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Pyroxferroite, a new calcium-bearing iron silicate from Tranquillity Base

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Abstract—Pyroxferroite from Tranquillity Base, Moon is defined as the iron-rich analog of pyroxmangite. Pyroxmangite is redefined as the manganese-rich member of the Siebenerketten pyroxenoids. Pyroxferroite is triclinic, a 6·62, b 7·54, c 17·35Å, α 114·4, β 82·7, γ 94·5°; optically biaxial, α 1·753, β 1·755, γ 1·766, 2 V + 35°. A typical unit cell content is close to 14 $(Fe_{0\cdot84}Ca_{0\cdot13}Mg_{0\cdot02}Mn_{0\cdot02})(Si_{0\cdot99}Al_{0\cdot01})O_3$. Density 3·82 calc., 3·76 obs. Yellow color.

INTRODUCTION

SCIENTIFIC study of the rocks and minerals collected during Apollo 11 mission to Tranquillity Base, Moon was carried out under the unusual circumstances of high emotion, haste and deliberate duplication. To avoid problems of priority, the mineralogists agreed to prepare a joint publication for each new mineral discovered on the Moon. This report was initially prepared by J. V. Smith (JVS) on behalf of the groups of investigators, and was rewritten on the basis of comments received from the latter.

Pyroxferroite was first recognized by the LSPET (1969) as an unidentified yellow mineral that seemed to be concentrated in vuggy areas of the Type B rock. The first data showing that it is isostructural with pyroxmangite were reported by several investigators in the special issue of *Science*, January 30, 1970 (Vol. 167). These data were necessarily abbreviated and have been expanded in the present paper. The sources of the present data are identified by the initial letters of the authors, viz. CM (Chao, Minkin), FKD (Frondel, Klein, Drake), FT (Fuchs, Tani), SAMZ (Smith, Anderson, Moore, Zechman), TPDD (Traill, Plant, Douglas, Dence).

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* Names in alphabetical order of first author of each laboratory.

HISTORICAL BACKGROUND

Pyroxmangite was first described by FORD and BRADLEY (1913) from Iva, S. Carolina, and distinguished from rhodonite because of the very different optical axial angle (~ +30° vs. −74°) and some other less distinctive optical and crystallographic properties. FORD and BRADLEY distinguished it from babingtonite because of its chemical composition, and concluded that it is a "new member of the Pyroxene Group, belonging in the triclinic section". "The name pyroxmangite was given to the mineral in order to indicate that it is a manganese pyroxene." Nowadays, of course, the pyroxene group is split into true pyroxenes and various pyroxenoids characterized by the repeat distance of the silicate chain (see later).

PALMGREN (1917) assigned the name sobralite to an 'asymmetrical pyroxene' coexisting at Tunaberg, Sweden with an iron-rich rhodonite, diopside, olivine and spessartite. SUNDIUS (1931) compiled the available data on triclinic manganiferous 'pyroxenes', and obtained new optical and chemical data on certain samples. In particular, he demonstrated that both coarse and fine parallel intergrowths of chain silicates occur, and that identification had not always been correct. From chemical analyses plotted on the $MnSiO_3$, $CaSiO_3$, $(Fe,Mg)SiO_3$ ternary diagram, SUNDIUS distinguished composition fields for wollastonite (mostly Ca), bustamite (near $Ca_{0\cdot5}Mn_{0\cdot5}$), rhodonite (mostly Mn, but with extensive Fe and Ca substitution), sobralite (undetermined, but with data near $Mn_{0\cdot5}Fe_{0\cdot5}$) and hedenbergite (near $Fe_{0\cdot5}Ca_{0\cdot5}$).

SUNDIUS distinguished between sobralite and iron rhodonite on the basis of the optic axial angle. He noted that pyroxmangite from Iva, S. Carolina could not clearly be equated with sobralite on the basis of the data on the optical orientation, though the optic axial angles are similar. An 'iron rhodonite' described by Weibull in 1884 (see SUNDIUS, 1931) was found by SUNDIUS to be similar optically and chemically to sobralite.

The situation was clarified by HENDERSON and GLASS (1936) whose identification of pyroxmangite from an uncertain locality in Idaho prompted them to a detailed study of the original Iva material, and comparison with the Swedish sobralite. Correction of an error in the original determination of the optic orientation of the Iva material, plus new detailed optical and powder X-ray data of all the samples led to satisfactory proof of the essential mineralogic identity of sobralite and pyroxmangite. In spite of the incomplete description of the Iva material by FORD and BRADLEY, the name pyroxmangite has been generally adopted.

The dimensions of the unit cells of pyroxmangite and rhodonite were determined by PERUTZ (1937) from specimens described optically and chemically by TILLEY (1937). LIEBAU (1959) showed that pyroxmangite has a chain structure with a repeat of seven tetrahedra. PREWITT and PEACOR (1964) demonstrated that all the pyroxenes and pyroxenoids can be described in terms of sheets of approximately close-packed oxygens, between which tetrahedrally- and octahedrally-coordinated cations are bonded. Oriented, intergrown pyroxenes and pyroxenoids can be interpreted in terms of common layers of oxygens. The restricted composition ranges of the different types of chain silicates indicate a close structural relation between the kind of octahedrally-coordinated cations and the chain length. Pyroxmangite has a silicate chain

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whose repeat distance is seven tetrahedra, and is therefore classified as a Siebenerketten member of the pyroxenoids.

There are still further confusions in the old literature which require clarification. Not all 'iron rhodonite' turned out to be a true iron-bearing rhodonite in the Fünferketten structural group. Perutz (1937) from single crystal X-ray work showed that the 'iron rhodonite' specimen 34, of Whiteley and Hallimond (1919) is a Siebenerketten material. Tilley (1937) had previously suggested that this 'iron rhodonite' was actually a pyroxmangite on the basis of optical studies. Whiteley and Hallimond (1919) had obtained FeO 35·0 and MnO 14·5 wt.%, but had not analyzed for the other elements.

Hlawatsch (1907) determined the morphology and density, but not the chemical composition, of a triclinic 'rhodonite-like' material from a slag of unknown source. For this, and a similar specimen from the Germania smelter at Salt Lake City, he proposed the name vogtite in honor of J. H. L. Vogt. Hallimond (1919) found that the morphology of pale-yellow crystals from a steel-furnace slag was sufficiently close to that of Hlawatsch's specimens that the materials should be isomorphous: Hallimond noted that vogtite was considerably less dense than pyroxmangite and sobralite, and that the optical schemes were quite different. Bowen (1933) found that the morphological parameters obtained by Hallimond and by Hlawatsch were consistent with those of wollastonite indicating isomorphism. No X-ray data on a vogtite specimen have been reported so far, but it is quite clear that vogtite specimens do not belong to the Siebenerketten group.

Returning now to pyroxferroite, it is necessary to consider the chemical composition in relation to the nomenclature. As shown later, the dominant octahedrally-coordinated cations in the Siebenerketten pyroxenoids are Mn and Fe with Ca the only other major cation. Calcium oxide reaches a maximum concentration of 6 wt.%. The most obvious names are pyroxmangite and pyroxferroite for the end-member compositions $MnSiO_3$ and $FeSiO_3$. The Iva, S. Carolina material is renamed as a calcian manganoan pyroxferroite since its Fe/Mn ratio is 55/45 on an atomic basis. The Apollo 11 material is a calcian pyroxferroite, and has by far the closest composition to $FeSiO_3$ of natural Siebenerketten materials.

Lindsley (1967) synthesized pyroxferroite of composition $Ca_{0\cdot15}Fe_{0\cdot85}SiO_3$ at pressures ranging from 10 to 17·5 Kbars and temperatures from 1130 to 1250°C. A section on the synthesis data kindly provided by D. H. Lindsley is given later in this paper. C. W. Burnham has confirmed that synthetic pyroxferroite has unit cell dimensions analogous to pyroxmangite, and has complete 3D X-ray structural analyses underway of both synthetic and lunar material.

Occurrence and Petrographic Environment

The lunar sample of pyroxferroite occurs in the Type B rocks brought back to Earth by the Apollo 11 mission from the Sea of Tranquillity. The Type B rocks (as designated by the LSPET (1969)) can be denoted as microgabbros or diabases. The principal minerals are sub-calcic augite, ilmenite and calcic plagioclase. Textural interpretation indicates that when crystallization of the liquid is almost complete minor amounts of several minerals appear. Of these late stage minerals, pyroxferroite, cristobalite and tridymite are probably the most common, while fluorapatite, fayalite and K-feldspar also appear. Also in the Type B rocks are intergrowths of troilite and iron metal interpreted as the product of a sulfide melt immiscible with the silicate melt.

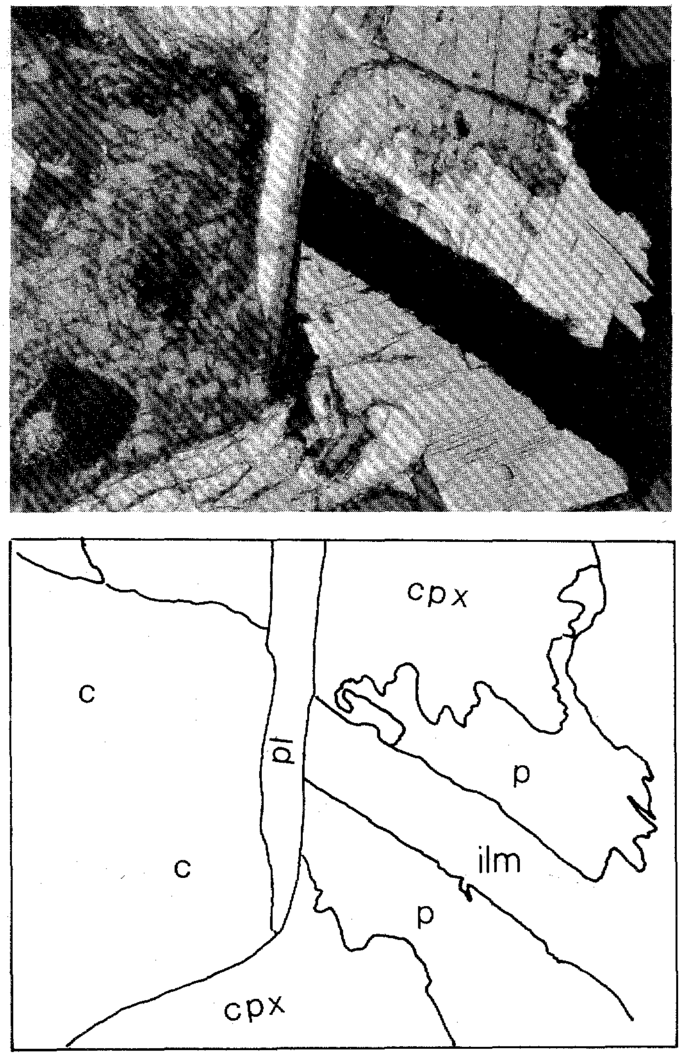

Fig. 1. (a) Photomicrograph using crossed polars of thin section 10025 of rock 10047. The polarization colors are rendered here in black and white.
(b) This key to the photomicrograph (a) identifies cristobalite (c), clinopyroxene (cpx), ilmenite (ilm), pyroxferroite (p) and plagioclase (pl). The interfingering of the pyroxferroite and clinopyroxene demonstrates an intimate growth relation. The tile texture of the cristobalite results from an inversion from the cubic symmetry at high temperature to the tetragonal symmetry at low temperature. The stripes in the plagioclase result from twinning. The numerous lines across the grains of pyroxene and pyroxferroite result from cleavages. (Provided by TPDD.)

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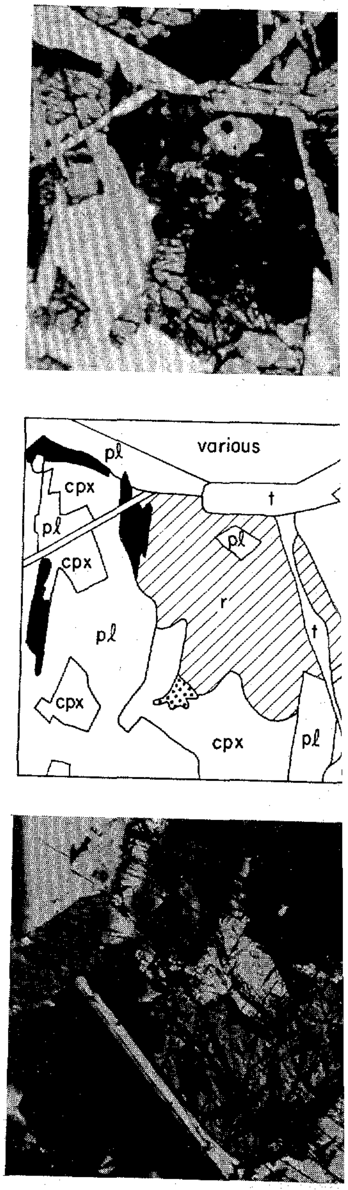

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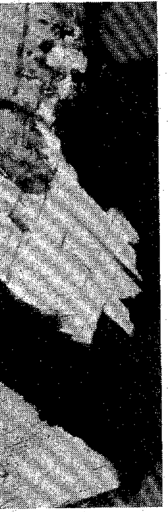

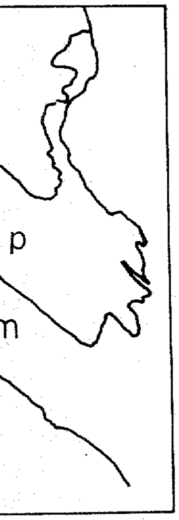

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The final product of crystallization of the silicate melt (called the residuum in Fig. 2 (c)) is extremely complex with a very fine grain size: it may involve separation of an immiscible silicate melt. Detailed mineralogic and petrologic descriptions are given in other papers of this issue and in the reports in the January 30, 1970 issue of *Science*.

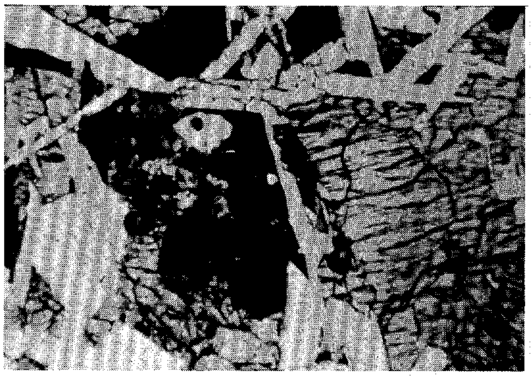
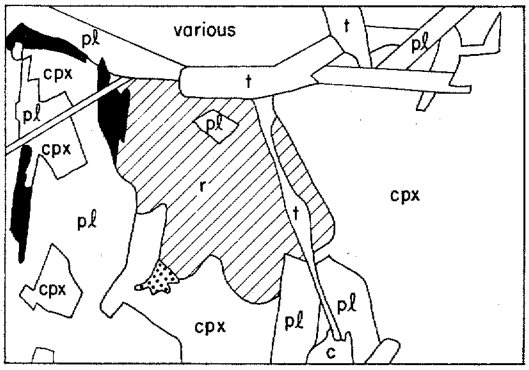
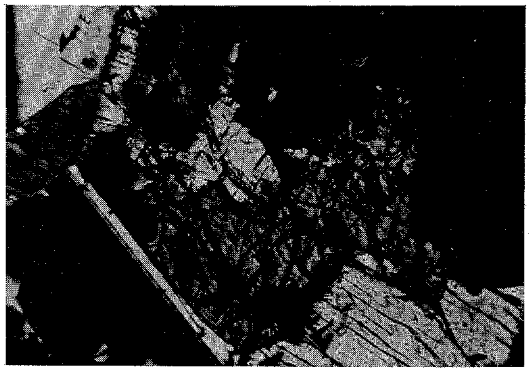


Fig. 2. (a) Photomicrograph using uncrossed polars of thin section 10052 of rock 10044. 0·15 mm across.



(b) Key to area showing cristobalite (c), clinopyroxene (cpx), ilmenite (black), pyroxferroite (dotted), plagioclase (pl), residuum (hatched) and tridymite (t).



(c) Photomicrograph using crossed polars and higher magnification of area to lower left of center in (a). Note that the slide was rotated a few degrees to obtain best intensity contrast. The triangular white patch at the center is pyroxferroite. All highly-colored material is pyroxene. The twin banding of the plagioclase is visible. (Provided by SAMZ.)

The present data on pyroxferroite were obtained on samples from rocks 10044 (FT, SAMZ) and 10047 (CM, FKD, TPDD). Figure 1, a photomicrograph with key, provided by TPDD shows pyroxferroite growing at the margins of clinopyroxene and as isolated grains. Figure 2 provided by SAMZ shows pyroxferroite in relation to the other minerals listed in the key. The relation to the late-stage residuum is well displayed.

Under a direct-vision binocular, the pyroxferroite is apparently distinguishable from the sub-calcic augite by its distinctive yellow color in contrast to the cinnamon color of the latter. However in thin section, distinction is not easy since the color effect is not readily visible. At least most of the pyroxferroite shows a sharp boundary to augite, but there is considerable suspicion that either intergrowths occur, or that there is overlap of chemical composition. Very careful study is needed to elucidate the relationships between the pyroxene and the pyroxferroite.

MORPHOLOGY

CM report that they studied vuggy crystals from rock 10047, but 2-circle goniometer data are not yet available. Other investigators worked with irregular fragments from crushed rock. SAMZ found that their crystals had rudimentary faces perhaps the result of cleaving during crushing of the host rock.

PHYSICAL AND OPTICAL PROPERTIES

TPDD discovered one good cleavage possibly (010), and one poor cleavage (001), indexed with respect to the X-ray determined unit cell. Cleaving does not seem to be as pronounced as in the Earth samples of ferroan pyroxmangite examined by HENDERSON and GLASS (1936) and by TILLEY (1937).

FKD report that pyroxferroite from 10047 is faintly pleochroic in thick grains showing pale yellow and yellow orange. The axes of the absorption indicatrix apparently do not coincide with those of the Fletcher indicatrix; the absorption scheme is $X' > Z'$. TPDD found that the pleochroism in pyroxferroite, also from rock 10047, was very weak or absent.

Table 1. Refractive indices and optic axial angle

	Rock 10047			Rock 10044					
	CM	FKD	TPDD	FT	Idaho‡	Iva‡	Silvberg‡	Tunaberg‡	Glen Beag§
α	1·753–1·756	1·752	1·750–1·753*	1·748†	1·737	1·748	1·737	1·726	1·732
β	1·755–1·758	1·758	1·752–1·755*	1·750†	1·740	1·750	1·740	1·728	1·735
γ	1·766–1·767	1·767	1·765–1·768*	1·768†	1·754	1·764	1·755	1·744	1·750
2 V	+35–40°	~ +35–40°	+35 ± 3°	+34 ± 4°	+39°	+37°	+41°	+40°	+41°

* Includes range and errors.
† ±0·003.
‡ HENDERSON and GLASS (1936).
§ TILLEY (1937).

Table 1 summarizes the data obtained on the refractive indices and the optic axial angle. The present data are insufficient to permit separation of a genuine variation of refractive indices from the various experimental errors. However the results do show a

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Table 2. Cell dimen

(a)	CM*
a	6·623 (8)
b	7·543 (5)
c	17·35 (2)
α	114·3 (1)
β	82·7 (2)
γ	94·5 (5)
V	783 (1)

Standard deviation in bracke
* Precession with least squares
† Front-reflection Weissenberg.
‡ Front-reflection Weissenberg
§ Using 25 unique reflections.
‖ Using 10 unique reflections.
¶ Using 23 unique reflections.

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Iva‡	Silv-berg‡	Tuna-berg‡	Glen Beag§
1·748	1·737	1·726	1·732
1·750	1·740	1·728	1·735
1·764	1·755	1·744	1·750
+37°	+41°	+40°	+41°

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significant increase of about 0·01–0·02 in the refractive indices with respect to those Siebenerketten pyroxenoids from Earth with approximately equal contents of Mn and Fe (see data for terrestrial specimens in Table 1). In addition the optic axial angle of the lunar pyroxferroite tends to be a few degrees smaller.

TPDD determined refractive indices on 4 grains in immersion oils at 25°C, and optic axial angles on 7 grains using conoscopic universal stage methods and spindle stage technique in Na light. They also recorded moderate dispersion with one black isogyre and one weaker and colored.

Observed values of the specific gravity are: CM, 3·76 ± 0·01; FT 3·68 ± 0·01; SAMZ, floats in liquid of 3·7.

X-RAY DATA

Table 2 summarizes the cell dimensions obtained from single crystal X-ray study. Just as for the data on the refractive indices it is impossible to separate genuine variation from experimental error.

Table 2. Cell dimensions from (a) single-crystal and (b) powder X-ray data

(a)	Single crystal			(b) Powder X-ray data		
	CM*	FT†	SAMZ‡	FT§	SAMZ‖	TPDD¶
a	6·623 (8)	6·63 (1)	6·61 (2)	6·62 (1)	6·615 (18)	6·62
b	7·543 (5)	7·58 (1)	7·52 (2)	7·54 (1)	7·556 (12)	7·55
c	17·35 (2)	17·43 (5)	17·37 (4)	17·34 (2)	17·35 (3)	17·38
α	114·3 (1)	114·5 (2)	114·28 (8)	114·3	114·38 (11)	114·34
β	82·7 (2)	82·6 (1)	82·72 (8)	82·8	82·7 (6)	82·69
γ	94·5 (5)	94·4 (1)	94·52 (8)	94·4	94·7 (5)	94·4
V	783 (1)		783 (6)		783 (3)	784·6

Standard deviation in brackets to same significance level.
* Precession with least squares refinement based on power data.
† Front-reflection Weissenberg.
‡ Front-reflection Weissenberg and precession.
§ Using 25 unique reflections.
‖ Using 10 unique reflections.
¶ Using 23 unique reflections.

In the belief that the structural resemblance of the pyroxenoids is of such importance that the cell dimensions should readily show the mathematical relations, Table 2 uses the orientation chosen by LIEBAU (1959). This choice of axes violates the rules set down by DONNAY *et al.* (1963), and is based on the structural analogy of the chain direction of the Siebenerketten pyroxenoids with the Zweierketten repeat of pyroxene along the *c*-axis.

The paucity of pyroxferroite made X-ray powder diffraction study difficult. All investigators used Debye–Scherrer techniques with a specimen made of at most a few grains. Because of the overlap of some lines and the difficulty of detecting weak lines from the background, it is not surprising that the reported data differ in certain features.

Table 3 compares the X-ray powder data for pyroxferroite with those for material from Iva, S. Carolina, and for a pyroxmangite from Kamiotomo, Japan.

Table 3. X-ray powder data for pyroxferroite and pyroxmangite

Apollo 11 mean*			Iva, S.C.†		Kamiotomo, Japan‡	
d	*I*	*hkl*	*d*	*I* (dens.)	*d*	*I* (vis.)
6·87	20	010	6·88	10	6·88	10
6·55	25	100	6·58	15	6·61	10
5·56	5?	011?	5·52	5	—	—
4·93	5?	$1\bar{1}2$?	5·25	5	5·24	3
4·68	40	110	4·68	30	4·70	15
4·20	15	$\bar{1}11$	4·21	15	4·20	8
3·76	8	$0\bar{2}2$	3·91	5	3·89	3
3·68	6	$0\bar{2}1$, $0\bar{2}3$	3·68	10	3·68	3
3·53	8	013	3·54	10	3·54	8
3·44	15	020	3·43	25	3·45	15
3·38	5	$1\bar{2}2$	3·38	5	—	—
3·32	10	$1\bar{2}3$	3·32	25	3·32	20
3·28	12	200, 201	3·29	30	3·29	20
—	—	—	3·23	5	3·22	10
3·19	5	113	3·20	5	—	—
3·14	15	202, $\bar{2}01$	3·15	30	3·16	15
3·09	45	021, $2\bar{1}1$, $2\bar{1}2$	3·10	75	3·11	50
3·01	25	120, $0\bar{2}5$	2·997	55	3·02	20
2·973	20	$2\bar{1}3$	—	—	2·988	20
2·934	100	014, 210	2·941	100	2·947	100
2·838	10	211	2·842	15	2·856	10
2·805	8	$\bar{2}11$, $12\bar{1}$	2·806	20	2·806	10
—	—	—	2·773	5	2·768	5
2·674	60	$0\bar{2}6$	2·664	95	2·666	55
2·621	30	$\bar{1}14$	2·628	50	2·620	20
2·579	35	$2\bar{2}2$	2·586	65	2·586	20
2·509	5	$0\bar{3}3$	—	—	2·525	3
2·490	20	$0\bar{3}2$	2·496	5	2·489	15
2·446	15	$21\bar{4}$	2·440	35	2·442	15
2·409	10	$2\bar{2}0$	2·403	20	—	—
2·377	8	$1\bar{3}2$	2·377	15	—	—
2·311	8	$2\bar{1}6$	2·290	5	2·279	5
2·284	8	$13\bar{3}$, 030	2·273	15	—	—
2·234	8	$0\bar{3}6$	—	—	—	—
2·217	8	$2\bar{2}6$, $22\bar{4}$	2·223	20	2·224	5
2·186	25	024	2·193	75	2·192	20
2·156	40	206, $3\bar{1}2$	2·167	95	2·168	35
—	—	—	2·138	20	—	—
2·099	20	303, 124	2·105	40	2·110	10
2·044	25	$2\bar{3}2$, $13\bar{6}$	2·033	45	—	—
1·994	5	032	2·027	5	2·035	20
1·969	8	$3\bar{2}2$	2·970	15	1·970	10
1·952	8	207	—	—	—	—
1·925	5	—	1·929	10	1·924	2
1·850	15	—	1·847	20	1·858	5b
1·815	8	—	1·808	15	1·850	5b
1·797	5	—	—	—	1·811	5
1·773	5	—	1·766	5	1·799	1
1·750	5	—	1·745	20	1·749	5
1·706	20	—	1·708	50	1·708	25
1·692	20	0, $\bar{1}$, 10	1·691	40	1·689	20
1·659	20	—	1·662	60	1·666	22
1·640	20	—	1·647	55	1·652	18
1·615	5	—	1·613	25	1·615	13
1·607	5	—	—	—	—	—
1·594	10	—	1·592	20	1·589	10
—	—	—	1·577	20	1·575	1
1·567	8	—	1·569	30	1·568	20
1·548	8	—	1·557	35	1·554	15
1·523	8	—	1·530	10	1·535	10
1·515	8	—	1·517	20	1·521	12

Apollo 11 mean*	
d	*I*
1·472	25
—	—
1·432	8
1·410	35
1·380	8
1·370	8
1·361	8
1·299	10
1·284	10
1·260	5
1·247	5
1·230	5
1·060	10
1·022	5

* Combination of data by CM,
† Harvard 84908; data by B. Ta
‡ Field Museum M18172; data

The X-ray powder data
Scherrer methods. Althoug
satisfactory, it is quite obvi
resolve overlapping lines.
sample, and should be used
ness of the lunar sample.

The differences of intensi
are no obvious correlations
by over-exposure.

Although the various ind
high-angle lines did not agree
precession X-ray photograp
graphs only, and relied on c
tions. FT and TPDD indexe
a considerable fraction of th
graphs. CKD compared the
by Dr. C. W. Burnham on sy
complex structure like that
patterns is only reliable if a
single crystal patterns. Auto
cell dimensions can give spur
Table 2 may be too optimisti

Copies of the original dat
only one set of data is given.
and the indexing was obtaine

There are quite large dif
ferroite and pyroxmangite. T
result from an impurity.

yroxmangite

	Kamiotomo, Japan‡	
s.)	*d*	*I* (vis.)
	6·88	10
	6·61	10
	—	—
	5·24	3
	4·70	15
	4·20	8
	3·89	3
	3·68	3
	3·54	8
	3·45	15
	—	—
	3·32	20
	3·29	20
	3·22	10
	—	—
	3·16	15
	3·11	50
	3·02	20
	2·988	20
	2·947	100
	2·856	10
	2·806	10
	2·768	5
	2·666	55
	2·620	20
	2·586	20
	2·525	3
	2·489	15
	2·442	15
	—	—
	—	—
	2·279	5
	—	—
	—	—
	2·224	5
	2·192	20
	2·168	35
	—	—
	2·110	10
	—	—
	2·035	20
	1·970	10
	—	—
	1·924	2
	1·858	5b
	1·850	5b
	1·811	5
	1·799	1
	1·749	5
	1·708	25
	1·689	20
	1·666	22
	1·652	18
	1·615	13
	—	—
	1·589	10
	1·575	1
	1·568	20
	1·554	15
	1·535	10
	1·521	12

Table 3 (continued)

	Apollo 11 mean*		Iva, S.C.†		Kamiotomo, Japan‡	
d	*I*	*hkl*	*d*	*I* (dens.)	*d*	*I* (vis.)
1·472	25	—	1·478	60	1·477	17
—	—	—	—	—	1·444	2
1·432	8	—	—	—	1·432	5
1·410	35	—	1·408	—	1·413	35
1·380	8	—	—	—	—	—
1·370	8	—	—	—	—	—
1·361	8	—	—	—	—	—
1·299	10	—	—	—	—	—
1·284	10	—	—	—	—	—
1·260	5	—	—	—	—	—
1·247	5	—	—	—	—	—
1·230	5	—	—	—	—	—
1·060	10	—	—	—	—	—
1·022	5	—	—	—	—	—

* Combination of data by CM, FKD, FT, SAMZ and TPDD. FeK and CrK radiation.

† Harvard 84908; data by B. Tani, CrK radiation; intensities estimated by densitometer.

‡ Field Museum M18172; data by B. Tani; CrK radiation; intensities estimated by densitometer.

The X-ray powder data for lunar pyroxferroite were all obtained by Debye–Scherrer methods. Although the general level of agreement of *d* and *I* values is satisfactory, it is quite obvious that a high-resolution Guinier pattern is required to resolve overlapping lines. This technique, of course, would require considerable sample, and should be used preferably on synthetic material because of the preciousness of the lunar sample.

The differences of intensities obtained by the investigators are puzzling, and there are no obvious correlations to indicate preferred orientation or intensity distortion by over-exposure.

Although the various indexings of the low-angle lines agree quite well, those for high-angle lines did not agree. JVS had indexed his pattern using two complete sets of precession X-ray photographs about the *a* and *b* axes. CM used zero-layer photographs only, and relied on closeness of agreement of *d*-spacings for the other reflections. FT and TPDD indexed most of their lines from single crystal photographs but a considerable fraction of the possible reflections were not available on the photographs. CKD compared their low-resolution X-ray powder data with data obtained by Dr. C. W. Burnham on synthetic pyroxferroite. It is clear that for a low-symmetry, complex structure like that of pyroxferroite, indexing of X-ray powder diffraction patterns is only reliable if a complete set of intensities is available from indexed single crystal patterns. Automatic indexing programs with least squares analysis of cell dimensions can give spurious results, and the accuracies of the cell dimensions in Table 2 may be too optimistic.

Copies of the original data can be obtained from J. V. Smith. Here in Table 3, only one set of data is given. The *d* and *I* values were selected from all the patterns, and the indexing was obtained from single-crystal patterns.

There are quite large differences of intensity between the patterns for pyroxferroite and pyroxmangite. The 2·525 line of pyroxmangite is surprising and might result from an impurity.

TPDD found that the precession photographs taken around all three principal axes show extra reflections that are consistent for three different single crystals. They suggest that the unit cell of Table 2 is actually a sub-cell with axial dimensions *a*, *b* and *c* that are only one-quarter those of the true cell. JVS re-examined the SAMZ photographs and found no unequivocal superstructure reflections, though the situation was confused by small crystals apparently attached to the main crystals by irrational angles. However he did find that streaks occurred on layer lines taken about the 6·6 Å axis which is common to pyroxenes and pyroxenoids. This indicates stacking errors of cations in the octahedrally-packed oxygen anions. Indeed parallel intergrowths of pyroxferroite and pyroxene may occur in which the [110] axis of the latter is common to the *a* axis of the former.

CHEMICAL COMPOSITION AND CALCULATED DENSITY

All the chemical analyses of the pyroxferroite (Table 4) were obtained by electron microprobe methods. This technique did not permit determination of the valence state. The high state of reduction of the Apollo 11 rocks suggests that essentially all the iron is in the ferrous state. In addition it is possible that the titanium is in the 3- rather than the 4-valent state assumed in Table 4.

Table 4. Electron microprobe analyses

	CM	FKD	FT	SAMZ	TPDD
Rock number	47	47	44	44	47
SiO_2	46·8	45·0	46·3–47·1	44·7–46·4	45·5–47·0
TiO_2	0·5	0·5	0·4–0·7	0·3–0·5	0·2–0·5
Al_2O_3	0·3	0·2	—	0·5–1·2	0·2–0·4
FeO	44·6	47·2	45·9–47·7	45·0–46·4	46·0–47·9
MnO	0·8	1·0	0·6–0·9	0·6–1·3	0·1–0·5
MgO	0·8	0·9	0·3–1·2	0·6–0·9	0·4–1·0
CaO	6·0	6·0	4·7–5·6	5·7–6·3	5·4–6·1
Na_2O	tr.	—	—	—	—
Total	99·8	100·8	100·7	100·2	100·1

Although considerable progress has been made in setting up calibration standards and correction procedures for electron microprobe analyses, JVS cautions against any attempt to interpret in detail the cation location of the minor constituents Al and Ti which might fractionate between the octahedral and tetrahedral sites.

Although the data are subject to essentially unknown calibration errors, the spread of the data is sufficiently large to show that the lunar pyroxferroite has variable composition. However it is remarkable that the major elements Fe and Ca vary over only narrow ranges. The sub-calcic augite in the Apollo 11 Type B rocks is very variable in composition (see data in many articles of this issue), ranging from a composition near diopside to one near that of pyroxferroite. At this time it is not known if pyroxferroite has a composition range overlapping that of the sub-calcic augite.

Table 5 shows the chen

Table 5.

CM	$(Fe_{0·81}Ca_{0·14}Mg_{0·03}$
FKD	$(Fe_{0·85}Ca_{0·14}Mg_{0·03}$
FT	$(Fe_{0·83}Ca_{0·12}Mg_{0·03}$
SAMZ	$(Fe_{0·82}Ca_{0·13}Mg_{0·02}$
TPDD	$(Fe_{0·84}Ca_{0·13}Mg_{0·02}$

Specific gravities calcul
CM 3·82; FT 3·83; TPD
given earlier, possibly expl

Dr. D. H. LINDSLEY of
New York at Stonybrook)
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9·5 kbar, 1190°C; 10 kbar
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The octahedral cations
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is controlled by the size of
(Mn, Fe, Mg)(Ca, Mg)SiO_3.
its cation radius is actually s

Table 5 shows the chemical formulae recalculated to 3 oxygen atoms.

Table 5. Chemical formulae calculated to 3 oxygens

CM	$(Fe_{0\cdot81}Ca_{0\cdot14}Mg_{0\cdot03}Mn_{0\cdot02})$	$(Si_{0\cdot98}Ti_{0\cdot01}Al_{0\cdot01})$	O_3
FKD	$(Fe_{0\cdot85}Ca_{0\cdot14}Mg_{0\cdot03}Mn_{0\cdot02})$	$(Si_{0\cdot97}Ti_{0\cdot01}Al_{0\cdot01})$	O_3
FT	$(Fe_{0\cdot83}Ca_{0\cdot12}Mg_{0\cdot03}Mn_{0\cdot02})$	$(Si_{0\cdot997}Ti_{0\cdot003})$	O_3
SAMZ	$(Fe_{0\cdot82}Ca_{0\cdot13}Mg_{0\cdot02}Mn_{0\cdot01}Ti_{0\cdot004}Al_{0\cdot01})$	$(Si_{0\cdot98}Al_{0\cdot02})$	O_3
TPDD	$(Fe_{0\cdot84}Ca_{0\cdot13}Mg_{0\cdot02}Mn_{0\cdot01})$	$(Si_{0\cdot986}Al_{0\cdot007}Ti_{0\cdot007})$	O_3

Specific gravities calculated from the chemical analyses and the cell volumes are: CM 3·82; FT 3·83; TPDD 3·83. These values are higher than the observed values given earlier, possibly explainable by presence of considerable void space.

SYNTHESIS OF PYROXFERROITE

Dr. D. H. LINDSLEY of the Geophysical Laboratory (now at State University of New York at Stonybrook) kindly supplied the following passage.

BOWEN *et al.* (1933) synthesized Fe–Ca metasilicates approaching the composition range of lunar pyroxferroite. X-ray powder photographs suggested a pyroxenoid structure of wollasonite type. LINDSLEY and MUNOZ (1969) later showed these iron-rich pyroxenoids to be metastable at atmospheric pressure. LINDSLEY (1967) recently synthesized pyroxferroite of composition $Ca_{0\cdot15}Fe_{0\cdot85}SiO_3$ at pressures from 10 to 17·5 kbar and temperatures from 1130 to 1250°C. More recently, phase equilibrium studies to be reported by LINDSLEY and BURNHAM indicate a triangular stability field for pyroxferroite of that composition lying between invariant points at approximately 9·5 kbar, 1190°C; 10 kbar, 1040°C; and 17·5 kbar, 1270°C. At lower pressures pyroxferroite decomposes to a Ca-enriched pyroxenoid (or clinopyroxene), fayalitic olivine and a SiO_2 phase, whereas at lower temperatures it transforms into a clinopyroxene. Although all phase equilibrium and synthesis studies were made in equilibrium with metallic iron, pyroxferroite is probably stable up to oxygen fugacities at which the oxidation reaction pyroxferroite $\rightarrow$ magnetite + Ca-enriched metasilicate + SiO_2 phase takes place. This is presumably near the range of the fayalite–magnetite–quartz buffer (EUGSTER and WONES, 1962; LINDSLEY *et al.*, 1968).

DISCUSSION

The octahedral cations of the lunar pyroxferroite, and of the synthetic pyroxferroite, have concentrations fairly close to those required for one large cation to every six small cations. It is not unlikely that the detailed structure analysis now being carried out by C. W. Burnham will show that the large cations concentrate into one site. LIEBAU (1959) suggested that the formula of the Siebenerketten metasilicate is controlled by the size of the cations and that the chemical formula is given by $(Mn, Fe, Mg)(Ca, Mg)SiO_3$. It is not clear why Mg should go into both sites since its cation radius is actually smaller than those of Mn and Fe.

Figure 3 summarizes graphically the relation between cations of the Siebenerketten metasilicates as indicated by their oxides. Dr. M. Fleischer and Mrs. J. V. Smith kindly carried out the literature reviews which provided the data. Table 6 lists the oxides, specific gravity and refractive indices of all the Siebenerketten silicates located by Dr. M. Fleischer. Although some so-called pyroxmangites in mineral museums are actually rhodonite, most of the specimens reported in the table have been characterized accurately either by optical, X-ray, or both methods.

Table 6. Chemical analyses, specific gravity and optical properties of Siebenerketten silicates (wt. per cent)

No.	MnO	FeO	Fe_2O_3	MgO	CaO	G	α	γ	β	γ–α	+2 V
1	52·42	0·39	tr.	0·68	0·46	3·69	1·732	1·751	1·736	0·019	43–46
2	51·91	—	0·96	0·83	0·32	3·65	1·735	1·755	1·738	0·020	—
3	51·10	1·39	—	1·46	0·92	3·73	1·730	1·748	1·733	0·018	46
4	45·53	1·28*	0·29	3·84	0·68	3·61	1·728	1·746	1·732	0·018	41–42
5	45·02	5·69	—	3·13	0·93	—	1·730	1·748	1·732	0·018	—
6	40·91	—	0·68	0·37	3·60	3·26	1·717	1·732	—	0·015	40
7	39·96	9·72	0·21	0·72	2·68	—	1·732	1·748	1·734	0·0165	42
8	33·96	17·94	1·02†	1·54	1·57	—	—	—	—	—	—
9	33·37	12·35	0·66	3·48	2·88	3·68	1·731	1·749	1·734	0·018	40
10	29·98	11·08	4·65	3·74	2·24	3·6	—	—	—	—	—
11	29·34	19·12	—	1·96	2·94	3·76	1·738	1·754	1·742	0·016	39·5
12	29·22	12·50	3·69	3·92	2·21	3·56	1·746	1·763	—	0·017	40‡
13	28·25	15·02	1·45	4·56	3·00	3·63	1·732	1·750	1·735	0·018	41
14	27·06	20·91	1·50	2·14	2·62	3·66	1·737	1·754	1·740	0·017	39
15	24·25	22·44	—	1·20	5·60	—	—	—	—	—	41
16	21·09	22·32	2·37	3·11	4·64	3·73	1·734	1·751	1·737	0·017	37·5
17	20·63	28·34	—	—	1·88	3·80	1·748	1·764	1·750	0·016	30
18	20·50	24·69	0·85	1·39	5·46	3·72	1·738	1·755	1·740	0·017	42
19	20·25	25·10	2·46	1·15	3·07	3·66	1·745	1·763	—	0·018	42
20	20·08	26·01	2·94	1·32	2·57	3·75	—	—	—	—	—
21	—	—	—	—	—	—	1·726	1·744	1·728	0·018	40

1. Lee (1955). Ajiro Mine, Japan.
2. Momoi (1964). Kigotaki Mine, Nagano Pref., Japan.
3. Momoi (1964). Takamoi Mine, Yamaguchi Pref., Japan.
4. Lee (1955). Kinko Mine, Japan.
5. Momoi (1964). Taguchi Mine, Aichi Pref., Japan.
6. Yoshimura *et al.* (1958). Ichinomata Mine, Japan.
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9. Hietanen (1938). Simsiö, Finland.
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12. Omori and Hasesawa (1955, 1956). Iwaizumi, Japan.
13. Tilley (1937). Glen Beag, Scotland.
14. Henderson and Glass (1936). Idaho.
15. Sundius (1931). Vester Silfberg, Sweden.
16. Hietanen (1938). Simsiö, Finland.
17. Ford and Bradley (1913). Iva, S. Carolina.
18. Sundius (1931). Vester Silfberg, Sweden.

19, 20. Tatekawa (1964). Tango Peninsula, Japan.

21. Henderson and Glass (1936). Tunaberg, Sweden.

* Also contains ZnO 0·23 per cent.
† Equals $Fe_2O_3 + Al_2O_3$.
‡ Stated to be "biaxial negative, +2 V = 40°".

It is clear that the calciu
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cal properties of

β	γ-α	+2 V
1·736	0·019	43–46
1·738	0·020	—
1·733	0·018	46
1·732	0·018	41–42
1·732	0·018	—
—	0·015	40
1·734	0·0165	42
—	—	—
1·734	0·018	40
—	—	—
1·742	0·016	39·5
—	0·017	40‡
1·735	0·018	41
1·740	0·017	39
—	—	41
1·737	0·017	37·5
1·750	0·016	30
1·740	0·017	42
—	0·018	42
—	—	—
1·728	0·018	40

gites in mineral museums
the table have been char-
ods.

It is clear that the calcium content tends to increase with the iron content, and that the magnesium content is uncorrelated. In addition it is clear that the Siebenerketten pyroxenoid is not characterized by the LIEBAU formulae unless some of the chemical analyses are wrong. Detailed X-ray, Mössbauer and electron microprobe studies are desirable in order to determine the concentrations of the cations and their distribution among the cation sites.

If ordered and disordered forms of the Siebenerketten silicates are found, it will be necessary to expand the nomenclature. However this should be done with suitable prefixes. The mineral nepheline provides a good example since it has a composition range on both sides of the ideal formula $(Na_3K)(Al_4Si_4O_{16})$. The lunar pyroxferroite may turn out to be essentially $Fe_6CaSi_7O_{21}$.

Since the Apollo 11 rocks are not in the original position of crystallization, there is no geological control to indicate depth of crystallization. If pyroxferroite crystallized stably, LINDSLEY's data indicate a minimum pressure of 9·5 kbar corresponding on the Moon to a static pressure found only at several hundreds of kilometers below the surface. It would be remarkable if the Type B specimens crystallized more than a fraction of a kilometer below the present surface of the Moon, since they have probably been broken away from near-surface lava flows. Furthermore the close association of cristobalite and tridymite argues against high pressures. The simplest explanation is that pyroxferroite crystallized metastably as did the pyroxenoids in the experiments of BOWEN *et al.* (1933). Although the oxygen fugacity during crystallization of the lunar rocks was very low ($\sim 10^{-13}$ atm: see several reports in *Science*, January 30), D. H. LINDSLEY points out such a low fugacity need not be necessary for formation of pyroxferroite. Certainly iron-enrichment of the liquid is needed, and certainly the iron must remain in the ferrous state if it is to enter pyroxferroite.

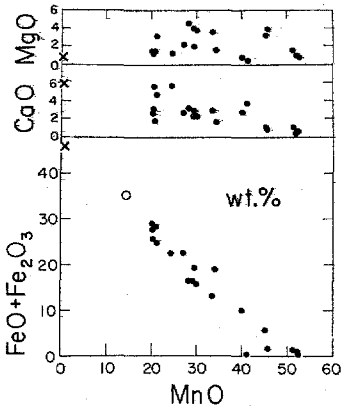

Fig. 3. Chemical relationships of Siebenerketten pyroxenoids. See Table 6 for the data for terrestrial minerals shown as solid dots. The cross shows the mean for the Apollo 11 data. The circle shows the FeO and MnO data for blast-furnace sample described by WHITELEY and HALLIMOND (1919).

However Lindsley suggests that oxygen fugacities as high as those for the fayalite–magnetite–quartz buffer should probably permit iron-enrichment of a basaltic magma and sufficient reduction of the iron.

Unfortunately the Agrell *et al.* group of investigators were unable to complete all their measurements in time for this paper but their preliminary results were published in the January 30, 1970 issue of *Science*. Briefly their preliminary optical study of specimens from rocks 10013, 10045 and 10058 indicated higher 2V and a more fibrous and curved character. The chemical analyses showed a zoning trend towards the diopside composition. Dr. S. O. Agrell and his co-workers will publish their complete results later, and these will include a detailed study of vogtite made some years ago as part of a Ph.D. program.

Prof. G. M. Brown of Durham University kindly stated that he and co-workers had found pyroxferroite in thin-section 10058-23 to be completely free of Mg and to have the atomic ratio Ca_{15} Fe_{85}. In another paper of this issue, microprobe analyses of other grains in 10058-23 and in 10045-35 show a higher Mg content than in Table 4.

Acknowledgments—We particularly thank Dr. M. Fleischer of the U.S. Geological Survey for assistance with literature review and advice on the nomenclature. Dr. D. H. Lindsley of New York State University at Stonybrook very kindly prepared a summary of the synthesis conditions of pyroxferroite.

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