

## Methane pyrolysis in low-cost, alkali-halide molten salts at high temperatures Supplementary Information

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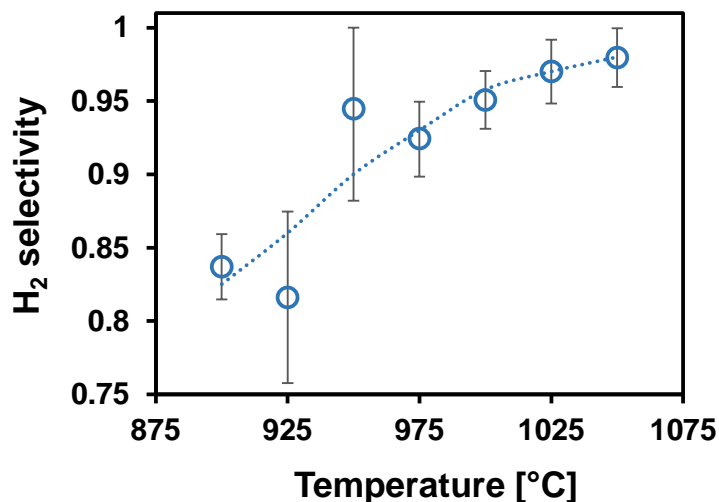
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### Table of Contents

1. Selectivity of products.....	2
2. Reactor modelling for kinetic parameter calculations .....	3
a. Differential model .....	3
b. Batch reactor model.....	4
3. Reaction rates versus bubble size .....	5
4. Scale-up calculations for industrial reaction rates.....	5
5. CH <sub>4</sub> -D <sub>2</sub> exchange .....	6
a. Modeling single exchange.....	6
b. Arrhenius plot of kinetic parameters for single exchange.....	7
6. Catalytic activity of solid carbon produced from MP .....	7
7. Carbon characterizations and processing.....	8
a. Scanning Electron Microscopy (SEM) images .....	8
b. Raman spectra.....	8
c. X-ray diffraction patterns .....	9
d. Chloride salt contamination levels.....	10

## 1. Selectivity of products



**Figure S1:** H<sub>2</sub> selectivity of gaseous products of methane pyrolysis (MP) in a molten KCl bubble column. 15 SCCM of CH<sub>4</sub> is bubbled into the melt at a depth of 18 cm with an approximated bubble residence time of 0.75 seconds. 30 SCCM of argon is introduced in the headspace of the reactor for quantitative product analysis and to minimize reactions in the headspace.

The selectivity of products (on a hydrogen basis) of methane pyrolysis (MP) is calculated by dividing the total amount of atomic hydrogen in a gas product by the total amount of atomic hydrogen that enters the reactor as methane. The selectivity for molecular H<sub>2</sub> versus temperature for a molten KCl bubble column is shown in **Figure S1**. The H<sub>2</sub> selectivity increases with temperature, rising from ~84% at 900 °C to ~98% at 1050 °C. The relatively large error can be attributed to the low conversions and the subtractions of the methane conversion in the headspace. The other atomic hydrogen exits mostly as ethylene and benzene (and also likely as some larger aromatic molecules that are not detected in the gas phase).

## 2. Reactor modelling for kinetic parameter calculations

### a. Differential model

The rate of methane consumption can be expressed using the following simplified rate equation:

$$\frac{d[\text{CH}_4]}{dt} = -k_f[\text{CH}_4]^n + k_r[\text{H}_2]^m \quad (1)$$

Using reaction conditions that result in <10% conversion of methane, the initial concentration of methane is substituted, the differential is expressed as a difference, and back reactions are ignored in the following preliminary model:

$$\frac{\Delta[\text{CH}_4]}{\Delta t} = -k_f[\text{CH}_4]^{0n} \quad (2)$$

The order in methane (i.e.,  $n$ ) is confirmed to be 1 by measuring the rate of methane consumption versus methane partial pressure at low conversions, where the concentration of methane is calculated using an ideal gas law assumption:

$$[\text{CH}_4] = \frac{P_{\text{CH}_4}}{RT} \quad (3)$$

By dividing both sides of the equation by the initial concentration (or pressure) of methane, the rate constant,  $k_f$ , can now be expressed using only the fractional conversion of methane ( $X_{\text{CH}_4}$ ) and the residence time ( $\tau$ ):

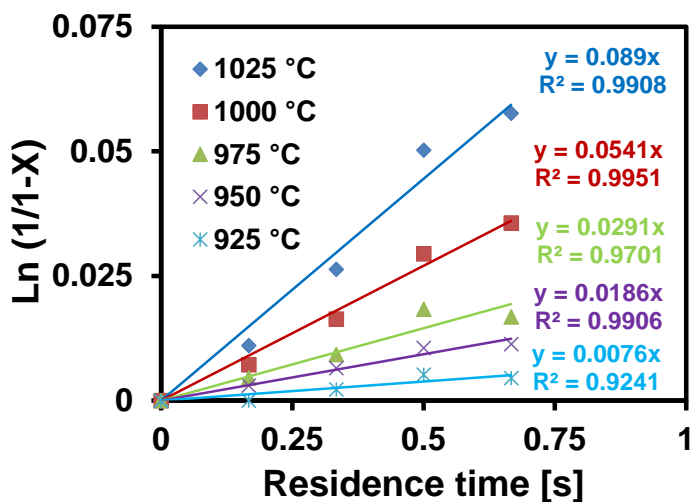
$$\frac{X_{\text{CH}_4}}{\tau} = -k_f \quad (4)$$

Once  $k_f$  has been calculated for each temperature, the Arrhenius expression can be used to find the effective kinetic parameters:

$$k = k^0 e^{-\frac{E_a}{RT}} \quad (5)$$

$$\ln k = \ln k^0 - \frac{E_a}{RT} \quad (6)$$

## b. Batch reactor model



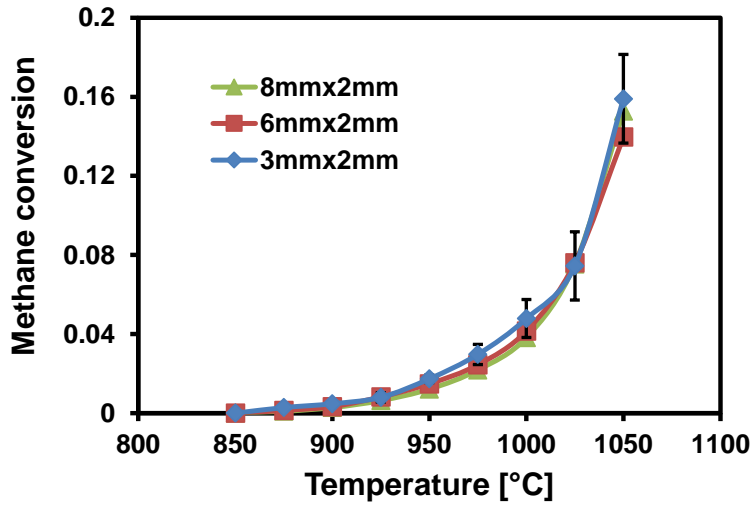
**Figure S2:** Plot of  $\ln(1/(1-X_{\text{CH}_4}))$  versus residence time for different temperatures in a molten KCl bubble column reactor at 1 atm. 15 SCCM of methane is bubbled into the melt and 30 SCCM of argon is injected into the headspace. The headspace conversion is subtracted from all points at each temperature.

Methane pyrolysis in molten salt bubble column reactors is also modeled using the batch reactor design equation, treating each individual bubble as a batch reactor:

$$k\tau = \ln \frac{1}{1-X_{\text{CH}_4}} \quad (7)$$

For each temperature, the depth of the inlet tube is adjusted and the conversion of methane ( $X_{\text{CH}_4}$ ) measured (with the headspace conversion subtracted). At each depth, the residence time ( $\tau$ ) is estimated by assuming the bubble rise velocity is 24 cm/s. The term  $\ln(1/(1-X))$  is then plotted against  $\tau$  for each temperature and the best-fit linear slope of the points is calculated as the rate constant,  $k$  (see Figure SX). This modelling approach is likely more accurate than the differential model derived in the previous section, as many more data points contribute to the estimation of the rate constant at each temperature; both the batch reactor model and the differential model (with repetition of measurements three times) yielded the same effective activation energies and pre-exponential factors (within error).

### 3. Reaction rates versus bubble size



**Figure S3:** Fractional methane conversion in a molten KCl bubble column versus temperature using quartz injector tubes submersed to a depth of 18 cm with the same inner diameters (IDs) of 2 mm and different outer diameters (ODs). Measured bubble diameters for the 8 mm, 6 mm, and 3 mm ODs are ~6 mm, ~7 mm, and ~8 mm, respectively. 15 SCCM of methane is bubbled into the melt and 30 SCCM of argon gas are sweeping the headspace.

### 4. Scale-up calculations for industrial reaction rates

The equation used to calculate the best-case scenario initial rates of methane decomposition in industrial bubble column reactors is as follows:

$$\text{rate} \left[ \frac{\text{mol}}{\text{m}^3_{\text{reactor}} \text{s}} \right] = \varepsilon \left[ \frac{\text{m}^3_{\text{gas}}}{\text{m}^3_{\text{reactor}}} \right] * k(T) \left[ \frac{1}{\text{s}} \right] * \frac{P_{\text{CH}_4}}{RT} \left[ \frac{\text{mol}}{\text{m}^3_{\text{gas}}} \right] \quad (7)$$

Here,  $\varepsilon$  is the gas holdup.

For an industrial steam methane reformer, a first-order approximation for the overall rate of reaction (assuming 100% conversion of methane to products) can be calculated using the following:

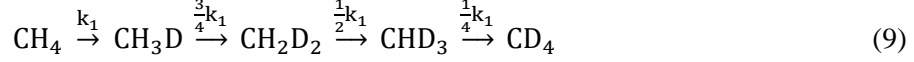
$$\text{rate} \left[ \frac{\text{mol}}{\text{m}^3\text{-s}} \right] = \frac{1}{\tau} \left[ \frac{1}{\text{s}} \right] * \frac{P_{\text{CH}_4}}{RT} \left[ \frac{\text{mol}}{\text{m}^3} \right] \quad (8)$$

Here, tau is the residence time. Assuming methane partial pressures of 10–15 atm and a residence time of 1–3 seconds, the overall rates are ~32–143 mol/m<sup>3</sup>-s at 1000 °C.

## 5. CH<sub>4</sub>-D<sub>2</sub> exchange

### a. Modeling single exchange

For the following model of single exchange of CH<sub>4</sub> and D<sub>2</sub>:



The set of differential equations representing the concentration of each species can be expressed as follows:

$$\frac{d[\text{CH}_4]}{dt} = -k_1[\text{CH}_4] \quad (10)$$

$$\frac{d[\text{CH}_3\text{D}]}{dt} = -\frac{3}{4}k_1[\text{CH}_3\text{D}] + k_1[\text{CH}_4] \quad (11)$$

$$\frac{d[\text{CH}_2\text{D}_2]}{dt} = -\frac{1}{2}k_1[\text{CH}_2\text{D}_2] + \frac{3}{4}k_1[\text{CH}_3\text{D}] \quad (12)$$

$$\frac{d[\text{CHD}_3]}{dt} = -\frac{1}{4}k_1[\text{CHD}_3] + \frac{1}{2}k_1[\text{CH}_2\text{D}_2] \quad (13)$$

$$\frac{d[\text{CD}_4]}{dt} = +\frac{1}{4}k_1[\text{CHD}_3] \quad (14)$$

Assuming there is an initial concentration of 0 for all species except for CH<sub>4</sub>, the above system of differential equations can be solved analytically to yield the following expressions:

$$[\text{CH}_4] = [\text{CH}_4]^0 e^{-k_1 t} \quad (15)$$

$$[\text{CH}_3\text{D}] = 4 [\text{CH}_4]^0 e^{-k_1 t} \left(-1 + e^{\frac{k_1 t}{4}}\right) \quad (16)$$

$$[\text{CH}_2\text{D}_2] = 6 [\text{CH}_4]^0 e^{-k_1 t} \left(-1 + e^{\frac{k_1 t}{4}}\right)^2 \quad (17)$$

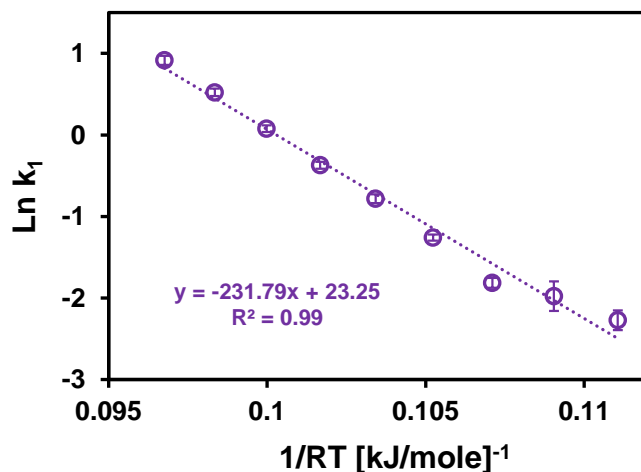
$$[\text{CHD}_3] = 4 [\text{CH}_4]^0 e^{-k_1 t} \left(-1 + e^{\frac{k_1 t}{4}}\right)^3 \quad (18)$$

$$[\text{CD}_4] = [\text{CH}_4]^0 e^{-k_1 t} \left(-1 + e^{\frac{k_1 t}{4}}\right)^4 \quad (19)$$

In the above five analytical expressions (Eq. S15–S19), there is only one unknown variable (the rate constant,  $k_1$ ) and one parameter (the initial concentration of methane,  $[\text{CH}_4]^0$ ). Values expressed in units of concentration can be replaced with expressions of partial pressures using the ideal gas law (see Eq. S3). The first-order rate constant,  $k_1$ , can be calculated at each temperature using Eq. S4 and then the effective kinetic parameters (pre-exponential factor,  $k_1^0$ , and activation energy,  $E_{a1}$ ) can be calculated using the

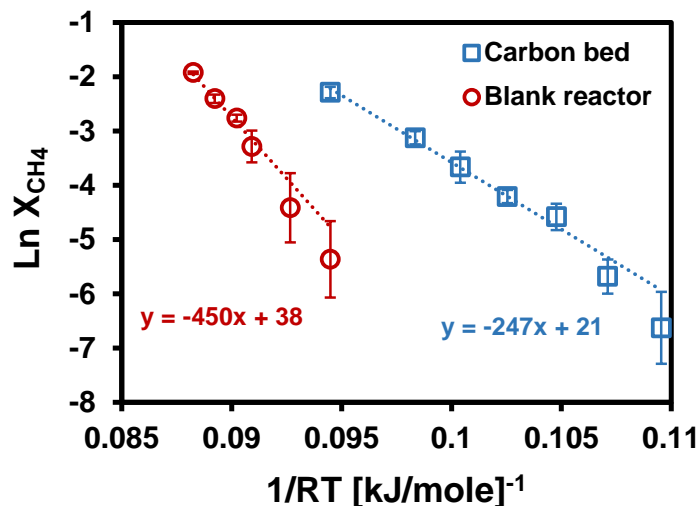
Arrhenius equation (Eq. S6 and Figure S4). The values of  $k_1$  and  $P_{\text{CH}_4^0}$  were then used to model the partial pressures of methane isotopologues using Eq. S15–S19.

### b. Arrhenius plot of kinetic parameters for single exchange



**Figure S4:** Arrhenius plot of calculated rate constant for  $\text{CH}_4\text{-D}_2$  exchange in a molten KCl bubble column. Initial methane partial pressure is 0.1 atm and initial deuterium partial pressure is 0.9 atm. Total bubbling flowrate is 20 SCCM with 30 SCCM of Ar sweeping the headspace of the reactor.

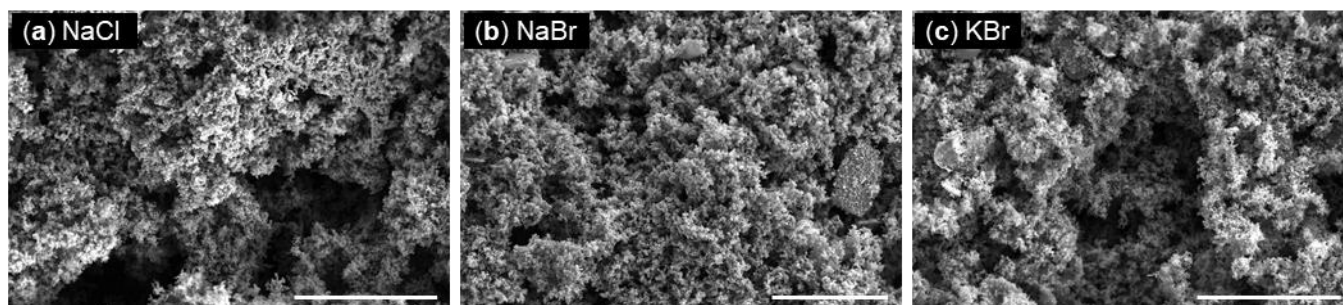
### 6. Catalytic activity of solid carbon produced from MP



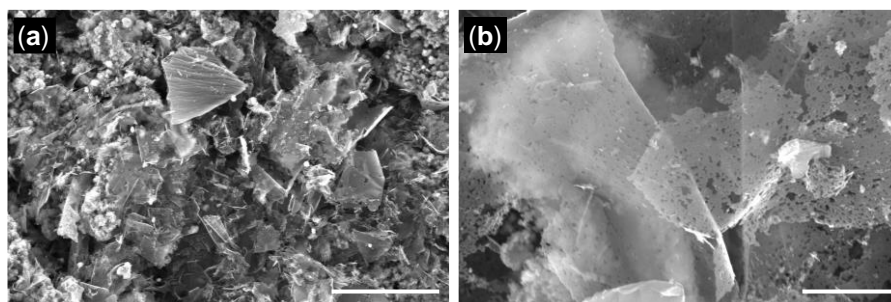
**Figure S5:** Arrhenius plots of  $\text{Ln } X_{\text{CH}_4}$  vs  $1/RT$  for a packed bed of water-washed carbon synthesized from MP in molten KCl and a blank reactor (i.e., the same reactor without a carbon bed). A  $\frac{1}{2}$ " quartz reactor is loaded with 0.2 grams of carbon supported on quartz wool for the experiment. Reactant gas is comprised of 30 SCCM of  $\text{CH}_4$  and 20 SCCM of argon.

## 7. Carbon characterizations and processing

### a. Scanning Electron Microscopy (SEM) images

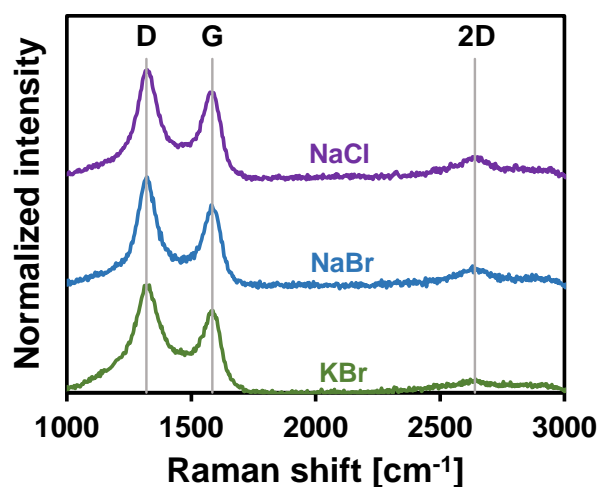


**Figure S6:** SEM images of the carbon synthesized from MP in different molten salt bubble columns at 1000 °C and 1 atm of CH<sub>4</sub>: (a) NaCl; (b) NaBr; and (c) KBr. All carbons have been washed with 70 °C water for two hours with constant stirring. Scale bars in all images correspond to 50 μm.



**Figure S7:** SEM images of the carbon synthesized from MP in molten KCl at 1050 °C and 0.13 atm of CH<sub>4</sub> (supplemented with argon to 1 atm). Scale bars correspond to (a) 50 μm and (b) 5 μm.

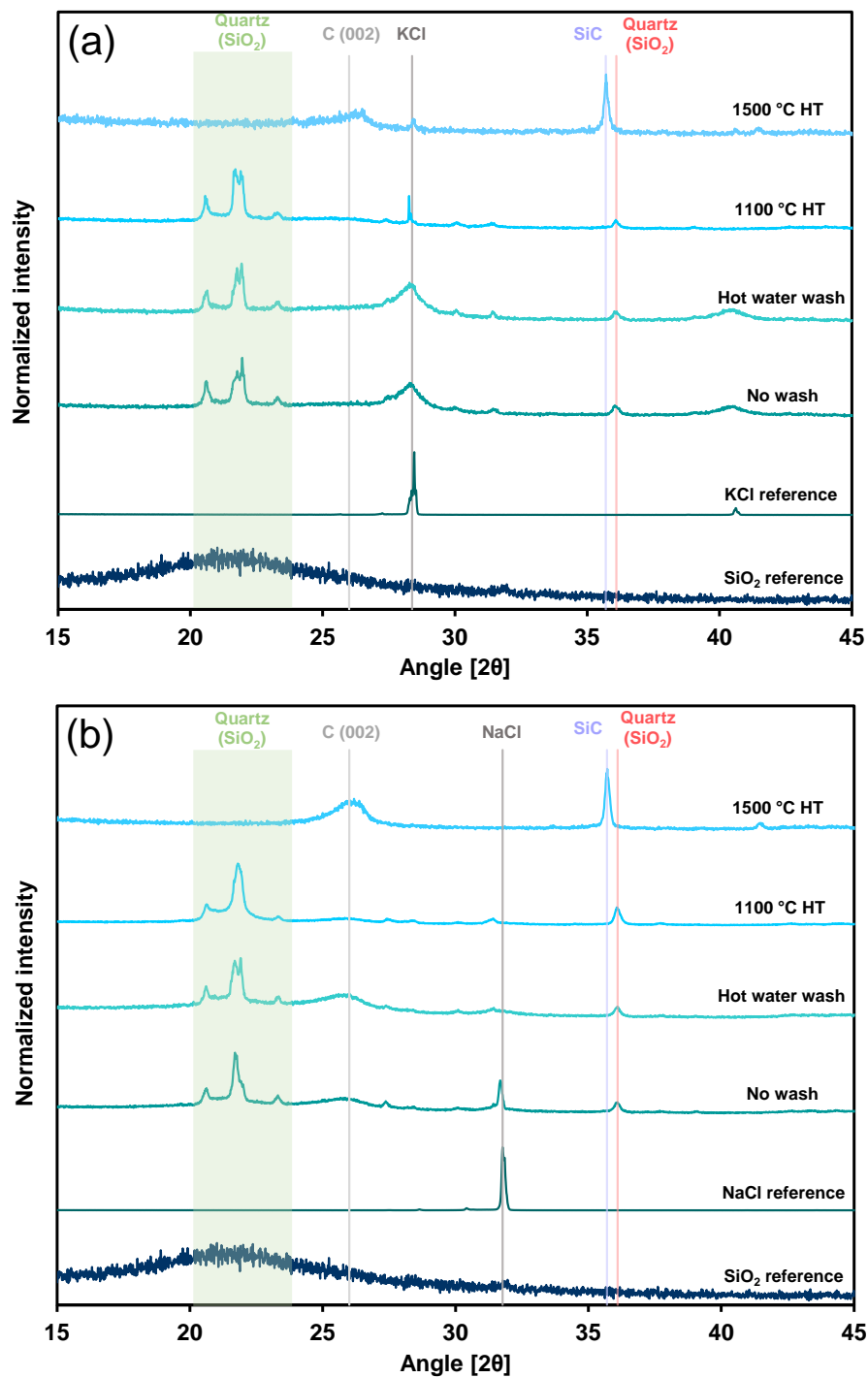
### b. Raman spectra



**Figure S8:** Raman spectra of carbon samples synthesized from methane pyrolysis in different molten salt bubble column reactors at 1000 °C. All samples have been washed with 70 °C water for 2 hours with constant stirring.



### c. X-ray diffraction patterns



**Figure S9:** XRD patterns of carbon products synthesized from MP in molten (a) KCl and (b) NaCl after various washing procedures. Quartz (SiO<sub>2</sub>) reactor material and neat salt (i.e., fresh NaCl and KCl powder) samples are included as references.

The XRD patterns for the carbon products synthesized in molten chloride bubble columns after various washing procedures are shown in Figure S9. The reflection corresponding to the (002) plane in graphite (at  $\sim 26\ 2\theta$ ) is broad or nonexistent in the samples that have not yet been washed, whereas the reflections for quartz ( $\text{SiO}_2$ ) and salt crystals are sharp and prominent. Hot water washing the samples for 2 hours at 70 °C with constant stirring significantly reduced the intensity of the NaCl peaks, but not the KCl peaks. A subsequent heat treatment at 1100 °C for 12 hours under flowing argon reduced the average intensity of the KCl peaks markedly. After an additional 1500 °C heat treatment for 12 hours under flowing argon, the remaining obvious reflections in the XRD spectra were those corresponding to disordered carbon, KCl, and silicon carbide (SiC). The presence of SiC (and absence of  $\text{SiO}_2$ ) can be explained by the reaction of the remaining  $\text{SiO}_2$  with the carbon powders.

#### d. Chloride salt contamination levels

**Table S1:** EDX analysis of solid carbon produced in alkali-halide molten salt bubble columns at 1000 °C after a 12-hour heat treatment at 1500 °C under flowing argon.

Alkali-halide salt	Weight %		
	Na or K	Cl	C
NaCl	$0.4 \pm 0.1$	$3.1 \pm 0.5$	$96.5 \pm 0.6$
KCl	$0.2 \pm 0.1$	$0.6 \pm 0.1$	$99.2 \pm 0.2$