



# Effect of solution composition on the recrystallization of kaolinite to feldspathoids in hyperalkaline conditions: limitations of pertechnetate incorporation by ion competition effects

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## ABSTRACT

The incorporation of pertechnetate ( $\text{TcO}_4^-$ ) into feldspathoids produced by alkaline alteration of aluminosilicate clays may offer a potential treatment route for  $^{99}\text{Tc}$ -containing groundwater and liquors. Kaolinite was aged in NaOH to determine the effect of base concentration, temperature, and solution composition on mineral transformation and pertechnetate uptake. In all reactions, increased temperature and NaOH concentration increased the rate of kaolinite transformation to feldspathoid phases. In reactions containing only NaOH, sodalite was the dominant alteration product; however, small amounts (6–15%) of cancrinite also formed. In experiments containing NaOH/Cl and NaOH/ $\text{NO}_3$  mixtures, sodalite and nitrate cancrinite were crystallized (at 70°C), with no reaction intermediates. The addition of  $\text{SO}_4^{2-}$  crystallized sulfatic sodalite at 40 and 50°C, but at higher temperatures (60 and 70°C) sulfatic sodalite transforms to vishnevite (sulfatic cancrinite). In experiments where a pertechnetate tracer was added (at  $\sim 1.5 \mu\text{mol l}^{-1}$ ), only 3–5% of the  $^{99}\text{Tc}$  was incorporated into the feldspathoid phases. This suggests that the larger pertechnetate anion was unable to compete as favourably for the internal vacancies with the smaller  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  anions in solution, making this method likely to be unsuitable for groundwater treatment.

**KEYWORDS:** kaolinite, alkaline, alteration, pertechnetate, sodalite, cancrinite.

## Introduction

THERE is a global legacy of contaminated land around nuclear facilities, specifically arising from leaking storage ponds and containers (Mon *et al.*, 2005; Perdrial *et al.*, 2011; Wang and Um, 2012). At the Sellafield nuclear facility, UK,  $\sim 20$  million  $\text{m}^3$

of soil may be contaminated, and  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$  and  $^{99}\text{Tc}$  have been identified as important contaminants (Hunter, 2004). In oxic environments, technetium is highly mobile in the form of its pertechnetate anion,  $\text{TcO}_4^-$  (Burke *et al.*, 2005), and its half-life of  $2.1 \times 10^5$  years (Szecsody *et al.*, 2014) means that  $^{99}\text{Tc}$  is particularly problematic. Hence there is a need for low cost, preferably non-invasive, techniques to be developed that might increase the pace of restoration at nuclear sites.

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Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , (Grim, 1968) is commonly found in sediments and soils around nuclear sites (Huertas *et al.*, 1999), and has a simple 1:1 sheet silicate structure (Bauer *et al.*, 1998). Under alkaline conditions, kaolinite dissolves, releasing  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  into solution, leading to the formation of secondary feldspathoid and zeolite phases (Mashal *et al.*, 2004; Qafoku *et al.*, 2003; Zhao *et al.*, 2004; Wallace *et al.*, 2013). The exact phase precipitated depends on the solution composition, base concentration, Si:Al ratio and temperature (Deng *et al.*, 2006b). Important features of the internal structure of these neo-formed minerals, such as cancrinite ( $[(\text{Ca},\text{Na})_6(\text{CO}_3)_{1-1.7}][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$ ) (Bonaccorsi and Merlino, 2005), sodalite ( $(\text{Na}_8\text{Cl}_2)[\text{Si}_6\text{Al}_6\text{O}_{24}]$ ) (Bonaccorsi and Merlino, 2005) and vishnevite ( $[(\text{Na},\text{Ca})_{6-x}\text{K}_x(\text{SO}_4)][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$ ) (Bonaccorsi and Merlino, 2005), are channels and cages, which are known to selectively incorporate guest anions/cations (Deng *et al.*, 2006b; Mon *et al.*, 2005). Alkaline altered sediments are known to incorporate  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  (Choi *et al.*, 2005, 2006; Chorover *et al.*, 2008; Deng *et al.*, 2006a; Mon *et al.*, 2005; Wallace *et al.*, 2013); however, there is no information available regarding the successful incorporation of  $^{99}\text{Tc}$ , in the form of pertechnetate ( $\text{TcO}_4^-$ ), into alkaline alteration products. Perrhenate ( $\text{ReO}_4^-$ ) has been incorporated into sodalite (Dickson *et al.*, 2014; Mattigod *et al.*, 2006) and the incorporation of this negatively charged, tetrahedral anion may support the hypothesis that  $\text{TcO}_4^-$  could be encapsulated into similar phases. This work investigates alkaline alteration of kaolinite, particularly the effect of base concentration, temperature, and solution composition during aging, with a view to encapsulating  $^{99}\text{Tc}$ , in the form of pertechnetate ( $\text{TcO}_4^-$ ), into a range of neoformed phases. Thus, potentially, this could provide a novel remediation treatment for land contaminated with  $^{99}\text{Tc}$ .

## Material and methods

### Materials

Two natural kaolinite samples were used as supplied; kaolinite from Fluka Chemicals (Switzerland) and sample K-Ga 1b from the Clay Mineral Society (Chantilly, USA). Ammonium pertechnetate was obtained from LEA-CERCA (France). All other reagents (sodium hydroxide, chloride, nitrate and sulfate) were obtained from VWR international (USA).

### Methods

In all instances, aerobic batch experiments were carried out in sealed 50 ml polypropylene Oakridge tubes. Initial experiments suspended 0.4 g of dry kaolinite (Fluka) in 20 ml of NaOH solution (0.05 M, 0.5 M, 5 M), at room temperature (RT) or 70°C in a temperature-controlled oven (5 M NaOH only). The same solid-to-solution ratio was used in all subsequent experiments. Samples were shaken on a daily basis. At intervals of 1, 7, 14 and 35 days (RT), and 7 and 10 days (70°C), tubes were removed from the oven. After cooling to RT, solid phases were extracted by centrifugation, at 6000 g for 10 minutes. The solid phase was washed four times with deionized water and dried, at room temperature, in a desiccator containing Carbosorb.

### Effect of solution composition and temperature

Temperature effects were determined when 0.4 g dry kaolinite (Fluka) was aged in 20 ml 5 M NaOH for 10 days at 40°C, 50°C and 60°C. In order to investigate the effect of changing the anion composition on the alteration products formed, three additional basic (5 M NaOH) solutions were used that contained either 1 M NaCl, 0.5 M  $\text{NaNO}_3$  or 4 M  $\text{Na}_2\text{SO}_4$ . Kaolinite (Fluka) was aged in the NaOH/Cl solution at 70°C for 10 days. Kaolinite (K-Ga 1b) was aged in the NaOH/ $\text{NO}_3$  solution at 40°C, 50°C and 60°C for 14 days and in the NaOH/ $\text{Na}_2\text{SO}_4$  solution, at 40°C, 50°C, 60°C and 70°C for 10 days. Additionally, seven-day time series experiments were performed at 70°C using kaolinite (K-Ga 1b) in NaOH, and kaolinite (K-Ga 1b) in the NaOH/ $\text{Na}_2\text{SO}_4$  solution, with daily sample-sacrifice.

### Pertechnetate sorption experiments

Four sets of triplicate experiment were performed where ammonium pertechnetate was added at tracer concentrations (1.5  $\mu\text{M}$ ) to each of the basic solutions described above (i.e. NaOH, NaOH/ $\text{SO}_4^{2-}$ , NaOH/ $\text{NO}_3^-$  and NaOH/ $\text{Cl}^-$ ) prior to the addition of kaolinite (K-Ga 1b) and incubated at 70°C for up to 72 days. At regular intervals, aqueous samples were separated by centrifugation and Tc activity determined by liquid scintillation counting on a Packard TriCarb 2100TR.

### Sample characterization

The starting material and alkaline alteration end products were analysed by a number of

complementary techniques. Powder X-ray diffraction (XRD) using a Bruker D8 diffractometer. Samples (50–100 mg) were mounted on silicon slides and scanned between  $2^\circ$  and  $70^\circ 2\theta$ . Rietveld refinement was carried out using *TOPAS 4.2* software (Bruker), providing quantitative analysis of the crystalline phases. (For the results presented in this study, the errors were  $\pm 10\%$  at the 50% level, i.e. between 40–60% present, and  $\pm 1\%$  close to the limit of detection, e.g. at the 3% level there was between 2–4% present). The  $N_2$ -specific surface area was measured using the BET method, with a Micrometrics Gemini V Surface Area Analyser, with samples degassed for a minimum of 19 hours, at *RT*, with nitrogen gas prior to analysis. Electron micrographs were produced using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) using a FEI QUANTA 650 FEG environmental SEM. Samples were mounted on a carbon pad and coated in platinum prior to analysis.

## Results

### *Preliminary investigation of alkaline alteration of kaolinite in NaOH solutions*

There was no evidence of new phases in the XRD patterns (not shown) where kaolinite was aged in 0.05 M and 0.5 M NaOH at room temperature for 35 days. A partial phase transformation to sodalite (data not shown), occurred when kaolinite was aged in 5 M NaOH; however, kaolinite peaks were still dominant at day 35. XRD patterns (data not shown) for the aging of kaolinite in 5 M NaOH, at  $70^\circ\text{C}$  indicated that full transformation to sodalite had occurred after 10 days. Based on these results, 5 M NaOH and elevated temperatures were used in subsequent experiments.

### *Effect of time and temperature on the alkaline alteration of kaolinite in 5 M NaOH*

Kaolinite was aged over 7 days in 5 M NaOH at  $70^\circ\text{C}$ . XRD patterns (Fig. 1a) show that the transformation from kaolinite to sodalite started after one day, evidenced by the sharp decrease in the main kaolinite (k) peak intensities and the formation of peaks from the neo-formed sodalite (s) and minor amount of cancrinite (c). Rietveld analysis of the day 1 and 2 samples indicated the presence of 8 and 15 wt.% of cancrinite (Fig. 2a),

respectively. By day 3, sodalite was the dominant phase, with only minor kaolinite peaks visible. There was no evidence of cancrinite after day 2. Throughout the next four days, the kaolinite peaks further reduced as the sodalite peaks increased, until only minor amounts of kaolinite were visible in the XRD patterns by day 7. Rietveld analysis (Fig. 2a) of day 7 samples quantified 81 wt.% sodalite and 19 wt.% kaolinite. BET (Fig. 4) analysis indicates an initial increase, from 12 to  $16\text{ m}^2/\text{g}$  in the surface area at day 1, followed by a consistent decrease in surface area up to day 6 ( $7\text{--}10\text{ m}^2/\text{g}$ ).

Rietveld analysis of XRD data from 10-day experiments at lower temperatures (Fig. 6c) showed 80 wt.% sodalite and 20 wt.% kaolinite at  $50^\circ\text{C}$ , and 24 wt.% sodalite, 70 wt.% kaolinite and 6 wt.% cancrinite at  $40^\circ\text{C}$ . This indicates that the rate of clay transformation increased with temperature.

### *Effect of time and temperature on the alkaline alteration of kaolinite in 5 M NaOH + 4 M Na<sub>2</sub>SO<sub>4</sub>*

The XRD patterns for kaolinite aged over 7 days, in 5 M NaOH and 4 M  $\text{Na}_2\text{SO}_4$  at  $70^\circ\text{C}$  are shown in Fig. 1b. We note sharp decreases in the kaolinite (k) peak intensities between the starting material and the 1 day aged sample. The decrease in the kaolinite peaks, and the appearance of small peaks at  $13.9^\circ$  and  $24.4^\circ 2\theta$  was consistent with the transformation from kaolinite to sulfatic sodalite/vishnevite. Rietveld analysis (Fig. 2b) of the day 1 samples quantified the neoformed feldspathoids as 2 wt.% vishnevite and 29 wt.% sodalite. After two days aging, the XRD patterns (Fig. 1b) showed further reductions in the kaolinite peak intensities (k) together with increasing sulfatic sodalite peak intensities (s). Rietveld analysis (Fig. 2b) for the day 2 samples showed that sulfatic sodalite had increased to 62 wt.%, vishnevite had increased to 2.5 wt.% and kaolinite had decreased to 35.5 wt.%. By day 3, peaks for vishnevite (v) increased in intensity (Fig. 1b), and only minor kaolinite peaks were visible. Throughout the next four days, the kaolinite peaks further reduced and the sodalite/vishnevite (s/v) peaks became more prominent until only minor amounts of kaolinite were visible in the XRD patterns by day 7. After 7 days, Rietveld analysis (Fig. 2b) showed that sodalite had decreased to 24 wt.%, vishnevite had increased to 53 wt.% and kaolinite had decreased to 23 wt.%. This suggested that the kaolinite transformed to

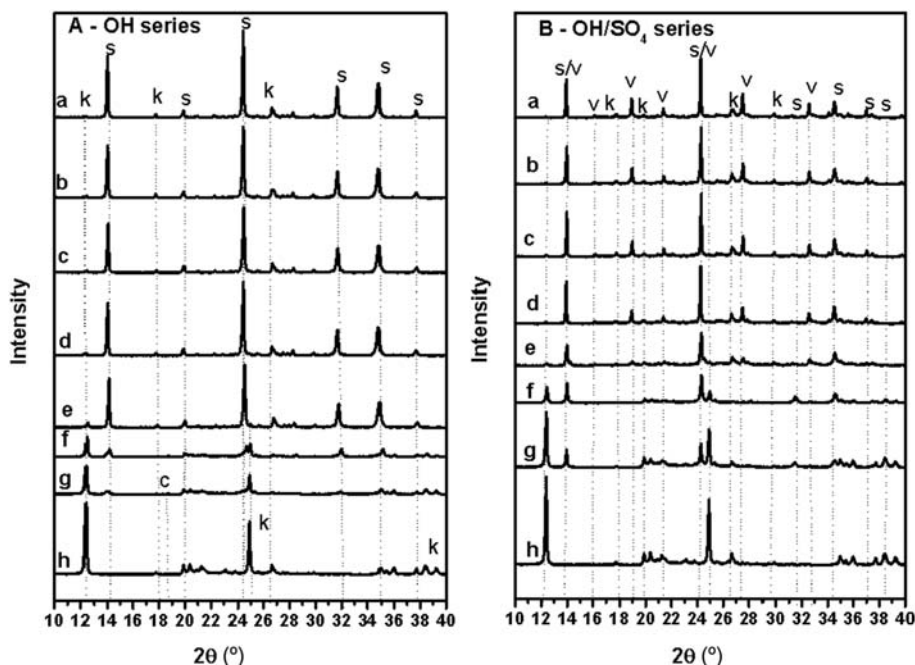


Fig. 1. X-ray diffraction (XRD) patterns of kaolinite aged in 5 M NaOH (A) and 5 M NaOH/SO<sub>4</sub> (B) at 70°C for (a) 7 days, (b) 6 days, (c) 5 days, (d) 4 days, (e) 3 days, (f) 2 days and (g) 1 day. The XRD pattern of the kaolinite starting material is shown in (h). Minerals are annotated as s (sodalite), k (kaolinite), v (vishneville) and c (cancrinite).

vishneville via a sulfatic sodalite intermediate phase. No broad humps were observed in the XRD patterns at any time during the reaction indicating that there were no amorphous phases detected at any time during the transformations.

Scanning electron microscope images (Fig. 3) of the solid phases collected during the transformation show the kaolinite starting material and the sulfatic sodalite/vishneville alteration product at day 2 and 7. The kaolinite starting material (Fig. 3a) comprised multiple layers of stacked hexagonal plates ~20–30 μm in size. The EDS spectra of kaolinite showed the presence of Al, Si and O, with the Al and Si peaks present with equal intensities. After one day of aging, the overall crystal morphology of the kaolinite had evolved (data not shown). An interlocking desert rose morphology, characteristic of cancrinite (Deng *et al.*, 2006c), was observed after two days (Fig. 3b). These crystallites were ~2.5 μm in diameter and contained O, Al, Si, Na, and S by EDS analysis, consistent with formation of sulfatic sodalite or vishneville. By day 7, the sample crystal morphology comprised spheres of interlocking tabular crystals (Fig. 3c) with a diameter of ~3–5 μm. BET (Fig. 4) analysis

indicates similar change to those observed in the pure NaOH system with an initial increase (12 to 15 m<sup>2</sup>/g) in surface area at day 1 followed by a consistent decrease in surface area up to day 6 (4–6 m<sup>2</sup>/g).

The XRD patterns (Fig. 5) in respect of the aging of kaolinite in 5 M NaOH and 4 M Na<sub>2</sub>SO<sub>4</sub> at 70°C for 10 days, showed the presence of sulfatic sodalite and vishneville. Rietveld analysis (Fig. 6b) of a sample aged at 60°C for 10 days quantified the phases to be 34 wt.% sulfatic sodalite, 8 wt.% kaolinite and 58 wt.% vishneville. After 10 days aging at 50°C the reaction products were 69.5 wt.% sulfatic sodalite and 30.5 wt.% kaolinite. At 40°C the reaction products were 36 wt.% sulfatic sodalite and 64 wt.% kaolinite. This suggested that at lower temperatures kaolinite transforms to sulfatic sodalite, and to vishneville at higher temperatures.

#### *Alkaline alteration of kaolinite in 5 M NaOH + 1 M NaCl or 0.5 M NaNO<sub>3</sub>*

The addition of 1 M NaCl to the 5 M NaOH solution led (Fig. 5) to the transformation of

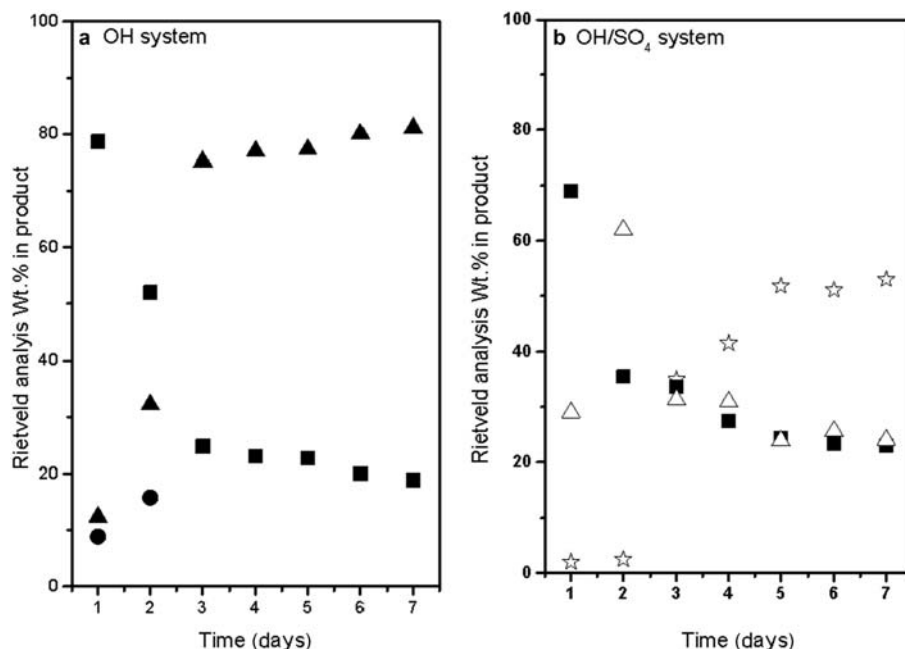


FIG. 2. Rietveld analysis for kaolinite aged in 5 M NaOH (a) and 5 M NaOH/SO<sub>4</sub> (b) at 70°C for 7 days. Mineral wt.% are shown for kaolinite (squares), sodalite (triangles), cancrinite (circles) and vishnevitte (stars). Muscovite impurity in the starting material is not shown.

kaolinite to sodalite after 10 days aging at 70°C. In contrast XRD data show that aging kaolinite in 5 M NaOH + 0.5 M NaNO<sub>3</sub> for 14 days at 60°C (Fig. 5) led to the formation of nitrate cancrinite. Trace amounts of kaolinite (Fig. 5) were still present after 14 days. Rietveld analysis (Fig. 6a) of the 14 day sample quantified the phases to be 98.5 wt.% nitrate cancrinite and 1.5 wt.% kaolinite, which suggested that the kaolinite to nitrate cancrinite

transformation was almost complete after 14 days. Experiments were also carried out at lower temperatures and showed an increase in the amount of kaolinite remaining after 14 days (i.e. 8 wt.% at 50°C and 31 wt.% at 40°C). This indicates that the rate of transformation from kaolinite to nitrate cancrinite increased as temperature increased, and no reaction intermediates were present.

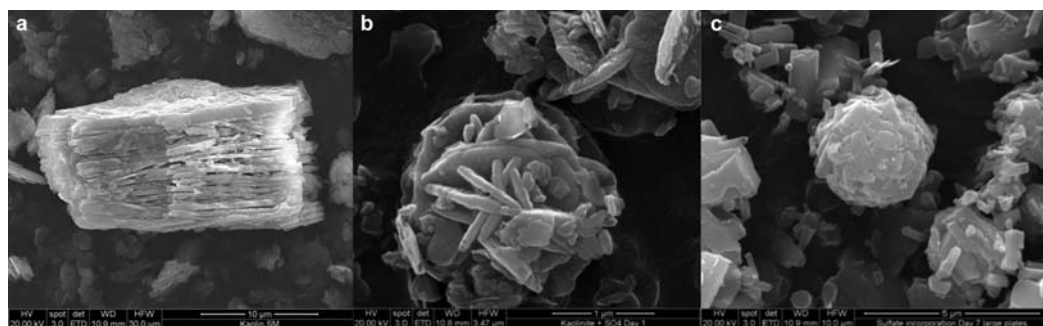


FIG. 3. SEM images for kaolinite (a) and the alkaline alteration product formed during the ageing of kaolinite in 5 M NaOH + SO<sub>4</sub> (4 M) at 70°C for (b) 2 days and (c) 7 days.

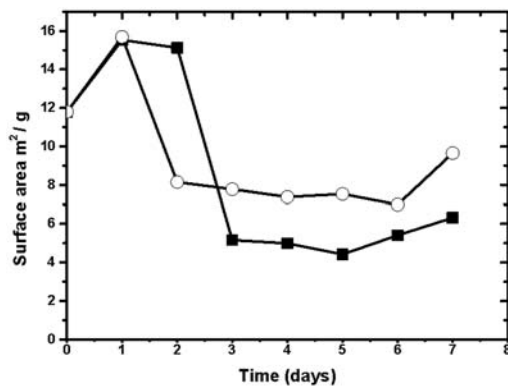


FIG. 4. Changes in mineral surface area during the reaction of kaolinite in 5 M NaOH (circles) and NaOH/SO<sub>4</sub> (squares) at 70°C for 7 days.

#### Pertechnetate incorporation behaviour during phase transformation

The % <sup>99</sup>Tc remaining in solution (Fig. 7) during the aging of kaolinite in either 5 M NaOH, 5 M NaOH + 1 M NaCl, 5 M NaOH + 0.5 M NaNO<sub>3</sub>, or 5 M NaOH + 4 M Na<sub>2</sub>SO<sub>4</sub>, was very high, ~95–97%, in all instances. This suggested that only a small uptake to solids (~3–5% <sup>99</sup>Tc; Fig. 7, inset) occurred during the first nine days of aging. Although these experiments continued for 72 days, no further uptake was observed.

#### Discussion

The end products which form during alkaline alteration of kaolinite vary depending on base concentration, temperature and solution composition. The lack of mineral transformation during the reaction of kaolinite in 0.05 M and 0.5 M NaOH, and partial transformation to sodalite in 5 M NaOH at *RT*, implied that there was a threshold concentration effect between 0.5 M and 5 M NaOH. Full transformation at higher [NaOH] is anticipated as the increased rate of a reaction is related to increases in base concentration. The rate of mineral transformation is also higher at higher temperatures (Mashal and Cetiner, 2010).

Our experiments showed that in 5 M NaOH, kaolinite started to transform to sodalite at 70°C after one day, with only trace kaolinite remaining after 7 days. In previous work on feldspathoid precipitation from both kaolinite (Rios *et al.*, 2009; Zhao *et al.*, 2004) and Si-Al solutions (Deng *et al.*,

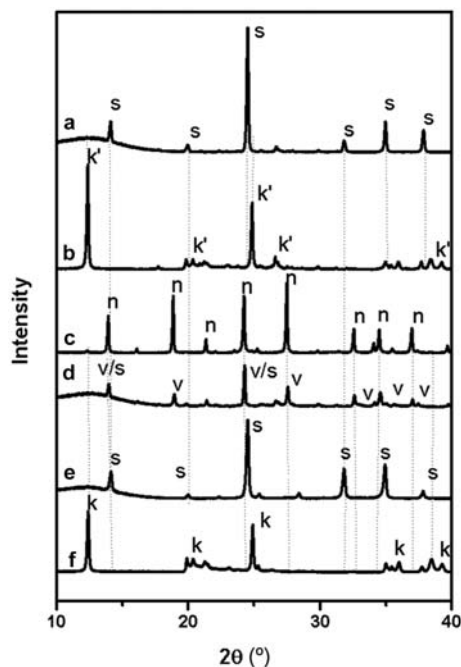


FIG. 5. XRD patterns of (a) sodalite, annotated as s, the alkaline alteration product of (b) kaolinite (Fluka), annotated as k, aged in 5 M NaOH + Cl at 70°C for 10 days; (c) nitrate-cancrinite, annotated as n, the alkaline alteration product of (f) kaolinite (K-Ga 1b), annotated as k reacted in 5 M NaOH + NO<sub>3</sub> (60°C, 14 days); (d) sulfatic sodalite/vishnevite, annotated as s/v, the alkaline alteration product of (f) kaolinite (K-Ga 1b), annotated as k, reacted in 5 M NaOH + SO<sub>4</sub> (70°C, 10 days) and (e) sodalite, annotated as s, the alkaline alteration product of (f) kaolinite (K-Ga 1b), annotated as k, reacted in 5 M NaOH (70°C, 10 days).

2006b), amorphous and zeolitic intermediates were observed before sodalite and cancrinite precipitation. However, we did not observe these intermediate phases in our experiments.

#### Effect of solution composition on alteration product formation

It is thought that guest anions form ion-pairs with Na<sup>+</sup> ions in solution, inducing the nucleation and growth of the neoformed feldspathoid end-products (Zhao *et al.*, 2004). As we have stated, the end products vary depending on which anions are present in solution (Choi *et al.*, 2006), and incorporation of guest ions is likely to be size dependent. The anion-Na<sup>+</sup> ion pairs must be able to

## ALKALINE ALTERATION OF KAOLINITE

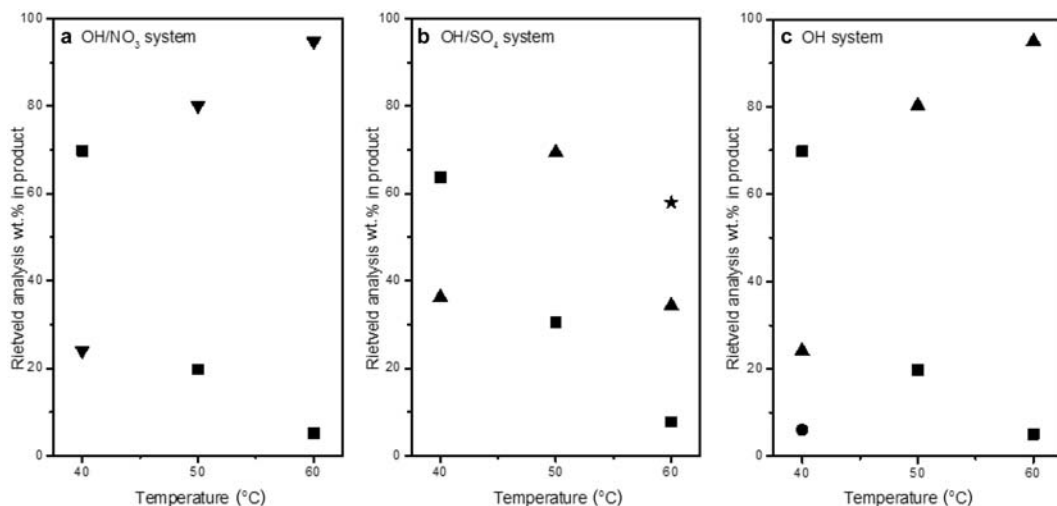


FIG. 6. Rietveld analysis for kaolinite aged in (a) 5 M NaOH + NO<sub>3</sub> for 14 days at 40, 50 and 60°C. Mineral wt.% are shown for kaolinite (squares) and nitrate cancrinite (inverted triangles), in (b) 5 M NaOH + SO<sub>4</sub> for 10 days at 40, 50 and 60°C. Mineral wt.% are shown for kaolinite (squares), sulfatic sodalite (triangles) and vishneville (stars) and in (c) 5 M NaOH for 10 days at 40, 50 and 60°C. Mineral wt.% are shown for kaolinite (squares), sodalite (triangles) and cancrinite (circles).

fit inside the cages and channels of the aluminosilicate minerals which grow around them (Barrer *et al.*, 1968). In this study, the addition of sodium sulfate, sodium nitrate and sodium chloride

produced end products of sulfatic sodalite/vishneville ( $[(\text{Na}, \text{Ca})_{6-x}\text{K}_x(\text{SO}_4)][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$ ), nitrate cancrinite ( $\text{Na}_6[\text{Si}_6\text{Al}_6\text{O}_{24}] \cdot 2\text{NaNO}_3$ ) and sodalite ( $(\text{Na}_8\text{Cl}_2)[\text{Si}_6\text{Al}_6\text{O}_{24}]$ ), respectively. The

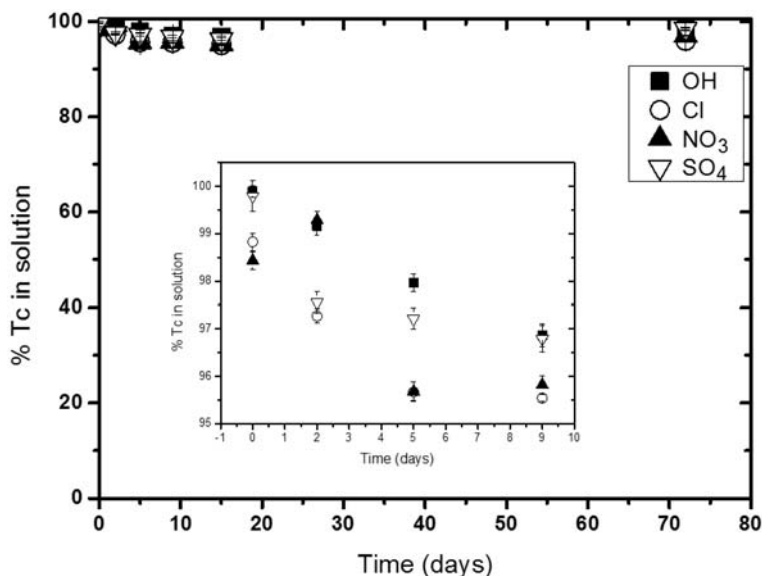


FIG. 7. % <sup>99</sup>Tc (30 Bq/ml) in solution after ageing kaolinite in 5 M NaOH (squares), 5 M NaOH + Cl (circles), 5 M NaOH + NO<sub>3</sub> (triangles) and 5 M NaOH + SO<sub>4</sub> (inverted triangles) at 70°C for 72 days.

formation of nitrate cancrinite and vishneville resulted in guest anion substitution of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  into the ideal cancrinite structure. The sodalite structure does not have the wide channels found in cancrinite, only cages. These cages contain a central anion, tetrahedrally bound to four cations. As the ideal sodalite structure has a central  $\text{Cl}^-$  anion, the formation of sodalite in the presence of sodium chloride is as anticipated (Barrer *et al.*, 1974; Zhao *et al.*, 2004).

In the  $\text{NaOH}/\text{NO}_3^-$  system no reaction intermediates were observed for the transformation of kaolinite to nitrate cancrinite (Fig. 5). The formation of nitrate cancrinite in high- $\text{NO}_3^-$  experiments has been previously reported (Buhl *et al.*, 2000; Zhao *et al.*, 2004). In our experiments, the degree of reaction for the  $\text{NaOH}/\text{NO}_3^-$  system was more than any of the other systems tested, with 69, 92 and 98 wt.% transformation from kaolinite to nitrate cancrinite at temperatures of 40, 50 and 60°C after 14 days.

#### Reaction pathway for the $\text{NaOH}/\text{SO}_4^{2-}$ system

The transformation of kaolinite aged in  $\text{NaOH}/\text{SO}_4^{2-}$  has not been reported previously; therefore, this reaction pathway was studied in more detail. The XRD patterns (Fig. 1*b*) observed for the alteration products are similar to those for sulfate-cancrinite which was synthesized from aluminosilicate solutions (Deng *et al.*, 2006*b*). The morphological changes, observed via SEM (Fig. 3), show blade-like spheres at day 2 which are similar to those which have been reported in the literature for cancrinite (Choi *et al.*, 2005), however that reaction was performed at a lower base concentration, (0.01 M NaOH instead of 5 M) and for a longer time period (190 days compared to 7 days). The appearance of peaks for Na and S in SEM-EDS analysis, which were not present in the starting material, support the formation of sulfatic sodalite/vishneville. In summary, XRD, SEM, EDS and surface area evidence all suggest that the partial alkaline alteration of kaolinite started after 1 day of reaction.

Vishneville (sulfatic cancrinite) formation was observed after three days of reaction. Rietveld analysis (Fig. 6*b*) shows a gradual increase in the % vishneville over days 4 to 7, to 53%, with the amount of sulfatic sodalite decreasing to 24% over the same period. This is consistent with the dissolution of sulfatic sodalite and the crystallization of vishneville. SEM images of the reaction products at day 7 (Fig. 3*c*) showed minor changes in

morphology, in that the spheres were smaller and more tabulated, which is similar to other SEM images reported for cancrinite (Deng *et al.*, 2006*c*). The smaller size of the day 7 spheres was reflected by a slight increase in the surface area, indicating some dissolution of sodalite and recrystallization to vishneville. After seven days 78% of the original kaolinite had reacted, producing vishneville at 70°C (via a sulfatic sodalite intermediate). The sodalite intermediate is more stable at lower temperatures evidenced by the lack of vishneville at 40 and 50°C.

#### Proposed incorporation of $^{99}\text{Tc}$ into alkaline altered clays

The potential incorporation of the technetium anion, pertechnetate ( $\text{TcO}_4^-$ ), into cancrinite or sodalite has received some support from other authors (Mattigod *et al.*, 2006; Dickson *et al.*, 2014); however, the successful incorporation of technetium into feldspaths has not yet been achieved. The results (Fig. 7) of the low-concentration pertechnetate experiments showed only a very small  $^{99}\text{Tc}$  uptake under any of the reaction conditions studied. Up to 5% sorption of  $^{99}\text{Tc}$  to alkaline alteration products was observed in all instances. Using sulfate to drive the reaction toward sulfate cancrinite did not produce any increased uptake over other anions such as chloride or nitrate (despite the analogous tetrahedral coordination of  $\text{SO}_4^{2-}$  and  $\text{TcO}_4^-$ ).  $\text{TcO}_4^-$  is a relatively large anion ( $\sim 2.5$  Å), and in cancrinite  $^{99}\text{Tc}$  is likely to have been incorporated into a channel rather than a cage due to size constraints. Sodalite does not have channels, so the incorporation of  $^{99}\text{Tc}$  would have been into the cages. The low  $^{99}\text{Tc}$  uptake could suggest that the large pertechnetate anion is unable to compete favourably for the internal sites with the smaller, and therefore more size appropriate,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , or  $\text{SO}_4^{2-}$  anions ( $\sim 1.4$ ,  $\sim 1.7$ ,  $\sim 2.0$  and  $\sim 2.3$  Å respectively), at these low concentrations. The successful incorporation of  $^{99}\text{Tc}$  into alkaline alteration end products such as cancrinite and sodalite could provide a substantial research contribution. However, very high concentrations of pertechnetate (and conversely low concentrations of other anions) are likely to be required to produce significant uptake of  $^{99}\text{Tc}$  into alkaline alteration end products.

#### Conclusions

Kaolinite undergoes alkaline alteration in the presence of 5 M NaOH (both with and without



Cl<sup>-</sup>) at 70°C to sodalite, to vishnevitte if sulfate is present (via sulfatic sodalite at lower temperatures), and to nitrate cancrinite in the presence of nitrate. The rate of reaction was faster for the OH and OH/NO<sub>3</sub><sup>-</sup> systems relative to the OH/SO<sub>4</sub><sup>2-</sup> system. Up to 5% <sup>99</sup>Tc tracer could be incorporated into these alkaline altered feldspathoids which is insufficient to consider alkaline alteration of clay minerals to be a remediation strategy for <sup>99</sup>Tc.

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