

Supplementary Information

for

Time-Resolved *in situ* Synchrotron X-ray Diffraction Studies of Type 1 Silicon Clathrate Formation

by

Peter T. Hutchins^{1†}, Olivier Leynaud^{1, 2††}, Luke A. O'Dell^{3†††},
Mark E. Smith³, Paul Barnes^{*1, 2} and Paul F. McMillan^{*1}

- 1: Department of Chemistry and Materials Chemistry Centre, Christopher Ingold Laboratory, University College London, 20 Gordon Street, London, WC1H 0AJ, UK.
- 2: School of Crystallography, Birkbeck College, University of London, Malet Street, London, WC1E 7HX, UK
- 3: Department of Physics, University of Warwick, Coventry CV4 7AL, UK.

† Present address: Infineum UK Ltd., Infineum Business & Technology Centre, PO Box 1, Milton Hill, Abingdon, Oxon. OX13 6AE, U.K.

†† Present address: Institut Néel, CNRS Université Joseph Fourier, B.P. 166, F-38042 Grenoble Cedex 9, France.

††† Present address: Steacie Institute for Molecular Science, National Research Council, 100 Sussex Drive, Ottawa ON, K1N 5A2, Canada.

Corresponding authors' E-mail: p.barnes@mail.cryst.bbk.ac.uk; p.f.mcmillan@ucl.ac.uk

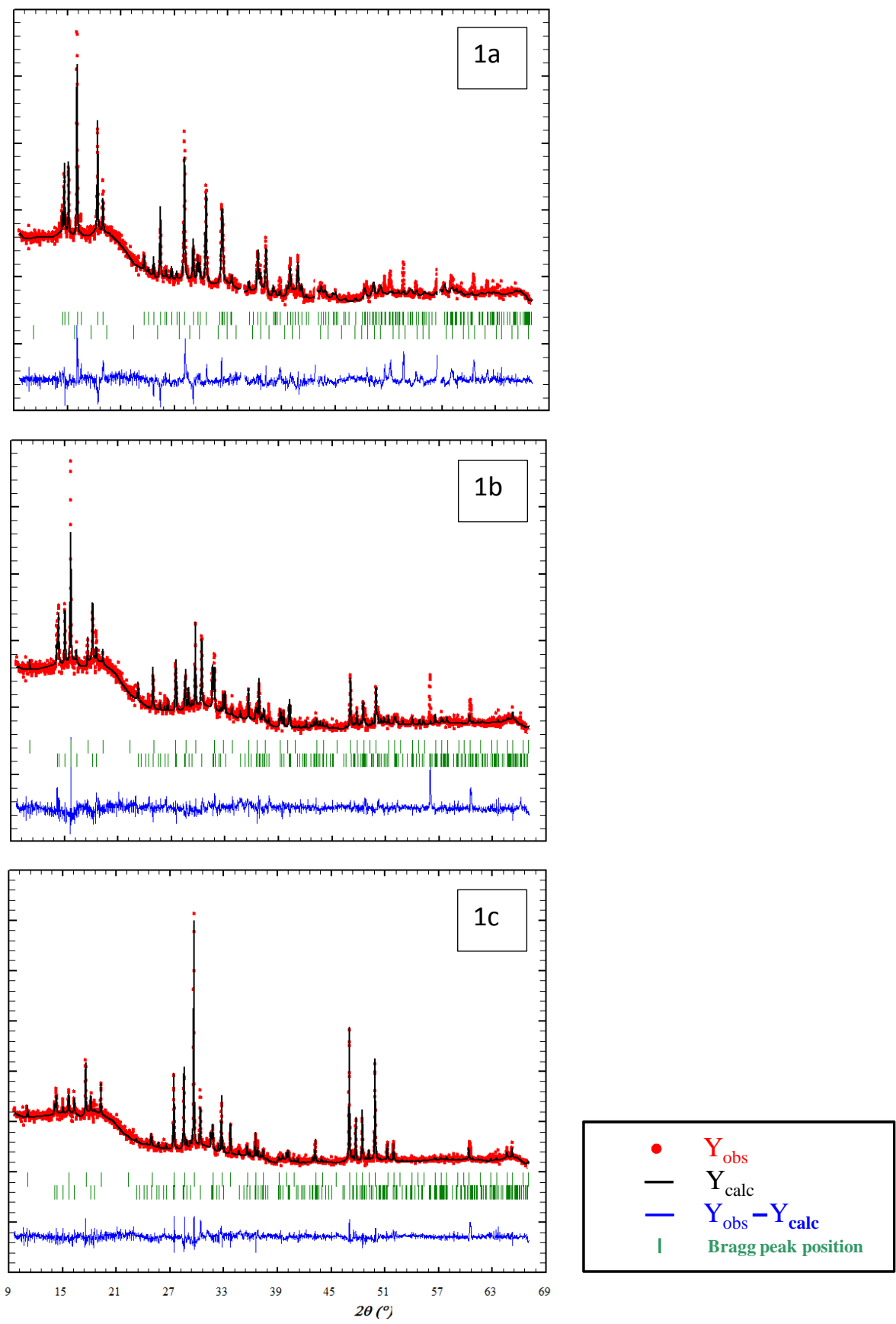


Figure 1:

Figure 1:

Three “Rietveld” diffraction plots (*Intensity* in arbitrary units *versus* 2θ ($^\circ$)) from the sample at representative stages of the overall synthesis of Si-clathrate-type-I from the NaSi precursor:

- upper plot: data set No.19 collected near the beginning of the synthesis, after 9.5 minutes with the temperature reaching 76°C ;
- middle plot: data set No.130 collected during the most active stages of the synthesis, after 65 minutes with the temperature reaching 500°C ;
- lower plot: data set No.300 collected, at the end point of the whole synthesis recipe after 150 minutes, with the temperature at 500°C .

The data are pre-fitted using the Le Bail procedure and the resulting unit cell parameters are then used as input parameters for a two-phase Rietveld fit to the NaSi and Si-clathrate structures. The various plot parameters (Y_{obs} etc.) are identified in the key box and the *Bragg peak position* markers relate to the NaSi and Si-clathrate structures with the upper row given as the dominant structure at that point in the synthesis (upper plot = NaSi dominant; middle and lower plots = Si-clathrate dominant). An as-yet unidentified contamination is evident within $2\theta=51-63^\circ$ for the first two plots, but this is removed in the heat treatment by the time of the third plot thereby improving the fit. Further associated refinement/structural data are given below.

Data Collection and Refinement Details

Pattern	time (min)	Temp ($^\circ\text{C}$)	$2\theta_{\text{min}}$ ($^\circ$)	$2\theta_{\text{max}}$ ($^\circ$)	2θ -step ($^\circ$)	λ (\AA)
19	9.5	76	8.5721	68.6807	0.014704	1.40000
130	65	500	8.5721	68.6807	0.014704	1.40000
300	150	500	8.5721	68.6807	0.014704	1.40000

Table 1: Summary of data collection parameters.

U	V	W	Phase	R_{Bragg}
0.2453	-0.0200	0.0062	NaSi	26.69
0.0200	-0.0067	0.0082	$\text{Na}_x\text{Si}_{46}$	67.65
0.0200	-0.0200	0.0112	NaSi	33.67
0.0351	0.0025	0.0007	$\text{Na}_x\text{Si}_{46}$	24.95
0.0200	-0.0200	0.0126	NaSi	41.66
0.0442	-0.0249	0.0068	$\text{Na}_x\text{Si}_{46}$	16.58

Table 2: Summary of Rietveld refinement parameters; U, V, W = peak width variation parameters using a pseudo-Voigt peak function and with R_{Bragg} are as per standard definition/units for FullProf refinement output.

a. NaSi (C2/c, monoclinic)						
Unit Cell:	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)
76°C, 9.5 min.	12.161(1)	6.5480(6)	11.144(1)	90	119.085(5)	90
500°C, 65 min.	12.297(1)	6.686(1)	11.353(1)	90	120.041(4)	90
NaSi coordinates						
76°C, 9.5 min.	<i>x</i>		<i>y</i>		<i>z</i>	
Na(1)	0.361(2)		0.660(3)		0.379(2)	
Na(2)	0.632(1)		0.895(1)		0.452(1)	
Si(1)	0.450(1)		0.248(1)		0.314(1)	
Si(2)	0.610(1)		0.438(1)		0.365(1)	
500°C, 65 min.	<i>x</i>		<i>y</i>		<i>z</i>	
Na(1)	0.351(2)		0.652(3)		0.379(2)	
Na(2)	0.627(1)		0.885(2)		0.428(1)	
Si(1)	0.467(1)		0.230(2)		0.318(1)	
Si(2)	0.619(1)		0.469(2)		0.356(1)	

b. Na_xSi₄₆ (Pm3n, cubic)						
Unit Cell:	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	γ (°)	β (°)	γ (°)
76°C, 9.5 min.	10.1965(6)	10.1965(6)	10.1965(6)	90	90	90
500°C, 65 min.	10.2238(5)	10.2238(5)	10.2238(5)	90	90	90
500°C, 150 min.	10.2285(3)	10.2285(3)	10.2285(3)	90	90	90
Na _x Si ₄₆ coordinates						
76°C, 9.5 min.	<i>x</i>		<i>y</i>		<i>z</i>	
Na(1)	0		0		0	
Na(2)	0.25		0.5		0	
Si(1)	0		0.308(2)		0.118(2)	
Si(2)	0.183(2)		0.183(2)		0.183(2)	
Si(3)	0.25		0		0.5	
500°C, 65 min.	<i>x</i>		<i>y</i>		<i>z</i>	
Na(1)	0		0		0	
Na(2)	0.25		0.5		0	
Si(1)	0		0.305(2)		0.119(2)	
Si(2)	0.180(1)		0.180(1)		0.180(1)	
Si(3)	0.25		0		0.5	
500°C, 300 min.	<i>x</i>		<i>y</i>		<i>z</i>	
Na(1)	0		0		0	
Na(2)	0.25		0.5		0	
Si(1)	0		0.3066(6)		0.1193(6)	
Si(2)	0.1811(5)		0.1811(5)		0.1811(5)	
Si(3)	0.25		0		0.5	

Table 3: Structural Refinement details for (a) the NaSi (silicide) and Na_xSi₄₆ (clathrate) phases at the same three representative points of the synthesis as used for Fig.1. The values in brackets represent the last given decimal place statistical error output obtained from the least squares refinement process (the amount of NaSi after 300 min. was considered too small for inclusion).

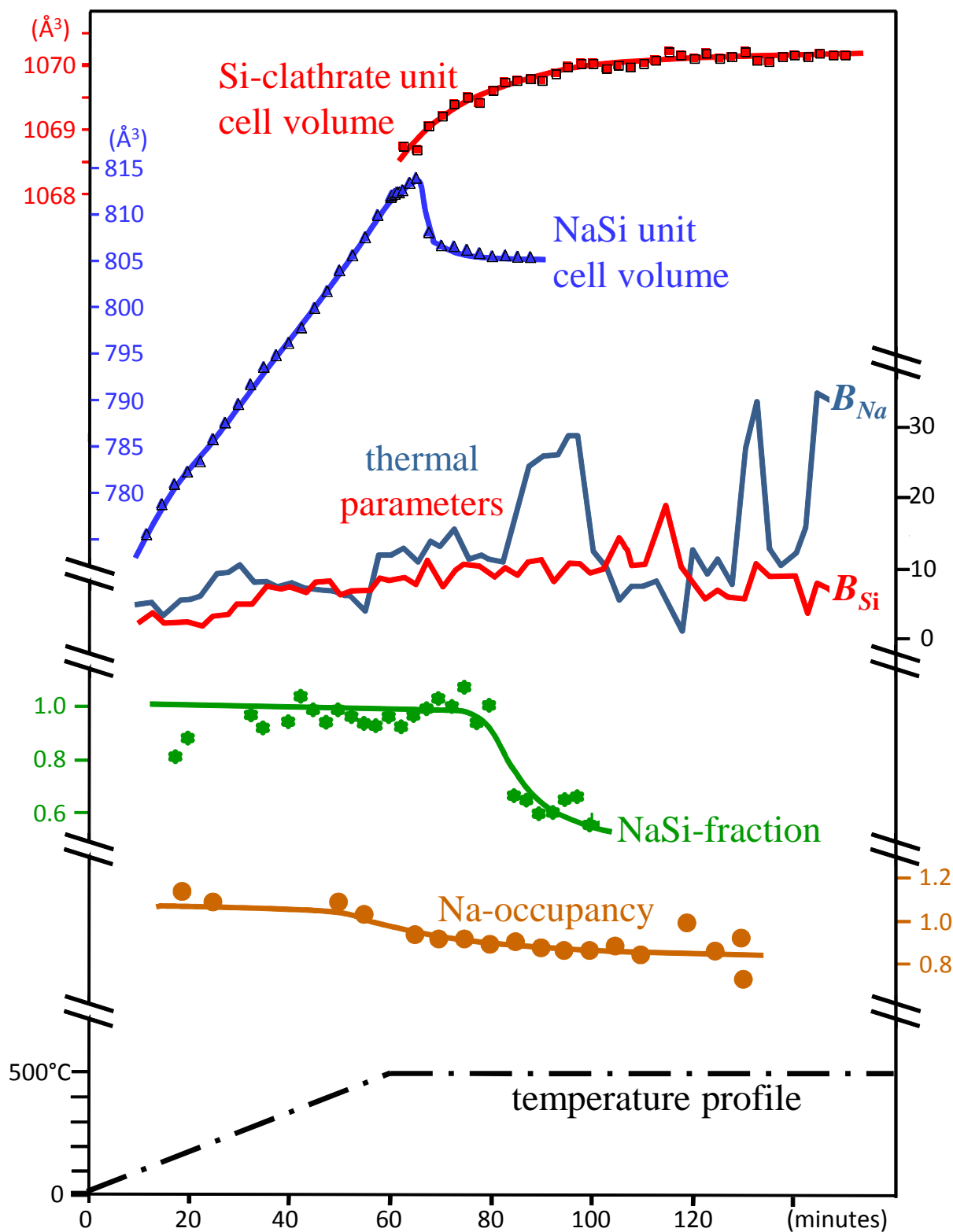


Figure 2: Variations in Unit Cell and other parameters *versus* time/temperature, as obtained from the *in situ* data after multi-phase refinement. The main article displays the same NaSi and Si-clathrate unit cell volumes *versus* time/temperature. In this plot other parameters, the thermal-B-factors (for Na and Si), the NaSi fraction, the average Na-occupancy of the Na structural sites, are additionally shown; the parameters are derived mainly from standard

FullProf output (with proportional values) and are expressed, as appropriate, in absolute units or in arbitrary/normalized (to unity) units. The overall perception from these combined plots would be that there are clearly significant structural/thermal/compositional changes occurring, at 500°C during the 60-100 minutes period, and that these changes include a large NaSi prior expansion, increased Na-mobility leading to loss of structural-Na and consequent promotion of the $\text{NaSi} \rightarrow \text{Na}_x\text{Si}_{46}$ -clathrate decomposition reaction. Such indications are very useful, but it must also be pointed out that many of the parameters in question, particularly the *B*-factors and occupancy, invariably become highly correlated during refinement and therefore great caution must be exercised in interpreting the combined behavior of these parameters.