Kinetics of spodumene recrystallisation

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This presentation reviews kinetic models that cast the decrepitation of α-spodumene to β-spodumene in terms of simple, and easy to apply, mathematical equations. This presentation also reveals the predictions from the models and their limitations, for typical operating conditions of the kilns in lithium refineries.

ALTA 2024, Perth, Australia (30 May 2024)

Presentation outline

1. Introduction

- Energy requirements and decarbonisation
- Spodumene polymorphs
- Mechanism of calcination (Abdullah et al., 2019)
- XRD models
- DTA/DSC-based models

2a. Kinetic models

- Model of Fosu, Kanari, Bartier, Hodge, Vaughan and Chagnes (Fosu et al., 2021)
- Model of Moore, Mann, Montoya and Haynes (Moore et al., 2018)
- Model of Botto, Cohen Arazi and Frenkel (Botto et al., 1975)

2b. Crucial information

- Experimental measurements
- Mechanism and kinetic parameters
- Predictions and fit to own data
- Comparison with experiments (Peltosaari et al., 2015)

3. Summary remarks

- Lack of particle size dependence; amorphous vs crystalline pathways
- Diffusion limitation
- Importance of recrystallisation of *β*-spodumene
- Effect of additives

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.
Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.
Dessemond, C., Soucy, G., Harvey, J.-P., Ouzilleau, P., Phase transitions in the α–γ–β spodumene thermodynamic system and impact of γ-spodumene on the efficiency of lithium extraction by acid leaching. Minerals, 2020, **10**, 519.
Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423.
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Peltosaari, O., Tanskanen, P., Heikkinen, E.-P., Fabritius, T., α → γ → β-phase transformation of spodumene with hybrid microwave and conventional furnaces. Minerals Engineering, 2015, **82**, 54-60.
Salakjani, N.K., Singh, P., Nikoloski, A.N., Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: Conventional heating. Minerals Engineering, 2016, **98**, 71-79.

1. Introduction

- Energy requirements and decarbonisation

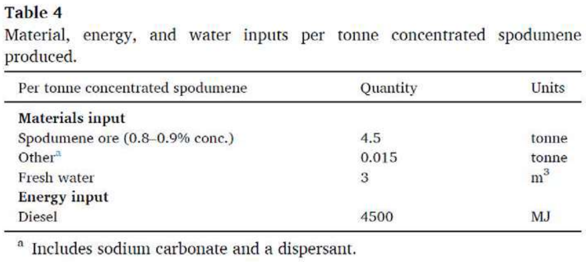


Table 4

Material, energy, and water inputs per tonne concentrated spodumene produced.

Per tonne concentrated spodumene	Quantity	Units
Materials input		
Spodumene ore (0.8–0.9% conc.)	4.5	tonne
Other[a]	0.015	tonne
Fresh water	3	m^3
Energy input		
Diesel	4500	MJ

[a] Includes sodium carbonate and a dispersant.

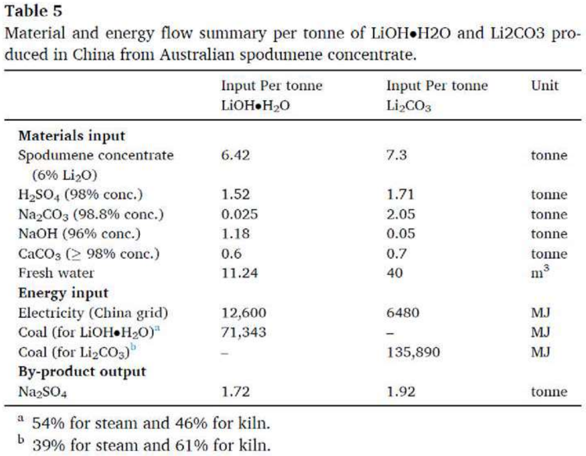


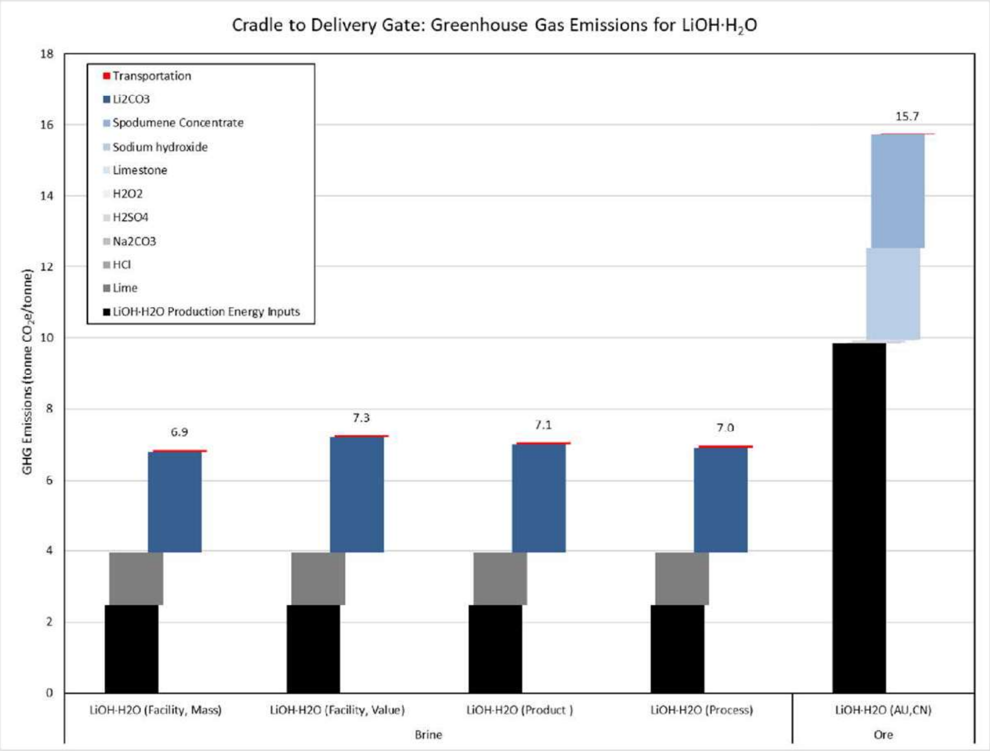
Table 5

Material and energy flow summary per tonne of LiOH•H2O and Li2CO3 produced in China from Australian spodumene concentrate.

	Input Per tonne $LiOH{\bullet}H_2O$	Input Per tonne Li_2CO_3	Unit
Materials input			
Spodumene concentrate (6% Li_2O)	6.42	7.3	tonne
H_2SO_4 (98% conc.)	1.52	1.71	tonne
Na_2CO_3 (98.8% conc.)	0.025	2.05	tonne
NaOH (96% conc.)	1.18	0.05	tonne
$CaCO_3$ ($\geq$ 98% conc.)	0.6	0.7	tonne
Fresh water	11.24	40	m^3
Energy input			
Electricity (China grid)	12,600	6480	MJ
Coal (for $LiOH{\bullet}H_2O$)[a]	71,343	–	MJ
Coal (for Li_2CO_3)[b]	–	135,890	MJ
By-product output			
Na_2SO_4	1.72	1.92	tonne

[a] 54% for steam and 46% for kiln.

[b] 39% for steam and 61% for kiln.



Kelly, J.C., Wang, M., Dai, Q., Winjobi, O., Energy, greenhouse gas, and water life cycle analysis of lithium carbonate and lithium hydroxide monohydrate from brine and ore resources and their use in lithium ion battery cathodes and lithium ion batteries. Resources, Conservation & Recycling, 2021, **174**, 105762.

1. Introduction

- Spodumene polymorphs

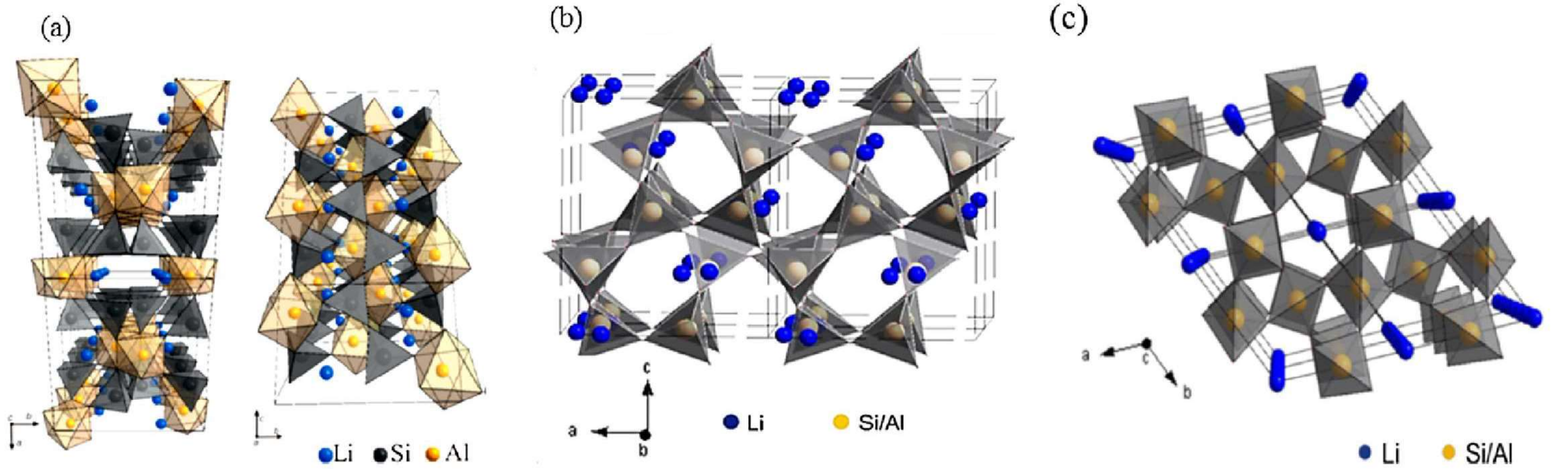
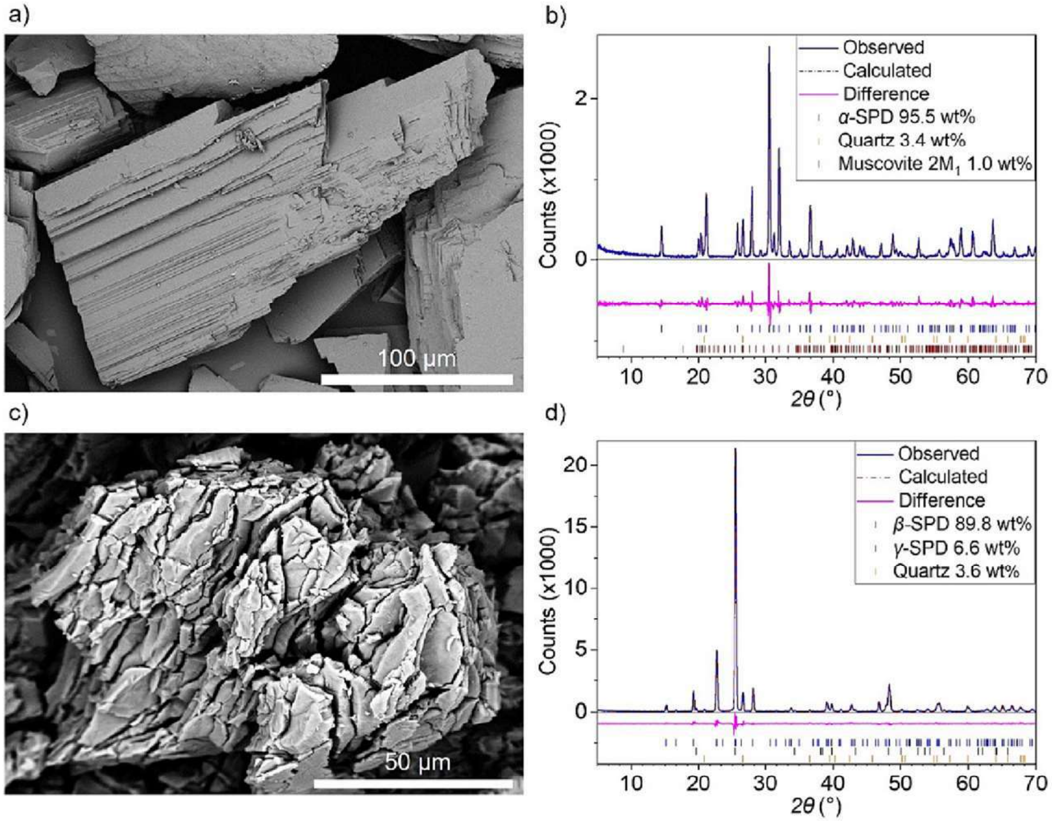


Fig. 1. Graphical representation of the structures of (a) α-spodumene of $V = 389.15\ \text{Å}^3$ and $\rho = 3.160\ \text{g cm}^{-3}$ (Clark et al., 1969), (b) β-spodumene of $V = 520.67\ \text{Å}^3$ and $\rho = 2.365\ \text{g cm}^{-3}$ (Li and Peacor, 1968), and (c) γ-spodumene of $V = 128.79\ \text{Å}^3$ and $\rho = 2.395\ \text{g cm}^{-3}$ (Li, 1968). (after Welsch et al., 2015).

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.
Clarke, P.T., Spink, J.M., The crystal structure of β spodumene, $LiAlSi_2O_6$-II. Zeitschrift für Kristallographie, 1969, **130**, 420-426.
Li, C.-T., The crystal structure of $LiAlSi_2O_6$ III (high-quartz solid solution). Zeitschrift für Kristallographie 1968, **127**, 327-348.
Li, C.-T., Peacor, D.R., The crystal structure of $LiAlSi_2O_6$-II ("β spodumene"). Zeitschrift für Kristallographie, 1968, **126**, 46-65.
Welsch, A.-M., Murawski, D., Prekajski, M., Vulic, P., Kremenovic, A., Ionic conductivity in single-crystal $LiAlSi_2O_6$: influence of structure on lithium mobility. Physics and Chemistry of Minerals, 2015, **42**, 413-420.

1. Introduction

- Spodumene polymorphs (2)



Before calcination

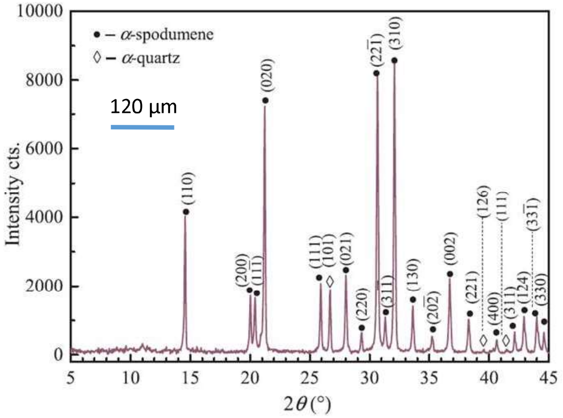
Morphology and mineralogy of concentrates of *α* and *β*-spodumene: a) BSE-SEM image of dense *α*-spodumene with typical cleavage planes; b) XRD and Rietveld refinement of *α*-spodumene; c) BSE-SEM image of *β*-spodumene with cracks due to the thermal treatment at 1100 °C for 2 h; d) XRD and Rietveld refinement of *β*-spodumene

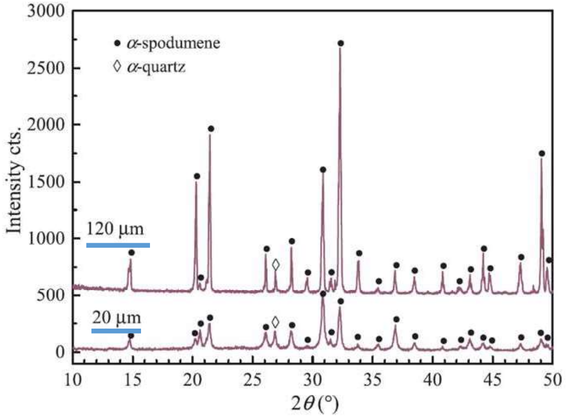
After calcination (1100 °C, 2 h)

Alhadad, M.F., Oskierski, H.C., Chishi, J., Senanayake, G., Dlugogorski, B.Z., Lithium extraction from *β*-spodumene: A comparison of keatite and analcime processes. Hydrometallurgy, 2023, **215**, 105985.
Salakjani, N.K., Singh, P., Nikoloski, A.N., Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: Conventional heating. Minerals Engineering, 2016, **98**, 71-79.

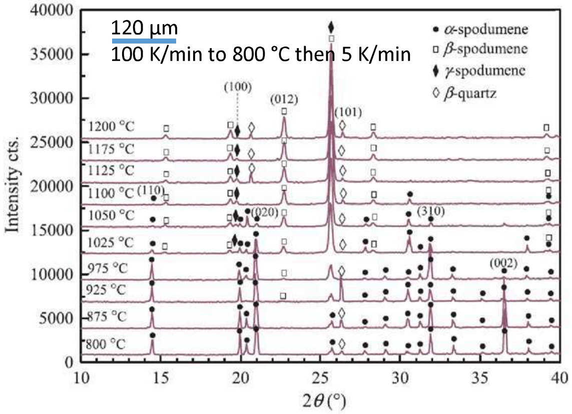
1. Introduction

- Mechanism of calcination (Abdullah et al., 2019)


120 µm


120 µm

20 µm


120 µm

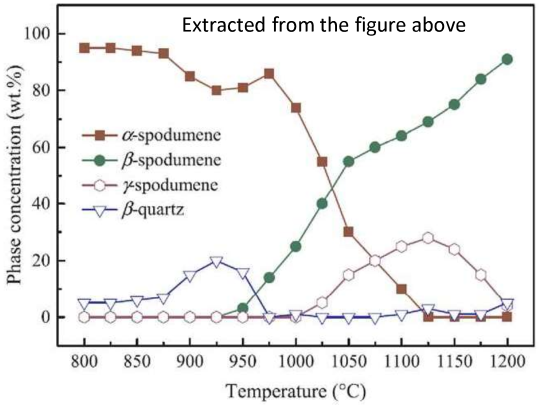
100 K/min to 800 °C then 5 K/min

(i) amorphous spodumene → γ-spodumene → β-spodumene

(ii) crystalline α-spodumene → β-quartz$_{ss}$ → β-spodumene

(iii) crystalline α-spodumene → γ-spodumene → β-spodumene; and

(iv) crystalline α-spodumene → β-spodumene


Extracted from the figure above

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.

1. Introduction

XRD-based models (Moore et al., 2018; Fosu et al., 2021)

- Based on quantitative (Rietveld) or semiquantitative analysis of X-ray diffraction spectra
- Include conversion of α-spodumene and formation of γ-spodumene and β-spodumene
- Assume homogeneous first order reaction models (no particle size dependence)
- Reaction mechanism (cf. Abdullah et al. for the initial $k_{\mathrm{iii}} \approx k_{\mathrm{iv}}$)

  α-spodumene → φ β-spodumene + $(1 - \varphi)$ γ-spodumene (k_1)

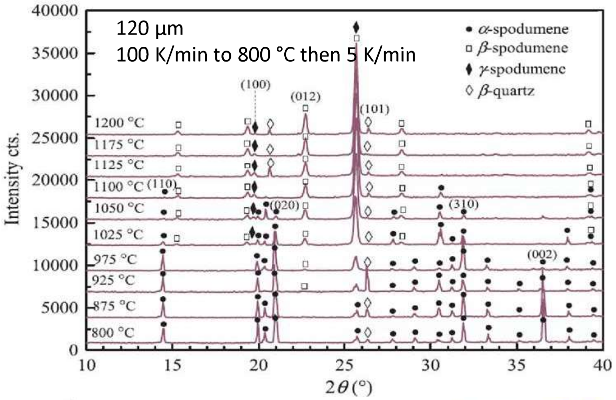
  γ-spodumene → β-spodumene (k_2)
- Equations

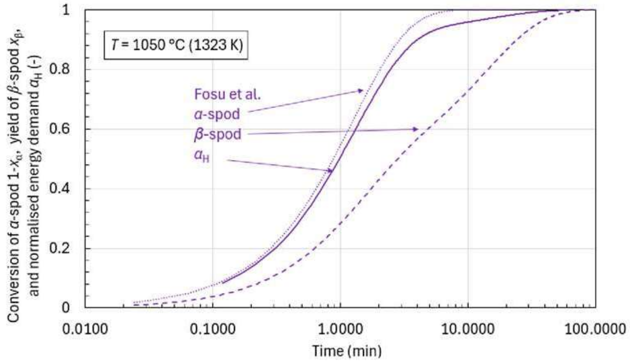
$$\frac{d\,x_\alpha}{dt} = -k_1 x_\alpha \qquad k_1 = A_1 \exp(-\frac{E_1}{RT})$$

$$\frac{d\,x_\beta}{dt} = \varphi k_1 x_\alpha + k_2 x_\gamma \qquad k_2 = A_2 \exp(-\frac{E_2}{RT})$$

$$\frac{d\,x_\gamma}{dt} = (1-\varphi) k_1 x_\alpha - k_2 x_\gamma$$

$$\frac{d\,\alpha_H}{dt} = \frac{\varphi k_1 x_\alpha \Delta H_{\alpha\to\beta} + (1-\varphi) k_1 x_\alpha\, \Delta H_{\alpha\to\gamma} + k_2 x_\gamma\, \Delta H_{\gamma\to\beta}}{\Delta H_{\alpha\to\beta}}$$





Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Minerals Engineering, 2019, **140**, 105883.
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1. Introduction

- Heat demand models (Botto et al. 1975, Abdullah et al. 2024)

- Based on the endothermic heat demand measured by differential thermal analysis DTA (Botto et al., 1975) or differential scanning calorimetry DSC (Abdullah et al., 2024)
- Botto et al.

  α-spodumene (+ energy) → β-spodumene

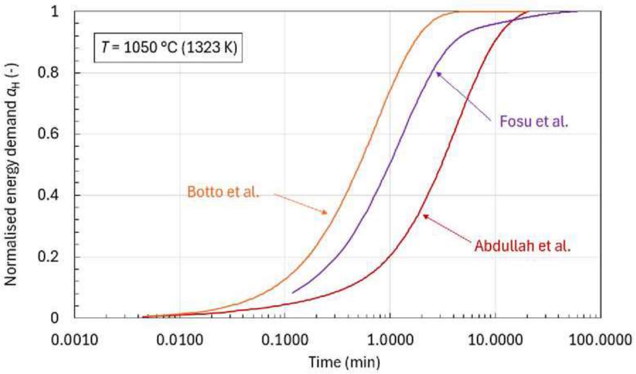
  $$\frac{d\,x_H}{dt} = -k x_H \qquad k = A\exp\left(-\frac{E}{RT}\right)$$

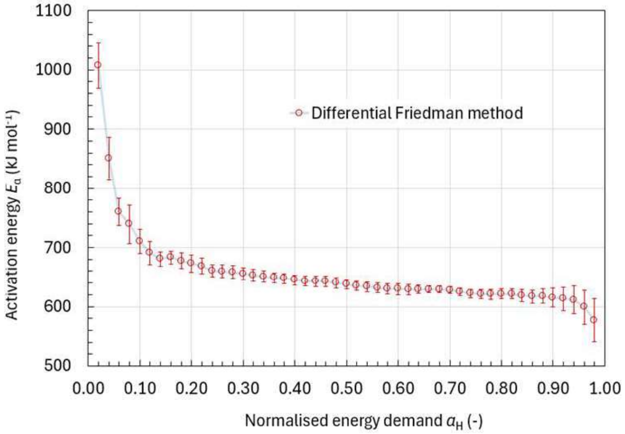
  Simple and approximate; covered in this presentation
- Abdullah et al.

  Isoconversional approach that produces $E(\alpha_H)$, $A(\alpha_H)$ and $f(\alpha_H)$, where $f(\alpha_H)$ is the reaction model

  $$\frac{\mathrm{d}\alpha_H}{\mathrm{d}t} = A(\alpha_H)\exp\left(-\frac{E(\alpha_H)}{RT(t)}\right) f(\alpha_H)$$

  Very accurate, can be applied to an arbitrary heating program, provides significant mechanistic insights; Not covered in this presentation





Abdullah et al., in review, 2024.

Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.

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2a. Kinetic models

- Model of Fosu, Kanari, Bartier, Hodge, Vaughan and Chagnes (Fosu et al., 2021)
- Model of Moore, Mann, Montoya and Haynes (Moore et al., 2018)
- Model of Botto, Cohen Arazi and Frenkel (Botto et al., 1975)

2b. Crucial information

- Experimental measurements
- Mechanism and kinetic parameters
- Predictions and fit to own data
- Comparison with experiments (Peltosaari et al., 2015)

3. Summary remarks

- Lack of particle size dependence; amorphous vs crystalline pathways
- Diffusion limitation
- Importance of recrystallisation of *β*-spodumene
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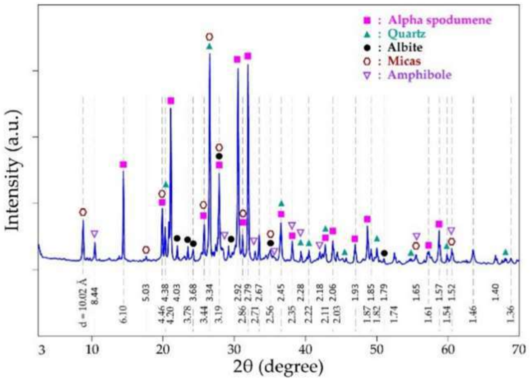
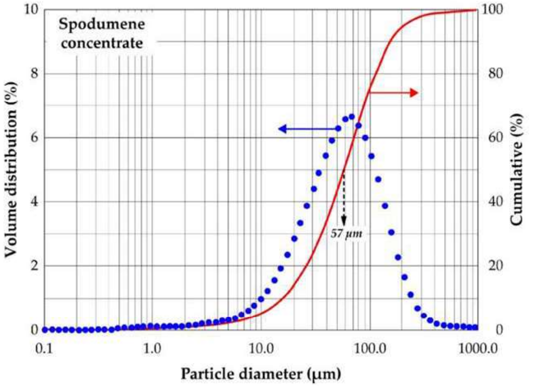
2. Kinetic models and their crucial information

▪ Model of Fosu et al. [Experimental measurements]

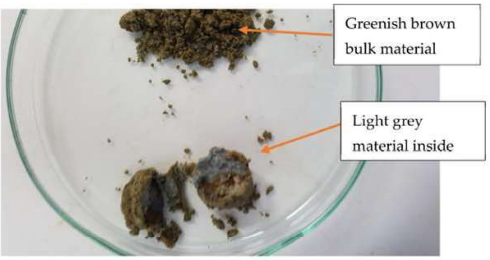
- Spodumene provenance, particle size and purity
  - ➢ Pilbara, Western Australia
  - ➢ d_{80} = 113 µm
  - ➢ 4.6 wt% Li_2O; 57.4 wt% purity





- Experimental
  - Ex-situ X-ray diffraction (XRD)

- Experimental methodology
  - ➢ Roasted isothermally in carbolite furnace at 1173, 1198, 1223, 1248, 1273, 1298, 1323 K
  - ➢ Residence time 7.5, 15, 60, 240 and 480 min
  - ➢ Residence time includes heating to the target temperature
  - ➢ Furnace preheated for 60 min



- Modal concentrations
  - ➢ Semi-quantitative relative abundances of phases from EVA software coupled to PDF2 data base
  - ➢ Peak relative heights, assuming that all crystalline phases add up to 100 %

Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423

2. Kinetic models and their crucial information

- Model of Fosu et al. [Mechanism and kinetic parameters]

- Reaction mechanism

  α-spodumene → $\varphi\ \beta$-spodumene + $(1-\varphi)\ \gamma$-spodumene (k_1)

  γ-spodumene → β-spodumene (k_2)

- Parameters

  k_1: $E_1 = 655\ (\pm 20)$ kJ mol^{-1}; $\ln(A_1/\text{min}^{-1}) = 59.3\ (\pm 2.0)$

  k_2: $E_2 = 730\ (\pm 19)$ kJ mol^{-1}; $\ln(A_2/\text{min}^{-1}) = 63.7\ (\pm 1.7)$

  Selectivity: $\varphi = 0.5$

  $\ln(A_{1,2}/\text{min}^{-1})$ and errors from Tables S23 & S24 of Fosu et al.

- Reaction model

  First order in mass fraction of α-spodumene and γ-spodumene

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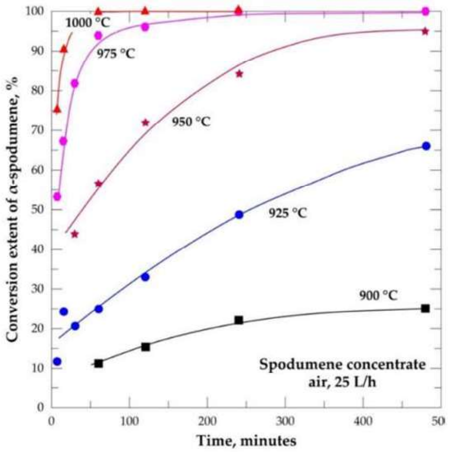
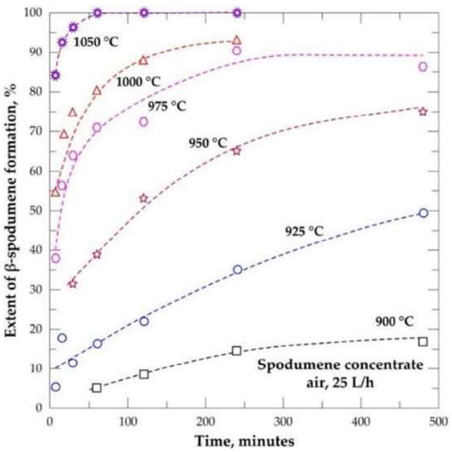
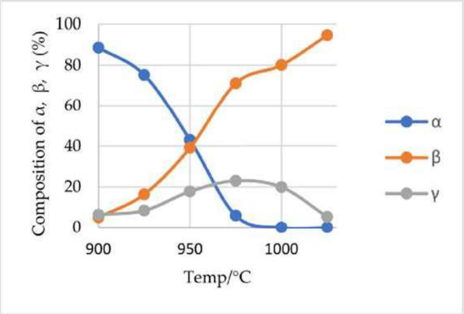
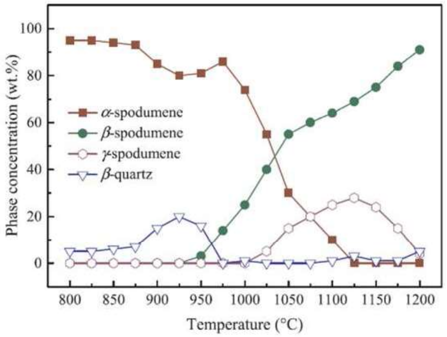






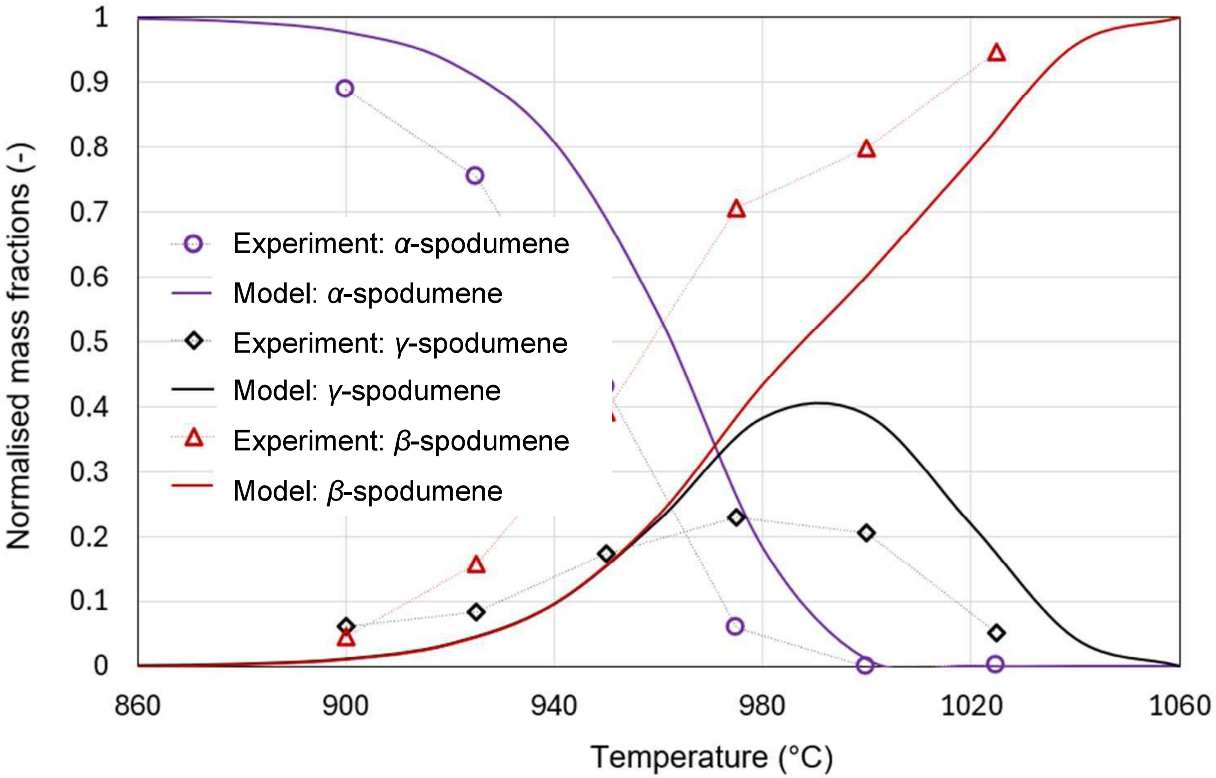
Fosu et al.



Abdullah et al.

2. Kinetic models and their crucial information

- Model of Fosu et al. [Predictions and fit to own data]



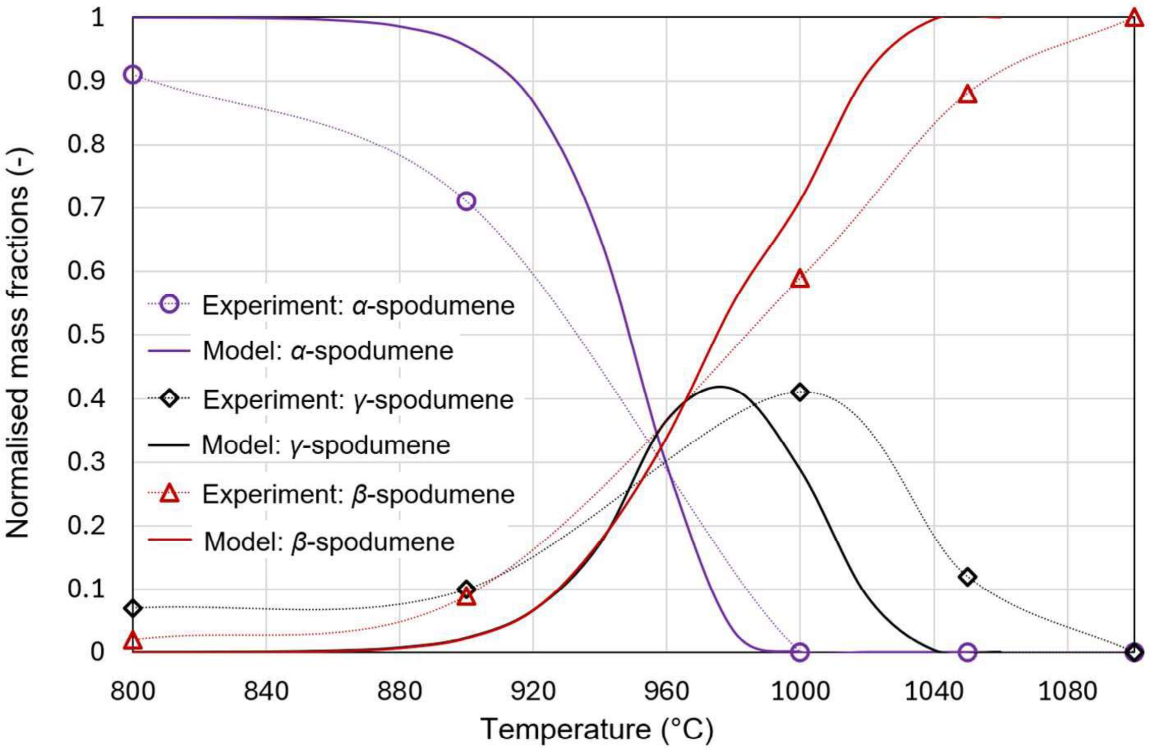
Predictions and fit to Fosu's et al. own measurements (Figure 11):

- polymorph distribution after 1 h of thermal treatment
- solid lines denote the modelling predictions and points are experimental measurement
- dotted line plotted as a guide to an eye

Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423

2. Kinetic models and their crucial information

- Model of Fosu et al. [Comparison with Peltosaari's et al. data]



Comparison of Fosu's et al. model with Peltosaari's et al. measurements:

- polymorph distribution after 2 h of thermal treatment
- solid lines denote the modelling predictions and points are experimental measurement
- dotted line plotted as a guide to an eye for the data of Peltosaari et al.

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2. Kinetic models and their crucial information

Model of Moore et al. [Experimental measurements]

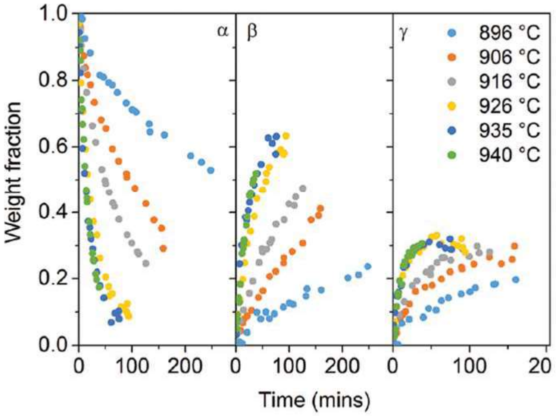
- Spodumene provenance, particle size and purity
  - Mt Cattlin mine, Western Australia
  - $d_{\text{Sauter}} = 4.67\ \mu\text{m}$
  - 7.2 wt% Li_2O; 90 wt% purity

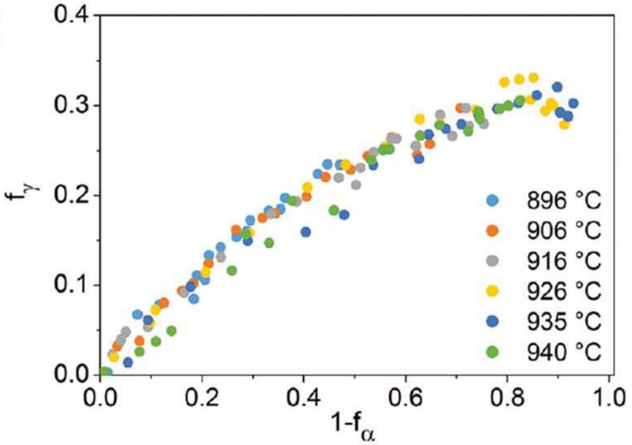
- Experimental

  In-situ synchrotron X-ray diffraction (XRD)

- Experimental methodology
  - Calcined isothermally in capillaries at 1169, 1179, 1189, 1199, 1208, 1213 K
  - Residence time up to 300 min
  - Air-gun heating, preheating time negligeable

- Modal concentrations
  - Rietveld refining





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- Reaction mechanism

  α-spodumene $\rightarrow \varphi\, \beta$-spodumene + $(1 - \varphi)\ \gamma$-spodumene (k_1)
  γ-spodumene $\rightarrow \beta$-spodumene (κk_1)

- Parameters

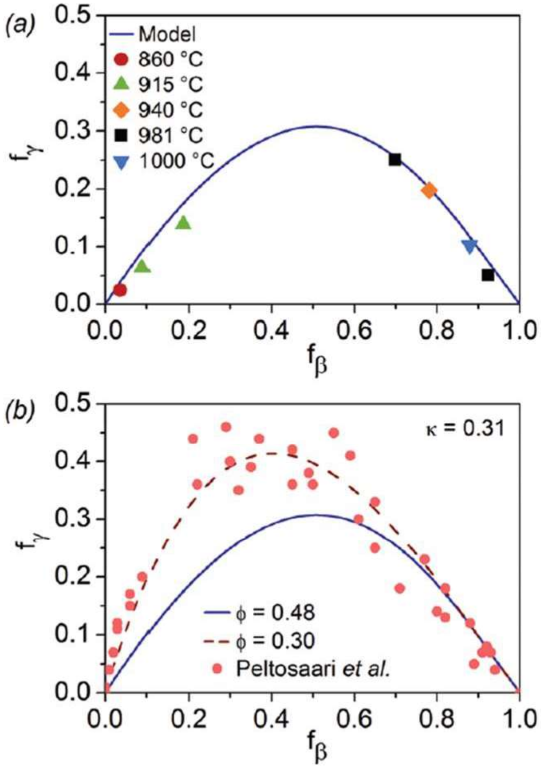
  k_1: $E_1 = 780\ (\pm170)$ kJ mol^{-1}; $\ln(A_1/\text{min}^{-1}) = 75\ (\pm7)$

  Selectivity: $\varphi = 0.48 \pm 0.01$ ($\varphi = 0.30$ for Peltosaari et al.)

  Parameter κ: $\kappa = 0.31 \pm 0.03$

- Reaction model

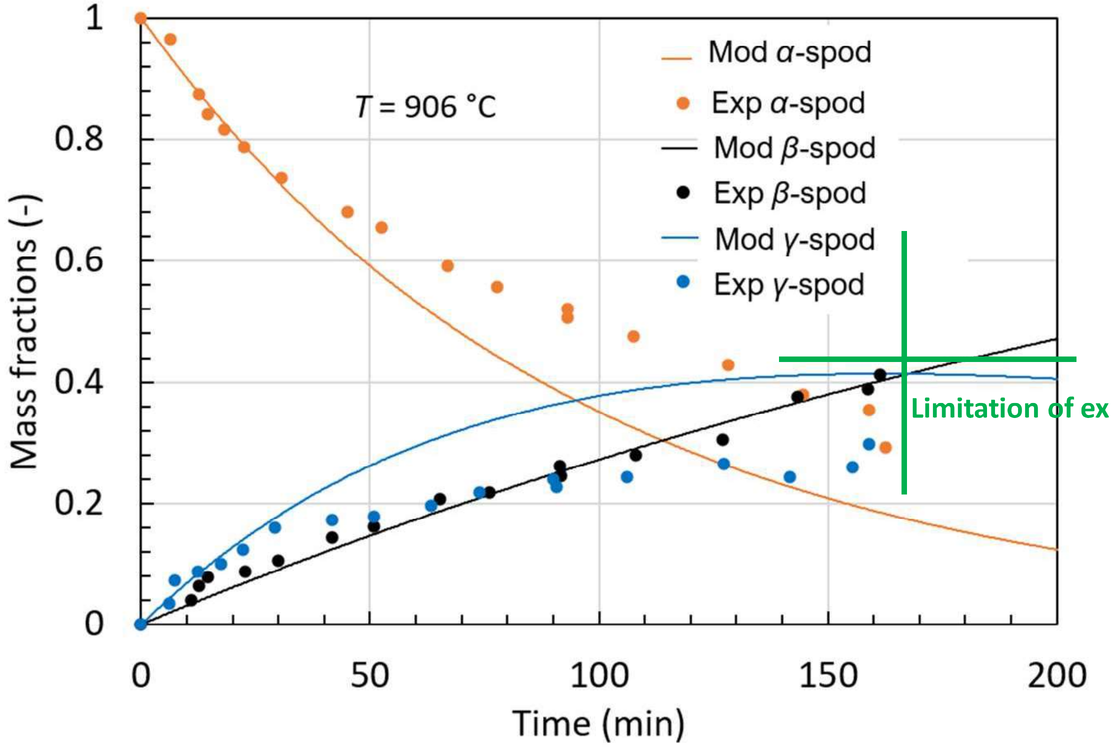
  First order in mass fraction of α-spodumene and γ-spodumene



Moore, R.L., Mann, J.P., Montoya, A., Haynes, B.S., *In situ* synchrotron XRD analysis of the kinetics of spodumene phase transitions. Physical Chemistry Chemical Physics, 2018, **20**, 10753-10761.
Peltosaari, O., Tanskanen, P., Heikkinen, E.-P., Fabritius, T., α → γ → β-phase transformation of spodumene with hybrid microwave and conventional furnaces. Minerals Engineering, 2015, **82**, 54-60.

2. Kinetic models and their crucial information

- Model of Moore et al. [Predictions and fit to own data]



Limitation of experiments

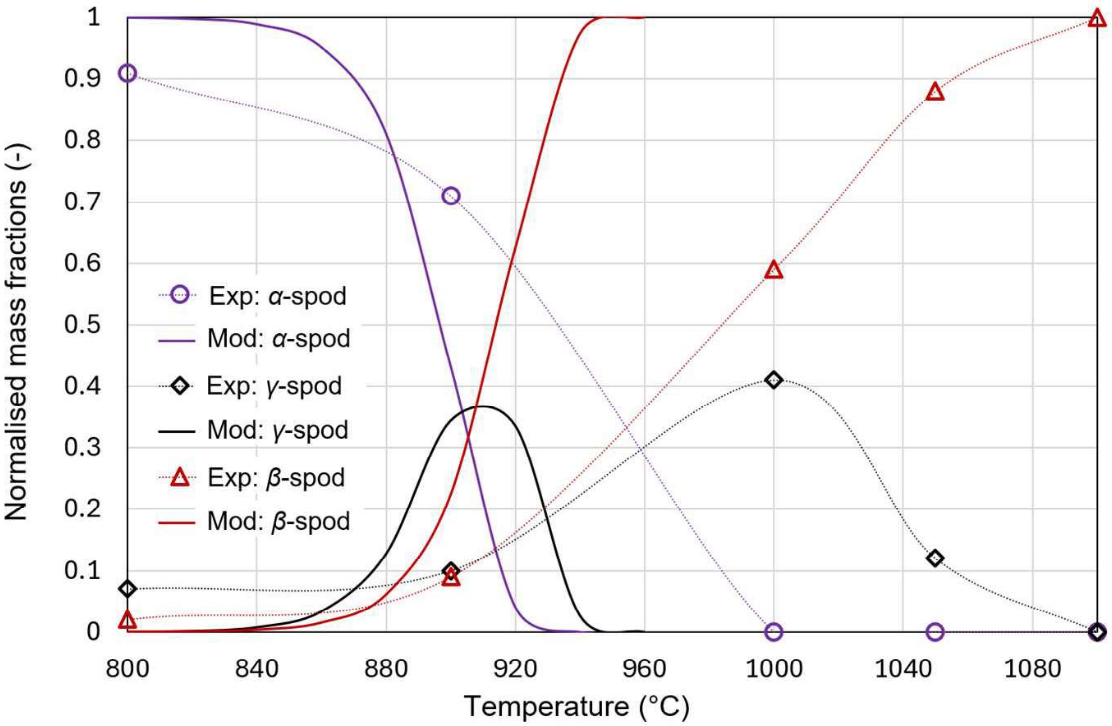
Predictions and fit to Moore's et al. own measurements (Figure 3, *T* = 906 °C):

- Recall large error in the activation energy
- Note good match for *β*-spodumene, but not for *α*- and *γ*-spodumene
- Note lack of measurements for large conversion, which are important for practical applications

Moore, R.L., Mann, J.P., Montoya, A., Haynes, B.S., *In situ* synchrotron XRD analysis of the kinetics of spodumene phase transitions. Physical Chemistry Chemical Physics, 2018, **20**, 10753-10761.

2. Kinetic models and their crucial information

- Model of Moore et al. [Comparison with Peltosaari's et al. data]



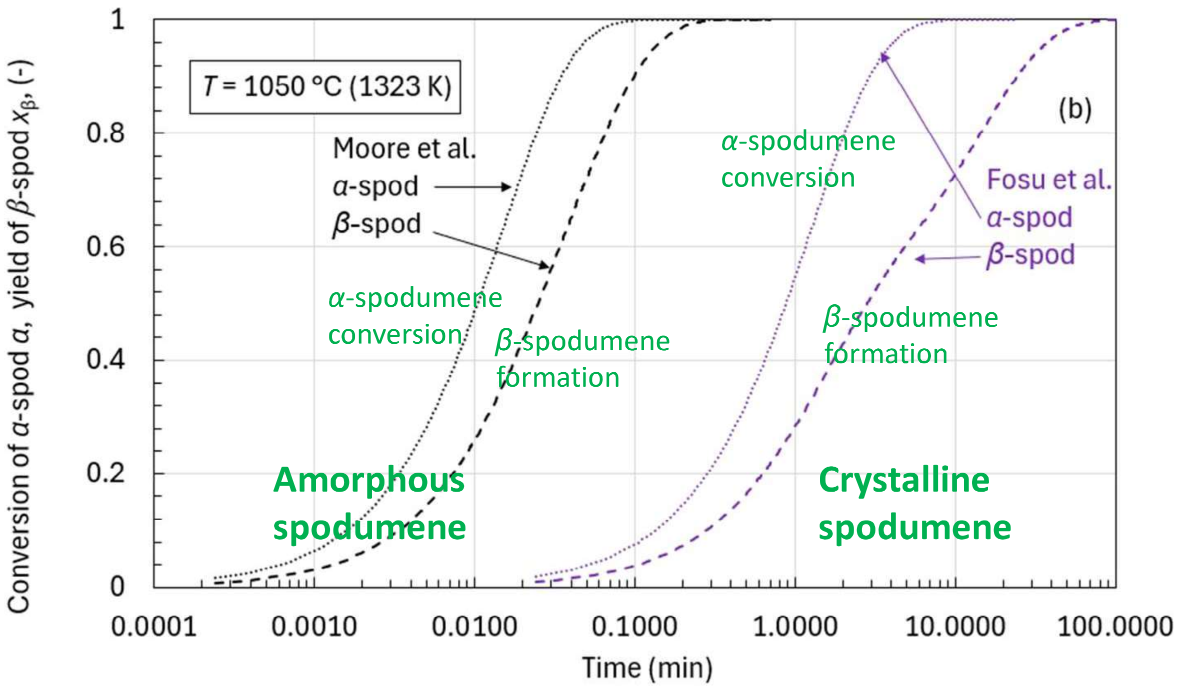
Comparison of Moore's et al. model with Peltosaari's et al. measurements:

- polymorph distribution after 2 h of thermal treatment
- solid lines denote the modelling predictions and points are experimental measurement
- dotted line plotted as a guide to an eye for the data of Peltosaari et al.
- Very fast, due to amorphisation & defects introduced during grinding

Moore, R.L., Mann, J.P., Montoya, A., Haynes, B.S., *In situ* synchrotron XRD analysis of the kinetics of spodumene phase transitions. Physical Chemistry Chemical Physics, 2018, **20**, 10753-10761.
Peltosaari, O., Tanskanen, P., Heikkinen, E.-P., Fabritius, T., α → γ → β-phase transformation of spodumene with hybrid microwave and conventional furnaces. Minerals Engineering, 2015, **82**, 54-60.

2. Kinetic models and their crucial information

- Model of Moore et al. [Comparison with Fosu’s et al. model]



Comparison of Moore’s et al. model with the model of Fosu et al. measurements:

- Moore’s et al. model is fast, due to amorphisation and defects introduced during grinding
- The model follows different kinetics, i.e., pathway (i) of Abdullah et al.
- *Apparent* size dependence, because of the switch in the mechanism

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.
Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423.
Moore, R.L., Mann, J.P., Montoya, A., Haynes, B.S., *In situ* synchrotron XRD analysis of the kinetics of spodumene phase transitions. Physical Chemistry Chemical Physics, 2018, **20**, 10753-10761.

2. Kinetic models and their crucial information

▪ Model of Botto et al. [Experimental measurements]

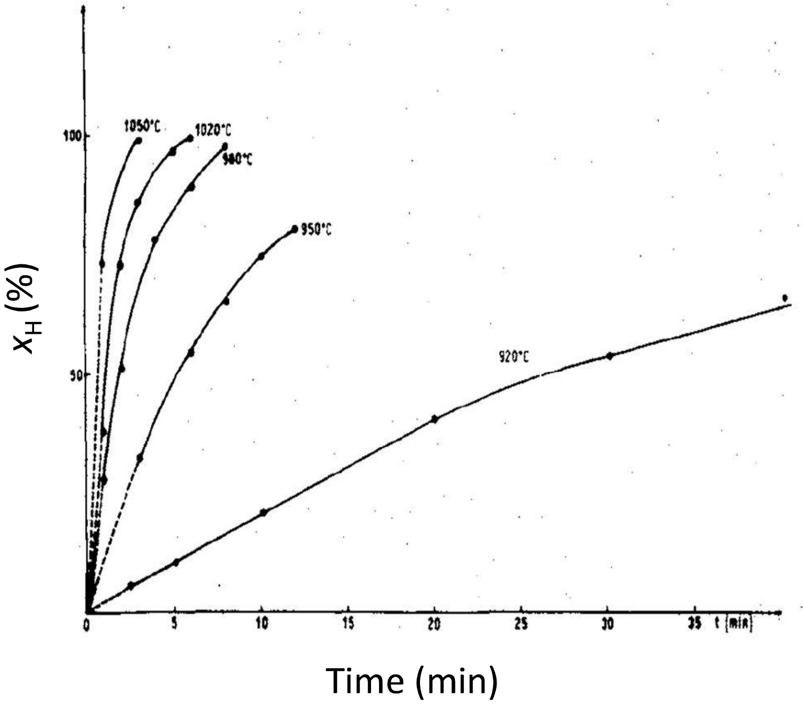
- Spodumene provenance, particle size and purity
  - San Luis Province, Argentina
  - < 74 µm
  - 5.5 wt% Li_2O; 68.5 wt% purity and 7.95 wt% Li_2O; 99 wt% purity

- Experimental: Differential thermal analysis

- Experimental methodology
  - Roasted isothermally in furnace at 1163, 1193, 1223, 1293, 1323 K
  - *Heated at 10 K min^{-1} to target temperature then isothermal*
  - Conversion factor, 26.4 (±0.5) kJ mol^{-1}
  - Assume JMAK (Avrami-Erofeev) nucleation, obtain *u* = 1, then kinetic analysis

x_α (%)

- Derivation of kinetic rates
  - Obtain *k* at different heating times at constant *T*
  - Apply Arrhenius equation to extract Arrhenius parameters



Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.

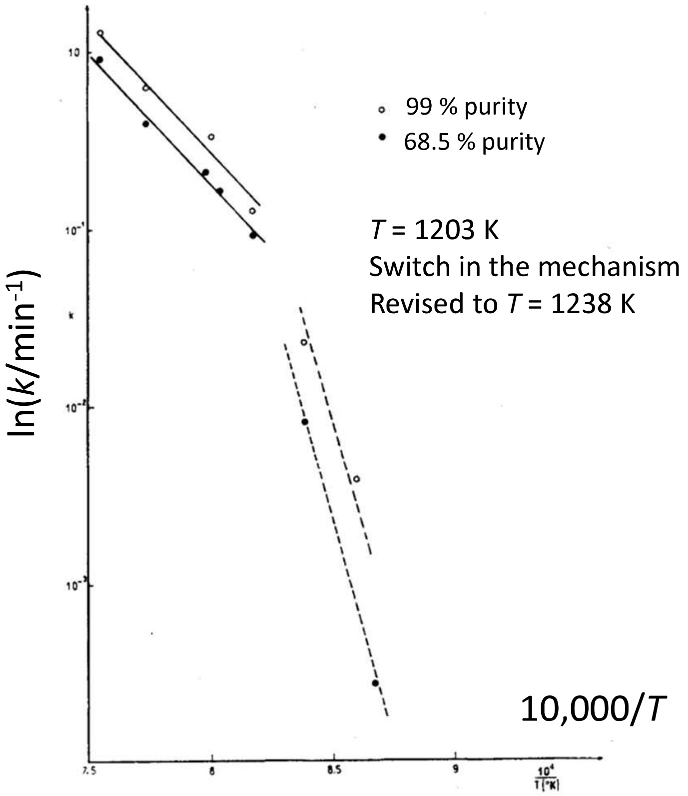
2. Kinetic models and their crucial information

- Model of Botto et al. [Mechanism and kinetic parameters]

- Reaction mechanism
  - Normalised heat demand
  - α-spodumene → β-spodumene

- Parameters
  - $T \leq 965$ °C
  - $E = 698\ (\pm 21)$ kJ mol^{-1}; $\ln(A/\text{min}^{-1}) = 66.6\ (\pm 2.1)$
  - $T \geq 965$ °C
  - $E = 275\ (\pm 19)$ kJ mol^{-1}; $\ln(A/\text{min}^{-1}) = 25.3\ (\pm 1.7)$

- Reaction model
  - First order in normalised energy demand

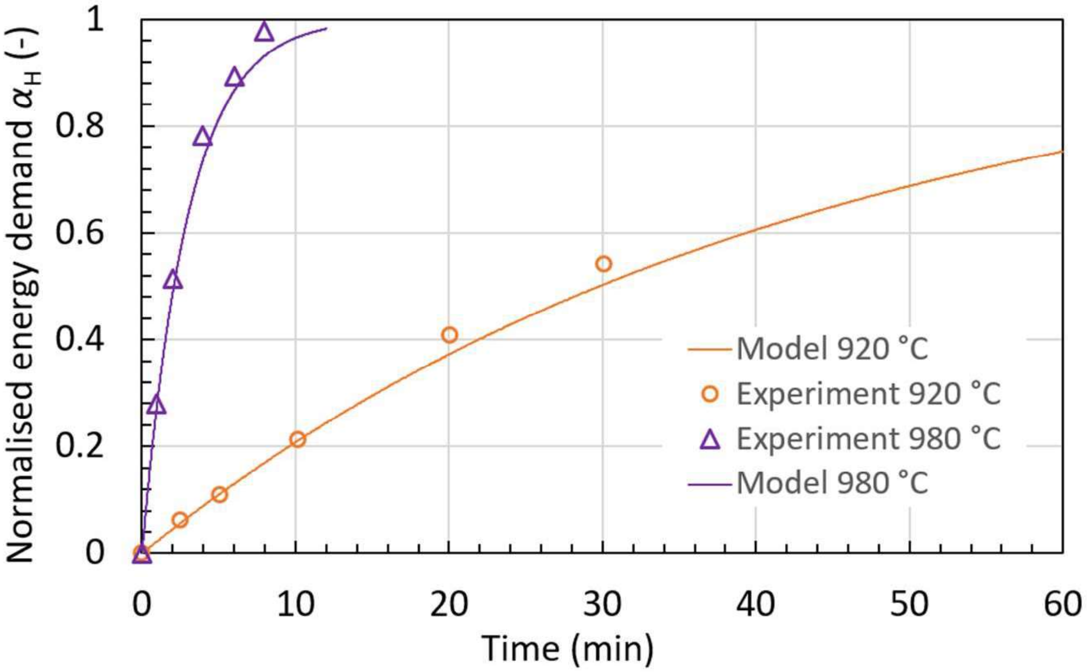


$T = 1203$ K
Switch in the mechanism
Revised to $T = 1238$ K

Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.

2. Kinetic models and their crucial information

- Model of Botto et al. [Predictions and fit to own data]



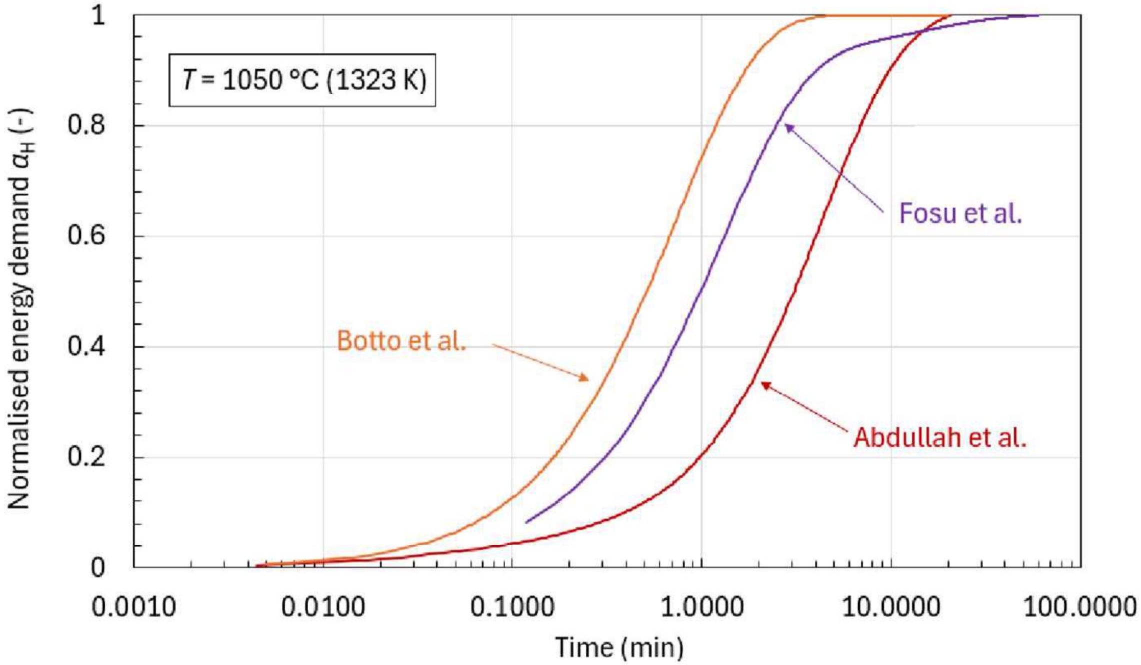
Predictions and fit to Botto's et al. own measurements (Figure 2c&d):

- Normalised energy demand (α_H)
- solid lines denote the modelling predictions and points are experimental measurement

Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.

2. Kinetic models and their crucial information

- Model of Botto et al. [Comparisons with other models]



Comparison of Botto's et al. model with models of Fosu et al. and Abdullah et al.:

- there are no isothermal measurements in the literature for the normalised energy demand
- Fosu's et al. predicts modal distribution of polymorphs and, with an additional energy equation, yields the normalised energy demand
- Abdullah's et al. model predicts the normalised energy demand directly

Abdullah et al., in review (2024)
Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.
Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423

Presentation outline

1. Introduction

- Energy requirements and decarbonisation
- Spodumene polymorphs
- Mechanism of calcination (Abdullah et al., 2019)
- XRD models
- DTA/DSC-based models

2a. Kinetic models

- Model of Fosu, Kanari, Bartier, Hodge, Vaughan and Chagnes (Fosu et al., 2021)
- Model of Moore, Mann, Montoya and Haynes (Moore et al., 2018)
- Model of Botto, Cohen Arazi and Frenkel (Botto et al., 1975)

2b. Crucial information

- Experimental measurements
- Mechanism and kinetic parameters
- Predictions and fit to own data
- Comparison with experiments (Peltosaari et al., 2015)

3. Summary remarks

- Lack of particle size dependence; amorphous vs crystalline pathways
- Diffusion limitation
- Importance of recrystallisation of *β*-spodumene
- Effect of additives

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.

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3. Summary remarks

- What have we learned?

1. Recrystallisation of amorphous (defect-laden) and crystalline spodumene proceeds along different pathways; pathway (i) vs pathways (iii) and (iv), in the mechanism of Abdullah et al. (2019); cf. (Fosu et al., 2021; Moore et al., 2018). No dependence on particle size.

2. Impurities, such as SiO_2, induce the appearance of additional pathways; pathway (ii) in the mechanism of Abdullah et al. (2019).

3. Diffusion is the limiting mechanism for the calcination of α-spodumene to β-spodumene; it is not nucleation nor crystallisation

4. The final recrystallisation of β-spodumene from γ-spodumene governs the temperature and the residence time of the calcination process (Abdullah et al., 2018; Dessemond et al., 2020; Fosu et al., 2021; Peltosaari et al., 2015; Salakjani et al., 2016).

5. Kinetic parameters in the Arrhenius relationship are correlated! Good predictions are possible for unphysical values of E and $\ln(A)$, as errors in E are offset by errors in $\ln(A)$.

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.
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Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423.
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Peltosaari, O., Tanskanen, P., Heikkinen, E.-P., Fabritius, T., α → γ → β-phase transformation of spodumene with hybrid microwave and conventional furnaces. Minerals Engineering, 2015, **82**, 54-60.
Salakjani, N.K., Singh, P., Nikoloski, A.N., Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: Conventional heating. Minerals Engineering, 2016, **98**, 71-79.

3. Summary remarks

3.1 Lack of particle size dependence; amorphous vs crystalline pathways

(i) **amorphous** spodumene → *γ*-spodumene → *β*-spodumene

(ii) crystalline α-spodumene → *β*-quartz$_{ss}$ → *β*-spodumene

(iii) **crystalline** *α*-spodumene → *γ*-spodumene → *β*-spodumene; and

(iv) **crystalline** *α*-spodumene → *β*-spodumene

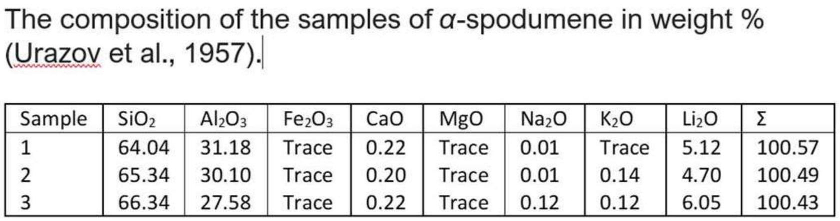
- XRD models are very specific and, at present, cannot differentiate between pathways (i) and (iii – iv) and do not include (ii).
- The mechanistic pathways switch for concentrates dominated by amorphous and crystalline materials. This manifests itself in the apparent dependence on particle size. There is minor size-dependence due to heating of the particles.
- Pathway (ii) is naturally included in the isoconversional DSC-based models (not presented today) but is yet to be included in the XRD-based models.
- We estimate the particles of d_{80} = 20 μm to be 75 % amorphous and only 30 % amorphous if characterised by d_{80} = 50 μm; based on Abdullah et al. (2019).
- Isoconversional DSC models must be developed for each concentrate. At present, this is also true for the XRD models. It should be possible to incorporate pathways (i) and (ii) as separate corridors in future XRD models.

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.

3. Summary remarks

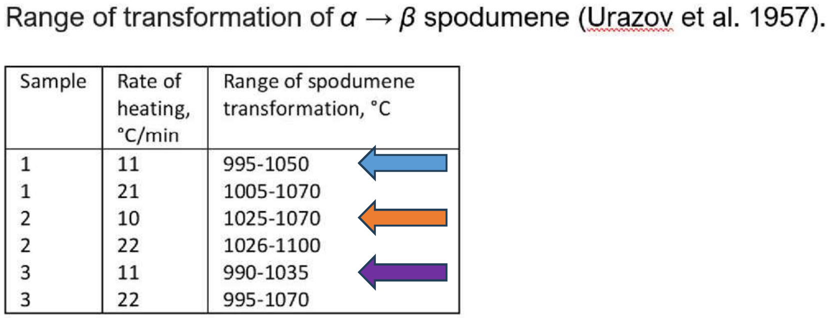
3.2 Additional pathways due to impurities

(ii) crystalline α-spodumene → β-quartz$_{ss}$ → β-spodumene (Abdullah et al., 2019; Urazov et al., 1957)



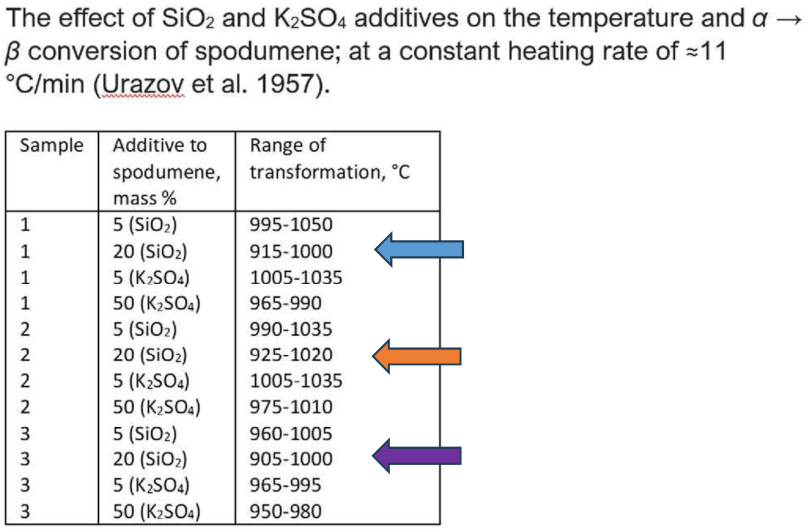
The composition of the samples of α-spodumene in weight % (Urazov et al., 1957).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Li_2O	Σ
1	64.04	31.18	Trace	0.22	Trace	0.01	Trace	5.12	100.57
2	65.34	30.10	Trace	0.20	Trace	0.01	0.14	4.70	100.49
3	66.34	27.58	Trace	0.22	Trace	0.12	0.12	6.05	100.43



Range of transformation of $\alpha \rightarrow \beta$ spodumene (Urazov et al. 1957).

Sample	Rate of heating, °C/min	Range of spodumene transformation, °C
1	11	995-1050
1	21	1005-1070
2	10	1025-1070
2	22	1026-1100
3	11	990-1035
3	22	995-1070



The effect of SiO_2 and K_2SO_4 additives on the temperature and $\alpha \rightarrow \beta$ conversion of spodumene; at a constant heating rate of ≈11 °C/min (Urazov et al. 1957).

Sample	Additive to spodumene, mass %	Range of transformation, °C
1	5 (SiO_2)	995-1050
1	20 (SiO_2)	915-1000
1	5 (K_2SO_4)	1005-1035
1	50 (K_2SO_4)	965-990
2	5 (SiO_2)	990-1035
2	20 (SiO_2)	925-1020
2	5 (K_2SO_4)	1005-1035
2	50 (K_2SO_4)	975-1010
3	5 (SiO_2)	960-1005
3	20 (SiO_2)	905-1000
3	5 (K_2SO_4)	965-995
3	50 (K_2SO_4)	950-980

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.
Urazov, G.G., Plyushchev, V.E., Shakhno, I.V., On monotropic transformation of spodumene (in Russian). Doklady Akademii Nauk SSSR, 1957, **113**, 361-363.

3. Summary remarks

3.3 Diffusion is the limiting mechanism of calcination

Diffusion is the limiting mechanism for the calcination of α-spodumene to β-spodumene; it is not nucleation or crystallisation

Compare $k = A\exp(-\frac{E}{RT})$ and $D = D_0\exp(-\frac{\Delta H}{RT})$

ΔH is the activation enthalpy for diffusion

This also the reason for the mechanism of Moore et al. (2018) and Fosu et al. (2021) to be equivalent to pathways (iii) and (iv) of Abdullah et al. (2018).

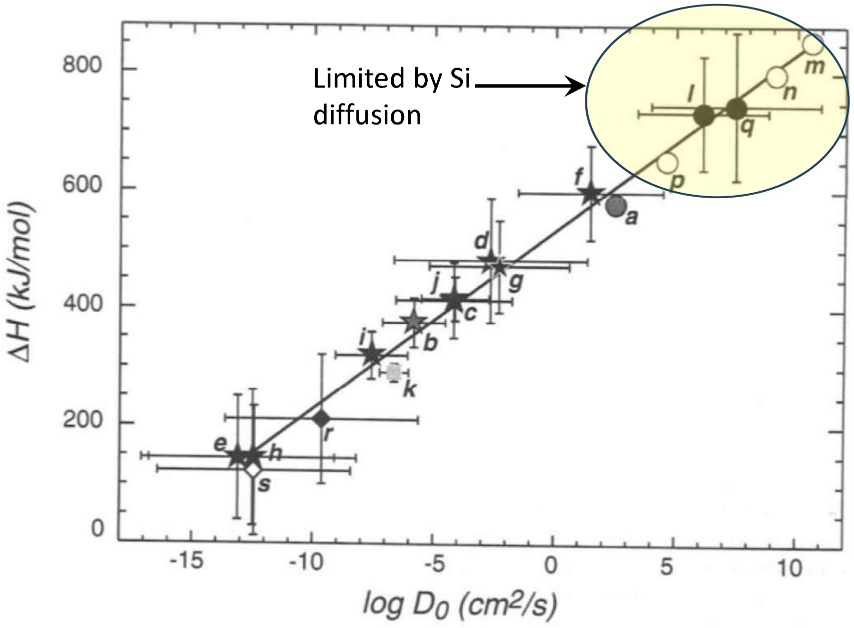
Moore et al. and Fosu et al.

α-spodumene → φ β-spodumene + $(1 - \varphi)$ γ-spodumene (k_1)

γ-spodumene → β-spodumene (k_2)

Abdullah et al.

amorphous spodumene → γ-spodumene → β-spodumene



Limited by Si diffusion

Compensation relationship for diffusion (Béjina and Jaoul, 1997)

Abdullah, A.A., Oskierski, H.C., Altarawneh, M., Senanayake, G., Lumpkin, G., Dlugogorski, B.Z., Phase transformation mechanism of spodumene during its calcination. Minerals Engineering, 2019, **140**, 105883.
Béjina, F., Jaoul, O., Silicon diffusion in silicate minerals. Earth and Planetary Science Letters, 1997, **153**, 229-238.
Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A., Physico-chemical characteristics of spodumene concentrate and its thermal transformations. Materials, 2021, **14**, 7423.
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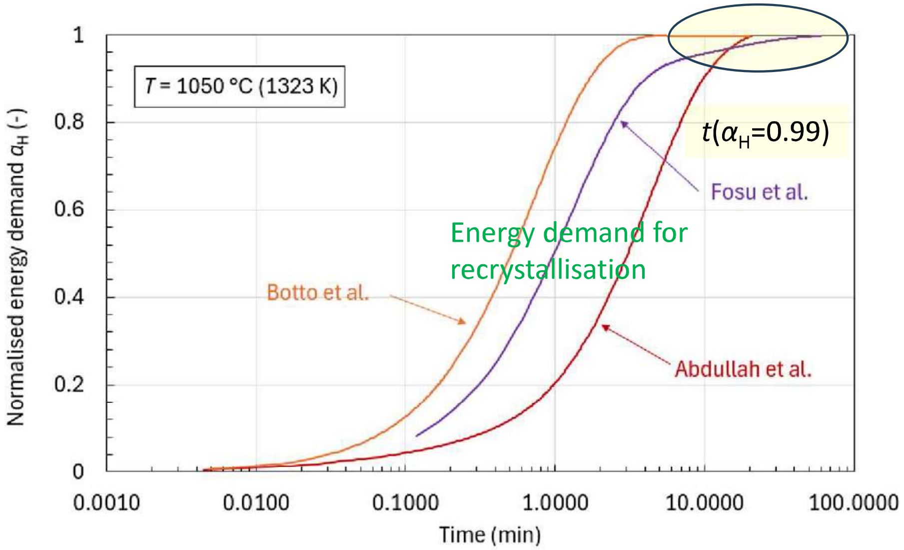
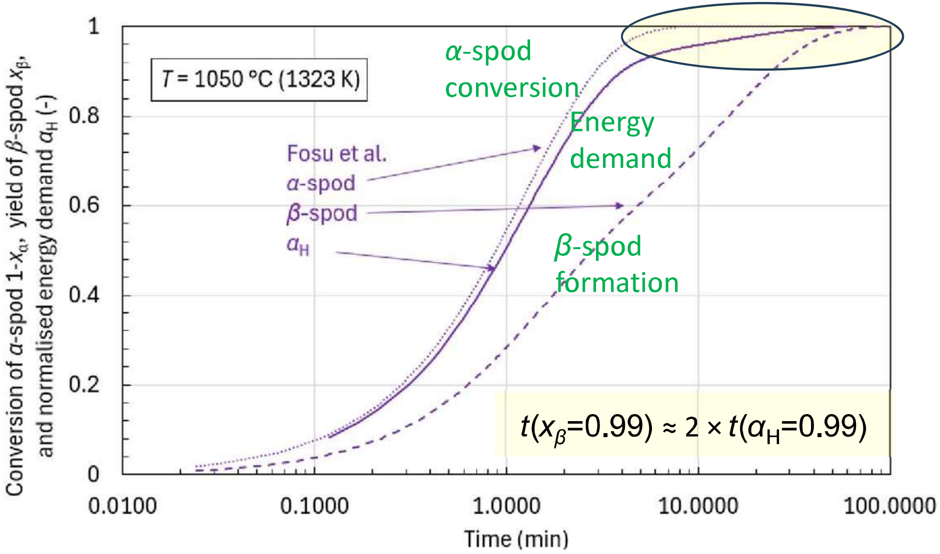
3. Summary remarks

3.4 Recrystallisation of β-spodumene from γ-spodumene

The final recrystallisation of β-spodumene from γ-spodumene governs the temperature and the residence time of the calcination process (Dessemond et al., 2020; Fosu et al., 2021; Peltosaari et al., 2015).





Abdullah et al., in review (2024)

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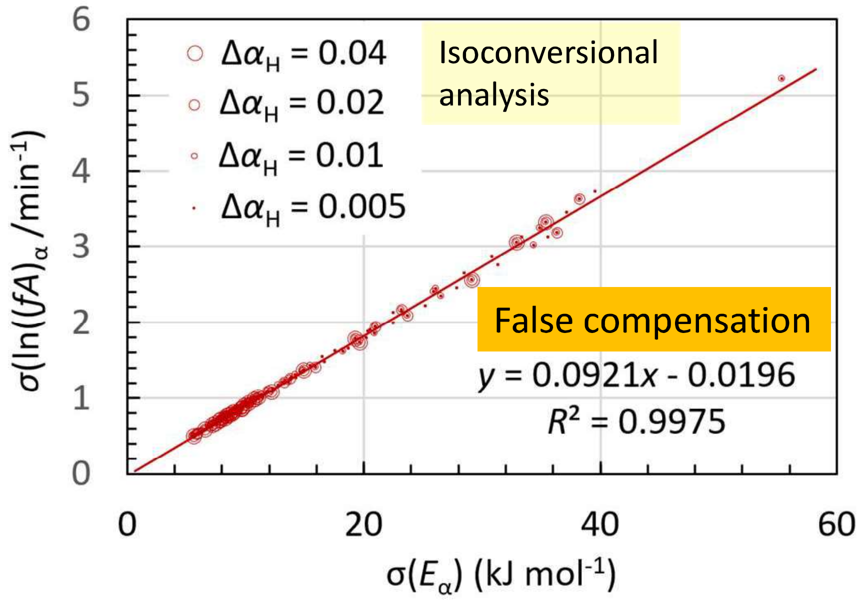
3. Summary remarks

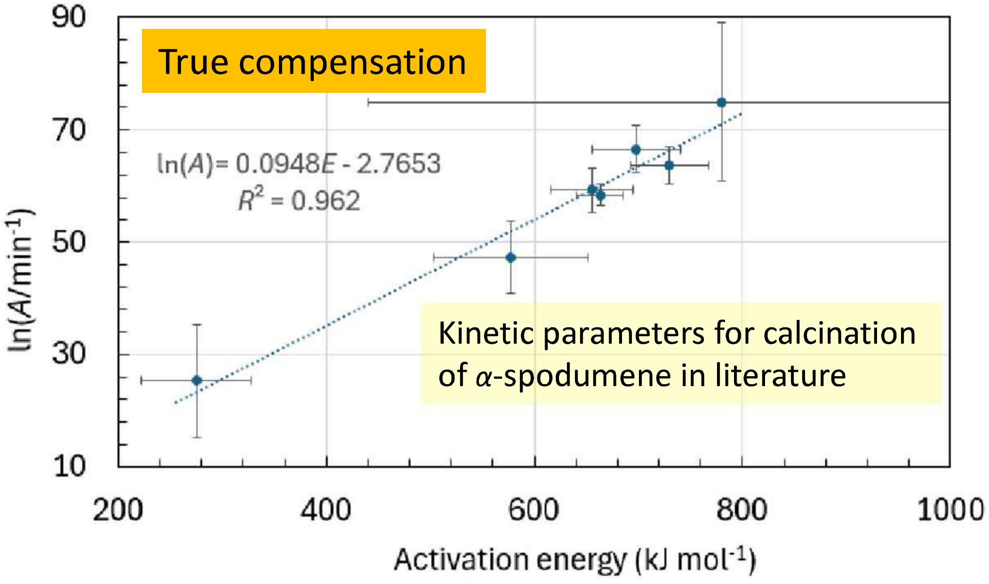
3.5 Compensations

Fitting Arrhenius relationship to experimental data “invites” compensations. *E* and ln(*A*) are independent, but their statistical estimators are “falsely” compensated. This is because errors in $\sigma(E)$ and $\sigma(\ln(A))$ are correlated.



Isoconversional analysis

False compensation



True compensation

Kinetic parameters for calcination of α-spodumene in literature

Abdullah et al., in review (2024)

Botto, I.L., Cohen Arazi, S., Krenkel, T.G., Kinetic study of polymorphic transformation of spodumene I into spodumene II (in Spanish). Boletín de la Sociedad Española de Cerámica y Vidrio, 1975, **14**, 433-440.

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