

# Problems of Iron Gain and Loss during Experimentation on Natural Rocks: The Experimental Crystallization of Five Lunar Basalts at Low Pressures [and Discussion]

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## Problems of iron gain and loss during experimentation on natural rocks: the experimental crystallization of five lunar basalts at low pressures

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It is extremely difficult to conduct melting experiments on iron-bearing silicate compositions under conditions where the oxygen fugacity and iron oxide content of the charges are controlled precisely at the relevant values, due to reactions between the charge, the container and the adjacent atmosphere. Possible effects are illustrated by discussion of the experimental data for five lunar basalts. At low oxygen fugacities the techniques using molybdenum capsules in an atmosphere whose oxygen fugacity is controlled by passage of a  $\text{CO}_2/\text{H}_2$  mixture, and that of enclosing (better, sealing) the charge inside a high purity iron capsule inside a sealed, evacuated silica glass tube yield results which are relatively close to the desired run conditions.

### 1. INTRODUCTION

This paper directs its attention to two specific problems of composition control which have been analysed from the copious data obtained for the experimental crystallization of low titanium lunar mare basalts in several laboratories and by a variety of techniques at or below atmosphere pressure (a similar analysis cannot yet be performed for a single terrestrial basalt). These problems, which are of course linked, are the control of oxygen fugacity in the system, and the gain or loss of iron by the charge reacting with various types of container. The intentions of the paper are to quantify the problems for specific cases, to illustrate the value of two data projections in the evaluation of the data, and to relate to each other and to the changes in composition consequent upon the technique used, the results observed in different laboratories for the crystallization sequences in selected samples. It is our hope that this paper will improve general understanding of the problems inherent in the experimental study of natural basalts.

The preparation of this paper would not have been possible without the generous provision of unpublished microprobe analyses of experimental charges by D. Walker.

The basalts, whose experimental crystallization is discussed here, are the picrite basalts 12002 and 12040 from Oceanus Procellarum (Apollo 12), picrite basalt 15555 and pigeonite-porphyrines 15065, 15058 from the vicinity of Hadley Rille (Apollo 15). Each of these samples represents a material which has been assumed to be a primary magma derived directly from the lunar mantle. The arguments in favour of, or against the validity of those assumptions depend in part upon the precise values of iron–magnesium ratio developed in the liquids and crystals during low pressure experimental crystallization of the samples. In addition to illustrating some general aspects of the problems of experimentation with natural basalts and a convenient graphical method for their evaluation, this paper emphasizes the dangers inherent in reasoning from the fine detail of experimental results without due regard to the problems of composition control. This latter point has been pursued further by O'Hara *et al.* (1975) and is not expanded here.

Natural crystallization of the five samples occurred at low pressures and at low oxygen fugacities, where most iron was present as  $\text{Fe}^{2+}$ , and iron metal was close to being in equilibrium with the sample. The picrite basalts have olivine or chrome spinel as liquidus phase (at  $> 1325^\circ\text{C}$ ) at low pressure, joined soon by the other of these phases. Later in their crystallization, calcium-poor pyroxene appears, and eventually anorthite-rich plagioclase begins to crystallize (at *ca.*  $1160^\circ\text{C}$ ). The pigeonite porphyries crystallize some olivine, but spinel, calcium-poor pyroxene and anorthite-rich plagioclase dominate the crystallization sequences.

Further accounts and discussions of the experimental crystallization of the rocks can be found in Biggar, O'Hara, Peckett & Humphries (1971), Biggar, O'Hara & Humphries (1972), Green *et al.* (1971*a*), Green, Ware, Hibberson & Major (1971*b*), Grove, Walker, Longhi, Stolper & Hays (1973), Humphries, Biggar & O'Hara (1972), Longhi *et al.* (1972), Walker, Kirkpatrick, Longhi & Hays (1976). (The debate (see O'Hara & Humphries (1977)) about the manner in which these rock compositions are related to the actual magmas which erupted onto the lunar surface is irrelevant here. This paper is solely concerned with the problems of experimenting under control upon five rock samples distributed by N.A.S.A.).

## 2. DATA REPRESENTATION

Because the amount of the spinel which crystallizes is small (estimated at less than 3% by mass from consideration of the  $\text{Cr}_2\text{O}_3$  balance), it is convenient to represent the rock and mineral compositions in a projection from the sum of all spinel components into the 'plane' of the other major minerals which are calcic plagioclase, calcium-poor pyroxene and olivine. A suitable projection is that from the 'spinel' point of the four-component, isostructural, equivalent weight projection (used by O'Hara 1968; Jamieson 1970) into the plane  $\text{XO} \cdot \text{R}_2\text{O}_3\text{-YO-ZO}_2$  which bisects the four-component tetrahedron. This plane, which is analogous to  $\text{CaO} \cdot \text{Al}_2\text{O}_3\text{-MgO-SiO}_2$ , contains the compositions of anorthite (with which is combined the albite as an equivalent number of feldspar molecules), forsterite and enstatite (with which are combined, on a molecularly equivalent basis the appropriate FeO- and MnO-bearing molecules). Iron oxide gain from the containers or iron oxide loss from the charges is expressed in such a projection by movement of the charge composition respectively towards or away from the  $\text{YO}(\text{MgO})$  apex along a control line passing through the initial bulk composition of the sample.

Gain or loss of iron changes the  $\text{MgO}/\text{FeO}$  ratio of the silicate charge, and alters the silica-saturation level (e.g. in terms of C.I.P.W. normative minerals). A second projection which is extremely useful in representing the mineralogical effects of gain and loss of iron is that from the feldspars, apatite, the  $\text{CaSiO}_3$ -component of pyroxene, and  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ , ( $\text{Fe}_2\text{O}_3$ ) into the plane  $\text{MgO-FeO-SiO}_2$ . This plane contains the compositions of the olivines and the calcium-free pyroxenes. Gain or loss of iron appears in this projection as a movement of the charge composition respectively towards or away from the  $\text{FeO}$ -apex along a control line passing through the initial bulk composition of the sample. Phase equilibria between the liquidus fields of olivine, calcium-poor pyroxene and silica minerals encountered in the natural rocks should be (and are) analogous to those reported by Bowen & Schairer (1935) and Roeder & Osborn (1966).

When projected into these two projections, the results are expected to conform *approximately* with the pseudo-ternary phase diagrams shown in figures 1 and 2.

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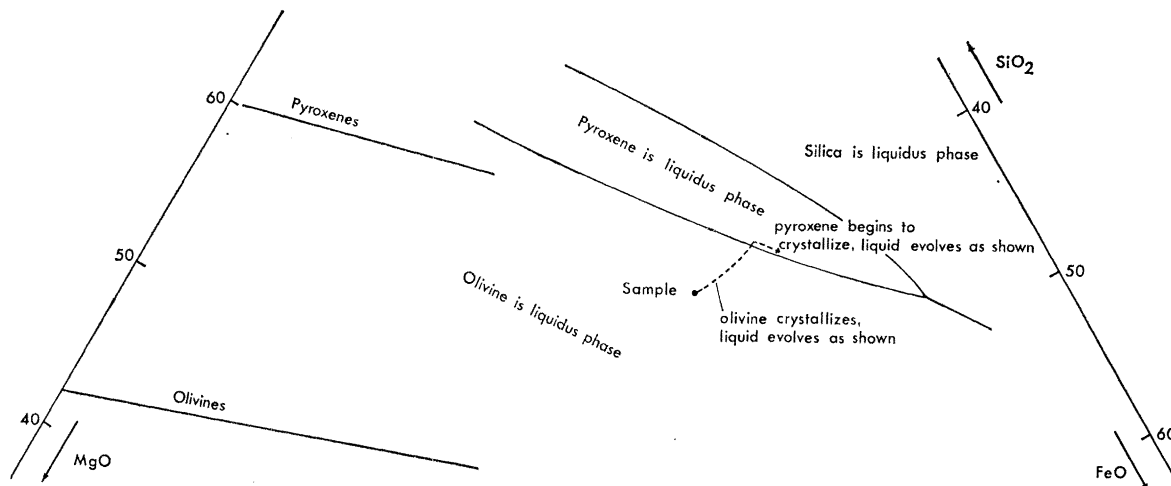


FIGURE 1. Projection into plane MgO-FeO-SiO<sub>2</sub> from feldspar, CaSiO<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> etc. as in Ford *et al.* (1972), showing expected liquidus phase fields.

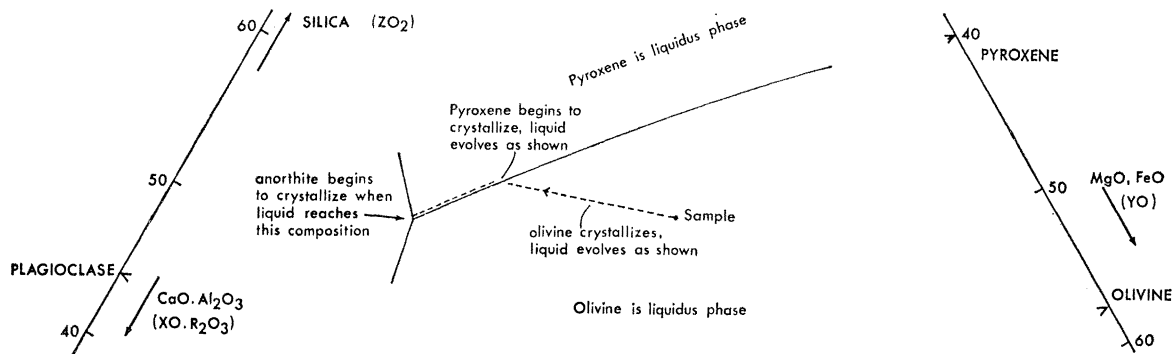


FIGURE 2. Projection into plane XO.R<sub>2</sub>O<sub>3</sub>-YO-ZO<sub>2</sub> (including anorthite-olivine-silica) from spinel (YO.R<sub>2</sub>O<sub>3</sub>) in scheme of O'Hara (1968), Jamieson (1970).

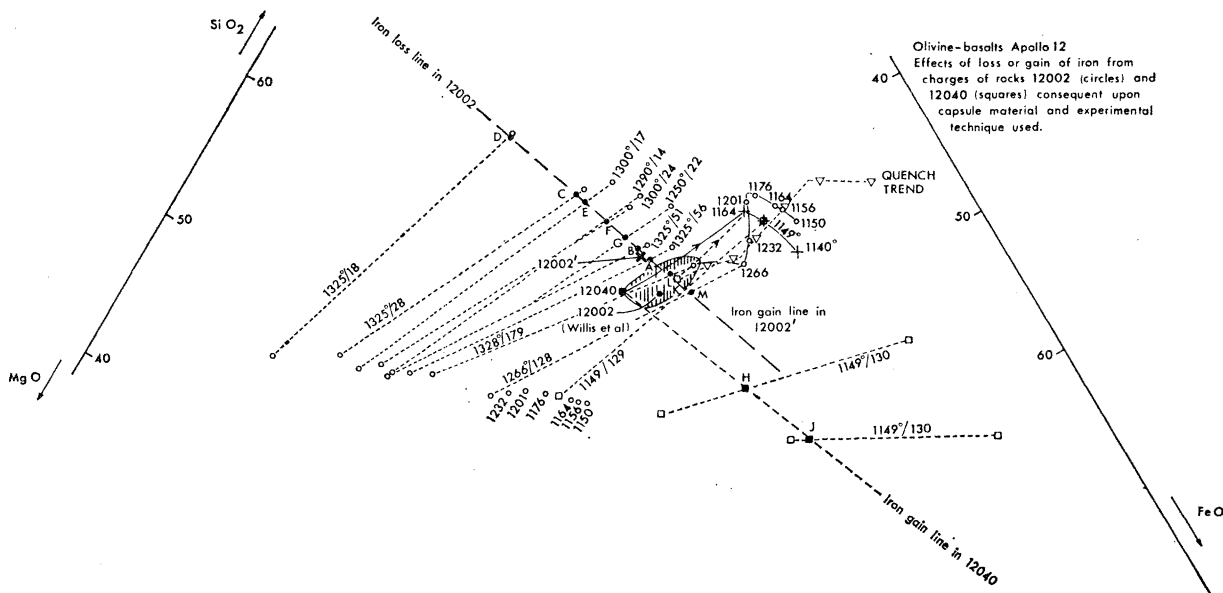


FIGURE 3. Projection into plane MgO-FeO-SiO<sub>2</sub> of data for samples 12002, 12040. Explanation in the text. Remember: pyroxene is present in most runs at or below 1180 °C. Corrigendum: the upper line labelled 1149°/130 should be 1149°/130a, and the lower, 1149°/130b.

Residual liquids saturated with olivines and calcium-poor pyroxene, even when simultaneously saturated with plagioclase, will not in fact project exactly along a unique curve as implied by figure 1 because of differences in the chromium, titanium and alkali contents of the systems. Likewise they will not project exactly along a unique position of the olivine-pyroxene liquidus interface, or attain a unique composition at simultaneous saturation with olivine, pyroxene and anorthite, because of differences in the FeO/MgO ratio, the alkali, Cr<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> or normative diopside content of the liquids concerned. Nevertheless, the figures illustrate the way in which residual liquids should evolve from any one fixed bulk composition during cooling in equilibrium experiments.

### 3. RESULTS FROM LOW TITANIUM LUNAR BASALTS

#### (a) *Picrite basalts 12002 and 12040: variations in Fe/Mg ratio and silica contents*

Figure 3 illustrates, in terms of variations in Mg/Fe ratio and silica-saturation level, the effect of loss or gain of iron upon bulk sample, liquid and olivine composition obtained from natural olivine-basalt samples 12002 (Grove *et al.* 1973) and 12040 (Biggar, O'Hara & Humphries, unpublished). The shaded field encloses all analyses of Apollo 12 olivine basalts, except that of 12002 by Grove *et al.* (cross, 02') which is based upon microprobe analysis of an all-glass charge obtained in a graphite capsule at 5 kbar†. The compositions of natural samples 12040 (Kushiro & Haramura 1971) and 12002 (Willis *et al.* 1971) are indicated. The analysed compositions of olivine and liquid from four different experiments (56, 51, 28, 18) at 1325 °C are plotted, together with the bulk compositions of the charges A, B, C, D inferred from the observation that the actual charges consist of olivine and glass only, and that the bulk compositions differ from 12002' only by gain or loss of FeO.

The techniques used by Grove *et al.* (1973) were to enclose the charges in molybdenum or iron capsules enclosed in evacuated sealed silica glass tubes, or to run at a controlled oxygen fugacity in a molybdenum container. At the low inherent oxygen fugacity of the charges, in which the activity of metallic iron is close to one, iron is very soluble in the molybdenum capsules. Iron is lost from the charge to the capsule, and oxygen is released to the atmosphere inside the capsule, raising the oxygen fugacity until the iron activity is reduced to the point where no further iron dissolves in the molybdenum. The size of this effect will be, to an extent time dependent, but it will also depend upon the size and configuration of the charge, and the extent to which released oxygen can escape from the molybdenum capsule.

Even greater losses of iron from the charge may occur when a similar technique is utilized but a capsule of spectrographic purity iron is substituted for the molybdenum. If the iron contains any carbon (not reported in the analysis) even more extensive reduction of the charge may occur than in the previous case.

Of the four experiments on 12002 at 1325 °C, run 18 (bulk composition D) was carried out in an iron capsule for 19.5 h, and has lost more iron (about half of its original 21.66 % FeO) than run 28 (bulk composition C) run for 10.1 h in a sealed molybdenum capsule. Run 56 (bulk composition A) which appears to have lost little or no iron, was run in molybdenum at a controlled oxygen fugacity of 10<sup>-11</sup> atm‡ for 1.25 h. Run 51 (bulk composition B), by the same technique, and for only 0.5 h at the slightly lower oxygen fugacity of 10<sup>-11.4</sup> atm

† 1 kbar = 10<sup>8</sup> Pa.      ‡ 1 atm ≈ 10<sup>5</sup> Pa.

has likewise retained most of its original iron. At lower oxygen fugacities, iron losses to molybdenum capsules become severe (see discussion of run 12040/129 below, and see O'Hara, Humphries & Waterston (1975)).

Also shown (figure 3) are analysed olivine-liquid assemblages from experiments at 1300 °C (runs 17, 24), 1290 °C (run 14) and 1250 °C (run 22) and their respective inferred bulk charge compositions, E; F; F and G.

Runs 17 and 14 at 1300 °C, 1290 °C respectively were also carried out in sealed iron capsules for 21.8 and 3.8 h respectively, whereas runs 24 and 22 at 1300 °C, 7.7 h and 1250 °C, 6.5 h respectively were carried out in sealed molybdenum capsules and appear to have lost less, but still significant amounts of iron.

Results reported by Grove *et al.* (1973) at 1225 °C for iron and molybdenum capsules show a range of olivine composition from Fo<sub>76</sub> to Fo<sub>88</sub> (in the iron capsule) which is as great as the range of composition reported at 1325 °C, implying that iron loss in the iron capsule at 1225 °C (a 40.7 h run) is at least as great as in run 18 at 1325 °C. A consequence of iron loss from the charges is that the olivine/calcium-poor pyroxene liquidus interface is likely to be encountered by the residual liquids at a higher temperature than would have otherwise been the case, and the same is true for the first appearance of plagioclase when the residual liquids meet the olivine-pyroxene-plagioclase cotectic. Grove *et al.* (1973) bracket the first appearance of plagioclase in 12002 at 1165 ± 10 °C in molybdenum capsules, or 1170 ± 5 °C in iron capsules, which may be compared with *ca.* 1160 °C reported by Biggar *et al.* (1971) for rocks 12040, 12018, 12020 which belong to the same petrographic group.

Serious iron loss appears to have affected most of the experiments on 12002 carried out in sealed silica tubes. The experimentally produced residual liquids from charges in which most of the iron has been retained as FeO are represented here by the heavy curves expressing the evolution of residual liquids from 12040 (figure 3) in experiments carried out in controlled atmospheres in molybdenum capsules (Biggar *et al.* 1971). The sealed silica glass tube technique using molybdenum or iron capsules of spectrographic purity does not appear to be a viable method of experimentation on lunar samples.

Subsequently Walker *et al.* (1976, Table 1) carried out further experiments on 12002, utilizing the sealed silica tube technique, but with capsules of the highest purity ('carbon-free') iron available. The apparent trend of liquid evolution in these experiments is shown by the sequence of open circles linked by a continuous line starting from the open square, K, which marks the bulk composition of an all glass charge obtained at 1350 °C. K is displaced from the starting composition 12002' along the iron-gain control line. The bulk compositions of two other charges run at 1328 °C (run 179) and 1266 °C (run 128) are shown by L, M respectively along this same iron-gain control line. All the charges run at temperatures above 1201 °C by this technique appear to have gained a small amount of iron oxide relative to the starting material 12002'. Oxygen diffuses through silica-glass tubes at high temperatures (Gray, Reid & Jones 1974) and will react at the charge/container interface to add FeO to the silicate charge at an oxygen fugacity well below that at which iron metal itself begins to oxidize (i.e. the reaction may have occurred despite the fact that the outside of the capsule is un-tarnished). This effect has also been demonstrated to affect results for lunar high titanium basalts (O'Hara *et al.* 1975).

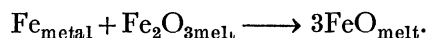
The series of inverted triangles linked by a broken line ('quench trend') represents the path of liquid evolution in the charge 12002' during cooling experiments at various rates of

less than 50 °C/h (Walker *et al.* 1976, Table 2) in which olivine and spinel crystallization is enhanced at the expense of a delayed appearance of pyroxene, and an even more delayed appearance of plagioclase. These results, gained by the same basic technique as the equilibrium run data, also appear to be subject to comparable amounts of iron-oxide gain.

Contrasting with the severe loss of iron which resulted in the experiments with spectrographically-pure iron capsules and the small gain in iron which resulted in the experiments with high purity iron capsules reported above, extensive gain of iron is liable to occur when iron capsules are used in experiments at controlled oxygen fugacities which, while above those at which iron metal is in equilibrium with the original sample, are nevertheless below those at which pure iron oxidizes to FeO.

The effect of iron loss to molybdenum and gain from iron capsules is shown by experiments 129 and 130 on sample 12040, which were run side by side in the same controlled atmosphere furnace at the relatively low oxygen fugacity of  $10^{-12.5}$  atm at 1149 °C. Experiment 129 used a molybdenum capsule. Because the oxygen fugacity is a power of ten lower than that of the Fe/FeO equilibrium, a small amount of iron dissolved in the molybdenum capsule (this is not obvious from figure 3). Metallic iron is *not* produced from the charge until lower oxygen fugacities are attained. Experiment 130 used an iron capsule. Metallic iron is not in equilibrium with charge 12040 at this oxygen fugacity, hence oxygen from the gas atmosphere reacts with iron from the capsule to produce FeO which dissolves in the silicate liquid. Two olivine-liquid tie lines (130a, 130b) from different portions of the inhomogeneous charge which resulted from experiment 130 and two different bulk compositions (H, J) are shown, the more iron-rich presumably coming from a part of the charge which was closer to the capsule wall.

Results of experiments on 12040 by yet another technique have been reported by Green *et al.* (1971a). The sample was first fused at some high temperature in a gas furnace, then portions of the glass were run in tightly closed, high purity iron capsules sealed within platinum tubes packed with carbon. It is anticipated that the initial glass produced in this fashion will contain some Fe<sup>3+</sup>. During the experiment this will react with the iron container, adding iron to the charge thus:



Comparisons (O'Hara *et al.* 1975, Figure 4) between the olivine compositions reported from their charges and those reported by Biggar *et al.* (1971) indicate that Green *et al.*'s (1971a) experiments produced a series of residual liquids which would be displaced to the FeO-rich side of the trend for 12040 shown in figure 3. The temperature at which Green *et al.* (1971a) reported the first appearance of plagioclase in their charges is 20 °C below that reported by Biggar *et al.* (1971, 1972), consistent with an iron oxide gain of the type discussed. In the case of a high titanium basalt, the charges obtained by Green *et al.*'s (1971a) technique have apparently gained more iron oxide than charges run in high purity iron capsules in sealed silica tubes (O'Hara *et al.* 1975).

(b) *Picrite basalts 12002 and 12040: variations in feldspar, olivine and silica contents*

Figure 4 is a projection from spinel into the system  $\text{XO} \cdot \text{R}_2\text{O}_3 - \text{Z}\text{O}_2 - \text{Y}\text{O}$  (which contains the section anorthite-olivine-silica) of the data for samples 12002 and 12040. The compositions of 12002 (Willis *et al.* 1971) and 12040 (Kushiro & Haramura 1971) as well as the analysis (cross, 02') of 12002 provided by Grove *et al.* (1973) are shown.

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The effects of loss or gain of iron oxide upon silica saturation level and upon the ratio of feldspathic components to ferromagnesian silicate components in the experiments on 12002 and 12040 are illustrated in this projection (figure 4). Compositions which have lost or gained iron will fall along control lines drawn from the YO apex, extending through the bulk compositions of the starting materials. It is possible in this type of projection to draw a pseudo-quaternary phase diagram which describes the early crystallization of the natural samples showing boundaries between liquidus fields of olivine, pyroxene and anorthite, when all iron is retained as FeO. It is, however, impossible to draw a unique position of the boundary between the olivine liquidus and the pyroxene liquidus for the charges which have gained or lost iron; the boundary sought must be in a different position for each Mg/Fe ratio in the final bulk charge, as also must be the position of the anorthite liquidus field.

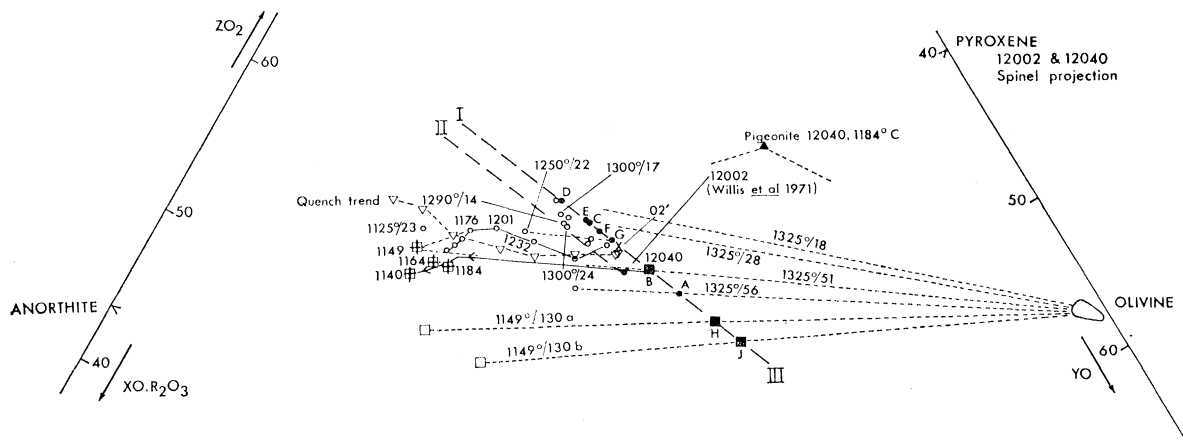


FIGURE 4. Projection from spinel into plane  $XO.R_2O_3$ - $YO$ - $ZO_2$  of data for samples 12002, 12040. Explanation in the text.

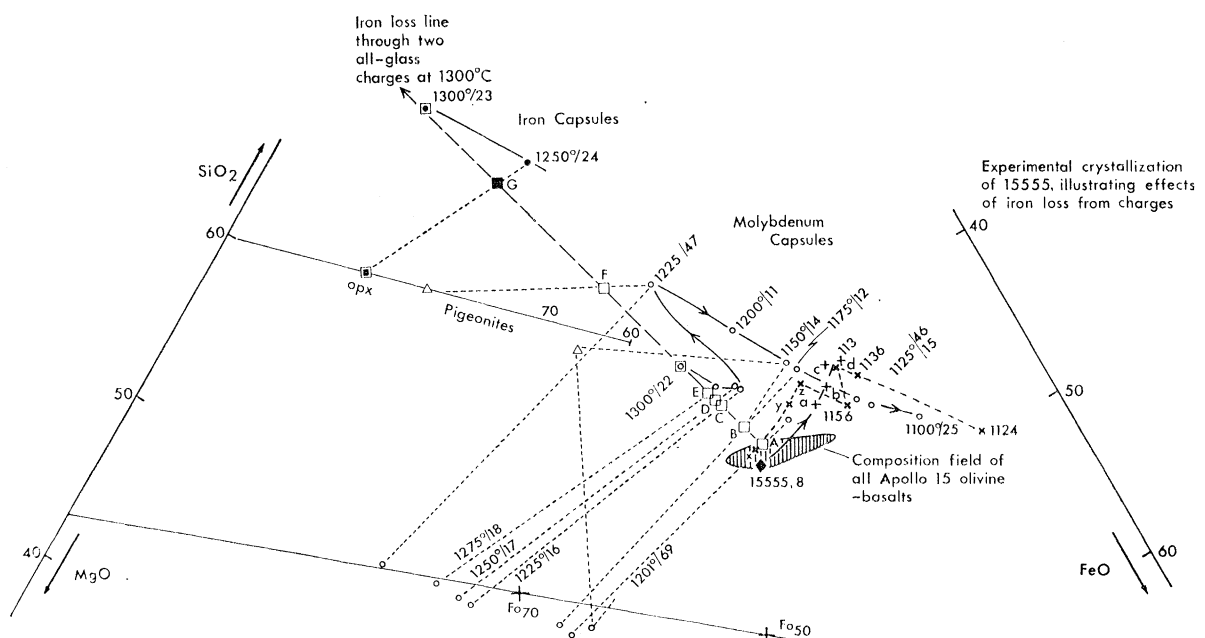


FIGURE 5. Projection into plane  $MgO$ - $FeO$ - $SiO_2$  of data for sample 15555. Explanation in the text.



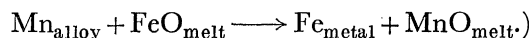
Liquid compositions in the experiments on 12002 at 1325 °C, 18, 28, 51 and 56, are shown by appropriately numbered small circles and tie lines. Tie lines linking these compositions to 'olivine' intersect the iron-loss line drawn through the original bulk composition of the material used for the experiments at points corresponding in this projection with the bulk compositions labelled D, C, B and A respectively in figure 3. Remarks made in connection with that figure again apply.

The residual liquid developed from 12002 at the lowest temperature (run 23 at 1125 °C), is also shown in relation to the trend of residual liquid evolution deduced from the crystallization of rock 12040 (Biggar *et al.* 1971) under conditions where little iron is lost. The evolution of liquids from 12002 in the equilibrium and quenching experiments of Walker *et al.* (1976) are shown as before. The iron gain in the higher temperature charges of both trends (construct the required bulk compositions L, M relative to 02') is conspicuous, the apparent liquid evolution being inexplicable in terms of the crystallization of olivine from a charge of fixed composition.

An iron-gain control line, virtually the same as that through 12002', has been drawn from the composition of 12040 towards the YO apex. The compositions of the two glasses obtained from a run (130) in an iron capsule at a controlled oxygen fugacity of  $10^{-12.5}$  atm (below that of the Fe/FeO equilibrium, but above that of the equilibrium appearance of iron in a silicate charge of 12040 composition) have been plotted and joined to olivine by dotted tie lines. Their intersections with the iron-gain control line mark the compositions of two of the glass compositions H, J, which were generated in this manifestly inhomogeneous run product. Since pyroxene is present in the glass from experiment 129, run in a molybdenum capsule at a controlled oxygen fugacity of  $10^{-12.5}$  atm, it is evident that some iron loss must have occurred. (The olivine-liquid tie line, coincident with 1325°/51, passes through the starting composition.)

Finally, it is evident from figures 3 and 4 that the sample 12002' falls outside (to the iron-poor side of) the field of Apollo 12 picrite-basalts (which extends in figure 4 to the olivine-poor side of 12040). The reasons for this are not clear, but may be connected with the previous use of the subsample for other types of experiment (see D'Amico *et al.* (1971)) which involved melting and remelting for unstated periods in an uncontrolled  $N_2-H_2-O_2$  atmosphere in contact with an undisclosed container material.

(Several investigators have used (inadvertently) iron capsules containing up to 50 parts Mn/10<sup>6</sup>. At the oxygen fugacities of these experiments, virtually all this manganese will be oxidized into the melt, and in closed systems, reduction of iron from the charge may occur, by the reaction:



(c) *Picrite-basalt 15555: variations in Fe/Mg ratio and silica contents*

Figure 5 illustrates for sample 15555, an Apollo 15 olivine-basalt, the effects of differing degrees of iron-loss upon the phase equilibria observed by different techniques. The filled diamond shows the analysed composition of sample 15555, 8 (Rhodes & Hubbard 1973). The curve rising from it passes through successive residual liquid compositions (crosses) obtained from charges held in molybdenum capsules in a controlled atmosphere at the oxygen fugacity of the Fe/FeO equilibrium (Humphries *et al.* 1972) under which conditions negligible iron is lost from the charge ( $a = 1200$  °C;  $b = 1173$  °C;  $c = 1150$  °C;  $d = 1145$  °C).

Longhi *et al.* (1972) report two experiments at 1300 °C from which glass only was obtained (run 23 in spectrographically-pure iron capsule in sealed silica tube; run 22 in a molybdenum

capsule in sealed silica tube; compositions shown by boxed circles). Both have lost substantial amounts of iron for reasons already discussed. A line, expressing possible bulk compositions of charges which might be generated by iron loss from the original sample has been drawn through these two bulk glass compositions towards the FeO apex of the diagram. This line passes close to 15555, 8. Experiment 69, at 1201 °C was carried out at a controlled oxygen fugacity of  $10^{-12}$  atm in a molybdenum capsule, under which conditions little iron loss should have occurred. Olivine and glass (both shown by open circles) were the only products, hence the bulk composition of the starting material is identified as A (open square).

Four experiments (12, 16, 17, 18 at 1175, 1225, 1250 and 1275 °C respectively) in molybdenum capsules inside sealed silica glass tubes are reported as yielding essentially olivine and glass (spinel is reported from 12, 16 and minor pyroxene from 12). These results enable the bulk compositions of these particular charges to be approximately located at B, C, D, E (open squares) respectively, the extent of iron loss apparently increasing with the run temperature.

A second rather lengthy experiment at 1225 °C (no. 47) by the same technique, however, yielded pigeonite and glass with only minor olivine and spinel. From these data it is possible to locate the bulk composition of this charge as lying close to F (open square), and a much greater iron loss than in the other experiments is indicated.

Where capsules of spectrographic purity iron were used inside sealed glass tubes still greater iron losses are reported. Experiment 24, at 1250 °C yielded calcium-poor orthopyroxene and glass only, enabling the bulk composition of the charge to be located at G. From 65–82 % of the iron present in the starting material has been lost from the charge in runs 23 and 24, while up to 45 % appears to have been lost in the runs made in molybdenum capsules. The two curved lines emanating from the bulk charge compositions at 1300 °C (runs 22, 23) express the *apparent* trends of liquid evolution in iron and molybdenum capsules inside sealed silica tubes. These bear no resemblance to that obtained in runs where the iron content of the charges has been maintained constant, and the phase equilibria observed along them are of little relevance to the sample 15555.

It might be argued that iron losses at the lower temperatures are less significant. Run 14 at 1150 °C, however, yielded pigeonite, olivine, spinel and anorthite. The bulk composition of the charge is, therefore, unlikely to fall closer to the starting composition than B, implying appreciable iron loss even at this temperature.

The iron losses are to be viewed in relation to the shaded field which encloses all analyses of the Apollo 15 olivine basalt hand specimens. The phase equilibria determined in iron and molybdenum capsules inside sealed silica glass tubes refer to bulk compositions which are significantly different from those of the rock group nominally under investigation.

Kesson (1975) has reported results also obtained in pure iron containers in sealed silica glass tubes for a synthetic mixture intended to simulate an average of 15016 and 15555. This yielded a glass of composition  $x$  (figure 5) and residual liquids at lower temperatures of compositions  $y$  (1237 °C),  $z$  (1162 °C) and at lower temperatures as indicated by labelled crosses for 1156, 1138, 1136 and 1124 °C. The run at 1156 °C in particular appears to have gained iron relative to the remainder, and the contrast in Fe/Mg ratio between the glass from the run at 1124 °C and that obtained by Longhi *et al.* (1972) in molybdenum at 1125 °C is most striking. The technique used by Kesson (1975) is one which may permit most of the alkali to be volatilized from the charge, and which in at least one other case (O'Hara *et al.* 1975, Fig. 5) has led to a small but very significant increase in FeO in the melt due to oxidation of the capsule.

*(d) Picrite-basalt 15555: variations in feldspar, olivine and silica contents*

Figure 6 is a projection from spinel into the plane  $XO.R_2O_3$ - $YO$ - $ZO_2$  showing the same data for rock 15555 as were plotted in figure 5. An iron-loss line, radiating from the  $YO$  apex has been drawn through the two all liquid charges from runs 22 and 23 as in figure 5. The liquid from run 69 at 1201 °C at a controlled oxygen fugacity of  $10^{-12}$  atm falls, in this projection also, close to the point representing the liquid at 1200 °C in experiments on 15555 by a similar technique (Humphries *et al.* 1972). The liquid-olivine tie-line for this experiment intersects the iron loss line at A (open square) which is taken to represent the bulk composition of the starting material for Longhi *et al.*'s (1972) experiments on 15555. This composition is appreciably more olivine rich than the analysis of 15555, shown by a filled diamond in the field of all Apollo 15 olivine-basalt hand specimen compositions (shaded). The discrepancy between A and 15555, 8 in figure 5, however, requires that A be poorer in spinel, as well as richer in olivine than 15555, 8. (Specimen 15555 was coarse grained, notoriously inhomogeneous basalt.)

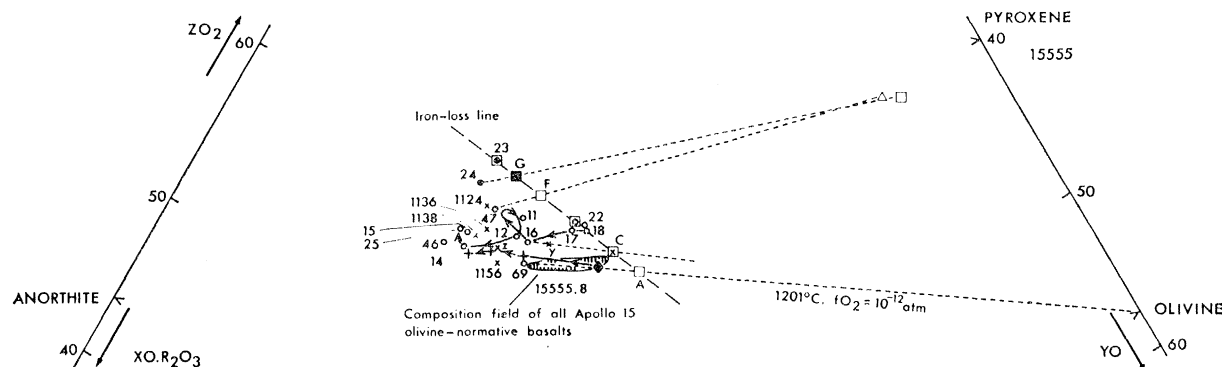


FIGURE 6. Projection from spinel into plane  $XO.R_2O_3$ - $YO$ - $ZO_2$  of data for sample 15555. Explanation in the text.

Liquid developed from a charge in a spectrographically pure iron capsule at 1250 °C (run 24) in equilibrium with orthopyroxene enables the bulk composition of that charge to be established at G. Similarly, the essentially pigeonite-liquid product in run 47 at 1225 °C enables the least iron-depleted composition possible for the charge, F, to be located. Again in run 16, also at 1225 °C, the olivine-liquid product enables the bulk composition of that charge to be located at C. The data are internally consistent, in that those runs which are seen to have lost more iron in the projection of figure 5, again appear to have lost more iron, and in the same relative order, in figure 6.

The apparent trend of residual liquid compositions in the experiments in molybdenum capsules is indicated, 22-18-17-16, etc., and may be contrasted with the residual liquid trend (crosses) developed from sample 15555 in experiments in which little iron was lost (Humphries *et al.* 1972). Also shown, as in figure 5, are the results ( $x$ - $y$ - $z$ , etc.) from a synthetic simulation of 15555 in which some iron may have been gained (Kesson 1975).

*(e) Pigeonite-basalts 15065, 15058: variations in Fe/Mg ratio and silica contents*

Figure 7 illustrates for sample 15065, an Apollo 15 pigeonite basalt, the effects of differing degrees of iron loss upon the phase equilibria.

The boxed open circle towards lower right of the diagram represents the composition of the glass in an all-glass run at 1201 °C in molybdenum foil at a controlled oxygen fugacity of  $10^{-12}$  atm; it is assumed to represent the composition of the sample in the absence of iron depletion. This may be compared with the composition field (shaded) of all other analysed quartz-normative basalts from the Apollo 15 site (Rhodes & Hubbard 1973).

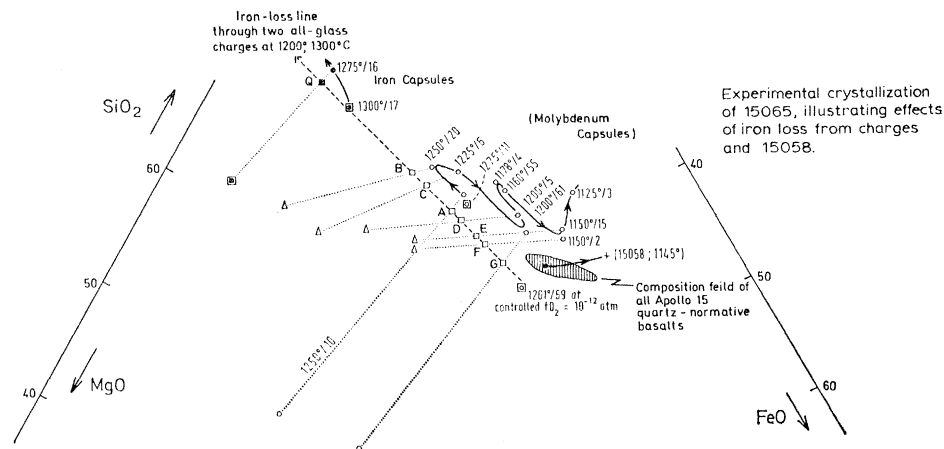


FIGURE 7. Projection into plane MgO-FeO-SiO<sub>2</sub> of data for samples 15065, 15058. Explanation in the text.

Longhi *et al.* (1972) report an experiment in a spectrographically-pure iron capsule in a sealed silica tube which yielded glass only (boxed filled circle 1300°/17). A broken line extends from the FeO apex through the composition of the glass from the 1201 °C run (no. 69) to the composition of the glass in the 1300 °C run in an iron capsule. Bulk compositions of charges which have been subject to iron loss ought to fall along this line. A further experiment in a spectrographically-pure iron capsule in a sealed silica tube was carried out at 1275 °C, yielding orthopyroxene (filled boxed square) and a glass. The inferred bulk composition of this charge is shown by a small filled square, Q. The apparent trend of liquid evolution with falling temperature is indicated; the charges in both experiments in spectrographically-pure iron capsules have clearly lost a great deal of FeO (up to 70 % of that originally present, or up to a total of 14 % FeO from the analysis).

A further experiment (1275°/11) in a sealed molybdenum capsule yielded an all glass charge whose composition (boxed open circle near the centre of the figure) falls a little to the silica-rich side of the iron-loss line previously constructed. About 20 % of the original FeO was lost, from this experiment. The discrepancy between the three glass charges and a single iron-loss control line raises the question of sample inhomogeneity, but may equally reflect an extreme case of the imprecision of analysis for SiO<sub>2</sub> on the microprobe.

Other glass compositions from experiments in sealed molybdenum capsules at 1250 (2 runs), 1225, 1200 (2 runs), 1178, 1160, 1150 (2 runs) and 1125 °C are shown by small open circles, connected by a sinuous line which expresses the *apparent* trend of residual liquid evolution with falling temperature in this group of experiments. Analysed pigeonites and olivines from some of these experiments are also plotted and linked to their respective glasses by dotted lines. A run at 1250 °C (run 10) consists of glass with olivine and clinopyroxene only. The glass-olivine tie-line intersects the iron loss control line at A (open square), which represents the least iron depleted bulk composition possible for this experiment. Another run at 1250 °C

(run 20) consists of glass and clinopyroxene only. The bulk charge composition is shown at B. Similar considerations apply to an experiment at 1225 °C (bulk composition C).

The remaining experiments at 1200 (run 15), and 1150 °C (runs 2, 15) whose pigeonite-liquid tie-lines are plotted, contain some spinel. Their bulk compositions cannot, therefore, be more depleted in iron than shown by open squares D, E, F and similar reasoning indicates that run 61 at 1200 °C, which contains olivine and spinel, cannot be more depleted in iron than G.

The bulk compositions attained by the 15065 charges, and the apparent liquid evolution trends, may be compared with the inferred evolution trend of liquids from another pigeonite-basalt, 15058 (small circle in shaded field) which reaches the composition shown by a cross at 1145 °C (Humphries *et al.* 1972) when run under conditions where little iron is lost to the capsule.

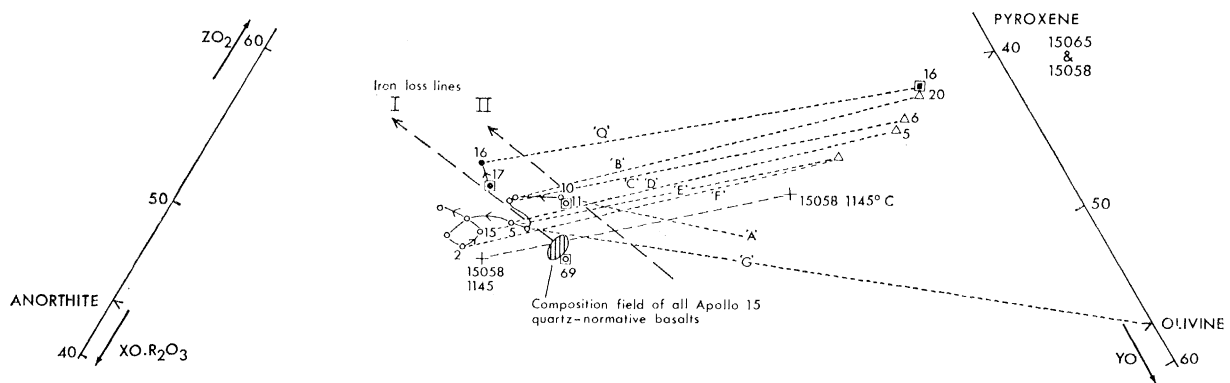


FIGURE 8. Projection from spinel into plane  $XO.R_2O_3-YO-ZO_2$  of data for samples 15065, 15058. Explanation in the text.

(f) *Pigeonite-basalts 15065 and 15058: variations in feldspar, olivine and silica contents*

Figure 8 represents the same data on quartz-normative pigeonite basalts 15065 and 15058 as does figure 7, but the projection is now from spinel into the section  $XO.R_2O_3-YO-ZO_2$ . Symbolism is the same as in figure 7. An iron-loss line passing through all glass charge compositions obtained from 15065 at 1275 °C in a molybdenum capsule at controlled  $fO_2$  of  $10^{-12}$  atmospheres (run 69) and 1300 °C in sealed iron capsule (run 17) is shown by the broken line labelled I. This is the same iron-loss line as drawn in figure 7. The composition of glass from run 69 was *in the first instance* assumed to represent the bulk composition of the starting material for all the experiments on 15065, and is seen in figure 6 to lie close to that of other Apollo 15 pigeonite basalts (shaded field). The dotted tie lines between pyroxene or olivine crystals and various glasses, labelled Q, A, B, C, etc. must intersect some iron-loss control line at the bulk compositions of the respective charges Q, B, C, etc. just as described in figure 7, and it is immediately apparent that the relative iron-loss implied can be in the same order as seen in figure 7, indicating satisfactory internal consistency in the data. However, the tie lines labelled Q, A, B, C and the all glass charge obtained from run 11, all require that iron-loss control lines displaced in some cases as far as that labelled II should be selected for the location of the bulk composition. The most obvious explanations are that the charges loaded did not homogeneously sample the rock 15065, an inhomogeneous distribution of pigeonite phenocrysts being the likely explanation.

If this is the correct explanation, the samples taken for runs 10 and 11 would have had to have contained about 20% more by mass of pigeonite crystals than did the sample taken for runs 16, 17.

Serious imprecision in microprobe analyses for silica does provide an alternative explanation, but the size of effect required is at least twice as large as that demonstrable from repeat determinations on 12002 samples 18, 28, 51 and 56.

The apparent trend of liquid evolution in the runs in spectrographically-pure iron and molybdenum capsules has again been indicated. It does not seem possible to explain the convolutions solely in terms of iron-losses, and imprecision in the analyses for silica may be a factor.

These liquid trends may be compared with the pigeonite-liquid tie-line (crosses) in sample 15058 at 1145 °C in a charge which has lost little iron; this tie-line passes through the bulk composition of 15058, and the actual path of liquid evolution during pigeonite and spinel crystallization may be assumed to have followed the tie line approximately (overlooking the appearance and resorption of a little olivine in this sample).

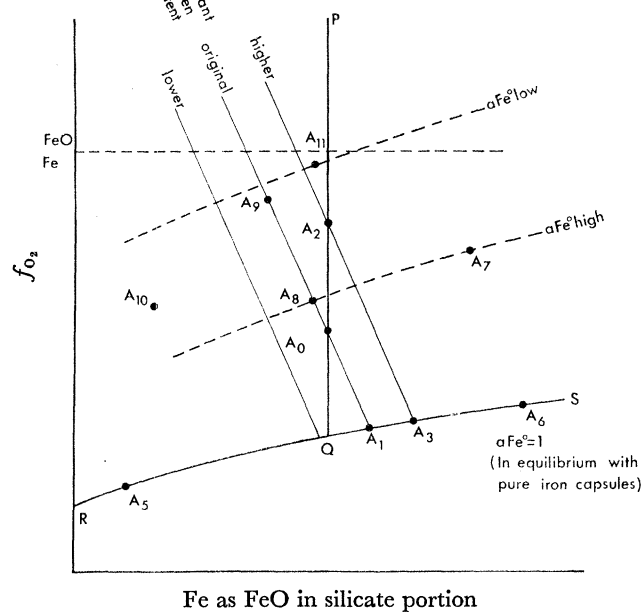


FIGURE 9. Summary figure showing variations of oxygen fugacity and oxidized iron content of the silicate charge resulting from various techniques at a single temperature.

#### 4. SUMMARY OF THE EFFECTS IN DIFFERENT EXPERIMENTAL TECHNIQUES

Figure 9 summarizes the changes involved in the bulk composition and oxygen fugacity of the silicate charge under different experimental conditions. The diagram plots the oxygen fugacity against the concentration of oxidized iron in the silicate fraction. At high oxygen fugacities all iron is oxidized, and its amount should be constant under ideal conditions of experimentation. The desired experimental conditions will fall somewhere along the vertical line P-Q. At the oxygen fugacity of Q, iron metal appears in the system (at an activity of iron

metal a little less than unity because the metal phase is not absolutely pure). At lower oxygen fugacities the oxidized iron content of the silicate fraction declines along curve Q–R.

Three isopleths representing activities of iron metal = unity, = some high value, and = some lower value are indicated.

Charges which are run in pure iron capsules will finally equilibrate at some oxidized iron content and oxygen fugacity lying along curve R–Q–S.

Isopleths showing constant oxygen content of the silicate fraction are also shown.

Let  $A_0$  represent the bulk composition and inherent  $fO_2$  of the charge whose phase relations it was desired to study.

If  $A_0$  is sealed inside a pure iron container and equilibrated, the final charge condition will be  $A_1$  ( $aFe^O = 1$ ; constant oxygen content).

If prior to being sealed inside the pure iron container,  $A_0$  was raised to higher oxygen fugacity (e.g. by fusing at some higher oxygen fugacity  $A_2$ ), then the final charge condition will be  $A_3$ .

If the charge  $A_0$  was not sealed inside the iron container, the oxygen content of the system may change (via the gas phase). Oxygen may gain access (as in the sealed silica tube technique) and since this is a progressive process the 'final' condition of the charge will be time dependent but will be represented by some state ( $A_4$ , not shown) which moves towards S in longer runs.

If on the other hand, the iron container were not pure, but contained carbon, oxygen would be lost from the silicate system (via the formation of CO) and the terminal state of the system would be represented by some condition,  $A_5$ , showing severe iron loss from the silicates, at low oxygen fugacity.

If the charge was contained in a pure iron container and held at some controlled oxygen fugacity, the final state of the system will be represented by a point lying somewhere along R–S, which will be determined by the externally controlled  $fO_2$ .  $A_6$  might represent the equilibrium state if the oxygen fugacity were to approach that of the original condition  $A_0$ , and the charge would show substantial iron gain.

Alternatively, some iron-bearing alloy might be used as a container. For any alloy there will be a unique  $aFe^O$  isopleth, say that labelled 'high' in figure 9. Final equilibration of the charge will then occur at some state,  $A_7$  determined by the oxygen fugacity (if this is externally controlled) or  $A_8$  when the oxygen fugacity might be greater or less than that appropriate to  $A_0$  (if the system is sealed and oxygen content remains constant). This type of container only offers advantages when both alloy and oxygen fugacity are chosen at precisely the correct values (and different values for each temperature of course).

If the charge was sealed initially in pure molybdenum capsules ( $aFe^O = 0$ ) continuous reaction sets in, and the state of the silicate charge moves in some time dependent way along some trend through  $A_8$  towards and perhaps beyond  $A_9$  (higher oxygen fugacity, lower oxidized iron content, constant oxygen content of system). Quasi-equilibrium can only be established as iron metal is removed from the charge to alloy with the container, thereby raising the  $aFe^O$  of the alloy in immediate contact with the melt. The extent of iron loss will be dependent on both time of run, ratio of charge mass/interface area, and the ratio of transport rates of iron in the charge and the alloy, but initial losses will be the most rapid.

If the charge is held in molybdenum capsules at some controlled oxygen fugacity final equilibration is again impossible. At low oxygen fugacity time dependent losses of the type already discussed will occur, yielding final states of the system such as  $A_{10}$ . When, however, the oxygen fugacity is held close to that of the equilibrium between Fe and FeO, iron metal

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activity in the system is very low, and the iron loss to the molybdenum container is also very low (condition  $A_{11}$ ).

N.B.  $\text{MoO}_2$  contents of the liquids in equilibrium with molybdenum capsules are low ( $< 0.1\%$ ) in the oxygen fugacity range under discussion, but the concentration of  $\text{MoO}_2$  in any spinel present is much higher (1–3%) and may reach levels of 20% if the oxygen fugacity has risen slightly above that of the Fe/FeO equilibrium.

The two figures, 10 and 11, summarize the main effects displayed in the previous diagrams, and show bulk compositions which correspond to the states of the system labelled  $A_0$ ,  $A_1$ ,  $A_3$ ,  $A_5$ ,  $A_6$ ,  $A_9$  and  $A_{11}$  in figure 9.

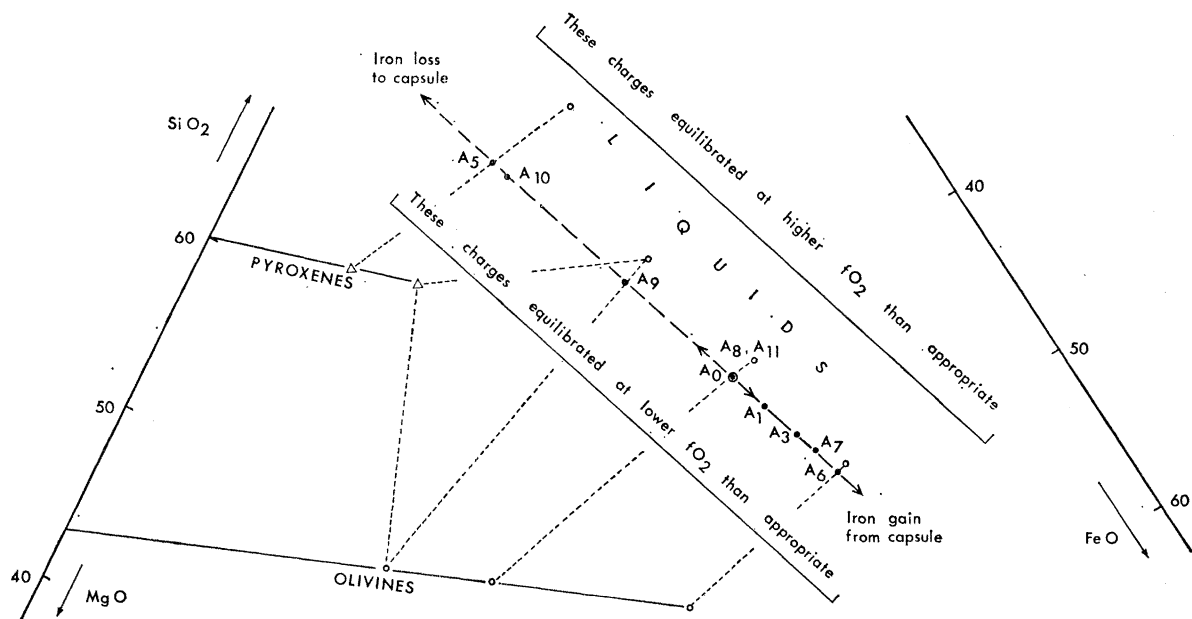


FIGURE 10. Summary figure showing effects of the variations outlined in figure 9 upon results in the MgO-FeO-SiO<sub>2</sub> projection.

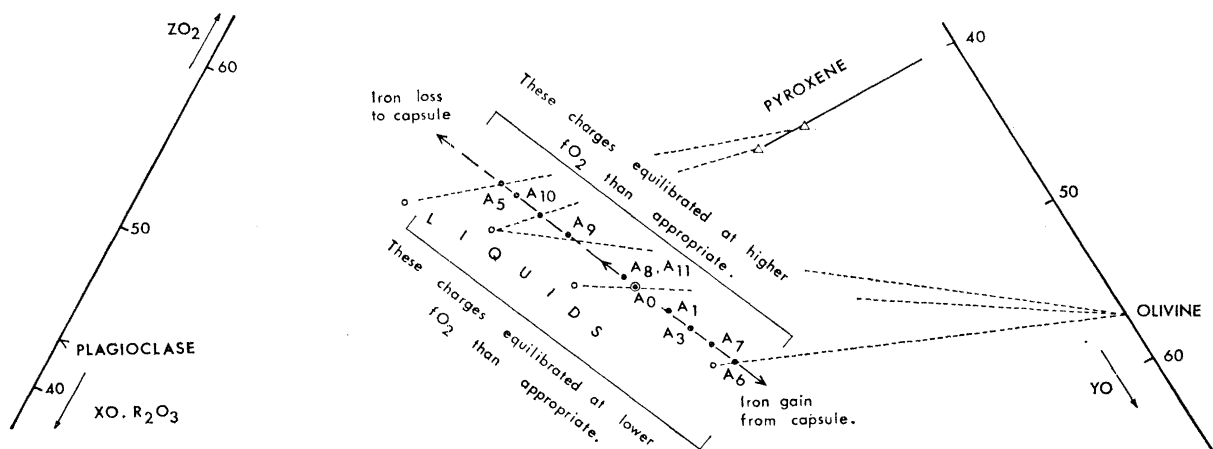


FIGURE 11. Summary figure showing effects of the variations outlined in figure 9 upon results in the spinel projection into plagioclase-olivine-silica.



Note that the projections used in figures 3–8 do not distinguish between the changes of oxygen fugacity and/or oxygen content which accompany the gain or loss of iron, depending upon the technique adopted. *These changes may lead to changes in the phase equilibria observed, independent of any changes connected with the change of oxidized iron content.*

This will be particularly true for any phase whose stability in the system is strongly dependent upon the oxygen fugacity (e.g. spinel, armalcolite) as shown by O'Hara *et al.* (1975).

## 5. CONCLUSIONS

There is no easy routine technique by which the iron-oxide content and oxygen fugacity of an iron-bearing silicate charge can be precisely controlled at freely chosen values. Severe limitation of the contact area between charge and container, as in the suspended wire loop technique (Presnall & Brenner 1974; Donaldson *et al.* 1975) will reduce the size of the effects discussed, but not eliminate them and problems will be experienced in effecting a proper control of alkali contents by this technique. Yet another alternative, that of *sealing* the charges inside pure iron capsules, has obvious attractions, but assumes that the relevant equilibria are those involving iron metal throughout, and presupposes that the present oxygen content of the sample is that relevant to its original crystallization. The best technique for future development appears to be those based on the use of the correct (i.e. selected by trial and error) iron–platinum alloy to balance exactly the iron activity of the charge when it has reached equilibrium. This technique may be extended to higher oxygen fugacities, more relevant to experimentation on terrestrial basalts.

Meantime, results obtained by the simpler techniques must be treated with appropriate caution. The better techniques will yield orders and temperatures of phase appearance and residual liquid evolutionary trends closely similar to those expected in the natural sample. Small differences between the natural rock petrography and results of experiments which arise in any parameter dependent upon the Fe/Mg ratio (e.g. olivine or pyroxene composition as a function of temperature, temperature of appearance or disappearance of a phase) should not, however, be refined upon in reaching petrogenetic conclusions from the experimental data.

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### Discussion

G. M. BROWN, F.R.S. (*Dept. of Geological Sciences, Durham University*). Do you propose that plagioclase was a liquidus or near-liquidus phase in all the mare basalt suites? Although, as you suggest, small mare basalt fragments may not be representative of the liquid compositions from which they crystallized, the use of soil fragments could introduce plagioclase contamination from impact-welded fragments of highlands feldspathic material. The Apollo 15 green glasses and Apollo 17 orange glasses may be more representative of large, homogeneous lava bodies than the crystalline mare basalt fragments. Do they yield comparable data on the plagioclase phase relations?

M. J. O'HARA AND D. J. HUMPHRIES. We believe that the hand specimens of mare basalts contain geochemical evidence of the compositions of the true liquids from which they formed (O'Hara & Humphries 1977), and that these liquids were just saturated with plagioclase, olivine, pigeonite and spinel at low pressure. This evidence stands independent of the estimates of average mare basalt compositions which may be made from the compositions of small glass particles, or small lithic fragments, in the soils. These averages might be liable to contamination in the manner suggested by Professor Brown, but the compositions obtained are very similar to the liquid composition indicated by analysis of the chemical variations of the hand specimens, and by the largest, least porphyritic hand specimens.

D. K. BAILEY (*Department of Geology, University of Reading*). It is clear that gain and loss of iron during experimentation on basaltic compositions can create serious problems. Does Professor O'Hara or his colleagues have any experience of similar problems in experiments below 1000 °C?

M. J. O'HARA AND D. J. HUMPHRIES. Rates of transfer of iron between charge and container are likely to be lower at temperatures below 1000 °C, and much lower when the charges are largely crystalline, but these effects may be offset, at least in part, by the longer duration of experiments below 1000 °C. We therefore have no information on the magnitude of the effects which will be encountered at lower temperatures, but expect the principles governing what transpires to be those set out in § 4 of this paper.

J. V. SMITH (*Dept. of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.*). In the title you referred to the experimental crystallization of five lunar basalts. Your work is extremely important in evaluating whether the basalts result from cotectic liquids produced by partial melting in the lunar interior. Would you care to draw conclusions from your work with respect to this question?

M. J. O'HARA AND D. J. HUMPHRIES. The key question in the petrogenesis of the mare basalts is whether the liquids from which they developed were low pressure cotectic liquids or unmodified high pressure partial melts of the lunar mantle. Elsewhere (O'Hara & Humphries 1977) we present the case for the former of these interpretations, and argue that the bulk compositions of most individual hand specimens, including all those discussed in this paper, are not those of true liquids. Phase equilibria observed in these samples are, therefore, of marginal relevance to the petrogenesis of mare basalts. The main purpose of this paper is to analyse and quantify a problem of technique which is general to all experimentation on natural basaltic rocks. The second is to warn against the use of fine detail from experimental runs in arguments allegedly supporting the choice of certain hand specimens as liquids, when such arguments would only have been valid if the control of bulk composition had been perfect (a point further explored by O'Hara *et al.* 1975).