

# FORMATION OF KANEMITE FROM PRECURSOR AS A MODEL FOR ASR GEL HYDRATION

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## Abstract

In the kanemite formation model for ASR,  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  reacts with  $\text{SiO}_2$  of the aggregates and water to Na-kanemite. Our investigations deal with the expansion, the water uptake and the structural changes during the reaction of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  and water vapour without any addition of  $\text{SiO}_2$  in order to explain the contribution of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  to the expansion process. There are used two samples with different content of the  $\text{Na}_2\text{Si}_2\text{O}_5$  modifications and alteration state.

It is shown that under restraint in the expansion cell, there is no proportional correlation between kanemite amount, water uptake and expansion.

Under free swelling conditions, kanemite formation is intermediate and most of the reaction products are amorphous sodium silicate hydrates. They seem to be responsible for the continuous water uptake observed over the whole period of 90 days. These gels have a lower degree of polymerisation than the original  $\text{Na}_2\text{Si}_2\text{O}_5$  samples.

**KEYWORDS:** kanemite formation, expansions, mass changes, gel silicate structure

## 1 INTRODUCTION

Although a lot of studies concerning the mechanism of Alkali-Silica Reaction (ASR) have been done, no unique model was established covering all observations related to real degradation of concrete. The so-called ASR gels which are generated during the reaction between the alkaline pore solution and the alkali-sensitive aggregates play an important role in understanding the phenomenon of swelling and expansion during the ASR. Investigations of field gels from damaged concrete structures and also synthetic gels with comparable composition showed [1,2,3,4,5] that these alkali silicate gels mainly consist of  $\text{SiO}_4$ -layers. In accordance with this, Wieker et al. [6,7,8] proposed the formation of kanemite as a model for the ASR. In this model, the reaction of the layer silicate  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  with  $\text{SiO}_2$  from the aggregate proceeds in the presence of water vapour and causes the formation of a hydrous layer silicate with water in the interlayer space ( $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ). This process is accompanied with an expansion of the reaction mixture. Besides these similarities to ASR there are still open questions, for instance the influence of the amorphous state of the real ASR gels on the water uptake. Xou et al. [2-5] found that the amount of water in the interlayer space is not sufficient to explain the expansion behaviour.

In this paper, we investigated the reaction of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  with water vapour without any additional  $\text{SiO}_2$ , because  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  can form kanemite itself according to equation:



Furthermore, the  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  used contains other structure modifications ( $\alpha$ -,  $\beta$ -,  $\gamma$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ) and is subject to alteration including carbonation, which could affect volume expansion if reacting.

## 2 MATERIALS AND METHODS

### 2.1 Materials

The used  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  samples (A and B) are commercially available from Clariant, Germany (product SKS 6) and consist of mainly  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ , with variable but minor amounts of the other structure modifications. The materials also differ in age, material A being five years old and material B only one month.

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## 2.2 Methods for assessment and analysis

### *Expansion measurements*

The  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  samples were pressed to tablets and stored in a device specially designed for expansion testing, as shown in Figure 1. The construction of the devices allows control the relative humidity (RH) in the closed system, because there is no direct contact between the tablet and liquid water. For kanemite formation, the RH of 88 % is optimal [8] and was controlled by a 20 wt% solution of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) in the reservoir serving as a humidity buffer. The weight of the plunger and the plate results in an inherent restraint of about 0.005 N/mm<sup>2</sup>.

### *Water sorption*

Another part of tablets was stored in an exsiccator with the same RH like in the expansion device (88 % RH at 20°C). The amount of water taken up from the atmosphere in the exsiccator was determined by weighting the samples.

### *X-ray diffraction (XRD)*

The phase composition of the starting and the expanded samples was determined by a X-ray diffractometer (XRD 3000 TT, Seifert GmbH). The samples were investigated as tablets without any additional preparation procedures in order to avoid structural changes. The upper surface of each tablet corresponded with the reflection plane of the goniometer. The XRD experiments were carried out with  $\text{CoK}\alpha$  radiation ( $\lambda=1.77889\text{\AA}$ ) on a total scan range  $2\theta=8-80^\circ$  with step size  $2\theta=0.05^\circ$  and a scan time per step of 3s. The operating conditions of the instrument were set at 40 kV and 30 mA.

In phase identification, following ICSD code numbers are used: No. 34669 ( $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ), No. 34668 ( $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ), No. 88662 ( $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$ ) and No. 88618 for kanemite.

For the quantitative determination of the crystalline phases, the POWDERCELL program [9] was used. Lower limits of detection are at about ~5wt%. Additionally, from baseline analysis, the amount of amorphous constituents can be determined.

### *<sup>29</sup>Si MAS-NMR*

For NMR investigations, the samples were prepared by careful dry powdering in a mortar with pestle. All spectra were recorded at room temperature on a BRUKER AVANCE 400 spectrometer, operating at a <sup>29</sup>Si resonance frequency of 79.48 MHz. The MAS-NMR measurements were performed using a 4 mm double-bearing MAS probe (BRUKER Biospin) at a spinning rate of 12 Hz. The <sup>29</sup>Si MAS spectra were obtained using single pulse excitation with pulse duration of 4.25  $\mu\text{s}$  ( $\pi/2$  pulse). To obtain a reliable signal-to-noise ratio, the spectra of the powdered samples were recorded by accumulating 590 – 860 FIDs with a recycle delay of 120s. Processing of the free induction decay was realized using the BRUKER XWINNMR software. The <sup>29</sup>Si spectra were externally calibrated to liquid TMS (tetra methyl silane) at 0 ppm.

## 3 RESULTS

### *Expansion*

Figure 2 shows the one-dimensional expansion behaviour of the two  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  samples until 14 and 33 days, respectively. Both samples show an expansion under the conditions selected. It is clearly to be seen, that the sample A is more reactive than sample B.

Although the expansion of both samples is different, the amount of water taken up during this expansion process is similar, ie. 17.5 wt% in A and 20.0 wt% in B.

### *Phase composition of reaction products*

Typical XRD patterns are shown in Figure 3 and 4. These diagrams contain the XRD pattern of the starting sample and the sample after 14 days reaction.

In Figure 3, the main peaks of sample A are assigned to the delta-phase. Peak heights are seen to decrease during the reaction period. After 14 days reaction at 88% RH, kanemite was formed. In addition, background noise after 14 days reaction is significantly increased. Sample B shows similar behaviour regarding the kanemite formation, but an important difference to sample A is the smaller background of the X-ray pattern curve (Figure 4).

To determine the composition of starting samples and samples after reaction, Rietveld analysis and peak deconvolution were performed with the software package POWDERCELL [9]. In Table 1, the composition of both samples is summarized. Figure 5 shows deconvolution of a XRD diffractogram from reaction product into several phase components by POWDERCELL, to

determine quantitative phase composition. This evaluation considers crystalline phases only. The amount of amorphous constituents was not determined. It is significant, that the original sample A contains less  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  but more  $\alpha$ - and  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  than sample B. After a reaction period of 14 days, sample A contains already 31.9 wt% kanemite, whereas sample B reaches nearly the same content (28.3 wt%) only after 33 days. In contrast to sample B, the content of  $\alpha$ - and  $\beta$ -modifications in sample A decreases during the reaction.

Both starting samples A and B were also investigated by  $^{29}\text{Si}$  MAS NMR with quantitative evaluation of the spectra, as shown in Figure 6. NMR assessment reveals that only crystalline  $\text{Na}_2\text{Si}_2\text{O}_5$  components exist in the original samples A and B. No evidence was found for amorphous or crystalline  $\text{SiO}_2$  that could potentially produce additional kanemite if in contact with  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  and water vapour. Under these experimental conditions,  $^{29}\text{Si}$  MAS NMR is unable to detect the small amounts of cristobalite that are detected by XRD. The signal at  $-91.8$  ppm could not be attributed to any known substance. The content of the related compound is, however, relatively small (3 wt% in A and 8 wt% in B) and is neglected in discussion. The quantitative data confirm the results from XRD experiments that the main difference between the original samples is the content of the  $\text{Na}_2\text{Si}_2\text{O}_5$  modifications, see Table 2. The values determined by XRD and NMR are in good agreement.

#### *Water sorption*

For more detailed investigations of the reaction of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  with water, sorption experiments in an exsiccator were held, so-called “free swelling”. With this set of experiments it was possible to correlate composition and water uptake, but no simultaneous expansion was included.

Sorption experiments during free expansion (Figure 7) show that there is a very similar water uptake of both samples, but the amount of water is remarkably smaller than by the samples in the expansion device.

#### *Structural changes*

Because of no proportional relation between volume expansion values, kanemite content and mass increase, respectively, the samples stored in the exsiccator were investigated by XRD POWDERCELL procedure with respect to the formation of amorphous components over a period of 90 days. The results of the XRD data analysis are shown in Figure 8 and 9.

The content of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  in sample A, Figure 8, decreases faster compared to sample B. The reaction is assumed to end at about 35 days. At this time, the amount of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  is still half of the starting value. At later times up to 90 days, the  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  amount does not change anymore. During the period of 35 days, the main changes occur with the other phases, too, especially the amount of both kanemite and amorphous phases increase in the same way as the  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  content decreases. Until the end of the reaction, the amount of kanemite decreases again while the amount of the amorphous phases increases further. At the end of the reaction, kanemite was detected in a very small amount in sample A and the content of the amorphous reaction products is about 35 wt%.

Sample B shows different behaviour. The amount of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  also decreases but in a more slow and continuous manner over the total time of reaction. At the end of the reaction, 67 wt % of  $\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  was still determined. In comparison to sample A, this represents a very small reduction only. Conversely, the amount of amorphous phases increased, especially in the second period of the reaction from 21 to 90 days.

Kanemite content increased too, and kanemite formation seems to stabilize after about 21 days at a very low content. Changes in the content of kanemite can not be observed at later times.

In both samples, the other constituents  $\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$  and  $\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$  participate in the reaction only to a small extend.

Because the existence of amorphous products was detected by XRD, additional  $^{29}\text{Si}$  MAS NMR experiments were made after 3 month of reaction in the exsiccator. The  $^{29}\text{Si}$  MAS NMR spectrum of the reacted sample A and its deconvolution in a part of crystalline and one part attributed to the amorphous components of the reaction mixture are depicted in Figure 10. There exists a fraction of unreacted  $\text{Na}_2\text{Si}_2\text{O}_5$  (spectrum b). Kanemite, however, was not detected in this sample. This is in accordance with the XRD results, where only small amounts (<5 wt %) were found. Furthermore, most of the silicates formed are amorphous, see spectrum c).

## 4 DISCUSSION

### *Expansion with restraint*

From results of the experiments in the expansion cell (swelling under restraint) and without restraint, was concluded that kanemite is formed from commercial  $\text{Na}_2\text{Si}_2\text{O}_5$  samples under both conditions. This confirms the validity of Equation (1), kanemite can be formed starting from  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  and water. However, the kanemite formation as the only effect can not explain the significant different expansions related to this reaction. The amount of kanemite formed as well as the increase of mass does not correlate with expansion values measured in the cell. So in our experiments, the formation of about 30 wt% kanemite is connected with a water uptake of about 18 to 20 wt%, but the extent of the expansion and the reaction rate of the two samples with these properties differ by almost 100 %. Hence, there is no proportional relation between expansion and increase in mass.

Further investigations of the crystalline part of the samples by XRD and  $^{29}\text{Si}$  MAS NMR show that the two samples A and B mainly differ in their content of the  $\text{Na}_2\text{Si}_2\text{O}_5$  modifications, whereas sample A with a lower content of the  $\delta$ -modification gives the higher expansion. This is contrary to the model of kanemite formation. Consequently, the lower content of the  $\delta$ -modification is only one aspect of the alteration process in the sample. Another fact is that the reacted sample A shows a higher background in the X-Ray pattern caused by the presence of amorphous constituents.

### *Free swelling*

From further investigations of the reaction of  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  with water without restraint was found that there are differences in swelling behaviour of the samples compared with the experiments in the expansion cell. The water uptake and the kanemite content are considerably lower. Thus, the reaction conditions strongly influence the changes of the samples. Especially, the expansion is sensitive for changes. XRD and  $^{29}\text{Si}$  MAS NMR experiments confirm the formation of amorphous phases.

In sample A, the main part of amorphous phases is formed by transforming kanemite because the amount of kanemite decreases after reaching a maximum at about 35 days. In sample B, the degradation of  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  might lead to an increase of the amorphous content. Kanemite remains at the same content from 21 to 90 days at a very low level. The contribution of the other  $\text{Na}_2\text{Si}_2\text{O}_5$  modifications to the formation of gel-like reaction products is small.

Detailed information about the amorphous species was obtained by comparing  $^{29}\text{Si}$  MAS NMR spectra of the samples A and B, Figure 11. Both spectra contain signals of  $\text{Q}^1$  (-78.8 ppm),  $\text{Q}^2$  (-86.4 ppm) and  $\text{Q}^3$  units (-94.6 ppm) caused by gels, besides signals for unreacted crystalline  $\text{Na}_2\text{Si}_2\text{O}_5$ . In contrast to the composition of field and adapted synthetic gels [1-4], no three-dimensional polymerisation occurs in the amorphous products, ie. no signal for  $\text{Q}^4$  groups. This points out that the formation of gels in this system is connected with the partial depolymerisation of the starting silicate anions of  $\text{Na}_2\text{Si}_2\text{O}_5$ , but not by connection of the silicate layers. This is typical for gels with a high Na/Si ratio which can be considered as the first stage of the real ASR gels.

## 5 CONCLUSIONS

The expansion of pressed tablets of two commercially available  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  samples at 88% RH is influenced by the composition of the original samples, especially the content of other modifications of the  $\text{Na}_2\text{Si}_2\text{O}_5$ . Under restraint in the expansion cell, the amount of kanemite formed and the water uptake during reaction with water vapour are equal, but connected with different expansions. Hence, the kanemite formation is not the only reason for the expansion process. A higher expansion level is connected with the fact that the reaction product of sample A consists partly of amorphous components and the other modifications of  $\text{Na}_2\text{Si}_2\text{O}_5$  also partially take part in the reaction forming additional products of unknown structure and expansion behaviour.

In contrast to the experiments in the expansion cell, the water uptake during “free swelling” was remarkably lower and very similar in both samples. However, it does not correlate with comparable contents in kanemite. The formation of amorphous products during free swelling seems to be responsible for further up take of water. After a storage time of 3 month, only very small amounts of kanemite could be detected and the reaction products are completely amorphous. So it is concluded, that kanemite is an intermediate product determining only the first step of swelling by water uptake. The alkali silicate gels formed have a lower degree of polymerisation than the starting samples. They contain dimer, chain-like and units with layer structure, but no fully polymerised units. It is likely that such gels can react with further  $\text{SiO}_2$  provided by reactive aggregates forming ASR gels with lower Na/Si ratios of about 0.2 that were observed in damaged concrete.

## 6 REFERENCES

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TABLE 1: Phase composition of the  $\text{Na}_2\text{Si}_2\text{O}_5$  samples before and after reaction with water vapour at 88 % RH, room temperature

<i>POWDERCELL</i>	A			B		
	0 days	14 days		0 days	33 days	
	wt%	wt%	$\Delta$ wt%	wt%	wt%	$\Delta$ wt%
$\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$	22.5	17.6	- 5.1	17.5	16.2	- 1.3
$\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$	13.7	9.4	- 4.3	1.8	3.2	+ 1.4
$\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$	63.7	39.1	- 24.6	75.3	49.5	- 25.8
Cristobalite	2.2	2.0	- 0.2	1.1	2.7	+1.6
Kanemite	0.0	31.9	+31.9	0.0	28.3	+28.3

TABLE 2: Phase composition of starting materials by  $^{29}\text{Si}$  MAS NMR, in wt%.  
(Un-attributed determined by mass balance)

<i><math>^{29}\text{Si}</math>-MAS-NMR</i>	A	B
	wt%	wt%
$\alpha$ - $\text{Na}_2\text{Si}_2\text{O}_5$	27	16
$\beta$ - $\text{Na}_2\text{Si}_2\text{O}_5$	11	3
$\delta$ - $\text{Na}_2\text{Si}_2\text{O}_5$	59	73
SUM totals	97	92
un-attributed	3	8

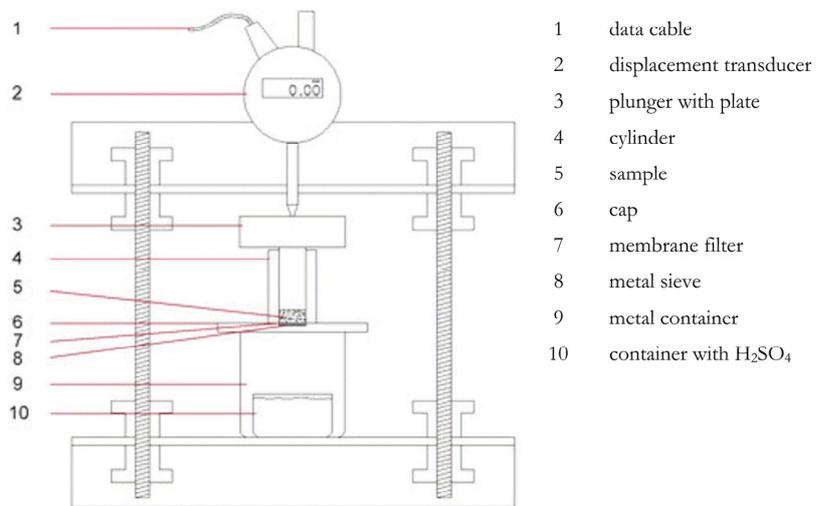


Figure 1: Device for one-dimensional expansion measurements

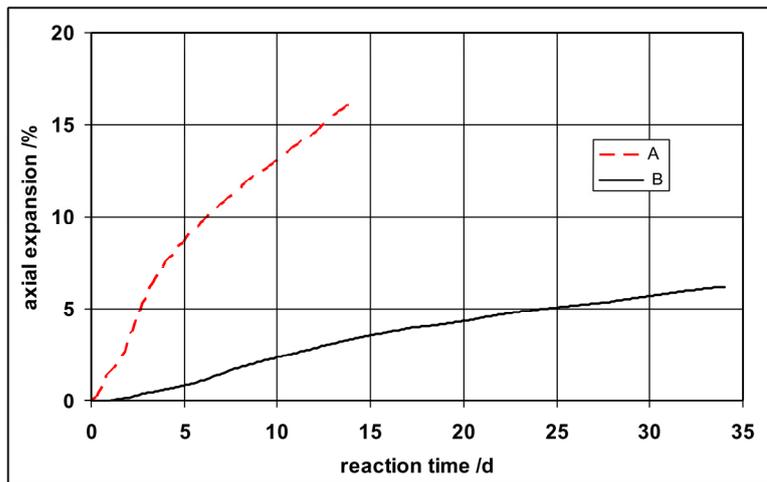


Figure 2: One-dimensional expansion of  $\delta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> samples at 88% RH, room temperature

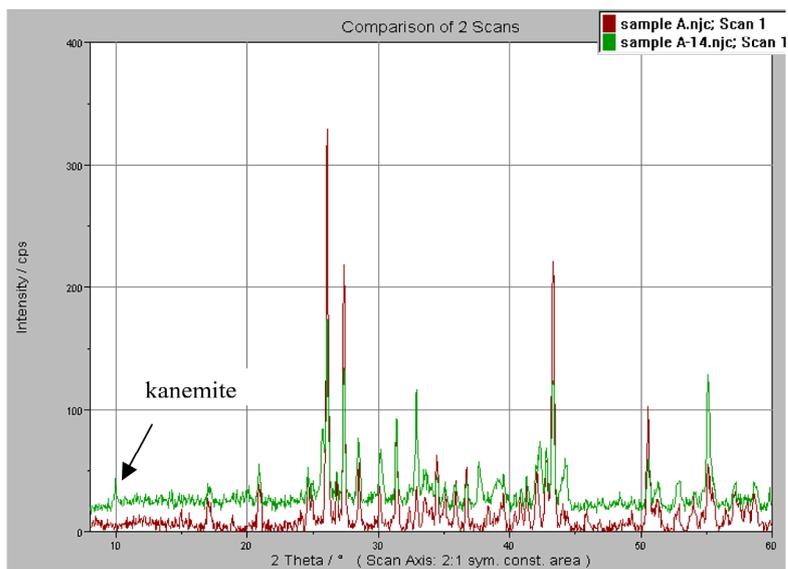


Figure 3: XRD pattern of sample A original and after 14 days reaction

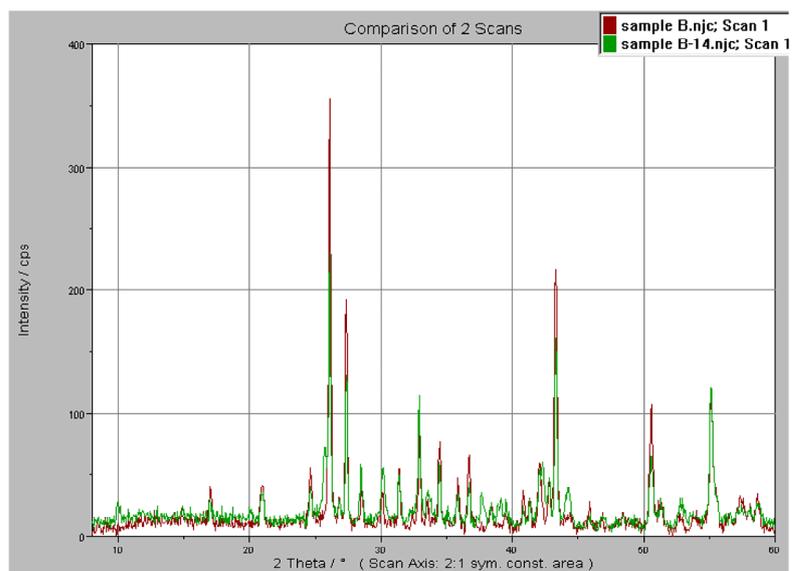


Figure 4: XRD pattern of sample B origin and after 14 days reaction

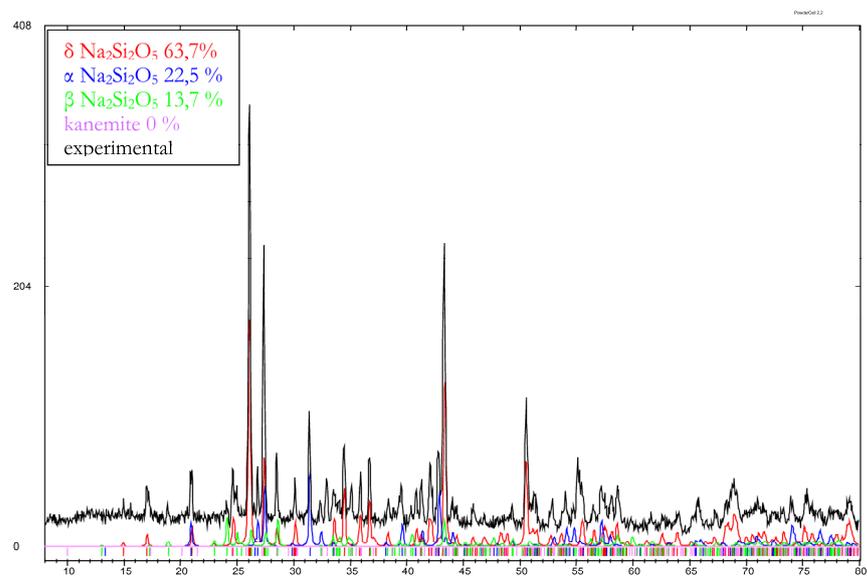


Figure 5: Sample A, original material evaluated by POWDERCELL

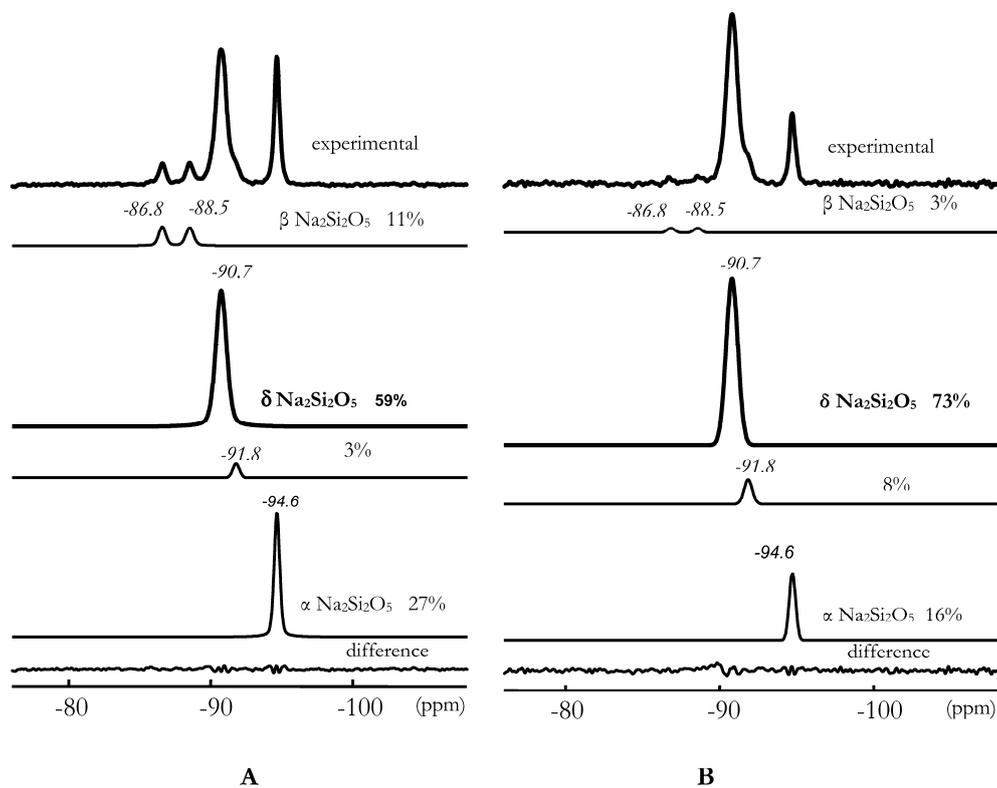


Figure 6:  $^{29}\text{Si}$  MAS NMR spectra of the original  $\text{Na}_2\text{Si}_2\text{O}_5$  samples A and B with deconvolution of spectra

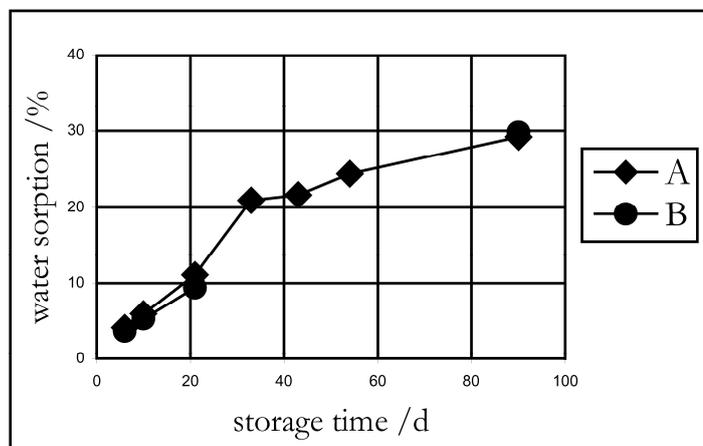


Figure 7: Water sorption of  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  samples A and B in water vapour with 88 % RH, room temperature

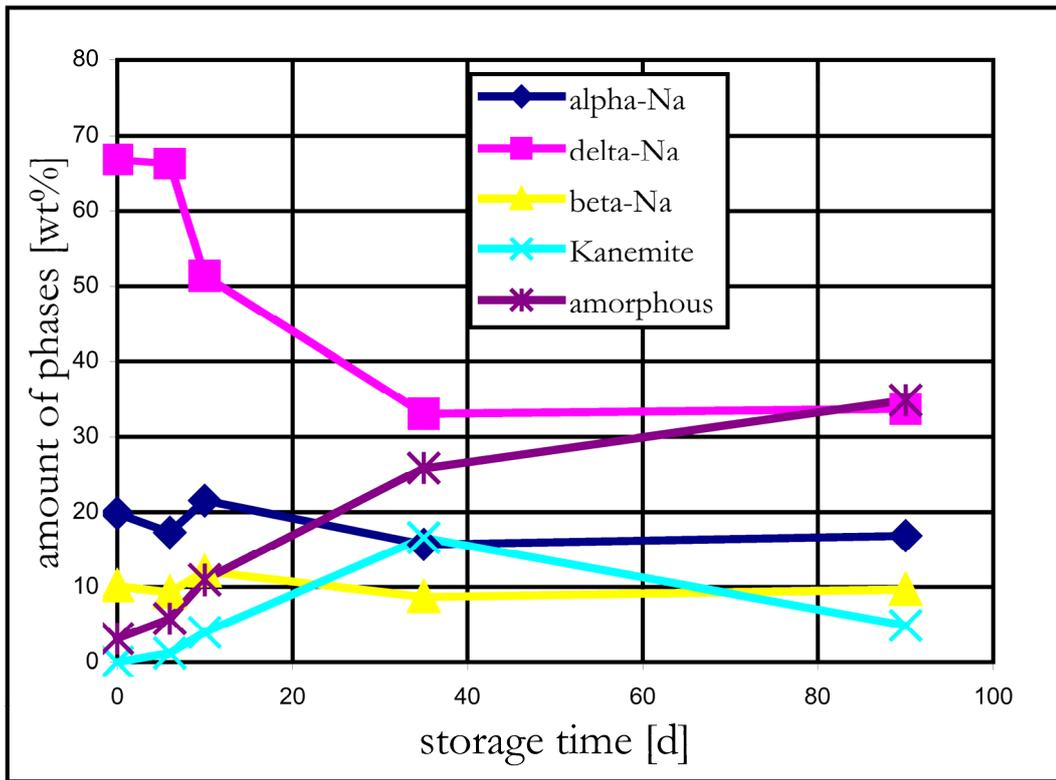


Figure 8: Composition of the sample A during reaction with water vapour at 88% RH, room temperature

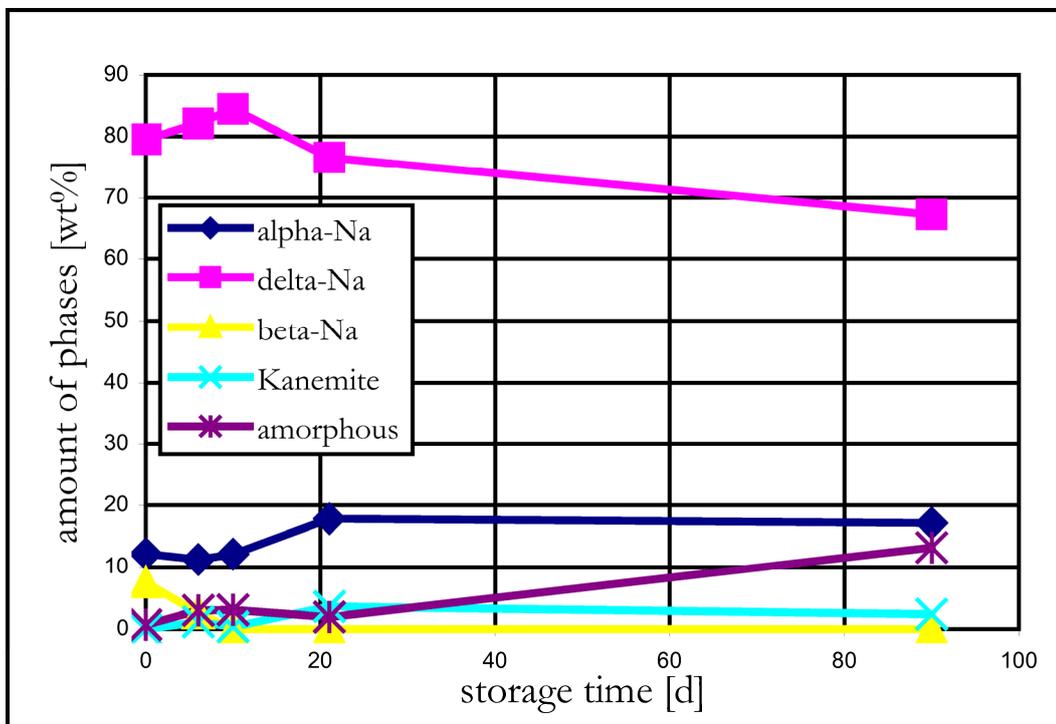


Figure 9: Composition of the sample B during reaction with water vapour at 88% RH, room temperature

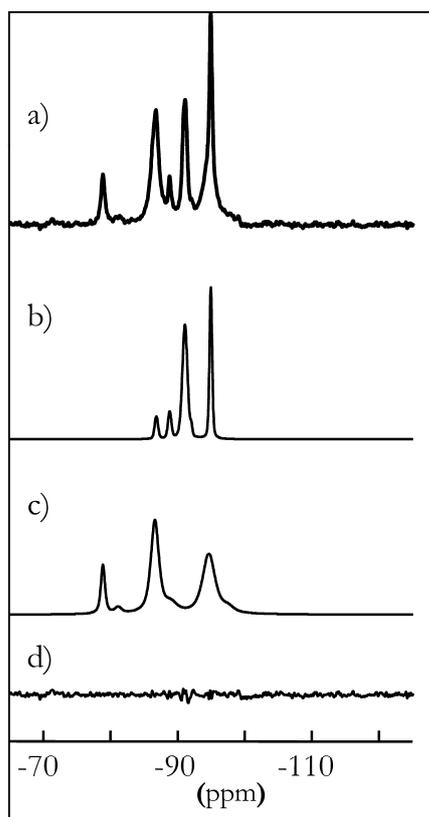


Figure 10:  $^{29}\text{Si}$  MAS NMR spectra of the reacted sample A (90 d)  
 a) experimental  
 b) simulated spectra of unreacted  $\text{Na}_2\text{Si}_2\text{O}_5$   
 c) simulated spectrum: a) minus b)  
 d) difference between experimental and simulated spectra

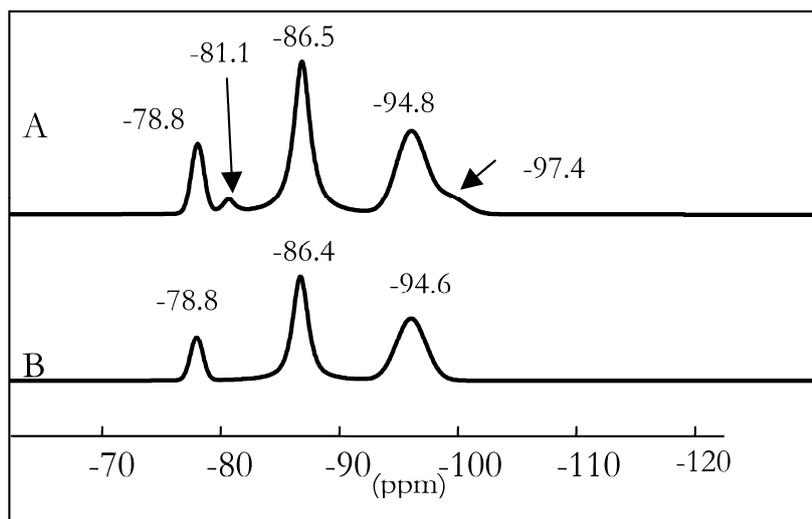


Figure 11:  $^{29}\text{Si}$  MAS NMR spectra of the amorphous reaction products formed in samples A and B after 3 month storage in a water vapour atmosphere with 87 % RH