

# Formation of aluminosilicate geopolymers from 1:1 layer-lattice minerals pre-treated by various methods: a comparative study

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**Abstract** Materials resembling aluminosilicate geopolymers have been prepared from the kaolinitic 1:1 layer lattice aluminosilicate clay mineral halloysite by reaction with sodium silicate solution under alkaline conditions. The effect on geopolymer formation of pretreating the clay mineral reactant by heating, high-energy grinding or exposure to acid or alkali was monitored by the ability of the samples to cure and harden, and by XRD,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  solid-state MAS NMR spectroscopy. Only samples prepared from the fully thermally dehydroxylated clay showed the typical XRD and NMR geopolymer characteristics. Less complete reaction was found in samples pretreated by highly energetic grinding, whereas samples exposed to chemical pretreatment with dilute acid did not react to form viable geopolymers. Pretreatment with dilute alkali produced a zeolite which reacted with sodium silicate, but the hardened sample was not X-ray amorphous and showed subtle differences in its NMR spectra. These results are discussed in terms of the vital role played in the early stages of the reaction sequence

by the presence of labile aluminium. The efficacy of the various pretreatment methods is related to their ability to render the aluminium source (the solid aluminosilicate clay) sufficiently soluble in alkali.

## Introduction

Aluminosilicate geopolymers were originally formalized by Davidovits [1] as consisting of tetrahedral  $\text{AlO}_4$  and  $\text{SiO}_4$  units condensed under highly alkaline conditions into a three-dimensional framework with charge stabilization by alkali metal ions. The recommended starting materials (a mixture of dehydroxylated clay mineral such as metakaolinite, sodium silicate solution and sodium hydroxide) [1] cure at ambient temperature to a robust solid characteristically amorphous to X-rays and containing solely tetrahedral aluminium and silicon, as judged by their solid-state MAS NMR spectra [2]. Thermal pre-treatment of the starting clay mineral to bring about its dehydroxylation is stated to be essential to the synthesis of geopolymers [1]; although building materials based on alkali-treated undehydroxylated kaolinite were described earlier [3], these products did not have the X-ray amorphous characteristics of geopolymers and were composed of crystalline hydroxysodalite. Thermal dehydroxylation of kaolinite minerals markedly influences the coordination state of the aluminium, rendering it more labile by converting it from 6-fold to a mixture of 6, 5 and 4-fold coordination [4]. Although complete dehydroxylation at 800°C is normally recommended for the synthesis of geopolymers, the extent to which the

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aluminium environment must be modified for the condensation reaction to produce a viable geopolymer has not been determined. Furthermore, there are other ways of changing the aluminium environment of an aluminosilicate mineral which may be effective in promoting geopolymerization; these include mechanochemical treatment, which gives a mixture of 4,5, and 6-fold Al coordination states, and chemical treatment with acid or alkali.

The aim of this work is to investigate the relative merits of thermal, mechanochemical and chemical pre-treatment of a 1:1 layer lattice silicate (halloysite) in preparation for its conversion to an aluminosilicate geopolymer. The effect of the various pre-treatment methods on the mineral structure was evaluated by X-ray powder diffraction and  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR. After pre-treatment, geopolymers were prepared, and the viability of the products was judged on the basis of several criteria [5], namely, development of strength at ambient curing temperature, attainment of an X-ray amorphous condition and the presence of solely tetrahedral Al and Si coordination as determined by solid-state MAS NMR.

## Experimental

The 1:1 layer lattice aluminosilicate used throughout this work was New Zealand halloysite (New Zealand China Clays Ultrafine grade). This mineral is low in iron ( $< 0.14\%$   $\text{Fe}_2\text{O}_3$ ) and alkali metals and is chemically identical to kaolinite but has tubular rather than platy morphology. The principal mineralogical impurities are quartz and cristobalite, estimated by semi-quantitative XRD to be  $< 3\%$ . The other reagents were sodium silicate solution type “O” (Fernz Chemical Co., concentration 668 g/l,  $\text{Na}_2\text{O}:\text{SiO}_2=0.3$  and reagent grade NaOH pellets.

Geopolymers were prepared using both undehydroxylated halloysite and halloysite which had been pretreated in various ways, as follows:

Thermal treatment was carried out by heating for 2 h at 200–1000 °C. The degree of dehydroxylation in each case was determined from the measured mass loss.

Mechanochemical treatment was carried out by two types of high-energy grinding. In one experiment, the sample was ground for 20 h at 400 rpm in a planetary ball mill (Frisch Pulverisette) fitted with a 100 mm dia. zirconia pot and 3 mm dia. zirconia balls. The mass ratio of sample: milling media was 1:50. Grinding was also carried out in a more energetic vibratory ring mill

(Bleuler, Switzerland) equipped with a tungsten carbide bowl and rings. In this case, the maximum grinding period was considerable shorter (15 min).

Chemical treatment was carried out by soaking 5 g aliquots of raw halloysite in 0.1 M HCl or 0.1 M NaOH for periods of 1–24 h. After chemical treatment the samples were recovered by filtration, washed and dried at 60 °C for 24 h.

Geopolymers were synthesized from all the pre-treated halloysite samples and the untreated control. The generic composition of all the geopolymer samples was:  $\text{SiO}_2:\text{Al}_2\text{O}_3 = 3.4$ ,  $\text{Na}_2\text{O}:\text{SiO}_2 = 0.4$ ,  $\text{H}_2\text{O}:\text{Na}_2\text{O} = 11.4$ . The calculated amount of NaOH was dissolved in water and allowed to cool before the addition of the calculated amount of sodium silicate solution with continuous stirring. The halloysite was then mixed in and the resulting paste poured into a cylindrical mould, sealed in plastic film and cured at 60 °C for 24 h. After curing, the plastic film was removed and the sample oven-dried at 60 °C overnight.

Both the halloysite starting materials and the corresponding geopolymers were characterized by X-ray powder diffraction (Philips PW 1700 computer-controlled goniometer with a graphite monochromator and Co K $\alpha$  radiation) and by  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR, using a Varian Unity 500 spectrometer (11.7T), with a 4 mm Doty MAS probe spun at 10–12 kHz, under the following conditions:

$^{27}\text{Al}$ : spectrometer frequency 130.224 MHz with a 1  $\mu\text{s}$  ( $\pi/10$ ) pulse for solution) and a 1 s delay, spectra referenced to  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,

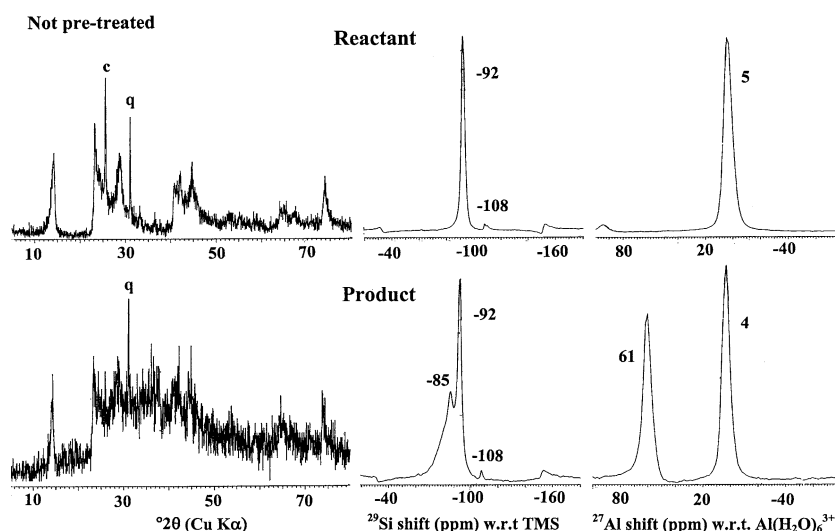
$^{29}\text{Si}$ : spectrometer frequency 99.926 MHz with a 6  $\mu\text{s}$  ( $\pi/10$ ) pulse and a 100 s delay, spectra referenced to tetramethylsilane (TMS).

## Results and discussion

### Geopolymer from untreated halloysite

Figure 1 shows the X-ray and solid-state NMR results of a control experiment in which the geopolymer synthesis was carried out using untreated halloysite. The reactant, shown in the upper panel of Fig. 1, displays an XRD trace fully consistent with halloysite of basal spacing 7.3 Å (ICDD file no 29–1487). The sharp peaks at 31.1 and 24.3°2 $\theta$  are due to the 101 and 100 reflections of the quartz impurity (ICDD file no. 33–1161), while the peak at 25.6°2 $\theta$  is due to the 101 reflection of cristobalite (ICDD file no. 39–1425). The  $^{29}\text{Si}$  NMR spectrum of this reactant shows the expected

**Fig. 1** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of untreated halloysite clay (upper panel) and the product formed when this material is subjected to a geopolymer synthesis reaction (lower panel). The unmarked XRD peaks correspond to halloysite with a 7.3 Å basal spacing (ICDD file no 29-1487) and the peaks labelled q and c are from quartz and cristobalite respectively



sharp resonance at  $-92$  ppm arising from the  $\text{Q}^3$  tetrahedral layer silicate units [4, 6], while the quartz impurity is responsible for the small peak at  $-108$  ppm [4]. The single  $^{27}\text{Al}$  NMR resonance at 5 ppm arises from the aluminium in solely octahedral coordination in this clay [4].

After being subjected to the geopolymer synthesis reaction, this material set and hardened to some extent, but did not achieve the texture and properties of a well-polymerized sample. The XRD trace (Fig. 1, lower panel) indicates some loss of crystallinity, but the basal spacing is retained and remnants of the other reflections are still discernable, as is the sharp 100 peak of the quartz impurity. The  $^{29}\text{Si}$  NMR spectrum retains the peaks at  $-92$  and  $-108$  ppm from the reactant, but a new, broad resonance at  $-85$  ppm indicates a degree of reaction involving the formation of new tetrahedral Si–O–Al structures [6]. The  $^{27}\text{Al}$  NMR spectrum of this material shows that about 40% of the original octahedral Al (5 ppm) has been converted to tetrahedral coordination (60 ppm). Thus, the combined evidence suggests that a degree of geopolymerization has occurred in this sample, but that the reaction is by no means complete, and that a significant proportion of the original unreacted halloysite is still present.

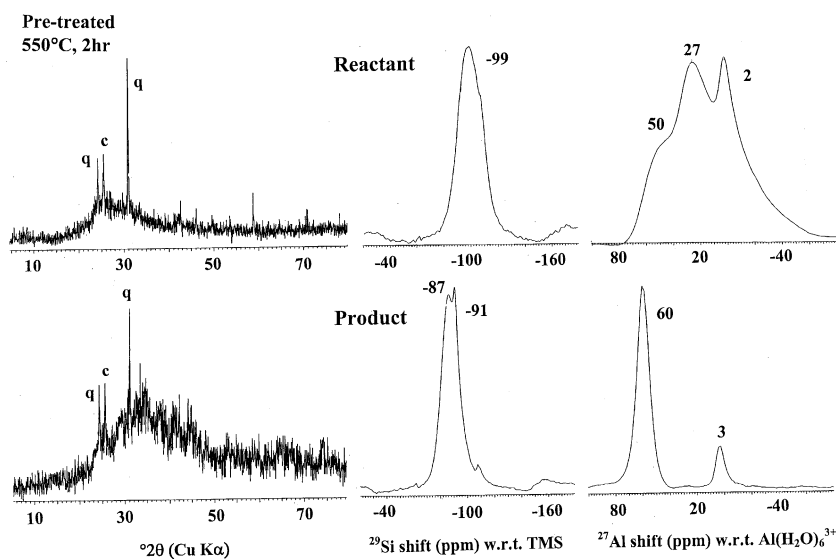
#### Geopolymers from thermally pretreated halloysite

Several dehydroxylation temperatures were employed; below  $550$  °C, dehydroxylation is incomplete, as judged by the measured mass loss. As dehydroxylation proceeds, the resulting reacted products exhibit increasingly geopolymer-like characteristics, becoming increasingly X-ray amorphous and containing increasing proportions of tetrahedral Al. Typical results for

halloysite pretreated by heating at  $550$  °C and  $1000$  °C are shown in Figs. 2 and 3, respectively. By  $550$  °C, dehydroxylation is well advanced, the sample having lost 77% of the mass loss corresponding to full dehydroxylation. The XRD pattern (Fig. 2, upper panel) is essentially X-ray amorphous but retains the sharp peaks of the crystalline silica impurities. The  $^{29}\text{Si}$  NMR spectrum shows the typical broad resonance of dehydroxylated halloysite at about  $-99$  ppm arising from a range of Si–O–Al(Si) bond angles associated with a flattening of the tetrahedral sheet [4, 6]. The progress of dehydroxylation in this sample is confirmed by the presence in the  $^{27}\text{Al}$  NMR spectrum of resonances at 2 ppm (octahedral Al), 27 ppm (usually ascribed to 5-fold coordinated Al) and a shoulder at 50 ppm (tetrahedral Al) [4]. The Al coordination changes are typical of dehydroxylated kaolinite or halloysite [4] and are a particularly sensitive indicator of dehydroxylation, since the structural hydroxyl groups removed by dehydroxylation are intimately associated with the octahedral Al layer.

After geopolymerization, this sample displays an increased amorphous content with respect to the crystalline silica reflections which are still visible (Fig. 2, lower panel). The  $^{29}\text{Si}$  NMR spectrum has narrowed and shifted to the more typical geopolymer position at about  $-90$  ppm, reflecting the incorporation of Al into the coordination sphere of the Si. The narrowness of this resonance allows it to be partially resolved into two peaks ( $-87$  and  $-91$  ppm) and reveals the  $\text{SiO}_2$  impurity resonance at  $-108$  ppm. The  $^{27}\text{Al}$  NMR spectrum (Fig. 2, lower panel) shows that most of the Al is in tetrahedral coordination, as expected for a true geopolymer, but a small amount of octahedral Al persists. Further heating at temperatures between

**Fig. 2** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of halloysite clay thermally dehydroxylated at 550 °C for 2 h (upper panel) and the product formed under geopolymer synthesis conditions (lower panel). The XRD peaks labelled q and c correspond to quartz and cristobalite respectively



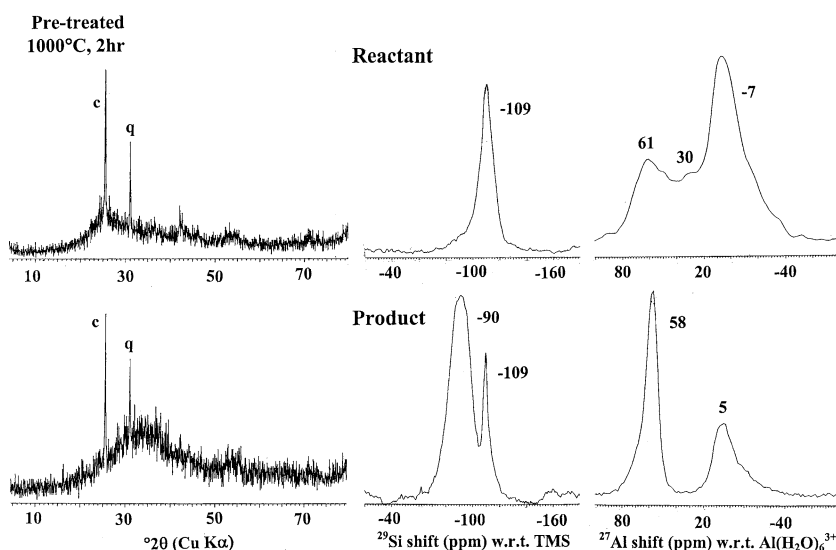
550 °C and the recommended temperature of 800 °C produces dehydroxylated halloysite from which geopolymers can be synthesized having diagnostic XRD and NMR characteristics [5]. However, the pretreatment temperature of 800 °C may be a maximum, since at higher pretreatment temperatures (1000 °C), geopolymerization appears to be less complete, as judged by the mechanical soundness of the product and the presence of unconverted octahedral Al (Fig. 3, lower panel). Although mullite (the high-temperature aluminosilicate thermal reaction product of halloysite) does not crystallize until about 1050 °C, and continues to evolve at higher temperatures [7], the present results suggest that thermal pretreatment at temperatures of incipient crystallization produces a precursor material which is less amenable to structural rearrangement

under geopolymerization conditions. At this stage, formation of the stable octahedral  $\text{AlO}_6$  columns of the mullite structure will render the transformation to a tetrahedral framework structure increasingly difficult. Thus, the optimum temperature for thermal pretreatment of the clay mineral is that which secures maximum lability of the Al configuration (i.e. maximum content of 4 and 5-fold coordination) without its transformation into the more stable octahedral units of higher-temperature crystalline phases.

#### Geopolymers from mechanically pretreated halloysite

Two types of mechanical treatment were investigated. The results of grinding for 20 h in a commonly-used

**Fig. 3** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of halloysite clay thermally pretreated at 1000 °C for 2 h. (upper panel) and the product formed under geopolymer synthesis conditions (lower panel). The XRD peaks labelled q and c correspond to quartz and cristobalite respectively



type of planetary ball mill are shown in Fig. 4 (upper panel). Comparison with the untreated material (Fig. 1, upper panel) shows that this grinding method has made very little difference to the XRD and  $^{29}\text{Si}$  characteristics; all the X-ray reflections of the starting material are still present and the position of the  $^{29}\text{Si}$  NMR resonance is unchanged. Small differences can be detected in the  $^{27}\text{Al}$  NMR spectrum, however, in which minor traces of tetrahedral and 5-coordinated Al can just be discerned at 56 and 30 ppm respectively. The properties of the geopolymer prepared from this precursor (Fig. 4, lower panel) are very similar to the geopolymer from the untreated clay, except for the appearance of slightly more tetrahedral Al in the mechanochemical sample, indicating a very slightly greater degree of reaction.

In view of this result, a much more vigorous grinding method was employed, using a vibratory ring-disc mill. Activation for 15 min under these conditions produces a much more marked effect on the clay mineral (Fig. 5, upper panel), rendering it essentially X-ray amorphous and broadening its  $^{29}\text{Si}$  NMR spectrum by the appearance of a shoulder at about  $-102$  ppm between the original halloysite and silica resonances at  $-92$  and  $-108$  ppm. This new  $^{29}\text{Si}$  resonance corresponds to that of dehydroxylated halloysite, as seen in the sample thermally pretreated at  $550^\circ\text{C}$  (Fig. 3). An even more striking change is seen in the  $^{27}\text{Al}$  NMR spectrum, with the appearance of significant amounts of tetrahedral and 5-coordinated Al suggesting that the lability of this sample has been increased significantly. This increased reactivity is evident from the product formed from this material (Fig. 5, lower panel). The XRD trace shows that the resulting geopolymer is essentially X-ray

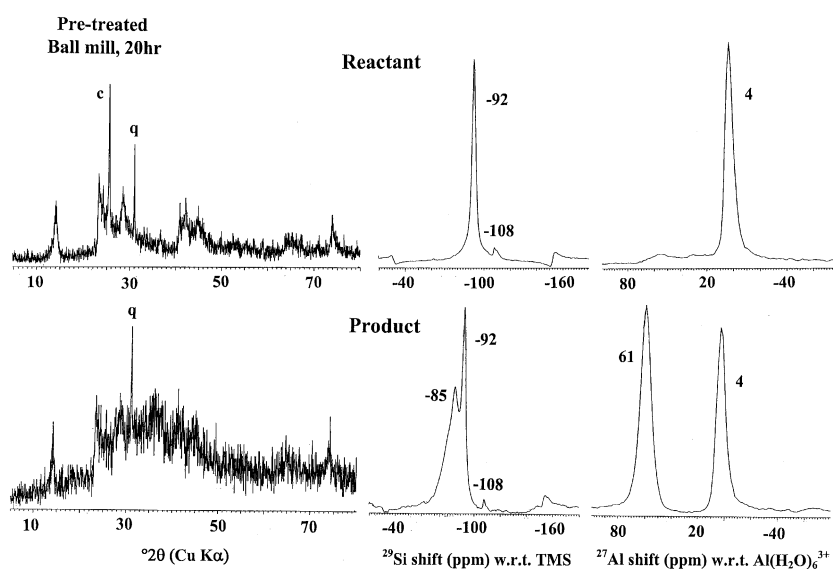
amorphous, but retains evidence of the original quartz impurity. The broad  $^{29}\text{Si}$  NMR resonance is centred at  $-86$  ppm; this downfield shift from the position of the peak in the ground reactant is consistent with the entry of Al into the coordination environment of the Si. Although the position of this resonance is less negative than usually found in these geopolymers, the slight shoulder at about  $-90$  ppm has the effect of moving the centre-of-gravity of this peak closer to the expected value. The presence of the quartz impurity is evidenced by the small sharp peak at  $-108$  ppm. The relatively advanced state of geopolymer formation can be gauged from the  $^{27}\text{Al}$  NMR spectrum (Fig. 5, lower panel), which shows that a high proportion of the Al is in tetrahedral coordination (58 ppm), with only a small amount of unreacted octahedral Al evident at 4 ppm. These results suggest that sufficiently vigorous mechanochemical pre-treatment of the clay mineral might be a viable alternative to thermal dehydroxylation.

#### Geopolymers from chemically pretreated halloysite

##### *Pretreatment with 0.1 M HCl*

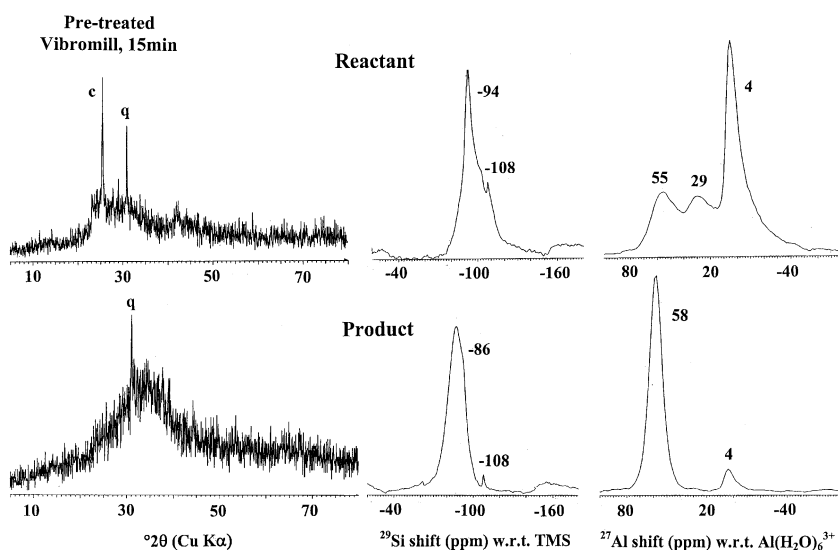
The result of acid treatment of raw halloysite for 24 h is shown in Fig. 6 (upper panel). Comparison with the results for the untreated mineral (Fig. 3, upper panel) shows that this pretreatment has produced no change in the clay. This result is consistent with previously published work on acid-leaching of aluminosilicate clays which indicates that the octahedral Al–O sheets are susceptible to acid attack only after thermal dehydroxylation [8] or mechanochemical treatment [9], both of which processes disrupt the aluminium coordination,

**Fig. 4** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of halloysite clay mechanochemically pretreated in a planetary ball mill for 20 h (upper panel) and the product formed under geopolymer synthesis conditions (lower panel). The XRD peaks labelled q and c correspond to quartz and cristobalite respectively

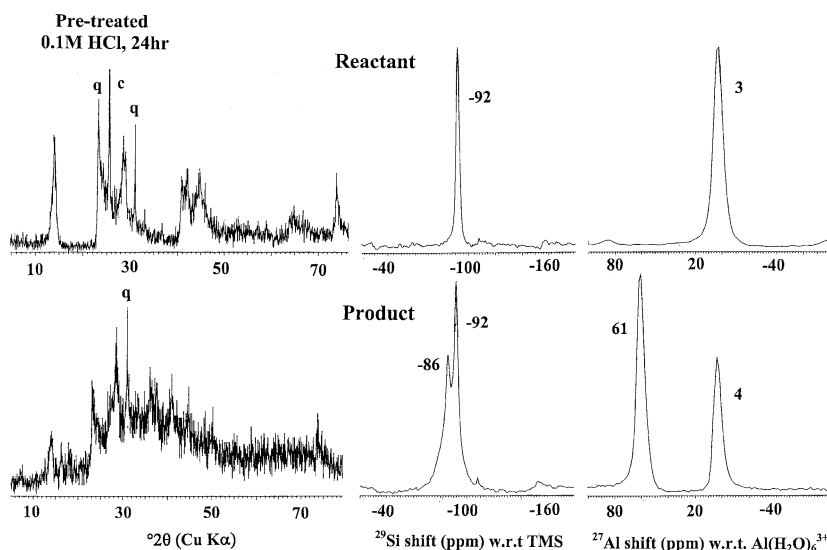




**Fig. 5** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of halloysite clay mechanochemically pretreated in a vibratory-type mill for 15 min (upper panel) and the product formed under geopolymer synthesis conditions (lower panel). The XRD peaks labelled q and c correspond to quartz and cristobalite respectively



**Fig. 6** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of halloysite clay chemically pretreated with 0.1 M HCl for 24 h (upper panel) and the product formed under geopolymer synthesis conditions (lower panel). The unmarked XRD peaks correspond to halloysite with a 7.3 Å basal spacing (ICDD file no 29-1487) and the peaks labelled q and c correspond to quartz and cristobalite respectively



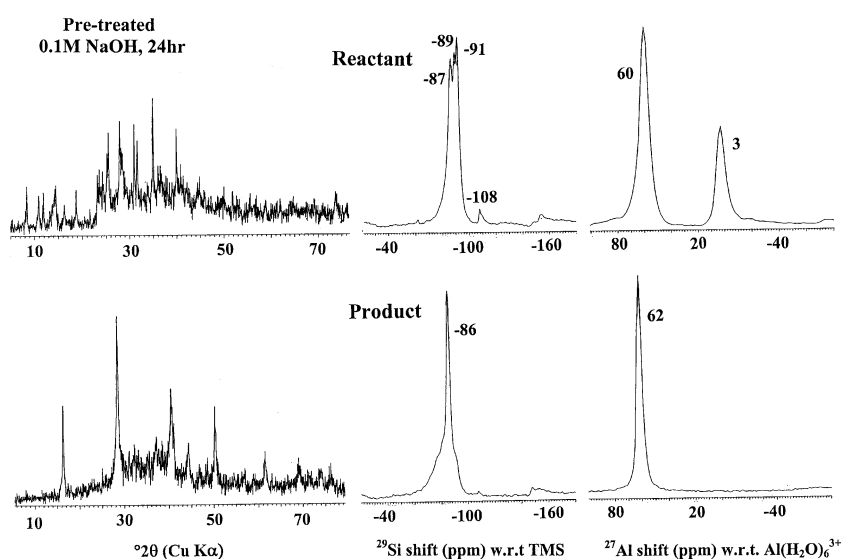
making it more reactive. The ineffectiveness of acid pretreatment is confirmed by the inability of the treated material to form a viable geopolymer (Fig. 6, lower panel). As was found for the untreated clay, the product from the acid-treated reactant showed very poor strength and its XRD and  $^{29}\text{Si}$  NMR characteristics were similar to the product from untreated halloysite. Comparison of the  $^{27}\text{Al}$  NMR spectra of these two geopolymers shows a slightly higher proportion of tetrahedral Al in the acid-treated sample, suggesting that acid treatment may have facilitated geopolymerization, but only to a small degree.

#### Pretreatment with 0.1 M NaOH

The effect of alkali pretreatment of raw halloysite for 24 h on the XRD and NMR characteristics is shown in

Fig. 7, upper panel. These results show that even this relatively mild alkali treatment has a considerable effect on the mineral, the sharp XRD peaks indicating its conversion to crystalline hydrated zeolite LTA,  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}\cdot 27\text{H}_2\text{O}$  (ICDD file number 73-2340). This significant chemical reaction is reflected in the  $^{29}\text{Si}$  NMR spectrum, in which three sharp resonances are resolved at  $-87$ ,  $-89$  and  $-91$  ppm, in addition to the small residual quartz impurity at  $-108$  ppm. The  $^{27}\text{Al}$  NMR spectrum of this material also indicates the conversion of a significant amount of the original octahedral Al to tetrahedral coordination, consistent with zeolite formation. Experiments carried out at shorter alkali treatment times show that after 2 h the Al retains its original exclusively octahedral coordination, but after 3 h, progressive conversion to tetrahedral coordination begins.

**Fig. 7** XRD,  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of halloysite clay chemically pretreated with 0.1 M NaOH for 24 h (upper panel) and the product formed under geopolymer synthesis conditions (lower panel). The unmarked XRD peaks in the upper panel correspond to  $\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$  (ICDD file number 73-2340) and the unmarked XRD peaks in the lower panel correspond to  $6\text{NaAlSiO}_4 \cdot \text{Na}_2\text{CO}_3$  (ICDD file number 24-1045)



Even though treatment with dilute alkali for 24 h has brought about significant changes in the chemical environment of both the Si and Al atoms, as evidenced by the NMR results, the conversion of crystalline halloysite to another crystalline compound does not facilitate geopolymerization on subsequent treatment with alkali silicate. The X-ray diffraction pattern of this product (Fig. 7, lower panel) shows it to contain a new crystalline phase, displaying the major peaks of sodium aluminium silicate carbonate,  $6\text{NaAlSiO}_4 \cdot \text{Na}_2\text{CO}_3$  (ICDD file number 24-1045) superimposed on a broad background from the presence of a small amount of residual X-ray amorphous material. The formation of this carbonate double salt apparently results from atmospheric carbonation of the excess alkali present. The crystallinity of this compound is reflected in the narrow linewidth of the  $^{29}\text{Si}$  NMR peak at  $-86$  ppm, superimposed on a broader underlying feature, presumably arising from the small amount of amorphous component. The Al is in exclusively tetrahedral coordination, but the narrowness of the NMR resonance by comparison with a conventional  $^{27}\text{Al}$  geopolymer NMR spectrum is consistent with a more crystalline environment. Thus, although this product sets, it does not have the typical XRD or NMR characteristics of a metakaolinite-based geopolymer, nor is it exactly similar to the product of kaolinite reacted directly with sodium silicate, which is reported [3] to form hydroxysodalite,  $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ .

#### Implications of these results for the geopolymerization mechanism

These results indicate that thermal dehydroxylation is the only pre-treatment of the clay mineral halloysite

capable of producing on reaction with alkaline sodium silicate solution a material with the unique XRD and NMR characteristics of a geopolymer. The next most effective pretreatment is grinding of sufficient intensity to promote the breakdown of the crystal structure. The most significant effect of thermal dehydroxylation is its disruption of the coordination sphere of the aluminate sheet, since the structural hydroxyl groups are associated with this part of the structure. High-energy grinding exerts a similar effect, lowering the coordination number of the octahedral aluminium to a mixture of 5 and 4-fold coordination, but under the present experimental conditions, to a lesser degree than thermal dehydroxylation. These observations emphasise the importance of the lability of the aluminium-containing component towards alkaline attack in the early stages of the reaction, and explain why only those pretreatments which assist this process are effective. The lability of the silicate part of the aluminosilicate structure is less important in the present reacting mixture, since the alkali silicate solution provides the necessary source of soluble silicate. The solubility of the solid silicate towards alkali will however be an important factor in the absence of alkali silicate solutions, where the only source of soluble silica is the solid aluminosilicate itself. The necessity of a source of soluble aluminium is supported by experiments in which viable solid materials with the XRD and NMR characteristics of typical aluminosilicate geopolymers have been prepared in the absence of solid aluminosilicates from alkaline solutions of sodium aluminate and sodium silicate [10].

From this it also follows that if the only available source of soluble aluminium is rendered less accessible to alkali attack by being locked into a crystalline phase,

the geopolymerization reaction will be hindered. This appears to be the reason why pretreatment of the clay with alkali did not in this case lead to a material with the typical XRD and NMR characteristics of a geopolymer, since this pretreatment produces a crystalline zeolite in which the aluminium may not be reactive to alkaline attack. It also suggests that thermal pretreatment carried out at too high a temperature, at which high-temperature crystalline phases begin to form, may hinder the reaction. Similar reasoning may explain our lack of success in producing geopolymers from the 2:1 layer-lattice aluminosilicate mineral pyrophyllite, in which the aluminate layer is protected from alkali attack by the two enclosing silicate layers, and not even thermal dehydroxylation produces the necessary aluminium solubility since the dehydroxylated product is also crystalline (unpublished results).

### Conclusions

1. The properties of geopolymer-like materials formed by reaction of an aluminosilicate clay (halloysite) with alkaline sodium silicate solution depend strongly on the way in which the clay is pretreated.
2. Thermal pretreatment at temperatures between 550 °C and 800 °C progressively removes hydroxyl water from the clay structure, changing the coordination number (CN) of the aluminium from 6 to a mixture of 4, 5 and 6-CN. The resulting geopolymer shows the typical curing characteristics, XRD,  $^{27}\text{Al}$  and  $^{29}\text{Si}$  MAS NMR spectra of a viable geopolymer. If the temperature of the thermal pretreatment is sufficiently high to initiate crystallization of the high-temperature phases, the subsequent formation of a viable geopolymer is compromised.
3. If sufficiently energetic, mechanochemical pretreatment (high-energy grinding) of the clay can bring about similar changes in the aluminium CN to thermal dehydroxylation. Geopolymers formed from this material show similar mechanical and

structural characteristics to the well-reacted materials prepared from the dehydroxylated clay.

4. Chemical pretreatment of the clay with dilute HCl brings about negligible change in the XRD and NMR spectra, and produces a poorly-set material with very similar characteristics to that synthesized from the untreated clay. By contrast, pretreatment of the clay with dilute alkali for >3 h produces a crystalline zeolite which cures and hardens during the subsequent geopolymer synthesis reaction. The product shows some of the characteristics of a typical geopolymer, but is not fully X-ray amorphous, containing a crystalline double salt of sodium aluminosilicate and carbonate.
5. These results can be understood in terms of the efficiency of the various pretreatments in converting the aluminium of the solid aluminosilicate (clay) to an alkali-soluble form. This emphasises the vital role played by labile aluminium in solution during the early stages of geopolymer formation.

### References

1. Davidovits J (1991) *J Thermal Anal* 37:1633
2. Barbosa VFF, MacKenzie KJD, Thaumaturgo C (2000) *Int J Inorg Mater* 2:309
3. Berg LG, Demidenko BA, Remiznikova VA, Nizamov MS (1970) *Stroit Mater* 10:22
4. MacKenzie KJD, Smith ME (2002) *Multinuclear solid state NMR of inorganic materials*, Pergamon Materials Series, vol 6. Pergamon/Elsevier, Oxford
5. MacKenzie KJD (2003) *Adv. In Ceram. Matrix Composites IX*, *Ceram. Trans.* 153:175
6. Singh PG, Bastow T, Trigg M (2005) *J Mater Sci* 40:3951
7. Brown IWM, MacKenzie KJD, Bowden ME, Meinhold RH (1985) *J Amer Ceram Soc* 68:298
8. Okada K, Shimai A, Takei T, Hayashi S, Yasumori A, MacKenzie KJD (1998) *Microporous Mesoporous Mater* 21:289
9. Temuujin J, Burmaa G, Amgalan J, Okada K, Jadambaa Ts, MacKenzie KJD (2001) *J Porous Mater* 8:233
10. Brew DRM, MacKenzie KJD (2005) Fresh insights into geopolymer formulations: the roles of sodium silicate and sodium aluminate. *Proc. World Geopolymer Conf.*, St. Quentin, France, p 27