In situ synchrotron XRD analysis of the kinetics of spodumene phase transitions

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ELECTRONIC SUPPLEMENTARY MATERIAL

S1 Australian Synchrotron technical information

In this section we provide the technical specifications of the powder X-ray diffraction beamline at the Australian Synchrotron, in addition to the calibration curve provided to convert the set-point temperature of the FMB Oxford hot-air blower to the operating temperature.

Table S1 Technical specifications of the PXRD beamline.

Source	Bending magnet
Available energy range	5-30 keV (0.41-2.4 angstroms)
Mirrors	Si, Rh, Pt coated

	2-3 mrad incidence angle
	VCM - collimates beam
	VFM - focuses beam in vertical
DCM	Si(111) flat crystal pair, energy range 5-20 keV Si(311) flat/bent crystal pair, energy range 7-30 keV
Nominal beam size at sample	(horizontal x vertical) 5 mm (H) x 2 mm (V) Unfocussed <0.5 mm (H) x <0.5 mm (V) Focussed
Harmonic content	<1% in the case of two mirrors

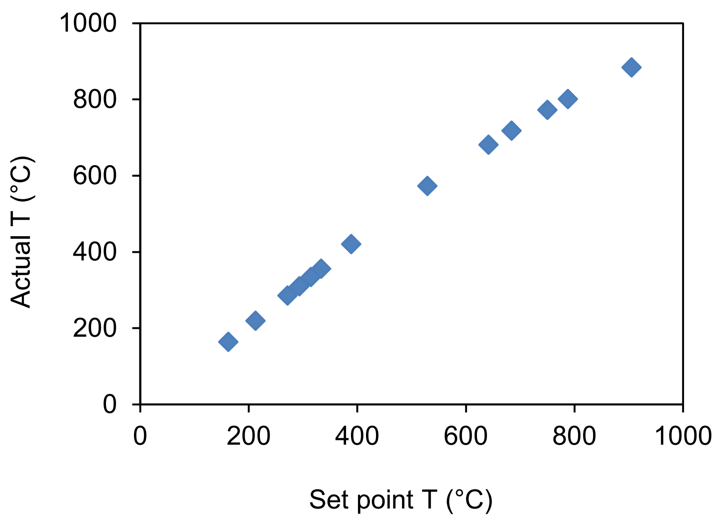


Fig. S1 Calibration curve for the hot-air blower set-point provided by the Australian Synchrotron.

S2 XRD patterns of the pure phases of spodumene

For our analysis of the phase distribution of α-, β-, and γ-spodumene, we selected peaks in the XRD pattern unique to each phase. This section illustrates the profiles of the three phases individually, as generated from their CIF files, in addition to providing their crystal structures and unit cell parameters. The unique peaks selected for identification of each phase is marked by an asterisk.

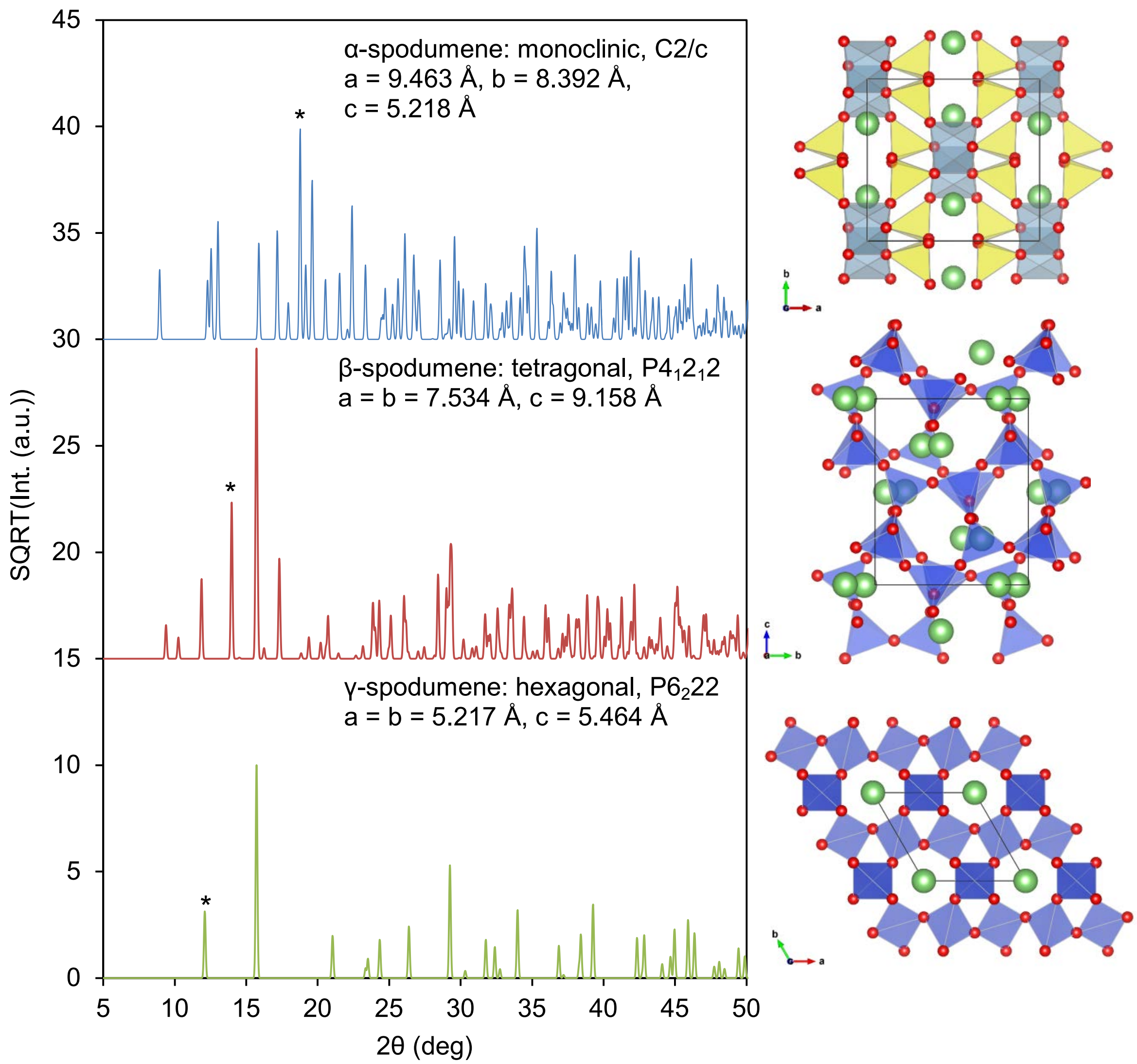
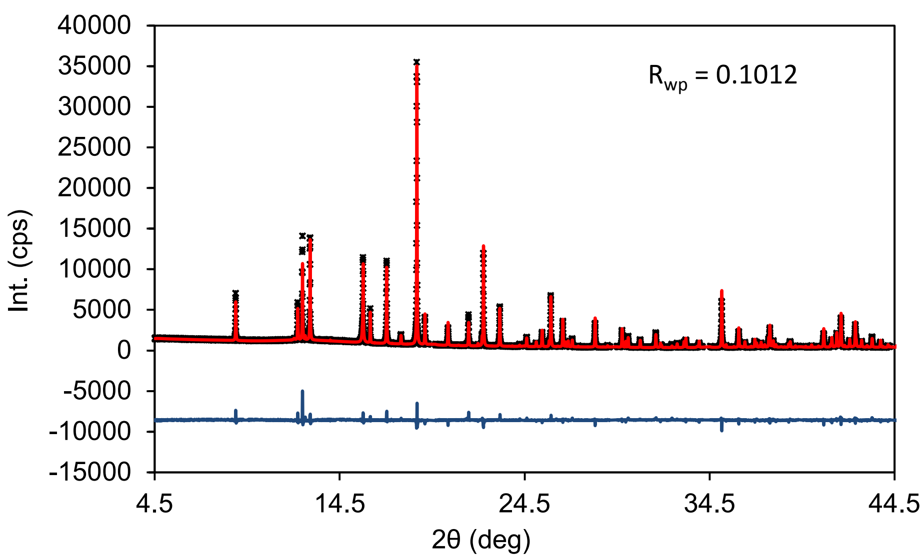


Fig. S2 XRD profiles and crystal structures of the three phases of spodumene: (a) α-spodumene,[1] (b) β-spodumene,[2] and (c) γ-spodumene.[3] Diffractograms are vertically offset by 15 units for clarity. Si positions are shown in yellow and Al positions in grey in α-spodumene. (Al,Si)O_4 tetrahedrons in which Al,Si are distributed randomly in a 1:2 ratio are in blue. Li is shown in green and O in red. Crystallographic structures prepared using Vesta.[4] Peaks used to monitor the respective phases are shown with asterisks (*).

1. M. Cameron, S. Sueno, C. T. Prewitt and J. J. Papike, *American Mineralogist*, 1973, **58**, 594-618.
2. P. T. Clarke and J. M. Spink, *Zeitschrift fur Kristallographie, Bd.*, 1969, **130**, S. 420-426.
3. C.-T. Li, *Zeitschrift für Kristallographie*, 1968, **127**, 327-348.
4. K. Momma and F. Izumi, *Journal of Applied Crystallography*, 2011, **44**, 1272-1276.

S3 Further information on Rietveld refinements

Two examples of typical Rietveld refinement results are shown (Fig. S3), illustrating the calculated patterns fit the observed pattern well.



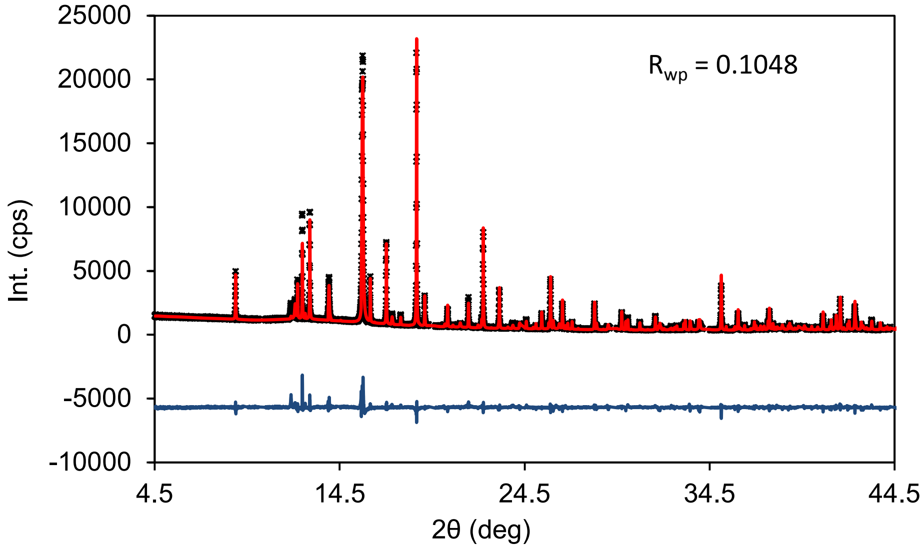


Fig. S3 Examples of refined peaks indicating observed pattern (crosses), calculated pattern (red) and difference (blue). The difference is offset for clarity.

S4 *Ex situ* XRD patterns

Ex situ XRD experiments were performed to determine the long term stability of the γ-spodumene phase. The XRD patterns, as obtained, are given in Fig. S4.

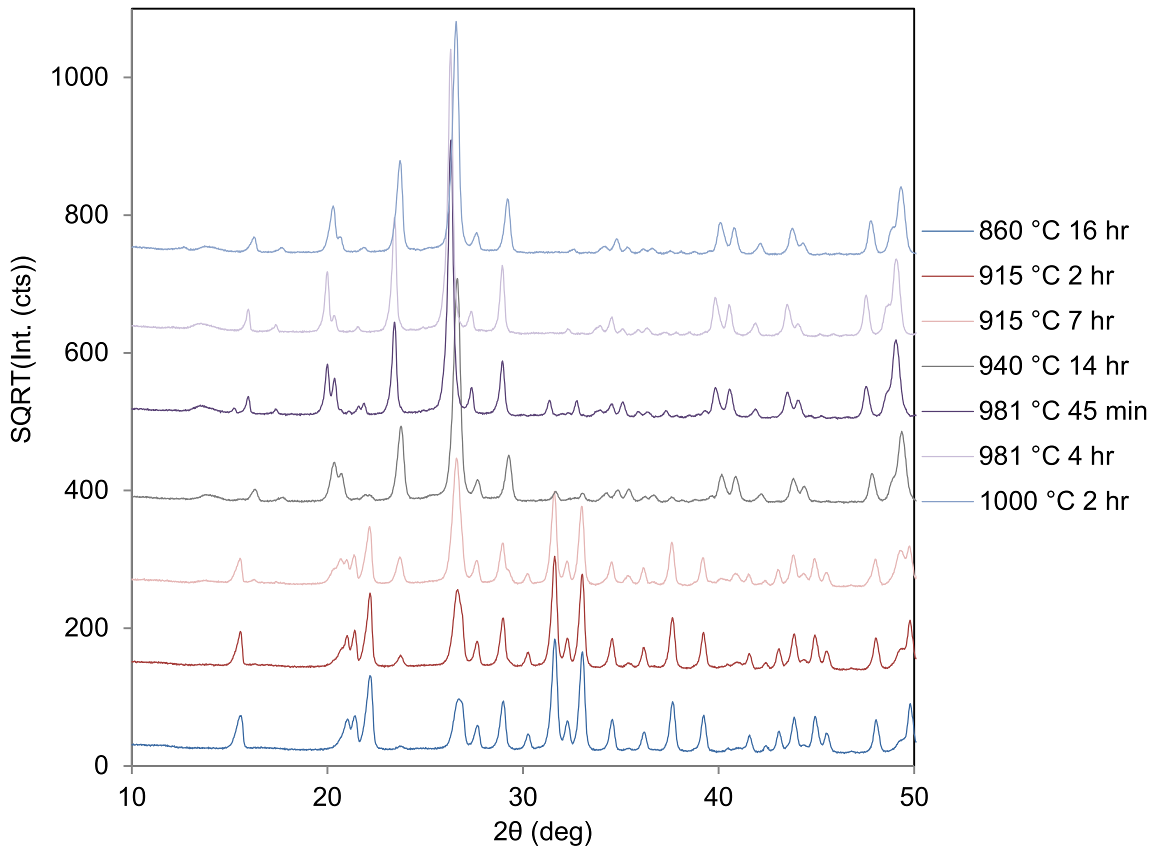


Fig. S4 XRD patterns observed during *ex situ* experiments. Diffractograms have been truncated to the range of 10 to 50 ° 2θ and are offset for clarity.

S5 Full derivation of rate equations

The complete derivation of the expressions for f_α, f_β, and f_γ are provided in this section. As noted in the text, the decay of f_α is described by the standard first-order kinetic model:

$$\frac{df_\alpha}{dt} = -k_1 f_\alpha$$

Integrating and using the initial condition $f_\alpha(t = 0) = 1$ yields:

$$f_\alpha = exp(-k_1 t)$$

The decay of α-spodumene is given by the transformation scheme:

$$\alpha \overset{k_1}{\rightarrow} \phi\beta + (1-\phi)\gamma$$

The subsequent decay of γ-spodumene is also assumed to have first order kinetics:

$$\gamma \overset{k_2}{\rightarrow} \beta$$

Following the stoichiometry of the transformation schemes, the rate of change in f_β is given by:

$$\frac{df_\beta}{dt} = \phi k_1 f_\alpha + k_2 f_\gamma$$

Since $f_\gamma = 1 - f_\alpha - f_\beta$:

$$\frac{df_\beta}{dt} = \phi k_1 f_\alpha + k_2\left(1 - f_\alpha - f_\beta\right)$$

$$= k_2 + (\phi k_1 - k_2)\, f_\alpha - k_2 f_\beta$$

$$= k_2 + (\phi k_1 - k_2)\, exp(-k_1 t) - k_2 f_\beta$$

$$\therefore\ exp(k_2 t)\frac{df_\beta}{dt} + k_2 f_\beta\, exp(k_2 t) = k_2(k_2 t) + (\phi k_1 - k_2)\, exp\big((k_2 t - k_1)t\big)$$

$$\therefore\ \frac{d}{dt}\left[f_\beta\, exp(k_2 t)\right] = k_2 exp(k_2 t) + (\phi k_1 - k_2)\, exp(k_2 t - k_1 t)$$

$$\therefore f_\beta\, exp(k_2 t) = exp(k_2 t) + \frac{\phi k_1 - k_2}{k_2 - k_1} exp(k_2 t - k_1 t) + C_1$$

$$\therefore f_\beta = 1 + \frac{\phi k_1 - k_2}{k_2 - k_1} exp(-k_1 t) + C_1 exp(-k_2 t)$$

C_1 is determined by observing the initial condition: $f_\beta = 0\ at\ t = 0$.

$$\therefore\ C_1 = -\frac{(\phi k_1 - k_2)}{k_2 - k_1} - 1 = \frac{-\phi k_1 + k_2 - k_2 + k_1}{k_2 - k_1} = \frac{k_1(1-\phi)}{k_2 - k_1}$$

$$f_\beta = \frac{(\phi k_1 - k_2)}{k_2 - k_1} exp(-k_1 t) + 1 + \frac{k_1(1-\phi)}{k_2 - k_1} exp(-k_2 t)$$

$$f_\beta = -\left[\frac{k_1(1-\phi)}{k_2-k_1}+1\right]exp(-k_1t)+1+\frac{k_1(1-\phi)}{k_2-k_1}exp(-k_2t)$$

$$f_\beta = -\left[\frac{k_1(1-\phi)}{k_2-k_1}\right]exp(-k_1t)+[1-exp(-k_1t)]+\frac{k_1(1-\phi)}{k_2-k_1}exp(-k_2t)$$

$$f_\beta = \frac{k_1(1-\phi)}{k_2-k_1}[exp(-k_2t)-exp(-k_1t)]+[1-exp(-k_1t)]$$

$$f_\beta = \frac{k_1(1-\phi)}{k_2-k_1}[exp(-k_2t)-f_\alpha]+[1-f_\alpha]$$

Since $f_\gamma = 1-f_\alpha-f_\beta$, we see by inspection that

$$f_\gamma = -\frac{k_1(1-\phi)}{k_2-k_1}[exp(-k_2t)-f_\alpha]$$

We note that

$$exp(-k_2t) = [exp(-k_1t)]^{k_2/k_1} = f_\alpha^{\;k_2/k_1}$$

Therefore we can rearrange the equation for f_β as

$$f_\beta = \frac{k_1(1-\phi)}{k_2-k_1}\left[f_\alpha^{\;k_2/k_1}-f_\alpha\right]+[1-f_\alpha]$$

$$= \frac{(1-\phi)}{k_2/k_1-1}\left[f_\alpha^{\;k_2/k_1}-f_\alpha\right]+[1-f_\alpha]$$

And

$$f_\gamma = \frac{-(1-\phi)}{k_2/k_1-1}\left[f_\alpha^{\;k_2/k_1}-f_\alpha\right]$$

S6 Binomial expansion of f_γ

Consider

$$f_\gamma = \frac{-(1-\phi)}{\kappa - 1}\left[f_\alpha^\kappa - f_\alpha\right]$$

We can write

$$f_\alpha^\kappa - f_\alpha = f_\alpha\left(f_\alpha^{\kappa-1} - 1\right)$$

The solution to the model can be written as

$$\frac{1}{1-\phi} \cdot \frac{f_\gamma}{f_\alpha(1-f_\alpha)} = \frac{1}{(\kappa-1)} \cdot \frac{1-f_\alpha^{\kappa-1}}{1-f_\alpha}$$

Substitute

$$x = 1 - f_\alpha$$

$$r = -(\kappa - 1)$$

Then we obtain

$$\frac{1}{(\kappa-1)} \cdot \frac{1-f_\alpha^{\kappa-1}}{1-f_\alpha} = \frac{-1}{r} \cdot \frac{1-(1-x)^{-r}}{x}$$

Now, since $|x| < 1$ we can use the negative binomial series as

$$(1-x)^{-r} = 1 + rx + \frac{1}{2!}r(r+1)x^2 + \frac{1}{3!}r(r+1)(r+2)x^3 + \cdots$$

we obtain

$$\frac{-1}{r} \cdot \frac{1-(1-x)^{-r}}{x} = \frac{rx\left[1 + \frac{1}{2!}(r+1)x + \frac{1}{3!}(r+1)(r+2)x^2 + \cdots\right]}{rx}$$

$$= 1 + \frac{1}{2!}(r+1)x + \frac{1}{3!}(r+1)(r+2)x^2 + \cdots$$

Reverting to our original variables, we obtain

$$\frac{1}{1-\phi}\cdot\frac{f_\gamma}{f_\alpha(1-f_\alpha)} = 1 + \frac{1}{2!}(2-\kappa)(1-f_\alpha) + \frac{1}{3!}(2-\kappa)(3-\kappa)(1-f_\alpha)^2 + \cdots$$