

## SYNTHESIS OF KENYAITE AND MAGADIITE IN THE PRESENCE OF VARIOUS ANIONS

**Key Words**—Anions, Kenyaite, Magadiite, Quartz, Silicate, Synthesis.

### INTRODUCTION

Eugster (1967, 1969) reported kenyaite and magadiite interlayered with extensive formations of chert in the Magadi basin, Kenya. Other occurrences of these minerals have been reported in Trinity County, California (McAtee *et al.*, 1968), at Alkali Lake, Oregon (Rooney *et al.*, 1969), at Kanem near Lake Chad (Maggiore, 1970), in alkali lakes of central Wyoming (Surdam *et al.*, 1972), in the Nigerian Manga (Icole *et al.*, 1981), and in the McBean Formation, South Carolina (Houser, 1982). In most of these deposits the minerals were formed from sodium carbonate-rich alkaline lake waters.

The minerals have the approximate chemical composition:  $\text{Na}_2\text{Si}_4\text{O}_{29} \cdot 9\text{H}_2\text{O}$  (magadiite) and  $\text{Na}_2\text{Si}_{22}\text{O}_{45} \cdot 10\text{H}_2\text{O}$  (kenyaite) and can be readily synthesized from aqueous sodium silicate solutions. Lagaly *et al.* (1973) discussed the preparation of magadiite in a hydrothermal system at 100°C and the subsequent preparation of intercalated organic derivatives. More recently, Beneke and Lagaly (1983) described the synthesis of kenyaite temperatures of 100°–150°C. A “speculative field boundary” for kenyaite and magadiite formation was proposed. Solutions having  $\text{SiO}_2\text{:NaOH}$  ratios of <150:12 yielded magadiite which then transformed to kenyaite; at higher ratios, kenyaite formed directly.

Kenyaite and magadiite have also been produced as by-products in the synthesis of high-silica zeolites (Araya and Lowe, 1985; Van der Gaag *et al.*, 1985). In some preparations magadiite was synthesized from systems having  $\text{SiO}_2\text{:NaOH}$  ratios >150:12. The reason for the formation of magadiite at these high ratios could have been the presence of  $\text{Cl}^-$ ; however, few data are available on the effects of high levels of anions other than  $\text{OH}^-$  on the synthesis of silicates. In recent years industrial interest in the synthesis of new silicate systems has increased markedly, particularly with respect to catalyst production for use in industrial processes and to modifications to improve the yield of existing silicate synthesis mechanisms. We report here results of a preliminary investigation into the effects of anions on the formation of two potentially useful silicates, kenyaite and magadiite.

### MATERIALS AND METHODS

Materials used were Aerosil 200, a fumed silica having a surface area of 200 m<sup>2</sup>/g (Degussa), and analytical reagent grades of NaOH and sodium salts of a variety of anions. Preliminary experiments were carried out in sealed stainless steel reaction vessels at 150°C under autogenous pressure, and using molar ratios of  $\text{SiO}_2\text{:NaOH} = 1$  and  $\text{H}_2\text{O:NaOH} = 15$ . Crystalline material suitable for X-ray powder diffraction analysis was obtained after 3 days. The effect of various anions was studied by replacing two-thirds of the sodium hydroxide by an equimolar amount of the sodium salt of the selected anion.

Reaction products were air dried at room temperature and identified by X-ray powder diffraction (XRD) (CoK $\alpha$  radiation, using a scanning rate of 1°2 $\theta$ /min and the following peaks (after Eugster, 1967):

Magadiite: 15.41, 3.435, 3.146 Å;  
Kenyaite: 19.68, 9.925, 4.965 Å.

The approximate ratios of kenyaite to magadiite were estimated by the sum of the peak areas of these major XRD peaks for each mineral.

### RESULTS AND DISCUSSION

The behavior of silicate species in the presence of different anions is not well understood. Iler (1979, p. 230) reported that NaCl causes the precipitation of products having Si:Na ratios greater than those present in solution. Thus, kenyaite, with its relatively high Si:Na ratio, might be preferred to magadiite in the presence of  $\text{Cl}^-$ , as was found (Table 1). The kenyaite-magadiite ratio also decreased with an increase in the atomic number of the halide used. The addition of  $\text{F}^-$  resulted in the formation of kenyaite within a few hours. Either magadiite was not produced or the transformation reaction proceeded so quickly that the amount of magadiite remaining was below the detection limit of the XRD technique (~10%). The addition of  $\text{I}^-$  slowed the reaction, and even after 7 days at 150°C no evidence was found for kenyaite formation. The conversion of kenyaite to  $\alpha$ -quartz also proceeded much more rapidly in the presence of  $\text{F}^-$  than in the presence of  $\text{Cl}^-$ .

Table 1. Products from anion replacement.

Anionic species	Product <sup>1</sup>
Fluoride	Abundant kenyaite; no evidence of magadiite
Chloride	Abundant kenyaite; 10% magadiite
Bromide	Abundant magadiite; 10% kenyaite
Iodide	Abundant magadiite; no evidence of kenyaite
Sulfate	Abundant magadiite; no evidence of kenyaite
Carbonate	Abundant kenyaite; 15% quartz
Phosphate	Abundant crystalline kenyaite
Cyanide	Magadiite: kenyaite, ~3:1
Thiocyanate	Poorly crystalline magadiite and kenyaite
Acetate	Abundant kenyaite; 10% magadiite
Borate	No crystalline product

All syntheses carried out with same  $\text{SiO}_2:\text{Na}$  ratio but two thirds of the NaOH was replaced by the appropriate sodium salt.

<sup>1</sup> Identifications by X-ray powder diffraction (see text).

Table 1 also shows that the presence of  $\text{PO}_4^{3-}$  or  $\text{CH}_3\text{COO}^-$  resulted in the production of kenyaite, whereas  $\text{SO}_4^{2-}$  and  $\text{CN}^-$  tended to produce magadiite. The presence of the  $\text{B}_4\text{O}_7^{2-}$  resulted in the formation of a noncrystalline gel only. Even after 10 days, when all other syntheses (with the exception of the  $\text{I}^-$ -containing synthesis) had proceeded to  $\alpha$ -quartz, no evidence of any reaction was found in the  $\text{B}_4\text{O}_7^{2-}$ -containing system. This lack of silicate precipitation was presumably due to a condensation reaction between  $\text{B}_4\text{O}_7^{2-}$  and the various silicate anions to form a relatively stable gel structure (Iler, 1979, p. 190).

It is somewhat surprising that in view of the widespread occurrence and presumed stability of magadiite produced from  $\text{CO}_3^{2-}$ - (or  $\text{HCO}_3^-$ ) rich solutions and its coexistence with trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), kenyaite was produced here so readily in the presence of  $\text{CO}_3^{2-}$ . The present laboratory studies, however, were not intended to reproduce the situation in nature, and reaction temperatures and reactant composition can significantly affect the final products.

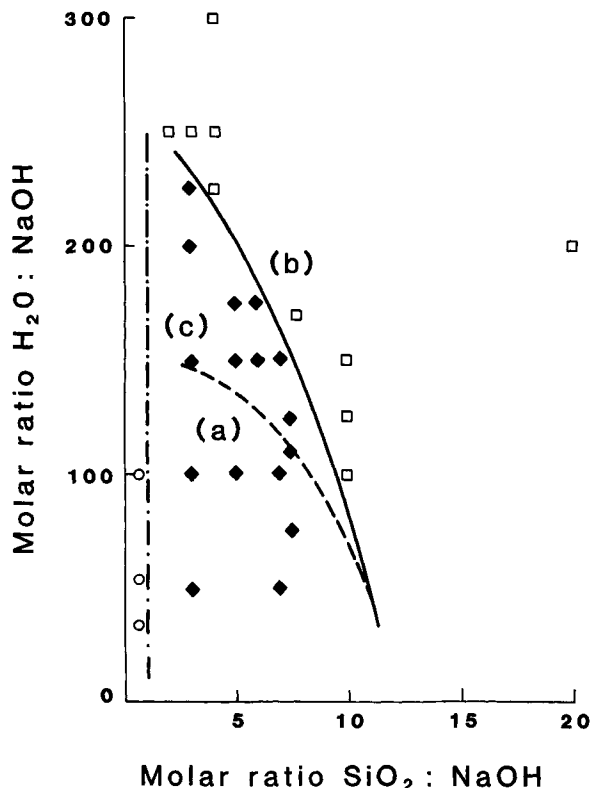


Figure 1. Synthesis of kenyaite and magadiite as a function of  $\text{H}_2\text{O}:\text{NaOH}$  vs.  $\text{SiO}_2:\text{NaOH}$  at  $150^\circ\text{C}$ .  $\blacklozenge$  = magadiite;  $\square$  = kenyaite;  $\circ$  = solution. Dotted line (a) is the "speculative stability field boundary" of Beneke and Lagaly (1983); solid line (b) shows the boundary determined in the present study. Total solubility field is left of (c), parallel to the  $\text{H}_2\text{O}:\text{NaOH}$  axis.

The crystallinity of the products was also affected by the nature of the anion present. The presence of  $\text{CN}^-$  and  $\text{SCN}^-$  resulted in low yields of poorly crystalline kenyaite and magadiite. Extending the reaction times

Table 2. Comparison of products from hydroxide and carbonate syntheses.<sup>1</sup>

$\text{H}_2\text{O}:\text{Na}$	$\text{SiO}_2:\text{Na}$	Time (hr)	Hydroxide-only system	Carbonate system <sup>2</sup>
50	3	40	Magadiite only	Magadiite only
		96	Magadiite = kenyaite	Magadiite = kenyaite
100	3	40	Magadiite only	Kenyaite, poorly crystalline; 10% magadiite
		96	Magadiite; 10% kenyaite <sup>3</sup>	Very abundant kenyaite
100	5	96	Magadiite; 10% kenyaite	Abundant kenyaite only
100	10	96	Abundant kenyaite only	Abundant kenyaite; 10% magadiite
150	3	40	Kenyaite; 10% magadiite	10% kenyaite only
		96	Magadiite = kenyaite	Highly crystalline kenyaite
200	3	40	Highly crystalline magadiite	No crystalline product
		96	Abundant kenyaite; 10% magadiite	Highly crystalline kenyaite
200	20	96	Poorly crystalline kenyaite	Highly crystalline kenyaite

<sup>1</sup> Identifications by X-ray powder diffraction (see text).

<sup>2</sup> Same  $\text{SiO}_2:\text{Na}$  ratio, but with two thirds of the sodium hydroxide replaced with sodium carbonate.

<sup>3</sup> 10% represents the minimum detectable limit of the mineral by the analytical method employed.

beyond 5 days under the conditions used here increased the amounts of  $\alpha$ -quartz in the product but did not increase the amounts of kenyaite and magadiite.

Table 2 shows the results of the synthesis carried out to confirm the position of the proposed "speculative stability field boundary" (Beneke and Lagaly, 1983) (Figure 1) and to determine the effect of  $\text{CO}_3^{2-}$  addition. The position of this proposed boundary suggests that kenyaite should form directly at  $\text{SiO}_2$ :NaOH ratios of 3 and  $\text{H}_2\text{O}$ :NaOH ratios  $>140$ . Magadiite formed, however, as an intermediate product at a  $\text{H}_2\text{O}$ :NaOH ratio of  $<200$  (Figure 1). For a  $\text{SiO}_2$ :NaOH ratio  $>8$ , the proposed boundary appears to be substantially correct, although the position of the boundary at  $\text{SiO}_2$ :NaOH ratios  $>10$  could not be established because the reactant mixtures were too viscous to yield adequately mixed reactants. At  $\text{SiO}_2$ :NaOH ratios  $<2$  no solid products were formed under the experimental conditions used, as is indicated by the second line in Figure 1, which intersects the  $\text{SiO}_2$ :NaOH axis at about 2 and which is almost parallel to the  $\text{H}_2\text{O}$ :NaOH axis.

The replacement of two-thirds of the NaOH by equimolar amounts of  $\text{Na}_2\text{CO}_3$  yielded products similar to those reported by Beneke and Lagaly (1983). In the presence of  $\text{CO}_3^{2-}$  at  $\text{H}_2\text{O}$ :NaOH ratios  $>150$ , kenyaite formed directly (see Table 2), whereas magadiite formed at  $\text{H}_2\text{O}$ :NaOH ratios  $<100$ . The conversion of magadiite to kenyaite also appeared to proceed more rapidly in the presence of  $\text{CO}_3^{2-}$  and the products were more crystalline. Table 2 also shows the effect of  $\text{CO}_3^{2-}$  at different  $\text{SiO}_2$ :NaOH ratios and confirms that kenyaite formed preferentially.

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