INVESTIGATIONS OF PYROXFERROITE STABILITY IN LUNAR BASALTS;

Introduction. The conditions that allow pyroxferroite to form as a residual phase in lunar volcanic rocks remain an enigma. Pyroxferroite crystallizes as a late stage residual mineral in Apollo 11 low-K (1), Apollo 12 pigeonite porphyritic (2) and Apollo 15 quartz normative basalts QNBs (3). Pyroxferroite is a 7-repeat pyroxenoid (4) whose composition lies in the forbidden zone of the pyroxene quadrilateral. Lindsley and Burnham (5) determined that Ca.14 Fe.86 SiO3 becomes stable only at pressures greater than 10 kbar, and the stable low-pressure phase assemblage is fayalitic olivine, hedenbergite and a silica polymorph. Lunar pyroxferroites contain small amounts of Mg, Al and Ti. Lindsley and Burnham suggested that the addition of these other components would further reduce the pyroxferroite stability field.
Heating experiments on lunar pyroxferroite from 12021 (6) produced breakdown to the stable assemblage hedenbergite + fayalite + quartz at 990°C in 68 hours. The result led Lindsley et al. (6) to conclude that 12021 (and other pyroxferroite bearing basalts) cooled rapidly (to 990°C in 3 days) in order to preserve pyroxferroite. This conclusion was supported by the observation (7) that fayalite + silica + hedenbergite symplectites in Apollo 11 basalts were relict pyroxferroite grains that decomposed to the equilibrium assemblage on slow cooling. Cooling rate experiments on lunar basalts (8) indicate that pyroxferroite sometimes persists metastably under very slow cooling conditions. Basalts 12021 and 15065 contain mm-sized grains of pyroxferroite that show no evidence of breakdown to the stable assemblage. Cooling rate estimates for these basalts are <1°C/day. Several investigators (2,7,9) also concluded that textural evidence in 12021 suggested that pyroxferroite persisted under conditions of slow cooling. They observed that pyroxferroite coexisted with, clinopyroxene, plagioclase, a silica phase and oxides, but that fayalite was absent. Our own observations on 15065 (10) are that pyroxferroite crystallization is restricted to clinopyroxene-bounded pockets in which olivine did not nucleate. Other pockets in 15065 contain fayalitic olivine, tridymite and hedenbergite, but not pyroxferroite. This observation suggested the present set of experiments.

Experiments. A residual liquid composition (597-75) was chosen from a dynamic experiment on 15597 cooled from 1223°C to 1060°C at 0.5°C/hour. Glass starting material was prepared and used for equilibrium and controlled cooling rate experiments. This residual liquid should be a likely starting composition for inducing pyroxferroite crystallization, because it corresponds to the composition of the late stage liquid that crystallizes the groundmass phases, plagioclase, clinopyroxene, silica, ilmenite and ulvöspinel. Equilibrium and 0.5°C/hr cooling rate experiments were performed in high-purity Fe capsules. The experimental results were previously reported (10). Additional cooling rate experiments have been performed using Fe-Pt alloy loops and diopside crucibles. These experiments were run in CO-CO2 gas mixtures with fO2 monitored at iron-wüstite using CaO-ZrO2 oxygen cells.

Results. The results of the experiments are depicted in Fig. 1. Fayalitic olivine appears at 1049°C in equilibrium experiments. In dynamic crystallization experiments carried out in Fe capsules or using the Fe-Pt loop technique the temperature of olivine appearance is 1017°C. Thus, olivine crystallization temperature is suppressed by 30°C. The presence of olivine precludes the possibility of pyroxferroite crystallization, and the
abundant late stage phases in these experiments are hedenbergitic pyroxene, silica, plagioclase, ulvöspinel and ilmenite. We had hoped that the use of the glass bead and Fe-Pt alloy loop technique would further suppress olivine nucleation and allow the formation of pyroxferroite. Unfortunately this technique produced olivine crystallization at the same temperature as the Fe capsule experiments.

Previous investigators (2, 9) noted that pyroxferroite nucleated on clinopyroxene and suggested that the clinopyroxene substrate allowed pyroxferroite to grow outside of its stability field. To test this suggestion we fabricated a crucible from slabs of Tamela diopside and ran a cooling experiment at 1°C/hr from 1070°C to 904°C. This experiment produced clinopyroxene, plagioclase, silica, ilmenite, but fayalite was absent. The compositions of the pyroxenes produced in this experiment are shown in Fig. 2a. The zoning trend is similar to the groundmass pyroxene trend observed in slowly cooled Apollo 15 QBs, and a late-stage pyroxferroite-like phase is produced. This synthetically produced phase is slightly richer in iron than lunar pyroxferroites (Fig. 2b). X-ray diffraction patterns of the run product do not show the diagnostic peak for pyroxferroite (010). If there is a peak, it is barely distinguishable above background. Since the pyroxferroite-like phase constitutes a <10% of the run product, it may be present in quantities too small to be detected by x-ray.

Conclusions. Continued difficulties have been encountered in our endeavor to produce pyroxferroite as a late-stage low-pressure phase in lunar basalts. We have been able to suppress olivine nucleation by performing our experiments in diopside crucibles, and have produced a phase compositionally similar to pyroxferroite. We are now attempting to synthesize this material in large enough quantities to permit characterization by x-ray powder techniques.

FIGURE 2. A) Compositions of pyroxenes produced by cooling 597-75 glass in a diopside crucible at 1°C/hr and at an fO₂ near Fe-wüstite. The run also contained plagioclase, silica, ilmenite and ulvöspinel. Fayalite is absent. B) Compositions of pyroxferroite found in Apollo 11, 12 and 15 basalts.