during the run.

Figure 1A shows the amount of FeO (total Fe as FeO) remaining in the liquid as a function of time, and in Figure 1B this is recalculated in terms of percentage loss of original FeO. For all capsule materials the rate of iron loss is greatest in the first hour, and progressively less in succeeding hours. After 1 hour, 70 percent of the original FeO is lost to

TABLE 1. Microprobe Analyses of Andesitic Glasses (Initial Composition Tonalite 101) Held as Liquids in Noble Metal Capsules for Various Times at 30 Kbar\*

Capsule	← Ag <sub>75</sub> Pd <sub>25</sub> →				← Ag <sub>30</sub> Pd <sub>70</sub> →				← Pt →				Tonalite 101
	1100	1100	1200	1200	1100	1100	1100	1100	1100	1100	1200	1200	
Temp. °C	1100	1100	1200	1200	1100	1100	1100	1100	1100	1100	1200	1200	
Wt. % H <sub>2</sub> O	18	18	5	5	15	15	15	15	15	15	5	5	
Time hr.	1	3	1	5	1	3	5	1	3	10	1	3	
SiO <sub>2</sub>	61.8	60.5	60.5	62.0	61.6	64.2	62.5	63.6	64.0	63.9	62.6	63.8	60.3
TiO <sub>2</sub>	0.8	0.8	0.9	0.9	0.8	0.8	0.8	0.8	0.9	0.8	0.9	0.9	0.8
Al <sub>2</sub> O <sub>3</sub>	18.5	20.2	19.1	19.4	19.3	19.2	19.6	20.7	20.3	20.2	20.0	19.8	18.5
FeO	4.7	4.3	5.1	2.2	4.7	3.6	3.3	1.6	0.8	0.8	1.8	0.8	5.8
MgO	3.6	3.4	2.6	2.8	2.5	2.9	2.7	2.8	2.7	2.7	2.8	2.7	2.5
CaO	5.2	5.0	5.9	6.5	5.9	5.8	5.7	5.7	5.6	5.7	6.0	5.9	6.0
Na <sub>2</sub> O	3.3	3.5	3.7	3.9	2.7	1.4	3.0	2.7	3.1	3.0	3.7	3.8	3.9
K <sub>2</sub> O	2.1	2.3	2.2	2.3	2.5	2.1	2.4	2.2	2.6	2.7	2.2	2.3	2.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.1	100.0	99.8	100.0	100.0	100.0
% FeO Loss	19	26	12	62	19	38	43	72	86	86	70	86	

\*All analyses are normalized to total 100.0, with all Fe as FeO.

the Pt capsule. After 3 hours, the percentages of original FeO absorbed by the capsules are 85 percent for Pt, 35 percent for  $\text{Ag}_{30}\text{Pd}_{70}$ , and 25 percent for  $\text{Ag}_{75}\text{Pd}_{25}$ . This confirms the well-known fact that the use of Ag-Pd capsules, when temperatures permit, reduces the iron loss considerably compared with the nearly total loss to Pt that occurs within a few hours. Nevertheless, the loss of 30-40 percent iron with the use of Ag-Pd capsules is significant.

#### Effect of Different Temperatures and Water Contents

In Figures 1C and D, the 1100°C results for Pt and  $\text{Ag}_{75}\text{Pd}_{25}$ , respectively, transferred from Figure 1A, are compared with results at 1200°C. The 1200°C runs were located just above the liquidus, similar to the 1100°C runs, and this condition was achieved by adding only 5 percent  $\text{H}_2\text{O}$ ; the liquidus with 5 percent  $\text{H}_2\text{O}$  is 1190°C for 1 hr runs (Stern and Wyllie, 1973), and slightly lower for runs of longer duration (see Fig. 3 and discussion below). For short duration runs it appears that the effect of increasing temperature is overcome by the effect of decreasing  $\text{H}_2\text{O}$  content.

Greater loss of iron from samples held at lower temperatures but containing more dissolved water (Fig. 1, C and D) may result from differences in the oxygen fugacity in sample charges containing different amounts of  $\text{H}_2\text{O}$ . Loss of iron frees oxygen. For two runs losing similar amounts of iron, the sample with the lower water content will have a higher  $\text{O}_2/\text{H}_2\text{O}$  ratio, and thus a higher oxygen fugacity. This will cause a decrease in the activity of metallic iron, which may offset the increased diffusion rates and increased absorbency of capsule materials at higher temperature. This effect has been demonstrated by Boettcher and Allen (personal communication, 1974). They found that in a Mount Hood andesite with 20 wt percent  $\text{H}_2\text{O}$  run at 13 kbar and 900°C for 12 hrs in a Pt capsule with the N-NO buffer, iron loss is 40 percent. In a similar run at 920°C with the M-H buffer, no iron loss was detected.

Figure 1C for Pt shows three similar curves for 1100°C, 1200°C, and the dashed line *a* for basaltic liquid with 0.38 percent  $\text{H}_2\text{O}$  at 1250°C, 10 kbar (Merrill and Wyllie, 1973). These indicate increased iron loss with temperature for runs longer than 2 hours. For shorter runs the iron loss increases with increasing  $\text{H}_2\text{O}$  content, regardless of temperature, although differences are small.

Figure 1D for  $\text{Ag}_{75}\text{Pd}_{25}$  shows a larger temperature effect in runs longer than 2 hours. 1200°C is close to the melting temperature of  $\text{Ag}_{75}\text{Pd}_{25}$  at 30 kbar, and

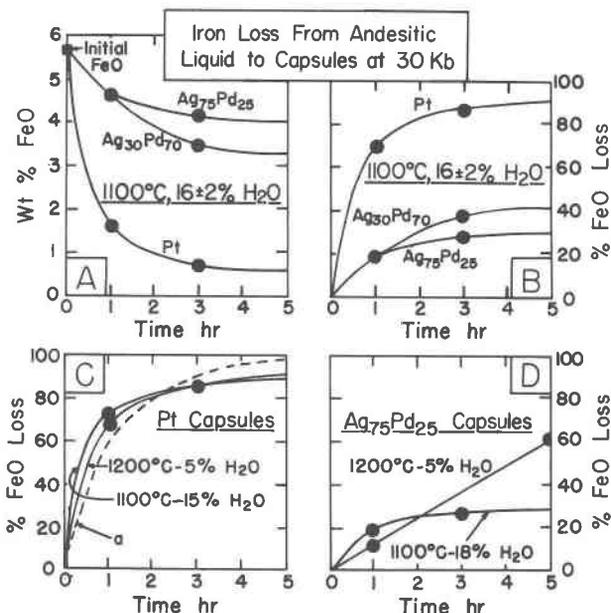


FIG. 1. Iron loss from andesitic liquid containing initially 5.7 percent FeO (all Fe as FeO) as a function of sample container, time, temperature, and water content. See Table 1 for data. Curve *a* is from Merrill and Wyllie (1973), giving results for basaltic liquid with initially 14 percent FeO and 0.38 percent  $\text{H}_2\text{O}$  at 1250°C and 10 kbar in Pt capsules. (A) shows measured iron contents of quenched liquid. The other diagrams show this expressed as percentage of initial FeO lost from the sample.

the results suggest that the properties of the alloy change considerably between 1100°C and 1200°C.

#### Iron Loss from Liquid + Crystal Assemblages

Rock-melting experiments are primarily concerned with equilibrium conditions between liquid and crystals. The results in Figure 2 (Table 2 for details) show the extent to which the crystals maintain equilibrium with the liquid through which iron is diffusing into the capsule walls.

Figures 2A and B show  $\text{Ag}_{75}\text{Pd}_{25}$  results for the phase assemblage garnet(Ga) + clinopyroxene(Cpx) + liquid(L), with 80 percent liquid. The iron loss curve for 100 percent liquid, transferred from Figure 1B, is compared in Figure 2A with the iron lost in 4 hours from the phases in the assemblage. Garnet and clinopyroxene were not present in the starting material, and the 4-hour values were calculated as the difference in iron content of the phases after a 1-hour run, taken as the initial iron content, and the iron content of the phases after a 5 hour run. An unknown but probably significant amount of iron is lost from the crystals + liquid during the hour of mineral readjustment (Fig. 1D). These results are plotted in Figure 2B in terms of the ratio  $\text{Mg}/(\text{Mg} + \sum \text{Fe})$ .

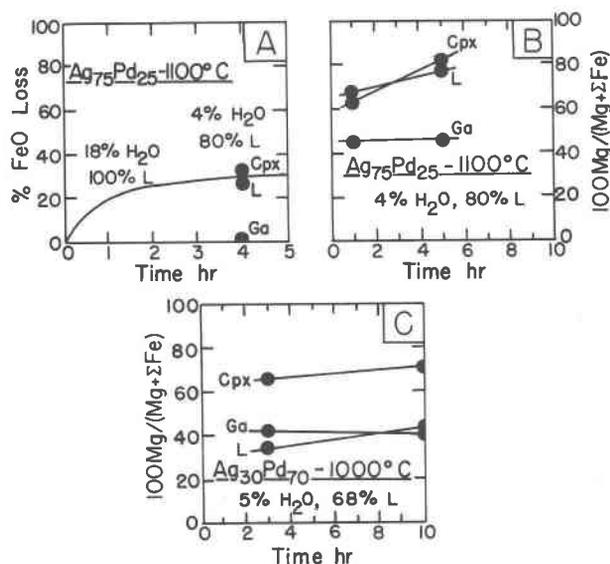


FIG. 2. Iron loss from liquid + crystal assemblages in the crystallization interval of andesite at 30 kbar. See Table 2 for data. (A) The curve for andesitic liquid at 1100°C is transferred from Figure 1B. With 4 percent H<sub>2</sub>O at the same temperature, the charge consists of 80 percent liquid, with clinopyroxene and garnet. The percentages of FeO lost by these phases during a 4-hour interval are plotted. (B) Shows the same data expressed in terms of the magnesium/iron ratio. (C) Similar results at 1000°C with higher percentage of crystals. Abbreviations: Cpx, clinopyroxene; Ga, garnet; L, liquid.

During the 4-hour interval no iron is lost from garnet, but both liquid and clinopyroxene lose about 30 percent, slightly more from clinopyroxene than from liquid. There are significant changes in the Mg/(Mg + ΣFe) ratios for clinopyroxene and liquid.

Distribution coefficients for Fe and Mg between the liquid and minerals therefore vary as a function of run duration. Larger changes in the distribution coefficients can be produced by varying the oxygen fugacity (Mysen and Boettcher, 1973).

Results for essentially the same composition in Ag<sub>30</sub>Pd<sub>70</sub> at 1000°C, where the liquid content is 68 percent (Stern, 1973), are listed in Table 2, and plotted in Figure 2C. During a 7-hour interval between 3 and 10 hour runs, the iron content of garnet barely changed, while it decreased slightly in clinopyroxene and liquid. The rates of change of the ratios Mg/(Mg + ΣFe) in liquid and clinopyroxene are much smaller at 1000°C than at 1100°C, probably due more to the lower temperature than to the smaller proportion of liquid in the assemblage. These results suggest that at 1000°C and below, iron loss is not a serious problem for Ag-Pd capsules in runs of 10 hours duration.

#### Effect of Capsule Size

The amount of iron loss may be a function of surface area of capsule in contact with sample, and the volume ratio of sample/metal, as well as the capsule material. Our Pt capsules had internal diameter 0.0525 inches before being flattened, and held approximately 5 mg of material; our Ag-Pd capsules had internal diameter 0.070 inches and held approximately 10 mg of sample. Irving (1971) determined the iron loss from a nepheline mugearite melt with 2 percent water (20-30% liquid + crystals) to capsules with 0.078 inches internal diameter and 15 mg of sample. After 50 minutes in Ag<sub>75</sub>Pd<sub>25</sub> at 1200°C and

TABLE 2. Microprobe Analyses of Glasses, Garnets, and Clinopyroxenes Quenched from Runs with Andesite Composition Within the Melting Interval at 30 Kbar\*

Conditions	Ag <sub>75</sub> Pd <sub>25</sub>				1100°C		4% H <sub>2</sub> O		Ag <sub>30</sub> Pd <sub>70</sub>		1000°C		5% H <sub>2</sub> O	
	Liquid (L)		Garnet (Ga)		Clinopyroxene (Cpx)		Liquid (L)		Garnet (Ga)		Clinopyroxene (Cpx)			
Time hr.	1	5	1	5	1	5	3	10	3	10	3	10		
Coexisting Phases	Ga	Ga	L	L	L	L	Ga	Ga	L	L	L	L		
	Cpx	Cpx	Cpx	Cpx	Ga	Ga	Cpx	Cpx	Cpx	Cpx	Ga	Ga		
SiO <sub>2</sub>	66.7	66.4	39.1	38.4	51.8	50.9	72.6	73.0	37.6	37.7	49.6	50.6		
TiO <sub>2</sub>	0.7	0.8	1.4	1.2	0.7	0.7	0.7	0.7	2.4	1.4	0.9	0.7		
Al <sub>2</sub> O <sub>3</sub>	18.2	20.1	22.1	22.0	15.7	16.3	17.1	17.3	21.1	20.8	13.8	13.6		
FeO	1.6	1.2	18.7	18.4	7.4	4.0	1.4	1.1	21.1	21.9	9.0	7.6		
MgO	1.8	2.4	8.5	8.5	7.4	9.7	0.4	0.4	8.1	6.7	9.9	10.0		
CaO	3.6	3.8	9.9	10.0	12.9	14.1	3.1	2.8	9.4	11.2	12.6	13.7		
Na <sub>2</sub> O	4.1	3.4	0.2	0.2	4.1	4.3	1.3	1.5	0.2	0.2	4.2	3.9		
K <sub>2</sub> O	3.2	3.0	0.1	0.1	-	-	3.4	3.2	0.1	0.1	-	-		
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0		
100 Mg / Mg+Σ Fe	67.3	78.3	44.9	45.1	63.7	81.5	35.3	42.2	40.6	36.0	66.5	70.1		

\*All analyses are normalized to 100.0, with total Fe as FeO.

30 kbar only 4 percent of the initial FeO was lost (*cf* Fig. 1D). After 45 minutes in Pt at 1130°C and 10 kbar, 32 percent of the initial FeO was lost (*cf* Fig. 1C). Nehru and Wyllie (1975) showed that the rate of iron loss to platinum from partly melted peridotite does decrease with larger capsules.

In different kinds of apparatus where larger capsules can be used, iron losses may be kept within reasonable limits with Ag-Pd alloys (Holloway and Burnham, 1972; Helz, 1973). Fudali (1965) used large Ag-Pd capsules at 1 atm with negligible iron loss even at 1200°C. It is in the small runs in the half-inch diameter piston-cylinder apparatus buffered only by the apparatus that the losses become excessive. They may be reduced by changing oxygen fugacity in buffered runs, as discussed above, but this conventionally requires larger apparatus.

### Attainment of Equilibrium

It is difficult to prove that equilibrium has been established in multicomponent rock-water systems. The phase boundaries determined are commonly the beginning or end of a reaction interval, rather than the univariant reactions of simple systems. Yoder and Tilley (1962) evaluated in detail many of the problems involved, including that of water dissociation and hydrogen migration, which can also affect the amount of iron absorbed by the capsule.

Merrill and Wyllie (1973), referring to iron loss in Pt capsules at 1250°C, concluded that: "Experimental designs must balance the need to keep runs as short as possible in order to minimize the iron loss, against the need for the runs to be of duration sufficient to attain a reasonable approach to equilibrium among phases in the silicate sample." Results in Figures 1 and 2 indicate that this conclusion is valid also for Ag-Pd capsules down to temperatures in the range 1100°C to 1000°C, for the small samples used in piston-cylinder apparatus.

### Experimental Approaches for Equilibrium in Rock Studies

There has been much discussion about the inadequacy of synthesis runs and the necessity for reversal runs in phase equilibrium studies, and the papers by Fyfe (1960) and Yoder and Tilley (1962) include good reviews. In rock systems, demonstration of reversible equilibrium requires more time at high temperatures than do synthesis runs, and the additional iron loss may be sufficient to negate any prospect of equilibrium, even if a phase boundary is apparently reversed. Experimentalists are well aware of the fact

that not all claims of reversibility demonstrate the attainment of equilibrium, and other petrologists who wish to use experimental results should be aware of the problems.

Experimental approaches for evaluating the attainment of equilibrium include comparison of results (1) in runs of varying duration, (2) achieved with different starting materials (crystalline assemblages, oxide mixtures, gels, glasses, and materials seeded with mineral grains of the anticipated product), and (3) obtained using different routines for subjecting samples to run conditions.

All experiments are synthesis runs, in the sense that the products are synthesized from a different starting material. A reversal is simply a pair of synthesis runs using starting materials stable on either side of a phase boundary. Incomplete synthesis is an acceptable test for reversal runs in simple systems, provided that the reactions proceed far enough for directions to be unambiguously established. In multicomponent rock systems, however, it is much harder to establish the direction of equilibrium from incomplete reaction. It is not sufficient to produce a phase; the phase must have the equilibrium composition. As Biggar and O'Hara (1972) have stated: "It is difficult to devise a foolproof reversal of any composition-dependent boundary between two multivariant equilibria fields, particularly when there may be an asymmetric nucleation hysteresis strongly dependent upon the variable structural state of one of the phases (notoriously glass)."

There are problems associated with all starting materials (Yoder and Tilley, 1962; Green and Ringwood, 1972; Kennedy and Ito, 1972). We prefer finely crushed crystalline rock powder, and believe that this is the only material suitable for determination of the solidus (Lambert and Wyllie, 1972). Glasses have some advantages near the liquidus, but Gibb (1974) demonstrated problems in plagioclase nucleation at temperatures below the liquidus.

Figure 3 is a schematic diagram of the different routines used for subjecting samples to run conditions. A is the starting material, either glass or crystalline assemblage, and D, B, and C are multiphase high-pressure assemblages formed at increasingly higher temperatures. The dashed line is a phase boundary between the assemblage B and C. The only test for equilibrium is to synthesize C from B and to reverse this by synthesizing B from C. This cannot be accomplished in one-stage runs using glass or crushed rock as starting material.

One-stage runs are illustrated by routine 1. The

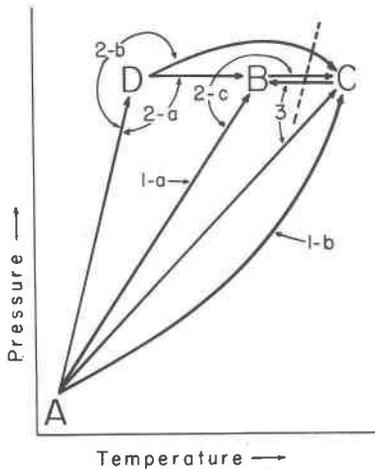


FIG. 3. Experimental routines for locating high-pressure phase boundary between the phase assemblages B and C. Assemblage A represents crushed, crystalline rock in our experiments, but the same applies for glass. 1-a and 1-b are one-stage runs. 2-a, 2-b, and 2-c are two-stage runs from low to high temperatures. 3 is a two-stage run from high to low temperatures. All of these are synthesis runs. Demonstration of reversible equilibrium requires a pair of two-stage runs, 2-c and 3, with all phases in each assemblage reaching appropriate compositions. At temperatures where iron loss is significant (see Fig. 1 and 2), the requirement for two-stage runs ensures that the phase compositions cannot have the correct  $Mg/(Mg + \Sigma Fe)$  ratios.

crystalline starting material A (equally applicable to glass starting material) is brought directly to run conditions where assemblage B is synthesized (routine 1-a), and to a higher temperature where assemblage C is synthesized (routine 1-b). The synthesis phase boundary is drawn between these two runs.

In two-stage low-to-high temperature runs, the low pressure starting material is first converted to a high pressure assemblage, D, then taken to higher temperature conditions where assemblages B (routine 2-a) and C (routine 2-b) are produced. The synthesis phase boundary is drawn between B and C, and if this agrees with the results using routine 1, it indicates that problems of nucleation and kinetics of reaction are not significant. Routine 2-c is another two-stage synthesis, where the starting material A is first run at conditions where the product is B (previously determined from routine 1-a), and then changed to C by increased temperature; but this is now one half of a reversal.

The two-stage high-to-low temperature run 3 is another synthesis run, where the starting material A is first run at conditions where the product is C (previously determined from routine 1-b), and then changed to B by decreased temperature; this is the second half of the reversal.

Two-stage reactions are required to determine the positions of both reactions B→C (routine 2-c) and C→B (routine 3) which bracket the equilibrium position of the phase boundary for the reversal B⇌C. This bracket may not be symmetrical (e.g., MacGregor, 1964) and if there are problems of nucleation or metastable persistence of phases, the bracket may be wide.

The boundaries in many published phase diagrams for rocks were located using one-stage synthesis runs, routine 1. When these boundaries are checked for equilibrium by using reversal routines, the two-stage runs required cause continued iron loss from the sample, especially for the high-to-low temperature runs. Consequently, the Fe-bearing minerals have different compositions by the time the reversal check is completed, and their stability fields should differ from those determined by one-stage synthesis runs. The problem is worse for runs near the liquidus where higher temperatures not only cause more iron loss, but may also increase the errors introduced by thermocouple contamination (Mao, Bell, and England, 1971; Presnall, Brenner, and O'Donnell, 1973).

#### *Clinopyroxene-Out and Garnet-Out Boundaries in Tonalite and Gabbro*

Experimental attempts to establish equilibrium positions for phase boundaries in tonalite and gabbro at 30 kbar are listed in Tables 3 and 4 and plotted in Figures 4 and 5.

The tonalite starting material (A, Fig. 3) consists of plagioclase, quartz, orthoclase, biotite, hornblende,

TABLE 3. Experimental Runs to Check Equilibrium with Tonalite and 10% H<sub>2</sub>O at 30 Kbar in Ag<sub>30</sub>Pd<sub>70</sub> Capsules

Temperature °C	Time hr	Phases Produced
<u>One-stage runs</u>		
925	2	Ga, Cpx, Ky, L
950	1	Ga, L
1125	1	Ga, L
1150	1	L
950	11	Ga, L
1100	11	Ga, L
1125	8	L
<u>Two-stage runs. First stage, 2 hr at 900°C, produced Ga+Cpx+Ky+L</u>		
950	2	Ga, Cpx, Ky, L
950	11	Ga, Cpx, Ky, L
975	2	Ga, L
<u>Two-stage runs. First stage, 1 hr at 1000°C, produced Ga+L</u>		
1125	1	Ga, L
1150	1	L
890	12	Ga, Cpx, Ky, L
910	12	Ga, Ky, L
925	10	Ga, Ky, L

and 10 percent H<sub>2</sub>O. Figure 4 shows the results of attempts to reverse the Cpx-out boundary in the tonalite, near 950°C, where the assemblage changes from Cpx + Ga + Ky + L (B, Fig. 3) to Ga + Ky + L (C, Fig. 3) (Stern and Wyllie, 1973; Stern, Huang, and Wyllie, in preparation). The effects of iron loss in Ag<sub>80</sub>Pd<sub>70</sub> capsules are minor at temperatures below 1000°C (Fig. 2C).

Short duration, two-stage low-to-high temperature runs (routines 2-a and 2-b in Fig. 3, with assemblage D the same as B) bracket the boundary at 25°C higher than the one-stage runs. Long duration two-stage high-to-low temperature runs (routine 3 in Fig. 3) bracket the boundary approximately 40°C lower than the one-stage runs. These results show that Cpx is slower to nucleate in the assemblage Ga + L than in the low-pressure crystalline assemblage, and that Cpx does not nucleate in the latter assemblage in the temperature interval (about 25°C) where Cpx persists, perhaps metastably, in the Cpx + Ga + Ky + L assemblage. The pair of runs comprising the reversal are at 890°C and 975°C, giving a very wide bracket.

TABLE 4. Experimental Runs to Check Equilibrium with Gabbro at 30 Kbar in Pt Capsules, with 10% and 30% H<sub>2</sub>O

Temperature °C	Time hr	Phases Produced
<u>10% H<sub>2</sub>O, one-stage runs</u>		
1150	1	Ga, Cpx, L
1175	1	L
1200	1	L
1150	6	Ga, Cpx, L
1175	6	Cpx, L
1150	12	Cpx, L
1200	12	L
<u>10% H<sub>2</sub>O, two-stage runs.</u>		
<u>First stage, 1 hr at 1000°C,</u>		
<u>produced Ga+Cpx+L</u>		
1125	1	Ga, Cpx, L
1150	1	Ga, Cpx, L
1175	0.5	L
1225	0.5	L
1175	2	Cpx, L
1200	2	L
1150	6	Ga, Cpx, L
1175	5	Cpx, L
1125	12	Ga, Cpx, L
1150	12	Cpx, L
<u>30% H<sub>2</sub>O, one-stage runs</u>		
1075	1	Ga, Cpx, L, V
1100	1	L, V
1050	6	Ga, Cpx, L, V
1075	6	Cpx, L, V
1100	6	L, V
1050	12	Ga, Cpx, L, V
1075	12	Cpx, L, V
1100	12	L, V
<u>30% H<sub>2</sub>O, two-stage runs.</u>		
<u>First stage, 6 hr at 950°C,</u>		
<u>produced Ga+Cpx+L+V</u>		
1050	12	Ga, Cpx, L, V
1075	10	Cpx, L, V

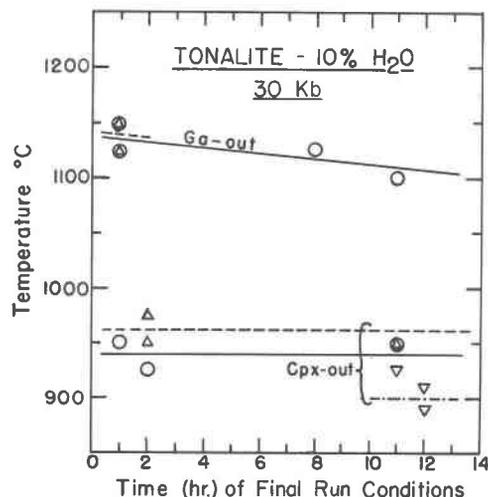


FIG. 4. Effect of run duration and experimental routines (Fig. 3) on the recorded positions of phase boundaries in tonalite with 10 percent H<sub>2</sub>O at 30 kbar, in Ag<sub>80</sub>Pd<sub>70</sub> capsules. Circles are one-stage runs (solid lines), triangles with apex upwards are two-stage low-to-high temperature runs (dashed line), triangles with apex downwards are two-stage high-to-low temperature runs (dot-dash line). For two-stage runs, the time plotted is for the second stage only. See Table 3 for run data. Abbreviations: Ga, garnet; Cpx, clinopyroxene.

For the Ga-out boundary in Figure 4, which is the liquidus (Stern and Wyllie, 1973), one-stage and two-stage low-to-high temperature runs give the same bracket in 1-hour runs. One-stage runs show that the boundary moves to lower temperatures with increased time. This could be due to progressive thermocouple contamination, which causes recorded temperatures to be lower than actual temperatures, although this is not normally found to be a problem at temperatures below 1300°C (e.g., Hensen, 1973). Alternatively, it is due to the changing relative compositions of liquid and garnet (Fig. 2).

Figure 5 compares one-stage runs with two-stage low-to-high temperature runs (routines 1 and 2, Fig. 3) for determination of the liquidus of gabbro in Pt capsules. Times plotted are for the second stage of the two-stage runs. Two-stage high-to-low temperature runs (routine 3, Fig. 3) for completion of reversals from the liquid field are not shown because too much iron is lost during the first stage (Fig. 1), and thermocouple contamination at the higher temperatures becomes more of a problem. The gabbro starting material consists of plagioclase, augite, serpentine, and magnetite.

Figure 5A shows results near 1175°C using 10 percent H<sub>2</sub>O. In runs of 1 to 2 hours the boundary between the assemblages Ga + Cpx + L and L is

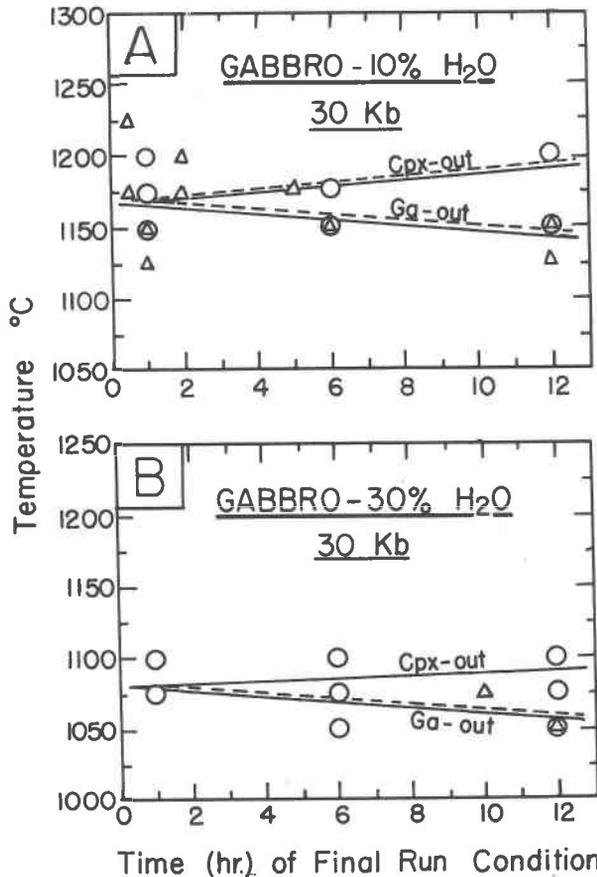


FIG. 5. Effect of run duration, temperature, and experimental routines (Fig. 3) on the recorded positions of phase boundaries in gabbro in platinum capsules at 30 kbar with (A) 10 percent H<sub>2</sub>O and (B) 30 percent H<sub>2</sub>O. Circles are one-stage runs (solid lines), triangles with apex upwards are two-stage low-to-high temperature runs (dashed lines). For two-stage runs, the time plotted is for the second stage only. See Table 4 for run data. Abbreviations: Ga, garnet; Cpx, clinopyroxene.

bracketed within a 25°C interval using either routine. With one-stage runs of longer duration, garnet disappears below the liquidus, as the Ga-out boundary moves to lower temperatures, and the Cpx-out boundary moves to higher temperatures. The same changes are shown by the two-stage runs. In Figure 5B, the liquidus is lowered through about 100°C by using 30 percent H<sub>2</sub>O, and the one-stage runs show similar results, with divergence of the Cpx-out and Ga-out phase boundaries after a few hours. It was not established that the Cpx-out boundary increased in temperature. The long-duration two-stage runs agree with the one-stage runs. The increasing Mg/(Mg + ΣFe) in clinopyroxene as a function of run duration (Fig. 2) is consistent with increased temperature for the Cpx-out boundary in Figure 5A.

## Conclusions

Iron loss from rock-H<sub>2</sub>O systems to Ag-Pd capsules at 1100°C and above is significant in runs of duration 1 hour or more. Iron is not lost uniformly from all phases in crystal + liquid assemblages, and the distribution of Fe and Mg among crystals and liquid therefore changes as a function of run duration.

Consistency between one-stage and two-stage low-to-high temperature runs for tonalite and gabbro with at least 10 percent H<sub>2</sub>O and at temperatures between 1050°C and 1200°C suggests a close approach to equilibrium after 1 hour runs, with no kinetic problems or problems of nucleation for garnet and clinopyroxene under these conditions. The longer run times and exposure to higher temperatures that would be required to demonstrate reversible equilibrium, however, cause the recorded positions of the Cpx-out and Ga-out phase boundaries to change temperature in different directions, with discrepancies reaching 25–50°C after 12 hours in both Ag-Pd and Pt capsules. Reversible equilibrium cannot be closely defined in a system with progressively changing bulk composition.

At 950°C where iron loss is much lower, Figure 4 shows that clinopyroxene is reluctant to nucleate in the high-pressure phase assemblage, and the Cpx-out phase boundary is reversible only within the wide bracket 890–975°C. It is well established that garnet is reluctant to nucleate under these conditions (Green, 1972; Lambert and Wyllie 1972, 1974).

In their experimental study of equilibrium with granitic rocks, Piwinski and Martin (1970) concluded thus: "Future investigators of granite-water systems, or of rock-water systems simulating anatectic processes, should be cognizant of, and rigorously evaluate, all factors influencing reaction kinetics; '... valuable and reliable results can be obtained if the experimenter is willing to make experiments of months, and not days' (Fyfe, 1960)." In high-temperature rock-water systems a close approach to equilibrium appears to be attainable in runs measured in hours rather than in days (Figs. 4 and 5), but in systems with low water contents, or with compositions approaching rhyolites where reactions are more sluggish, the longer runs required to achieve satisfactory reaction and to test for reversible equilibrium may cause sufficient iron loss and possibly thermocouple contamination to shift the positions of recorded phase boundaries. Compromise is required.

In his review of the manuscript by Nehru and Wyllie (1975) about a partly melted peridotite, J. Hol-

loway wrote: "I think they are to be commended for exposing some of our dirty linen, but I think a plea should now be made to stop doing experiments which yield unacceptably poor data. Either a new capsule material must be found or we must confine ourselves to iron-free systems, or we must become theoreticians!" (personal communication, 1974). On the other hand, we can argue that the outline of a phase diagram for an Fe-deficient rock is better than no diagram at all, as long as those who use it are aware of its limitations. Theoreticians need numbers to work with, and in extrapolating calculations from low pressures to phase relations involving liquids at 30 kbar, we suspect that errors may be larger than an experimental error of  $\pm 50^\circ\text{C}$ .

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