

SUPPLEMENTARY MATERIALS (LINDSLEY ET AL. PIGEONITE)

Starting materials. We used CaSiO_3 as the source of CaO in the mix (because CaO has a high affinity for moisture in the air, and thus cannot be weighed accurately into a mix). To make CaSiO_3 we mixed equimolar amounts of CaCO_3 and SiO_2 , and ground them together. To get rid of CO_2 , we heated the mix slowly (over 1-2 days) to $\sim 1300^\circ\text{C}$, holding it at that temperature for at least one week. (Slow heating is essential to prevent violent decarbonation, which would cause loss of sample.) The amount of SiO_2 weighed into the final mixes was adjusted for the amount contributed by CaSiO_3 .

The Fe sponge used in the mixes contains 2.293 wt % oxygen. This was determined by reducing sponge under a stream of hydrogen at 800°C ; the oxygen content was calculated from both the weight loss of the sponge and the weight gain of a small u-tube filled with magnesium perchlorate. Analyzed sponge was stored in an evacuated desiccator to minimize additional gain of oxygen.

“Pre-reaction” of starting mixes. The mixtures were placed in silver-foil-lined silica-glass tubes sealed at one end. Typically each tube held 2 to 3 grams of mix. A capillary was drawn above the sample and pieces of freshly reduced Fe^0 sponge were placed at the top of the capillary to prevent oxidation. The tube and its contents were dried under vacuum at 800°C for 10 minutes with the iron “oxygen getter” at $\sim 600^\circ\text{C}$. The tubes were then sealed under vacuum at the capillary by a torch and placed in a horizontal furnace at $900\text{--}920^\circ\text{C}$ (safely below the melting temperature of silver) for approximately 2 weeks. Although the stable assemblage for

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pigeonite bulk composition at 900-920 °C is augite (high-Ca clinopyroxene) + orthopyroxene, the latter rarely nucleates in experiments at low pressure, so the products of pre-reaction were augite, olivine, and quartz.

Details of final synthesis. Most samples required multiple cycles of heating and grinding to produce the materials reported here. Details are given in Table S1. Microprobe analyses are in Table S2. The Mn contents of most samples are greater than the detection limit of ~600 ppm. The Mn was probably introduced by exchange with the Fe capsules, which contain 0.16 wt. % Mn for most (13 ppm in the capsules for $\text{Wo}_{10}\text{X}=\text{60 T}$). Note that that last sample has reported MnO contents only 1 to 2 times the detection limit.

Most samples plot to the Mg-rich side of the target composition; one possible explanation (suggested by Steve Huebner) is that reducing components present in the Fe capsules may have reduced a small fraction of the FeO in the starting materials; that hypothesis is consistent with the excess SiO_2 present in all samples. According to the manufacturer, the capsules for $\text{Wo}_{10}\text{X}=\text{60 T}$ contain 100 ppm C, 67 ppm S, and 49 ppm Si – any of which might have reducing capacity.

X-ray diffraction. XRD data were collected in steps of $0.01^\circ 2\theta$ and a scan speed of $4^\circ/\text{minute}$. (Tests showed that slower scanning speeds did not significantly improve the quality of the data.) The cell parameters we report here are one to two orders of magnitude more precise (and probably more accurate) than those given by Turnock et al. (1973). In the three cases where

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direct comparison is possible, our unit cells are slightly larger than those reported by Turnock et al (1973, Table 2); some of the differences exceed the uncertainties reported by the earlier workers. We believe that the differences between our results and those of Turnock et al. (1973) largely reflect technical improvements in the intervening 45 years. Turnock et al. (1973) estimated peak positions from strip charts, and were only able to read and index peaks up to $\sim 75^\circ$ 2θ ($d \approx 1.265 \text{ \AA}$ for Cu radiation). We collected data to $128^\circ 2\theta$ ($d \approx 0.86 \text{ \AA}$) and had the luxury of a computer to locate and index the peaks, thereby obtaining far more (and more precise) data. We were also able to use both the $K\alpha_1$ and $K\alpha_2$ peaks.

To the extent that the differences between our results and those of Turnock et al. (1973) are real (that is, not due to analytical uncertainty), we suggest that their samples may have lost iron during synthesis as their samples were made by suspending pellets in a CO-CO₂ gas mixture (an open system). Fe loss through the formation of Fe(CO)₅ as a gaseous species in a gas-mixing furnace is a problem not widely recognized in gas-mixing experiments but observed over the years by one of us (DHL). Although details of the Turnock et al. (1973) syntheses are no longer available, DHL recalls that the authors had to use multiple cycles of heating and grinding that would have enhanced Fe loss through this process. Loss of Fe would result in smaller unit cells. A reviewer suggested additional possible explanations for the disagreements: incorrect estimation of diffractometer zero; and overlapping $K\alpha_1$ and $K\alpha_2$ peaks. Turnock et al. (1973) used $K\alpha$ ($\lambda = 1.54178 \text{ \AA}$) for peaks below $30^\circ 2\theta$ and were able to separate $K\alpha_1$ and $K\alpha_2$ peaks at higher angles. Our refinements used the Match!3 program to make that distinction.

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We were able to locate one of the original Turnock et al. (1973) XRD slides (Wo₁₀ X = 30; Turnock's E13-G2) and x-rayed it under the same conditions as we used for our samples. The results are shown in the table below

Wo ₁₀ X=30	a	b	c	Beta	Volume
Our data (Wo ₁₀ X=30 I)	9.6918(5)	8.9084(4)	5.2300(2)	108.487(4)	428.246(7)
Turnock et al. (1973) (E13-G2)	9.684(3)	8.907(2)	5.227(2)	108.51(2)	427.6(3)
Turnock sample x-rayed 2018	9.6885(20)	8.9056(17)	5.2298(10)	108.535(15)	427.827(14)

This comparison, shows that our analysis of the Turnock et al. (1973) sample is very similar to their analysis. This suggests that the differences may be due more to compositional differences than differences in XRD technique and refinement. We note that the uncertainties for the Turnock et al. (1973) sample measured in 2018 are 2 to 4 times larger than those for our sample; this might result from lower crystallinity or larger compositional variation in his sample – or both.