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PYROXFERROITE: BREAKDOWN AT LOW PRESSURE AND HIGH TEMPERATURE;

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Heating experiments at 950-990°C confirm the hypothesis that lunar pyroxferroite is metastable at low pressures with respect to the three-phase assemblage Ca-rich clinopyroxene plus fayalite plus tridymite. Rate studies of the breakdown reaction may provide information on the cooling rates of lunar igneous rocks containing pyroxferroite.

The discovery of the new mineral pyroxferroite in a number of lunar igneous rocks has posed an enigma, for phase equilibrium studies had shown that synthetic Mg-free pyroxferroite is stable only at pressures greater than 10 kb (Lindsley & Burnham, Science, 1970). The lunar occurrences--late-stage minerals associated with tridymite, cristobalite, and glass in volcanic or near-surface rocks--strongly suggested, on the other hand, that the natural material crystallized at very low pressure. One possible explanation was that lunar pyroxferroite might be stabilized by minor constituents that are missing in the synthetic material. However, the metastable crystallization from synthetic glasses of Ca-Fe pyroxenoids approaching pyroxferroite in composition (Bowen, Schairer, and Posnjak, Am. J. Sci., 1933; see also Lindsley and Munoz, Am. J. Sci. 267A, 1969) suggested that pyroxferroite may have crystallized metastably and was then cooled so rapidly that a more stable assemblage was unable to form. This hypothesis received support from observations of an apparent breakdown symplectic--fayalite, a silica mineral, and a Ca-enriched metasilicate--after pyroxferroite (Ware and Lovering, Science, 1970) which indicates that at least some pyroxferroites may have cooled sufficiently slowly to permit transformation to a more stable assemblage.

Single crystals of pyroxferroite were separated from samples 12021,38 and 12021,109 by E. Dowty for Mössbauer studies. Selected crystals, from 0.1 to 0.2 mm, were mounted in epoxy, polished, and analyzed by electron microprobe for Fe, Ca, Mg, Si, Al, Ti, and Mn; the range of compositions $Wo_{12}En_{13}Fs_{75}$-$Wo_{14}En_{4}Fs_{82}$ is closely similar to that reported by Boyd et al. for another sample of rock 12021. Single-crystal precession x-ray diffraction photographs confirmed that the crystals are pyroxferroite; some showed minor amounts of oriented clinopyroxene (Table I). It is not yet clear whether this clinopyroxene occurs as fine lamellae or as epitaxial discrete crystals. Next the pyroxferroite crystals were wrapped in envelopes of $Ag_{70}Pd_{30}$ foil, sealed in evacuated silica-glass tubes, heated to temperatures ranging from 950-990°C, and quenched in water.

In initial experiments (14163, 14168, Table I), the crystals were converted to Fe-depleted clinopyroxene + tridymite, apparently by incongruent vaporization of FeO-rich components (although the silica-glass capsules were made as small as convenient, their capacity was approximately 10^5 times the volume of the pyroxferroite crystals). To counteract this effect, the free space within the capsules was reduced and a separate charge of synthetic pyroxferroite with several hundred times the mass of the lunar crystal was added. In experiments utilizing these precautions (14167 and 14166, Table I), one pyroxferroite crystal (14166) heated for a total of 5 days, 23 hours, at 960±3°C did not break down but did develop weak reflections in the x-ray diffraction photographs attributable to the appearance of oriented clinopyroxene. Another (14167) was transformed completely in 68.5 hours at 990±3°C to an intimate intergrowth of clinopyroxene + fayalite + tridymite (Fig. 1); the grain size of the clinopyroxene and fayalite was just coarse enough to be resolvable by electron microprobe techniques (analyses given in Table I). Precession photographs and optical examination reveal that the fayalite and tridymite occur as minute, randomly oriented inclusions within a single crystal of clinopyroxene that presumably formed topotaxially with respect to the parent pyroxferroite.

These preliminary findings may indicate that lunar basalts containing pyroxferroite have cooled to temperatures below 990°C in less than 3 days.

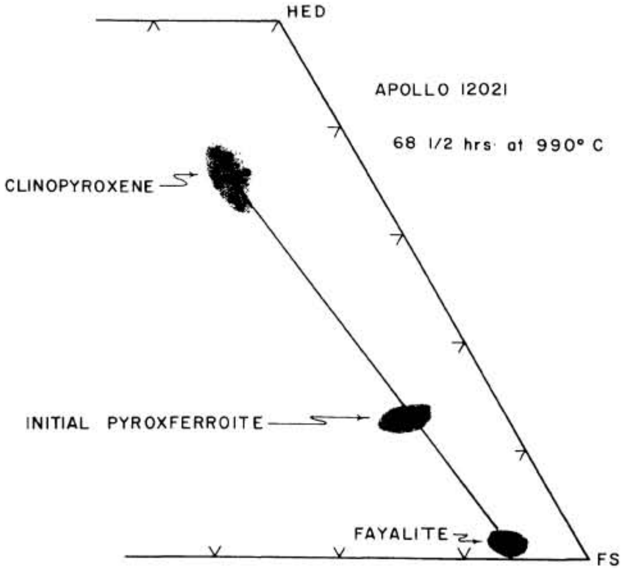

Fig. 1. Portion of pyroxene quadrilateral showing compositions of pyroxferroite crystal 14167, and of the breakdown products clinopyroxene and fayalite + tridymite (projected).

Pyroxferroite Breakdown

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Table I. Data for heating experiments on pyroxferroite.

Starting Materials Crystal No.	14163	14168	14167	14166
Probe Composition	$Wo_{12}En_{11}Fs_{77}$	$Wo_{13}En_{5}Fs_{82}$	$Wo_{12}En_{9}Fs_{79}$	$Wo_{12-13}En_{6-11}Fs_{76-81}$
Pyroxferroite				
a(Å)	6.62	6.62	6.64	6.64
b(Å)	7.53	7.55	7.56	7.55
c(Å)	17.36	17.39	17.40	17.37
α(deg)	114.1	114.2	114.1	114.1
β(deg)	82.8	82.7	82.8	83.1
γ(deg)	94.5	94.4	94.3	93.6
V($Å^3$)	783	786	791	789
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Pyroxene present in starting crystal	YES	NO	NO	NO
Temperature, °C	960±5	990±5	990±3	960±3
Duration	15d 11h	15d 11h	68½h	5d 23h
Run Products				Mainly pyroxferroite
Pyroxene	$Wo_{50}En_{37}Fs_{13}$	$Wo_{39}En_{35}Fs_{26}$	$Wo_{36}En_{11}Fs_{53}$	(minor pyroxene)
a(Å)	9.80	9.79	9.82	---
b(Å)	8.98	8.98	9.08	---
c(Å)	5.28	5.27	5.29	---
β(deg)	106.0	105.8	106.0	---
V($Å^3$)	447	446	453	---
Space Group	C^2/c	C^2/c	C^2/c	---
Tridymite	YES	YES	YES	---
Fayalite	NO	NO	Fo_7	---