

SPINELS AND THE PETROGENESIS OF SOME APOLLO 12 IGNEOUS ROCKS¹

F. D. BUSCHE, MARTIN PRINZ, AND KLAUS KEIL, *Department of
Geology and Institute of Meteoritics, University of New Mexico,
Albuquerque, New Mexico 87106*

AND

T. E. BUNCH, *Space Sciences Division, NASA Ames Research
Center, Moffett Field, California 94035*

ABSTRACT

Spinels in four Apollo 12 igneous rocks have been analyzed with the electron microprobe. Spinel composition is complex and reflects solid solution between five end members that can best be represented in a modified spinel prism in which Ti^{4+} replaces Fe^{3+} . Some rocks (12036, 12038) contain two main spinel groups with divergent compositional trends. In addition, 12036 contains rare hercynite-rich spinels in pyroxene melt inclusions; these have not previously been reported in lunar samples. Rock 12039 contains only one ulvöspinel-rich late spinel group. Rock 12051 has spinels which are often continuously zoned from chromite- to ulvöspinel-rich end members with no compositional discontinuities. Conclusions: (1) A three-dimensional representation of the complex spinel solid solutions in Apollo 12 rocks and a knowledge of textural and paragenetic relationships of spinels and coexisting phases are necessary for interpreting their petrogenetic significance. (2) The presence of two groups of spinels with divergent trends, commonly found in Apollo 12 igneous rocks, is the result of crystallization of early chromite-rich spinel and olivine, terminated by a peritectic reaction of the type described by Irvine (1967), and later crystallization of ulvöspinel-rich spinel, either simultaneously with, or later than, pyroxene. The "gap" in composition between the two spinel groups is the result of a change in composition of the melt during the course of crystallization. In rock 12039, complete resorption of early spinel (and olivine) may have resulted in the formation of only one, late spinel group. In 12051, rapid crystallization of early chromite-rich spinel simultaneously with pyroxene, rather than olivine, results in continuously zoned crystals, trending towards the Fe_2TiO_4 end member. No divergence in compositional trends is noted, apparently because there is no intervening peritectic reaction. (3) No evidence is found in support of several other hypotheses suggested in explanation of the divergent Apollo 12 spinel trends, such as the presence of an immiscibility field, or reaction of early chromite-rich spinel and melt to yield late ulvöspinel-rich spinel. (4) Melt of the composition of rock 12038 could not be the parent of an olivine-pyroxene cumulate rock such as 12036 (or 12040) because early 12038 spinels differ markedly from early 12036 spinels. However, a melt intermediate in composition between 12036 and 12038 could be parental to both rocks. The residual melt of this parent,

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after olivine and pyroxene crystal settling, would be enriched in feldspar components and this could explain the unusual major and trace element composition of rock 12038.

INTRODUCTION

Irvine (1965, 1967) has shown that the compositions of chromian spinels may be used as indicators of the physicochemical conditions of formation for terrestrial ultramafic rocks, especially if the mineral content and the composition of coexisting phases is known. Jackson (1969) studied the compositional variations in coexisting chromite and olivine in chromitite zones of the Stillwater complex, using a similar approach, and was able to achieve much insight into conditions of crystallization.

In Apollo 12 igneous rocks, spinels ranging in composition from FeCr_2O_4 to Fe_2TiO_4 (e.g., Haggerty and Meyer, 1970) are commonly found as accessory minerals. This is in contrast to Apollo 11 igneous rocks where these phases are sparse (Agrell *et al.*, 1970). Others who have analyzed and/or discussed the implications of Apollo 12 spinels include Brett *et al.* (1971), Brown *et al.* (1971), Cameron (1971), Champness *et al.* (1971), Drake *et al.* (1970), El Goresy *et al.* (1971), Gibb *et al.* (1970), Haggerty (1971a, 1971b, 1972), Keil *et al.* (1971), Kushiro *et al.* (1970), Kushiro and Haramura (1971), Muan *et al.* (1971, 1972), Reid (1971), Simpson and Bowie (1971), Taylor *et al.* (1971), Walter *et al.* (1971), and Weill *et al.* (1971).

In surveying this literature it becomes apparent that several problems with regard to Apollo 12 spinels require further clarification. One problem is the graphical portrayal of the complex compositions of spinels which may be represented by five components: FeCr_2O_4 (Cm), MgCr_2O_4 (Pc), FeAl_2O_4 (Hc), MgAl_2O_4 (Sp), and Fe_2TiO_4 (Uv) (the abbreviations will be used throughout this paper). Any graphical method of portrayal which stresses only two of these end members (e.g., Cm and Uv), as was commonly done in the cited literature, loses the subtle distinctions that may exist in spinel compositions within a given rock and/or between rocks. Haggerty (1971a) also points out that spinels are more complex than initially realized and their representation by a binary solid solution series between Cm and Uv is invalid.

Another unresolved problem is that of the presence or absence of a gap or discontinuity (Haggerty and Meyer, 1970; Haggerty, 1971a) in the so-called chromite-ulvöspinel series of Apollo 12 spinels. Haggerty (1971a) suggests that a distinct discontinuity exists between Uv_{40} and Uv_{65} in the chromite-ulvöspinel series of Apollo 12 spinels,

and that few points fall into this gap. Workers who have shown that Apollo 12 rocks contain spinels which do not have a compositional gap are Brown *et al.* (1971), El Goresy *et al.* (1971), Keil *et al.* (1971), Reid (1971), and Walter *et al.* (1971). Haggerty (1972) has shown that no compositional gap is present in Apollo 15 sample 15555.

The significance of the gap or discontinuity in the composition of Apollo 12 spinels has been interpreted in several ways: (1) as a miscibility gap in the chromite-ulvöspinel series (Haggerty and Meyer, 1970; Walter *et al.*, 1971); (2) a peritectic reaction of the early Cm-rich spinels with the melt resulting in the formation of later Uv-rich spinels (Brett *et al.*, 1971; El Goresy *et al.*, 1971; Kushiro *et al.*, 1970; Kushiro and Haramura, 1971); (3) a combination of hypotheses (1) and (2) (Taylor *et al.*, 1971); (4) termination of early crystallization of Cm-rich spinel and olivine by a peritectic relation, as outlined by Irvine (1967), when a new phase (pyroxene) crystallizes (Cameron, 1971; Champness *et al.*, 1971; Gibb *et al.*, 1970; Weill *et al.*, 1971); (5) a combination of hypotheses (2) and (4) (Haggerty, 1972); (6) termination of crystallization of Cm-rich spinel as a result of rapid change of physicochemical conditions accompanying eruption of the magma to the surface (Weill *et al.*, 1971); and (7) as the result of a very steep "liquidus slope" of equilibrium crystallization during the interval in which the liquid is saturated with spinels of these compositions (Weill *et al.*, 1971).

The purposes of this paper are, therefore, as follows: (1) to find a suitable method of plotting the complex compositions of lunar spinels such that relationships within and between rocks can be observed and described; (2) to present spinel data for four Apollo 12 igneous rocks (12036, 12038, 12039, 12051) which have different spinel populations, and to relate the spinel compositions to the petrology of each sample; and (3) to discuss the significance of the compositional gap or discontinuity for each sample and the insight it may provide for the petrogenesis of each rock.

ANALYTICAL METHODS

Spinel was analyzed with an ARL-EMX electron microprobe using chemically analyzed minerals and synthetic glass for standards: Cr_2O_3 , Al_2O_3 , and V_2O_5 were analyzed using chromite; FeO , TiO_2 , MgO , and MnO were determined using ilmenite; and CaO was analyzed using a synthetic basaltic glass. All analyses were corrected for drift, deadtime, background, mass absorption, secondary fluorescence by characteristic radiation, and atomic number using procedures described by Keil (1967). Because of the inhomogeneity exhibited in some lunar spinel grains (especially in rock 12051), great care was taken to return to the same analytical points for all elements on successive analyses of the same grain. Since no wet-chemical bulk analyses of rocks 12036 and 12039 are available, thin

sections of those samples were analyzed for bulk composition using the broad electron beam technique described by Prinz *et al.* (1971).

PRESENTATION OF DATA

The complex compositions of lunar spinel solid solutions can best be represented in a triangular prism, modified after Irvine (1965) (Fig. 1). The major modification is that Fe^{3+} is replaced by Ti^{4+} along the upper edge of the prism, giving rise to the components Mg_2TiO_4 and Fe_2TiO_4 . This modification appears to be justified because Ti is

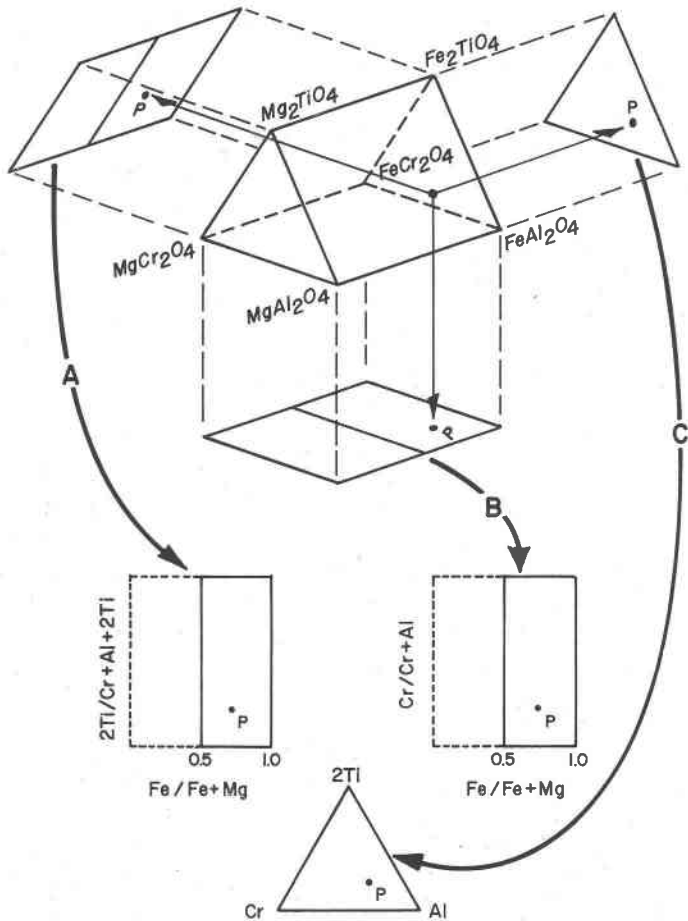


FIG. 1. The spinel prism of Irvine (1965), modified to fit the compositions of lunar spinels. Major modifications are the substitution of Mg_2TiO_4 and Fe_2TiO_4 for Fe_2FeO_4 and Mg_2FeO_4 which corresponds to substitution of Ti^{4+} for Fe^{3+} . Projections to sides A, B, and C are shown.

a major constituent of lunar spinels and no evidence for the presence of Fe³⁺ has been found in our data (in contrast with Haggerty and Meyer, 1970).

The length axis of the prism represents the relative proportions of Fe and Mg, with the front of the prism being Mg-rich and the rear being Fe-rich. A triangular cross section gives the relative proportions of Al, Cr, and Ti for a given Fe/Fe + Mg ratio. The small amounts of Mn and Ca were added to Fe, and V was added to Cr. The six corners correspond to each of the components; Mg₂TiO₄ is not needed in our calculations and, therefore, spinel analyses are recalculated into five components (Table 1).

In order to completely describe a spinel analysis, a point P (representing that analysis) is projected to three sides of the prism, as shown in Figure 1. These projections are shown as sides A, B, and C and all analyses are plotted as mole ratios since end members are calculated. A projection to side A is made by plotting 2Ti/(Cr + Al + 2Ti) against Fe/(Fe + Mg) which projects the point P to side A horizontally, parallel to the base. A projection to side B is made by plotting Cr/(Cr + Al) against Fe/(Fe + Mg) and the point P projects vertically downward to the base. A projection to side C is made by plotting mole percentages of 2Ti, Cr, and Al (recalculated to 100 percent) in a triangular plot and this projects the point P horizontally, parallel to the base. Since no spinels were found with a Fe/(Fe + Mg) ratio less than 0.5, the lefthand sides of the projections

Table 1: Electron microprobe analyses of selected spinels in four Apollo 12 igneous rocks

Group No.	Oxides (weight percent)									
	Rock 12036			Inter-mediate Rock 12038		II	Rock 12039	Rock 12051		
TiO ₂	5.7	26.4	1.18	5.0	21.8	39.1	31.5	6.5	23.7	32.8
Al ₂ O ₃	10.1	4.1	55.0	17.1	6.7	2.90	3.5	10.8	5.2	2.48
Cr ₂ O ₃	45.6	15.7	4.6	41.5	17.1	5.8	2.26	42.8	17.3	0.03
V ₂ O ₃	1.01	0.63	0.06	0.98	0.58	0.41	0.47	0.74	0.48	0.22
FeO	28.1	48.3	33.4	27.6	48.6	62.1	63.5	36.8	53.2	62.2
MnO	0.28	0.33	0.16	0.26	0.34	0.32	0.28	0.23	0.24	0.25
MgO	7.6	4.0	5.6	7.4	3.3	0.04	0.21	1.30	0.46	0.21
CaO	0.42	0.22	0.46	0.36	0.44	0.13	0.20	0.31	0.39	0.47
Total	98.81	99.68	100.46	100.20	98.86	101.80	100.92	99.48	100.97	98.76
	Spinel Components* (mole percent)									
Cm	56.1	5.4	5.3	54.4	25.9	8.8	3.7	60.3	25.2	1.0
Pc	8.0	17.8	-	0.01	-	-	-	-	-	-
Hc	-	-	75.2	-	5.5	6.4	7.7	16.6	8.5	5.7
Sp	20.9	4.1	18.2	33.1	8.9	-	-	5.9	2.4	-
Uv	15.0	72.7	1.3	12.4	59.7	84.8	88.6	17.2	63.9	93.3

*See text for method of calculation

For 72 individual analyses see Busche et al. (1971).

A and B are shown as dashed lines, and are omitted in subsequent diagrams (Figs. 2-4). The orientations of sides A, B, and C are maintained in Figures 2-4 for ease of viewing.

Haggerty (1971a) has made a similar modification of the spinel prism of Irvine (1965) for terrestrial spinels by substituting Ti^{4+} for Fe^{3+} . However, his $MgAl_2O_4$ - $FeAl_2O_4$ and $MgCr_2O_4$ - $FeCr_2O_4$ edges are the reverse of ours; he has projected to the same three sides but has used weight percentage oxide ratios rather than mole ratios; and his projection to the triangular rear of the prism is presented as a plot of $TiO_2/(Al_2O_3 + Cr_2O_3 + TiO_2)$ against $Cr_2O_3/(Al_2O_3 + Cr_2O_3)$ (weight percentages). Thus, his plots cannot be directly compared with ours, although points in sides A and B have the same general orientation.

Some selected spinel analyses are presented in Table 1 and the end members are given below each analysis. These end members were calculated as follows: (1) all Mn and Ca are added to Fe^{2+} , and V is added to Cr, as is the case for the data plotted in Figures 2-4. (2) Fe_2TiO_4 is calculated using up all available Ti; excess Ti never occurred and therefore Mg_2TiO_4 was not calculated; (3) $FeCr_2O_4$ is calculated; any excess Cr is calculated as $MgCr_2O_4$; (4) $FeAl_2O_4$ is calculated; any excess Al is calculated as $MgAl_2O_4$. A small excess sometimes remains but it is generally less than 0.5 mole percent and is ignored.

SPINEL COMPOSITIONS AND PETROLOGICAL RELATIONSHIPS

One hundred fifty spinels have been analyzed in four Apollo 12 rocks (12036, 12038, 12039, 12051). Seventy-two complete analyses, including structural formulae, have previously been published (Busche *et al.*, 1971). The remaining 68 spinels have been analyzed for Fe, Ti, Cr, Al, and Mg only and these data are included in Figures 2-4. It should be noted that, because of the small concentrations of Ca, Mn, and V, a complete analysis [$(Fe + Mn + Ca)/(Fe + Mn + Ca + Mg)$, $2Ti/(Cr + V + Al + 2Ti)$, and $(Cr + V)/(Cr + V + Al)$] versus an incomplete analysis [$Fe/(Fe + Mg)$, $2Ti/(Cr + Al + 2Ti)$, and $Cr/(Cr + Al)$], on the scales of Figures 2-4, plot very close to each other. Hence, the use of complete and incomplete analyses in the same diagram does not alter the spinel compositional patterns.

In the following section spinel compositions are related to texture, mineral content and composition, and bulk composition of each rock.

Rock 12036

Rock 12036 is a feldspathic peridotite and has been studied in detail by Prinz *et al.* (in prep.). This rock is a complex cumulate with early

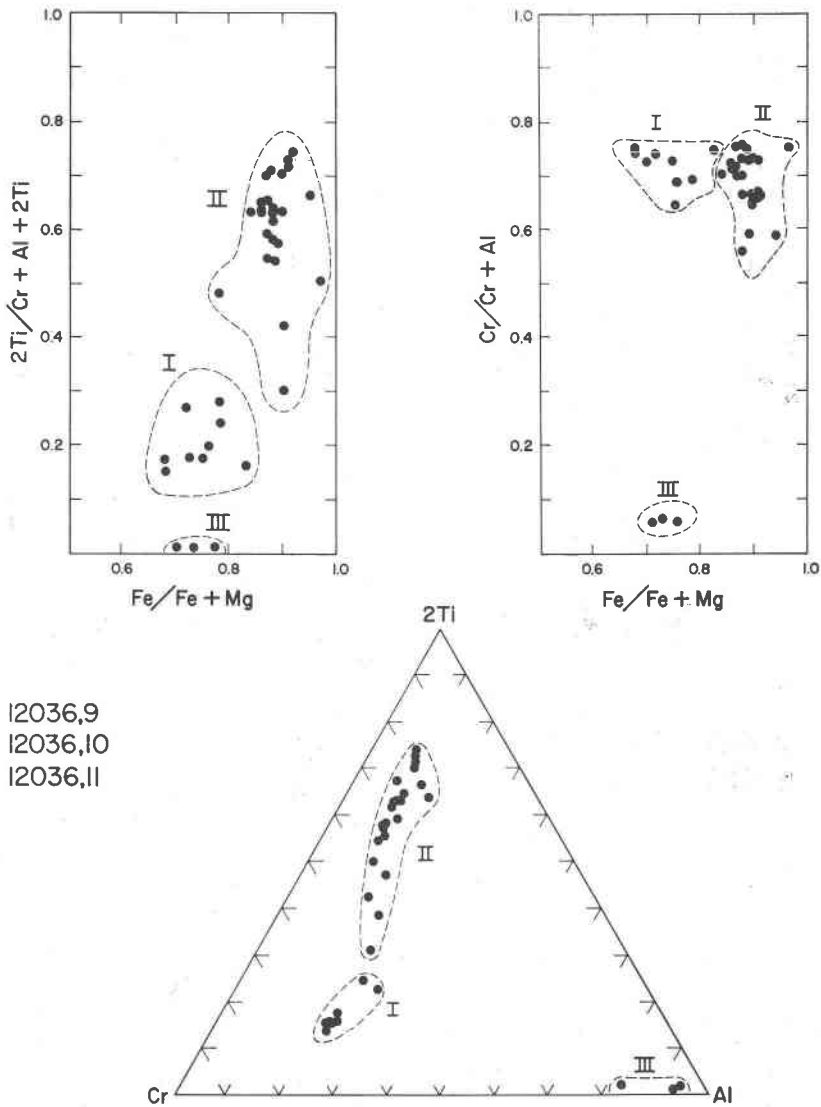


FIG. 2. Compositions of spinels from rock 12036 plotted as projections to sides A, B, and C of the spinel prism shown in Figure 1 (in mole ratios). Group I, II, and III spinels are outlined by dashed lines.

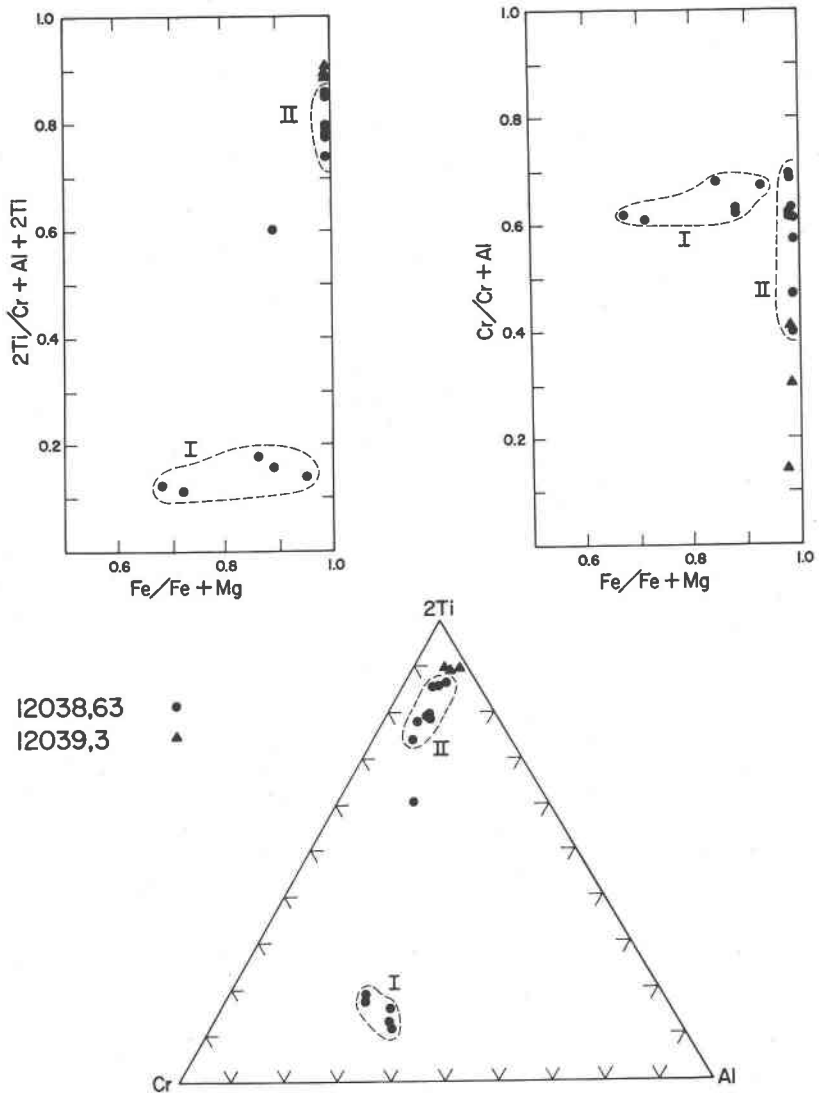


FIG. 3. Composition of spinels from rocks 12038 and 12039 plotted as projections to sides A, B, and C of the spinel prism shown in Figure 1 (in mole ratios). Group I and II spinels in rock 12038 are outlined by dashed lines.

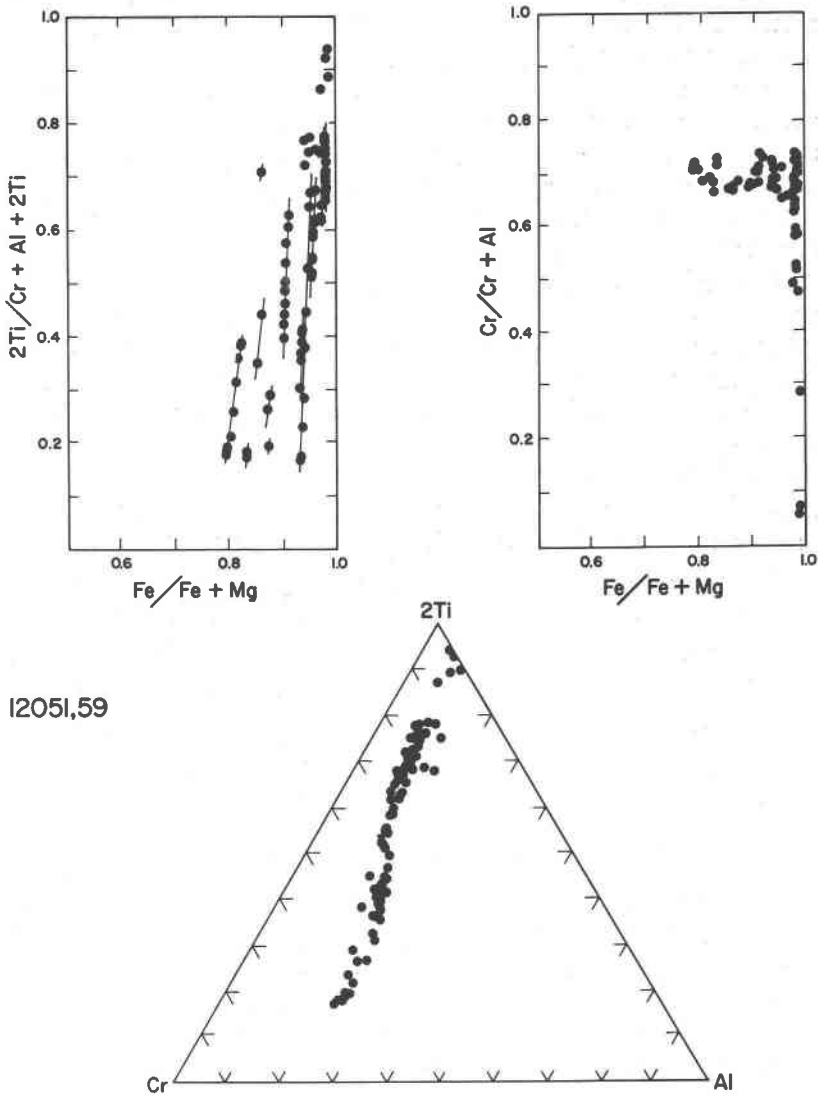


FIG. 4. Compositions of spinels from rock 12051 plotted as projections to sides A, B, and C of the spinel prism shown in Figure 1 (in mole ratios). Ranges in composition of individual spinel grains are indicated by solid lines but, for reasons of clarity, are only shown in the projection to side A (Fig. 4A).

crystallized Cm-rich spinel and olivine (F_{064-60}) poikilitically enclosed in chemically homogeneous pigeonite-augite megacrysts up to 5 mm across. These megacrysts are incorporated into a second stage assemblage; this assemblage includes cumulus olivine (F_{059-36}), followed by plagioclase (An_{90-77}), spinels intermediate between Cm and Uv, chemically inhomogeneous pyroxene which rims the early pyroxene megacrysts and, finally, accessory minerals. A bulk analysis of three thin sections of this rock by broad beam electron microprobe techniques is listed in Table 2 and in general is similar but somewhat more mafic than the analysis of rock 12040 (Kushiro and Haramura, 1971). Modally, the rock contains 24 percent olivine, 58 percent pyroxene, 12 percent plagioclase, 5 percent opaques, and 0.7 percent melt inclusions (in volume percentages) (Prinz *et al.*, in prep.).

The composition of spinels is shown in Figure 2, representing analyses of grains in three thin sections. Spinel of this rock may be divided into three groups (Fig. 2). Group I spinels are Cm-rich but also contain significant proportions of Sp, Uv, and Pc (Table 1). They are euhedral, often intergrown octahedra that are chemically homogeneous and represent cumulus phases. This group presumably represents a

Table 2: Bulk compositions of four Apollo 12 igneous rocks (in weight percentages)

Sample No.	1 12036	2 12038,24	3 12039,3	4 12051,34
SiO ₂	42.2	47.05	47.3	45.54
TiO ₂	2.57	3.22	3.04	4.74
Al ₂ O ₃	6.2	12.12	10.7	9.95
Cr ₂ O ₃	0.59	0.34	0.23	0.36
FeO	22.7	17.91	21.1	20.19
MnO	0.27	0.24	0.19	0.28
MgO	17.0	7.09	5.3	6.82
CaO	7.8	11.46	12.1	11.33
Na ₂ O	0.17	0.64	0.36	0.31
K ₂ O	0.02	0.07	0.09	0.04
F ₂ O ₅	0.06	0.02	0.09	0.07
S	n.d.	n.d.	n.d.	0.10
H ₂ O-	n.d.	n.d.	n.d.	0.03
Subtotal	99.58	100.16	100.50	99.76
Less O = S	-	-	-	0.05
Total	99.58	100.16	100.50	99.71

n.d. = not determined

1. Broad beam electron microprobe analysis; average of three thin sections (12036,9; 12036,10; 12036,11) (Prinz *et al.*, in prep.)
2. Kushiro and Haramura (1971)
3. Broad beam electron microprobe analysis of one thin section (this paper)
4. Maxwell and Wiik (1971)

solid solution series, with the earliest spinels having the lowest Fe/(Fe + Mg) ratios. These spinels crystallized essentially simultaneously with early olivine (Fe_{64-60}) and vary mainly in Fe/(Fe + Mg) and relatively little in Cr/(Cr + Al) and $2Ti/(Cr + Al + 2Ti)$ ratios. The compositional variations appear to be the result of partitioning of these elements between spinel and olivine.

Group II spinels formed together with other minerals in a later, second stage assemblage of minerals and are Uv-rich, but also contain significant proportions of Pc, Cm, and Sp (Table 1). These spinels are usually subhedral to anhedral and are sometimes zoned with the Uv component increasing toward the rim. There is a small hiatus in compositions between group I and II spinels, especially as seen in Figure 2A. More significant than this compositional hiatus, however, is the major change in the compositional trend from group I to group II spinels: whereas group I spinels vary mainly in Fe/(Fe + Mg) but little in Cr/(Cr + Al) and $2Ti/(Cr + Al + 2Ti)$, group II spinels vary little in Fe/(Fe + Mg) but mainly in Cr/(Cr + Al) and $2Ti/(Cr + Al + 2Ti)$. Group II appears to represent a solid solution series, with the earliest spinels presumably being those with lowest $2Ti/(Cr + Al + 2Ti)$ ratios. Group II spinels formed in a second stage mineral assemblage and essentially simultaneously with later pyroxene that rims the pigeonite-augite megacrysts. Apparently, the compositional variations in the spinels are the result of element partitioning between spinel and pyroxene.

Group III spinels are rare; only three grains were found. They are rich in the Hc component and are the first spinels of this composition to be reported in lunar samples. The three analyses are presented in Busche *et al.* (1971; Table 38) and one analysis is given in Table 1. All three grains were found in early pyroxene melt inclusions which are described in detail by Prinz *et al.* (in prep.). One of the melt inclusions in which group III spinels were found is relatively Al_2O_3 -rich (approximately 17 weight percent) and this may be partly responsible for the aluminous nature of the spinel.

A number of noteworthy facts become apparent from a comparison of spinel compositions in rock 12036 and other Apollo 12 samples studied. The earliest group I spinels have the lowest Fe/(Fe + Mg) ratios of Cm-rich spinels, and group II spinels have the lowest Fe/(Fe + Mg) ratios of intermediate to Uv-rich spinels in Apollo 12 rocks. This appears to be a reflection of the low Fe/(Fe + Mg) ratio of the rock as indicated by the bulk analysis and of the melt from which 12036 crystallized. Since 12036 is a cumulate rock, the bulk analysis of the rock cannot be taken as the composition of its parent

melt and, in fact, the parent melt must have had an even lower Fe/(Fe + Mg) ratio. Furthermore, the Cr/(Cr + Al) ratio of group I spinels are among the highest of Apollo 12 Cm-rich spinels, indicating a high Cr/(Cr + Al) ratio of the parent melt.

Rock 12038

Rock 12038 is a fine-grained basalt that is unique among Apollo 12 wet chemically analyzed igneous rocks because of its relatively high Al_2O_3 and Na_2O and low FeO contents (Table 2). This rock is also relatively rich in rare earth elements as compared to other Apollo 12 igneous rocks (Schnetzler and Philpotts, 1971). Biggar *et al.* (1971) interpret the melt from which rock 12038 formed as being a low-pressure cotectic liquid that is probably parental to such magnesian rocks as 12018, 12020, and 12040; *i.e.*, the latter three rocks are essentially 12038 melt with the addition of cumulus olivine, some pyroxene, and chromian spinel. Since rock 12036 is very similar to rock 12040, as shown by Prinz *et al.* (in prep.), this hypothesis presumably applies to rock 12036 as well. Schnetzler and Philpotts (1971) point out that a melt of 12038 composition cannot be the direct parent of the magnesian Apollo 12 igneous rocks cited by Biggar *et al.* (1971) but that rock 12038 may have formed from a later liquid differentiated from a melt parental to those rocks which has been enriched in plagioclase, and perhaps, clinopyroxene.

Compositionally, spinels in rock 12038 fall into two widely separated groups that are shown as groups I and II in Figure 3 (note that groups I and II of rock 12038 are similar but not identical to groups I and II of rock 12036). Group I spinels are Cm-rich, but contain considerable Sp and Uv. They are compositionally homogeneous euhedral octahedra and are very sparse. One grain of a group I spinel was found associated with a grain of olivine (Fo_{60}) (olivine is very rare in this rock). Since the rock also contains late fayalitic olivine, the presence of Cm-rich spinel and olivine of Fo_{60} indicates that the latter phases are either the result of crystal settling or early crystallization from melt of 12038 composition and incomplete resorption. However, group I spinels are markedly aluminous (approximately 17 percent Al_2O_3) [Table 1; Busche *et al.* (1971)]. In fact, these are the most aluminous Cm-rich spinels yet reported from Apollo 12 rocks. Since rock 12038 is the most aluminous Apollo 12 igneous rock it is suggested that these spinels crystallized from this melt and, hence, are not the product of extensive crystal settling and accumulation. Furthermore, the Cr_2O_3 content of spinels in rock 12038 is low, and the Cr/(Cr + Al) ratios are among the lowest of

Apollo 12 spinels. Rock 12038 also has a low bulk Cr_2O_3 content (Kushiro and Haramura, 1971), giving additional support to the proposition that Cm-rich spinels (group I spinels) crystallized from this liquid.

Group I spinels have variable $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios but vary little in $2\text{Ti}/(\text{Cr} + \text{Al} + 2\text{Ti})$ or $\text{Cr}/(\text{Cr} + \text{Al})$ ratios. Apparently, group I spinels represent a solid solution series similar to that of group I spinels in rock 12036. However, a major difference between the two groups is that group I spinels of rock 12038 are much richer in Al_2O_3 and poorer in Cr_2O_3 than group I spinels of rock 12036. Since both these groups crystallized simultaneously with olivine it is presumed that this type of compositional trend is again the result of element partitioning between spinel and olivine.

Group II spinels are sparse; they are generally anhedral and inhomogeneous, with enrichment of Uv towards the rim. They are highly enriched in FeO and very poor in MgO; in fact, the Uv-content may be as high as 85 percent. In addition to the Uv component, they also contain some Cm and Hc (Table 1); apparently, group II spinels are members of a solid solution series. They are among the latest phases to crystallize and probably form as late as the fayalitic olivine.

A single spinel analysis is intermediate between group I and II spinels (Fig. 3; Table 1); the significance of this spinel is not clear.

Rock 12039

Rock 12039 is a medium-grained basalt or microgabbro and one of the most Fe-rich and Mg-poor Apollo 12 igneous rocks (Table 2). It is most similar in composition to rock 12064 analyzed by Kushiro and Haramura (1971). Early olivine was not observed, and the rock contains tridymite and cristobalite (Keil *et al.*, 1971; Bunch *et al.*, 1972). Plagioclase and pyroxene are the predominant minerals; and pyroxferroite often mantles clinopyroxene.

Spinel in rock 12039 are subhedral and interstitial, and appear to have formed late in the crystallization history of the rock. They are relatively homogeneous and grain to grain compositional variations are small. The compositions of three grains are shown in Figure 3 and individual, complete analyses are given in Busche *et al.* (1971); one representative analysis is given in Table 1. Reconnaissance study of other spinel grains in this thin section indicates near-uniformity in composition with the grains reported here and, hence, no additional quantitative analyses were made. The spinels in rock 12039 are very Uv-rich and contain some Cm and Sp. The similarity between rocks 12039 and 12064 is further expressed in the composition of spinels;

both contain Uv-rich spinel only. The relatively uniform composition of these spinels, therefore, indicates that immiscibility was not a factor in their formation. Comparison of the mineralogical and chemical compositions of rocks 12039 and 12064 indicate close similarity.

Biggar *et al.* (1971) suggest that rock 12064 is a low-pressure cotectic liquid and rocks such as 12021, 12065, and 12052 are samples of this lava to which pigeonite and, to a lesser extent, olivine and spinel have been added. They also show that a liquid of rock 12064 composition crystallized early olivine and Cm-rich spinel and that their disappearance is due to reaction with the liquid. They also note that there is no evidence of a discontinuous reaction of Cm-rich spinel and liquid to form Uv-rich spinel in rock 12064. Thus, because of early resorption, rock 12064 contains no Cm-rich spinel, and crystallization of late Uv-rich spinel is the result of the composition of the melt and the physicochemical conditions under which it crystallized. Similar arguments appear to account for the Uv-rich spinels in rock 12039. The possibility that early Cm-rich spinels settled out of this melt rather than were resorbed back into it, seems less likely since Biggar *et al.* (1971) show that the composition of rock 12039 is very close to a low-pressure cotectic liquid. If significant crystal settling of Cm-rich spinel and olivine occurred then the melt would not be close in composition to that cotectic liquid.

Rock 12051

Rock 12051 is a fine-grained basalt relatively rich in iron in comparison to most other wet chemically analyzed Apollo 12 igneous rocks (Table 2). Brown *et al.* (1971) refer to this rock as a ferrobasalt. No early olivine was found in our sections, but Brown *et al.* (1971) note its rare occurrence in their material. Fayalitic olivine and silica are commonly present (Keil *et al.*, 1971). Brown *et al.* (1971) note that the texture indicates cotectic crystallization of plagioclase and pyroxene, and we are in agreement with this interpretation.

The spinels in rock 12051 differ from those of most Apollo 12 igneous rocks. Many grains are inhomogeneous and some are zoned from a more Cm-rich core to a Uv-rich rim. However, the Cm-rich spinel has a relatively high $Fe/(Fe + Mg)$ ratio and zoning is continuous across the so-called Apollo 12 spinel gap (as was also shown by Brown *et al.*, 1971). The zoning is diffuse and sharp boundaries or mantled grains are not observed. Some grains appear to have more complex compositional inhomogeneities (Keil *et al.*, 1971, Fig. 8), and these may be due either to unusual growth patterns as the result of rapid crystallization, or to geometrical effects as a result of the particular cut in thin section through a zoned grain.

Nevertheless, the compositional patterns of spinels in rock 12051 (Fig. 4) differ markedly from those of rocks 12036, 12038, and 12039 (Figs. 2, 3). The spinel composition of rock 12051 is most clearly shown in the $2\text{Ti}/(\text{Cr} + \text{Al} + 2\text{Ti})$ versus $\text{Fe}/(\text{Fe} + \text{Mg})$ plot (Fig. 4A). The lines connecting points indicate the extent of compositional variability within individual grains; these lines are omitted from the other two projections for the purpose of clarity. The patterns in Figure 4A indicate that early spinels with lowest $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios grade continuously into Uv-rich compositions. Apparently, a solid solution relationship exists between early, $\text{Fe}/(\text{Fe} + \text{Mg})$ -poor and late, Uv-rich spinels, and no immiscibility gap is observed. The major variations are in $2\text{Ti}/(\text{Cr} + \text{Al} + 2\text{Ti})$, although there is some variation in $\text{Fe}/(\text{Fe} + \text{Mg})$ and $\text{Cr}/(\text{Cr} + \text{Al})$. The variation in $\text{Fe}/(\text{Fe} + \text{Mg})$ is nearly entirely a variation in Fe, as Mg is near constant in all zoned grains that were analyzed (see Keil *et al.*, 1971, Fig. 8). As crystallization proceeded, Cm-rich spinel increased in $\text{Fe}/(\text{Fe} + \text{Mg})$ ratio and the slope of the line through points in individual grains (as shown in Fig. 4A) increases nearing vertical on the right side of the diagram. Later spinels have increasingly Uv-rich cores and rims and plot in the upper right corner of the plot; these may be a later solid solution series.

Early spinels of 12051 crystallized essentially simultaneously with pyroxene and plagioclase and in this respect, are analogous to group II spinels in rocks 12036 and 12038. The major difference is that these grains are sometimes cored by Cm-rich spinels, with relatively high $\text{Fe}/(\text{Fe} + \text{Mg})$ ratios, and are continuously zoned.

CONCLUSIONS

The following conclusions have been drawn from the study of spinel compositions for the four Apollo 12 igneous rocks studied:

(1) There appears to be no evidence for a miscibility gap in the spinel system in any of the four rocks studied. This finding is in agreement with the experimental work of Muan *et al.* (1972): they have shown that no two-phase region is present at temperatures down to 1000°C in that portion of the spinel prism where Apollo 12 spinels plot (note that there is no evidence for subsolidus reactions in the spinels studied here). These rocks have spinels that may be divided into either one (12039), two (12038), or three (12036) groups. Rock 12051 has Cm-rich spinels which are zoned continuously to Uv-rich spinels. Spinel form continuous solid solution series in rocks with one spinel group. Separate spinel groups in rocks 12036 and 12038 appear to be the result of crystallization at different stages in the crystallization history of the rocks.

(2) There is no textural evidence in the rocks studied here for a peritectic relation involving reaction of early Cm-rich spinel with liquid to produce Uv-rich spinel as suggested by Kushiro *et al.* (1970). A peritectic relation of this type should be manifested in textural evidence, such as resorption of Cm-rich spinel, which is not observed. Cameron (1971) and Weill *et al.* (1971) have reached similar conclusions.

(3) Mineralogical and chemical data for spinels and coexisting phases, and the textures and bulk compositions of the rocks, point to a peritectic relationship for the origin of spinels of the type described by Irvine (1967). Early Cm-rich spinel forms simultaneously with early olivine; formation of these phases is terminated and is followed by pyroxene crystallization, often simultaneously with plagioclase. If new spinel crystallizes shortly thereafter, the compositional hiatus between old and new spinel is small, as in rock 12036. If new spinel crystallizes much later, then the compositional gap is large, as in rock 12038. If early Cm-rich spinel is totally resorbed or settled out of the melt, only one Uv-rich spinel series is present, as is the case in rock 12039. There is no clear evidence that suggests that crystallization of Cm-rich spinel is terminated by eruption of the lava to the surface, or that a change in the "liquidus slope" of equilibrium crystallization has changed, as suggested by Weill *et al.* (1971).

(4) Rock 12051 contains spinels with trends somewhat analogous to group II spinels of rocks 12036 and 12038. Early Cm-rich spinel, with low $Fe/(Fe + Mg)$ ratio, is absent but the rare occurrence of early olivine was noted by Brown *et al.* (1971). It appears that the rapid crystallization of this fine-grained rock resulted in the inhibition of crystallization of early spinel and olivine before the peritectic reaction took place that results in the onset of pyroxene and plagioclase crystallization. Therefore, Cm-rich spinel with relatively high $Fe/(Fe + Mg)$ ratios crystallized simultaneously with pyroxene and plagioclase and, since there was no interference from a peritectic relationship, resulted in a continuous crystallization series between Cm- and Uv-rich compositions. Again, this observation points to the lack of a miscibility gap in the complex spinel systems observed in Apollo 12 rocks.

(5) Haggerty (1971a) has surveyed the literature on Apollo 12 spinels and plotted their compositions in a modified spinel prism similar to the one used in this paper. Most of the data points fall into two groups similar to groups I and II of rocks 12036 and 12038. We interpret this finding as an indication that many Cm-rich spinels formed early, before the crystallization of pyroxene, and that many Uv-rich spinels

formed after the peritectic relationship which produced pyroxene, or even later in the crystallization history of the rock. We suggest that the extent of a compositional gap between early and later spinels is a function of the time of crystallization of the spinel in the melt. The major change in the compositional trends between the two spinel groups is interpreted as the result of the differences in element partitioning between spinel and co-existing phases, especially spinel and olivine for early Cm-rich spinels, and spinel and pyroxene for later Uv-rich spinels. However, we would caution any interpretation of spinel data without the detailed knowledge of the composition and zoning of spinel grains in relation to composition, texture and time of crystallization within the specific rock.

(6) Biggar *et al.* (1971) suggest that melts of rock 12038 composition may be the parent of olivine-rich rocks such as 12018, 12020, and 12040. Prinz *et al.* (in prep.) have shown that rock 12036 is very similar to rock 12040. Hence, by analogy, a melt of rock 12038 composition may be the parent of rock 12036. However, Schnetzler and Philpotts (1971) argue that rock 12038 could not be parental to these rocks and must have formed from a later liquid to which plagioclase, and perhaps, clinopyroxene were added. However, their proposition was not supported by textural evidence.

Data on the composition of spinels for rocks 12036 and 12038 are relevant to these hypotheses: The early Cm-rich spinels in rock 12038 are more Al-rich and Cr-poor than those in rock 12036 and, therefore, the latter could not have formed in a liquid of 12038 composition. However, a liquid intermediate in composition between rocks 12036 and 12038 could be parental to both, as well as to the other magnesian Apollo 12 igneous rocks. From this parent, 12036-type Cm-rich spinels as well as early olivine and pigeonite-augite megacrysts could have crystallized. This differentiated melt would then be greatly enriched in the feldspar component and resemble the composition of rock 12038. This model is then in essential agreement with the proposition of Schnetzler and Philpotts (1971) and would avoid the problem of not observing textural evidence for plagioclase enrichment.

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