Delineation of the One Atmosphere Augite-Pigeonite Miscibility Gap for Pyroxenes from Lunar Basalt 12021

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Abstract

Single crystals of lunar clinopyroxene containing a second exsolved clinopyroxene have been investigated by stepwise heating experiments combined with X-ray diffraction techniques. Results show that the pigeonite-augite two-phase region narrows with increasing temperature, but is intersected by the solidus. Exsolution lamellae in pyroxenes from lunar basalt 12021 are homogenized into the host pyroxene at a temperature close to that of the solidus for a given pyroxene composition. The earliest pyroxenes in rock 12021 crystallized at 1175°C; pyroxene crystallization continued to approximately 960°C.

Introduction

Many pyroxenes from volcanic and intrusive rocks contain a second, exsolved pyroxene phase. This exsolution, submicroscopic in scale, is especially well developed in lunar basalts, which often contain primary host augite and pigeonite that have unmixed pigeonite and augite, respectively. Since pyroxenes crystallize over a wide range of temperatures in basaltic rocks, an understanding of pyroxene crystallization history is of use in understanding the crystallization history of the whole rocks. In order to further understand the subsolidus pyroxene phase relations as they pertain to volcanic rocks, we have undertaken heating experiments on pigeonites and augites from lunar basalt 12021. The experiments involved the stepwise heating and homogenization of clinopyroxenes of various compositions under controlled oxygen pressures. Although the lunar pyroxenes crystallized in a somewhat simpler system than most terrestrial pyroxenes (no water was present to lower the solidus nor was the oxygen fugacity high enough to produce significant amounts of ferric iron), we believe that significant information can be obtained from experiments on lunar pyroxenes which will be applicable to our understanding of the phase relations of terrestrial pyroxenes and their host rocks. The experiments delineate the augite-pigeonite miscibility gap for Al,Ti bearing clinopyroxene, the pyroxene phase relations at the beginning of melting, and place limitations on the temperatures at which pyroxenes of different compositions crystallized.

We have determined the phase relations of both clinopyroxenes and orthopyroxenes with compositions near to those of the pyroxene composition plane enstatite-diopside-hedenbergite-ferrosilite. This paper is the first of a series of studies detailing pyroxene phase relations. Work in progress treats the orthopyroxene=clinopyroxene (pigeonite) reaction (Ross, Huebner, N. L. Hickling), pyroxene phase diagram topology (Huebner and A. C. Turnock), and natural pyroxene melting relations (Huebner, Ross, and N. L. Hickling). Preliminary results of the present study have been reported by Ross et al (1971a,b).

The exact characterization of pyroxenes from lunar basalts is a difficult, complex, and time-consuming task, for often those phases are highly zoned both with respect to chemical composition and to structure type. Fortunately a number of investigators have thoroughly examined pyroxenes from basalt 12021, and we rely heavily on their work in describing the various clinopyroxenes used in our experiments. Particularly we refer the reader to the studies of Boyd and Smith (1971), Bence et al (1970, 1971), Papike et al (1971), Weill et al (1971), Klein et al (1971), Walter et al (1971), and Dence et al (1971).
Apollo 12 Basalts and Rock 12021

James and Wright (1972) distinguish three major groups of Apollo 12 basaltic rocks: olivine-pigeonite basalts, ilmenite-bearing basalts, and feldspathic basalts. The only olivine-free basalt of the first type is rock 12021, of immediate interest to us. This rock is porphyritic with phenocrysts of chrome spinel and pigeonite rimmed with augite in a variolitic groundmass consisting of plagioclase (An$_{50-90}$), augite, and minor pyroxferroite, silica, and oxides. The observed mode (in wt percent) obtained from our complete mineral separation is: silica, 2 percent; plagioclase (An$_{10-70}$), 27 percent; Mg-rich pigeonite (ave. Wo$_{10}$ En$_{30}$ Fs$_{50}$), 10 percent; Mg-rich augite (ave. Wo$_{30}$ En$_{45}$ Fs$_{25}$), 13 percent; ferro-pigeonite (ave. Wo$_{15}$ En$_{35}$ Fs$_{50}$), and moderate to high-iron ferro-augite (ave. Wo$_{26}$ En$_{32}$ Fs$_{50}$), 41 percent; pyroxferroite, 2 percent; and oxides, sulfides and metal, 5 percent.

Chemical analyses of the whole rock, as determined by four different groups of investigators, are given in Table 1. A calculated mode (James and Wright, 1972) based on analysis 3 given in Table 1 is: pyroxene (ave. Wo$_{21}$ En$_{38}$ Fs$_{40}$), 66.65 percent; plagioclase (ave. An$_{50}$), 27.02 percent; ilmenite, 4.66 percent; apatite, 0.03 percent; SiO$_2$, 1.08 percent; and glass, 0.61 percent. The excellent agreement for total pyroxene, plagioclase, and opaque phases indicates that little material was lost during the separation.

The sequence of appearance inferred from the textural relations of basalt 12021 is: (1) spinel and pigeonite, (2) Mg-rich augite, (3) plagioclase, ferropigeonite, intermediate ferro-augite, ilmenite, (4) iron-rich ferro-augite, pyroxferroite, and (5) silica.

### Table 1. Chemical Analyses of Apollo 12 Basalt 12021

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
<th>Sample 5</th>
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<td>P$_2$O$_5$</td>
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<tr>
<td>MnO</td>
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</tr>
<tr>
<td>S</td>
<td>--</td>
<td>&lt; 0.1</td>
<td>--</td>
<td>--</td>
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<tr>
<td>Cr$_2$O$_3$</td>
<td>--</td>
<td>0.26</td>
<td>0.40</td>
<td>0.38</td>
<td>0.41</td>
</tr>
<tr>
<td>Total</td>
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<td>100.0</td>
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</table>


The crystallization sequences for the major phases appearing in basalt 12021 have been investigated experimentally (Table 4) using whole-rock compositions by quenching from various temperatures below the temperature of complete melting. Green et al. (1971) observed olivine, pigeonite, and spinel crystallizing on the liquidus at 1155°C and 1 bar. The olivine (Fo$_{98}$) was consumed by reaction with liquid to precipitate pigeonite at approximately 1140°C. Plagioclase began to crystallize at 1130°C and coprecipitated with clinopyroxene. Ilmenite began to crystallize at 1090°C and the solidus is estimated to be 1050°C. The authors concluded that plagioclase could have begun to crystallize in rock 12021 before rapid crystallization of the groundmass. Biggar et al. (1971) obtained somewhat different results: At one bar with $f_{O_2} = 10^{12.5}$ bar the crystallization sequence was: spinel at temperatures $>$ 1180°C, followed by “protohypersthene” + pigeonite at 1180°C. Plagioclase + augite began to crystallize at 1142°C, then at 1128°C “protohypersthene” reacted to pigeonite. Ilmenite began crystallizing at 1097°C, and the solidus temperature is 1073°C. It is not clear what Biggar et al. (1971) mean by “protohypersthene.” It is apparently a pyroxene with parallel extinction and low CaO content—probably orthopyroxene. Experimental work (Ross and Huebner, unpublished data) suggests that Mg-rich orthopyroxenes could crystallize at temperatures as high as 1210°C and then react with the liquid in the temperature interval 1200–1170°C to form pigeonite close to the composition Wood$_{10}$En$_{46}$Fs$_{5}$.

It appears that most of the crystallization from the parent melt of rock 12021 took place at or near the lunar surface. The Mg-rich, Ca-poor pigeonite phenocrysts, however, could have formed at some depth prior to eruption. We do not believe that there is any persuasive evidence that these phenocrystals crystallized under high pressure (>5 kbar). The presence of large amounts of aluminum (as much as six wt percent) in the augite certainly cannot be due to high pressure for their zoning and textures indicate rapid growth from a fractionating liquid. We thus assume that all pyroxenes, except perhaps the Mg-rich, Ca-poor pigeonites, crystallized at low pressure (<1 kbar) and at oxygen pressures at or below the iron-wustite buffer curve.

Pyroxenes in Rock 12021—Previous Work

Extensive electron microprobe examinations of large pyroxene phenocrysts (as much as 2 cm in length) in polished thin sections of lunar rock 12021
have been made by Boyd and Smith (1971), Bence et al (1971), and Weill et al (1971). Generally the phenocryst pyroxenes are zoned so that they reflect the entire pyroxene crystallization history (Bence and Papike, 1972). Individual pyroxene grains from bulk pyroxene grain separates were analyzed by us and show the same range of composition.

The first pyroxene to crystallize forms the phenocryst cores and is Mg-rich pigeonite of nearly constant composition (Wo16En62Fs28). The pigeonite cores are always more calcium-rich at their outer boundaries, where they approach the composition Wo15En60Fs29. A discontinuous augite mantle usually surrounds the core and varies in composition from Wo22En47Fs21 to Wo30En46Fs30. A thin band of ferro-pigeonite of the approximate composition Wo15En45Fs35 may appear outside this augite mantle (Boyd and Smith, 1971, p. 442). Lastly, ferro-augite is usually found on the very exterior surfaces of the pyroxene phenocrysts and has compositions as iron-rich as Wo28En12Fs85 (Boyd and Smith, 1971, p. 442).

This pyroxene crystallization sequence (1) Mg-rich pigeonite; (2) Mg-rich augite and ferro-pigeonite; and (3) ferro-augite, is plotted diagrammatically in Figure 1 and is shown clearly in the pyroxene quadrilateral composition plots of Boyd and Smith (1971, Figs. 1, 2), Weill et al (1971, Figs. 3 a-d), and Bence et al (1971, Fig. 6). This chemical zoning is sometimes complicated by preferential crystal growth in certain crystallographic directions and development of different compositions behind crystallographically distinct growth faces (sector zoning). For a thorough discussion of sector zoning in lunar basalts similar to 12021, the reader is referred to the study of Hollister et al (1971).

In addition to the complex pyroxene zoning found with respect to Ca, Mg, and Fe, there is also complex zoning with respect to the minor components Al, Ti, and Cr. For our present purposes, however, we will ignore the effect on clinopyroxene subsolidus phase relations of Al2O3, TiO2, and Cr2O3 which, except in extraordinary cases, make up less than 5 wt percent of the pyroxene composition.

### Sample Separation and Characterization

Four pyroxene concentrates (A, B, C, and D) were prepared for our present study from rock chips 12021,29 and 12021,103 by crushing to pass 100 mesh, magnetic separation, centrifuging in heavy liquids, and hand picking. Some of the grains from the four fractions may be portions of the large phenocrysts and some are probably groundmass pyroxenes that crystallized contemporaneously with the portions of the phenocrysts that are chemically similar. The pyroxenes from each separate were characterized as to structural state and chemical composition with single crystal X-ray precession photographs, point chemical analyses on representative grains using the electron microprobe, and wet chemical analyses on portions of fractions A, B, and C (Table 2).

The “mode” of 10 to 15 crystals from each of the four separates was determined from the single...
crystal X-ray precession photographs of the h0l and 0kl reciprocal lattice nets. Usually 72 hour exposures with molybdenum unfiltered X-radiation were made of each net. Unit-cell parameters for the host and included phases were determined from measurement of the quartz calibrated films. The cell edges are generally accurate to $\pm 0.2$ percent and angles to $\pm 0.1^\circ$. The relative amounts of host, exsolved, and epitaxially overgrown pyroxenes were estimated by visually comparing the intensities of the h0l reflections having identical index, because the scale of exsolution is too fine to be detected by optical or microprobe methods. Such procedures were first used by Ross et al. (1969) in their study of exsolution in amphiboles. The h0l diffraction patterns of typical low calcium and high calcium Mg-rich pigeonites which compose fraction A are shown in Figure 2A and 2B. Typical Mg-rich augite (fraction B) and ferro-augite (fraction C) patterns are shown in Figure 2C and 2D.

Electron micrographs taken by E. J. Dwornik (U.S.G.S.) of our fraction A and B clinopyroxenes and those of Fernandez-Moran et al. (1971) of pyroxenes from a chip of the same lunar basalt show exsolution lamellae only a few hundred angstroms thick. With the optical microscope we observed only one grain with visible exsolution lamellae. Due to the very small size and generally even distribution of the exsolution lamellae as shown by these electron microscope studies, the chemical compositions as determined by the electron microprobe over a 2 to 5 micron region are believed to represent closely the average or bulk compositions which existed prior to exsolution.

Fraction A is composed entirely of Mg-rich pigeonite crystals 0.05 to 0.5 mm long, euhedral to subhedral, and often showing prominent \{110\} cleavage forms and occasionally \{100\} and \{010\} forms. There is very little visible evidence of any epitaxial overgrowth of the more reddish augite which is seen mantling the large pyroxene phenocrysts. Ninety-five percent or more of the pigeonites in fraction A have a low calcium content (Wo$_{8-11}$); a few grains were found to have a higher calcium content (Wo$_{11-15}$). The bulk grain compositions as determined by repeated electron probe analyses on

*Fig. 2. h0l precession photographs (MoK\(_\alpha\), unfiltered X-radiation) of (A) low-calcium Mg-rich pigeonite fraction A containing 10 percent augite oriented on (001) and 2 percent augite oriented on (100); (B) high-calcium, Mg-rich pigeonite from fraction A containing 35 percent augite on (001); (C) Mg-rich augite from fraction B containing 35 percent pigeonite on (001); and (D) ferro-augite containing 50 percent ferro-pigeonite on (001). The reciprocal axes a* and c* are designated as follows: P-pigeonite host, A-augite host, A(100)-augite on (100), A(001)-augite on (001), P(001)-pigeonite on (001).*
several low calcium grains varies slightly, from Wo$_{9}$ to 11, En$_{59}$ to 63, and Fs$_{28}$ to 31. The average composition represented by probe analyses of low-Ca grains is Wo$_{10}$En$_{59}$Fs$_{29}$ (Fig. 3). Wet chemical analysis of a 50-mg portion of fraction A gives the average composition of Wo$_{11.3}$En$_{59.9}$Fs$_{28.7}$ (Table 2) for the aggregate of fraction A pigeonites. These compositions are in good agreement with composition of core pigeonite in large phenocrysts analyzed by Boyd and Smith (1971), Weill et al (1971), and Bence et al (1971), which are, respectively, Wo$_{12}$En$_{61}$Fs$_{27}$, Wo$_{10}$En$_{62}$Fs$_{28}$, and Wo$_{6}$En$_{65}$Fs$_{28}$. Some of the low calcium pigeonite crystals examined by us zone to slightly more calcium-rich compositions, approaching an apparent limit of about Wo$_{15}$En$_{53}$Fs$_{30}$. The phenocryst cores also show this type of zoning, particularly in the “(100) sector” (Boyd and Smith, 1971, Fig. 2). The high-calcium pigeonite grains from fraction A have bulk compositions that are similar to that of the grain margins of the low calcium pigeonites.

X-ray precession photographs show that calcium-poor pigeonites contain 5 to 10 percent exsolved augite oriented on (001) and 1 to 2 percent exsolved augite oriented on (100). Calcium-rich pigeonite grains contain 20 to 35 percent augite oriented only on (001).

Electron probe analyses of the Mg-rich augite composing fraction B show that there is a preferential grouping in the compositional range Wo$_{29}$-38, En$_{42}$-49, and Fs$_{20}$-24, averaging Wo$_{33}$En$_{43}$Fs$_{29}$ (Fig. 3). Wet chemical analysis of a 50 mg portion of fraction B (Table 2) gives an average composition of Wo$_{30.4}$En$_{42.4}$Fs$_{26.6}$, suggesting that the selection of grains for probe analysis was somewhat biased to the more Mg-rich augites. Crystals from fraction B are equivalent to the augite, forming the inner part of the phenocrystal mantle in contact with the pigeonite core described by Boyd and Smith (1971, p. 442) as having the composition Wo$_{12}$En$_{43}$Fs$_{38}$. X-ray photographs show that the ferro-pigeonite host contains about 35 percent exsolved augite oriented on (001) and that the intermediate ferro-augite host invariably contains 50 percent exsolved ferro-pigeonite oriented on (001).

It is in the clinopyroxenes from fraction C that we see clear evidence of epitaxial overgrowth of one clinopyroxene on another. The best example of epitaxy is seen in grain 13D from fraction C which consists of ferro-pigeonite of average composition Wo$_{32}$En$_{46}$Fs$_{38}$ epitaxially overgrown by ferro-augite of average composition Wo$_{32}$En$_{46}$Fs$_{38}$. Eighteen electron probe analyses made over the polished surface of the grain clearly delineate the pigeonite-augite overgrowth boundary, shown as a dashed line in Figure 4A. These analyses are plotted within a portion of the pyroxene quadrilateral in Figure 4B.

The intensities of the X-ray reflections displayed in the precession photographs of grain 13D show that it was originally composed of approximately 80 percent host pigeonite and 20 percent host augite; the ratio of the two host phases (4.0) corresponding well (considering the difficulty in estimating the crystal “mode”) to the apparent ratio (2.9) obtained from multi-point electron probe analysis (Fig. 4A). The host pigeonite (a 9.714, b 8.937, c 5.232 Å, β 108.68°) now contains about 20 percent augite (a 9.709, b 8.937, c 5.266 Å, β 106.08°) exsolved on (001). The host augite (a 9.733, b

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*Only the most optically homogeneous, clear yellow augite grains were selected for microprobe analysis.*
Fig. 4A. Sketch of polished surface of grain 13D showing Wo mole percent values determined at 18 locations by microprobe analyses. Note the presence of a sharp boundary between pigeonite (Wo 11–15) and augite (Wo 21–24).

8.937, c 5.265A, β 105.98°) now contains about 50 percent pigeonite (a 9.741, b 8.937, c 5.229A, β 108.85°) exsolved on (001). The present mode of the grain is: host pigeonite—64 percent, host augite—10 percent, (001) pigeonite—10 percent, and (001) augite—16 percent.

Clinopyroxene grains in which there is an epitaxial overgrowth of a second clinopyroxene such as that described above have X-ray patterns that differ from those of clinopyroxenes in exsolution intergrowth. In composite grains the two clinopyroxenes, augite and pigeonite, share a common b-direction. However, neither the a nor the c axes of the two phases are parallel but deviate from one another by approximately 1°15', a value very close to Δβ/2, where Δβ = β_{pigeonite} − β_{augite}. The axial relationships within the (010) plane of such a pigeonite-augite overgrowth are shown diagrammatically in Figure 5. This type of overgrowth is easily distinguished in lunar pyroxenes from (001) and (100) exsolution intergrowths, for in exsolution intergrowth the a or the c axes of the co-existing pair are always parallel within a few minutes arc.

The densest fraction (D) is composed of very iron-rich augite and corresponds to Boyd and Smith's (1971, p. 442) "outer mantle" ferro-augite for which they report a composition of WO_{2.9} En_{12} F_s_{22} (Fig. 3). Augite grains in this fraction also invariably contain 50 percent pigeonite unmixed on (001). Epitaxial overgrowths of iron-rich pigeonite are generally not seen in grains from this fraction.

Fig. 4B. The same 18 points plotted on part of the pyroxene quadrilateral.

Experimental

X-ray examination

Small crystals, 0.1 to 0.3 mm in length, were selected from the various fractions for single crystal X-ray study. The crystals that gave well resolved and sharp X-ray reflections were then used in the

Fig. 5. Sketch of the axial relations within the common (010) planes of epitaxially related augite and pigeonite, crystal 13D. The sketch exaggerates the value of Δβ, actually Δβ = β_{pig} − β_{aug} = 1.25°.
subsequent heating experiments. Such crystals show restricted chemical zoning and very little epitaxial overgrowth of a second clinopyroxene as indicated by well defined temperatures of homogenization, by electron microprobe analysis, and by X-ray analysis. In all 24 crystals were used in these experiments.

After the initial X-ray examination the single crystals were heated, quenched, and again X-rayed. Complete unit-cell parameters for both host and exsolved phases were then obtained from h0l and 0kl photographs. The same crystals were then returned to the furnace for the next heating step and the whole process repeated for as many as nine heating cycles.

The change in the unit-cell parameters and the change in the relative X-ray intensities of the host and exsolved clinopyroxene describe the amount of exsolved phase that has dissolved back into the host at any particular heating temperature. The "beta" (β) angle is particularly sensitive to changes in the calcium content of both augite and pigeonite (Papike et al., 1971; Turnock et al., 1973) and is thus very useful in delineating a section of the augite-pigeonite solvus; however, absolute Wo values are not well known from the present b-β plots.

Heat treatment

Heating experiments were conducted in a vertically mounted, platinum wound quenching-style furnace. The temperature variation in the hot zone was ±1°C over 1 cm and ±3°C over 3 cm. Temperature was measured with Pt-PtRh thermocouples sheathed by enclosure with an oxygen "probe" (see below). The temperature range of interest is 900° to 1200°C; the thermocouples were calibrated against gold (melting point 1064.4°C, IPTS '68) enclosed in glass capsules suspended in the sample position. The uncertainty in bracketing the gold melting point was ±0.1°C. Thermocouple EMF was recorded continually on one channel of a two-pen strip chart recorder; with a 20 mV full-scale range, the uncertainty (expressed as temperature) due to reading of the chart is less than ±2°C. Recorded temperature variation during a run was commonly less than 3°C. Overall temperature uncertainty is estimated to be within ±7°C. Run data are summarized in Table 3.

Runs designated ESt (Table 3) were made in evacuated silica tubes at the beginning of this investigation. Pyroxene crystals were individually wrapped in Pt foil packets, and one or more packets were sealed in an evacuated silica tube. The tubes were hung in the hot zone of the furnace in air or CO₂. The air pressure in the vacuum line was monitored during the scaling of the tube; calculation of conditions within the tube at the run temperature indicates that the oxygen fugacity was such that magnetite would be the stable iron oxide phase. Quench crystals were examined for evidence of oxidation—oxides on surface of grain, dusty inclusions, or reddish discoloration—but none was found. However, precession photographs of crystals heated in evacuated silica tubes commonly showed a weak, spotty ring pattern of cristobalite. In the absence of direct evidence for oxidation, we believe the source of this cristobalite is the silica tube itself. In a successful effort to avoid silica contamination, we conducted later series of experiments in which crystals were exposed directly to a reducing furnace atmosphere. In none of these runs was cristobalite ever identified, only rare occurrences of tridymite (see crystals 2D and 26D in Table 3). This tridymite could conceivably be part of the lunar rock 12021 mesostasis that is attached to the crystals, yet overlooked during selection of the crystals.

Runs designated OFA in Table 3 were equilibrated with a furnace atmosphere of mixed CO₂ and H₂. At T, P, and equilibrium, the oxygen fugacity of this gas mixture is proportional to the initial mixing ratio $P_{CO_2}/P_{H_2}$ (Nafziger et al., 1971). The flow rates of CO₂ and H₂ were individually regulated by a gas apparatus train (Fig. 6) consisting of pressure regulators, capillaries, and valves. The gas pressure regulators maintain a constant pressure (1-3 psi) on the upstream side of a minute orifice (capillary or low flow rate valve). Gas is permitted to "leak" through the orifice. A flow rate may be changed by varying a gas pressure "head" or the size of an orifice; mixing ratios of 1000:1 can be obtained at low flow rates with a single mixing stage. The nominal flow rate was approximately six liters per hour checked with a ball-type flowmeter calibrated for air at NPT, yet used for the input or exhaust gases. Equivalent flow rates in the furnace (16 mm diameter) are 0.94 cm/sec (next to the oxygen cell) and 0.80 cm/sec above the oxygen cell. This range of flow rate corresponds well with the 0.9 cm/sec recommended by Darken and Gurry (1945) as being satisfactory for this kind of work. This simple and inexpensive equipment is sufficient to maintain a $P_{CO_2}/P_{H_2}$, so constant that the $f_o_2$ of a furnace atmosphere varies less than 0.1 log atm unit over a week's duration.
Oxygen fugacity was measured directly in the hot spot of the furnace, adjacent to the samples, using the calcia-stabilized zirconia electrolyte cell.

Reference Gas (O₂) Pt [(Zr₀.₈₅Ca₀.₁₅)O₂] Pt, Furnace Gas

Sato (1971) reviews the use of such devices. Elements of the cell are shown by Sato (1970, Fig. 1), but details of construction used here differ. Cell EMF was monitored continuously on the second channel of a two-pen recorder. The uncertainties of electrochemical oxygen fugacity determinations themselves have been discussed by Huebner and Sato (1970). The direct fₒ measurement obviates the uncertainties (mixing ratio, gas flow and reaction

Fig. 6. Simplified diagram of the gas train used to maintain a constant, predetermined oxygen fugacity in the furnace.
rates, impurities, leaks into or out of the gas stream) associated with the traditional calibrat ed gas-mixer methods. This apparatus will measure oxygen fugacity in the desired \( f_0 \) range, that is, several tenths of a log atm unit below that of the iron-wustite assemblage, to at least 0.05 log atm unit.

Most heating experiments lasted 15–200 hours; several experiments were much longer. A homogenization step was judged to be essentially completed during an overnight run because repeated heatings at the same temperature did not result in observed additional homogenization. At the termination of an experiment, a sample was removed from the furnace and quenched in mercury. The platinum foil sample container of an \textit{OFA} run (Table 3) was cooled to room temperature within one second after removal from the furnace hot zone; due to the thermal insulation afforded by silica tubing, \textit{EST} runs were quenched to room temperature more slowly, probably within several seconds. Experiments described below show that the rate of growth of exsolution lamellae is so slow that detectable back-reaction could not have occurred during any quench.

Single crystals for \textit{OFA} runs were wrapped in platinum foil, selected because of its high melting point and the fact that the outer electrode of the
Fig. 7A. Microprobe analyses of heated (but unmelted) crystals plot within the compositional range of the fractions A, B, or C from which the crystals were selected, indicating no appreciable loss of iron to the platinum foil containers. Analyses by A. E. Bence and by Huebner.

We chose an oxygen fugacity several tenths of a log atm unit of 16, below that of the assemblage Fe * Fe_{1-x}O in order to avoid decomposing the pyroxene (by oxidation or reduction) and to approximate the oxygen fugacity of the lunar environment in which the pyroxene single crystals formed. At the time we initiated the study, the crystallization history of the Apollo 12 samples had not been thoroughly investigated. However, many investigators had indicated the exceedingly reduced nature of the Apollo 11 basalts, and by analogy, we selected similarly reducing conditions. Subsequent work, including the discovery of nearly pure iron metal in both pyroxene and groundmass of basalt 12021 (Walter et al., 1971; Weill et al., 1971), attests to the reducing environment of crystallization for Apollo 12 basalts.

Results

Run conditions and data pertinent to phase characterizations are summarized in Table 3 and Figure 9. Heating experiments for each crystal are arranged (Table 3) top to bottom in the order in which the experiments were actually performed. Experiments in which we attempted to reverse the homogenization process are apparent because the temperature first increases, then decreases as listed in the table. Methods used to determine the parameters listed in Table 3 are described below.

Precession photographs of the h01 net of a typical Ca-rich pigeonite crystal from fraction A, taken before and after various heat treatments, are shown in Figure 8. The a* axes of host pigeonite and exsolved (001) augite move closer together (Δβ = β_{aug} - β_{pige} decreases) with increasing temperature, indicating that the calcium contents of the two phases approach one another. During melting, augite and pigeonite a* axes again separate, indicating increasing differences in the calcium content of the two phases. In addition to (001) augite, a small amount of augite oriented on (100) is present in some low-calcium fraction A pigeonites. We made no attempt to record the cell dimensions of this augite because of the weakness of the reflections and their early disappearance in the heating sequence.

The β angles of coexisting augite and pigeonite vary regularly with the temperature of a homogenization experiment. The β angle is dependent on the Wo content of pyroxene, but relatively independent of En/Fs (Turnock et al., 1973). Changes in β are a sensitive indicator of changes in the mole percent Wo of a pyroxene, but there is a relatively great uncertainty in assigning a specific percent Wo to a particular value of β, due to the lack of good standards. We have made an estimate by considering...
the β angles, bulk compositions, and proportions of phases in unheated grains, and the β angles at which these grains become homogenized, but at present the precision greatly exceeds the accuracy of the method. However, it is clear that with increasing temperature, Δβ decreases, corresponding to a narrowing of the augite-pigeonite miscibility gap.

The b of a clinopyroxene varies greatly with En/Fs, but is relatively insensitive to variations in Wo content except for very En-rich compositions (see Turnock et al., 1973). The b unit-cell parameter is also greatly dependent on Al content; thus care must be taken not to underestimate Fe content because of aluminum (J. J. Papike, personal communication). Differences in the b-dimensions of intergrown augite and pigeonite could not be distinguished on the X-ray precession photographs. Furthermore, b remained constant (within the uncertainty of measurement) until a crystal began to melt (Table 3), indicating constancy of Fe/Fe+Mg in the bulk grain, further confirmed by microprobe chemical analyses (Figs. 7A and 7B).

Measurement of the unit-cell parameters of augite or pigeonite lamellae in (001) orientation with respect to the host pigeonite or augite shows that the a-dimensions of host and exsolved phase are identical within the accuracy of measurement, whereas the c-dimensions vary from one another significantly. The reverse is true for clinopyroxene lamellae in (100) orientation; the a-dimensions of host and lamellae deviate significantly and the c-dimensions are nearly identical. These observations definitely indicate that the lattices of the host and exsolved phase are constrained to fit one another along either a or c. Since both the (100) and (001) lamellae

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*Fig. 8. h0l precession photographs (MoKα, unfiltered X-radiation) of Ca-rich pigeonite crystal 3R originally containing about 30 percent augite exsolved on (001). Photographs taken before heating and after heating to 950°, 1164°, 1211°, and 1274°C — a° and c° axes are designated as in Figure 2.*

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...Microprobe chemical analyses of partially melted ortho- and clinopyroxenes demonstrate that, when enough glass has formed to rim the crystals and wet the platinum foil, most of the iron is lost from the crystal and liquid.
have their b-axes oriented parallel to b of the host, the b-dimensions of host and lamellae must also be so constrained. This accounts for our inability to observe splitting of the (0k0) reflections in X-ray photographs of exsolved pyroxenes. If such a constraint exists, it would clearly indicate that the use of the b unit-cell edge to determine accurate En and Fs content is suspect. Thus, the En and Fs content of the exsolved phases, plotted as circles in Figure 10, are probably not reliable and may account for some of the odd tie-line orientations, particularly Nos. 4 and 5.

The subsolidus homogenization data is portrayed on T-β diagrams (Fig. 9) which also show the change of Wo content of co-existing augite and pigeonite as a function of temperature. The Wo, En, and Fs content of the bulk grain are known, but the exact content of these components in the host and exsolved phases, as explained above, cannot be ascertained quantitatively.

The melting relations depicted in Figure 9 are not at constant bulk composition because iron leaves the pyroxene and liquid and enters the platinum. The melting relations thus shown in the solidus portion of the diagrams are for the nearly iron-free pyroxene system.

The proportion of exsolved pyroxene, relative to the total amount of the pyroxene present, is an index of the degree to which the pyroxene has been homogenized. We consistently observed that the pyroxene crystals were essentially homogenized to a single-phase pyroxene crystal just below or at the solidus temperature. Above the solidus the homogenized augite grains partially melted to yield liquid plus more Ca-rich augite (as in Figs. 9B, C, D). However, for the Ca-rich pigeonites, augite reappeared during the melting process, after the original crystal has been homogenized (see Fig. 9A). This phenomenon occurs because these bulk compositions pass into the 3-phase region L+P+A with increasing temperature; a pyroxene phase diagram explaining this behavior is being prepared (Huebner and A. C. Turnock, unpublished data; see also Huebner and Ross, 1972).

We have made no attempt to report the degree to which a crystal has melted. Estimation of the percentage of glass is exceedingly difficult unless an ultra-thin section is made of the crystal. The nature of the melting process is being actively investigated by Huebner, Ross, and Hickling. At this time, it is only important to note evidence for first melting—tiny bubbles, and anastomosing tubules of glass. An "H" in Table 3 indicates that a crystal was intensively scrutinized for small amounts of glass, yet none was found. Melting is not observed until the liquid has coalesced into visible droplets at a temperature in excess of the actual temperature of first melting.

X-ray photographs of some augite grains which were homogenized or partially melted show the presence of two, sometimes more, augite lattices having significantly different β angles. This is noted in Table 3 (also see Fig. 9) as multiple entries of unit-cell dimensions at a single temperature of heat treatment. For example, at 1243°C, augite grain 1D (Fig. 9b) contains glass plus two crystallographically distinct augites having β angles of 106.77° and 106.08°. The presence of compositionally different augites within the same grain may be partly due to original compositional zoning where the part of the grain with higher iron content reacts at lower temperatures than does the Mg-rich portion of the grain. This is most often seen in the more highly zoned ferro-augites. Additional chemical zoning and disequilibrium conditions leading to the appearance of augites of different compositions may be caused by loss of iron from the grain to the platinum foil during the melting of pyroxene (Huebner and Ross, unpublished data).

The T-Wo sections at the temperatures of first melting, which are also the temperatures of homogenization, have been superimposed upon the pyroxene quadrilateral in Figure 10 by the addition of analytical data for En and Fs as determined by electron microprobe analysis of five homogenized clinopyroxene crystals plotted in Figure 7b. Approximate compositions for the other homogenized crystals and for the unmixed clinopyroxenes just before homogenization were determined, as previously mentioned, from the b unit-cell edge and the β
experiments on other crystals showed no apparent reversal of the homogenization process.

Discussion

Unmixing Process

Our experimental work shows that the lunar clinopyroxene host crystals redissolve the unmixed augite or pigeonite readily in the temperature range 800°C to 1200°C. All experimental runs of 19 hours or greater duration appear to have come to equilibrium. The laboratory demonstration of unmixing in these same pyroxenes has proven to be much more difficult than the demonstration of homogenization. In only a few runs did we observe a significant reversal of the mixing process. The apparently large difference in rates of mixing versus unmixing suggests that the reaction mechanisms of the two processes are different.

The preservation of the compositional zoning and delicate exsolution textures in the clinopyroxenes from basalt 12021 shows that no intergranular recrystallization took place. The exsolution must be entirely intragranular, dependent only on the original composition of the grain and on pressure, temperature, cooling rates, and possibly stress. Conceivably, trace amounts of small ions, particularly hydrogen, might have some effect on the exsolution rates. We know of no experiments on silicates which would enlighten us on this problem. Our experiments on unmixing would suggest, tentatively, that the pyroxenes in lunar basalt 12021 cooled to 800°C or less over a period of at least many weeks or months.

At temperatures not far below the homogenization temperature, host pigeonites and pigeonite lamellae within augites should, if equilibrium obtains, react to form orthopyroxene ("inverted pigeonite") plus augite (Ross and Huebner, unpublished data). Such a reaction did not occur, to our knowledge, in any unshocked lunar basalt nor do we know of any observation of pigeonite lamellae in terrestrial augite reacting to form orthopyroxene. "Inverted pigeonite" textures are relatively rare, and are usually seen only in slowly cooled intrusive rocks. The nature of the process of "inversion" of pigeonite to orthopyroxene remains unknown. It appears to involve intergranular recrystallization and thus the probable presence of a fluid phase in the rock.

Subsolidus Phase Relations

The data plotted in Figures 9 and 10 delineate a subsolidus miscibility gap between augite and pi-
geonite compositions that extends across much of the quadrilateral. The gap is asymmetric toward pigeonite; the pigeonite solvus is steeper than the augite solvus for relatively Mg-rich compositions. This asymmetry is in accord with observed pyroxene exsolution relations in lunar rock 12021: augite exsolves 25–50 percent pigeonite, whereas pigeonite exsolves only 20–35 percent augite.

The miscibility gap does not close because these lunar pyroxenes begin to melt before the crest of the solvus is reached. At the solidus, the width of the gap narrows with increasing Fe/Fe + Mg, from about 20 percent Wo at Fe/Fe + Mg = 0.30, to about 10 percent Wo at 0.85. We have found no evidence that the solidus passes over the crest of the solvus at one atmosphere pressure; the gap persists to the most iron-rich of pyroxenes. At any Fe/Fe + Mg value, the gap for lunar basalt 12021 is narrower than the pigeonite-augite gap for any known terrestrial rock, presumably a reflection of higher fO2 and alkalis in terrestrial magmas. At higher pressure (15–16 kbar) on a synthetic join En0.2Fs0.8-wollastonite Smith (1972) has found a symmetrical solvus with a crest at 915–950°C. The differences in shape and position are attributable to experimental error and differences in pressure and composition.

The melting temperatures observed in this study, 960°C–1175°C, are considerably lower than the temperatures found in phase-relation studies of synthetic pyroxene systems. Roedder (1965) found that the lowest liquidus temperature for synthetic (En–Fs–Hd–Di) quadrilateral compositions was 1160°C on the Hdi–Fs join, implying solidus temperatures no lower than 1160°C. Yoder et al. (1964) melted natural pyroxenes and pyroxene mixtures; they found solidus temperatures between those found by Roedder and those presented in this study. These differences may be due to the presence of minor additional components (Huebner and Turnock, unpublished data; Huebner, Ross, and Hickling, unpublished data; see also Huebner et al., 1972).

**Geothermometry**

Our work places constraints on the crystallization temperature range of lunar rock 12021 and similar rocks. Exsolution features develop from initially homogeneous pyroxenes; therefore, a pyroxene must have crystallized at a temperature equal to or exceeding its homogenization temperature. However, a pyroxene will crystallize from a natural magma at a temperature that is lower than the melting temperature of pyroxene alone. The homogenization and melting temperatures, which seem to be indistinguishable, suggest cotectic crystallization of the two pyroxenes in the original rock and provide an excellent estimate of the possible range of pyroxene crystallization temperature: 1175°C ± 15°C to 960°C ± 15°C. Since these pyroxenes crystallized throughout much of the crystallization process of lunar rock 12021, these temperatures also indicates the approximate range of crystallization for the bulk rock. Consideration of the textural relationships indicates that some of the spinel may have crystallized at temperatures higher than 1175°C; most pyroxferroite and all silica crystallized below 960°C. Our estimate of the temperature of initial pyroxene crystallization (Table 4) is in general agreement with the temperatures obtained from whole-rock crystallization and melting studies; however, we are

**Table 4. Crystallization Temperatures: Lunar Rock 12021 at 1 Atm.**
better able to define the lower temperature crystallization range (1100°–960°C), and we have shown that pyroxene crystallization continued to at least 960°C.

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