ages of iron-bearing minerals derived from the Mössbauer areas for 84-14 and 45-24; the assumptions and possible errors in these values will be discussed elsewhere. However, it is apparent that the iron content of 84-14 is much greater than that for 45-24, whereas 45-24 has appreciably more ilmenite, pyroxene, and olivine than 84-14.

Mössbauer spectra at 80°K of two pyroxene separates from 44-43 are shown in Fig. 2; the inner peaks in B are due to ilmenite. Fraction A (density 2.85 to 3.50) is ordered ($\text{area}_{\text{inner}}/\text{area}_{\text{total}} = 0.67$), whereas fraction B (density 3.70 to 3.90) is essentially disordered ($\text{area}_{\text{inner}}/\text{area}_{\text{total}} = 0.52$). This surprising result agrees with the optical, x-ray, and microprobe work reported here and elsewhere that this rock contains both a clinopyroxene (A) and a pyroxenoid (B) of the pyroxmangite type. For B, the line widths of the inner peaks are greater than those of the outer peaks (0.48 and 0.40 mm/sec, respectively), and the room-temperature areas are not consistent with those obtained at 80°K. Although this evidence could be interpreted as implying there are more than two cation sites with appreciably different Q.S. values, it could also be due to a lack of homogeneity caused by exsolution.

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Lunar Clinopyroxenes: Chemical Composition, Structural State, and Texture

Abstract. *Single-crystal x-ray diffraction, microprobe, optical and electron optical examinations of clinopyroxenes from Apollo 11 lunar samples 10003, 10047, 10050, and 10084 show that generally the crystals are composed of (001) augite-pigeonite intergrowths in varying ratios. Transmission electron micrographs reveal abundant exsolution lamellae, many only 60 Å thick. In addition to the phase inhomogeneities, primary chemical inhomogeneities are clearly demonstrated. There are reciprocal relationships between calcium and iron and between* $Ti^{4+} + 2Al$ *and* $R^{2+} + 2Si$. *Our evidence suggests that a chemically inhomogeneous subcalcic* C2/c *augite was the only primary pyroxene from which pigeonite later exsolved.*

The lunar clinopyroxenes, augite and pigeonite, from rocks 10003,38 10047,27, 10050,32, and soil 10084,100 collected by the Apollo 11 astronauts were examined by standard petrographic microscopy, by the Buerger single-crystal x-ray precession technique, by transmission and scanning electron microscopy, and by electron-microprobe analyses of single crystals mounted in epoxy cement and polished to expose a plane surface.

Examination of the clinopyroxenes with the petrographic microscope shows intercumulus textures and, within the grains, complex patterns of color varying from very light pink to fairly dark reddish brown. The characteristic properties of the lunar clinopyroxenes are the "sectorial" extinction and the apparent warping or bending of the (110) cleavage planes. These effects are caused by lattice rotation of two or more blocky, sometimes pie-shaped, "domains" contained within a crystal. Precession photographs of crystals containing such domains reveal that they are offset from one another by rotation about a common *b* axis (*1*). The rotation is generally 1° to 5°, and often a one-to-one correlation can be made between the number of domains seen optically in a crystal and the number observed in its *h0l* diffraction pattern. Color variations occur across the domain boundaries. The "sectorial" extinction so commonly displayed by the pyroxenes when examined in plane polarized light is caused by this offset domain structure.

Single-crystal x-ray diffraction patterns were made of 25 crystals or crystal chips. Almost all the crystals consisted of augite plus pigeonite oriented on (001). The approximate amount of pigeonite contained in the host augite was determined by comparing the relative intensities of the *h0l* reflections (*2*). The ratios of augite to pigeonite in some of these single crystals are as follows: rock 10003, 4 : 1, 7 : 3, 1 : 1, 1 : 1, 2 : 3, 1 : 4; rock 10047, 17 : 3, 13 : 7, 1 : 0, 7 : 3; rock 10050, 19 : 1, 19 : 1, 3 : 7, 17 : 3, 1 : 0, 17 : 3, 3 : 2, 50 : 1; rock 10072, 17 : 3; soil 10084, 13 : 5, 17 : 3, 17 : 3.

Cell parameters obtained from measurements of precession patterns can be summarized as follows: augites, *a* 9.68 to 9.76 Å, *b* 8.90 to 8.95 Å, *c* 5.25 to 5.28 Å, β 105.8° to 106.8°; pigeonites, *a* 9.68 to 9.76 Å, *b* 8.90 to 8.94 Å, *c* 5.21 to 5.24 Å, β 108.8° to 109.1°. The augites have space group *C2/c*, and the pigeonites, $P2_1/c$. The reflections violating *C2/c* symmetry in a crystal

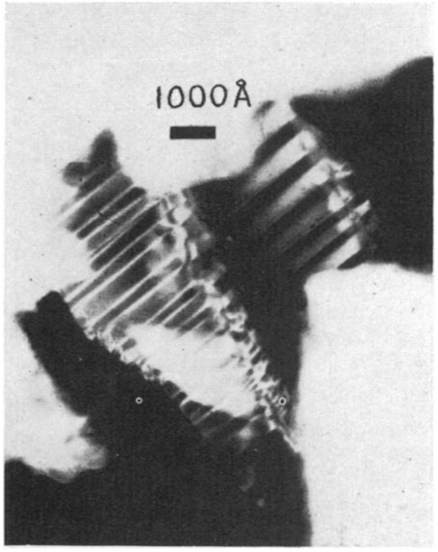

Fig. 1. Transmission electron photomicrograph of a small crystal fragment of clinopyroxene from rock 10047. The narrow lamellae to the left of the photograph (thin white bands) vary in thickness from 60 to 100 Å and are interpreted as being pigeonite unmixed on (001) from augite host (wide, dark bands 200 to 500 Å thick). Coalescence of the thin pigeonite lamellae into much thicker lamellae may be occurring to the right of the photograph (light bands approximately 400 Å thick). The discontinuity in the center of the grain trending 11 to 5 o'clock may be a domain boundary with the left domain becoming more augitic, the right, more pigeonitic.

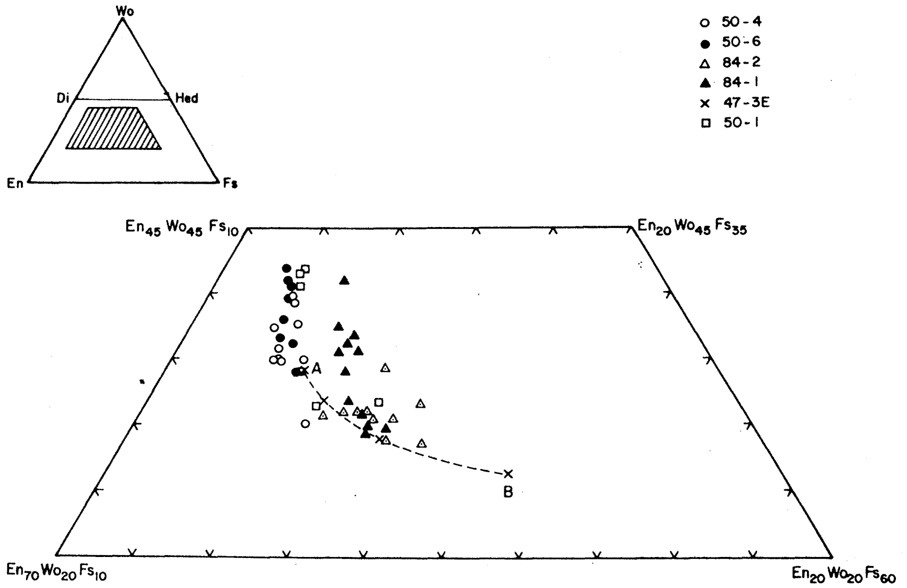

Fig. 2. Plot of electron-microprobe chemical analyses of six lunar clinopyroxenes on a part of the pyroxene quadrilateral. Separate analyses were made at several points on each crystal.

from rock 10003 with augite-pigeonite ratio 1 : 4 are found to be diffuse, similar to those observed by Morimoto and Tokonami (*3*) for pigeonite from andesite, Isle of Mull, Scotland. With one exception, the pigeonites included in the augite hosts are oriented with the (001) planes and *a* and *b* axes in common with those of the host. Pigeonite oriented on (100) of augite was observed within a prismatic crystal growing into a vug of rock 10072,33.

Only occasionally are pigeonite exsolution lamellae observed with the petrographic microscope. Transmission electron microscopy, however, reveals a complex array of (001) pigeonite lamallae, some only 60 Å thick (Fig. 1). Generally the lamellae are thinner than 1000 Å, so that identification by observations made with the petrographic microscope is difficult. The pigeonite contains more iron than the augite host and is thus denser and more opaque to electrons. We therefore assume that the less transparent pigeonite lamellae appear in the electron photomicrographs as gray to white zones and the more transparent augite areas appear as dark gray to black zones. Usually the small crystal fragments show abundant exsolved pigeonite at the crystal margins, and on some margins there appears to be more pigeonite than augite host. We have found no direct evidence for primary pigeonite in the rock samples studied, with the possible exception of crystal 10072-1 where a (100) overgrowth of primary pigeonite on augite may have occurred.

We conclude that the crystal fragments containing more pigeonite than augite originated from a much larger crystal which was initially a subcalcic augite. This primary augite unmixed a large amount of pigeonite and then underwent partial *intra*granular recrystallization such that parts of the grain became pigeonitic and others, augitic. A chip from such a grain, containing mostly pigeonite, could be misinterpreted as being a primary host phase. Such *intra*granular recrystallization textures are known in terrestrial rocks, for example: the inversion of pigeonite to orthopyroxene, and the unmixing and segregation of cummingtonite and actinolite to opposite ends of a grain that was originally a very subcalcic actinolite (*2*).

Additional evidence for unmixing of about 50 weight percent pigeonite from primary subcalcic augite appears in the *h0l* diffraction pattern of crystal 10003-8. This diffraction pattern shows the crystal to be composed of a single domain and indicates a present 1 : 1 ratio of augite to pigeonite. The x-ray reflections are generally sharp, but a diffuse streaking parallel to the *c** direction appears along a line connecting the equivalent *h0l* reflections of the two clinopyroxenes. For example, there is an intense streak between the 10,0,0 reflections of pigeonite and augite. This diffuse streaking is thought to be due to the diffraction effects produced by "islands" or "zones," some perhaps only a few unit cells in volume, of clinopyroxenes possessing a variety of compositions and possibly structural states. Such streaking would not be expected from primary intergrowth of augite and pigeonite but would be the expected result of incomplete exsolution and structural transformation over a range of temperature. Another interesting feature of the pigeonite unmixing is that those crystals which display multiple domains do not necessarily have the same amount of pigeonite in each domain. For example, crystal 10050-8 contains three domains, divided into augite-pigeonite ratios as follows: 3 : 7, 7 : 3, and 1 : 1.

Fifty electron-microprobe chemical analyses were made at various points on six single crystals previously examined by optical and x-ray methods (*4*). The results of these analyses are plotted in the pyroxene quadrilateral (Fig. 2). This plot ignores Al, Ti, Na, Cr, and Mn, which together correspond to about 3 mole percent of the clinopyroxene components, but this should not appreciably affect the usefulness of the diagram. The augite-pigeonite ratios for the crystals analyzed are: 10050-4, 19 : 1; 10050-6, 1 : 0; 10084-2, 13 : 5; 10084-1, 17 : 3; 10047-3E, 13 : 7; 10050-1, 19 : 1. Knowledge of the amount of unmixed pigeonite in the grains enables us to separate the primary chemical inhomogeneities appearing in the single crystal from secondary chemical inhomogeneities due to pigeonite unmixing from the primary clinopyroxene.

Four of the crystals analyzed show a striking distribution of compositions which trend nearly normal to the En-Fs join when plotted on the quadrilateral. The variation of composition for these crystals is as follows: 10050-6, $\mathrm{En_{45}Wo_{42}Fs_{14}}$ to $\mathrm{En_{47}Wo_{34}Fs_{19}}$; 10050-4, $\mathrm{En_{45}Wo_{40}Fs_{16}}$ to $\mathrm{En_{48}Wo_{30}Fs_{21}}$; 10084-1, $\mathrm{En_{41}Wo_{41}Fs_{18}}$ to $\mathrm{En_{45}Wo_{29}Fs_{26}}$; 10050-1, $\mathrm{En_{43}Wo_{42}Fs_{15}}$ to $\mathrm{En_{43}Wo_{32}Fs_{25}}$. Three of these crystals (10050-1, -4, -6) contain very little pigeonite, so that the analytical results reflect primary chemical inhomogeneities. Crystal 10050-6 is composed of six domains of unequal size rotated from one another by a few degrees. The chemical composition of this crystal varies from domain to domain.

The vertical trend demonstrated by these nearly pigeonite-free crystals is thought to be due to a concentration of iron into the *M*2 site at the expense of calcium, with only small change in total Mg content. This enrichment of Fe over Ca in *M*2 is believed to be related to the persistent crystallization of An-rich plagioclase. Ordinarily, in layered intrusive igneous rocks, we would expect plagioclase to trend from An_{80-70} at the early stages of crystallization to An_{40-30} at the later stages. The plagioclases in these rocks, however, are persistently calcic, ranging from approximately An_{85} to An_{73} (*5*). It appears that the primary *C2/c* clinopyroxenes crystallizing in these rocks became more and more depleted in Ca as they grew because of depletion of Ca in the melt by the continued precipitation of An-rich plagioclase. Magnesium tends to remain in the *M*1 site, and enrichment of Fe in the ordinarily Ca-rich *M*2 site must therefore occur. Once the concentration of Fe into *M*2 becomes significantly high, the crystallization trend can turn toward the ferrosilite corner of the pyroxene quadrilateral by Fe replacing Mg in *M*1.

Crystals 10084-2, 10047-3E appear to be lowest in Ca (Fig. 2). The scatter for crystal 10084-2 seems somewhat random. Crystal 10047-3E shows a continuous variation of Si, Fe, Ca, Mg, Ti, Al, Cr, and Mn from one end of the grain to the other (Fig. 3). Four complete analyses were made along the path of the traverse (dashed line, Fig. 2). The composition varies continuously from $En_{47}Wo_{34}Fs_{19}$ at the calcic end to $En_{37}Wo_{26}Fs_{36}$ at the other end. Unmixed pigeonite is undoubtedly concentrated into the more subcalcic portions of the crystal. Chemical formulas for the four analyzed positions (marked by *X*, Fig. 2) are, in order of decreasing Ca content, as follows: $Ca_{0.671}Na_{0.005}Mn_{0.010}Fe_{0.374}Mg_{0.921}Ti_{0.053}Cr_{0.011}Al_{0.084}Si_{1.871}O_{6.000}$, $Ca_{0.628}Na_{0.006}Mn_{0.011}Fe_{0.427}Mg_{0.0923}Ti_{0.047}Cr_{0.009}Al_{0.076}Si_{1,873}O_{6.000}$, $Ca_{0.569}\ Na_{0.006}\ Mn_{0.013}\ Fe_{0.525}\ Mg_{0.879}\ Ti_{0.039}Cr_{0.007}Al_{0.066}Si_{1.896}O_{6.000}$, $Ca_{0.518}\ Na_{0.006}\ Mn_{0.015}\ Fe_{0.709}\ Mg_{0.735}\ Ti_{0.032}\ Cr_{0.006}Al_{0.060}Si_{1.918}O_{6.000}$.

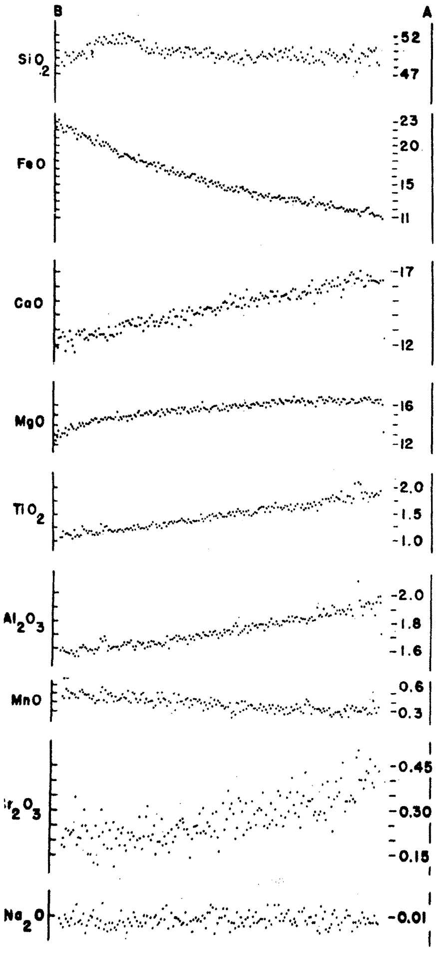

Fig. 3. Chemical trends in weight percent oxides for SiO_2, FeO, CaO, MgO, TiO_2, Al_2O_3, MnO, Cr_2O_3, and Na_2O obtained from an electron-probe traverse at 1 micron intervals from one end of crystal 10047-3E to the other end approximately parallel to the *c* axis.

The six crystals are generally lower in Ca and richer in Fe at the margins; the Ca and Fe vary nearly inversely in probe scans across the grain. The six crystals also show a nearly exact coupling of Ti and Al with Si and R^{2+} which can be interpreted as replacement of $R^{2+} + 2Si^{4+}$ by $Ti^{4+} + 2Al^{3+}$. Thus one Ti^{4+} would replace Mg, Mn, or Fe^{2+} in the *M*1 site, and charge balance would be maintained by simultaneous substitution of two Al^{3+} for two Si cations in the tetrahedral sites. This nearly exact coupling with Ti^{4+} suggests that little or no Ti^{3+} is present, for otherwise we should observe an octahedral Ti^{3+}–tetrahedral Al couple.

The change from low to high $Ti+Al$ is observed from a probe scan that crosses a color boundary, the high Ti and Al being associated with an intense reddish brown color. In turn, these sharp color boundaries often appear to be associated with the boundaries of the adjacent domains. The TiO_2 and Al_2O_3 contents each vary from about 1.5 weight percent in the nearly colorless areas to about 3 weight percent in the reddish brown areas. This distribution of Ti and Al found in the lunar pyroxenes has been found in certain terrestrial pyroxenes (*6*). The coupled relationship between Ca and Fe appears to be largely independent of the Ti and Al content, so that color is not necessarily related to pigeonite content.

The chaotic phase and chemical inhomogeneities displayed by these lunar clinopyroxenes suggest rapid crystallization from a melt of changing composition. We believe that a single *C2/c* clinopyroxene began to crystallize on the liquidus and above the augite-pigeonite solvus. We know from the studies of Smyth (*7*) and Prewitt, Papike, and Ross (*8*) that at high temperatures the low-temperature $P2_1/c$ pigeonite changes to the *C2/c* structure type, a fact which suggests a potential closing of the augite-pigeonite miscibility gap. Whether we call the primary *C2/c* lunar pyroxene subcalcic augite or calcic pigeonite may then be merely academic. The extreme chemical inhomogeneities found in the lunar clinopyroxenes may be due partly to the presence of a very flat solidus, such that small changes in melt composition would have an appreciable effect on the composition of the solid. The primary chemical inhomogeneities are further complicated by the subsolidus unmixing of two clinopyroxenes. The multiple domain structure is believed to be related to complex conditions of high-temperature crystal growth rather than to any later shock effects.

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