

1 **Supporting information**

2 *Rietveld refinement parameters*

3 The nesquehonite structure is taken from Giester et al. (2000). Peaks were modelled using the  
4 pseudo-Voigt function and the model of Stephens (1999) to account for anisotropic peak  
5 broadening for nesquehonite. The temperatures reported for nesquehonite decomposition during  
6 X-ray diffraction experiments were defined based on loss of most diffraction peaks, including the  
7 overlapping (1 0 1) and (1 0 1) peaks. This excluded the (0 2 1) peak of nesquehonite ( $40^\circ 2\theta$ )  
8 which persisted following the loss of all other nesquehonite peaks. From a crystal chemistry  
9 perspective, a sample containing only the (0 2 1) peak is no longer nesquehonite. Structureless  
10 pseudo-Voigt peaks were fitted to the background to account for the appearance of unidentified  
11 X-ray amorphous phase/s directly following the decomposition of nesquehonite. The  
12 oxymagnesite ( $3\text{MgO}\cdot 2\text{CO}_2$ ) structure was taken from Watabe et al. (2009), and the structures for  
13 magnesite ( $\text{MgCO}_3$ ), periclase ( $\text{MgO}$ ) and corundum are from the International Centre for  
14 Diffraction Data Powder Diffraction Files (ICDD PDF-2).

15 The March-Dollase model (Dollase, 1986; March, 1932) was used to model the preferred  
16 orientation of crystallites, while a 5<sup>th</sup> order Chebychev polynomial and a  $1/x$  function were used  
17 to fit the background. For quantitative laboratory experiments 6 x 10 second data sets were  
18 summed together to improve particle statistics for quantitative analysis. Due to poorly resolved  
19 peaks for periclase (which overlap with magnesite), onset of periclase is reported when the phase  
20 is higher than ~10 wt%, while remaining phases are reported at >1 wt% (the detection limit of  
21 XRD).

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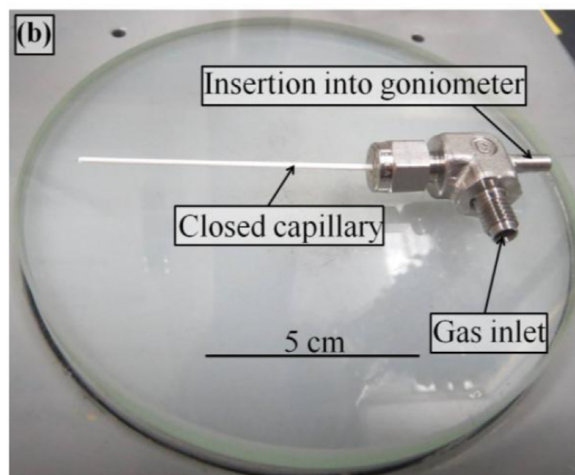
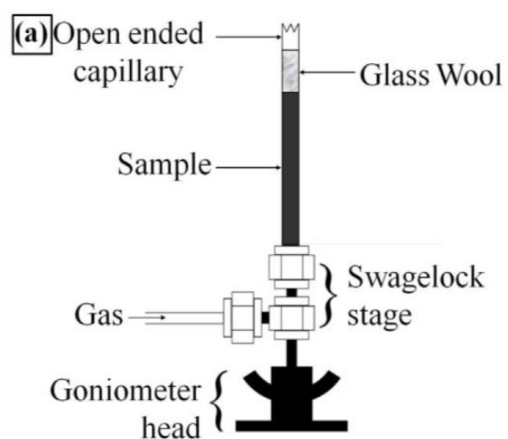
**Table S1:** Quantitative XRD data for the maximum wt% of system phases and the range of temperatures, over which they persist, in the thermal decomposition of nesquehonite between 25–650°C in an open system, or a closed system, fed with either 100% N<sub>2</sub> or 100% CO<sub>2</sub>.

	Open		Closed	
	100% N <sub>2</sub>	100% CO <sub>2</sub>	100% N <sub>2</sub>	100% CO <sub>2</sub>
Nesquehonite	97wt% (RT–139°C)	95wt% (RT–141°C)	85wt% (RT–170°C)	85wt% (RT–181°C)
Oxymagnesite	3.2wt% (326–459°C)	4.4wt% (321–520°C)	3.1wt% (322–497°C)	3.3wt% (322–493°C)
Magnesite	Not formed	51wt% (400–567°C)	15wt% (442–525°C)	32wt% (409–530°C)
Periclase	32wt% (379–600°C)	30wt% (507–600°C)	31wt% (481–600°C)	31wt% (505–600°C)
Amorphous	88wt% (RT–459%)	87wt% (RT–487%)		

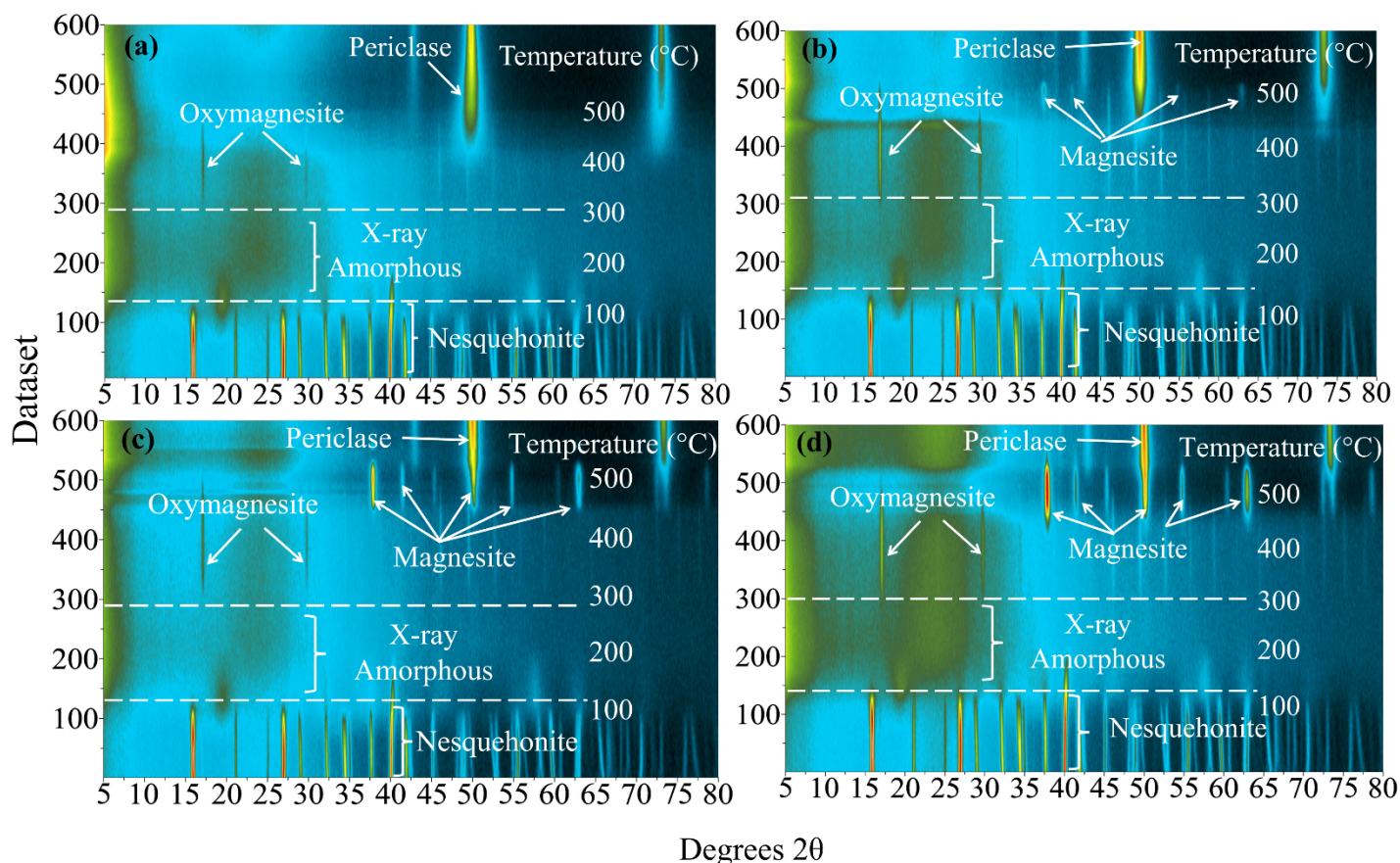
\* Values = maximum wt% (temperature range)

RT = Room temperature

Amorphous values corrected for gas loss



**Figure S1:** Preparation of nesquehonite into a (a) open, and (b) closed cell for XRD experiments.



**Figure S2:** Laboratory based in situ X-ray diffraction data displayed in surface plots (viewed down the intensity axis), for thermal decomposition of synthetic nesquehonite between 25–650°C with a temperature ramp rate of 5°C/min. Nesquehonite (N) was heated in open-ended quartz capillaries (1 mm diameter) with (a) 100% N<sub>2</sub> (b) 15% CO<sub>2</sub> in N<sub>2</sub> (c) 50% CO<sub>2</sub> in N<sub>2</sub> and (d) 100% CO<sub>2</sub> continuously flushed over the sample. Other crystalline phases include oxymagnesite (MgO·2MgCO<sub>3</sub>), magnesite (MgCO<sub>3</sub>) and periclase (MgO).