

Synthesis of “large” pigeonite crystals for Lunar Spectroscopic and Space Weathering Studies

A. Sinclair,¹ D. H. Lindsley,¹ H. Nekvasil,¹ and T. Glotch.¹ Stony Brook University, Dept. of Geosciences, Earth and Space Science Building, Stony Brook, NY 11794. Alexandra.Sinclair@stonybrook.edu.

Introduction: Apollo and Luna samples as well as the lunar meteorites have provided invaluable information on the nature of mineral phases expected to be found on the Moon and potentially on other airless bodies. Detecting such minerals by remote sensing (using for example, infrared (IR) spectroscopy) requires well characterized mineral standards. Obtaining such standards is particularly challenging if a mineral abundant on such planetary bodies cannot be readily found on Earth, commonly undergoes changes (e.g., exsolution), or is found on Earth only over a limited compositional range.

Pigeonite has been described in a variety of Apollo samples, from those of the Apollo 12 pigeonite basalt suite [1] to samples from the Apollo 14 (e.g., [2]) and 15 landing sites (e.g., [3]). Pigeonite has also been reported in lunar meteorites (e.g., NWA 4936 [4] and 4884 [5]). These occurrences suggest that pigeonite is common in lithologies on the lunar surface and the ability to identify it remotely is important. Unfortunately, terrestrial pigeonite suitable for optical standards is not readily available. Pigeonite is stable only at elevated temperature. Under conditions of slow cooling (as in plutonic rocks) it readily exsolves to form two pyroxenes: high-Ca (augite) and low-Ca (either clinopyroxene or Opx). For these reasons, pure pigeonite on Earth is almost exclusively limited to relatively fine-grained volcanic rocks (and is thus, difficult to separate). Original pigeonite in coarser-grained plutonic rocks, has almost universally “inverted”, that is, it has exsolved to intergrowths of augite lamellae in a low-Ca (usually Opx) host.

In order to address the need for pigeonite standards we have launched a concerted effort to synthesize pigeonites for the planetary science community. The intent is to synthesize the pigeonites within their high-temperature stability field and then quickly cool them far below their breakdown/inversion temperatures. Done properly, this should yield a single phase (at least at the X-ray diffraction level) that is metastable with respect to two pyroxenes.

Experimental goals: Most natural pigeonites have calcium contents close to 10% (Wo_{10}), but with varying ratios of Fe/ (Fe + Mg). Our synthesis program focuses on the range of pigeonite compositions ($Ca_{0.1}(Mg_{1-x}Fe_x)_{0.9}Si_2O_6$ where $x = 0.60, 0.40, 0.30, \text{ and } 0.20$). These compositions are shown by the orange symbols in Fig. 1. A synthesis technique was sought that produces crystallites of these compositions with dimension

between 30 to 100 μm , making them suitable for a variety of infrared spectroscopic studies.

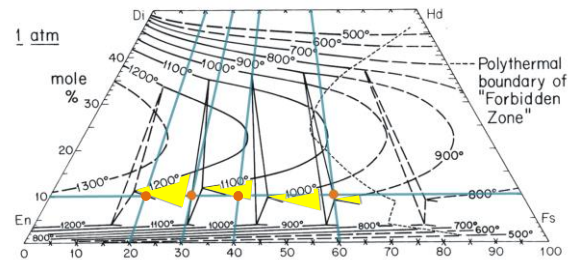


Figure 1. Target compositions of synthetic pigeonites (orange circles) superimposed upon the 1 atm pyroxene stability diagram of [6], with regions of low pressure pigeonite stability at various temperatures shaded in yellow.

Experimental Method: Stoichiometric mixes were prepared from dried $CaSiO_3$, MgO , Fe_2O_3 , SiO_2 , and “Fe-sponge”. The first four reagents were ground together for 2 hrs under ethanol in an agate mortar. Following this initial grinding, Fe-sponge, sufficient to convert all Fe_2O_3 to FeO , was added and homogenized by minimal amounts of additional grinding. These powders were first pre-reacted, which helps minimize the amount of unreacted starting material that could become trapped within the synthesized pyroxene [7]. Pre-reaction took place by loading each mix into an Ag foil “capsule” that had been loaded into a silica glass tube. Prior to sealing the tube, the samples were dried at 800°C under vacuum, (with a Fe-sponge “getter” to prevent oxidation) at $\sim 600^\circ\text{C}$ for 20 minutes to remove any moisture or residual ethanol from grinding. The tubes were then sealed while still under vacuum. These ampules were heated in a horizontal tube furnace at $\sim 900^\circ\text{C}$ for two weeks for this pre-reaction step.

After pre-reaction, the material was packed into Fe-capsules with tight-fitting lids, which were then inserted into silica glass tubes. The tubes were dried (with “getter”), evacuated, and sealed again, producing glass ampules. Because the thermal stability of pigeonite depends strongly on Fe/ (Fe+Mg) (see Fig. 1; also Fig. 6 in [8]), each composition was subjected to different thermal synthesis conditions for the final synthesis. Initially we attempted the final synthesis in the solid state, that is, at temperatures just below the solidus. These experiments yielded good pigeonites, but the grain size (≤ 30 microns) was smaller than desired.

To increase grain size, we heated the samples to between 50-20° C above the solidus temperature (Fig. 2) for 30 min. and then slowly (at approximately 1°C/hr) cooled them to just below the solidus temperature. The samples were held at this temperature for 3-5 days and then quenched in air. Temperature conditions for each composition are shown in Table 1.

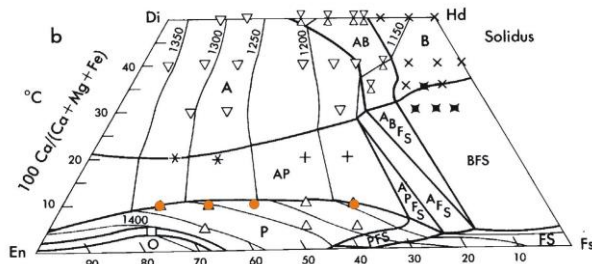


Figure 2. Solidus diagram (mol %) from [9] with target compositions indicated. P marks primary phase-field for pigeonite; AP shows primary phase field of augite plus pigeonite.

Target Composition		Initial <i>T</i> (°C)	Xln <i>T</i> (°C)
Wo ₁₀ En ₃₆ Fs ₅₄	(Ca _{0.1} Mg _{0.36} Fe _{0.54}) ₂ Si ₂ O ₆	1230	1180
Wo ₁₀ En ₅₄ Fs ₃₆	(Ca _{0.1} Mg _{0.54} Fe _{0.36}) ₂ Si ₂ O ₆	1270	1250
Wo ₁₀ En ₆₃ Fs ₂₇	(Ca _{0.1} Mg _{0.63} Fe _{0.27}) ₂ Si ₂ O ₆	1330	1280
Wo ₁₀ En ₇₂ Fs ₁₈	(Ca _{0.1} Mg _{0.72} Fe _{0.18}) ₂ Si ₂ O ₆	1370	1330

Table 1. Target compositions, with initial (super-solidus) temperatures and final crystallization temperatures.

Synthesis results:

All syntheses yielded sintered grey powders with individual grain sizes up to >100 microns in long dimension. Microscopic observations in index oil show only pyroxene with minor amounts of metallic Fe from the capsules. Powder X-ray diffraction patterns (Cu, K α source) index to the monoclinic space group $P2_1/c$, as shown in Fig. 3. *a* and *b* values depend largely on Ca (Wo) content, whereas *b* mainly reflects Fe/(Fe+Mg) [7]. Sharp peaks for (150) show little or no zoning in Fe/(Fe+Mg); and sharp peaks for (220), (311), and (310) likewise show minimal zoning of the pigeonite in Ca; and the peak positions fit well with the target compositions. However, weak shoulders at lower 2-theta on (220), (311), and (310) suggest the presence of minor (<<10%) amounts of higher-Ca augite in all samples. We conclude that the Wo₁₀ compositions for these samples probably fell just within the pigeonite + augite (AP) field of [9] at some stage during their synthesis; note that all compositions fall very close to the boundary between the P and AP fields of Fig. 2. We

plan to repeat the syntheses at very slightly lower Wo contents.

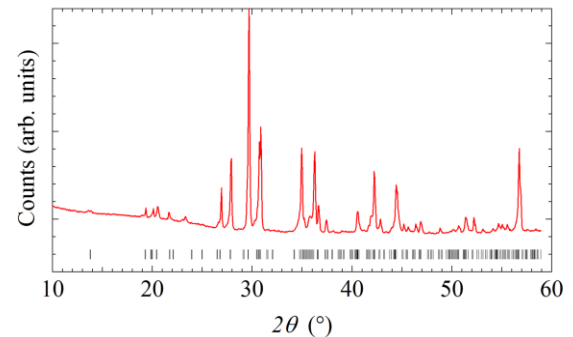


Figure 3. Powder diffraction pattern for Wo₁₀En₅₄Fs₃₆ in red. Black reflection markers for monoclinic space group $P2_1/c$ with lattice parameters $a = 9.732(1)$ Å, $b = 8.931(1)$ Å, $c = 5.2485(7)$ Å and $\beta = 108.583(7)^\circ$.

Acknowledgements: This work was supported by the RIS⁴E program, a SSERVI science team.

References: [1] Meyer, C. (2011) Lunar Sci. Compendium. [2] James, O.B. (1973) Geol. Soc. Prof. Paper 841. [3] Bouquain, S. & Arndt, N.T. (2006) Geophys. Res. Abstr. 00624. [4] meteorites.wustl.edu/lunar/stones/nwa4936.htm. [5] meteorites.wustl.edu/lunar/stones/nwa4884.htm. [6] Lindsley, D.H. (1983) Am. Min. **68**, 477. [7] Turnock, A., Lindsley, D.H., Grover, J.E. (1973) Am. Min. **58**, 50 [8] Davidson, P.M. & Lindsley, D.H. (1985) Contr. Min. Pet. **91**, 390. [9] Huebner, J.S. & Turnock, A. (1980) Am. Min. **65**, 225.