

## SYNTHESIS OF “LARGE” PIGEONITE CRYSTALS FOR LUNAR SPECTROSCOPIC AND SPACE WEATHERING STUDIES

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**Introduction:** We continue our efforts to synthesize pigeonites for use as standards in remote sensing. Our earlier attempts yielded substantial portions of pigeonite, but most samples were more magnesian (more En-rich) than the target compositions, and they were accompanied by detectable amounts of a silica phase and a high-Ca pyroxene and/or melt. In an attempt to grow relatively large crystals (~100 microns), we used near-solidus temperatures, and our results (especially evidence for melt at what should have been subsolidus conditions) led us to suspect – erroneously – that the published phase diagrams [1] might be in error. We have since learned that the problem stemmed from a relatively new supply of SiO<sub>2</sub> for our mixes: it is so coarse-grained that our standard grinding times (2-3 hours) were inadequate to reduce all grains to a size suitable for reaction with the other components during typical heating periods of 1 to 2 weeks. The presence of unreacted silica grains means that the remainder of the sample had significant olivine content, and we interpret that melting resulted from the cotectic between pigeonite and olivine. We now thoroughly grind the SiO<sub>2</sub> prior to combining it with the other components in our mixes, which appears to have solved the problem.

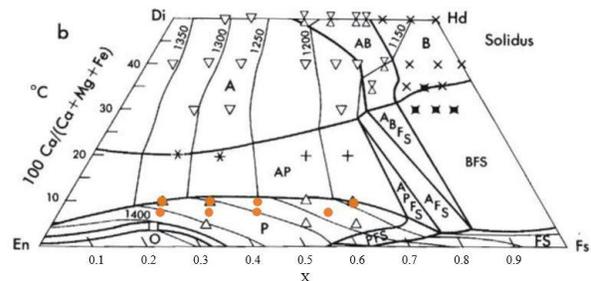
**Context:** Apollo and Luna samples as well as the lunar meteorites have provided invaluable information on the nature of mineral phases expected to be found on the Moon and potentially on other airless bodies. Detecting minerals on these bodies by remote sensing (using methods such as infrared (IR) spectroscopy) requires well characterized mineral standards.

Pigeonite has been described in a variety of Apollo samples, from those of the Apollo 12 pigeonite basalt suite [2] to samples from the Apollo 14 (e.g., [3]) and 15 landing sites (e.g., [4]). It has also been reported in lunar meteorites (e.g., NWA 4936 [5] and 4884 [6]). These occurrences suggest that pigeonite is common in lunar surface lithologies, making capacity for remote identification desirable. Unfortunately, terrestrial pigeonite suitable for optical standards is not readily available. Pigeonite is stable only at elevated temperature, and under conditions of slow cooling (as in plutonic rocks) readily exsolves to form high-Ca (augite) and low-Ca (clinohypersthene or orthopyroxene) pyroxenes. As a result, pure pigeonite on Earth is almost exclusively limited to relatively fine-grained volcanic rocks and is difficult to separate. Original pigeonite in

coarser-grained plutonic rocks is consistently “inverted”; that is, it has exsolved to intergrowths of augite lamellae in a low-Ca (usually orthopyroxene) host.

We have launched a concerted effort to synthesize pigeonite standards 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:** Many natural pigeonites have approximately 10% CaSiO<sub>3</sub> component (Wo<sub>10</sub>), but with varying ratios of Fe/(Fe+Mg), expressed here as X. Our synthesis program focuses on compositions with Wo<sub>8</sub> and Wo<sub>10</sub>, with a range of X between 0.2 and 0.6. The target compositions are shown in Figure 1.



**Figure 1:** Solidus diagram (mol%) from [1] with target compositions indicated in orange. P marks the primary phase field for pigeonite; AP marks the primary phase field of augite+pigeonite.

**Experimental Methods:** Stoichiometric mixes were prepared from dried CaSiO<sub>3</sub>, MgO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and “Fe-sponge”. To avoid the problem of coarse silica grains persisting unreacted during synthesis, we now grind the starting silica for several hours prior to weighing. The first four reagents were ground together for ~3 hrs under ethanol in an agate mortar. Fe-sponge, sufficient to convert all Fe<sub>2</sub>O<sub>3</sub> to FeO, was then added and homogenized by minimal additional grinding (30-40 minutes). We have found that if these oxide mixes are taken directly to final synthesis temperature, a significant amount of intermediate reaction products (e.g., silica phase; olivine; wüstite) becomes trapped within the growing pyroxene crystals and is therefore essentially unavailable for further reaction [7]. That problem is minimized by “pre-reaction” of the oxide mixes: each

powder was loaded into an Ag foil capsule which was placed in a silica glass tube; dried for 10 minutes at 800°C under vacuum (with a Fe-sponge “getter” at ~600°C to prevent oxidation); then sealed while still under vacuum and heated in a horizontal tube furnace at ~900°C for 10-21 days. This “pre-reaction” step produces an intermediate product mainly consisting of olivine, silica, and augite. That material was ground for 1-2 hours to yield a fine-grained sample suitable for final reaction at temperatures within the stability field for pigeonite of the appropriate X value.

After pre-reaction and grinding, the material was packed into Fe-capsules with tight-fitting lids, which were then inserted into silica glass tubes. The tubes were dried, evacuated, and sealed as for the pre-reaction. The thermal stability of pigeonite depends strongly on X (see Fig. 6 in [8]), so each composition was subjected to different thermal conditions during final synthesis.

**Synthesis Results:** We are just beginning to complete and analyze samples made with sufficiently fine-grained silica to permit complete reaction. The composition  $Wo_8 X=0.2$  reacted at a temperature (1150°C) well below the solidus yielded pigeonites 5-30 microns across – suitable for some but not all spectroscopic techniques. We attempted to produce larger grains by heating just above the solidus, followed by slow cooling to slightly below the solidus. A portion of that same  $Wo_8 X=0.2$  sample reheated slightly above the solidus temperature (1350°C); cooled over a period of 2 days to 1330°C; and held at temperature for 4 days produced excellent crystals 80-120 microns across with only small amounts of poorly quenched melt. Microprobe analysis is needed to determine the extent of zoning (if any), but it appears as if we now have a suitable protocol for producing gram quantities of pigeonites with usable grain sizes.

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