

## Lunar Mineralogy: A Heavenly Detective Story Presidential Address, Part I<sup>1</sup>

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### Abstract

A general introduction emphasizes the strong interactions between mineralogy and related sciences, and the need for cooperative programs among the various mineralogical groups.

To provide maximum access to the literature, the bulk of lunar rock types are classified into ANT, FETI, and KREEP groups. The Anorthositic-Noritic-Troctolitic compositions mostly occur as metabreccias, and are believed to come from the crust. The basalts rich in Fe and Ti result from late lava flows in mare basins. The KREEP suite of basaltic compositions occurs mostly as glasses and metabreccias rich in K, REE, P, and other large-ion elements; it probably results from a late liquid in primary differentiation of the Moon, or partial melting of ANT rocks, or both. Some lunar rocks are hybrids formed by melting of soils. Metamorphism is widespread. Minor rock types include peridotite, spinel allivalite and troctolite, and other fragments containing Mg-rich minerals. Granitic material occurs rarely. Minor meteoritic fragments occur.

Major mineral groups are pyroxene, feldspar, olivine, spinel, pseudobrookite (armalcolites), silica (quartz, tridymite, cristobalite), Fe-rich types (iron, troilite, ilmenite), phosphates (apatite, whitlockite), and Zr-minerals (zircon, baddeleyite). Minor silicates include pyroxferroite, amphibole, garnet, and tranquillityite. Minor sulfides are mackinawite, pentlandite, cubanite, chalcopyrite, and sphalerite. Minor oxides are rutile and corundum. Minor metals include copper, brass, and tin. A Zr-rich mineral is either zirkelite or zirconolite. Schreibersite, cohenite, and niningerite probably derive from iron meteorites. Rusty areas probably consist of goethite perhaps associated with hematite and magnetite; presence of Cl suggests possible terrestrial oxidation of meteoritic lawrencite.

Important features of feldspars are: mostly calcic plagioclase, but rare K,Ba-feldspar in residua; correlation of Mg,Fe,K, and Na with rock type giving test of differentiation models; Eu anomaly depends on temperature, oxidation state, etc; solid-solution of Ca(Mg,Fe)Si<sub>2</sub>O<sub>8</sub> in FETI plagioclase; exsolution of pyroxene, silica, and Fe in ANT plagioclase.

Important features of olivines are: correlation of  $mg$  [= atomic Mg/(Mg + Fe)] with rock type giving test of differentiation models; Ca may distinguish volcanic from plutonic environment; Cr enters as divalent ion, and may provide guide to oxidation state; Mg,Fe ordering of some olivines indicates long annealing; melt inclusions give magma composition; high Al in some olivines may correlate with spinel exsolution; melt inclusions give magma composition.

### Introduction

*This written address differs considerably from the oral presentation. Because of time limitations, the general introduction was omitted. Several hundred mineralogists and petrologists worked on the lunar program, and most ideas were discovered almost simultaneously by several persons or groups. In the oral presentation, references to individual scientists were deliberately omitted to avoid tedious repetition and invidious selection of names. In this written*

*presentation many references are given, but these are highly selective and chosen for convenience and not for priority or prestige. In particular, references tend to concentrate on controversial items and on papers submitted for publication. Matters of common knowledge are not fully documented.*

The Presidential Address provides an opportunity for the Retiring President to philosophize or to review some aspect of his work or of mineralogy in general. I shall briefly pontificate, and then use a review of lunar mineralogy as an implicit illustration of my main theme: that the distinctions between mineralogy and allied sciences (including geochemis-

<sup>1</sup> Presidential Address, Mineralogical Society of America. Delivered at the 54th Annual Meeting of the Society, 13 November 1973.

try, geophysics, petrology, and crystallography) are blurring so rapidly that research mineralogists should become competent in as many areas as possible, and should collaborate closely with scientists with related and overlapping interests.

It is quite impossible to understand the phase equilibria of (say) plagioclase feldspars without information on the following: (1) controlled laboratory syntheses at high temperature with X-ray diffraction and electron-optical characterization of the products; (2) chemical, X-ray diffraction, and electron-optical characterization of plagioclases from natural rocks ranging from volcanic to metamorphic; (3) heating studies of natural specimens. In addition, calorimetry and resonance techniques, plus many others, provide further knowledge. A crystallographer without a thermodynamic background might misinterpret the phase relations, while a geochemist might overlook the importance of domain texture in the occurrence of trace elements. The electrical conductivity and diffusion coefficients of ferromagnesian minerals depend strongly on structural defects and the oxidation state, thereby having a profound effect on geophysical interpretation of phenomena such as creep in the mantle and the temperature profile of the Moon. The routine use of the electron microprobe (hopefully to be joined by the ion microprobe for trace elements and isotopic ratios) brings geochemical data within the immediate control of the mineralogist and petrologist. The organization of research is beginning to utilize the power of coordinated studies, as in the mineralogy-petrology-geochemistry consortia for lunar specimens. Many mineralogical problems must be studied by groups of investigators, often geographically dispersed; such investigators should be diplomats as well as scientists.

Fortunately, not all mineralogy requires the big battalions with the kilo- or mega-buck. A perennial joy of mineralogy is the scope for the collector and the artist, for the field man and the museum curator. Some modern artists examine the world for existing natural beauty; collectors of minerals have been doing this for centuries. Mining operations continually reveal new mineral deposits of spectacular interest, such as the one at St. Hilaire. Some mineral museums expand their collections and put on magnificent displays; others deteriorate. Probably most mineralogists recognize the value of a pluralistic approach, and appreciate the mutual interests and different styles of the various types of mineralogists.

Unquestionably, it is important to develop strong cooperative programs among the various mineralogical groups (and also among the various geological societies); otherwise prolonged isolation leads to distrust and antagonism. It would be tragic if the world of mineralogy split up into separate camps, each fearful and contemptuous of the others.

Finally, I want to mention the practical uses of minerals. Agriculture depends on the proper interaction between the inorganic minerals and the organic content of soils. Many chemical and all metallurgical industries depend on extraction of minerals, some of which are becoming scarce. Novel uses of minerals, such as the employment of zeolites as catalysts in the petroleum industry and the application of mineral analogs as lasers and solid-state devices, should attain increasing importance; for example, several rare minerals with strong pleochroism may have potential electronic uses. For this reason, mineralogical societies should also collaborate closely with chemical and physical societies.

No mineralogist can rest on the knowledge gained in his formal education. One of the great advantages of the lunar program was the opportunity for the scientists to meet closely with practitioners in other disciplines. Some mineralogists gained a working knowledge of such apparent esoterica as a europium deficiency and the time relation of BABI and ADOR. It is extremely important to provide opportunities for mineralogists to expand their knowledge, and the Mineralogical Society of America should become active in organizing short courses and symposia, and in publishing critical monographs and treatises.

So much for the pontificating; now for lunar mineralogy with its illustration of the strong interconnections between mineralogy, petrology, geochemistry, and geophysics.

## Lunar Mineralogy

### Introduction

The completion of the Apollo missions provides a suitable time to evaluate the status of lunar mineralogy. An article "How the Apollo program changed the geology of the Moon: suggestions for future studies" by Smith and Steele (1973) gives a general background. Briefly, the Moon was in orbit around the Earth at least 4 giga-years ago; it underwent major chemical differentiation at least 3.9 giga-years ago (and perhaps as early as 4.5 giga-years ago) producing a crust, a mantle, and perhaps a core; in-

tense bombardment devastated the surface to depths of several tens of kilometers, perhaps with significant late accretion of the incoming projectiles; lava flows covered impact basins with the last activity occurring near 3 giga-years ago (though some unexplored areas of the Moon may have later extrusions); and continuing bombardment by relatively small projectiles produced a surface covered by debris (regolith). Geophysical and geological data show that the present crust of the Moon consists of a loose regolith some meters thick lying on some tens of kilometers of material with low seismic velocity. In the mare regions, the upper parts are dominated by basalts rich in Fe and Ti, whereas in the highland regions, the dominant rocks are probably rich in calcic plagioclase with subordinate pyroxene and olivine. The nature of the hypothetical mantle is controversial, but many workers believe that it is dominated by magnesian olivines and pyroxenes. Figure 1, a model of the Moon proposed after the Apollo 11 mission, may provide a crude description for a time prior to 4 giga-years ago. There are some very dif-

ficult geochemical and geophysical problems, especially concerning (1) the sources of energy and the timing of igneous events on the Moon, and (2) the ultimate origin of the bulk chemistry of the Moon.

The mineralogy and petrology of the Moon provides a fascinating challenge to the lunar detective. Few samples returned to Earth are simple igneous rocks. Most consist of complex breccias or fine-grained soils. In spite of careful selection of prospecting sites and detailed documentation (too detailed for the temper of many lunar investigators faced with sample description forms!), it is very difficult to pin down the actual starting point of most lunar samples. Fortunately the mineralogy of the Moon is rather simple compared to that on the Earth, comprising only some few dozens of species compared to several thousand (ultimately, of course, the full range of meteoritic minerals should be found on the Moon). There are few rock types (though one might not think so from the confusing nomenclatures in the literature!). In general, it is possible to arrange most of the information on lunar rocks and minerals into plausible sequences consistent with crystal-liquid differentiation, metamorphism, hybridization. The major uncertainties relate to geochemical and geophysical problems: what were the time sequences of crystal-liquid fractionation; what was the extent of late accretion; how important were remelting and metamorphism; what are the implications for the internal structure and the bulk composition of the Moon? In attempting to answer these questions, the mineralogic detective must bear in mind that the regolith is dominated by crustal material, and that deep-seated material should be sparse and found mainly as fragments in breccias from major impacts.

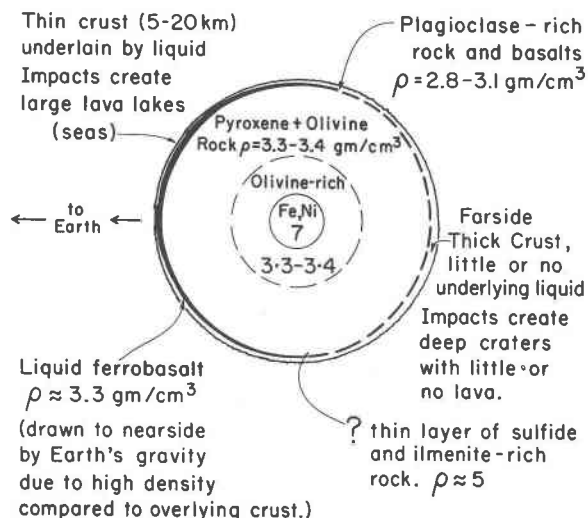


FIG. 1. A possible model for the Moon during primary differentiation prior to 4 giga-years ago. This model was proposed in 1970 before detailed characterization of KREEP rocks. Major reworking of the outer part of the Moon would occur in the next giga-year, and the FETI (mare) basalts would appear in this period. The ANT group might consist of the "plagioclase-rich rock and basalts" plus further differentiates from the ferrobasalt. The KREEP group might arise from both the late "ferrobasalt" and remelting of the ANT group. The FETI basalts might result from remelting of cumulates of pyroxene and oxide minerals followed by complex fractional crystallization. Minor ultrabasic rocks might be cumulates from the upper mantle and crust. From Smith *et al* (1970).

#### General statement on lunar rock types

The nomenclature of the lunar rocks is in a shambles. Unfortunately many lunar rocks are actually metamorphosed breccias or remelted regolith, and some names are given on the basis of bulk chemistry rather than the petrology and mineralogy. Furthermore, the chemistry of the minerals is biased towards alkali-poor compositions and reduced states of transition metals with respect to terrestrial analogs, thereby causing problems when terrestrial names are applied to lunar rocks.

The following nomenclature and description of the major rock types are chosen to maximize initial access to the literature:

**ANT suite:** (name from Anorthositic-Noritic-Troctolitic; Keil *et al*, 1972) comprised mainly of calcic plagioclase, orthopyroxene, and olivine; ranging from anorthositic to noritic and troctolitic in bulk composition. Mostly occurs as metamorphosed breccias (often monomict), fragments, or glasses. Commonly assigned to crust. Believed to result from early differentiation with gravity separation of crystals and liquid. Terms like gabbro, anorthositic gabbro, and highland basalt are also used.

**FETI suite:** (new name referring to high Fe and Ti content) comprised of basalts rich in Fe and Ti; dominated by zoned pyroxenes (mostly augitic), calcic plagioclase, and ilmenite. Olivine may or may not occur. The final residuum contains several rare minerals and has a granitic component. Mostly occurs as rock fragments, but some glasses occur. Interpreted as the result of late lava flows in mare basins, probably mostly from the tops of lava columns several kilometers thick. Origin controversial but perhaps from remelting of cumulates rich in pyroxenes and opaque minerals, modified by near-surface differentiation in lava suites. Usually called mare basalt in literature.

**KREEP suite:** (name is acronym given by Hubbard *et al*, 1971a) a description introduced for basaltic compositions rich in K, REE, P, Zr, Ba, U, and Th. Mostly occurs as glasses and meta-breccias but a few crystalline rocks with basaltic texture occur. Dominated by plagioclase, low-Ca pyroxene and minerals such as apatite and zircon which contain the above characteristic elements. Origin controversial but perhaps results from either liquid produced at the crust-mantle interface during primary differentiation, or liquid from partial melting of ANT crustal rocks, or both. Other terms including high-alumina basalt are also used.

There are some problems with this three-fold nomenclature: (1) There is evidence of both low- and high-K anorthosites (*e.g.*, Hubbard *et al.*, 1971b); perhaps the former were produced by flotation of plagioclase during formation of the crust, and the latter from crystal-liquid differentiation of a K-rich liquid produced by partial melting of the crust; if so, the former might be assigned to ANT, and the latter to KREEP. (2) Some rocks such as 14310 almost certainly were produced by remelting of regolith (*e.g.*, Dence and Plant, 1972), and therefore have a bulk composition derived from many components including meteoritic infall (Morgan *et al*, 1972); many breccias show metamorphic tex-

tures (*e.g.*, Anderson *et al*, 1972; Chao, Minkin, and Best, 1972; Warner, 1972), and it is not always obvious what rocks and minerals composed the original breccia. (3) The applicability of the terms high-alumina basalt and very high-alumina basalt (*e.g.*, Bansal *et al*, 1973) with respect to other rock descriptions is not fully clear at the moment (see later); whether such rocks represent a distinct igneous suite, or whether they are hybrids formed by melting of regolith, or both, is unclear.

On the whole the above three-fold grouping covers many of the lunar rocks, correlates fairly well with the chemistry of the component minerals, and perhaps also correlates with chronological development of lunar rocks. It certainly allows a preliminary examination of the petrogenetic significance of mineralogical properties.

The nature and extent of the minor rock types is rather uncertain. Crystal-liquid differentiation of basaltic compositions leaves a final immiscible liquid with granitic affinity (*e.g.*, Roedder and Weiblen, 1970). Minor glassy or crystalline representatives were found in the lunar samples, but whether large rock bodies of granitic composition occur is uncertain. Grains of olivine and pyroxene with very Mg-rich compositions occur as a minor constituent in all the lunar soils (see many papers), and spinel allivite and troctolite samples (*e.g.*, Agrell *et al*, 1973; Prinz *et al*, 1973a), a peridotite clast (Anderson, 1973) and ultrabasic fragments (*e.g.*, Steele and Smith, 1972) have been described. All these materials are more Mg-rich than equivalents from the broad ANT suite. A possible source is the upper mantle, but crustal processes or accretion must be considered. Rare fragments of iron meteorites have been found with characteristic textures, and other iron specimens are believed to represent melted or metamorphosed meteorites on chemical evidence. Contributions of stony meteorites to the lunar fines have been recognized from bulk chemistry (*e.g.*, Ganapathy *et al*, 1970), and an enstatite chondrite has been found (Haggerty, 1972a).

#### *Types of Lunar Minerals*

The major minerals to be described in detail later are:

Pyroxene	(Mg, Ca, Fe, Al, Ti, Cr, <i>etc</i> ) (Si, <i>etc</i> )O <sub>3</sub> . Very low in Na and K.
Feldspar	Mostly anorthite and bytownite, but rare K, Ba-feldspar in residua.

Olivine	Mostly Mg-rich but rare fayalite in residua. Divalent Cr.
Spinel	~ MgAl <sub>2</sub> O <sub>4</sub> in Mg-rich rocks. Chromite zoned to ulvöspinel in FETI basalts.
Pseudobrookite	Armalcolite group with divalent iron. Low Cr and Zr in FETI basalts and high Cr and Zr in metamorphosed Mg-rich rocks.
Silica	Tridymite, cristobalite, and quartz.
Fe-rich	Iron, troilite, and ilmenite occur, especially in FETI basalts.
Phosphates	Apatite and whitlockite, especially common in KREEP rocks. High in REE, Cl, and F.
Zr-minerals	Zircon and baddeleyite typical of KREEP rocks; also in residua of FETI basalts.

Minor silicate minerals are: pyroxferroite (analog of pyroxmangite, common in residua of FETI basalts; Chao *et al.*, 1970; Burnham, 1971), amphiboles (single occurrences of alumino-tschermakite (Dence *et al.*, 1971), and magnesio-arfvedsonite-richterite (Gay, Bancroft, and Bown, 1970) in FETI basalts; high in halogens), garnet (almandine-rich grains in a FETI basalt; Traill, Plant, and Douglas, 1970), tranquillityite (residua of basalts; Lovering *et al.*, 1971), melilite? (uniaxial grains in fines, no X-ray or chemical data; Masson *et al.*, 1972), phyllosilicates?? (in fines, probably terrestrial contaminants; Drever *et al.*, 1970), sphene?? (perhaps in devitrified spherule, tentative X-ray powder data; Gay, Bancroft, and Bown, 1970).

Minor sulfide minerals are: mackinawite, pentlandite, cubanite, chalcopyrite (all associated with troilite at margins or as inclusions consistent with exsolution or inversion; optical and chemical identification but no X-ray data; *e.g.*, Taylor and Williams, 1973), sphalerite (*e.g.*, El Goresy, Taylor, and Ramdohr, 1973).

Minor oxide minerals are: rutile (associated with ilmenite as lamellae and inclusions indicative of exsolution, *e.g.*, Haggerty, 1972b; as distinct grains in a peridotite, Anderson, 1973; and as blue grains in soils, Jedwab, 1973), corundum (in fines as aggregates, Kleinmann and Ramdohr, 1971; and as large crystal twinned on (0001), Christophe-Michel-Levy *et al.*, 1973; vapor deposit?, meteoritic? or terrestrial contaminant?), hematite? (lamellae in ilmenite, and associated with goethite? in "rusty"

rocks, *e.g.* Taylor, Mao, and Bell, 1973), and magnetite? (in "rusty" rocks).

Hydroxylated mineral: "rusty" areas on some rocks contain goethite? or another iron oxide hydroxide (Agrell *et al.*, 1972), perhaps with hematite and magnetite; presence of Cl suggests possibility of terrestrial oxidation of lawrencite, originally derived from cometary or meteoritic contamination on the Moon (El Goresy *et al.*, 1973; Taylor, Mao, and Bell, 1973), but lead isotope data suggest that the material is indigenous to the Moon (Nunes and Tatsumoto, 1973).

Minor minerals, probably largely from iron meteorites, are: schreibersite, cohenite, and niningerite.

The nature of the lunar mineral variously compared with terrestrial zirconolite or zirkelite is controversial, and X-ray structural data are needed to provide a control for assignment of atoms: either (Ca, Fe, *etc*) (Zr, *etc*)<sub>2</sub>O<sub>7</sub> for zirconolite or 1:1:5 for zirkelite (Wark *et al.*, 1973; Busche *et al.*, 1972; Peckett, Phillips, and Brown, 1972; Brown *et al.*, 1972). Other Zr, Ti-rich minerals may occur (*e.g.*, Zl: Haggerty, 1972b).

Minor metallic minerals are: copper (tiny grains near Fe metal, ilmenite, or troilite), brass (variable composition extending outside terrestrial range), tin (embedded in Fe metal), and indium (contaminant from rock box).

Aragonite (Gay, Bancroft, and Bown, 1970), SiC (Jedwab, 1973), and graphite may be contaminants.

#### *Important Aspects of Feldspars*

In this and succeeding sections, some aspects of the major mineral groups important for understanding the genesis of lunar rocks and minerals are outlined.

The great majority of lunar feldspars are calcic plagioclases. K,Ba-feldspars crystallize in the residua of FETI basalts and occur in KREEP basalts; they may occur with silica minerals as a granitic rock type (*e.g.*, fragment of hedenbergite granophyre, Mason *et al.*, 1971). Sodic plagioclases are very rare and may result from minor meteoritic contamination.

The plagioclases in the FETI basalts range from sector-zoned hollow tubes to anhedral grains intergrown with pyroxene. Plagioclases from ANT rocks usually show textures ranging from fine-grained "equilibrium" mosaics to irregular shock textures; probably most textures result from one or more episodes of metamorphism (both thermal and shock types) following an earlier igneous stage.

Electron microprobe analyses of ANT plagioclase are consistent with the  $MT_4O_8$  formula, but interpretation of analyses of FETI plagioclase is unclear. The location of the Mg and Fe atoms is uncertain, and the closest fit to an  $MT_4O_8$  formula is obtained if these elements are mostly in the tetrahedral sites. Weill *et al* (1971) outlined the problem, and Wenk and Wilde (1973) coordinated the available data. Mössbauer and electron-spin resonance data show that a small part of the iron is ferric while most is ferrous, and that the iron enters two structural sites, one of which is tetrahedral (*e.g.*, Schürmann and Hafner, 1972a; Hafner, Niebuhr, and Zeira, 1973); see also optical absorption data (Bell and Mao, 1973).

The composition of the calcic plagioclases correlates with the host rock. Figure 2 is a plot of wt percent Fe *vs* mole percent Ab inferred from the Na content. The plagioclases from the FETI basalts have the highest Fe contents, and there is a definite tendency for the Fe content to increase from about 0.5 wt percent at  $Ab_5$  to 1 wt percent near  $Ab_{12}$ . The plagioclases from the KREEP basalts tend to be more sodic, mostly occurring in the range from  $Ab_{10}$  to  $Ab_{25}$ ; again the Fe content correlates with Ab, but the concentration is lower than for FETI basalts. The third main group of plagioclases, that from ANT rocks, tends to be highly calcic with most compositions near  $Ab_5$ . The composition ranges of ANT and

KREEP plagioclases appear to overlap. The Mg and K contents appear to be distinctive for the three types of plagioclase, but the data are probably confused by relatively low accuracy of electron microprobe analyses for these elements. Smith (1971) noted that the composition bands seemed to diverge from a composition near  $Ab_3$ ; K 0.03, Fe 0.1, Mg 0.01 wt percent, and this turned out to be a common composition for plagioclase in anorthosites (*e.g.*, Steele and Smith, 1971). Plagioclases from a peridotite and a pink-spinel troctolite fall near the main concentration range for ANT rocks. As an illustration that the situation is not simple, data points are shown in Figure 2 for a feldspathic basalt with igneous texture but Fe content even lower than for KREEP basalts (Steele and Smith, 1973).

The well-known preference of Na for liquid over coexisting plagioclase (*e.g.*, Kudo and Weill, 1970) allows the Na content of lunar plagioclase to be used as a test of differentiation models. The low Ab content of ANT plagioclase is consistent with their origin as cumulates from liquids which later produced KREEP plagioclase (note the very calcic plagioclase in the pink-spinel troctolite); alternatively, partial melting of ANT rocks could yield liquids which give rise to KREEP plagioclase. If FETI basalts result from partial melting of a plagioclase-bearing source material, that plagioclase would be extremely low in Ab content, assuming that equilibrium occurred.

Unfortunately there are few laboratory data on the partition of Fe, Mg, K, *etc* between plagioclase and basaltic liquids, though one might expect that the substitution of Mg and Fe in plagioclase would decrease with temperature, and that the Mg/Fe ratio will depend both on the oxidation state and the Mg/Fe ratio of the coexisting liquid. Green *et al* (1972) and Akella and Boyd (1972) reported 0.3–0.6 MgO and 0.5–1.0 wt percent FeO in plagioclases synthesized in the presence of liquid from lunar basaltic compositions, which values are comparable with those observed in FETI basalts. Systematic data are badly needed to allow use of these elements for testing differentiation models. The *mg* ratio of the plagioclase (where *mg* = atomic Mg/(Mg + Fe)) may prove valuable in giving an indication of the parent liquid (*e.g.*, Walker *et al*, 1973); sparse data of low accuracy suggest that *mg* tends to be higher for KREEP than for FETI plagioclase, as expected by comparison with the data for pyroxenes. Crawford (1973) found that *mg* of zoned FETI plagioclase was the same as

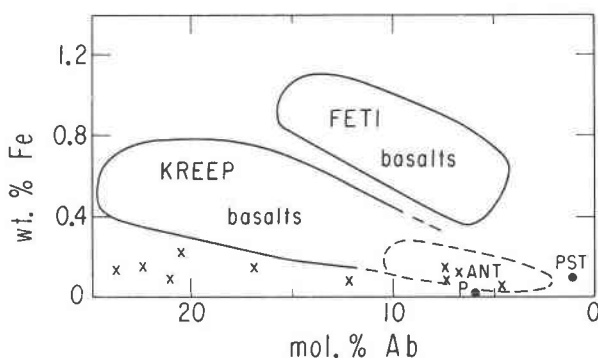


FIG. 2. Fe *vs* Na content of lunar plagioclases. Schematic drawing showing principal ranges for FETI basalts, KREEP basalts, and ANT materials. P shows the plagioclase in peridotite clast 15445,10 (Anderson, 1973) and PST that for pink-spinel troctolite (Prinz *et al*, 1973a). The ranges for plagioclases from KREEP and ANT rocks probably overlap. The crosses show data for 67747 feldspathic basalt which contains large poikilitic olivines enclosing feldspar laths and intergranular pyroxenes (Steele and Smith, 1973). Data from many sources. Data for Mg, Mg/Fe, and K to be published elsewhere.

for pyroxene crystallizing simultaneously. Detailed measurements of the alkali and alkaline-earth elements are badly needed as tests for differentiation models; unfortunately the concentrations of these elements, except for Na and K, are too low for accurate measurement with an electron microprobe, but hopefully detailed ion-microprobe data will be forthcoming (see Andersen, Hinthorne, and Fredriksson, 1970, for indicative data).

Interpretation of the minor element content of plagioclases from ANT rocks, metamorphosed breccias, and fines must take into account the effect of solid-state reactions which change the content of minor and trace elements. Steele and Smith (1974) pointed out that the pyroxene and silica minerals occurring as inclusions inside ANT plagioclase, and as grains at plagioclase boundaries (*e.g.*, James, 1972), may result from solid-state expulsion from plagioclase which originally showed high contents of Fe and Mg, perhaps comparable to those for FETI plagioclase. They proposed that with falling temperature the component  $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_3\text{O}_8$  broke down into pyroxene  $\text{Ca}(\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$  and silica  $\text{SiO}_2$ . If this is true, the pyroxenes in some lunar anorthosites consist partly or perhaps wholly of material exsolved from plagioclase. Nevertheless the *mg* content of the pyroxene may provide a guide to that of the liquid from which the plagioclase crystallized. The best evidence for exsolution is that of Lally *et al* (1972) who obtained electron micrographs of pyroxene grains lying in twin boundaries of plagioclase. Brett *et al* (1973), and others, reported tiny oriented rods of  $\text{Fe}_{99}\text{Ni}_{1}$  metal in plagioclase grains from Luna 20, and preferred sub-solidus reduction as the explanation.

The europium anomaly has figured in many geochemical discussions of lunar rocks. Unfortunately all accurate data obtained to date are on bulk samples using neutron activation or mass spectrometric analyses. Under reducing conditions, europium becomes divalent, whereas its neighboring rare earths remain trivalent. In the divalent state, europium tends to enter the feldspar structure preferentially, thus giving a positive anomaly in a feldspar and a negative anomaly in a coexisting basaltic liquid. Unfortunately, the europium anomaly depends in a complex way on the temperature, oxygen fugacity, and bulk composition (*e.g.*, Weill and Drake, 1973) and careful study will be needed before quantitative evaluation of lunar rocks can be made. Nevertheless it seems reasonably certain

that the europium anomalies in lunar rocks can be ascribed largely to plagioclase-liquid fractionation.

There are many electron-diffraction and X-ray diffraction studies of lunar plagioclases which show complex domain textures indicative of exsolution and order-disorder. Unfortunately, the phenomena depend in a complex way on the bulk chemical composition and on the crystallization and post-crystallization history. At the moment the data are of more value in providing evidence on the phase relations of plagioclase in general than on the specific problems of lunar mineralogy.

It is quite certain that lunar plagioclase can provide many clues to the discerning lunar detective.

### Important Aspects of Olivines

The *mg* value of lunar olivines provides a valuable guide to crystal-liquid differentiation. Figure 3 summarizes the principal ranges of *mg* for lunar olivines together with corresponding data for pyroxenes (see next section).

The ANT group of rocks carries olivines mostly in the range of  $mg = 0.85 - 0.65$  whereas the FETI group carries olivines ranging mostly from 0.7 to 0.3 with rare fayalites in the final residua.

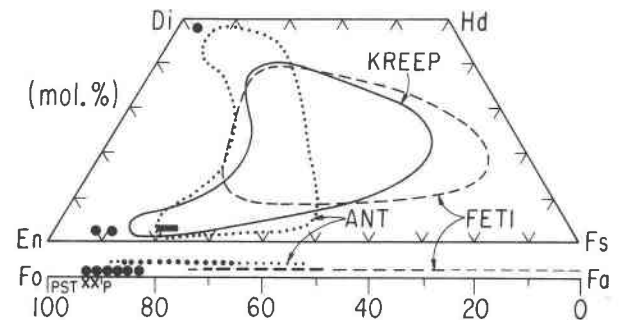


FIG. 3. Schematic drawing of major-element concentrations of lunar olivine and pyroxene. Note that considerable zoning occurs and that the ranges cover the principal but not the total ranges of composition. The pyroxenes of FETI basalts show final zoning to pyroxferroite or Fe-rich pyroxenes, while the olivines zone into fayalite. Both KREEP and FETI pyroxenes give compositions which tend to concentrate at the Mg-rich side of the ranges. Data from many sources. The data for ultrabasic fragments (filled circles) are from Steele and Smith (1972). P and PST refer to peridotite and pink-spinel trocolite (see Fig. 2). The rectangle shows the composition range of large crystals of orthopyroxene in Apollo 17 fines which may result from a true norite with coarse texture: veins of diopside have the same composition as the filled circle (Irving *et al*, 1974).

Ultrabasic rocks and fragments carry olivines with  $mg = 0.93 - 0.83$ ; seven compositions found by Steele and Smith (1972) for clasts and fragments are shown in Figure 3 along with that of 0.91 for the peridotite clast of Anderson (1973) and of 0.92 for the pink-spinel troctolite of Prinz *et al* (1973a). Other data in the literature for fragments, clasts, and single grains fall in the same range. Olivine is rare or absent in KREEP rocks. Figure 4 is a simplified version of Figure 6 of Steele and Smith (1973) which shows data on  $mg$  of olivines, Ca-poor pyroxenes, and basaltic liquids. Roeder and Emslie (1970) determined the fractionation of Mg between olivine and terrestrial basaltic liquids, and Medaris (1969) evaluated the fractionation of Mg between olivine and low-Ca pyroxene. Electron microprobe analyses of synthetic lunar samples yield a single band displaced to the left of the one for terrestrial samples, and there is no clear distinction between olivines and low-Ca pyroxenes. At liquidus temperatures,  $mg$  is similar for low-Ca and high-Ca pyroxene, but at low temperature,  $mg$  is higher for the low-Ca pyroxene. In general, for crystal-liquid fractionation on the Moon this diagram provides a good test of differentiation models, irrespective of the precise details of temperature and pressure.

Consider the olivines of the ultrabasic group. If these are phenocrysts which accumulated from a basaltic liquid, that liquid must have  $mg$  ranging from about 0.6 to 0.8. This is actually the range

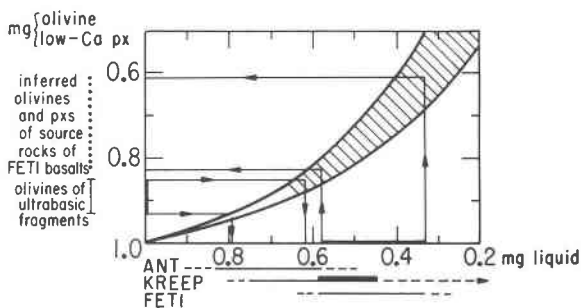


FIG. 4. Relation between  $mg$  for coexisting liquid and either olivine or low-Ca pyroxene. The shaded area shows the range of synthetic data for lunar basaltic compositions obtained by various workers including Biggar *et al* (1971), Green *et al* (1971, 1972) and Kushiro (1972). The ranges below the abscissa show the bulk composition for the three major rock types. For KREEP-type material, the  $mg$  value drops to zero for extremely-differentiated residua. See text for further explanation. [Modified from Steele and Smith (1973, Fig. 6)].

of  $mg$  for the bulk composition of most ANT rocks. If the FETI basalts result from partial melting of a rock dominated by olivines and pyroxenes, the  $mg$  range of the latter should be about 0.6 to 0.8. Partial melting of the ANT suite should give liquids with  $mg$  mostly from 0.4 to 0.6, which overlaps the ranges for the bulk values of FETI and KREEP basalts.

The minor elements in olivines vary considerably, and have petrogenetic value. Smith (1971) cautioned about problems arising from inaccurate electron-microprobe analyses, especially for secondary fluorescence of transition metals. Review of the extensive data in the literature shows the following:

(1) Mn correlates positively with Fe and has no petrogenetic significance (indeed major deviations from the correlation probably indicate an incorrect analysis).

(2) Ca tends to increase with Fa content ranging from 0.1–0.4 wt percent CaO near forsterite to 0.4–0.9 wt percent for the rare fayalites in residua of FETI basalts (Fig. 5). The ranges for the FETI and ANT groups overlap, but the latter tend to be richer in Mg and poorer in Ca. Note that many specimens in the ANT group are breccias, often recrystallized. Simkin and Smith (1970) found that the Ca-content provides a distinction between terrestrial olivines from plutonic rocks and those from volcanic or hypabyssal rocks. In Figure 5 all the olivines from FETI basalts lie in the region for volcanic and hypabyssal terrestrial olivines; furthermore, the dominant range of FETI olivines is close to the data points found by several investigators for olivines synthesized in the presence of liquid from lunar basaltic compositions. The ANT group overlaps both the plutonic and the volcanic-hypabyssal ranges suggesting that this group derives both from volcanic and plutonic rocks. Smith (1971) noted a distinction between a high-Ca and a low-Ca group on the basis of just Apollo 11 and 12 data, but examination of all available data shows that there is a continuous gradation—*e.g.*, the data by Prinz *et al* (1973b) for ANT fragments in the Luna 20 sample. The effect of metamorphism on the Ca content of olivine has not been quantified so far, but available data on diffusion rates (*e.g.*, Buening and Buseck, 1973) suggest that metamorphism in a thick ejecta blanket may cause significant migration of Ca from the olivine. Hence a low Ca content may indicate either a plutonic origin, or metamorphism, or both. The possibility



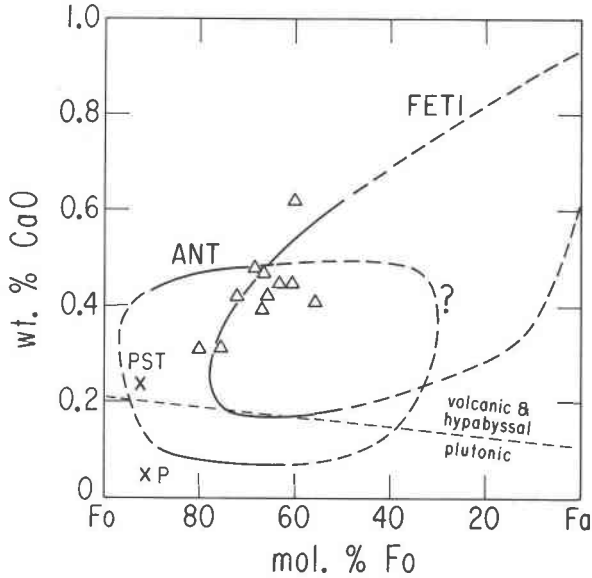


FIG. 5. Relation between wt percent CaO and mole percent Fo for lunar olivines. The two ringed areas show the ranges of electron microprobe analyses for ANT and FETI olivines. Most specimens fall in the regions of Fo marked by the continuous lines. P and PST stand for a peridotite and a pink-spinel troctolite (see Fig. 3). The dashed line marks the boundary between terrestrial olivines from plutonic vs volcanic and hypabyssal rocks. The triangles show olivines crystallized from liquids of lunar rock compositions (Biggar *et al*, 1971; Green *et al*, 1971, 1972; Kushiro, 1972).

of metastable crystallization with interaction between olivine and other Ca-bearing minerals must be evaluated; furthermore the bulk Ca content of the host rock must be considered. Butler (1972) gave detailed data on the zoning trends of four FETI basalts, and found a correlation of Ca content with texture indicating the effect of temperature of crystallization or of cooling rate.

(3) Cr tends to correlate with Mg, but may also correlate with the Cr content of the host liquid and more importantly with the oxidation state. In terrestrial olivines, the Cr content is undetectable by normal electron microprobe methods presumably because the Cr is trivalent and is not accepted easily by the olivine structure. In lunar olivines, the Cr content may rise to 0.n wt percent, presumably because divalent Cr is similar to  $Mg^{2+}$  and is accepted by the olivine structure. Haggerty *et al* (1970) reported optical absorption bands characteristic of  $Cr^{2+}$ , but not of  $Cr^{3+}$ , in olivine from a FETI basalt, but no comprehensive study of lunar olivines has been reported. Figure 6 shows the ranges for lunar olivines. The band for FETI olivines cor-

relates nicely with data obtained by several workers for olivines synthesized from melts of lunar basaltic composition. The band for ANT olivines is displaced to higher Mg values and lower Cr concentrations. Particularly noticeable are the low Cr concentrations for the peridotite and pink-spinel troctolite. Currently there is no definitive explanation for the wide range of Cr-contents (when normalized for the Mg correlation). A simple explanation might be that outgassing of the Moon resulted in reduction of  $Cr^{3+}$  to  $Cr^{2+}$ . Alternatively one might invoke effects from the bulk composition of the rock, from the temperature of equilibration, and from the effects of simultaneous crystallization of minerals such as spinel and pyroxene (*e.g.*, Butler, 1973). Dodd (1973) reported Cr contents in olivines from the Sharps (H-3) chondrite. These occupy the range from 0.02–0.2 wt percent  $Cr_2O_3$  and 100–70 mole percent Fo, without any correlation between Mg and Cr. Dodd found a weak correlation between Cr and Al, and favored the occurrence of some of the Cr as trivalent with a coupled substitution of  $Cr^{3+} + Al^{3+} = (Mg,Fe)^{2+} + Si^{4+}$ .

(4) Al is a puzzle. Accurate analysis of Al by electron microprobe methods is difficult because

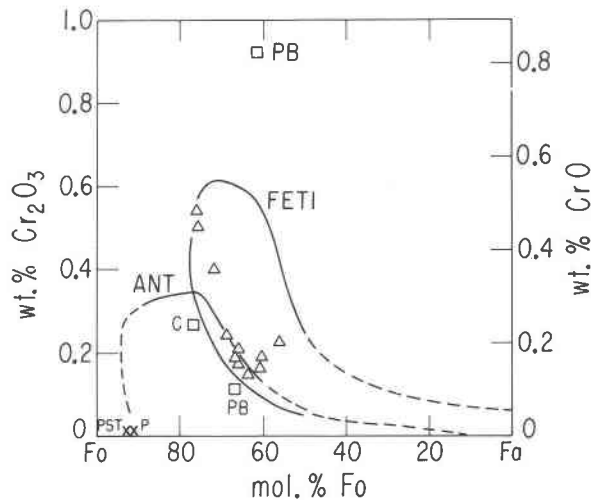


FIG. 6. Relation between wt percent  $Cr_2O_3$  (or CrO) and mole percent Fo for lunar olivines. The two ringed areas show the ranges of electron microprobe analyses for ANT and FETI olivines. The majority of the specimens fall in the regions of Fo marked by the continuous lines. P and PST stand for a peridotite and a pink-spinel troctolite (see Fig. 3). The triangles show synthetic olivines crystallized from liquids or lunar rock compositions (Biggar *et al*, 1971, Green *et al*, 1971, 1972; Kushiro, 1972). PB and C stand for olivine from two picritic basalts and a clast (Gay *et al*, 1972).

of the non-linear background. Gay, Bown, and Muir (1972) reported curved threads of tiny beads of spinel from a clast (C) and a picrite basalt xenolith (PB) in breccia 14321 (see Fig. 6 for Cr content). The Al contents (Fig. 7) of the olivines (1.12 wt percent in C, 0.38 and 0.19 in PB) are unusually high, and should be much greater than any possible experimental error. Simkin and Smith (1970) found no Al at the 0.01 wt percent level in terrestrial olivines, but more recent analyses by several investigators show 0.0n wt percent. Dodd (1973) reports up to 0.07 wt percent  $\text{Al}_2\text{O}_3$  in olivines from the Sharps chondrite. Figure 7 summarizes the data for olivines from FETI basalts and ANT materials. Most of them fall below 0.2 wt percent but a few are higher. The synthetic olivine synthesized by Kushiro *et al* (1971) at 10 kbar and 1290°C has 0.07 wt percent  $\text{Al}_2\text{O}_3$  which is near the average for all the olivines from FETI basalts. Akella and Boyd (1972) found 0.04 and 0.43 wt percent  $\text{Al}_2\text{O}_3$  in olivines synthesized at 1100°C and 1 bar, and at 1350°C and 30 kbar. Perhaps the substitution of Al increases rapidly with temperatures over 1300°C. Attention is now focused

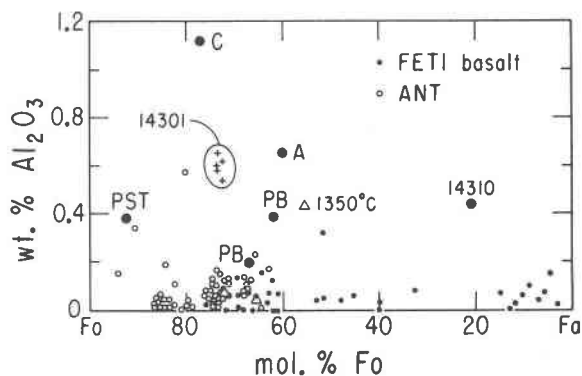


FIG. 7. Relation between wt percent  $\text{Al}_2\text{O}_3$  and mole percent Fo for some lunar olivines. A representative selection of data for FETI basalts and ANT materials is shown: note that the former data actually should concentrate near  $\text{Fo}_{50}$ - $\text{Fo}_{70}$ , but that there is a tendency for tables of analysis to quote unusual Fe-rich specimens. For the ANT specimens, some data points from the main cluster have been omitted. The unusual data are: C and PB, clast and picritic basalt in 14321 breccia (Gay, Bown, and Muir, 1972); PST and A, pink-spinel troctolite and anorthosite (Prinz *et al*, 1973a); 14301, microbreccia (Prinz *et al*, 1973c); 14310, basalt (Gancarz, Albee, and Chodos, 1971). The triangles are for olivines synthesized by Kushiro *et al* (1971) at 1290°C and 10 kbar ( $\text{Fo}_{72}$ ,  $\text{Al}_2\text{O}_3$  0.07 wt percent) and by Akella and Boyd (1972) at 1100°C and 1 bar ( $\text{Fo}_{66}$ , 0.04) and at 1350°C and 30 kbar ( $\text{Fo}_{66}$ , 0.43).

on olivines with high analyses of  $\text{Al}_2\text{O}_3$ . The brecciated anorthosite and pink-spinel troctolite fragment from Apollo 16 samples (Prinz *et al*, 1973a) are coarse-grained rocks for which there should be no difficulty in obtaining an accurate analysis of Al. The 14301 microbreccia is fine-grained but the analyses are very consistent (Prinz *et al*, 1973c). Only one datum is given for an olivine from the 14310 basalt. A few scattered analyses of ANT olivines lie above 0.2 wt percent  $\text{Al}_2\text{O}_3$ . At this time, there is no explanation for these very high analyses of  $\text{Al}_2\text{O}_3$ . The analysts have excellent reputations but the data should be rechecked in other laboratories. Perhaps some problems arise if samples are polished with alumina instead of preferred diamond.

(5) Ti analyses are mostly in the range below 0.1 wt percent, but it is possible that careful studies will show interesting features. Unquestionably, careful re-analysis of minor elements in olivines is desirable by electron microprobe methods together with data on trace elements (especially transition metals) by other techniques.

Other interesting features of olivines are: (1) the  $M_1$  octahedral site of some lunar olivines is favored by Fe over Mg atoms, suggesting prolonged annealing (see references in Brown and Prewitt, 1973); (2) late-stage reduction of fayalite yields Fe metal + silica mineral + glass (*e.g.*, El Goresy, Taylor, and Ramdohr, 1972); (3) occurrence of inclusions yields an estimate of the composition of the parent magma when homogenized (*e.g.*, Roedder and Weiblen, 1972).

#### Acknowledgments

Sincere thanks go to A. T. Anderson and I. M. Steele for their creative collaboration on lunar studies, to many other faculty members at Chicago for their advice, to I. Baltuska, R. Banovich, O. Draughn, T. Solberg, and others for meeting so many technical guidelines. An unpublished glossary of lunar minerals by J. W. Frondel was very helpful. Technical and financial help from the National Aeronautics and Space Administration is gratefully acknowledged; indeed, I have been amazed at the general competence of the Apollo program, and not surprised at the occasional incompetence when compared to problems in my own laboratory. Many thanks go to the National Science Foundation for providing basic support which allowed establishment of necessary equipment and know-how. I. M. Steele kindly reviewed the manuscript.

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