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Thermal reactions of alkali-leached aluminosilicates studied by XRD and solid-state ^{27}Al , ^{29}Si and ^{23}Na MAS NMR

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The interactions of dehydroxylated Zettlitz kaolinite with NaOH solution have been studied using X-ray powder diffraction and solid-state MAS NMR to characterise the crystalline and amorphous products, respectively, and to provide further information about the reaction sequence of kaolinite. Under the present conditions, leaching for very short times (*ca.* 10 min) preferentially removes uncombined amorphous silica (but not the quartz impurity), and also introduces Na into the remaining amorphous aluminosilicate phase. Leaching for longer times continues to remove Si from the amorphous phase, with a concomitant increase in Na incorporation and an increase in the proportion of available Al. On reheating to 1140 and 1300 °C, the resulting crystalline phases reflect the increase in Al and Na content with increased leaching time, forming α -alumina and, in samples leached for > 60 min, a nepheline solid solution at the expense of mullite, residual quartz and cubic spinel-type phase.

When aluminosilicate minerals such as kaolinite are heated, they pass through an amorphous or semi-amorphous state *en route* to crystalline high-temperature phases such as mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and cristobalite (SiO_2).¹ The constitution of the amorphous phases is difficult to determine; they may include poorly crystalline mullite, amorphous silica, amorphous aluminosilicates and a cubic spinel phase in amounts which vary depending on the crystallinity of the starting mineral, the impurities present and the thermal treatment.¹ The composition of some of these phases, especially the spinel, has also been the subject of considerable speculation for many years.² Although solid-state nuclear magnetic resonance with magic-angle spinning (MAS NMR) is a promising technique for studying amorphous phases, its usefulness in studying the present system is limited by the fact that the aluminium in octahedral and tetrahedral sites has similar ^{27}Al NMR chemical shifts in all the phases, and the ^{29}Si NMR spectra are broad and relatively featureless, spanning a range of Si environments.³ To facilitate the study of the aluminosilicate phases in heated kaolinite, Chakravorty and Ghosh have developed methods for selective dissolution using NaOH solutions under carefully controlled conditions.⁴ During leaching experiments of heated kaolinite, it has been noted that dissolution appears to occur in two steps.⁵ In the first step, representing the first *ca.* 30–40 min of reaction, dissolution is very rapid, and is thought to involve only the removal of uncombined SiO_2 , representing 35 mass% after 40 min reaction. Samples leached to this point did not form cristobalite on heating to higher temperatures. At longer leaching times, when the dissolution rate becomes much slower, it is thought that the amorphous aluminosilicate phase reacts next, followed by the poorly crystalline mullite component. The cubic spinel phase is considered to be the most stable to NaOH treatment. Samples leached for > 40 min formed corundum ($\alpha\text{-Al}_2\text{O}_3$) on heating to higher temperatures.⁵

These observations suggest that the interpretation of the ^{27}Al and ^{29}Si MAS NMR spectra of heated kaolinite could be facilitated by the progressive removal of the various phases using NaOH dissolution techniques. This paper reports the results of such a study, which also addressed the question of Na incorporation during leaching, using ^{23}Na MAS NMR.

Experimental

The kaolinite used in this study was a well characterised material from Zettlitz, calcined at 980 °C for 4 h to remove all

structural (hydroxy) water. The calcined kaolinite was treated with 5% NaOH solution on a boiling water bath for 10–90 min. The leached material was then recovered and washed thoroughly to free it of adsorbed alkali. Combined TG–DSC experiments were performed on these samples (Polymer Laboratories PL-STA thermal analyser) in air, heating rate 10 °C min⁻¹ to 1350 °C. Two sub-samples of this material were then heated in air as follows: (i) to 1140 °C at 5 °C min⁻¹ with no dwell time at 1140 °C; (ii) to 1300 °C at 5 °C min⁻¹, 30 min dwell time at 1300 °C. All samples were examined by X-ray powder diffraction (Philips PW 1700 computer-controlled diffractometer with graphite monochromator and Co-K α radiation). Their room-temperature ^{27}Al , ^{29}Si and ^{23}Na MAS NMR spectra were acquired at 11.7 T (Varian Unity 500 spectrometer with 5 mm Doty MAS probe spinning at 10–12 kHz), with parameters as follows: ^{27}Al : 1 μs ($\pi/10$ solution) pulse width, 1 s delay, shifts referenced to 1 mol dm⁻³ $\text{Al}(\text{NO}_3)_3$; ^{29}Si : 6 μs ($\pi/2$) pulse width, 10 s delay, referenced to tetramethylsilane (Me_4Si); ^{23}Na : 1 μs ($\pi/10$ solution) pulse width, 1 s delay, referenced to 1 mol dm⁻³ NaCl.

The samples heated to 1140 °C were analysed for Al, Si and Na by atomic absorption spectroscopy (AAS). Where appropriate, analyses for quartz (SiO_2) and corundum ($\alpha\text{-Al}_2\text{O}_3$) were made by quantitative X-ray powder diffraction (QXRD) with an internal standard of 20 mass% Cr_2O_3 (JCPDS Intensity Standard 674), calibrated with quartz and corundum standard phases diluted in finely ground (< 44 mesh) glass.

Results and Discussion

Leached samples without further heating

Representative XRD traces of both unheated and heated materials are shown in Fig. 1. The unleached unheated material (Fig. 1A) contains a significant proportion of amorphous material, evidenced by the broad baseline hump centred at $2\theta \approx 25^\circ$, with a small amount of a crystalline quartz impurity (estimated as 1.6% by QXRD) and poorly crystalline mullite. Broad reflections are also present, corresponding to a cubic spinel phase with a cell parameter similar to $\gamma\text{-Al}_2\text{O}_3$ (PDF no. 10-425).

Leaching for 10–30 min progressively reduces the amount of amorphous material, but never entirely removes it; the other poorly crystalline phases become more clearly visible with the

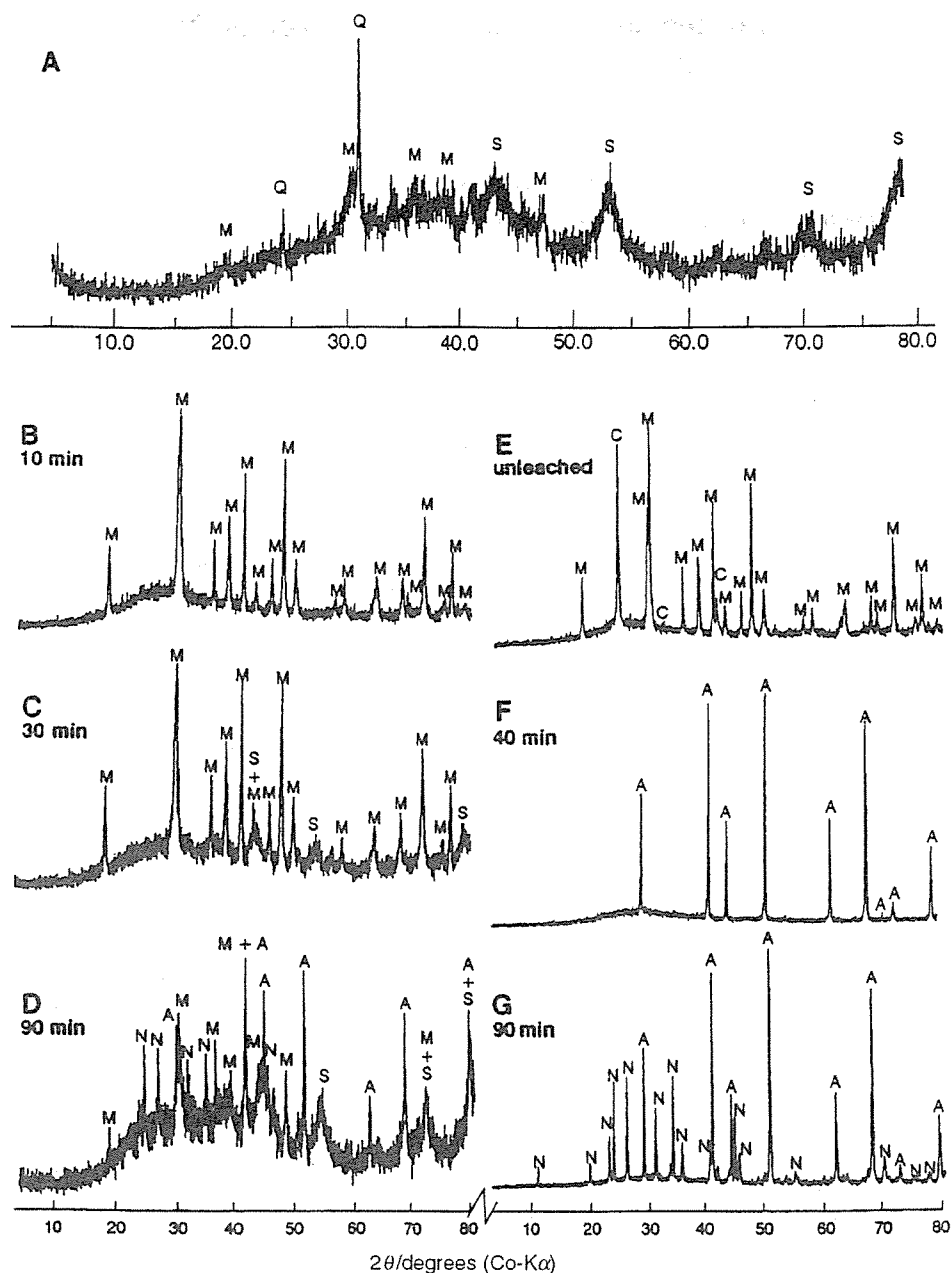


Fig. 1 Representative XRD traces of Zettlitz kaolinite, heated at 980 °C for 4 h, then leached in NaOH for the indicated times. A, Leached but not reheated; B–D, reheated at 1140 °C; E–G, reheated at 1300 °C. M=mullite (PDF no. 15-776), Q=quartz (PDF no. 33-1161), S=spinel-type γ -alumina (PDF no. 10-425) C=cristobalite, A=corundum, N=nepheline-type solid solution.

reduction of the amorphous component. Leaching for 40–90 min has little further effect on the remaining amorphous material, but may produce a slight deterioration in the crystallinity of the other phases. The 1.4–1.5% quartz content remains unaffected by any of these leaching treatments. The XRD results are summarised in Table 1, which also includes the

phases identified by XRD in leached samples which were reheated to 1140 and 1300 °C. The DSC traces of these samples are shown in Fig. 2, on which are also marked the mass losses of each sample at 1350 °C.

XRD of the samples after thermal analysis shows that the unleached sample, which gave rise to an exotherm at 1232 °C

Table 1 Phases detected by XRD in NaOH-leached Zettlitz kaolinite, listed in approximate order of decreasing significance

leaching time/min	as-leached	reheated to 1140 °C	reheated to 1300 °C
0	M, S, Q, am	M, Q, S(tr), am	M, C, am
10	M, S, Q, am	M, am	M, am
20	M, S, Q, am	M, S(tr), am	M, A, am(tr)
30	M, S, Q, am	M, S, am	A, M, am(tr)
40	M, S, Q, am	M, S, A(tr), am	A, am(tr)
60	M, S, Q, am	A, N, S, M, am	A, N
90	M, S, Q, am	A, N, S, M, am	A, N

Key: M=mullite, S=cubic spinel-type phase, Q=quartz, C=cristobalite, A=corundum, N=nepheline-type solid solution, am=amorphous phase, tr=trace amount.

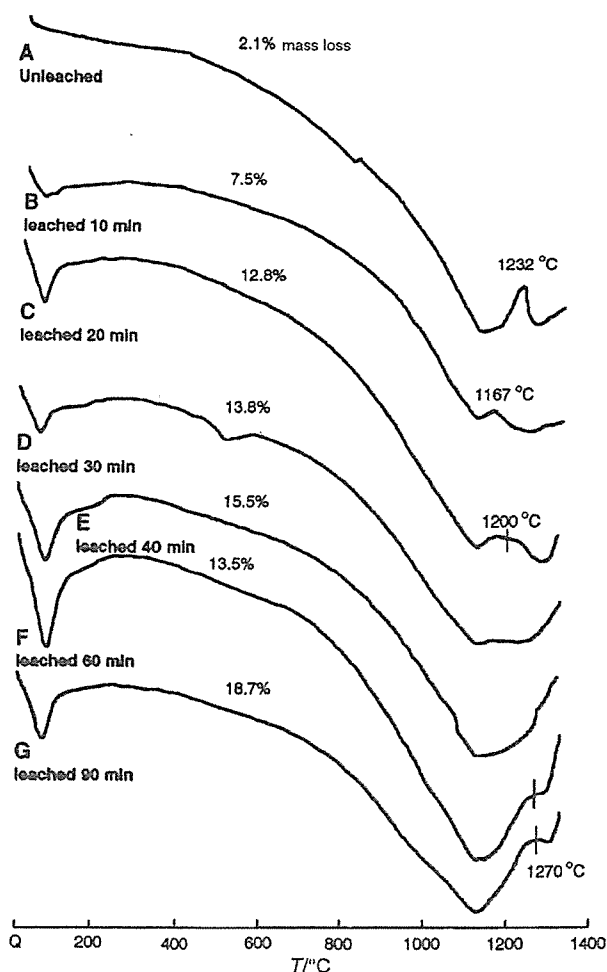


Fig. 2 DSC traces of Zettlitz kaolinite, heated at 980 °C for 4 h, then leached in NaOH for the indicated times. Heating rate 10 °C min⁻¹ in air.

with an enthalpy of $-25.28 \text{ cal g}^{-1}$ (Fig. 2A),† contains reasonably crystalline mullite, cristobalite, quartz and some residual amorphous material. Leaching for 10 min reduces the size and sharpness of the exotherm to an enthalpy of $-12.42 \text{ cal g}^{-1}$, and also lowers its peak temperature to 1167 °C (Fig. 2B). The product after heating this sample to 1350 °C in the DSC is mullite and a small amount of residual amorphous material. In the DSC trace of the sample leached for 20 min, the high-temperature exotherm is broadened, and possibly consists of two merged peaks with a mid-point temperature of *ca.* 1200 °C and a combined enthalpy of $-23.12 \text{ cal g}^{-1}$ (Fig. 2C). The product after thermal analysis is well crystallised mullite and a small amount of residual amorphous material. Leaching for 30 min essentially removes the high-temperature exotherm (Fig. 2D), but a small endotherm at *ca.* 500 °C suggests the removal of some hydroxy water. The product from this sample consists of mullite, corundum and some amorphous residue. Leaching for 40 min produces little difference from the sample leached for 30 min, but the heated product now contains significantly more corundum than mullite. After 60 min leaching, the first signs of an exothermic plateau are found at *ca.* 1270 °C (Fig. 2F), which becomes better defined after 90 min leaching (Fig. 2G). The crystalline products in both these samples are corundum and an aluminium-rich alkali-metal silicate similar to a nepheline solid solution (PDF no. 23-475), but in view of the present reaction conditions, our material must be the Na analogue.

Typical ²⁷Al and ²³Na MAS NMR spectra of both unleached

and heated samples are shown in Fig. 3, and a selection of typical ²⁹Si NMR spectra are shown in Fig. 4. The ²⁷Al spectra (Fig. 3A,B) all contain an octahedral and a tetrahedral resonance at δ *ca.* 6 and 58, respectively. The apparent growth of the tetrahedral resonance with respect to the octahedral as leaching progresses is misleading; the octahedral peaks have a high-field tail, probably arising from distortion of these sites. When the spectral intensity of the tail is taken into account by curve-fitting a third peak in this region, the proportion of octahedral spectral intensity ranges from 60 to 63%, *i.e.* within error it is essentially constant in all these spectra, but is considerably greater than expected for pure mullite (43%).^{6,7} The widths of the curves fitted to the octahedral region remain essentially constant with leaching time, but the fitted tetrahedral width decreases smoothly up to *ca.* 60 min leaching time, suggesting that the phases developing during leaching are better ordered than the amorphous phases originally present, at least with respect to the tetrahedral sites.

As expected, the ²⁹Si NMR spectra of the unleached samples (Fig. 4A–G) show considerable changes as leaching progresses. The resonance in the unleached sample (Fig. 4A) is at δ *ca.* -110, in the region of uncombined SiO₂, but it may also partially mask a small signal at δ *ca.* -88. On leaching for 10 min, the total Si intensity decreases and the δ -88 peak becomes proportionally more intense (Fig. 4B), a trend which continues with further leaching (Fig. 4C). The resonance at δ -88 arises from Si substituted by Al, and is in the spectral region of mullite,⁶ as well as other aluminosilicate phases. In order to satisfactorily simulate the ²⁹Si NMR spectra several curves had to be fitted, the positions of which varied somewhat from sample to sample. In general, the fitted peaks occurred at δ *ca.* -114, -108, -101 and -88, but not all the spectra required all these peaks for a satisfactory fit. Some typical curve-fitted ²⁹Si NMR spectra are shown in Fig. 5. The relative contributions of these fitted peaks to the total spectral intensity changes with leaching time, as shown in Fig. 6, in which the site distributions are shown as a percentage of the unleached Si remaining. The integrated intensities of the ²⁹Si NMR spectra fall off with leaching time up to about 40 min leaching time (Fig. 7).

From the chemical shifts and changes on leaching of the fitted ²⁹Si NMR peaks (Fig. 6), the following assignments are suggested. (i) The species at δ *ca.* -114 decreases to zero after 20 min leaching, and is probably due to amorphous and uncombined SiO₂. (ii) The species at δ -108 to -110 is removed more gradually, and eventually levels out at *ca.* 4–5% of the total Si intensity after 60 min leaching. Since the chemical shift of this resonance is in the region for quartz and cristobalite,⁸ it must contain the quartz phase which is not removed by leaching, and probably represents the 4–5% residual ²⁹Si intensity. The remainder of this resonance, which is removed slowly by leaching, could contain another silica-rich phase, since the fitted peak tends to be broad. The greater resistance of this species to alkali attack in comparison with the δ -114 resonance may indicate the presence in this phase of the impurities originally occurring in the kaolinite (0.55% Na₂O, 0.84% K₂O, 0.29% CaO, 0.27% MgO and 0.65% Fe₂O₃). (iii) The species at δ *ca.* -101 has a chemical shift suggesting a degree of Al substitution, and is similar to the ²⁹Si chemical shift of metakaolinite.³ This species is relatively insignificant in the unleached sample, but it becomes more prominent during the initial stages of leaching, and disappears after 30 min reaction. Since no crystalline phase demonstrating this behaviour is detectable by XRD, it is assumed to be amorphous also, possibly a product of reaction with the sodium hydroxide. The disappearance of this species after longer reaction times may reflect the formation of other more stable alumina-rich alkali-metal silicates (see below). (iv) The resonance at δ *ca.* -88, which becomes progressively more significant with leaching time, represents the most heavily Al-substituted species,

† 1 cal = 4.184 J.

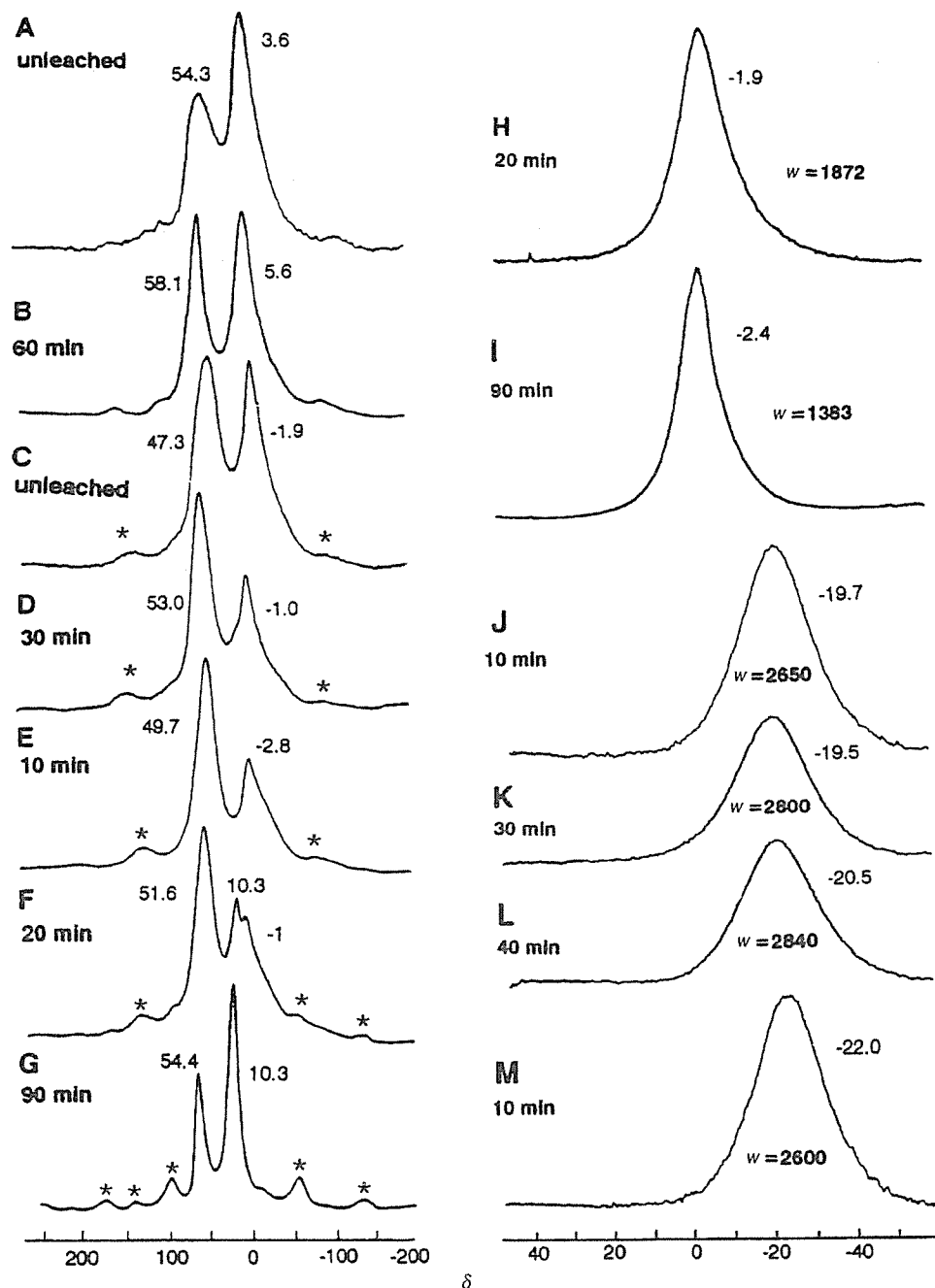
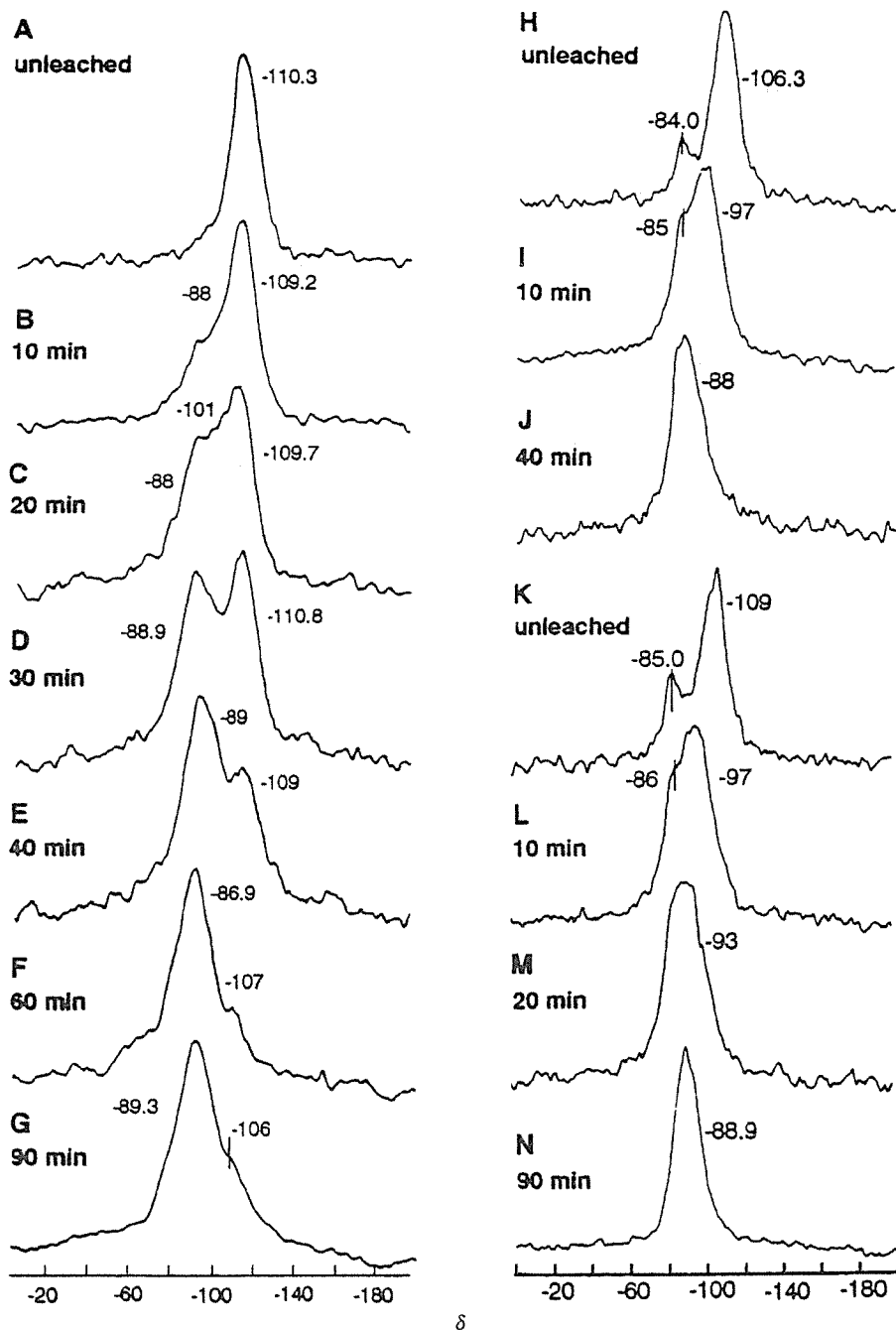


Fig. 3 Typical 11.7 T MAS NMR spectra of Zettlitz kaolinite, heated at 980 °C for 4 h, then leached in NaOH for the indicated times. A–G, ^{27}Al NMR; [ref. $\text{Al}(\text{H}_2\text{O})_6^{3+}$]; H–M, ^{23}Na NMR (ref. NaCl solution) A, B, H, I, Not reheated; C, D, J, reheated at 1140 °C; E–G, K–M, reheated at 1300 °C. Asterisks denote spinning side bands.

and will include the mullite-like parts of the structure, together with other aluminosilicates; the nepheline solid solution which crystallises from the amorphous phases in samples leached for 60–90 min is expected to have a ^{29}Si chemical shift similar to nepheline (δ –85 to –88)⁹ and should therefore appear under this envelope.

The ^{23}Na NMR signal from the unleached material was so weak as to be virtually indistinguishable from noise, but, by contrast, all the leached samples, both unleached and heated, show strong signals resulting from the incorporation of significant concentrations of Na (Fig. 3H,I), apparent even after 10 min leaching. The amount of Na present, estimated from NMR peak area measurements, increases almost linearly with leaching time, up to 40 min, after which it becomes essentially constant. A very good linear correlation ($R=0.99$) exists between the decreasing total Si intensity seen by NMR and the increasing Na NMR peak intensity as leaching progresses,

suggesting that the NaOH is not just dissolving silica to form soluble sodium silicate species, but insoluble sodium silicate or aluminosilicate species must also be forming concurrently. The resonance position and width at half height are essentially identical in all the unleached leached samples, independent of leaching time (Fig. 3H,I), and are typical of less shielded, more isotropic Na environments such as those found in hydrothermally treated sodium aluminosilicate glasses.¹⁰ The present resonance positions (δ ca. –2 to –3) are even closer to the hydrated Na^+ ion reference (δ 0) than in hydrothermally altered glass previously reported (δ –7.7),¹⁰ but are similar to the ^{23}Na shifts found in halloysites hydrothermally treated with NaOH at 600–800 °C containing incipient zeolite A (δ –1.9 to –4.5) and in commercial crystalline sodium zeolite A (δ –1.6) (our own unpublished results). These ^{23}Na NMR shifts are all downfield of the values for Na in the interlayer sites of smectites, δ –9.8 for Na-montmorillonite, δ –9.0 for



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Fig. 4 Typical 11.7 T ^{29}Si MAS NMR spectra (ref. Me_4Si) of Zettlitz kaolinite, heated at 900 °C for 4 h, then leached in NaOH for the indicated times. A–G, not reheated; H–J, reheated at 1140 °C; K–N, reheated at 1300 °C.

Na-bentonite and $\delta -5.3$ for Na-hectorite, our own unpublished results), consistent with the Na in the present leached samples being more highly hydrated than would be possible if the Na were in regular smectite-like interlayer sites. Removal of this hydration water by heating results in the expected upfield shift and broadening of the ^{23}Na resonance (Fig. 3J–M) to an extent determined by the leaching time, and thus by the Na:Si ratio. The increased broadening and upfield shift may be predominantly due to an increased electric-field gradient (efg) at the Na, but chemical shift effects may also be present. At leaching times <60 min, the resonance position ($\delta -18.3$ to -22 , Fig. 3J–M) is typical of unhydrated sodium aluminosilicate glass and rhyolite glass at 11.7 T ($\delta -18.4$).¹¹ At longer leaching times (*i.e.* lower Si content) the resonances move downfield and become narrower, especially in samples heated to 1300 °C. The resonance positions in these samples (δ ca. -13) are similar to those reported in nepheline-kalsilite

solid solutions, arising from the preferential occupation by Na of the crystallographically smaller of the two available alkali-metal sites in nepheline.¹² Thus, the present ^{23}Na NMR results are consistent with the incorporation of Na into the aluminosilicate structure at the earliest stages of leaching, initially in a highly hydrated amorphous phase which on heating forms an anhydrous amorphous sodium aluminosilicate or an aluminous crystalline nepheline solid solution, according to the amount of Si available. A good linear relationship ($R=0.94$) also exists between the ^{23}Na NMR intensity of the leached samples and the percentage of Si in the ^{29}Si NMR peak at $\delta -88$. The $\delta -88$ resonance probably contains contributions from several phases, including mullite and various possible alkali-metal aluminosilicates which have ^{29}Si peaks in this region [*e.g.* nepheline ($\text{NaAlSi}_3\text{O}_8$) $\delta -84$, -88 ; jadeite [$\text{NaAl}(\text{SiO}_3)_2$] $\delta -91.8$; albite ($\text{NaAlSi}_3\text{O}_8$) $\delta -92.8$ to -104.7 , natrolite ($\text{Na}_2\text{Al}_2\text{Si}_5\text{O}_{10}\cdot\text{H}_2\text{O}$) $\delta -87.7$, -95.4].⁸ Thus, the NaOH may

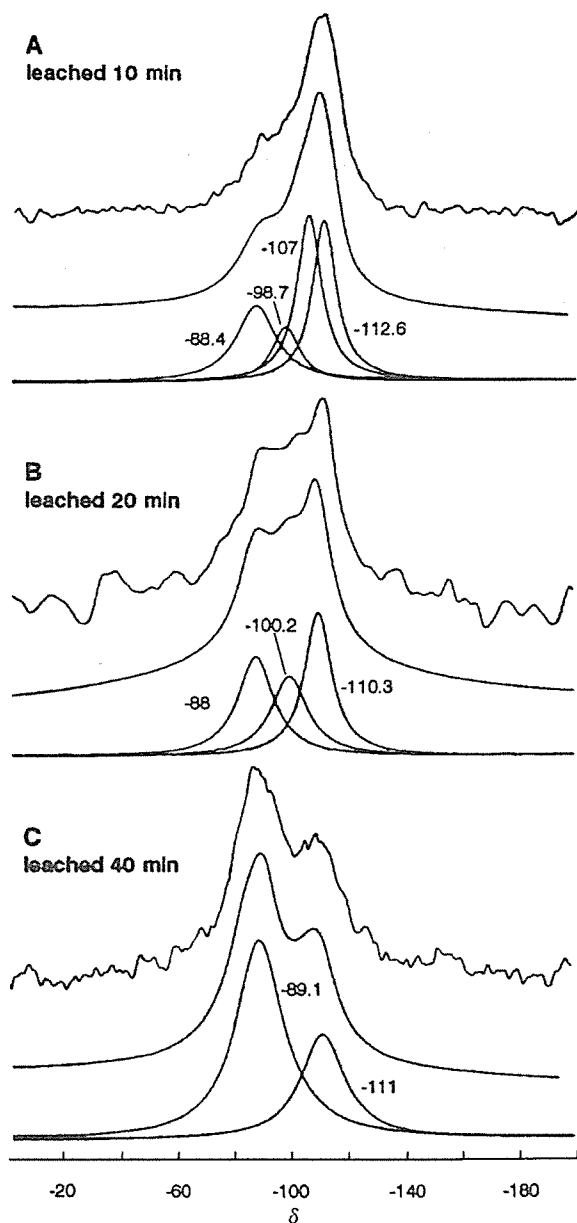


Fig. 5 Curve-fitted ^{29}Si MAS NMR spectra of Zettlitz kaolinite, leached as indicated. Observed spectrum is upper trace of each group, fitted envelope in middle and component peaks at bottom of group.

be reacting to form insoluble sodium aluminosilicates which are providing a major contribution to the $\delta -88$ NMR resonance.

Leached samples heated to 1140 and 1300 °C

A selection of typical XRD traces of samples heated to 1140 and 1300 °C are shown in Fig. 1B–G. The chemical analyses of the samples heated to 1140 °C are shown in Table 2. On heating to 1140 °C, the XRD trace of the sample leached for 10 min (Fig. 1B) shows only reasonably well crystallised mullite, in contrast with the unleached material which under the same heat treatment contains mullite, unreacted quartz, a trace of cubic spinel and significant amorphous material. Heating to 1300 °C for 30 min produces mullite of better crystallinity in both the 10 min leached and unleached samples; in the latter the quartz was completely converted to cristobalite, there was no trace of cubic spinel, and the amount of amorphous phase had been considerably reduced, as judged from the curvature of the diffraction baseline.

The 20 min leached sample heated at 1140 °C contained mullite and a small trace of cubic spinel. Heating this sample

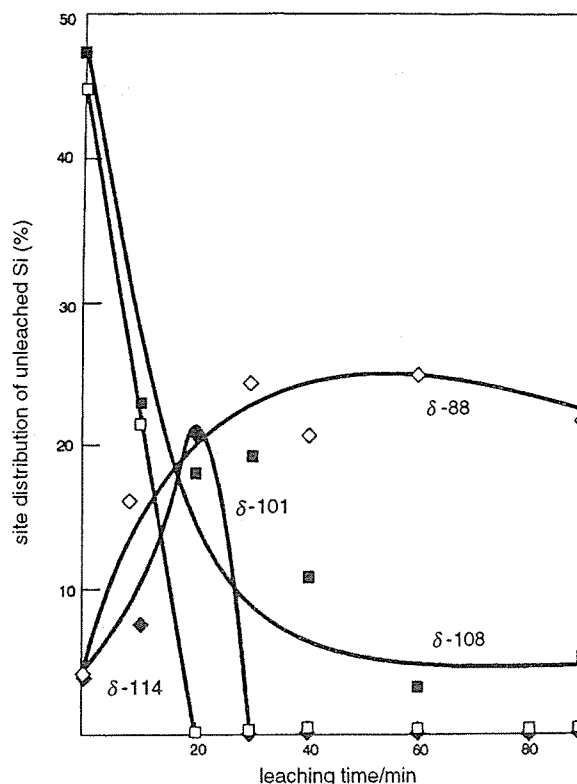


Fig. 6 Distribution of Si amongst the various sites in leached Zettlitz kaolinite, estimated from the fitted ^{29}Si NMR spectra, as a function of leaching time

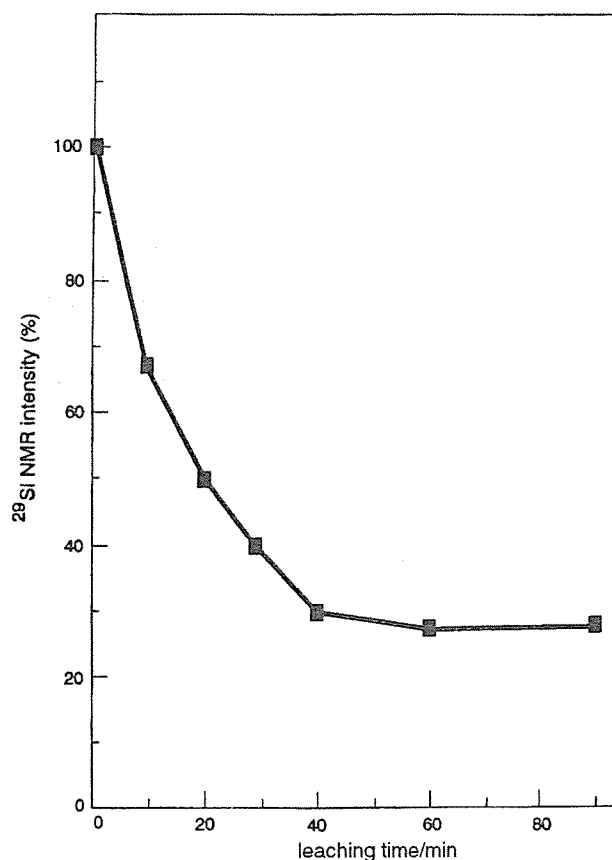


Fig. 7 Integrated intensity of total ^{29}Si NMR signal in leached Zettlitz kaolinite, as a function of leaching time

Table 2 Chemical analyses of unleached and leached Zettlitz kaolinite, heated to 1140 °C

leaching time/min	SiO ₂ (%)	Al ₂ O ₃ (%)	Na ₂ O (%)
0	54.5	45.1	0.28
10	45.2	51.4	2.98
20	36.3	58.5	4.11
30	32.8	61.9	4.31
40	29.2	64.5	5.10
60	25.5	65.2	7.27
90	25.9	64.4	7.05

at 1300 °C improved the mullite crystallinity and led to the formation of a small amount of corundum (α -Al₂O₃), at the expense of both the spinel and the amorphous phase; apparently even at this early stage in the leaching, the amorphous phase is becoming aluminium-rich.

The sample leached for 30 min and heated at 1140 °C (Fig. 1C) contains mullite and cubic spinel which appears more distinctly crystalline than with 20 min leaching. Heating this sample at 1300 °C produces a small amount of mullite and a considerable amount of corundum, again with the disappearance of spinel and a reduction in the amount of amorphous phase.

Spinel is still evident in the sample leached for 40 min and heated at 1140 °C, together with mullite and small amounts of corundum and amorphous phase. Heating at 1300 °C produces only crystalline corundum, with some residual amorphous phase still evident (Fig. 1F).

When heated to 1140 °C, the samples leached for 60 and 90 min contain, in addition to corundum, the nepheline solid solution (PDF no. 23-475) identified in the thermal analysis samples (see above), together with a small amount of mullite, the cubic spinel phase and a significant amount of amorphous material (Fig. 1D). Heating to 1300 °C completes the conversion of the mullite, spinel and amorphous material to crystalline corundum and nepheline solid solution (Fig. 1G). The XRD results for the reheated samples are summarised in Table 1.

The ²⁷Al NMR spectra of samples leached for up to 30 min and heated at 1140 °C (Fig. 3D) are all broadly consistent with previously published spectra of mullite,^{6,7} containing an octahedral resonance at δ -1.9 with a marked upfield tail, and a tetrahedral resonance at δ 47–53, which, however, shows no evidence of partial resolution into two components which is characteristic of highly crystalline mullite.⁶ The proportion of tetrahedral signal, estimated by curve-fitting the spectra, progressively increases from 51% in the unleached sample to 60% in the sample leached for 30 min; this is within the range previously reported for mullite derived from heated clay.⁷ Similar spectra were recorded for the mullite-containing samples heated at 1300 °C (Fig. 3E,F).

The onset of corundum formation is marked by the appearance of the characteristic octahedral resonance at δ ca. 10–11 in samples leached for 40–90 min and heated at 1140 °C, and in samples leached for 20–90 min heated at 1300 °C (Fig. 3F,G). The proportion of tetrahedral resonance decreases in these samples as the corundum resonance grows with leaching time and heating temperature. The position of the single tetrahedral resonance in the samples containing nepheline solid solution (Fig. 3G) is in the range expected for fully polymerised framework aluminosilicates,¹¹ but differs from the spectra reported for natural nepheline, which contain two resolvable tetrahedral resonances corresponding to two distinct Al sites.¹² The ²⁷Al NMR spectra are thus generally consistent with the XRD data.

The ²⁹Si NMR spectra of the samples heated at 1140 °C (Fig. 4H–J) are simpler than the corresponding unleached spectra (Fig. 4A–G). The unleached sample consists of two clearly resolved components, that at δ -84 corresponding reasonably to the major mullite resonance at δ -86.8,⁶ and that at δ -106.3 corresponding to uncombined silica and quartz

(δ -107.1).⁸ The change in this peak position to δ -109 on heating to 1300 °C (Fig. 4K) reflects the conversion of the quartz to cristobalite (δ -108.5 ppm).⁸ In the samples leached for 10 min the presence of mullite is still indicated by the shoulder at δ ca. -85 to -86 (Fig. 4I,L), but the major component of the resonance intensity (probably associated with the residual amorphous phase) has moved downfield to δ -97. The ²⁹Si NMR spectra of samples leached for times >10 min and reheated at 1140 and 1300 °C, all contain a single broad, featureless peak, the centre of which progressively moves downfield with increasing leaching time. This single peak envelope must contain contributions from the mullite and alkali-metal aluminosilicate phases, both amorphous and crystalline; all these spectra were therefore fitted with between one and four curves, some of which are shown in Fig. 8.

Satisfactory fits for most spectra were obtained with three peaks (Fig. 8A,B), which in all the samples containing XRD indications of mullite and amorphous phase (but no significant cubic spinel) occur at δ ca. -84, -95 and -102 (Fig. 8A). Samples containing mullite, cubic spinel and amorphous phase are best fitted by three similar peaks (Fig. 8B), and show no indication of an additional peak at δ ca. -80, the calculated position of an Si-containing spinel;³ this question is discussed further below. The heated sample containing only corundum and amorphous phase would be expected to contain only ²⁹Si resonances from the amorphous phase, and is best fitted by two peaks, at δ -88.5 and -96.1 (Fig. 8D), suggesting that the peaks at δ ca. -90 and -100 in the spectra of less-reacted samples are associated with the amorphous phase. By this reasoning, the peak at δ -84 to -85 in the mullite-containing samples must arise from mullite. Although this peak is slightly downfield of the resonance reported for well crystallised mullite (δ -86.8),⁶ it is within the error expected in the fitting of broad spectra. The sample containing only crystalline nepheline solid solution and corundum is best fitted by two peaks, at δ -86.5 and -92.4 (Fig. 8C), in reasonable agreement with the reported peak positions for nepheline (δ ca. -84 and -89);¹² the incorporation of additional Al into this phase does not appear to change its ²⁹Si NMR spectrum greatly. The similarity between the fitted ²⁹Si NMR spectra of nepheline solid solution (Fig. 8C) and the amorphous phase (Fig. 8D) suggests that the latter is the source from which the nepheline solid solution crystallises, and must therefore approach a similar composition in the later stages of leaching.

During the course of the ²⁹Si NMR curve-fitting, considerable effort was made to locate and fit peaks below δ -85, in the region expected for Si contained in the cubic spinel phase. Although the results for the reheated samples containing XRD indications of spinel were not convincing, inspection of the ²⁹Si NMR spectra of some of the unleached leached samples (Fig. 4) suggests the presence of extra spectral intensity in this region, to which a small peak could be fitted in some cases. Fig. 8E shows an example of such a fit, in which the downfield shoulder has been fitted by a peak at δ -76.2, representing a highly Al-substituted Si site such as could arise from an Si-containing γ -alumina-like spinel. Assuming this peak assignment, and taking into account the significant amount of spinel indicated by XRD in this sample, the small number of such silicons, representing 0.9% of the total Si intensity, suggests a rather low degree of Si substitution in this spinel. Another possible explanation of this result is that early-stage leaching may remove Si from the spinel originally formed at 980 °C, producing the observed cubic phase with a composition more like pure γ -Al₂O₃.

Constitution of the amorphous phases deduced from AAS and QXRD analyses

The analysis of the unleached material (Table 2) indicated an excess of ca. 20% SiO₂ above that required to ultimately form

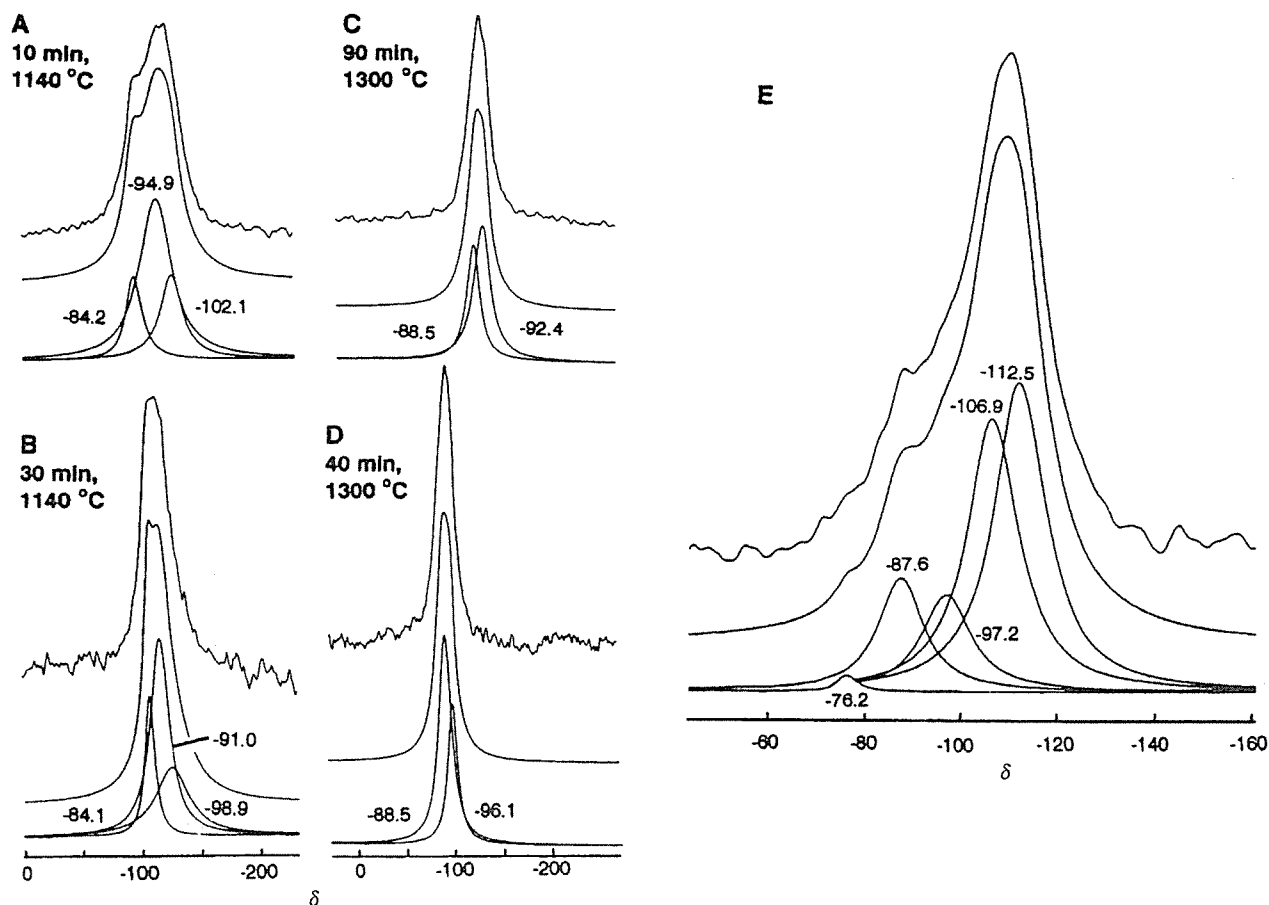


Fig. 8 Typical curve-fitted ^{29}Si NMR spectra of Zettlitz kaolinite, leached, then reheated as indicated. E, leached in NaOH for 10 min, curve-fitted to five peaks.

3:2 mullite; the low Na content suggests that this SiO_2 is relatively pure, but the analysis figures provide no indication of possible substitution of the Si into the spinel phase in the unleached sample.

On leaching for 10 min, SiO_2 is removed with a corresponding incorporation of Na_2O in the sample. Based on the 3:2 mullite composition which is ultimately achieved, this sample will contain 25% SiO_2 which is surplus to its requirements for mullite formation, which, together with the analysed Na content, calculated to an Na:Si:O ratio of 1:4.3:9.1, *i.e.* if the sodium is assumed to be associated with the amorphous silica component, its composition will be close to NaSi_4O_9 .

Applying similar reasoning to the sample leached for 20 min, but correcting the mullite composition for the 11.3% corundum estimated by QXRD in the sample heated at 1300°C , the composition of the amorphous phase (17.8% SiO_2 to 4.1% Na_2O) calculated to an Na:Si:O ratio of 1:2.2:5, *i.e.* the amorphous phase approximated to NaSi_2O_5 .

The same calculation for the sample leached for 30 min leads to the same composition for the amorphous phase; although further SiO_2 has been removed from the sample, this is compensated for by the ultimate formation at 1300°C of a greater amount of corundum (26.6%), maintaining the Na:Si:O ratio at 1:2.27:5, corresponding to an amorphous phase composition of approximately NaSi_2O_5 .

In contrast, after leaching for 40 min, the only detected crystalline phase, after the thermal reactions are completed at 1300°C , is corundum, estimated by QXRD to be 66.7%, in satisfactory agreement with the value for total Al_2O_3 (64.5%). The analysed SiO_2 and Na_2O contents, which must eventually end up solely in the amorphous phase, correspond to an Na:Si:O ratio of 1:3:6.4, *i.e.* a composition of approximately NaSi_3O_6 .

After leaching for 60–90 min, the compositions of the

samples are virtually unchanged, but QXRD indicates the formation of 39.3% corundum, the balance being a nepheline-type solid solution with a calculated composition of $\text{NaAl}_{1.2}\text{Si}_{1.9}\text{O}_{7.5}$. If the total Na content of this sample is assumed to be associated with a normal nepheline, $\text{NaAlSi}_3\text{O}_8$, the additional material forming the solid solution contains both Al and Si, with a composition $\text{Al}_{1.2}\text{Si}_{0.9}\text{O}_{3.5}$, *i.e.* the additional phase corresponds to 0.27 moles of 3:2 mullite. Thus, the nepheline-like phase has a composition which can be written $0.27(\text{Al}_6\text{Si}_2\text{O}_{13})\cdot\text{NaAlSi}_3\text{O}_8$. The structure of such a compound, if indeed it can be formed, is presently unknown.

Conclusions

When Zettlitz kaolinite is heated at 980°C then leached with NaOH for short times (*ca.* 10 min), the first species to be removed is uncombined amorphous SiO_2 , characterised by a ^{29}Si NMR peak at δ *ca.* -114 . Crystalline SiO_2 (quartz) is largely resistant to alkaline attack. A significant amount of Na and associated hydration water also comes into combination, probably with an amorphous aluminosilicate phase which is also relatively stable to NaOH attack, and contributes significantly to a ^{29}Si NMR peak at δ *ca.* -88 . The removal of *ca.* 30% of the total Si in this stage (based on NMR measurements) is sufficient to produce an overall mullite stoichiometry, since heating this material to 1300°C converts all the spinel and quartz and essentially all of the amorphous phase to mullite.

Leaching heated kaolinite for 20–30 min removes 50–60% of the total Si, principally from the amorphous phase which continues to retain Na, and contains Si sites not unlike nepheline, although even at this stage, it may be Al-rich with respect to nepheline composition. The system now contains insufficient Si to form mullite with all the available Al, since on heating to 1140°C the crystalline silica and most of the

spinel is taken into the amorphous phase, which forms a mixture of corundum and mullite on heating to 1300 °C.

Leaching for 40 min removes a further 10% Si from the amorphous aluminosilicate phase, bringing about the formation of some corundum even at 1140 °C. Heating to 1300 °C produces crystalline corundum at the expense of the mullite, spinel and amorphous phase still present at 1140 °C. The remaining Si is located in a small amount of residual amorphous phase which also contains Na and tetrahedral Al, according to ²⁷Al NMR data.

After 60–90 min leaching, no further Si is removed, but the system now contains sufficient Na and Al to form a solid solution of nepheline with alumina when heated at 1140 °C. Heating to 1300 °C converts all the remaining mullite, spinel and amorphous phase into the nepheline solid solution, the excess Al appearing as corundum.

The leaching sequence and subsequent thermal reactions can therefore be understood in terms of the progressive removal of Si from the system, principally from the amorphous silica and aluminosilicate phases, the latter becoming progressively substituted by Na.

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