

MARIA LAVAS, MASCONS, LAYERED COMPLEXES, ACHONDRITES AND THE LUNAR MANTLE

G. M. BIGGAR, M. J. O'HARA and D. J. HUMPHRIES

Grant Institute of Geology, University of Edinburgh, Scotland

and

A. PECKETT

Department of Geology, University of Durham, England

Abstract. Experimental data show Apollo 11 and 12 lava compositions to be controlled by fractional crystallization close to the lunar surface, in a process which yields achondrite-like igneous rocks as underlying complementary crystal accumulates. Volatilization losses during eruption can account for most other chemical differences between lunar lavas and common terrestrial magmas. No specific hypotheses of the composition, mineralogy, or origin of lunar interior can be sustained until the extent of these processes is known. A terrestrial upper-mantle-type lunar interior cannot yet be excluded. The assumption that maria surface lavas are primary partial melts is unjustified and leads to a postulated lunar interior with too low Mg/Mg+Fe to serve as a source for Apollo 14 and other igneous liquids. Other workers' uncontrolled visual estimates of crystallinity in experimental charges, purporting to show that maria lavas were not modified by low pressure fractionation, are irreconcilable with the chemistry of the residual liquids developed in our 'reversed' equilibrium experiments. The undesirability of using glass as a starting material for this type of experiment is re-emphasized.

1. Introduction and Statement

The preferred interpretation (Biggar *et al.*, 1971) of available lunar samples involves at least the following sequence of events:

- (1) Lunar accretion.
- (2) Primordial differentiation to yield crust by partial melting of interior.
- (3) Continued but rapidly declining rate of meteoritic impacts, including formation of maria basins.
- (4) Triggered release of further partial melts from the interior to fill maria basins with *lakes* of lava. (see 8)
- (5) Slow consolidation of the lava lakes with strong fractional crystallization in each liquid body. (see 12)
- (6) Random or intermittent eruption of underlying residual differentiated liquid through the crusts of the lava lakes to form the surface lavas sampled by Apollo 11 and 12 missions.

The age of these events is ~ 4.5 b.y. Apparent younger Rb/Sr isochron ages date one or more metamorphic events.*

Significant facets of this interpretation are that:

- (7) There is no evidence that the lunar interior, or the *primary* partial melts derived from it, differ significantly in composition from those present in the *outer* parts of the Earth: there is some evidence that the two groups of materials are similar.

- (8) Fire fountaining during initial lava eruption (see 4) led to small droplet forma-

* See footnote, p. 137.

tion and selective volatilization of elements, as well as fall in oxygen fugacity to the point where metallic iron began to separate. Two of the four major chemical peculiarities of maria lavas (great depletion in all the volatile elements, and most siderophile elements) result directly from the loss of vapour phase at stage (4) coupled with the settling out of a layer of metal phase at the floor of the lava lake after fire fountain droplets had fallen back into the lake.

(9) The extent of metal phase production determines the mass concentration effects.

(10) Prolonged fractional crystallization, just as in large terrestrial lava bodies, greatly reduced the residual liquid volume while concentrating the remaining FeO, the TiO₂, and rare-Earth elements (REE) in that reduced volume, thus producing the third chemical peculiarity of maria surface lavas.

(11) Volatilization losses of Na₂O (in particular) at stage (4) caused excessive precipitation of calcium-poor pyroxenes accompanied by very calcic plagioclase from the differentiating lava lake. Prolonged plagioclase extraction aided by volatilization produced the fourth chemical peculiarity, the marked europium deficiency in the late residual liquids, which occasionally spilled out over the crust as lava flows.

(12) The petrographic character of the crystal accumulates in the underlying maria structure is such that fragments of them observed to fall upon the Earth would be classified as achondrites, irons or stony irons. The essence of the interpretation is conveyed in Figure 1.

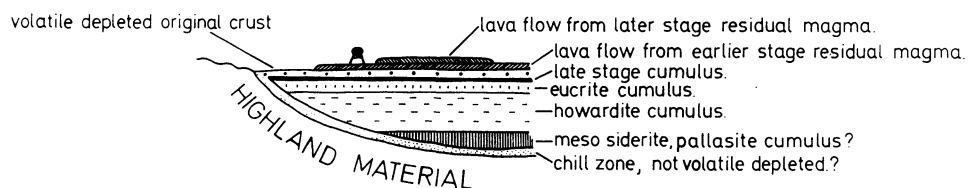


Fig. 1. Hypothetical cross section of lunar maria illustrating disposition of rock types consistent with experimental and petrological observations, topography, and Duke and Silver's (1967) interpretation of the achondrites (reproduced from Biggar *et al.*, 1971, Figure 10). Because both the chill zone and the first crust on the lake are formed from magma which may have fire-fountained on eruption, they will have suffered some volatilization losses, and iron precipitation, but not fractional crystallization. Impact melted glasses of howardite/eucrite-like composition are reported from soils at some sites (Marvin *et al.*, 1972).

This paper summarises the arguments demonstrating (i) that the maria are fractionated lava lakes, and not piles of successive individual flows. (ii) That their surface lavas represent strongly fractionated residual liquids from those lakes. (iii) That selective volatilization was a significant event. (iv) That the true age of the major igneous events is 4.5 b.y.* and (v) that the Mg/Fe + Mg of the lunar interior closely resembles that of the Earth's upper mantle.

The obscuring effect of the near-surface events which modify lunar rock compositions make it difficult to place any valid constraints on the nature of the lunar interior, beyond those already imposed by inference from astronomical observations. Firm

* See footnote p. 137.

choice between early fission, capture and conjugate birth as the origin of the Moon is impossible, as yet, on the strength of petrological or chemical data.

The interpretation presented above is founded upon certain observations of phase equilibria produced in our laboratory. Much of this paper is concerned with establishing the accuracy, sufficiency and relevance of these data. Experimental data from another laboratory have been alleged to invalidate our conclusions; some attention is given below to identifying serious discrepancies both within, and between those data and our own results, and to understanding the reasons for the discrepancies.

2. Maria Surface Lavas Are not Primary Partial Melts of Lunar Interior; Lunar Maria Are Sites of Extreme Fractional Crystallization

Strom (1971 and pers. comm.) reports stratigraphic sequences of very extensive thin flows emanating from wrinkle ridges in Mare Imbrium. The older lava flows are 'red', and the upper later flows are 'blue', indicating increase in TiO_2 . Final effusions from the fractures appear to be small volumes of very viscous light coloured lava. The telescopic evidence for differentiation increasing with passage of time in a mare surface eruption sequence is strong.

Large lakes or chambers of magma undergo *extreme* differentiation by fractional crystallization during their solidification (Wager and Brown, 1968). At a late stage a very small fraction of the original liquid volume becomes grossly enriched in those rare elements selectively rejected by the crystals forming and sinking to the floor of the body to form cumulates. Periodic escape of such residual liquids onto the surface (due to foundering or impact fracturing of the lava-lake crust) will then give chemical sequences inverted with respect to those expected in a direct partial melting sequence, the latest lava flows being the most enriched in rare elements.

The elements which are selectively rejected by crystalline or immiscible liquid, phases separating at an early stage from basaltic magmas and which might, therefore, be expected to become enriched in the residual liquids developed during consolidation of the lava-lakes, may be subdivided as follows:

(i) *Volatile* e.g. H_2 , O_2 , H_2O , CO_2 , F, Cl, Br, I, S, Se, Na, K, Rb, Cs, Zn, Cd, Hg, B, In, Tl, N, P, As, Sb, Te, Bi, Pb. These, however, will not reach high concentrations in residual liquids if a gaseous phase has separated at low pressure.

(ii) *Chalcophile* These include some of the volatile group, and will not reach high concentrations in residual liquids if a sulphide phase (crystal or liquid) has separated.

(iii) *Siderophile* e.g. Co, Ni, Pd, Pt, Os, Rh, Ag, Au. These will not reach high concentrations in residual liquids if oxygen fugacity has been low enough to cause the separation of an iron-rich metal phase.

(iv) *Lithophile* Any Fe remaining oxidised in the liquid after filling of the lava-lake will thereafter be strongly concentrated by fractional crystallization into the residual liquids together with Li, Sr, U, Th, Ce, Nb, Ba, Y, R.E.E., Ti, Zr, V, Cr. These will be progressively concentrated in the residual liquids regardless of volatilization, sulphide or metal phase precipitation, subject to the following provisos:

(a) Fe, Cr and V will remain high or be progressively concentrated provided there has not been precipitation of spinel (chromite, magnetite) or abundant Ca-rich pyroxene (diopside, augite).

(b) The light and heavy REE elements will be comparably concentrated provided that large amounts of Ca-rich pyroxene have not precipitated.

(c) Europium will not be concentrated if abundant plagioclase feldspar has precipitated, and *may have been selectively volatilized*.

The chemistry of maria surface lavas is marked by high concentration of Fe, Ba, Y, REE, Ti, Zr, V, Cr, without marked relative fractionation of the REE, but with a spectacular relative depletion of Eu. Extreme fractional crystallization and separation of calcic plagioclase and calcium-poor pyroxene, with little spinel or Ca-rich pyroxene is indicated.

In maria lavas great depletion of siderophile elements indicates extraction of a metal phase. Allowing for the initial Fe depletion caused by this, the present Fe/Mg ratio and high concentrations of REE, Ti, Zr, are such as might be generated in the final 1–2% of liquid in a consolidating lava lake.

The fractionated lava lake hypothesis *predicts* that the very high concentrations of elements such as Ti will be found in less than 2% of the total mass of the maria, and that these concentrations will increase in the surface lava flows from any one lava lake as they become younger, consistent with Strom *et al.*'s observation of increasing 'blueness' with passage of time, at least until a late stage when Ti-rich mineral begins to crystallize. Essene *et al.*'s (1970) hypothesis of successive flows of primary partial melts, each representing a very small fraction (less than 1%) of the source lunar mantle requires on the contrary (i) that concentrations of titanium should decrease, rather than increase with passage of time, and (ii) that huge volumes of the Moon's interior should have been 'worked over' and depleted of a minute fraction of partial melt, the mechanics of whose flow and collection into a few lava reservoirs presents severe problems. The mass balance problem is a principal objection to the successive lava flow hypothesis – it does not arise in the fractionated lava lake hypothesis because only 1–2% as much lunar mantle needs to be processed to yield the observed element concentrations in the last extreme differentiate of the lava lake.

One of the very minor but characteristic late stage rocks produced by extreme crystal fractionation in large terrestrial lava bodies is a hedenbergite-granophyre (Wager and Brown, 1968). Mason *et al.* (1971) now report a fragment of hedenbergite-granophyre from regolith at the Apollo 12 site.

3. Lunar interior; High Mg/Mg + Fe

Phase equilibria data from Apollo 11 samples did not exclude the possibility of a lunar mantle of terrestrial upper mantle composition (O'Hara *et al.*, 1970). Figure 2 summarises available relevant information on the partition of Mg and Fe between coexisting olivines and liquids, and the inferences which may be drawn from them about the Mg/Mg + Fe of the source regions of the liquids. The solid curve represents

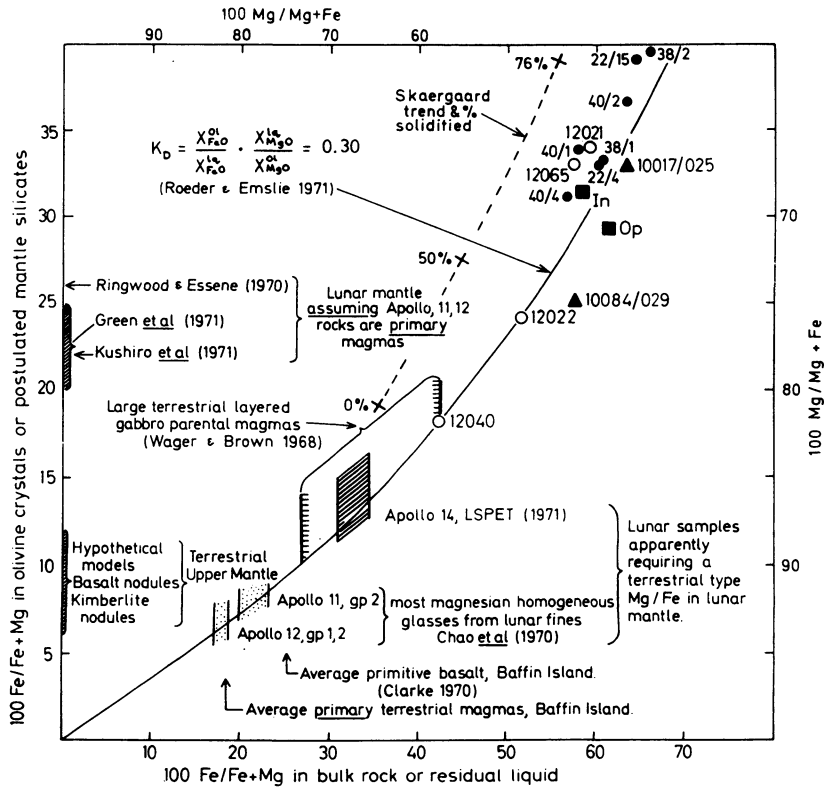


Fig. 2. Fe/Mg distribution between olivine crystals, or postulated lunar mantle and liquid, for Apollo 11, 12 and 14 samples; small filled circles and triangles from experimental data of Biggar *et al.* (1971); open circles from liquidus data of Green *et al.* (1971), filled squares from petrographic observation (James and Jackson, 1970) of the first olivines in the Apollo 11 intersertal (In) and ophitic (Op) group lavas.

an empirical partition function found to fit most terrestrial data. It is seen to fit data from quenching experiments on Apollo 11 samples (Biggar *et al.*, 1971, triangles), Apollo 12 samples (Biggar *et al.*, 1971, filled circles), liquidus olivine compositions quoted for four rocks (Green *et al.*, 1971, open circles) and phenocryst core compositions (James and Jackson, 1970 filled squares) in two groups (Op, ophitic; In, intersertal) of Apollo 11 lavas, plotted against average compositions of these groups (Compston *et al.*, 1970).

On the assumptions that Apollo 11 and Apollo 12 lavas represented primary partial melts, Ringwood (1970) and three other groups of workers have deduced relatively low Mg/Mg + Fe (0.75–0.80) in the silicates of the lunar mantle, as noted on the left side of the figure.

However, Apollo 14 samples have much higher Mg/Mg + Fe than the maria surface lavas, implying equilibration against silicates with Mg/Mg + Fe ~ 0.87. These lavas cannot be interpreted as more advanced partial melts of some more iron-rich mantle

because they have higher concentrations, than do lavas collected from maria-surfaces, of some incompatible elements which partition almost wholly into whatever volume of liquid is available. Nor can they be interpreted as partial melts depleted in metallic iron because relative to lavas collected from maria surfaces, they are richer in nickel, which dissolves preferentially in, and would be eliminated with a metal phase. These Apollo 14 liquids are clearly more primitive in $Mg/Mg+Fe$ than those erupted at the Apollo 11 and 12 sites, which are presumably derived by fractional crystallization from some primitive parent. Brown *et al.* (1971) and Brown (pers. comm. 1971) report olivines with $Mg/Mg+Fe \sim 0.88-0.90$ and comment on their implications for the lunar mantle. It may transpire that Apollo 14 magmas have the characteristics of primary magmas developed on a large scale during the initial differentiation and crust formation of the Moon (LSPET 1971) in a period when incompatible element concentrations and Fe/Mg ratio were sharply reduced in the lunar mantle. Still more magnesian basic glasses are reported by Chao *et al.* (1970) from the lunar fines, requiring a source region whose silicates have $Mg/Mg+Fe \sim 0.91-0.94$ similar to that demanded by the most primitive terrestrial partial melts (Clarke 1970) and evidenced in the ultramafic nodules blasted to the Earth's surface in kimberlite eruptions.

4. Lunar Maria, Layered Intrusions, Mascons

The distinctive feature of terrestrial layered intrusions is the decrease of $Mg/Mg+Fe$ in the residual liquids resulting from prolonged fractional crystallization. The dashed line (Figure 2) links points for cumulus olivine and coexisting liquid deduced for the successive residual liquids of the Skaergaard intrusion at various percentages of solidification of the original parental liquid (from Wager and Brown, 1968, Figure 119).

O'Hara *et al.* (1970) and Biggar *et al.* (1971) have proposed that solidification of the lunar maria lava lakes proceeds in a manner analogous to that seen in large terrestrial layered intrusions, with the modification that early precipitation of metallic iron has depleted siderophile elements and inhibited equivalent decrease of $Mg/Mg+Fe$ in the liquid until larger percentages of the parental liquid have solidified. Early precipitation of c. 3.7% of the initial magma as metallic iron would inhibit the evolution of a Skaergaard-type trend so that more than 90% crystallization would be necessary for the liquid to reach the $Mg/Mg+Fe$ ratios of lunar maria surface lavas.

The extent of metallic iron precipitation, and the resulting excess mass in the early stages of maria filling will vary with volatilization losses and hence with the mechanics of the first eruption process, and will, therefore, vary from one mare to another. This is only one of many possible internal explanations of mascons (O'Hara *et al.*, 1971), but the one which is supported by the experimental and petrological data (Biggar *et al.*, 1971).

If circumstances were such that a constant hydrostatic head and constant *volume* of liquid were maintained in the maria basins (possible if the level of the surface is maintained by a 'water-table' effect reflecting *widespread* partial melting at some depth) the process of densification of the erupted magma by loss of O_2 , Na_2O and K_2O with

accompanying precipitation of metallic iron might lead to c. 5% extra mass being consolidated in the basin. An excess mass $\sim 10^5 \text{ g cm}^{-2}$, is required beneath the maria to yield observed mascon effects, equivalent to an extra 6% mass present in what would otherwise have been a gabbro column c. 6 km deep (well within the depth range possible in the lunar maria, and evident in terrestrial layered bodies e.g. Stillwater complex 5.2 km; Bushveld complex 7.3 km, with lateral extent of $300 \times 400 \text{ km}$). Thus far, therefore, we find no constraints which exclude the possibility of a lunar interior and derived liquids comparable with those present in the Earth's upper mantle, and some evidence which points to considerable similarities.

All other factors being equal, the above hypothesis predicts that surface lavas from maria with larger mascons should exhibit higher non-volatile incompatible element concentrations at the same Fe/Mg ratio. The information required to test this prediction will take time to accumulate. It also predicts that lunar volcanic rocks will show some positive correlation between higher alkali retention and lesser depletion of siderophile elements (e.g. Ni) – this is true of Apollo 14 igneous rocks compared with Apollo 11 and 12 materials.

5. Selective Volatilization from Lunar Lavas

The rate of mass loss of Na_2O from a basic magma which is necessary to extract 1% Na_2O by weight from the liquid is readily calculated.

During fire fountaining, droplet surfaces will not be rapidly cooled because they are surrounded by other equally hot droplets. Assuming an ejection velocity of $\sim 10^4 \text{ cm s}^{-1}$, flight time $\sim 10^2 \text{ s}$ and a droplet size of $\sim 10^{-2} \text{ cm}$, a loss rate of $\sim 2.5 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ at 1500 K would suffice. Loss rates of 10^{-4} to $10^{-5} \text{ g cm}^{-2} \text{ s}^{-1}$ are required for similar losses from thin sheets of liquid flowing up to a hundred kms across the lunar surface, or fire fountain droplets averaging up to 1 cm in size.

Experiments on a terrestrial iron-rich tholeiite magma near its liquidus temperature are summarised in Table I. The mass loss rate of Na_2O is $> 10^{-5} \text{ g cm}^{-2} \text{ s}^{-1}$ at $\sim 1450 \text{ K}$ and $f\text{O}_2 \sim 10^{-11}$ to 10^{-15} bar and is appreciably higher than reported by O'Hara *et al.* (1970) when $f\text{O}_2 \sim 10^{-8}$ to 10^{-9} bar . This directly measured loss rate is similar to those inferred by application of the Langmuir equation ($\text{rate} = P_v \sqrt{(\text{mol wt} / 2\pi RT)}$, vaporization coefficient of 1) to De Maria *et al.*'s (1971) vapour pressures, or by assuming a rate $\sim 10^2$ times greater than for pure SiO_2 or bulk tektite compositions (Chapman and Scheiber 1969). The lower loss rates for K than Na presumably reflect the lower activity of potassium in the melt.

Selective loss of Na_2O at least *must have occurred during eruption* of lunar lavas, and the gross depletion of these rocks in all volatile elements points to the general nature of this conclusion.

Restoration of alkalis and other volatiles including oxygen to the lunar lava compositions leads, among many other possible parents, to compositions familiar among terrestrial basalts. It is unsafe to assume that the present lava compositions are those

TABLE IA
Volatilization study on Scourie iron-rich tholeiite dike; $fO_2 \sim 10^{-12}$ bar

Time h	Temp °C	Pressure (torr)	Comments	Na ₂ O wt %	K ₂ O wt %
Start	-	-		2.38 + ^a	0.92 + ^a
V. 63	1	1150-60	10 ⁻⁴ } part devitrified } bubbled surface, black glass powder	1.93	0.88
V. 62	5	1160	10 ⁻⁴ } part devitrified } bubbled surface, brown glass powder	1.51	0.97
V. 64	24	1160	1.5 × 10 ⁻⁴ } trace devitrification } smooth surface, brown glass powder	0.60	0.91
V. 57	60	1175	2 × 10 ⁻⁵ } trace devitrification } smooth surface, brown glass powder	0.16	0.25
V. 58	240	1175	2 × 10 ⁻⁵ } trace devitrification } smooth surface, brown glass powder	0.13	0.12
V. 59	430	1175	~5 × 10 ⁻⁵ } trace devitrification } smooth surface, brown glass powder	0.20	0.21

^a Not adjusted for H₂O, Fe₂O₃ in rock sample. Alkalis determined by flame photometer. Surface area of sample exposed ~2.9 cm²

TABLE IB

	I	II	III	IV
SiO ₂	50.49	51.29	53.43	52.19
TiO ₂	2.87	2.81	2.82	2.97
Al ₂ O ₃	12.48	12.44	12.96	12.91
FeO	16.57	16.28	16.03	17.13
MnO	0.26	(0.26)	(0.26)	0.27
MgO	4.85	4.84	4.92	5.02
CaO	8.89	8.97	9.24	9.19
Na ₂ O	2.41	2.13	0.09	0.09
K ₂ O	0.93	0.98	0.25	0.25
P ₂ O ₅	0.25	-	-	-
	100.00	100.00	100.00	100.02

I – Scourie dike, 10727 from thin vein at Geodh Eanruig (O'Hara, 1961; Table III, locality II, p. 856, plate XVIII), recalculated less H₂O and with all iron as FeO, from complete wet method analysis by M. R. Saunders.

II – Same material after 2 h at 1200°C in molybdenum capsule at $pO_2 \sim 10^{-12.0}$ bar, recalculated to 100% less P₂O₅ from microprobe analyses of glass fragments.

III – Same material as I after 60 h at 1175°C in molybdenum crucible at low pO_2 and total pressure of 2×10^{-5} torr. Electron microprobe analysis.

IV – Analysis I recalculated less P₂O₅ and appropriate alkalis to compare with III.

Note: alkali loss apparent between I and II; apparent loss of FeO from glass III (? reduced and reacted with crucible) and pick-up of SiO₂ (? from cracking of silicones oil of diffusion pump).

of the pre-eruption liquids, let alone the primary partial melts, and premature to ascribe their volatile-poor characteristics to the Moon as a whole on the strength of that assumption.

The feldspar phenocrysts in samples 14073, and 14310 record pre-eruption levels of Na_2O and K_2O in the liquids *at least* 2–3 times higher than the levels on final consolidation of these lavas (Brown and Peckett, 1971). Restoration of the missing alkalis and c. 0.25% O_2 to the present composition of 14310 leads to a composition quite familiar among *inter alia* the Kamchatka calcalkaline volcanics.

Volatilization which would have accompanied eruption and which selectively separates Rb from Sr, would have destroyed the orderly 4.5 b.y. model ages and the 4.5 b.y. isochron defined by the different bulk rock samples collected at the Apollo 11 (ophitic group) and Apollo 12 sites. Therefore, no igneous event can have affected these rocks since 4.5 b.y. (compare Urey *et al.*, 1971) and the internal mineral isochrons from individual rocks may date devitrification or other metamorphic events. 3.3–3.7 b.y. ago. (Liquids low in volatiles, alkalis and Fe^{3+} such as were produced in the experiments of Table I, were very slow to nucleate and some did not devitrify even in cooling times of 1 h from 1175 °C to 700 °C.)*

6. Accuracy Precision and Significance of the Experimental Data

Experiments performed on lunar samples and related compositions define, at various pressures, the (liquidus) crystalline phases stable with a liquid of the sample composition. This information can then be used to deduce the crystalline species present in the solid material with which the liquid last equilibrated *provided that* the pressure of that last equilibration is indicated by other information, or can be reliably estimated.

If that pressure is *assumed*, provisional conclusions only can be reached (O'Hara *et al.*, 1970); but addition of 10% of what you fancy to produce a more convenient liquidus phase is less than objective.

We have presented experimental evidence that maria surface lava compositions have low pressure cotectic character, controlled by crystal-liquid equilibria at low pressure, leading to the preceding interpretation of maria structure and origin. Others claim there is no evidence of significant low pressure control; go further in claiming that there has been no control of particular lunar lava compositions at any pressure other than that of genesis by partial melting of the lunar mantle; and assume the depth of that partial melting process. From this basis they deduce a model of a volatile depleted, strongly reduced pyroxenite or olivine-pyroxenite lunar interior. If our experimental observations are correct, maria surface lavas are not primary magmas and the model developed by Ringwood and Essene (1970), Ringwood (1970) and Green *et al.* (1971) is a chimera.

The controversy centres on the accuracy of our observation of close approach to cotectic character at low pressure, which has been criticized by Ringwood (1970) and

* Wasserburg and Papanastassiou (1971) suggest crustal or soil contamination of the lavas, vitiating this argument and most petrogenetic discussion based on minor element chemistry.

Green *et al.* (1971), on the strength of their visual estimates of crystallinity, in their products obtained from starting material long deprecated for its propensity to yield metastable products. Moreover, much information necessary for the evaluation of their statements was not presented by Green *et al.* (1971). The temperatures and durations of individual experiments were not given, nor is it clear which experiments used natural and which used synthetic materials (p. 602*). Without these data, claims to have produced the same result by different techniques are insubstantial. Details of the containers, atmospheres, temperatures and durations used in the initial glass preparations are needed to define the nature of the starting material. No calibration of the temperature or oxygen fugacity actually achieved in the charges was reported, and the pressure of some experiments is apparently unspecified (p. 610*). There were no data to establish the precision achieved in their visual estimates of percent crystallinity (Figure 2 caption*) which yield unrealistic residual liquid compositions.

There seem to be several inconsistencies in the data which were reported. For example, 12040 is given as showing plagioclase entry between 1120 and 1140°C (Figure 1*), near 1140°C (p. 603*), or between 1150°C and (presumably) 1140°C (p. 607*; but no 1150°C run is shown in their Figure 1). The percentage of crystals when plagioclase first appears in 12040 is reported variously as 70% (Figure 2*) or 50–60% (text on same page). There are no runs (Figure 1*) to substantiate the remark (p. 603*) that ilmenite enters at close to 1100°C in 12040. The percentage of crystals at plagioclase entry in 12021 and 12065 are given as 40% and 45% (Figure 2*), but as 20–30%, and 30–40%, respectively, in the text (p. 607*). It was claimed (p. 611*) that 12021 could be derived by extraction of olivine, spinel and minor pigeonitic pyroxene from 12009, yet the data (Figure 2*) indicate that a pyroxene olivine ratio of 3/1 would be required in the extract from 12009 to yield a residuum with the phase behaviour of 12021 at temperatures of c. 1160°C. Unlisted experiments of unknown bracket width and duration, which were apparently no more than syntheses from different starting materials *as loaded*, (see Figure 18, sequence 5 below) were presented (p. 608*) and claimed as reversals, and the reader is not told which compositions were used for these experiments.

Green *et al.* (1971) exploit small composition differences between experimental and natural minerals to stress the importance of ‘direct supporting evidence from each sample’; but surely there is a prior need to place the experimental observations on a quantitative and objective basis.

Ringwood and Green (1972) have published a further criticism of our results which is disappointing for its misrepresentation of our statements, and for its reliance yet again on subjective visual estimates of crystallinity as a basis for criticism of our quantitative data. We have *never* stated that plagioclase was liquidus phase in natural Apollo 11 or 12 basalts**, nor that the rocks were *on* the plagioclase-precipitating cotectic under the conditions encountered on the lunar surface, nor have we ‘qualified’ our original position that the lavas have compositions *close to* the 1 atmosphere cotectic (too close

* All page and figure references are to Green *et al.* (1971a).

** 10084 was a soil sample.

for this to be a coincidence). Our position is adequately stated by Biggar *et al.* (1971), p. 634, para 2. We did not *claim* that other workers results were invalid because of the use of glass as a starting material; we have *suggested* that it may have had something to do with the discrepancies in observations between ourselves and Ringwood and Essene (1970) while clearly recognizing that the other two groups whom Ringwood and Green (1972) introduce into the argument worked on compositions substantially removed from those under discussion (Biggar *et al.*, 1971, p. 631, para 2). The reader must judge for himself, in the light of the following remarks, however, how much of the actual disagreement stems from the choice of starting material, how much from inadequate calibration of techniques, and how much from uncertainties in more subjective observations. The loss of alkalis was not “claimed to cause an expansion of the primary fields of crystallization of mafic minerals”: no variation in an intensive variable can change the extent of primary phase fields, and, therefore, of cotectic liquid compositions in a system of fixed composition. The effect of the loss of alkalis and oxygen is to shift the composition of the remaining condensed system towards ferromagnesian minerals as claimed by Biggar *et al.* (1971, p. 634) who showed (*ibid.*, p. 635, Equation (2)) a reaction in which the plagioclase declines from 64% to 55.5% consequent on alkali loss. The key question is whether the change in normative feldspar composition from An₅₀ to An₈₀, combined with the increase in pyroxene at the expense of olivine will offset the reduction in total plagioclase; and problems raised by possible reduction of iron oxides further complicate the issue.

The reader may want more proof that addition of alkalis suppresses rather than enhances the initial appearance of plagioclase than the difference between the two approximate visual estimates of 40–50% (at $1125 \pm 5^\circ\text{C}$) and 35–50% (at $1115 \pm 5^\circ\text{C}$) crystallinity at plagioclase entry with or without alkalis respectively, given by Ringwood and Green (1972, Table II; what the alkali addition does to the *temperature* of plagioclase or other phase entries is, of course, irrelevant). We cannot yet provide a definitive answer for the iron rich composition of maria basalts; for the more magnesian compositions of Apollo 14 samples addition of alkalis *alone* undoubtedly lowers the temperature of plagioclase appearance and (visual estimates!) moves the composition towards the cotectic liquid composition *from* the plagioclase liquidus field. Raising or lowering $f\text{O}_2$ opposes this effect.

Contrary to Ringwood and Green's (1972) suggestion, nothing in any of the reported phase data, nor any conceivable data for effusive rocks could ever support the view that certain basalts were derived from regions below those at which plagioclase was a stable phase in the lunar interior. Such an interpretation depends upon totally different criteria. Their statement is only valid if 'residual' is inserted after 'stable' and the magmas are truly primary.

This disagreement is becoming long on immoderate wording and adrelin, rather than on discussion of scientific data and techniques; we must, however, thank Ringwood and Green (1972) for pointing out our error in drawing of one of our figures from our data table. Biggar *et al.* (1971, p. 633) carries an error (9.1% TiO₂) in the text. 9.2% is correct; in Table IV, column 1, Cr₂O₃ = 0.46%, not 0.06%.

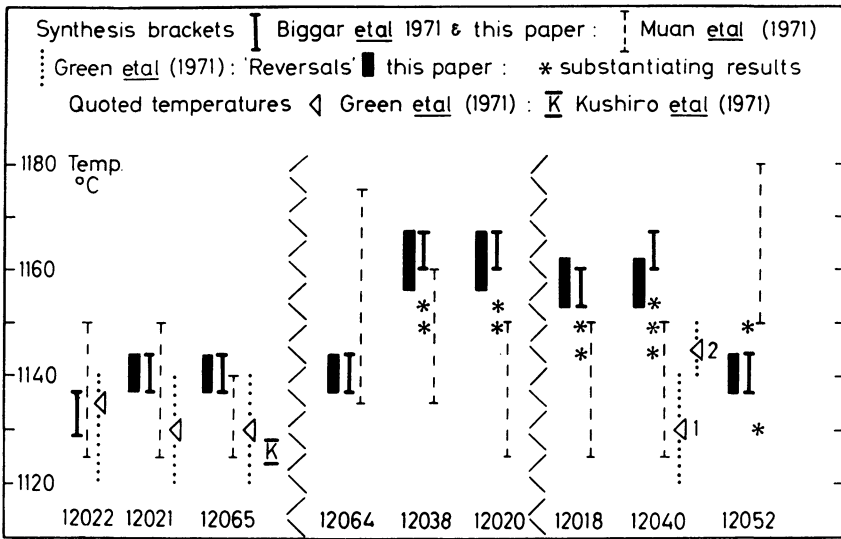


Fig. 3. Comparison of atmospheric pressure quenching data on the temperature of plagioclase appearance for 9 rocks reported on by four laboratories. Results substantiating one side of a bracket are shown where relevant by asterisks. Muan *et al.* (1971) finally reported plagioclase entry at 1125–1150°C in 12052; Green *et al.* (1971b) now concede ± 5° control precision and ± 10°C accuracy in their data. See Table IX, footnote (h).

TABLE II
Results of calculations of crystallinity contrasted with visual estimates^a

100 % rock =	% residual liquid	+	%	sp	ol	pig	plag	Estimated % crystals at plagioclase entry	% crystals visual estimates Green <i>et al.</i> (1971)
12040 ^b	60	cotectic glass	1160	1	29	9	–	40	{ 50 to 60 (text)
12040 ^b	54	12038 rock		1	32	10	3	46	{ 70 (Figure 2)
12052 ^c	74	} 12064 cotectic glass at 1137°C } Plagioclase already fairly common		1	3	17	6	< 25	
12065 ^c	77		1	4	12	6	< 20	~ { 40 (text)	
12021 ^c	80		tr	1	14	5	< 15	~ { 45 (Figure 2)	
12064 ^c	88		tr	1	7	4	~ 5	~ { 30 to 40 (text) ~ { 40 (Figure 2)	
12022 ^c	71	cotectic glass	1129°C	1	23	0	5	< 25	~ 45 (Figure 2)

^a These and subsequent calculations are advanced to show a *major* discrepancy between estimates of crystallinity by different methods. Quibbling over the choice of mineral compositions for the calculations could be endless, but would not lead to large changes in the final results.

^b Calculation in Table III.

^c These calculations used chrome spinel (Table IV, note 5), plagioclase (An₈₅), and pigeonite and olivine from 12038/2 (Biggar *et al.*, 1971, Tables III, IV).

TABLE III
Solutions to calculations for 12040

	12040 ^a		12038 +		12040	
	(Kushiro and Haramura, 1971)	(Scoon, 1971)	46% crystals ^b	1160°C glass + 40% crystals ^c	liquid at plagioclase entry Calculated ^d	Actually ^e
SiO ₂	43.59	43.82	43.88	44.02	37.93	46.86
TiO ₂	2.48	2.74	1.96	2.70	8.30	4.17
Al ₂ O ₃	7.34	7.40	7.71	7.22	27.40	11.50
Cr ₂ O ₃	0.70	0.70	0.67	0.76	-0.05	0.17
FeO	20.87	20.81	21.37	21.19	11.15	17.58
MnO	0.26	0.26	0.28	0.24	tr	0.20
MgO	16.66	16.08	16.43	15.83	-8.48	7.10
CaO	7.90	7.86	7.31	7.73	22.79	11.93
Na ₂ O	0.16	0.20	0.39	0.31	0.67	0.51
K ₂ O	0.05	0.04	0.04	0.05	0.21	0.07
P ₂ O ₅	0.02	0.07	0.02	-	0.08	-

^a Normalised to 100%.

^b 32.1% olivine (Fo₆₈ 12040, 1160°C), 10.4% pigeonite (12040, 1160°C Biggar *et al.*, 1971) 1.0% spine, (12009, Green *et al.*, 1971) and 2.5% An₈₅ calculated to fit Kushiro and Haramura analysis.

^c 29.3% olivine (Fo₆₈), 9.2% pigeonite, 1.2% spinel; calculated to fit Scoon analysis.

^d Extracting 30% olivine, 45% pigeonite (1136°C, Biggar *et al.*, 1971), 1% spinel (12009, 1150°C, Green *et al.*, 1971); mineral proportions measured from Green *et al.* (1971, Figure 2 first version issued at Houston conference, showing plagioclase entry at c. 1130°C as per their Figure 1. Later revised values dealt with in Table IV). Note the extraordinary values of CaO, Al₂O₃, very low SiO₂ and excessive depletion in ferromagnesian constituents.

^e From Biggar *et al.* (1971, Table V).

^f Biggar *et al.* (1971, p. 619) required at least three lava flows for the simplest admissible explanation of their experimental data. Precise calculations by James and Wright (unpublished) convince us that a more complicated model, involving a greater number of flows is required to explain the detailed geochemistry.

We emphasize that:

(1) The data of Biggar *et al.* (1971) establish significantly higher temperatures of plagioclase entry (Figure 3) than those claimed by Green *et al.* (1971). Muan *et al.* (1971), also using natural rock powder as starting material, could compromise with Biggar *et al.* (1971) on plagioclase entry at 1140–1160 °C in most cases. Green *et al.* (1971) and Kushiro *et al.* (1971), both using glass as a starting material, would select a temperature in the 1120–1140 °C range, but also agree with Muan *et al.* (1971).

(2) Calculations of percent crystallinity based on analyses of the coexisting phases in experimental products from Apollo 12 rocks (Tables II to IV) indicate much less crystallization at observed plagioclase entry (Figure 4) than claimed by Green *et al.* (1971) if levels of MgO, Al₂O₃, SiO₂ in the liquids are to be realistic.

(3) Products obtained from glass starting materials can be so fine grained (plate I) that percent crystallinity and crystalline-phase ratios are difficult to estimate, microprobe analysis of the residual glass is nearly impracticable, phases such as plagioclase are very difficult to detect in small amounts, and augite becomes difficult to distinguish optically from pigeonite.*

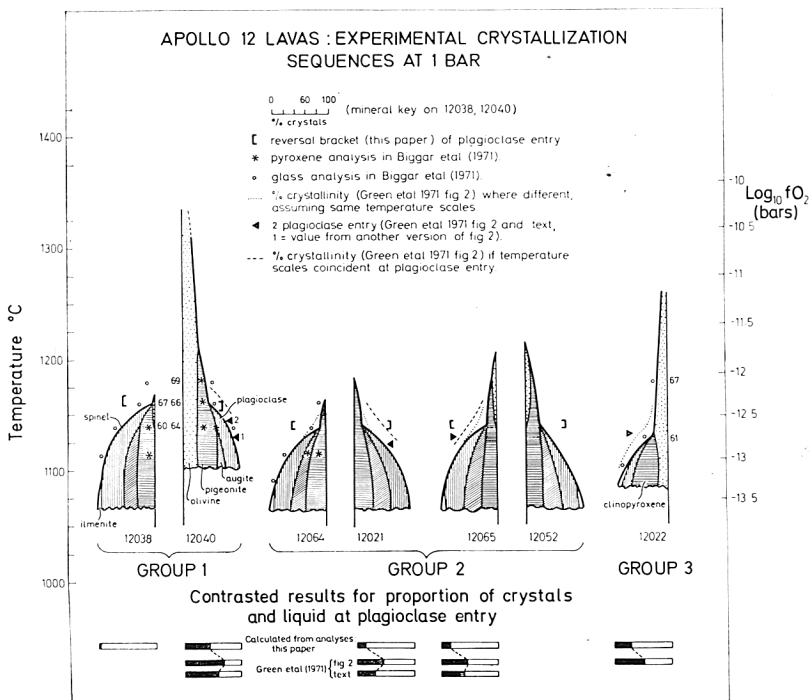


Fig. 4. Graphical representation of co-variation in f_{O_2} , temperature, phase assemblage and percentage crystallinity in Apollo 12 rock compositions (after Green *et al.*, 1971, Figure 2, but with percent crystallinity based on calculations, and the calcium-rich and calcium-poor clino-pyroxenes distinguished except in 12022; note contrast between our calculated, and Green *et al.*'s estimated crystallinity at plagioclase entry, shown by proportional length of black bars).

* Green *et al.* (1971b) refer to this problem, but were confident they could distinguish pigeonite from inverted protohpersthene!

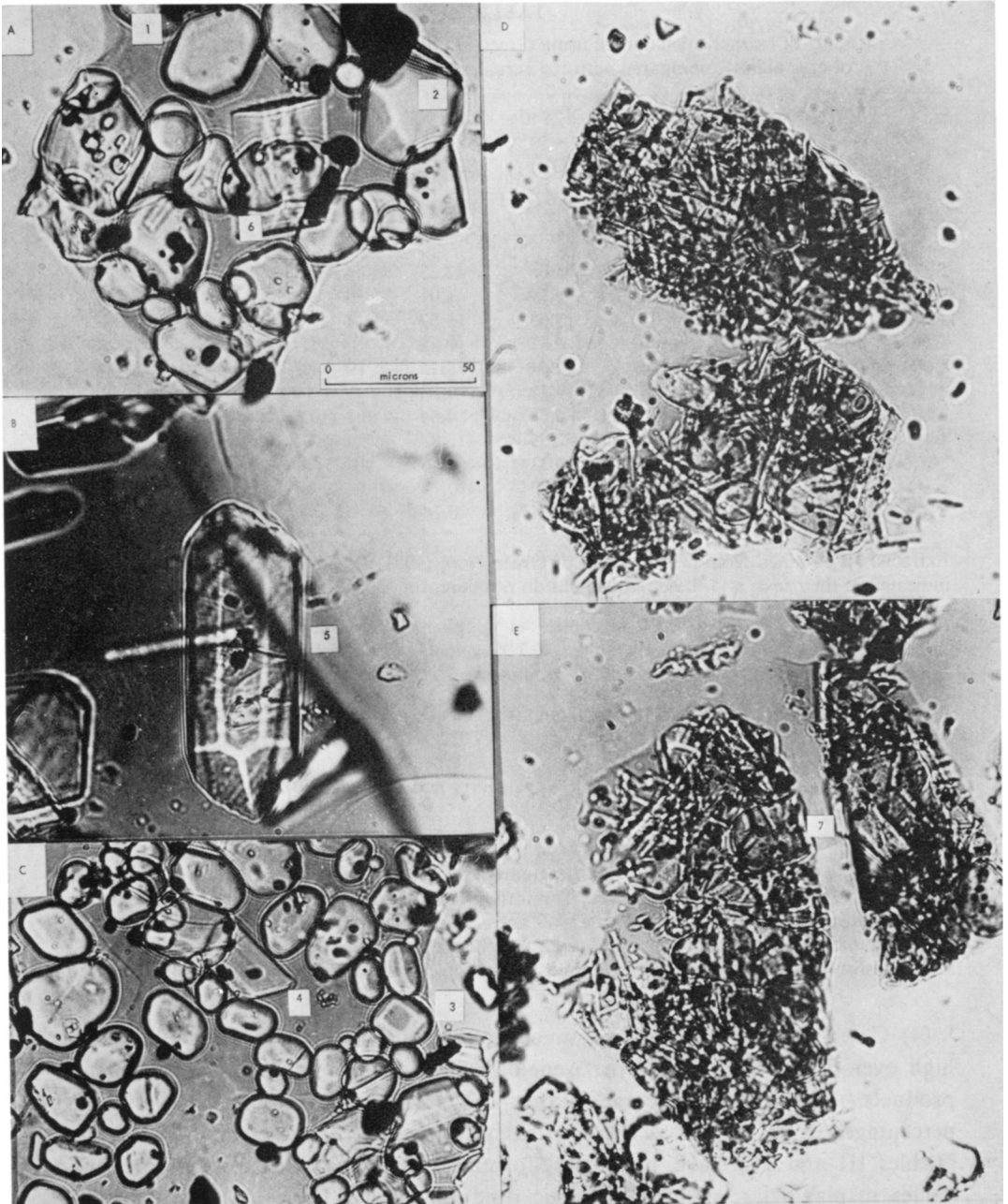


Plate I. Microphotographs (all same scale, see A) of products from reversal experiments on 12040 at 1162°/1153°C; A, B, C from rock powder starting material (experiment 035) showing euhedral olivines (1–3), pyroxene (4) and, again, with curving crack (5), plagioclase (6) and opaque spinel in glass. D, E from largely glass starting material (experiment 117) containing large olivines (7) as in A, C, but interlocking mesh of acicular pyroxenes whose minuscule width makes phase identification, estimation of crystallinity and microprobe analysis extremely difficult.

TABLE IV

Results of extract calculations, using Green *et al.*'s (1971, Figure 2) visual estimates of crystallinity, compared with the actual analysed cotectic liquid compositions

	12021 – 40% (A)	12065 – 45% (B)	12040 – 70% (C)	12040 – 50% (D)	12009 – 50% (E)	Observed real values 12038, 40, 64 cotectic liquids	12022 – 43% (F)	12022/15 observed 1129 °C
SiO ₂	43.16	41.77	37.68	41.06	42.33	46 ± 1	48.15	43.77
TiO ₂	5.09	5.30	6.71	4.29	4.91	4 ± 0.5	– 2.62	6.76
Al ₂ O ₃	16.56	18.29	22.08	13.63	15.67	11.4 ± 1	15.20	9.92
Cr ₂ O ₃	– 0.56	– 0.55	– 0.08	0.37	– 0.28		0.53	0.12
FeO	21.09	21.78	20.33	20.64	18.75	19 ± 1.5	17.20	20.53
MnO	0.23	0.22	0.37	0.21	0.25		0.14	0.30
MgO	– 2.14	– 3.56	– 6.69	6.68	4.64	6.1 ± 0.5	5.84	5.72
CaO	15.89	16.18	18.83	12.56	12.88	11.5 ± 0.4	14.51	11.36
Na ₂ O	0.54	0.40	0.53	0.32	0.46		0.51	0.73
K ₂ O	0.12	0.13	0.17	0.10	0.13		0.12	0.13
P ₂ O ₅	0.02	0.04	0.07	0.04	0.14		0.43	

Extracts, all obtained from measurement of Green *et al.* (1971, Figure 2). Slightly lower figures are indicated in their text, and these reduce, but do not cure, the discrepancies.

A pigeonite¹ 39%, spinel² 1%; B pigeonite¹ 44%, spinel² 1%; C olivine³ 26%, pigeonite⁴ 43%, spinel⁵ 1%; D olivine³ 18.6%, pigeonite⁴ 30.7%, spinel⁵ 0.7%; E olivine⁶ 7%, pigeonite⁷ 42%, spinel² 1%; F olivine⁸ 13%, pigeonite⁹ 19%, ilmenite¹⁰ 11%.

1 = 12021, 1150 °C; 2 = 12009, 1150 °C; from Green *et al.* (1971).

4 = 12040/2, 1137 °C; 7 = 12064/5, 1114 °C; 8 = 12022/15, 1129 °C; 9 = 12040/2, 1137 °C; from Biggar *et al.* (1971).

3 = Fo₆₅ + 0.5 Cr₂O₃, 0.3 CaO; 5 = 12064, 6 (Haggerty and Meyer, 1970).

6 = Fo₅₅; 10 = 12022, 1103 °C (unpublished).

Note that all solutions based on Green *et al.* (1971) visual estimates have attained *conspicuously* higher Al₂O₃, CaO concentrations than the analysed cotectic liquids which are already saturated with these components (as plagioclase). This results from gross overestimation of percentage of olivine, pyroxene. Solutions to 12021, 12040 and 12065 show excessive depletion in SiO₂, MgO because estimates of the amount of pyroxene present are excessive. In 12022, high SiO₂, low FeO and negative TiO₂ result from excessive ilmenite extract. Negative Cr₂O₃ values are not significant.

(4) Green *et al.*'s (1971) visual estimates of crystallinity yield values which are too high overall, and too high in pyroxene/olivine ratio, to apply to our experimental products. Residual liquid compositions, calculated by extracting their estimated percentages of crystals at plagioclase entry, frequently have negative components (Tables III and IV) have plagioclase-forming oxides well in excess of measured values in plagioclase-saturated cotectic residual liquids (Table IV), and are either grossly depleted, or are excessively rich in SiO₂ relative to the analysed residual liquids (Table IV). These discrepancies place the calculated liquids, when in positive composition space at all, in regions where plagioclase is likely to crystallize first and for some interval before the appearance of olivine or pyroxene (Figures 5 and 12).

(5) Similar criticisms apply to Ringwood's (1970) estimate of 30–50% crystallization

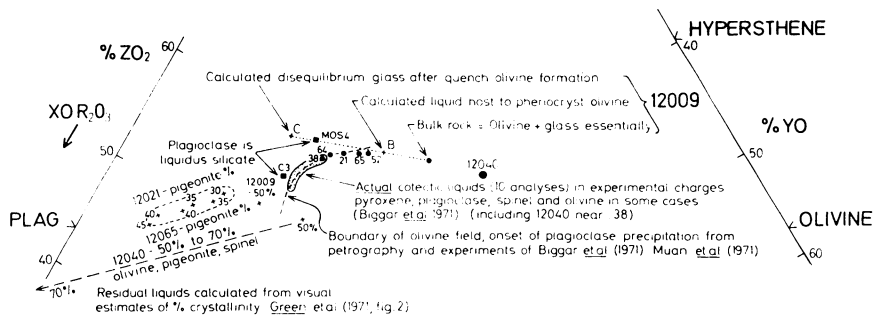


Fig. 5. Projection from diopside into the plagioclase-olivine-hypersthene-(silica) plane, of selected experimentally investigated natural and synthetic Apollo 12 materials, and analysed plagioclase-saturated liquids, to contrast with alleged plagioclase-saturated liquids, calculated by subtracting visual estimates of percentages of crystals in experimental charges. MOS 4 is from Muan *et al.* (1971). Calculated compositions with negative MgO plot within the figure provided there is sufficient FeO to compensate. The result would be unaffected by altering the Fe/Mg ratio in the pyroxene or olivine extracted *in this projection*.

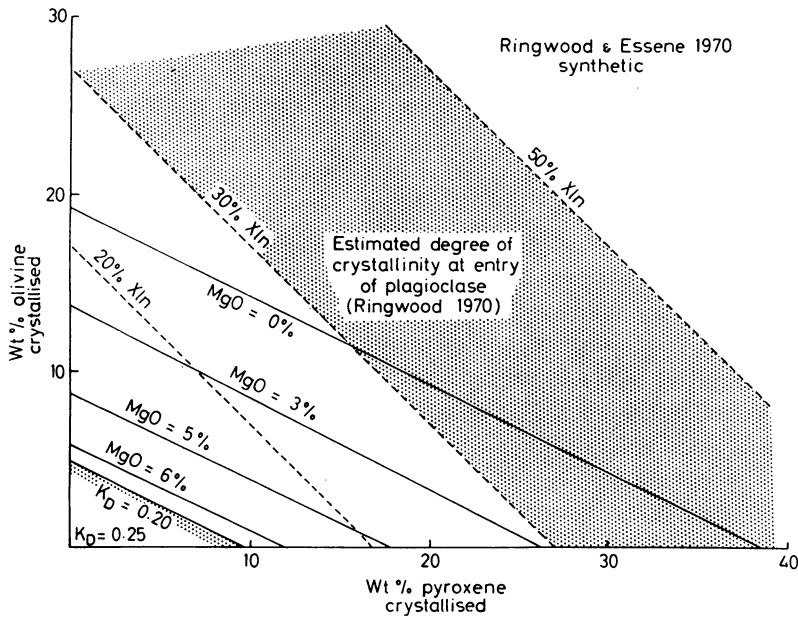


Fig. 6. Graphical presentation of results of extraction of 3% armalcolite (which reduces TiO_2 to cotectic levels at acceptable K_D and MgO figures) and variable combinations of olivine and pyroxene (Ringwood and Essene, 1970; Tables I(i), II(iii) and III, col. 1) from a synthetic Apollo 11 composition, contoured for resultant K_D olivine-liquid distribution coefficients, residual MgO in liquid, and total percentage of crystalline material present. High crystallinity is incompatible with acceptable K_D values and observed MgO contents of 6–7% (Biggar *et al.*, 1971; Table VI).

TABLE V
Apollo 11 lavas, cotectic liquid composition calculations

	I	II	III	IV	V	VI
SiO ₂	42.60	43.00	44.89	44.09	40.69	40.76
TiO ₂	8.86	8.76	8.25	8.31	11.92	11.98
Al ₂ O ₃	11.01	10.31	9.95	10.09	7.78	7.84
Cr ₂ O ₃	0.12	0.12	0.15	0.09	0.34	0.39
FeO	17.78	17.68	16.83	18.13	19.49	19.54
MnO	0.28	0.31	0.22	0.28	0.28	0.29
MgO	6.12	6.47	5.39	5.92	7.51	7.56
CaO	12.41	11.34	12.73	11.07	10.76	10.81
Na ₂ O	0.43	0.72	0.66	0.62	0.51	0.45
K ₂ O	0.09	0.37	0.39	0.59	0.30	0.43
P ₂ O ₅	0.12		0.24		0.18	
S	0.18				0.23	

- I – Apollo 11 ophitic group average (Compston *et al.*, 1970) minus 5% ilmenite, 4% olivine, 0.5% spinel.
 II – Cotectic liquids, average from 10017, 10084 (Biggar *et al.*, 1971, Table VI); note CaO, Al₂O₃ lower than in I.
 III – Apollo 11 intersertal group average, (Compston *et al.*, 1970) minus 10% ilmenite, 4% olivine, 4% pigeonite, 4% augite.
 IV – 10017 residual liquid at 1133°C (Biggar *et al.*, 1971), note CaO, lower than in III.
 V – Apollo 11, 10017 rock (Compston *et al.*, 1970).
 VI – Best fit to V using 10017 liquid at 1133°C plus 0.8% olivine (Fo₆₅), 0.2% spinel (10020–40 Haggerty *et al.*, 1970), 10.1% ilmenite (10020–40), 19.8% augite (10024 – 23/grain 14 Kushiro and Nakamura 1970) and – 2.6% pigeonite (10024 – 23/grain 14): K_D ol – lq = 0.26. Negative pigeonite shows that a more calcic augite should have been used.

of Apollo 11 lavas before plagioclase entry (Figure 6); excessive depletion, in MgO and, above all, in MgO relative to FeO result. Petrological observation (James and Jackson 1970; see Biggar *et al.*, 1971, p. 637) and various calculations (Table V and Figure 7) based on analysed residual liquids from experiments carried out on the natural rock samples, indicate that the Apollo 11 ophitic group (B) lavas precipitated plagioclase and 4 or 5 other crystalline phases when only 10% crystalline. The Apollo 11 intersertal group (A) lavas were nearer 25% crystalline on reaching the same condition. New data (Prinz *et al.*, 1971) for the average composition of lithic fragments at the Apollo 11 site yield more representative average compositions of the high potassium and low potassium lavas groups which are strikingly close in composition to the average of two cotectic liquids analysed by Biggar *et al.* (1971), Table VI. Selected oxide figures, listed in the above sample order, are: SiO₂ 42.8, 42.9, 43.0; TiO₂ 9.6, 8.7, 8.8; Al₂O₃ 10.6, 11.8, 10.3; FeO 18.0, 17.0, 17.7; MgO 7.0, 7.2, 6.5; CaO 10.7, 11.4, 11.3. These compositions will reach the plagioclase-precipitation cotectic at still lower amounts of crystallization.

(6) Primary magmas produced by partial melting of unknown source rocks at an elevated pressure are randomly chosen compositions with respect to the low pressure phase equilibria. The probability of such compositions exhibiting the close approach to low pressure cotectic character actually observed in Apollo 11 and 12 lavas by

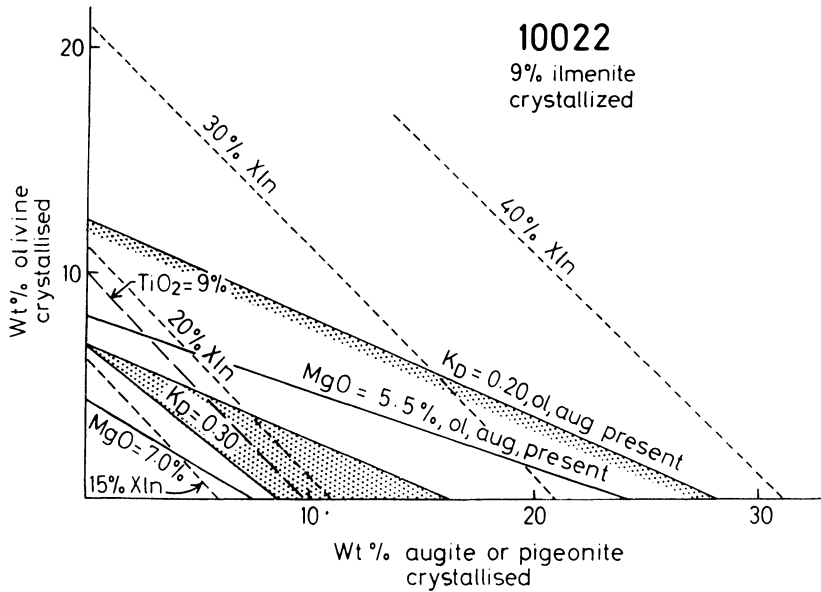


Fig. 7. Similar presentation to Figure 6 for rock 10022, using analysed mineral (core) compositions (Kushiro and Nakamura 1970) showing (shaded field) a range of acceptable MgO contents in the residual liquid at acceptable K_D values consistent with 15–25% crystallization. Results with $K_D < 0.20$ are deemed unacceptable. Alternative sets of K_D and MgO contours result from the choice of pigeonite or augite as the pyroxene crystallizing.

TABLE VI
Probabilities, ϕ , of observed approaches to cotectic behaviour being coincidence

Source	Laki 1783 Iceland			Kilauea Hawaii			Apollo 11		Apollo 12			
							Ophitic	Intersertal	12038	12064		
P^*	3			3			6	6	4	5		
X	0.10			0.05			0.10	0.25	0.05	0.10		
C	4	6	10	4	6	10	7	9	7	9	8	8
ϕ	0.028	0.033	0.22	0.007	0.022	0.071	0.00005	0.0004	0.0046	0.027	0.0036	0.0027

Calculated from the relationship

$$\phi = \sum_{P=P^*}^{P=C} \frac{(C-1)!}{(P-1)! (C-P)!} \cdot X^{(P-1)} (1-X)^{(C-P)}$$

where C = number of significant components, P^* = number of crystalline phases present, X = weight fraction present as crystals. This relationship is approximately true provided liquid loci are not strongly curved.

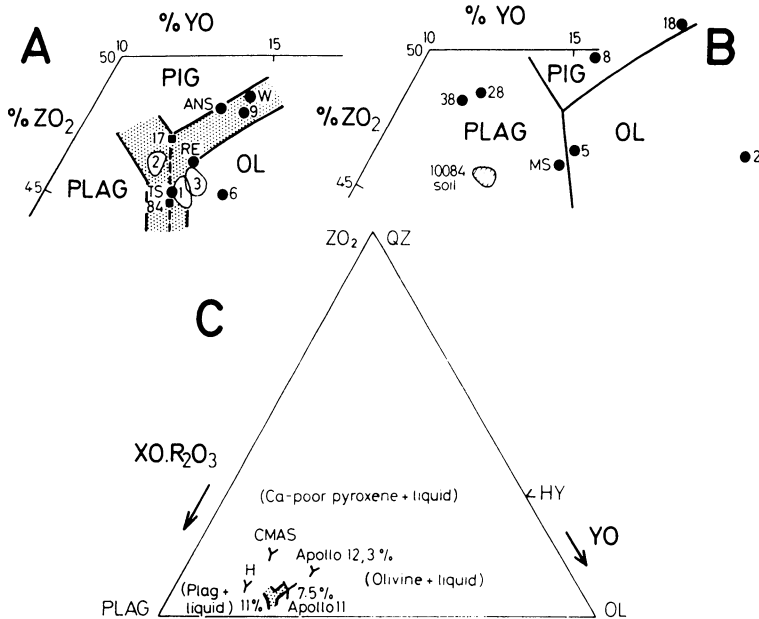


Fig. 8. Projection (O'Hara, 1968; Jamieson, 1970) from diopside into the plane plagioclase-olivine-hypersthene (quartz) showing the boundaries between the primary liquidus phase volumes of plagioclase, pigeonite and olivine as deduced from experimental and petrographic data for (A) synthetic and natural compositions of high TiO_2 content, ($\sim 11 \pm 1\%$) making no allowance for TiO_2 -rich phase crystallization at liquidus, and for (B) intermediate TiO_2 content ($\sim 7.5 \pm 1.5\%$). Compositions 2, 5, 6, 8, 9, 18, 28, 38 from O'Hara *et al.* (1970); ANS from Anderson *et al.* (1970); MS from Muan and Schairer (1971); RE from Ringwood and Essene (1970); TS from Tuthill and Sato (1970); W from Weill *et al.* (1970). Numbered fields enclose analyses of lavas of ophitic groups 1, 2; intersertal group 3, and 10084 soil as in Biggar *et al.* (1971, Figure 8), while 17, 84 mark the analysed residual liquids of rocks 10017, 10084 at the $8.75 \pm .5$ TiO_2 level (Biggar *et al.*, 1971, Table VI). Figure 7c compares the deduced cotectic liquid compositions with the analogous cotectic liquids in the Apollo 12 rocks at $\sim 3\%$ TiO_2 ; in Hawaiian tholeiitic lavas (H); and in the iron, sodium and titanium free system $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ (CMAS).

coincidence is measured in parts per ten thousand to parts per hundred at best (Table VI). When the new average compositions of Apollo 11 lavas (Prinz *et al.*, 1971), and the near coincidence of cotectic temperature and eruption temperature is taken into account these probabilities decline still further.

(7) Cotectic liquid compositions are best established by bracketing, i.e. by finding closely related compositions lying in different primary liquidus phase volumes. This has been done for Apollo 11 compositions (O'Hara *et al.*, 1970, Figures 2, 3; Biggar *et al.*, 1971, Figures 8, 9; and this paper Figures 8, 9 and 10). A bracket on plagioclase entry was established by two laboratories from synthetic compositions resembling Apollo 12 lavas (Figure 5). Cotectic character can also be established by analysing the cotectic liquids and other experimentally produced phases, and thence proving low percentage crystallinity by calculation, as done here (Tables II, III and V). Least

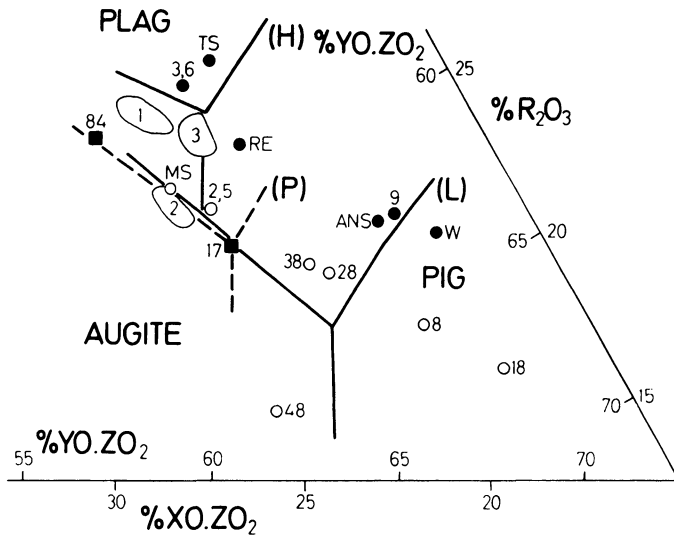


Fig. 9. Part of the projection from olivine into the plane hypersthene (YO.ZO_2)-wollastonite (XO.ZO_2)- R_2O_3 , treating the same data as in Figure 8 to deduce the apparent boundaries between the plagioclase, augite and pigeonite crystallization fields at saturation with olivine, when TiO_2 contents are high ($\sim 11 \pm 1\%$; boundaries (H), solid circle data points and natural rock, fields 1, 3; drawn without allowance for TiO_2 -rich phase crystallization), or low ($\sim 7.5 \pm 1.5\%$, boundaries L, open circle data points), and the preferred position (P) at simultaneous saturation with TiO_2 -rich oxides and the silicates, $\text{TiO}_2 \sim 8.75 \pm 0.5\%$ from probe analyses of experimentally produced residual liquids, and ophitic lavas group 2 (compare Biggar *et al.*, 1971, Figure 9). 10084 soil (not shown) falls in the plagioclase field of the (L) boundaries between MS, 84 and 1.

satisfactory is the indirect method of estimating, visually or otherwise, the percentage of crystals present on reaching cotectic crystallization, because it carries no internal check on consistency, and is susceptible to subjective and systematic errors in arriving at the estimates, particularly in fine grained products (plate I; D, E).

Close approach to cotectic composition is often, but not necessarily, accompanied by the appearance of many crystalline phases within a narrow temperature interval. However, neither the size of the temperature interval over which a number of crystalline phases appear, nor the size of the temperature interval between liquidus and solidus are criteria of closeness to cotectic composition. O'Hara *et al.* (1970) were incorrectly criticized (Ringwood, 1970, p. 6455) directly or by implication for the use of such criteria, but neither the abstract from which Ringwood drew his quotations, nor the full statement (O'Hara *et al.*, 1970, pp. 695, 704), is written in terms which excuse such a misrepresentation. The only authors who, to our knowledge, have attempted to utilize the size of the temperature interval as a criterion in this respect are Green *et al.* (1971, p. 608), in search of criticisms of Biggar *et al.* (1971), and Ringwood and Green (1971).

(8) The techniques used in the Edinburgh laboratory did not reveal a spuriously close approach to cotectic character in the random compositions represented by

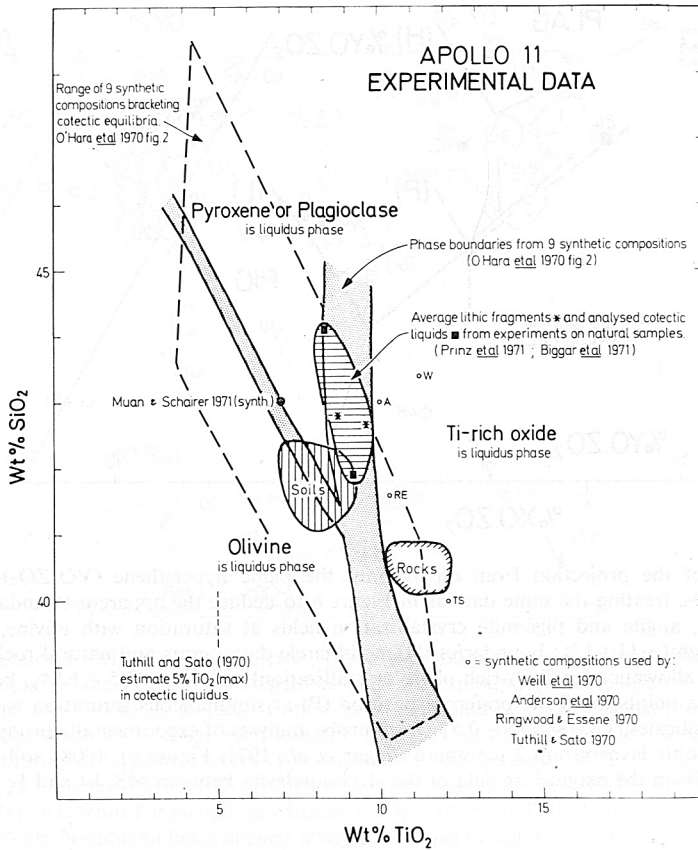


Fig. 10. Simplistic SiO_2 v. TiO_2 representation of liquidus fields, average rock compositions and cotectic liquid compositions encountered in Apollo 11 natural rocks and synthetic simulations. (N. B. Use of a higher oxygen fugacity caused plagioclase to appear as liquidus phase at the centre of the figure).

erroneous Apollo 12 analyses (Biggar *et al.*, 1971), nor has it revealed it in a suite of Reunion lavas known to depart somewhat from low pressure cotectic liquid compositions in their natural crystallisation (D. J. Humphries, in press). These techniques do, however, determine cotectic liquid compositions and temperatures identical (e.g. Figure 11) with those reported by other laboratories also engaged in long-term programs of atmospheric pressure experiments in systems of industrial and geological interest. With these techniques we also observe a close approach to cotectic character in the Laki fissure eruption (J. D. Bell and D. J. Humphries, in press) whose petrography demonstrates eruption with three phenocryst species when as little as 5% crystalline. Similar demonstrations of objectivity and applicability to natural circumstances are available for the technique used by Muan *et al.* (1971), these authors also remarking on the low degree of crystallinity at plagioclase entry.

(9) Available data from relevant synthetic systems (Figure 12) supports the bound-

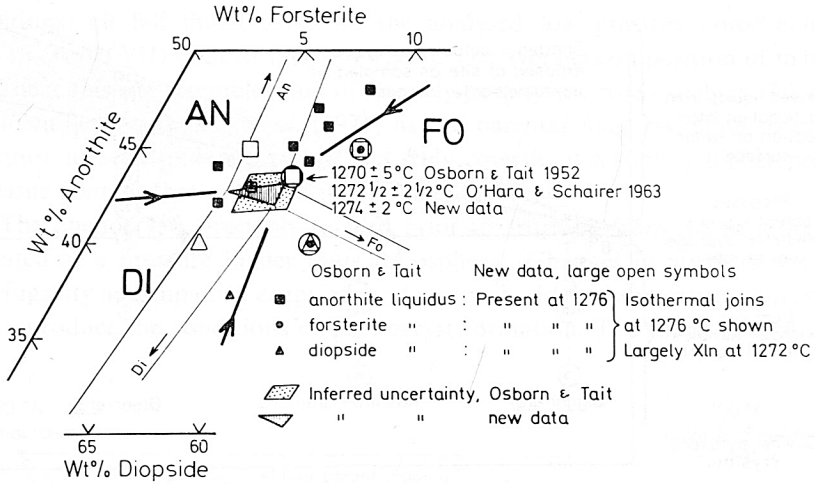


Fig. 11. Part of the plane anorthite-diopside-forsterite comparing atmospheric pressure phase boundaries (Osborn and Tait, 1952), and results for five compositions made and run in the Edinburgh laboratory illustrating close interlaboratory agreement on cotectic composition and temperature.

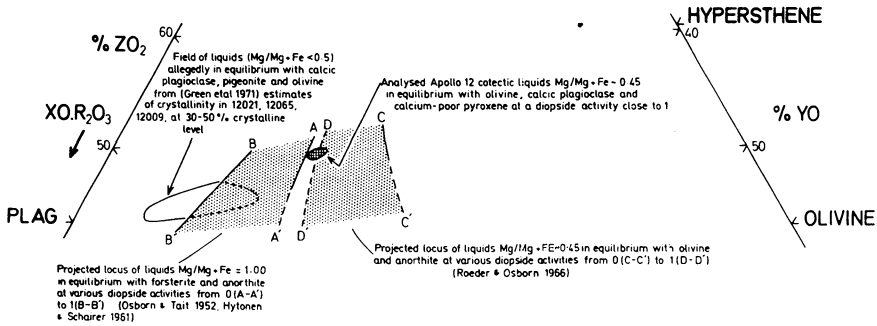


Fig. 12. Projection from diopside (as in Figure 6) into the plane plagioclase-olivine-hypersthene (silica) showing the loci of liquids in equilibrium in synthetic systems with olivine, plagioclase and one or two pyroxenes. Diopside activity has been set at zero in the olivine-plagioclase-silica plane, and at 1 when calcium-rich clinopyroxene coexists with olivine and plagioclase.

ary marking onset of plagioclase crystallisation found by Biggar *et al.* (1971) and Muan *et al.* (1971) in Apollo 12 compositions.

(10) Interpretation of the phase equilibria and lava chemistry turns on the *average* rock composition at the Apollo 12 site (Figures 13, and 14). The fundamental implications of this decision for lunar petrogenesis are illustrated by Figure 15. The hypothesis that 12009 or 12040 represent the parental magma at this site is untenable. The compositions of the average fines; average basaltic lithic fragments from the soils; impact melted glass fragments least affected by alkali depletion; and even the weighted average of the large rocks distributed for analysis (liable to bias towards extreme

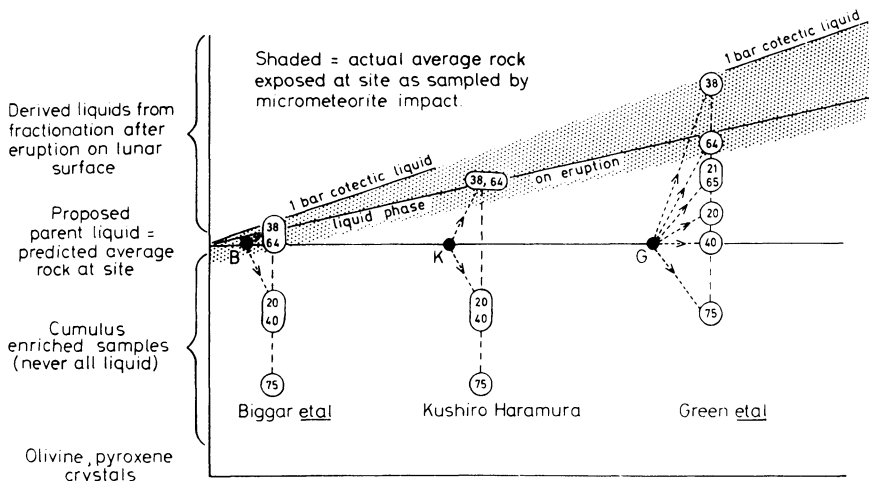
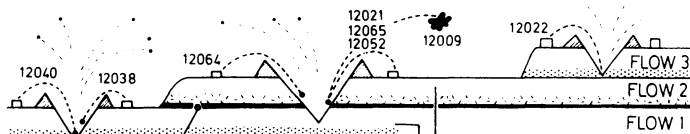


Fig. 13. Graphical summary of alternative interpretations of Apollo 12 site petrogenesis and their implications. The status of 12009, also regarded by Green *et al.* (1971) as possible parental liquid is discussed in the text. The alternative status of Apollo 12 rock samples (indicated by final two digits of sample numbers) in the three interpretations is apparent.

PREFERRED MODEL

Impacts sample whole sequence. Glass splash, as fragments, spheres, or large lumps chilled from >1200°C, reflects average composition.

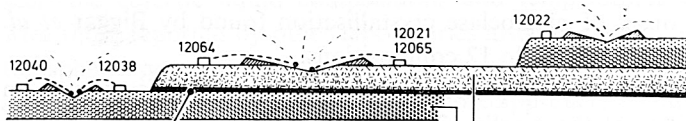


Basal chill devitrified by heat from overlying lava

Lavas erupted ~1150°C Phenocrysts already present sink, fairly rapid cooling leads to partial or complete crystallization of matrix.

A REJECTED ALTERNATIVE

Impacts sample only uppermost parts of flows (WHY?), obtaining selective sample of phenocryst depleted tops to flow



Basal chill quenched from 1200°C not devitrified (WHY; HOW EXPOSED?)

Lavas erupted ~1200°C, cool slowly to 1150°C (HOW?) with minor sinking of phenocrysts, then rapidly (WHY?) to form matrix.

Fig. 14. Schematic cross-sections corresponding with two extreme alternatives from Figure 13, illustrating their implications for Apollo 12 site geology. Individual globs of impact melt depart from average rock composition, but on average short travelled material reflects rock average.

compositions) all fall much closer to the analysed low pressure cotectic liquids (Figure 16, Table VII) than to 12009 or 12040. The average composition of materials exposed near this site resembles that of sparsely porphyritic rocks such as 12038, and 12064, identified by Biggar *et al.* (1971) as the parental magmas, close to cotectic composition at atmospheric pressure and truly cotectic at a slightly higher pressure and volatile content that prevailed within the lava lake.

(11) The phenocrysts probably formed prior to eruption from the lava lake and precipitated at a pressure higher than atmospheric. Changes in alkali content and oxygen fugacity accompanied eruption, and atmospheric pressure experiments do not exactly reproduce the conditions of phenocryst formation. Too much should not be

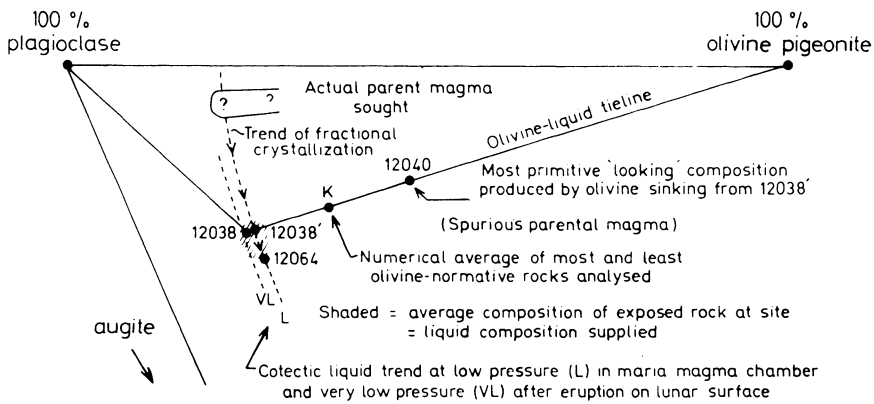


Fig. 15. Simplified phase diagram illustrating the experimental significance of the alternative interpretations of Figure 13, and their implications for studies of the lunar interior.

TABLE VII

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O
(1) Average basaltic lithic fragments ^a	47.2	3.0	14.0	tr	15.8	8.0	10.9	0.5	0.2
12038 rock ^b	47.1	3.3	13.0	–	17.7	6.6	11.4	0.7	0.1
(2) K 10 glass ^a	40.3	3.5	7.1	0.6	23.2	16.6	8.0	tr	tr
12040 rock ^b	43.9	2.7	7.4	0.7	20.8	16.1	7.9	0.2	tr
(3) K 9 glass ^a	43.1	4.4	8.5	0.3	23.0	11.0	9.4	0.4	0.2
12009? impact vitrophyre ^c	45.0	2.9	8.6	0.5	21.0	11.5	9.4	0.2	0.1

^a Keil *et al.* (1971); ^b Kushiro and Haramura (1971); ^c Compston *et al.* (1971).

- (1) Comparison of average of 28 basaltic lithic fragments in Apollo 12 soil with rock 12038 (suggested parental cotectic liquid to eruptive sequence) showing similarity; average fragments are *not* similar to 12040, 12009, below, in SiO₂, Al₂O₃, Cr₂O₃, MgO or CaO.
- (2) Comparison of impact melted glass fragment in Apollo 12 soil, with rock 12040, a coarsely crystalline potential target rock formed by crystal accumulation.
- (3) Comparison of impact melted glass fragment in Apollo 12 soil with rock 12009, a largely glassy sample with thermal history more akin to that of impact melts than to the great majority of the igneous rock samples.

TABLE
Summary of experimental data relevant to entry of

Run No.	Samples	Temperatures °C	Time (h)	Starting material as loaded
<i>A. Reversals</i>				
031	12021, 38, 52, 64, 65	1144; 1137	5; 5	rock powder
032	12018, 20, 38, 40	1167; 1156	5; 5	rock powder
033	12018, 20, 38, 40	1166; 1153	4; 12 ^a	rock powder
035	12018, 20, 38, 40	1162; 1153	4½ ^g ; 16	rock powder
111	12020	1167; 1156	5; 5	glass (1340, 1½ hr) ^{b, c}
112	12020, 12038	1166; 1153	4; 12 ^a	glass (1340, 1½ hr) ^{b, c}
117	12018, 20, 38, 40	1162; 1153	4½ ^g ; 16	glass (1330 1½ hr) ^{b, c}
<i>B. Syntheses from 'different' starting materials (pseudoreversals)</i>				
030	12038	1167	5	rock powder
034	12018, 20, 38, 40	1153	6½	rock powder
036	12018, 20, 38, 40	1153	72	rock powder
113	12020, 12038	1300; 1153	24; 6½	glass ^{b, c}
114	12020 only	1340; 1153	1½; 6½	glass ^{b, c}
116	12018, 20, 38, 40	1153	72	glass ^{b, c}
015	12022, 38, 52	1129	1½	rock powder
016	12022, 38, 52	1300; 1129	1; 1½	glass ^{b, c}
017	12022, 38, 52	1300; 1129	1; 1½	glass + 5% rock
109	12052	1300; 1041	24; 0.16	glass ^b
110	12020, 38, 52, 64	1340; 1041	1; 0.16	glass ^b
?	n. d.	n. d.	n. d.	glass ^{c, d}
?	n. d.	n. d.	n. d.	glass ^{c, d}
?	n. d.	n. d.	n. d.	devitrified glass ^e
?	n. d.	n. d.	n. d.	devitrified glass ^e
<i>C. Charges converted to liquid, or mainly liquid then temperature lowered substantially[†]</i>				
006	18, 20, 21, 22, 38, 40, 52, 64, 65	1250; 1154	1; 4½	rock powder
013	18, 20, 21, 22, 38, 40, 52, 64, 65	1306; 1110–1127	1; 1	rock powder
101	12022, 38, 64	1228; 1121	1, 24	rock powder
102	12022, 38, 64	1225; 1119	1, 1	rock powder
104	12022, 38, 64	1320; 1116	2, 1	rock powder
Muan and Schairer (1971)	Apollo 11 synthetic	1200; 1090	n. d.	devitrified glass
Roedder and Weiblen (1970)	Inclusions in olivine	> 1200; 1125/1065	many hours	glass

All Edinburgh experiments carried out at fO_2 of Fe/FeO equilibrium.

^a held 3 h each at 1159, 1156 during temperature reduction.

^b glass prepared, quenched, then reloaded. Picritic samples still retain some olivine.

^c glass may have devitrified while coming up to temperature (see 109, 110).

VIII

plagioclase and use of glass as starting material

Comments

plagioclase destroyed except in 12038; renucleated in all.
 plagioclase destroyed; renucleated 20, 38 only.
 plagioclase destroyed; renucleated 12038 only.
 plagioclase destroyed; renucleated in all four samples (less than in 034)

plagioclase renucleated
 plagioclase renucleated in both
 plagioclase renucleated in all samples

trace olivine only
 well distributed scarce plagioclase
 well distributed scarce plagioclase
 plagioclase present in 12038
 plagioclase present
 plagioclase present, pyroxene with multiple twinning
 { same phases present in all;
 { plagioclase less abundant in products from
 { glass bearing starting materials
 { variably devitrified on reaching 1041°C;
 { charges spent 9 mins > 1000°C; 17 mins > 700°C;
 { plagioclase in some. See text.
 { Green *et al.* (1971) "confirmed temperature
 { of disappearance of
 { plagioclase": claimed as reversal.

{ No plagioclase; large pyroxene prisms regenerated, showing curving cracks, some polysynthetic
 { twinning, in 12020, 40, 65
 { A few crystals free from cracks had straight extinction

No plagioclase; little pyroxene in 38, 64 (2–50°C below equilibrium entry).

No plagioclase in 12022 (contrast 016)

No plagioclase in 12022,64 (10–20°C below equilibrium)

No plagioclase in any (10–45°C below equilibrium)

No plagioclase (90°C below equilibrium entry)

No plagioclase or pyroxene renucleation.

^d glass prepared by few minutes heating at high temperature (Green, pers. comm).

^e conditions of devitrification not stated.

^f runs were kept in the furnace and not quenched, merely lowered to the second temperature quoted, and finally quenched.

^g 2½ h at 1160, then 2 h at 1162, lowered in 1½ h to 1153.

TABLE IX
Details of furnace assembly calibration

Carried out between run and run	Calibration point	Width of bracket solid-liquid °C	Date carried out 1970/1971	Correction to be applied temperature from e.m.f. (a) (b)
(initial calibrations)	Au	5.1	13 Oct. 19 Oct.	+0.8
	L ₂ S	3.2	21 Oct. 22 Oct.	-2.1
003 004	L ₂ S	3.5	5 Nov. 5 Nov.	-1.0 (c)
including 009	L ₂ S	2.0 (d)	25 Nov.	-1.6
including 010	Au	Solid (e)	26 Nov.	(+0.8)
019 020	L ₂ S	2.0 (d)	17 Dec.	-1.5
020 021	L ₂ S	Solid (f)	24 Dec.	(-1.5)
after 024	Diopside	2.7	4,5 Feb.	+1.5

Furnace used for other calibrated work at higher temperatures

initial calibration, then

101 102	L ₂ S	(d)	22 Apr. 1971	+3.6
102 103	Au	2.3	30 Apr. 1 May	+9.5
104 105	L ₂ S	4.4	10 May 11 May	+9.6

used for 106, 107, 108 (glass production) and the replaced by new thermocouple junction.

initial calibrations	L ₂ S	2.0 (d)	19 May	+4.0
	L ₂ S	(g)	20 May	
then used for 030, 031, 109, 110, 032, 111, 033, 112	Au	3.0	24 May 25 May	+6.6
033 034	L ₂ S	(g)	4 June	+4.0

- (a) These are the corrections applied to the measured e.m.f. to calculate the temperatures quoted by O'Hara *et al.* (1970), Biggar *et al.* (1971), and this paper.
- (b) A further linear interpolation between 0°C at 1064.4°C and 4.9°C at 1208°C must be added to these quoted temperatures to convert them to the International Practical Temperature Scale of 1968. This further correction mainly results from the redetermination of the melting point of lithium metasilicate as 1208°C on IPTS 1968 (Biggar, in press).
- (c) Based on the wide bracket (3.5°C). The next line of the table involved a smaller bracket and for greater accuracy the value -1.0 should be replaced by the value between -1.6 (the later and better result) and -2.1 (the value used earlier).
- (d) In melting interval known to be less than 2° (Biggar and O'Hara, 1969).
- (e) Thermocouple drift cannot have been greater than 0.8°.
- (f) Confirmed solid at 3.1° below the melting interval result of line 4. Therefore downward drift of thermocouple emf has not been greater than 3.1° in fact previous correction of -1.5 continued in use.
- (g) Confirmed solid at 2.0°C below result of 19th May.
- (h) Control precision is better than ±0.5°C (Biggar and O'Hara, 1969); accuracy relative to stated scales is ±2.5°C. Contrast Green *et al.* (1971b) who give ±5.0°C, ±10°C respectively.

impact-melted target material from the phenocryst-enriched base of one of the flows (Figure 14).

(14) Results presented here (Table VIII) and by Biggar *et al.* (1971) were obtained from close temperature brackets in thermally explored and properly calibrated furnaces

(Biggar and O'Hara, 1969; and Table IX, Figure 17 this paper), at controlled, known, and calibrated oxygen fugacities (Figure 5; Biggar *et al.*, 1971, Table II), in containers which do not react with the charges (Table X). All temperatures quoted in this and our previous work must be raised 2–5°C to correspond with the International Practical Temperature Scale (1968) and our revised melting point for Li_2SiO_3 (1208°C; IPTS, 1968) N.B. The emf of a thermocouple indicates nothing more than the temperature of the thermocouple tip (Figure 17). Sample preparation techniques do not

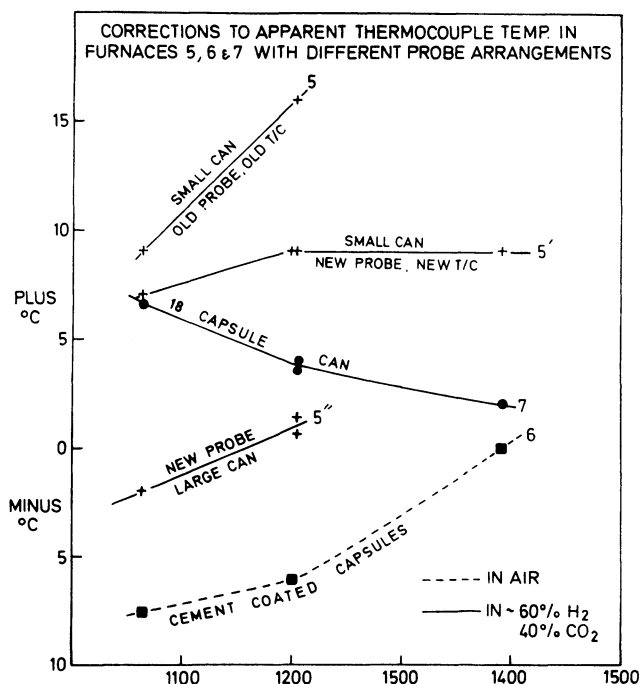


Fig. 17. Plot of corrections to be added to apparent thermocouple temperature as a function of temperature in furnaces of the type used in the studies at Edinburgh.

TABLE X

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO
12038 Rock	47.1	3.3	13.0	17.7	6.6	11.4
12038 1179°C, 5 h 0% crystals	46.9	3.4	12.4	17.6	6.8	11.2
12038 1160°C, 5 h <5% crystals ^a	46.8	3.5	12.3	17.7	6.6	11.2
12064 Rock	46.4	4.1	10.5	19.9	6.4	11.7
12064 1160°C, 5 h <5% crystals	46.4	4.0	10.6	19.4	6.6	11.6

^a cotectic liquid, plagioclase, olivine, spinel and two pyroxenes.

Table X, comparing glass analyses from all liquid, or nearly all liquid experiments with bulk rock composition, to illustrate composition control, absence of sampling errors conducive to premature plagioclase crystallization, and absence of iron loss. Data from Biggar *et al.* (1971) Table V.

bias the charge compositions, least of all towards excessive potential plagioclase (Table X).

The quenching and microprobe data refer to assemblages of homogeneous equilibrium phases, the apparent variation ($< \pm 2\%$ Fo in olivine; $< \pm 3\%$ Wo, 2–4% En in pyroxene; and $\pm 1\text{--}4\%$ major oxides in the glasses, equivalent to $\pm c. 1\%$ olivine in the norm) not greatly exceeding the precision of the method, and arising principally from the difficulty of ensuring that the volume sampled is located exclusively within one phase (c.f. Gibb, 1971) even in the relatively coarse-grained products from rock powder (plate I). No such check could be carried out on the much finer grained products from glass. Total reconstruction of the loaded natural minerals is of course

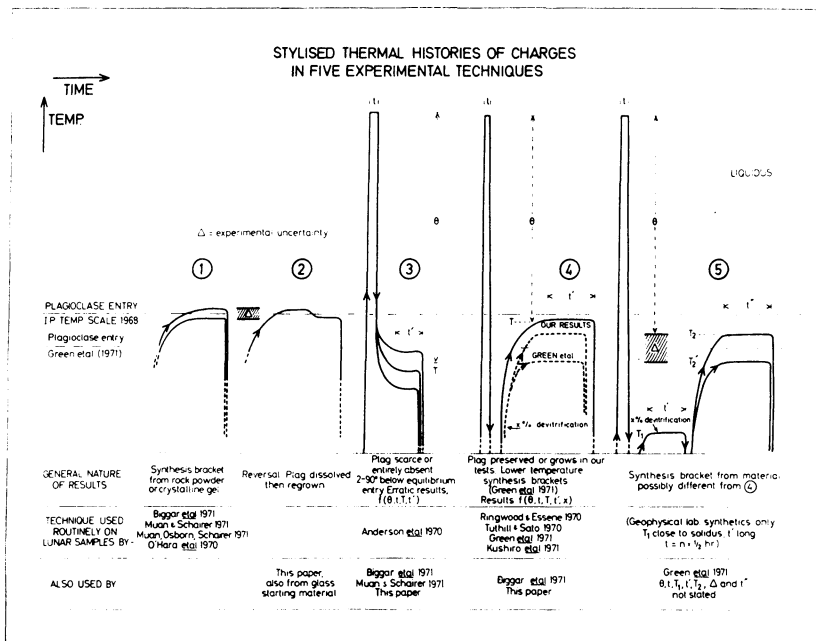


Fig. 18. Diagrammatic representation of thermal sequences used in various experiments.

TABLE XI

Microprobe analysis of cotectic plagioclase-bearing liquids in reversal experiments 1162°C/1153°C showing similarity of results from two starting materials

	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total
12038/035 (powder)	47.27	3.49	12.12	0.25	17.35	0.31	6.31	11.39	0.62	0.13	99.24
12038/117 (glass)	47.10	3.51	12.47	0.19	16.68	0.28	6.41	11.70	0.62	0.13	99.09
12040/035 (powder)	46.53	4.64	11.33	0.19	16.94	0.22	6.95	12.11	0.46	0.13	99.50
12040/117 (glass) ^a	47.21	4.06	10.46	0.28	17.17	0.25	7.94	11.42	0.33	0.13	99.25

^a Minute crystal size may mean that some pyroxene lay within sample area.

proved by the reduced Al_2O_3 content of the pyroxenes, and the destruction of the zoning.

(15) The only effects likely to arise from the presence of 0.25 bar H_2O in our furnace atmospheres are accelerated reaction rates, and a slight movement of the total liquid composition towards the primary phase volumes of olivine and pyroxene, which would diminish, not enhance, the appearance of cotectic character.

(16) Thermal sequences used by various workers on Apollo samples or synthetic simulations in different types of experiment are summarised in Figure 18. The entry of plagioclase has been 'reversed'* (Figure 18, sequence 2) in group 2 rocks 12021, 12052, 12064 and 12065 between 1144 and 1137 °C (Table VIII, run 031). Plagioclase has been demonstrated to be present in products of group 1 rocks 12018, 12020, 12038 and 12040 at 1153 °C (Figure 18, sequences 1 and 4), irrespective of whether rock powder or largely glass charges were used as starting material (Table VIII, runs 034, 036, 113, 114, and 116) or whether the runs lasted 6 h or 72 h. The appearance of plagioclase in these four rocks has been reversed (Figure 18, sequence 2) between 1162 and 1153 °C (Table VIII, runs 035, 117) using rock powder and largely glass starting materials. Microprobe analyses (Table XI) of the residual glasses conform, in each case, to the trend previously established by analyses of liquids developed in 5 h syntheses (Figure 18, sequence 1) at 1160, 1137 °C (Biggar *et al.*, 1971, Table V). In two of the samples plagioclase entry has been reversed between 1167 °C and 1156 °C (Table VIII, runs 032, 033) but in the other two even this small extent of superheating was sufficient to prevent renucleation of plagioclase.

(17) Charges loaded as glass may devitrify in our furnace atmospheres before arriving at run temperature (Table VIII, runs 109, 110). Experiments loading glass or devitrified glass may, therefore, arrive at temperature as the same phase assemblages and do not necessarily demonstrate even so much as syntheses from contrasted starting materials. Experiments in which liquid is created at high temperature, then lowered to run temperature (Figure 18, sequence 3) are particularly prone to delayed or deferred nucleation of plagioclase and pyroxene (Table VIII, section C), an effect beautifully displayed in the petrography of 12009 (see Figure 5). It is imperative to limit the superheating used in the first stage of glass preparation for 'reversal' experiments. Other experiments (Table VIII, runs 015, 016, 017) indicate that charges loaded as glass may yield less plagioclase than is obtained from rock powder under the same conditions. The two effects discussed last might be enhanced when dry atmospheres are used.

(18) Nucleation from glass does not always lead immediately, nor even rapidly, to stable phase assemblages (Ostwald, 1897; Volmer, 1939). Products are sensitive to the previous thermal history of the glass (Table VIII, sections B, C). When glasses have been prepared by the several (half-hour) fusions at very high temperature necessary to guarantee homogeneity (Schairer, 1959), and are then used without prior devitrification or annealing, difficulties must be expected. The accumulated experience of the past is worth repeating lest it be altogether overlooked,

* An absolutely valid reversal of an equilibrium involving a phase (e.g. glass) capable of inheriting a metastable internal structural state from the previous thermal treatment is very difficult to devise.

Nearly all silicate glasses readily undercool. Unless crystals are present in the glass before attempts are made to study phase changes with temperature erratic results and metastable equilibrium may be obtained.... In most silicate systems the determination of the appearance of a crystalline phase at equilibrium practically requires that that phase be present in the starting material. (Schairer 1959).

In glasses which devitrify to olivine, pyroxenes and plagioclase, metastable assemblages may form in minutes and persist for weeks unless devitrification is carried out close to the solidus (O'Hara and Schairer, 1963); these metastable crystals may subsequently enter into metastable crystal-liquid equilibria.

Summarising, then, we consider the assertions and criticisms by Ringwood (1970) and Green *et al.* (1971) concerning the atmospheric pressure phase equilibria to be unsubstantiated and somewhat authoritarian. We welcome any discussion of atmospheric pressure data on lunar or terrestrial materials which is based on fully reported, quantitative data obtained by well described techniques in calibrated equipment, preferably not relying solely on glass as a starting material.

Sparsely porphyritic rocks like 12038, 12064 are close in composition to low pressure cotectic liquids precipitating plagioclase, spinel, two pyroxenes, and olivine. The plausibility of the choice of these compositions as the parental magmas to local post-eruption differentiation at the Apollo 12 site must be judged by the reader in the light of two facts: The average rock exposed to meteorite bombardment resembles the sparsely porphyritic lavas (Figure 16): When erupted these lavas were in that early stage of crystallization which permits the creation of a small proportion of compositions such as 12040, 12052 by sinking of the dense crystals through the low viscosity liquid.

Whether vitrophyres, like 12009, with its extreme composition and distinctive thermal history which allies it directly with impact melted materials, can safely be interpreted as anything but impact 'splash' must also be judged by the reader.

Even neglecting the *certainty* of alkali and other element losses by volatilization during eruption, which must be restored before any lunar lava can be treated as a primary magma, it is our opinion that *none* of the rocks taken from the Apollo 11 or 12 sites represents even a volatile depleted primary magma from the deep lunar interior; the only identifiable parental magmas bear the stigmata of composition control by low pressure fractional crystallisation.

7. Summary of Conclusions

Protohypersthene*-crystallizing basic lavas from the Ocean of Storms were erupted as low pressure cotectic residual liquids from an underlying magma body, already as much as 80–98% crystallized. The lunar maria are differentiated lava lakes, filled by rock types familiar among the achondrites, floored by early metal precipitates which form mass concentrations, and capped by lava flows representing second-stage extrusion of the late residual liquids of the fractionation sequence. The distinctive geochemical and petrographic characteristics of this magmatic kindred relative to terrestrial ex-

* See addendum.

perience were controlled by volatilization losses during eruption and crystallization. The igneous events leading to maria formation may have been very early and triggered by major impacts.

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References

- Agrell, S. O., Long, J. V. P., and Reed, S. J. B.: 1971, 'A comparison of Glasses from the Apollo 11 and 12 Missions' (unpublished).
- Anderson, A. T., Crewe, A. V., Goldsmith, J. R., Moore, P. B., Newton, J. C., Olsen, E. J., Smith, J. V., and Wyllie, P. J.: 1970, *Science* **167**, 587.
- Biggar, G. M. and O'Hara, M. J.: 1969, *Mineral. Mag.* **37**, 1.
- Biggar, G. M., O'Hara, M. J., Peckett, A., and Humphries, D. J.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, Vol. 1, 617.
- Brown, G. M., Emeleus, C. H., Holland, J. G., Peckett, A., and Phillips, R.: 1971, *Proc. Second Lunar Sci. Conf. Geochim. Cosmochim. Acta Suppl. 2*, Vol. 1, 583.
- Brown, G. M. and Peckett, A.: 1971, *Nature* **234**, 262.
- Chapman, D. R. and Scheiber, L. C.: 1969, *J. Geophys. Res.* **74**, 6737.
- Chao, E. C. T., Boreman, J. A., Minkin, J. A., James, O. B., and Desborough, G. A.: 1970, *J. Geophys. Res.* **75**, 7445.
- Clarke, D. B.: 1970, *Contrib. Mineral. Petrol.* **25**, 203.
- Compston, W., Chappell, B. W., Arriens, P. A., and Vernon, M. J.: 1970, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 1*, Vol. 2, 1007.
- Compston, W., Berry, H., Vernon, M. J., Chappell, B. W., and Kaye, M. J.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, Vol. 2, 1471.
- De Maria, G., Balducci, G., Guido, M., and Piacente, V.: 1971, 'Mass Spectrometric Investigation of the Vaporization Process of Lunar Samples', *Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, Vol. 2, 1367.
- Duke, M. B. and Silver, L. T.: 1967, *Geochim. Cosmochim. Acta* **31**, 1637.
- Essene, E. J., Ringwood, A. E., and Ware, N. G.: 1970, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 1*, Vol. 1, 385.
- Gibb, F.: 1971, *Contr. Mineral. Petrol.* **30**, 103.
- Green, D. H., Ringwood, A. E., Ware, N. G., Hibberson, W. O., Major, A., and Kiss, E.: 1971a, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, Vol. 1, 601.
- Green, D. H., Ware, N. G., Hibberson, W. O., and Major, A.: 1971b, *Earth Planetary Sci. Letters* **13**, 85.
- Haggerty, S. E. and Meyer, H. A. O.: 1970, *Earth Planetary Sci. Letters* **9**, 379.
- Hytonen, K. and Schairer, J. F.: 1961, *Yearb. Carnegie Inst. Wash.* **60**, 125.
- James, O. B. and Jackson, E. D.: 1970, *J. Geophys. Res.* **75**, 5793.
- Jamieson, B. G.: 1970, *Mineral. Mag.* **37**, 537.
- Keil, K., Prinz, M., and Bunch, T. E.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, Vol. 1, 319.
- Kushiro, I. and Haramura, H.: 1971, *Science* **171**, 1235.
- Kushiro, I. and Nakamura, Y.: 1970, *Proc. Apollo 11 Lunar Sci. Conf. Geochim. Cosmochim. Acta Suppl. 1*, Vol. 1, 607.
- Kushiro, I., Nakamura, Y., Kitayama, K., and Akimoto, S.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl. 2*, Vol. 1, 481.
- LSPET (Lunar Sample Preliminary Examination Team): 1970, *Apollo 12 Preliminary Science Report*, NASA, Washington, D.C.
- LSPET (Lunar Sample Preliminary Examination Team): 1971, *Apollo 14 Preliminary Science Report*, NASA, Washington, D.C.

- Marvin, U. B., Reid, J. B. Jr., Taylor, G. J., and Wood, J. A.: 1972, *Abstracts 3rd Lunar Sci. Conf.*, NASA Houston.
- Muan, A., Hauck, J., Osborn, E. F., and Schairer, J. F.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 2, Vol. 1, 497.
- Muan, A. and Schairer, J. F.: 1971, *Yearb. Carnegie Inst. Wash.* **69**, 243.
- O'Hara, M. J.: 1961, *Mineral. Mag.* **32**, 848.
- O'Hara, M. J.: 1963, *Amer. J. Sci.* **261**, 32.
- O'Hara, M. J.: 1968, *Earth Sci. Rev.* **4**, 69.
- O'Hara, M. J., Biggar, G. M., Richardson, S. W., Jamieson, B. G., and Ford, C. E.: 1970, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 1, 695.
- O'Hara, M. J., Biggar, G. M., Richardson, S. W., Ford, C. E., and Jamieson, B. G.: 1971, *Phys. Earth Planetary Int.* **4**, 181.
- O'Hara, M. J. and Schairer, J. F.: 1963, *Yearb. Carnegie Inst. Wash.* **62**, 107.
- Osborn, E. F. and Tait, D. B.: 1952, *Amer. J. Sci.* **250A** (Bowen vol.) 413.
- Ostwald, W.: 1897, *Z. Phys. Chem.* **22**, 289.
- Prinz, M., Bunch, T. E., and Keil, K.: 1971, *Contrib. Mineral. Petrol.* **32**, 211.
- Ringwood, A. E.: 1970, *J. Geophys. Res.* **75**, 6453.
- Ringwood, A. E. and Essene, E.: 1970, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 1, 769.
- Ringwood, A. E. and Green, D. H.: 1972, 'Crystallization of Plagioclase in Lunar Basalts and Its Significance' (in press).
- Roedder, E. and Weiblen, P. W.: 1970, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 1, 801.
- Roeder, P. L. and Emslie, R. F.: 1971, *Contr. Mineral. Petrol.* **29**, 275.
- Roeder, P. L. and Osborn, E. F.: 1966, *Amer. J. Sci.* **264**, 428.
- Schairer, J. F.: 1959, in J. O'M. Bockris, J. L. White, and J. D. Mackenzie (eds.), *Physico-Chemical Measurements at High Temperatures*, Butterworths, 117.
- Scoon, J.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 2, Vol. 2, 1259.
- Strom, R. G.: 1971, *Mod. Geol.* **2**, 133.
- Tuthill, R. L. and Sato, M.: 1970, *Geochim. Cosmochim. Acta* **34**, 1293.
- Urey, H. C., Marti, K., Mei-Kao, L., and Hawkins, J. W.: 1971, *Proc. Second Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 2, Vol. 2, 987.
- Volmer, M.: 1939, *Kinetik der Phasenbildung*, Steinkopff, Dresden.
- Wager, L. R. and Brown, G. M.: 1968, *Layered Igneous Rocks*, Oliver and Boyd, Edinburgh.
- Wasserburg, G. J. and Papanastassiou, D. A.: 1971, *Earth Planetary Sci. Letters* **13**, 97.
- Weill, D. F., McCallum, I. S., Bottinga, Y., Drake, M. J., and McKay, G. A.: 1970, *Proc. Apollo 11 Lunar Sci. Conf., Geochim. Cosmochim. Acta Suppl.* 1, Vol. 1, 937.

Addendum. Green *et al.* (1971b) doubt our finding of protohypersthene on the strength of their experiments carried out under appreciably different conditions. The facts to bear in mind are: (i) Biggar *et al.* (1971) analysed inverted protohypersthene from 12040 (Ca₇Mg₆₇Fe₂₆) and observed inverted orthorhombic phase present in the range 1160–1200°C, and 1135–1160°C in 12021. Eruption temperatures lay within these ranges, hence inverted protohypersthene is to be expected in the rocks, all other factors being equal. (ii) Ross *et al.* (1971, Abstract, *2nd Lunar Science Conf.*) reported inversion of calcium-poor pigeonite cores (Ca₉Mg₆₃Fe₂₈) from 12021 to orthorhombic structures (? space group) at 1160–1215°C, in their heating experiments. (iii) Hollister *et al.* (1971, *Proc. 2nd Lunar Sci. Conf.*, p. 529–557) report orthorhombic cores in pigeonite from 12065. Aspects of their analysis 9-1-6 (Ca₈Mg₆₆Fe₂₈) are compared with our inverted protohypersthene (12040/4) TiO₂ 0.43, 0.43; Al₂O₃ 1.01, 1.08; Cr₂O₃ 0.77, 0.46 (misprint in earlier text); CaO 2.90, 3.39; FeO 17.96, 16.72; MgO 23.50, 23.81. (iv) Brown *et al.* (1971), Gay *et al.* (1971, *Proc. 2nd Lunar Sci. Conf.*, p. 377–392) suggest that curving cracks in pigeonite phenocryst cores of 12040, 12065 may reflect the C2/c → P2₁/c inversion in pigeonite; Ross *et al.* (1971) did not report C2/c structure formation but Prewitt *et al.* (1971, *Proc. 2nd Lunar Sci. Conf.*, p. 59) did for material of this general composition at 1000°C. A few cracks are present in the larger prisms of pigeonite in our runs, and the C2/c → P2₁/c inversion may also have occurred. Gay *et al.* (1971) comment on unusual pyroxene trends in 12065, matched by a terrestrial

protohypersthene precipitating rock. (v) Yoder, Tilley and Schairer (1964, *Yearb. Carnegie Instn. Wash.* 63, 121–129) reported an orthorhombic calcium-poor pyroxene stable at these relevant compositions and temperatures, identified as protohypersthene by the same authors (1963, *Yearb. Carnegie Instn. Wash.* 62, 84–95) with detailed discussion (1963, p. 90). (vi) Low-calcium-pyroxene cores comparable with Biggar *et al.*'s (1971) analysed protohypersthene form a smaller part of the rock powder as loaded, than do the large crystals with curving cracks which we interpret as inverted protohypersthene. Furthermore, had our protohypersthene been undissolved residual phenocryst cores it should have been more abundant in, not absent from, the lower temperature experiments. (vii) Finally we refer to results in Table VIII, run 006 which seem to eliminate worries about unmelted residual material.