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SUPPORTING INFORMATION

An amorphous sodium aluminate hydrate phase mediates aluminum coordination changes in highly alkaline sodium hydroxide solutions

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1.0 Stoichiometry calculations

Calculations to determine the amount of boehmite (AlOOH) and sodium hydroxide monohydrate ($NaOH \cdot H_2O$) needed to approximate the stoichiometry of nonasodium bishexahydroxyaluminate trihydroxide hexahydrate (NSA, $Na_9(Al(OH)_6)_2 \cdot (3OH) \cdot (6H_2O)$) are described.

1. Starting with the stoichiometry of NSA, first rearrange the molecular formula into units of Na_2O, Al_2O_3, and H_2O. The sodium, aluminum, and hydrogen balances are first calculated and then the oxygen balance is used to validate the calculation.

    - Sodium balance:

$Na_9(Al(OH)_6)_2 \cdot (3OH) \cdot (6H_2O) = 9$ Na total $= 4.5$ Na_2O

    - Aluminum balance:

$Na_9(Al(OH)_6)_2 \cdot (3OH) \cdot (6H_2O) = 2$ Al total $= 1$ Al_2O_3

    - Hydrogen balance:

$Na_9(Al(OH)_6)_2 \cdot (3OH) \cdot (6H_2O) = 27$ H total $= 13.5$ H_2O

    - Oxygen balance:

$Na_9(Al(OH)_6)_2 \cdot (3OH) \cdot (6H_2O) = 21$ O total $= 13.5$ $\{H_2O\} + [3 \cdot 1]$ $\{Al_2O_3\} + [4.5]$ $\{Na_2O\}$

$= 21 = 13.5 + 3 + 4.5$

Therefore, $Na_9(Al(OH)_6)_2 \cdot (3OH) \cdot (6H_2O)$ can be represented as $\{4.5\ Na_2O : 1\ Al_2O_3 : 13.5\ H_2O\}$.

2. Next, AlOOH is related to Na_2O, Al_2O_3, and H_2O

Given that $Al_2O_3 + H_2O = 2AlOOH$, AlOOH can be written as $\{0\ Na_2O : 1\ Al_2O_3 : 1\ H_2O\}$.

3. $NaOH \cdot H_2O$ is then related to Na_2O, Al_2O_3, and H_2O

First, $NaOH + H_2O = NaOH \cdot H_2O$

Then, $Na_2O + H_2O = 2NaOH$

Therefore, $2\ NaOH \cdot H_2O = Na_2O + 3\ H_2O$, and $NaOH \cdot H_2O$ can be written as $\{0\ Al_2O_3 : 1\ Na_2O : 3\ H_2O\}$

4. Analysis of the mole ratios indicates that to prepare a system approximating the composition of NSA, that one mole of AlOOH can be added to 4.5 moles of $NaOH \cdot H_2O$, shown below. Note that the approximation leads to a slightly water rich composition in the mixture of AlOOH and $NaOH \cdot H_2O$.

{4.5 Na_2O : 1 Al_2O_3 : 13.5 H_2O} ≈
1·{0 Na_2O : 1 Al_2O_3 : 1 H_2O} + 4.5·{0 Al_2O_3 : 1 Na_2O : 3 H_2O}

{4.5 Na_2O : 1 Al_2O_3 : 13.5 H_2O} ≈ {4.5 Na_2O : 1 Al_2O_3 : 14.5 H_2O} =
{9 $NaOH{\cdot}H_2O$: 2 AlOOH : 0 H_2O}

Using the molecular weight of AlOOH (59.973 g/mol) and $NaOH{\cdot}H_2O$ (58.012 g/mol), the mass of AlOOH and $NaOH{\cdot}H_2O$ can be determined to prepare a molar composition of {4.5 Na_2O : 1 Al_2O_3 : 14.5 H_2O}.
1 g of AlOOH · $(59.973\ g/mol)^{-1}$ · 4.5 (moles $NaOH{\cdot}H_2O$/moles AlOOH) · 58.012 g/mol = 4.3529 g $NaOH{\cdot}H_2O$

Note that the conversion between mole ratios of Na_2O : Al_2O_3 : H_2O and mass ratios of Na_2O : Al_2O_3 : H_2O is possible by using the molecular weights of Na_2O (61.9789 g/mol), Al_2O_3 (101.961 g/mol) and H_2O (18.0153 g/mol).

2.0 Additional experimental results

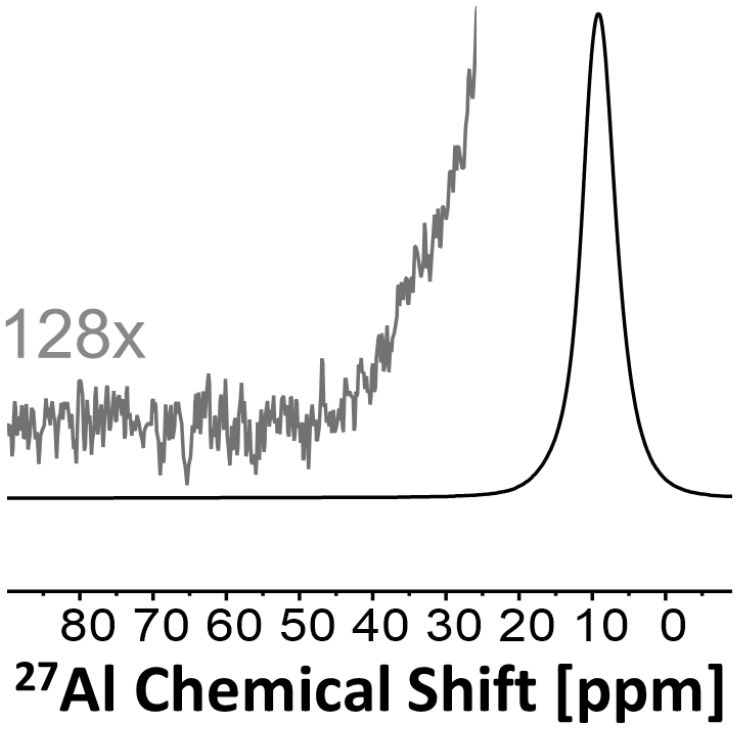

Figure S1. Single pulse, direct excitation *in situ* ^{27}Al MAS NMR spectra at a field strength of 14.1 T with 20.0 kHz spinning rate at approximately 25 °C characterizing the as-synthesized boehmite. A vertically magnified and offset spectrum is overlaid to show the lack of tetrahedral-coordinated Al in the as-synthesized boehmite. The ^{27}Al MAS NMR spectrum was acquired with a 0.45 μs pulse, 2048 transients, an acquisition time of 0.0185 s enumerated by 23148 complex points, and a recycle delay of 1 s. The spectrum was processed in Mestrenova, where the spectrum was zero-filled to 65536 complex points, and 20 Hz of exponential line broadening was applied.

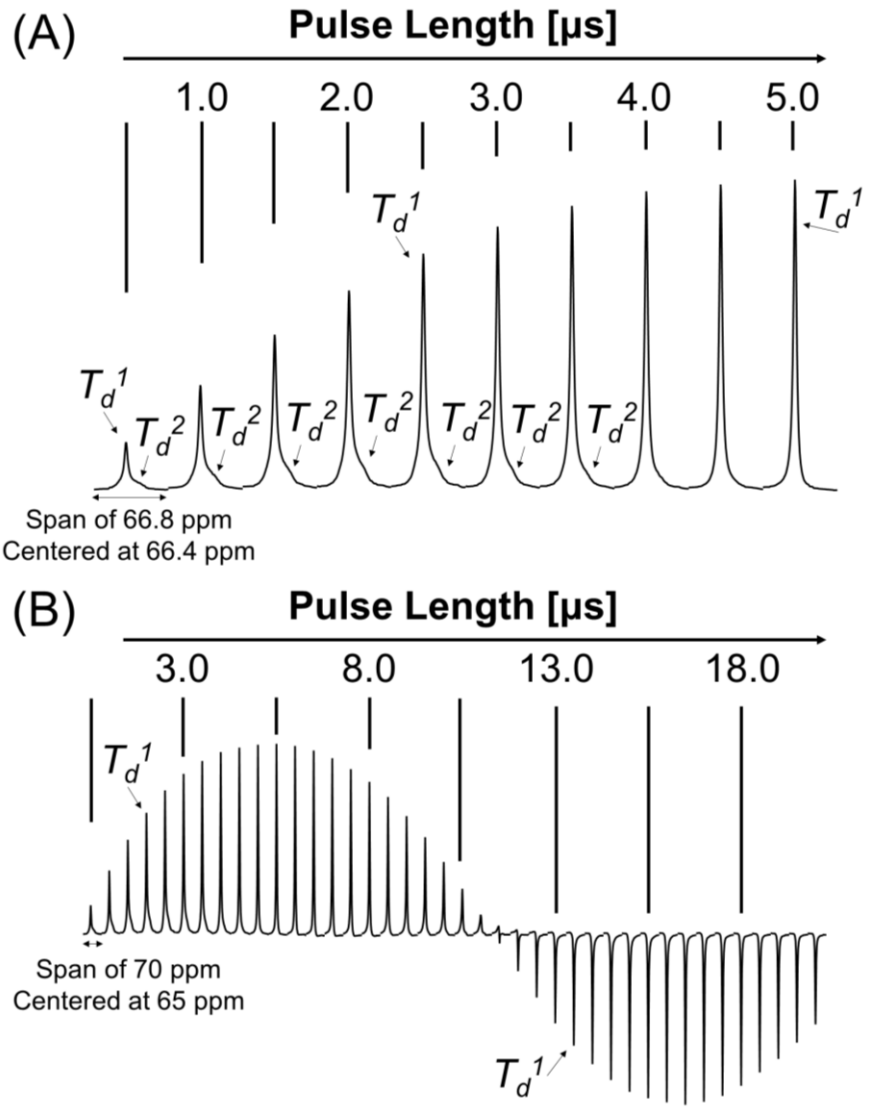

Figure S2. *In situ* ^{27}Al MAS NMR pulse length nutation experiment at a field strength of 14.1 T with approximately 3.4 kHz of spinning at 70 °C is shown. (A) Horizontally stacked ^{27}Al MAS NMR spectra acquired with between 0.5 and 5 µs duration pulses. Two tetrahedral resonances (T_d^1 and T_d^2) are visible, with T_d^2 exhibiting a shorter 90° pulse length. T_d^2 is assigned to amMSA based on X-ray diffraction, Raman spectroscopy, and high-field ^{27}Al MAS NMR spectroscopy as shown in the main text. (B) Horizontally stacked ^{27}Al MAS NMR spectra acquired with between 0.5 and 20 µs duration pulses. The quasi spin-1/2 behavior is evident based on inspection of the T_d^1 resonance over a longer range of pulse lengths, where a sinusoidal-dependence on pulse length is observed. Based on the sinusoidal dependence on pulse length, T_d^1 is assigned to solution-state aluminate species. To acquire these spectra, 64 transients were collected, with an acquisition time of 0.01984 s enumerated with 4096 complex points, and a recycle delay of 1 s was used. The spectra were processed in Mestrenova, where the spectra were truncated to 4000 points, zero-filled to 8192 points, and then 50 Hz of exponential line broadening was applied. The spectra are annotated with pulse lengths, assignments and vertical lines to guide the eyes. The span and center of the horizontally stacked spectra are also annotated.

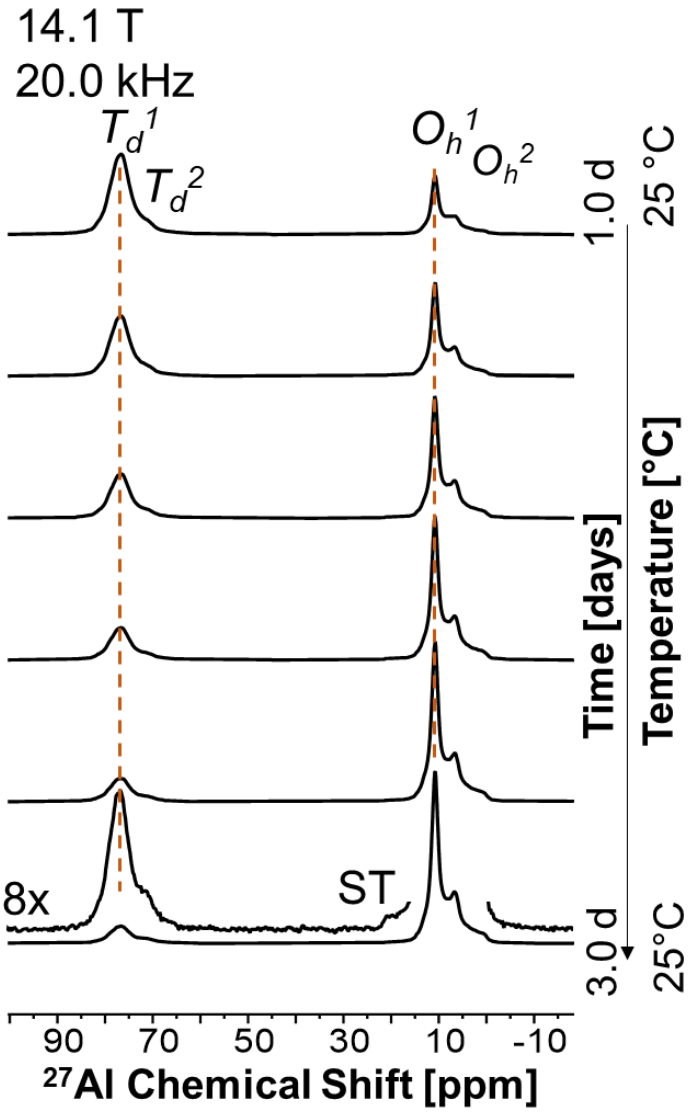

Figure S3. Single pulse, direct excitation *in situ* ^{27}Al MAS NMR spectra at a field strength of 14.1 T with 20.0 kHz spinning rate tracking amorphous monosodium aluminate hydrate transformation into NSA at approximately 25 °C. A magnified spectrum is offset from the final spectrum, with spectra assignments for the two tetrahedral resonances of amMSA and two octahedral resonances of NSA. The orange line is drawn to guide the eyes to the lack of any progressive changes in chemical shift. The satellite transition of the octahedral resonance is labeled ST, the octahedral resonances of NSA are labeled O_h^i and the tetrahedral resonances are labeled T_d^i, where *i* denotes the site number. In this figure, the time at t=0 h corresponds to the time at which the physical mixture of NaOH·H_2O and AlOOH were raised to a temperature of 70 °C. After approximately 1 day at 70 °C, the mixture was quenched to a temperature of approximately 25 °C, and acquisition of MAS NMR spectrum began at approximately 25 °C and continued over the next 2 days.

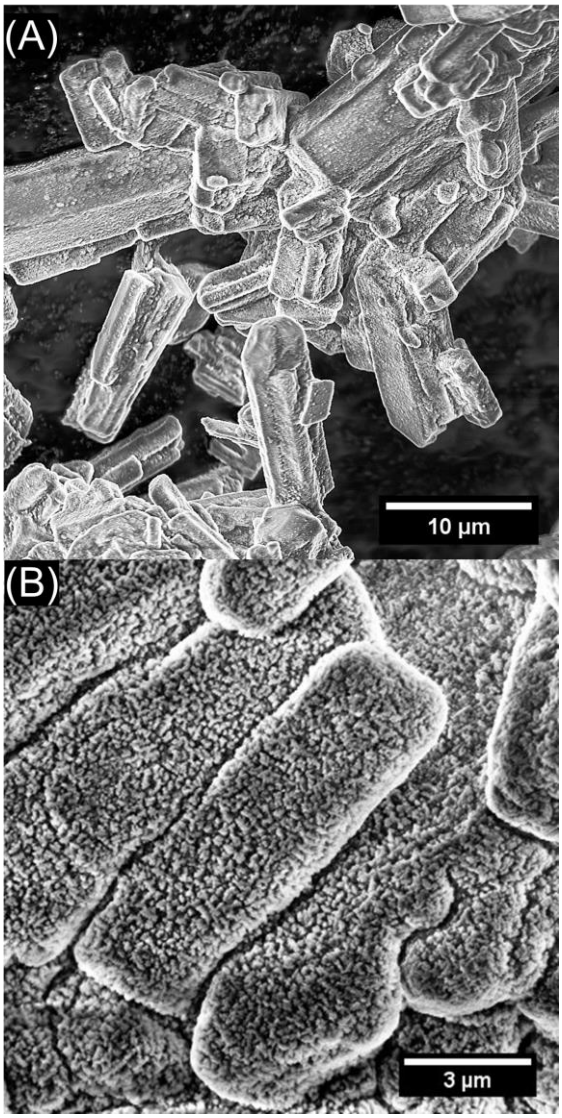

Figure S4. Representative scanning electron microscopy (SEM) of the amorphous monosodium aluminate hydrate phase, which is transforming into NSA, prepared *ex situ* via mixing AlOOH and $NaOH \cdot H_2O$ at 70 °C in a Parr vessel for 1 day. The SEM micrographs were obtained with a Helios NanoLab SEM (FEI, Hillsboro, Oregon) via the collection of secondary electrons using a through the lens detector (TLD) with an electron beam voltage of 5.0 kV and a current of 0.17 nA. Post-acquisition processing was performed in ImageJ (v 1.53c) where the contrast of the image was optimized for the micrographs. Note that the image shown in part (A) was digitally sharpened in ImageJ to better visualize the surface roughness. Comparable surface roughness is readily observable at higher magnifications, as shown in (B), with only optimization of the contrast. The SEM micrographs show the presence of approximately 10 micron sized columnar crystals coated with small crystallites.

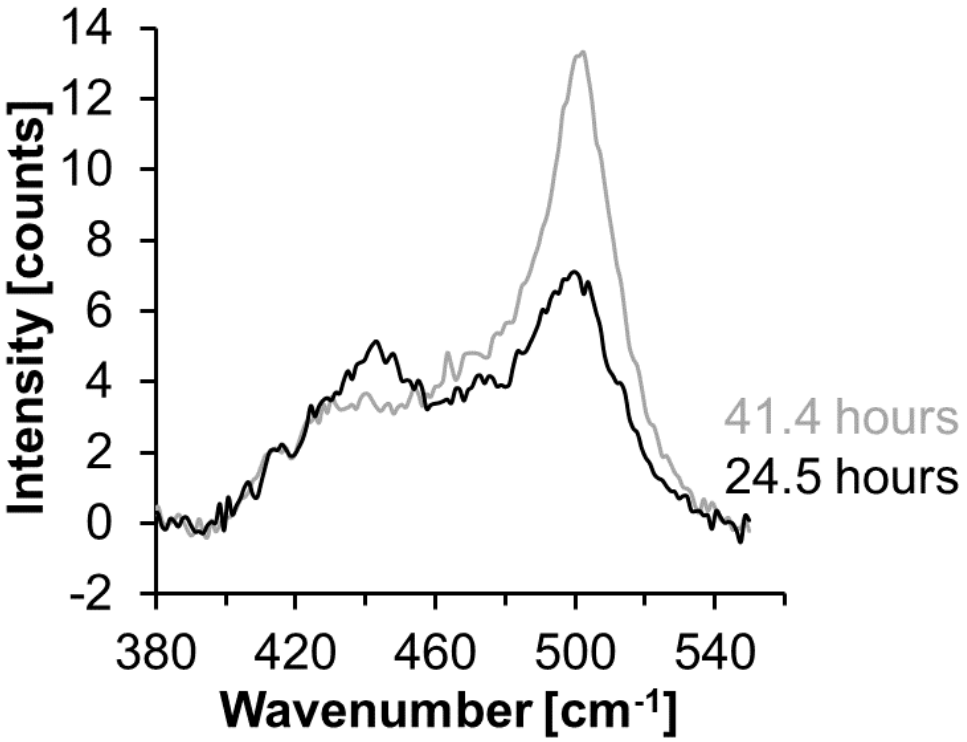

Figure S5. Raman spectra tracking the amorphous monosodium aluminate hydrate phase transforming into NSA at approximately 25 °C. The Raman spectra were acquired on the Horiba Labram HR spectrometer equipped on a Nikon Ti-E inverted microscope using a 10× objective via application of a continuous 632.81 nm laser at a temperature of ca. 25ºC. Spectra were acquired between 100 – 1300 cm^{-1}. The region spanning 380 – 550 cm^{-1} was deconvoluted using a single linear function to remove the background. The data shows that the Raman band assigned to NSA at ~500 cm^{-1} increases as a function of reaction time while the Raman band assigned to the amorphous tetrahedral Al component at ~ 440 cm^{-1} decreases as a function of reaction time, which is in agreement with the analysis of the *in situ* ^{27}Al MAS NMR results shown in the main text of the manuscript. In this figure, the time at t=0 h corresponds to the time at which the physical mixture of $NaOH \cdot H_2O$ and AlOOH were raised to a temperature of 70 °C. After approximately 1 day at 70 °C, the mixture was quenched to a temperature of approximately 25 °C, and acquisition of the Raman spectra began at approximately 25 °C. A total of 0.5 hours had elapsed between the temperature quench and the acquisition of the first Raman spectrum.

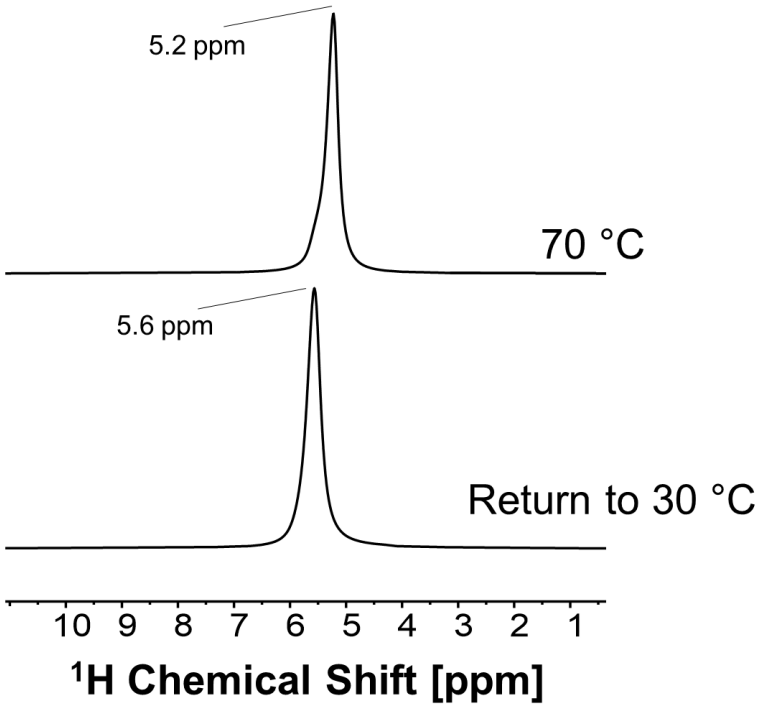

Figure S6. *In situ* ^{1}H MAS NMR spectra at a field strength of 7.05 T and a MAS spinning rate of 3.4 kHz of the boehmite and $NaOH \cdot H_2O$ mixture, heated in the instrument. At 70 °C the acquired ^{1}H MAS NMR spectrum appears as a single Lorentzian peak (albeit with some asymmetry) with a maximum at 5.2 ppm. Upon cooling to 30 °C and after 1 day (during which ^{27}Al MAS NMR scans were being acquired) the ^{1}H MAS NMR spectra shifts to appear as a single Lorentzian resonance at 5.6 ppm. In Figure S6, the spectra are normalized by their maximum peak height and annotated with the peak position of the Lorentzian line. The ^{1}H MAS NMR spectra at either temperature likely appear as a single Lorentzian line due to the chemical exchange of water and hydroxide between the different sites in the solution and solid at 70 °C, and between the different sites in the solids (amMSA and NSA) at 30 °C. Due to the lack of resolution of distinct ^{1}H environments, further analysis was not performed. The ^{1}H MAS NMR spectra were acquired with about 20 transients, an acquisition time of 200 μs, an excitation pulse width of 3.56 μs equivalent to a $\pi/4$ pulse length, and a recycle delay of 2 s between transients. The ^{1}H MAS NMR resonance of ethylene glycol at 30 °C was used as a chemical shift reference (δ = 3.75 ppm for the CH_2 resonance). The ^{1}H MAS NMR spectra were processed in Mestrenova, where 50 Hz of exponential line broadening was applied.

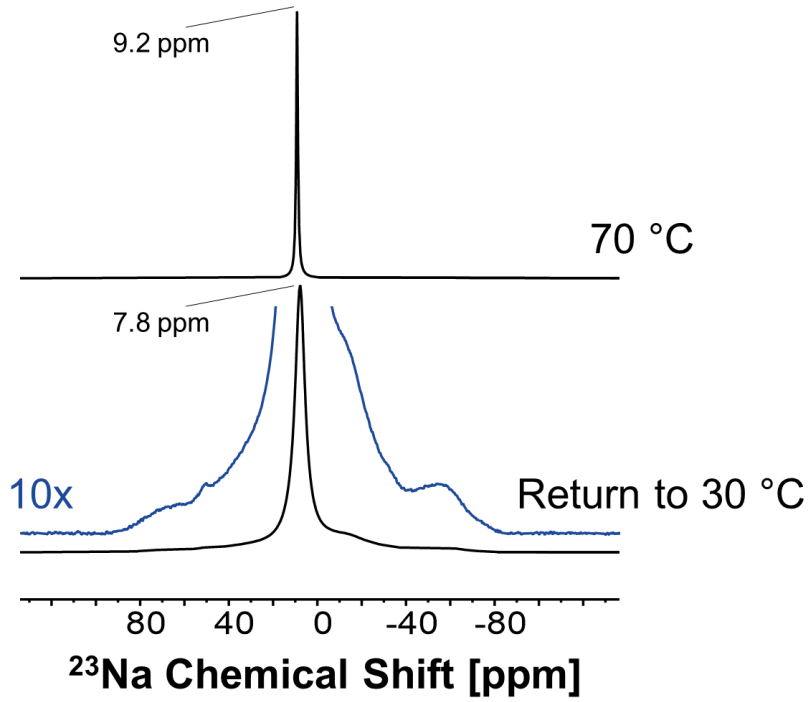

Figure S7. *In situ* ^{23}Na MAS NMR spectra at a field strength of 7.05 T and a MAS spinning rate of 3.4 kHz of the boehmite and $NaOH \cdot H_2O$ mixture, heated in the instrument. At 70 °C, the acquired ^{23}Na MAS NMR spectrum appears as a single Lorentzian peak with a maxima at 9.2 ppm. Upon cooling to 30 °C and after 1 day (during which ^{27}Al MAS NMR scans were being acquired) the ^{23}Na MAS NMR spectra develops into additional components. Specifically, the peak position of an apparently Lorentzian line appears at 7.8 ppm, and the Lorentzian line is superimposed on a broad component. In Figure S7, the spectra are normalized by their maximum peak height, annotated with the peak position of the Lorentzian line, and a vertically magnified (10x) spectrum is offset in blue to show the broad components which were of weaker intensity. The spectra are consistent with 6-coordinated Na^+ ions, but due to the low chemical shift range and the presence of many Na sites of NSA, further analysis was not performed. The ^{23}Na MAS NMR spectra were acquired with 128 transients, an acquisition time of 100 μs, an excitation pulse width of 1.5 μs equivalent to a $\pi/10$ pulse length calibrated on a sample of 1 M NaCl at 30°C, and a recycle delay of 1 s between transients. The ^{23}Na MAS NMR resonance of 1 M NaCl at 30 °C was used as a chemical shift reference ($\delta = 0$ ppm). The ^{23}Na MAS NMR spectra were processed in Mestrenova, where 5 Hz of exponential line broadening was applied.