EXPERIMENTAL CRYSTALLIZATION AND GEOCHEMICAL INTERPRETATION OF LOW TITANIUM BASALTS

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An effective argument in favour of primary origin of picritic low titanium magmas at the Apollo 12 and 15 sites and against their derivation by olivine enrichment in lower temperature eutectic liquids would appear to be that the experimentally produced liquidus olivine composition matches that observed in the cores of natural "phenocrysts" and is more magnesian than that observed in experiments conducted at the eutectic temperature (1, 2). The equilibrium olivine composition which will crystallize from a picrite basalt (e.g., 12040) at a given temperature reaches a minimum FeO content at a critical oxygen fugacity just below that of Fo/Fo equilibrium (fig. 1). Above that critical Fo, d(Fo)/d(Fo) is low, and control of the experiment easy. Below that Fo, metallic iron appears, Fo content of olivine rises rapidly, and d(Fo)/d(Fo) becomes very large, making precise control of experiment very difficult. Unfortunately the lunar basalts appear to have crystallized below the critical Fo; we (3, 4) have experimentally just above the critical Fo, for technical reasons of control of charge composition. Thus our experimentally produced olivines will be more iron-rich than would form in the natural rock at the same temperature. Where the charge has been run in a sealed, pure iron capsule after conversion of the sample to glass at some unspecified Fo (1), reaction between capsule and charge will occur, oxidizing and dissolving the container until an Fo is attained where iron metal is in equilibrium with the melt, which will, however, be Fo enriched, and precipitate too iron-rich an olivine at too high temperature, as well as showing suppression of the crystallization temperature of a 'phenocrystal'. Unless Fo and charge composition have been very precisely and accurately controlled, a direct comparison between experimental and natural olivine is not significant (fig. 2).

Fig. 1. Olivine composition as a function of oxygen fugacity at 1150, 1300°C (stylized) and relation to nickel-nickel oxide (NNO) and FeO/Fo equilibrium and actual oxygen fugacity in Apollo 12 basalts.

Fig. 2. Variation of olivine composition in natural rocks (horizontal bars) compared with experimental results at FeO/Fo oxygen fugacity (5 solid bars), oxidized in sealed iron capsule (1, small open circle 12065) and sealed in molybdenum (2, large open circle 12002) and in contact with melting natural olivine container (12026, crosses). Large open circles refer to non-determined charges at unknown Fo2 (2).

Moreover, during cooling iron metal is in equation relationship with iron-bearing silicate melts (5, 6) at that stage contain some FeO. Thus Mg/Mg+Fe²⁺ of the silicate system progresses during crystallization. It is, therefore, invalid to take either the Mg/Mg+Fe²⁺ total Fe (as in 2) or Mg/Mg+Fe²⁺ in the solidified hand specimen, and use a determined K to predict the equilibrium liquidus olivine composition - the true equilibrium liquidus olivine could be as much 5% Fo more magnesian.

When olivine crystals grow during rapid cooling of basaltic liquids, the effective distribution coefficient appears to be 0.18 ± 0.03 (7), lower than K (0.335) and causing more magnesian olivine to form than would be the case at equilibrium.

Grove et al. have provided microprobe data (8, 9, 10) which enable composition control during crystallization of Apollo 12 liquids to be evaluated further (figs. 3, 4). Fig. 3 illustrates the effect of loss or gain of iron upon bulk sample, liquid and olivine compositions obtained from natural olivine-basalt samples 12002 (8) and 12065 (Biggar et al. unpublished). The shaded field encloses all analyses of Apollo 12 olivine basalts, except that of 12002 by Grove et al. (cross, 0.0%). The compositions of natural samples 12040 (1) and 12000 (9) are indicated. Willis et al.'s analysis of 12002 is used in preference to Grove et al.'s (1973) analysis, which was made on a residue from other experiments, and yields a bulk composition which is incapable of yielding the results of Grove et al.'s (2) experiments 5, 6 at 1325°C (because the charges cannot have gained iron, and hence moved downwards in the diagram, in the technique used). The discrepancy might, however, be due to inhomogeneous mixing of the natural available.

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 and D inferred on the assumption that the actual charges consist of olivine and glass only, and that the bulk compositions differ from 12002 only by loss of FeO.

The techniques used (2) were to enclose the charges in molybdenum or iron capsules encased in evacuated sealed silica glass tubes or to run at a controlled oxygen fugacity in a molybdenum container. At the low inherent oxygen...
Fig 3. Projection from anorthite, albite, orthoclase, CaSiO₃, TiO₂, Cr₂O₃ into MgO-FeO-SiO₂. See text.

Fig 4. Projection from 'spinel' into the section X₀,R₂O₃ - Y₀-ZO₂ (includes anorthite-olivine-silica).
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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, size dependent, 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 an iron capsule is substituted for the molybdenum. If the iron contains any carbon (not normally reported in analyses) even more extensive reduction of the charge may occur than in the previous case.

Also shown in the analytical olivine-liquid assemblages from experiments at 1200°C (runs 17, 84), 1200°C (run 14) and 1250°C (run 22) and their respective inferred bulk charge compositions, E, F, G and H. A consequence of iron loss from the charges is that the olivine/olivine-poor pyroxene liquidus interface is likely to be encountered by the melt as temperature of run 84 is lowered. This otherwise has been true for the first appearance of plagioclase when the residual liquids meet the equilibrium residual liquids from charges in which all iron has been retained as FeO (as represented here by the heavy curves expressing the evolution of residual liquids in 12040 (from ref. 3).

Contrasting with the severe loss of iron which resulted in the sealed tube experiments with iron capsules reported above, the opposite is liable to occur where iron capsules are used in experiments at controlled oxygen fugacities. The effect of iron gain from iron capsules is shown by experiments 129 and 130 on sample 12040 at 1140°C. Run 129 was in the same controlled atmosphere furnace at an oxygen fugacity of 10−125 atmospheres 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. Metallic iron is not produced from the charge until lower oxygen fugacities are attained.

Experiment 130 used a capsule with iron. Molybdenum is not in equilibrium with charge 1300°C at this oxygen fugacity, hence oxygen from the gas atmosphere reacts with iron from the capsule to produce FeO which dissolves in the olivine liquid. Two olivine-liquid tie lines (130a, 130b) from experiment 129, and two inferred bulk compositions (H, J) are shown, as are the compositions of 12002 and 12040 as well as the analysis (cross G') of 12040 provided by Grove et al. (2).

Iron-loss lines, radiating from the YO apex of this projection, have been drawn through the two initial bulk compositions (Grove et al., Willis et al.) for sample 12040 (I and II respectively).

Liquid compositions in the four experiments on 12002 at 1200°C, experiments 18, 28, 51 and 56 are shown by appropriately numbered small circles. The lines linking these compositions to olivine should intersect the iron-loss line drawn through the original bulk composition of the material used for the experiments at points corresponding to the projection in this with the bulk compositions labeled D, C, B and A respectively in fig. 3. Again, it appears that the material analyzed by Grove et al. at 1200°C cannot be representative of the material lost into the capsules because the products of runs 51 and 56 are again inexplicable, requiring a starting material which, in mineralogical terms, would have been significantly depleted in plagioclase relative to feldspar in relation to the latter taken for bulk chemical analysis. From fig. 3 run 56 should contain very little olivine, while runs 51 and 28 will contain significantly more.

A single choice of a bulk composition and associated iron-loss line which would make such mineral proportions a reality would require selection of a starting material which, in mineralogical terms, would have been significantly depleted in plagioclase relative to feldspar in relation to the latter taken for bulk chemical analysis. From fig. 3 run 56 should contain very little olivine, while runs 51 and 28 will contain significantly more.

The residual liquid developed 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 under conditions where no iron is lost and where all available evidence, including microprobe analysis of all glass and 62 glass products, is consistent with reasonably homogeneous sampling of the powder provided. Run 129, which contains some pyroxene, has been joined to olivine dotted tie lines. Their intersections with the iron-loss control line mark the compositions of two of the glass compositions H, J, which were generated in this manifestly inhomogeneous run product.

Detailed discussion of equilibrium crystallization paths of individual hand specimens may, however, be superfluous. All hand specimen compositions at the Apollo 12 and 13 sites can be interrelated by the rock = rock + 'phenoocryst' cores + 'phenoocryst' rims indicating that chemical differentiation has involved the movement of the material in the rims of the crystals as well as the cores. The rim materials must be quenching products, since they are of compositions which are never in equilibrium with the liquid in the absence of abundant anorthite crystals. Phenocrysts cores also are frequently skeletal suggesting quenching rather than equilibrium phenocryst growth. It follows that individual hand specimen compositions represent neither liquid compositions nor any composition relative to the real liquid composition in terms of equilibrium crystal-liquid processes.


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