

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 cotectic 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 cotectic temperature (1,2). The equilibrium olivine composition which will crystallize from a picrite basalt (e.g. 12040) at a given temperature reaches a minimum Fo content at a critical oxygen fugacity just below that of Fe/FeO equilibrium (fig. 1). Above that critical fO_2 , $d(Fo)/d(fO_2)$ is low, and control of the experiment easy. Below that fO_2 , metallic iron appears, Fo content of olivine rises rapidly, and $d(Fo)/d(fO_2)$ becomes very large, making precise control of experiment very difficult. Unfortunately the lunar basalts appear to have crystallized below the critical fO_2 ; we (3, 4) have experimented at just above the critical fO_2 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_2 (1), reaction between capsule and charge will occur, oxidising and dissolving the container until an fO_2 is attained where iron metal is in equilibrium with the melt, which will, however, be FeO enriched, and precipitate too iron-rich an olivine at any given temperature, as well as showing suppression of the crystallization temperature of anorthite. Unless fO_2 and charge composition have been very precisely and accurately controlled, a direct comparison between experimental and natural olivine is not significant (fig. 2).

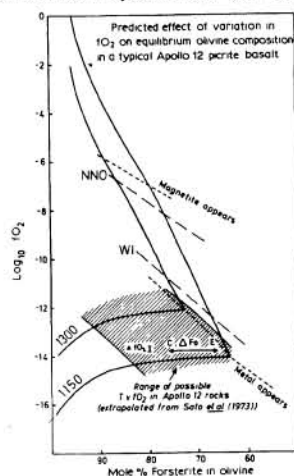


Fig 1

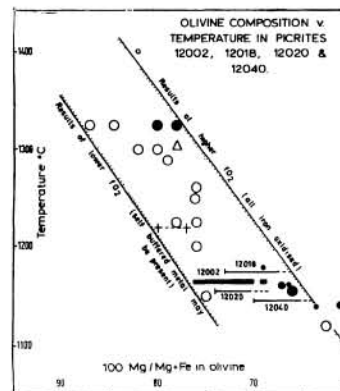


Fig 2

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

Fig. 2. Variation of olivine composition in natural rocks (horizontal bars) compared with experimental results at Fe/FeO oxygen fugacity (3, solid blobs), oxidised in sealed iron capsule (1, small open circle 12065) and sealed in molybdenum (2, large open circles 12002) and in contact with melting natural olivine container (12020, crosses). Large open circles refer to non depleted charges at unknown fO_2 (2).

Moreover, during cooling, iron metal is in reaction relationship with iron-bearing silicate melts (5, 6) which at that stage contain some Fe^{2+} . Thus $Mg/Mg+Fe^{2+}$ of the silicate system decreases during crystallization. It is, therefore, invalid to take either the $Mg/Mg + \text{total Fe}$ (as in 2) or $Mg/Mg+Fe^{2+}$ in the solidified hand specimen, and use a determined K_D to predict the equilibrium liquidus olivine composition - the true equilibrium liquidus olivine could be as much as ~5% Fo more magnesian.

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

Grove et al have provided microprobe data (pers comm) which enable composition control during crystallization of Apollo 12 picrites 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 (2) and 12040 (Biggar et al unpublished). The shaded field encloses all analyses of Apollo 12 olivine basalts, except that of 12002 by Grove et al (cross, 02'). The compositions of natural samples 12040 (8) and 12002 (9) are indicated. Willis et al's analyses 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 51, 56 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 sampling of the material 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, 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 enclosed in evacuated sealed silica glass tubes or to run at a controlled oxygen fugacity in a molybdenum container. At the low inherent oxygen

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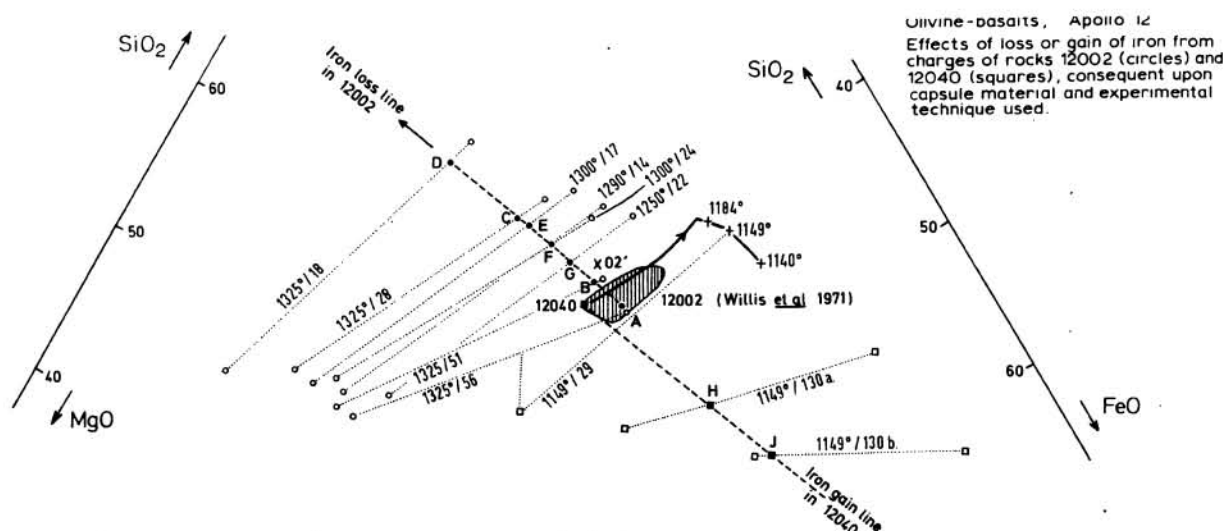


Fig 3. Projection from anorthite, albite, orthoclase, CaSiO_3 , TiO_2 , Cr_2O_3 into MgO-FeO-SiO_2 . See text.

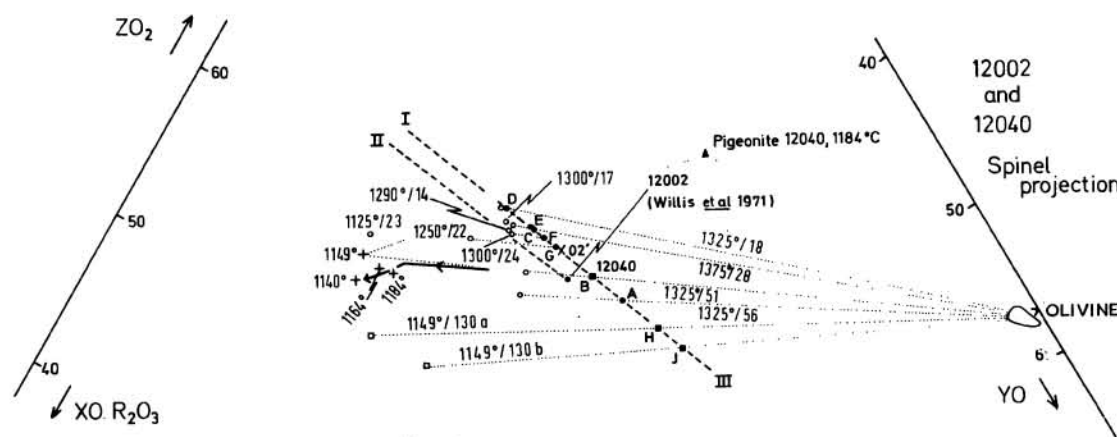


Fig 4. Projection from 'spinel' into the section $\text{XO.R}_2\text{O}_3 - \text{YO-ZO}_2$ (includes anorthite-olivine-silica).

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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, 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 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 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. 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 equilibrium residual liquids from charges in which all iron has been retained as FeO, 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 1149°C. Run side by side in the same controlled atmosphere furnace at an oxygen fugacity of $10^{-12.5}$ 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 dissolves in the molybdenum capsule. 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 experiment 130, and two inferred 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.

Figure 4 is a projection from spinel into the system $XO-R_2O_3-ZO_2-YO$ (which contains the section anorthite-olivine-silica) of the data for samples 12002 and 12040. The field occupied by all hand-specimen analyses of Apollo 12 olivine basalts (shaded) is shown, as are the compositions of 12002 and 12040 as well as the analysis (cross O2') of 12002 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.*) given for sample 12002 (I and II respectively).

Liquid compositions in the four experiments on 12002 at 1325°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 in this projection with the bulk compositions labelled D, C, B and A respectively in fig. 3. Again, it appears that the material analysed by Grove *et al.* as 12002 cannot be representative of the material loaded 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 pigeonite relative to feldspar in relation to the aliquot taken for bulk chemical analysis. From Fig. 3 run 56 should contain very little olivine, while runs 51 and 28 will contain significantly more yet from fig. 4 there is no single choice of a bulk composition and associated iron-loss line which would make such mineral proportions a reality - any single choice would lead to the prediction that the amount of olivine present in run 56 exceeds that in run 51, and that in turn exceeds the amount present in run 28. These results can be explained if the inhomogeneous nature of the sampling of the powder of rock 12002 extends to at least some of the aliquots taken for experimental charges.

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 or nearly all glass products, is consistent with reasonably homogeneous sampling of the powder provided. Run 129, which contains some pyroxene, has clearly lost some iron to the capsule.

An iron-gain line (III) has been drawn from the composition of 12040 towards the YO apex. The compositions of two glasses obtained from a run (130) in an iron capsule at a controlled oxygen fugacity 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.

Detailed discussion of equilibrium crystallization paths of individual hand specimens may, however, be superfluous. All hand specimen compositions at the Apollo 12 and 15 sites can be interrelated by

$$\text{rock}_1 = \text{rock}_2 \pm \text{'phenocryst' cores} \pm \text{phenocryst 'rims'}$$

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. Phenocryst 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 relatable to the real liquid composition in terms of equilibrium crystal-liquid processes.

References (1) Green, D.H. *et al.* 1971, *Proc. 2nd Lunar Sci. Conf.* 1, 601; (2) Grove *et al.* 1973, *Proc. 4th Lunar Sci. Conf.*, in press; (3) Biggar *et al.* 1971, *Proc. 2nd Lunar Sci. Conf.* 1, 617; (4) Biggar *et al.* 1972, *The Moon* ed. Urey, Runcorn, pp 129-164; (5) Barren, N.L. and Schairer, J.F. 1935, *Amer. J. Sci.* 229, 151; (6) Muan, A. 1958, *Amer. J. Sci.* 256, 171-207; (7) Cawthorn *et al.* in press; (8) Kushihiro, I. and Haramura, H. 1971, *Science* 171, 1235; (9) Willis *et al.* 1971, *Proc. 2nd Lunar Sci. Conf.* 2, 1123.