

## EXPERIMENTAL STUDY ON THE FORMATION OF ZEOLITES FROM OBSIDIAN BY INTERACTION WITH NaOH AND KOH SOLUTIONS AT 150 AND 200 °C

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**Abstract**—Experimental alteration of obsidian was performed in 0.001 to 0.5 N NaOH and KOH solutions at 150 and 200 °C for 1 to 30 d. The products were examined by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). Changes in chemical composition and pH value of solutions during the reactions were also measured. As the pH of reacting solutions was increased, smectite, phillipsite and rhodesite crystallized progressively in NaOH solutions, while smectite, merlinoite and sanidine grew successively in KOH solutions. In addition, a small amount of less-soluble, poorly ordered boehmite was present as products of all the experiments. Smectite mainly appeared at slightly high pH, Si/Al and Na/K conditions, whereas rhodesite should be produced in extremely high pH, Na/K and Si/Al conditions. Sanidine was also formed in conditions of very high pH and Si/Al and very low Na/K. In intermediate conditions of pH and Si/Al, crystallization of phillipsite was stimulated in solutions of Na/K > 10, while formation of merlinoite was favored in conditions of Na/K < 1.

**Key Words**—KOH solution, Merlinoite, NaOH Solution, Obsidian, Phillipsite, Rhodesite, Sanidine, Smectite.

### INTRODUCTION

Zeolites are abundant and widespread authigenic minerals formed from volcanic glass and various rock-forming minerals by interaction with aqueous solution or fluid in a wide variety of geochemical environments (Mumpton 1977; Hay 1986; Boles 1988). Natural zeolites have chemical and structural variations that must be related to the different geochemical environments in which they form. To clarify formation conditions of the variations of zeolites, numerous experimental studies on formation of zeolites have been conducted using starting materials such as natural and synthetic glasses, aluminosilicate gels, solution mixture and clay- and rock-forming minerals under a wide range of chemical and temperature conditions (Barrer 1982; Gottardi and Galli 1985). Zeolites are important materials for industrial utilization because of their molecular sieve, adsorption, ion exchange and catalytic properties. Thus, it is essential to develop a new efficient synthesis method of zeolites exhibiting higher functional properties in commercial applications (Sand 1980; Jansen 1991). However, conclusions of the experimental investigations were somewhat confusing because the kind of synthetic products varied sensitively with reaction conditions such as starting material and solid/liquid ratio as well as solution composition and reaction temperature. According to the earlier experimental investigations using rhyolitic glass as a starting material, it was found that phillipsite, analcime and nepheline were progressively formed at 200 °C reactions

with increasing NaOH concentration, but alkali feldspar appeared first and then merlinoite was subsequently produced as KOH concentration increased (Barth-Wirsching and Höller 1989). Alternatively, phillipsite, clinoptilolite and mordenite were obtained from solution containing both Na and K carbonates at 130 to 150 °C (Hawkins 1981). Therefore, it is important to carry out such experimental investigations under as many varied reaction conditions as possible to enable systematic consideration concerning zeolite formation. In this paper, we report the results of an experimental study on the formation of zeolites from obsidian in various concentrations of NaOH and KOH solutions, and discuss formation conditions of the zeolites and geological application to natural environments.

### EXPERIMENTAL

#### Starting Material

The starting material used in the experiments was obsidian from Mifune, Kagoshima Prefecture, Japan, and its chemical composition obtained by electron probe microanalyzer is: 80.04% SiO<sub>2</sub>, 12.27% Al<sub>2</sub>O<sub>3</sub>, 0.16% TiO<sub>2</sub>, 0.84% FeO, 0.18% MgO, 1.10% CaO, 3.14% Na<sub>2</sub>O and 3.04% K<sub>2</sub>O. The structural formula on the basis of 48 oxygens is: (Si<sub>20.31</sub>Al<sub>3.67</sub>Ti<sub>0.03</sub>Fe<sub>0.18</sub>Mg<sub>0.07</sub>Ca<sub>0.30</sub>Na<sub>1.54</sub>K<sub>0.98</sub>)O<sub>48</sub>. The obsidian was crushed in an agate mortar, and the 50 to 100 mesh-size grains were separated by dry sieving. The selected grains were cleaned ultrasonically in acetone to re-

Table 1. Experimental conditions and reaction products from obsidian in NaOH solutions.

Temp. (°C)	Obsidian (g)	NaOH (N)	Time (d)	pH	Reaction product
200	4.0	0.001	1	10.07	Boehmite
200	4.0	0.001	3	10.05	Boehmite
200	4.0	0.001	5	10.02	Smectite, Boehmite
200	4.0	0.001	10	9.95	†Smectite, Phillipsite, Boehmite
200	4.0	0.001	30	9.94	Smectite, Phillipsite, Boehmite
200	4.0	0.01	1	11.60	Boehmite
200	4.0	0.01	3	11.60	Phillipsite, Boehmite
200	4.0	0.01	5	11.60	Phillipsite, Boehmite
200	4.0	0.01	10	11.60	Phillipsite, Boehmite
200	4.0	0.01	30	11.60	Phillipsite, Smectite, Boehmite
200	4.0	0.1	1	12.75	Phillipsite, Smectite, Boehmite
200	4.0	0.1	3	12.71	Phillipsite, Smectite, Boehmite
200	4.0	0.1	5	12.69	Phillipsite, Smectite, Boehmite
200	4.0	0.1	10	12.65	Phillipsite, Smectite, Boehmite
200	4.0	0.1	30	12.62	Phillipsite, Smectite, Boehmite
200	4.0	0.5	1	13.42	Rhodesite, Boehmite
200	4.0	0.5	3	13.41	Rhodesite, Boehmite
200	4.0	0.5	5	13.41	Rhodesite, Boehmite
200	4.0	0.5	10	13.41	Rhodesite, Boehmite
200	4.0	0.5	30	13.41	Rhodesite, Boehmite
150	4.0	0.001	1	10.26	Boehmite
150	4.0	0.001	3	10.21	Boehmite
150	4.0	0.001	5	10.22	Boehmite
150	4.0	0.001	10	10.17	Boehmite, Smectite
150	4.0	0.001	30	10.15	Boehmite, Smectite
150	4.0	0.01	1	11.70	Boehmite
150	4.0	0.01	3	11.60	Boehmite
150	4.0	0.01	5	11.60	Boehmite
150	4.0	0.01	10	11.60	Boehmite
150	4.0	0.01	30	11.60	Phillipsite, Boehmite
150	4.0	0.1	1	12.95	Boehmite
150	4.0	0.1	3	12.95	Boehmite
150	4.0	0.1	5	12.91	Phillipsite, Boehmite
150	4.0	0.1	10	12.55	Phillipsite, Boehmite
150	4.0	0.1	30	12.12	Phillipsite, Boehmite
150	4.0	0.5	1	13.59	Phillipsite, Boehmite
150	4.0	0.5	3	13.48	Phillipsite, Boehmite
150	4.0	0.5	5	13.46	Phillipsite, Boehmite
150	4.0	0.5	10	13.45	Phillipsite, Boehmite
150	4.0	0.5	30	13.44	Phillipsite, Boehmite

† Bold letters represent major products identified by XRD.

move adhering ultrafine particles and were used for the experiments after drying in air.

#### Experimental Conditions

All experiments were conducted in a sealed Teflon bottle containing 4.0 g of starting material and 100 mL of 0.001, 0.01, 0.1 and 0.5 N NaOH or KOH solutions. Each bottle was placed in a pressure vessel and was maintained at 150 and 200 °C for 1, 3, 5, 10 and 30 d. After the hydrothermal treatment, the pressure vessel was quenched to room temperature, and then the reactant solid and solution were separated by centrifugation. Reaction products in the reactant solid were collected by ultrasonic cleaning and centrifugation, and were identified by XRD, SEM, TEM and EDX. The XRD patterns of the products were obtained from samples deposited on glass slides with a RIGAKU RU-200 diffractometer (CuK $\alpha$  radiation, 30 kV, 100

mA) equipped with a graphite monochromator. A JEOL JSM-25SII scanning electron microscope operated at an accelerating voltage of 25 kV was used for SEM; for TEM, a HITACHI H-700H transmission electron microscope was operated at an accelerating voltage of 200 kV using samples deposited on a Cu grid covered with a collodion film. For EDX, a JEOL JSM-840 scanning electron microscope equipped with EDX facilities used samples mounted on carbon folders and coated with carbon. Chemical compositions of solutions were measured by atomic absorption spectroscopy (AAS) for Al, Na, K, Mg and Ca, and by colorimetry for Si. The pH values of solutions were obtained with a TOA HM-20S digital pH meter using a glass electrode.

#### RESULTS

The experimental conditions and reaction products formed in the course of interactions between obsidian

Table 2. Experimental conditions and reaction products from obsidian in KOH solutions.

Temp. (°C)	Obsidian (g)	KOH (N)	Time (d)	pH	Reaction product
200	4.0	0.001	1	10.25	Boehmite, Kaolinite
200	4.0	0.001	3	9.96	Boehmite, Kaolinite
200	4.0	0.001	5	9.95	Boehmite, Kaolinite
200	4.0	0.001	10	9.95	† <b>Smectite</b> , Boehmite, Kaolinite
200	4.0	0.001	30	9.95	<b>Smectite</b> , Boehmite, Kaolinite
200	4.0	0.01	1	11.25	Boehmite, Kaolinite
200	4.0	0.01	3	11.72	Boehmite, Kaolinite
200	4.0	0.01	5	11.73	Boehmite, Kaolinite
200	4.0	0.01	10	11.72	<b>Merlinoite</b> , Boehmite, Kaolinite
200	4.0	0.01	30	11.72	<b>Merlinoite</b> , Boehmite, Kaolinite
200	4.0	0.1	1	12.98	Boehmite
200	4.0	0.1	3	12.77	Boehmite
200	4.0	0.1	5	12.72	<b>Merlinoite</b> , Sanidine, Boehmite
200	4.0	0.1	10	12.65	<b>Merlinoite</b> , Sanidine, Boehmite
200	4.0	0.1	30	12.54	<b>Merlinoite</b> , <b>Sanidine</b> , Boehmite
200	4.0	0.5	1	13.69	Merlinoite, Sanidine, Boehmite
200	4.0	0.5	3	13.60	Merlinoite, Sanidine, Boehmite
200	4.0	0.5	5	13.58	<b>Sanidine</b> , Merlinoite, Boehmite
200	4.0	0.5	10	13.57	<b>Sanidine</b> , Merlinoite, Boehmite
200	4.0	0.5	30	13.52	<b>Sanidine</b> , Merlinoite, Boehmite
150	4.0	0.001	1	10.38	Boehmite, Halloysite
150	4.0	0.001	3	10.19	Boehmite, Halloysite
150	4.0	0.001	5	10.16	Boehmite, Halloysite
150	4.0	0.001	10	10.15	Boehmite, Halloysite
150	4.0	0.001	30	10.15	Boehmite, Smectite, Halloysite
150	4.0	0.01	1	11.89	Boehmite, Halloysite
150	4.0	0.01	3	11.89	Boehmite, Halloysite
150	4.0	0.01	5	11.89	Boehmite, Halloysite
150	4.0	0.01	10	11.89	Boehmite, Halloysite
150	4.0	0.01	30	11.89	Boehmite, Halloysite
150	4.0	0.1	1	13.02	Boehmite
150	4.0	0.1	3	13.01	Boehmite
150	4.0	0.1	5	13.01	Boehmite
150	4.0	0.1	10	12.91	Boehmite
150	4.0	0.1	30	12.83	Boehmite
150	4.0	0.5	1	13.78	Boehmite
150	4.0	0.5	3	13.76	Merlinoite, Boehmite
150	4.0	0.5	5	13.75	Merlinoite, Boehmite
150	4.0	0.5	10	13.74	<b>Merlinoite</b> , Boehmite
150	4.0	0.5	30	13.72	<b>Merlinoite</b> , Boehmite

† Bold letters represent major products identified by XRD.

and NaOH solutions at 200 and 150 °C are listed in Table 1. Boehmite, smectite, phillipsite and rhodesite could be identified as reaction products in NaOH solutions by XRD and electron microscopy. Alternatively, smectite, merlinoite, sanidine and small amounts of boehmite, kaolinite and halloysite were produced in KOH solutions (Table 2). Figures 1a and 1b show XRD patterns of the products formed by 30-d reaction in both NaOH and KOH solutions.

#### Reaction Products in NaOH Solutions at 200 °C

Boehmite appeared in all of the experiments as an undetectable trace product by XRD; however, some aggregates of thin fibrous boehmite were clearly visible by TEM, as shown in Figure 2. These boehmite fibers gave an electron-diffraction exhibiting diffuse halo indicating a highly disordered structure. As indicated by EDX, the boehmite consisted mainly of Al

and very small amounts of Si. Such fibrous boehmite is well known as "pseudoboehmite", whose disordered structure is caused by random intercalation of water molecules into the octahedral layers (Tettenhorst and Hofmann 1980). Similar material can be easily produced by aging of amorphous Al-hydroxide prepared by neutralization of acidic solution containing Al ions (Souza-Santos et al. 1953; Violante and Huang 1985; Violante et al. 1993).

Smectite was primarily formed as a major reaction product using 0.001 N NaOH solution, and as a minor reaction product using 0.01 and 0.1 N NaOH solutions with accompanying phillipsite and less boehmite (Figure 1a). The TEM showed that the smectite occurred as aggregates of thin fibers curled inward or waved irregularly and was less than 1.0 µm in length (Figure 3a). As indicated by EDX, the fibers consisted mainly of Si and Al, and small amounts of Na, Mg and Ca

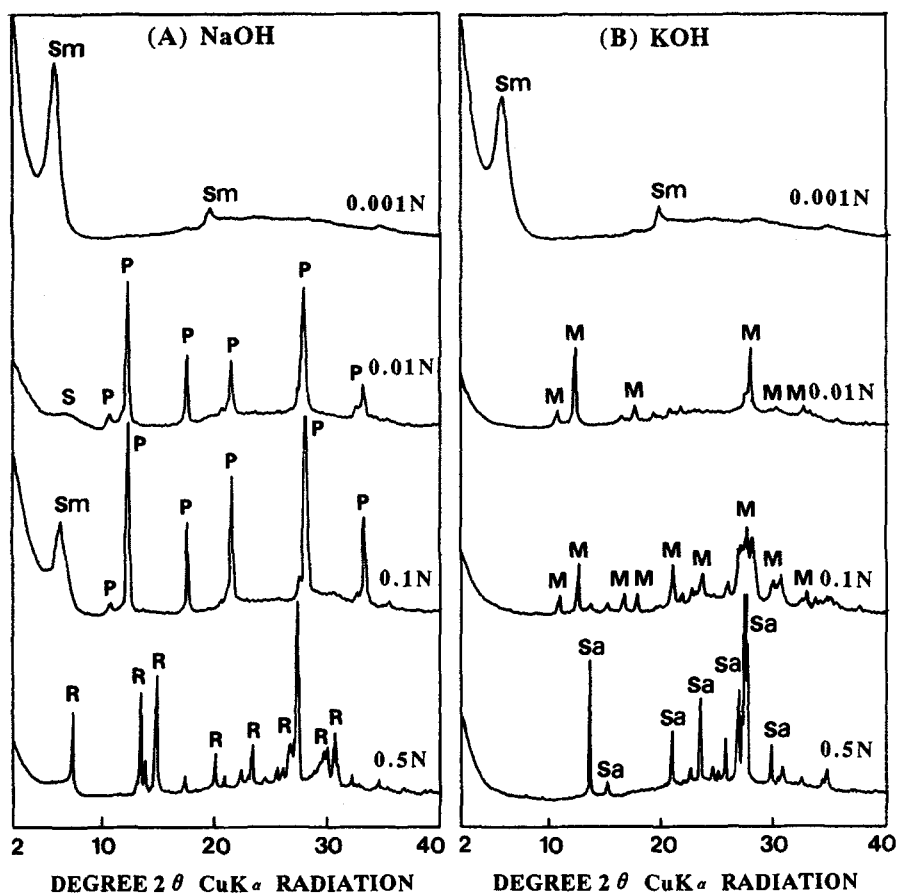


Figure 1. XRD patterns of reaction products formed by reactions at 200 °C for 30 d in 0.001 to 0.5 N A) NaOH and B) KOH solutions. Key: Sm = smectite; P = phillipsite; R = rhodesite; M = merlinoite; and Sa = sanidine.

(Figure 3b), which is very close to the composition of beidellite. Similar materials exhibiting circular fibrous habits have been synthesized from volcanic glass and obsidian by interactions with deionized water at 200 °C (Kawano and Tomita 1992; Kawano et al. 1993).

Phillipsite was the most abundant reaction product using 0.01 and 0.1 N NaOH solutions. A small amount of phillipsite was also produced in 0.001 N NaOH solution, whereas rhodesite appeared in 0.5 N NaOH solution instead of phillipsite. Figure 4a illustrates an SEM photograph of phillipsite crystals formed in 0.1 N NaOH solutions. The phillipsite formed in 0.01 N NaOH solution occurred as radial aggregates of thin fibers or needles less than 5.0  $\mu\text{m}$  in length. However, the morphology of phillipsite formed in 0.1 N NaOH solution is characterized by prismatic crystals or stubby laths 5–20  $\mu\text{m}$  in length and 1–5  $\mu\text{m}$  thick. As indicated by EDX, the phillipsite prisms consisted mainly of Si and Al and small amounts of Na, K, Ca and Fe (Figure 4b). The theoretical formula of phillipsite is:  $\text{K}_2(\text{Ca}_{0.5}\text{Na})_4\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$  (Gottardi and Galli 1985). For the present material, the structural formula calculated from the EDX analysis data is:

$\text{K}_{1.05}\text{Ca}_{0.46}\text{Na}_{1.35}\text{Fe}_{0.35}^{\text{II}}\text{Al}_{2.84}\text{Si}_{12.87}\text{O}_{32}$ , which is apparently richer in Si and poorer in Al compared with the chemical compositions of natural phillipsites (Gottardi and Galli 1985).

Rhodesite was formed only in 0.5 N NaOH solution, which exhibited similar prismatic morphology to that of phillipsite appearing in 0.1 N NaOH solution. Most of the rhodesite occurred as spherical aggregates as large as 50  $\mu\text{m}$  in diameter, with constructed prismatic crystals extended radically in all directions (Figure 5a). The EDX of the rhodesite crystals displayed a very strong peak of Si, relatively strong peaks of K and Ca and a weak peak of Al (Figure 5b). The structural formula on the basis of 40 oxygens calculated from the EDX analysis data is:  $\text{K}_{2.14}\text{Ca}_{3.56}\text{Mg}_{0.58}\text{Na}_{1.48}\text{Fe}_{1.21}^{\text{II}}\text{Al}_{0.53}\text{Si}_{16.03}\text{O}_{40}$ . Rhodesite occurs only rarely in natural environments; there are only 2 reports on natural occurrences of rhodesite from Kimberley, South Africa (Mountain 1957; Gard and Taylor 1957), and Trinity County, California (Eugster et al. 1967; Sheppard and Gude 1969). The XRD data and cell parameters calculated by least-squares refinement using the LCLSQ program (Burnham 1991) for the synthetic rhodesite are given

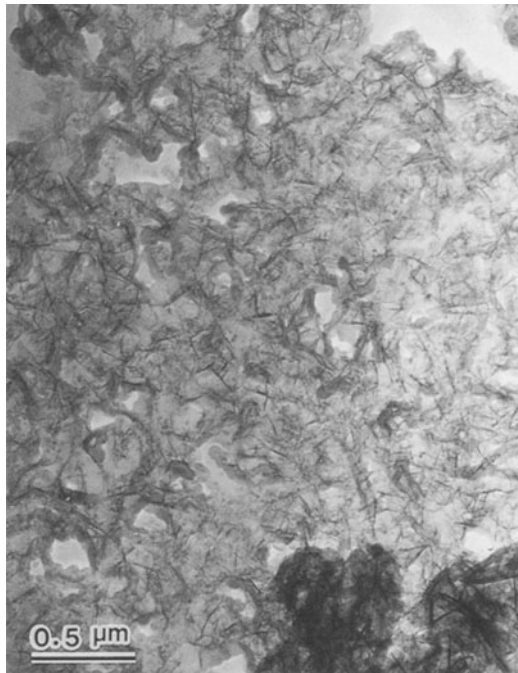


Figure 2. TEM of fibrous boehmite formed by reaction at 200 °C for 1 d in 0.001 *N* NaOH solution.

in Table 3 together with those of material from Trinity County.

#### Reaction Products in NaOH Solutions at 150 °C

The experimental conditions and reaction products formed by 150 °C experiments were also listed in Table 1. Based on XRD, formation of phillipsite in 0.01, 0.1 and 0.5 *N* NaOH solutions and of a small amount of rhodesite in 0.5 *N* NaOH solution were clearly recognized. In addition, TEM showed formation of small amounts of boehmite fibers in all experiments and of smectite exhibiting curled fibrous habit in 0.001 *N* NaOH solution.

#### Reaction Products in KOH Solutions at 200 °C

The hydrothermal reactions between obsidian and KOH solutions at 200 °C produced smectite, merlinoite, sanidine and small amounts of boehmite and kaolinite, depending strongly on the KOH concentration.

All reaction products contained small amount of boehmite which were undetectable by XRD, but clearly visible by TEM as thin fibers similar to the products in NaOH solution (Figure 2). A small amount of kaolinite was also observed by TEM in both 0.001 and 0.01 *N* KOH solutions. The kaolinite exhibited a characteristically spherical form less than 0.05 μm in diameter, which did not significantly increase in size and quantity with time, indicating a metastable phase. As indicated by EDX, the spherical kaolinite consisted of

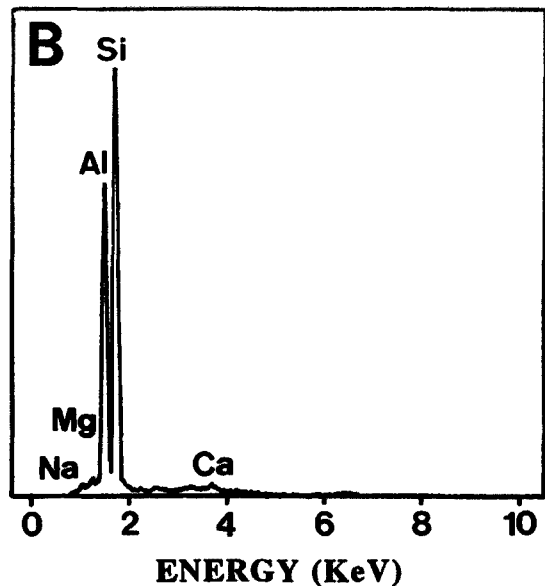
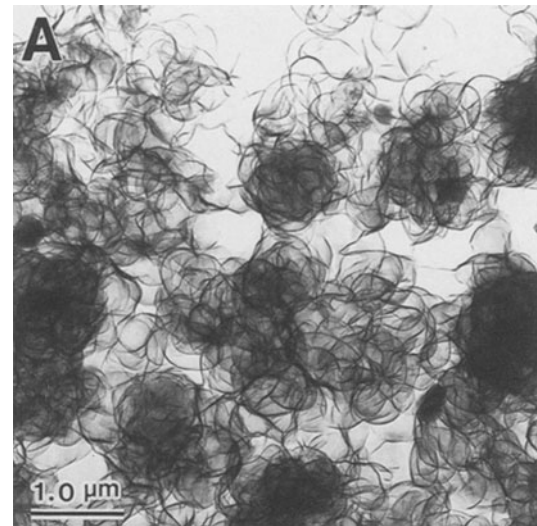


Figure 3. TEM and EDX spectrum of fibrous smectite formed by reaction at 200 °C for 30 d in 0.001 *N* NaOH solution.

similar amounts of Si and Al, which are compatible with those of natural kaolinite. Such spherical kaolinite is produced in large amounts from obsidian in acidic hydrothermal conditions and grows well as a stable phase (Kawano and Tomita 1995).

Smectite appeared only in 0.001 *N* KOH solution by the reactions for 10 and 30 d. As illustrated in Figure 1b, XRD of the smectite gave a pronounced 001 reflection ( $d = 15.0 \text{ \AA}$ ) which changed to 10.0 Å after heating and 17.2 Å after ethylene glycol solvation. The TEM and EDX indicated that the smectite exhibited curled or circular fibrous forms and consisted mainly of Si and Al, with small amounts of Na, K and Ca, suggesting that the smectite has morphological

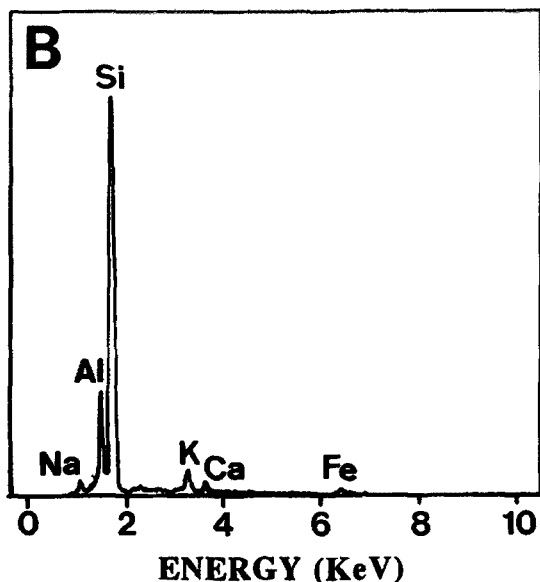
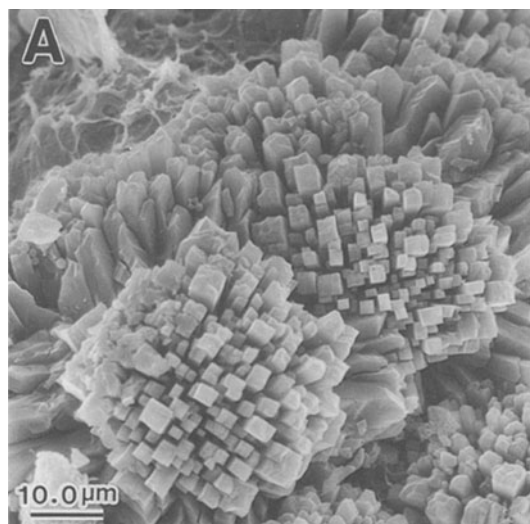


Figure 4. SEM and EDX spectrum of radiating aggregates of prismatic phillipsite formed by reaction at 200 °C for 30 d in 0.1 *N* NaOH solution.

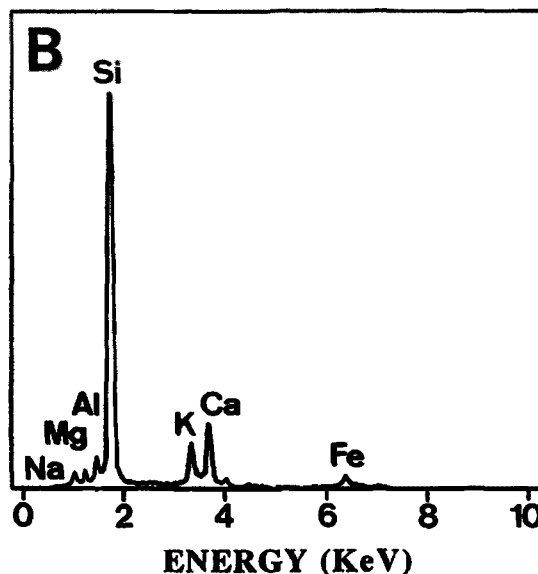
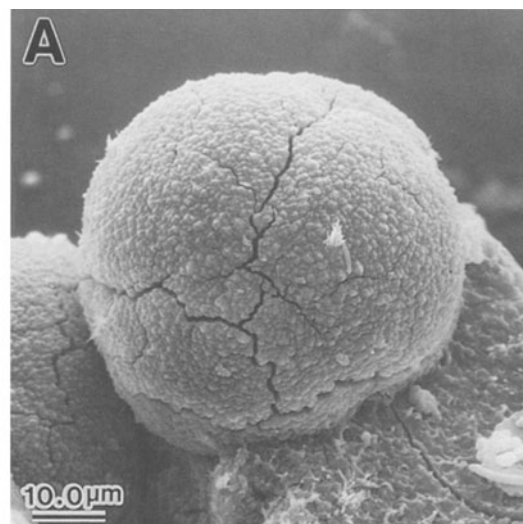


Figure 5. SEM and EDX spectrum of spherical aggregate of prismatic rhodesite crystals formed by reaction at 200 °C for 30 d in 0.5 *N* NaOH solution.

and chemical characteristics similar to the materials formed in 0.001 *N* NaOH solution (Figure 3a).

Merlinoite was formed mainly in 0.01 and 0.1 *N* KOH solutions by the reactions after 5 or 10 d. In 0.1 *N* KOH solution, merlinoite was produced as a major product with small amounts of sanidine and boehmite. Merlinoite appeared as a minor product coexisting with a large amount of sanidine in 0.5 *N* KOH solution (Figure 1b). The merlinoite occurred as aggregates of thin needle-like crystals less than 5 μm in length at the initial reaction stages, and it was developed to prismatic crystals up to 30 μm in length at the final reaction stages (Figure 6a). The chemical composition of the merlinoite is:  $K_{3.29}Na_{0.41}Al_{3.98}Si_{12.08}O_{32}$  obtained

from EDX analysis data (Figure 6b). Natural occurrences of merlinoite are apparently rare (Passaglia et al. 1977; Alberti et al. 1979; Khomyakov et al. 1981; Donahoe et al. 1984; Gottardi and Galli 1985). In contrast, syntheses of merlinoite have been performed extensively using various starting materials such as gels (Barrer and Baynham 1956; Barrer et al. 1959), rhyolitic pumice (Colella et al. 1977) and mixture of chemical reagents (Donahoe et al. 1984; Donahoe, Hemingway and Liou 1990; Donahoe, Liou and Hemingway 1990). Donahoe et al. (1984) found that formation of merlinoite was favored under hydrothermal reaction in solutions above pH 13.6 and below 0.5 of Na/(Na+K) ratio.

Table 3. XRD data and cell parameters for rhodesite.

hkl	Synthetic rhodesite†			Trinity County, Calif.‡	
	$d_c(\text{\AA})\S$	$d_o(\text{\AA})\S$	<i>I</i>	$d_c(\text{\AA})\S$	<i>I</i>
200	11.859	11.97	29	11.78	18
101				6.727	10
010	6.611	6.59	43	6.548	100
110	6.368	6.35	13	6.302	32
400				5.901	34
210				5.734	6
301				5.245	5
310	5.071	5.063	48	5.032	28
011				4.789	12
111					
211					
410	4.414	4.407	14	4.386	47
311				4.096	10
600	3.953	3.957	6	3.941	4
501				3.929	4
510	3.854	3.853	2	3.834	8
411	3.747	3.790	16	3.722	5
002				3.517	3
610, 202	3.392, 3.398	3.390	6	3.376	20
511					
020	3.305	3.320	15	3.274	7
120	3.274	3.280	100	3.242	16
112				3.071	19
320, 402				3.023	22
710				3.002	21
800	2.964	2.965	16	2.955	15
121				2.947	12
312	2.906	2.909	23	2.887	16
420	2.887	2.871	2	2.864	25
321				2.7784	6
711	2.775	2.770	6	2.7617	23

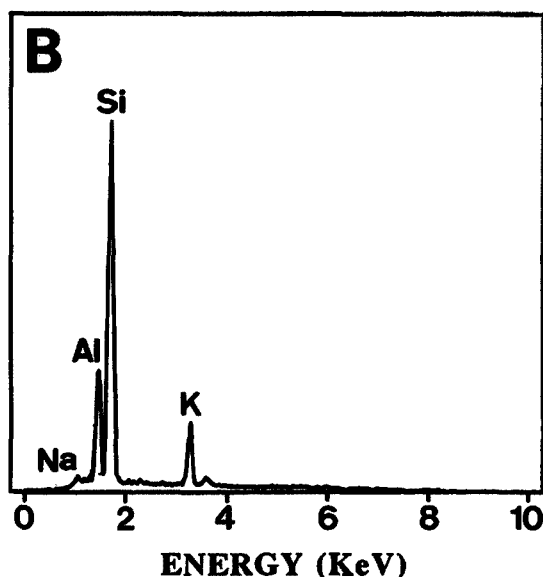
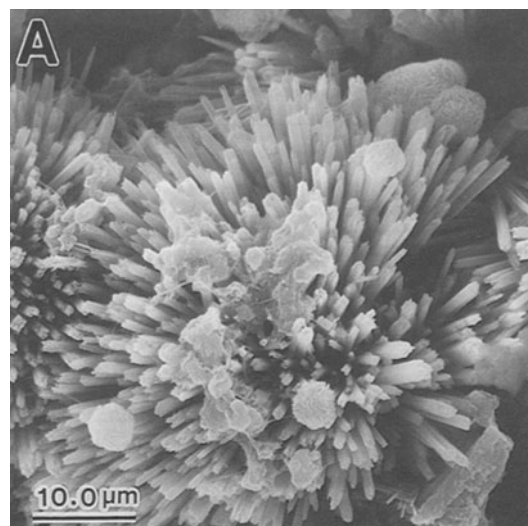
$a(\text{\AA}) = 23.71(3)$	$a(\text{\AA}) = 23.636 \pm 0.004$
$b(\text{\AA}) = 6.61(1)$	$b(\text{\AA}) = 6.549 \pm 0.001$
$c(\text{\AA}) = 7.09(1)$	$c(\text{\AA}) = 7.037 \pm 0.001$
$V(\text{\AA}^3) = 1112.4$	$V(\text{\AA}^3) = 1089.3 \pm 0.3$

† Present material.

‡ Data from Sheppard and Gude (1969).

§  $d_c$  = calculated *d*-values,  $d_o$  = observed *d*-values.

Sanidine was the predominant product in 0.5 *N* KOH solution, which occurred together with small amounts of merlinoite and boehmite, and which further increased in abundance with time. As shown by SEM, most of the sanidine occurred in the form of prisms or block of laths up to 30  $\mu\text{m}$  in length (Figure 7a). An EDX of the sanidine crystals gave a spectrum similar to that of K-feldspar,  $\text{KAlSi}_3\text{O}_8$  (Figure 7b). A structural formula calculated from the EDX analysis data is:  $\text{K}_{1.05}\text{Al}_{0.78}\text{Si}_{3.15}\text{O}_8$ . Sanidine is a high-temperature phase of K-feldspar, and it rarely occurs in natural environments as a low-temperature phase. However, it is well-known that K-feldspar most commonly occurs in high-grade alteration zones of saline, alkaline lake deposits (Sheppard and Gude 1968, 1973), burial diagenesis (Hay 1963) and hydrothermal alteration (Iijima 1974) as a replacement for alkali-rich zeolites; for example, analcime and phillipsite, formed by low-grade alterations.

Figure 6. SEM and EDX spectrum of prismatic crystals of merlinoite formed by reaction at 200 °C for 30 d in 0.01 *N* KOH solution.

#### Reaction Products in KOH Solutions at 150 °C

The experimental conditions and reaction products at 150 °C experiments were listed in Table 2. At this temperature, formation of merlinoite was detected by XRD as a major product in 0.5 *N* KOH solution. Additionally, TEM showed the presence of a trace amount of fibrous boehmite in all experiments and spherical halloysite in 0.001 and 0.01 *N* KOH solutions.

#### Chemistry of Solution

As listed in Tables 1 and 2, the pH of solutions remained high in alkaline, from about 9.9 to 13.8, with increasing NaOH and KOH concentrations. The reac-

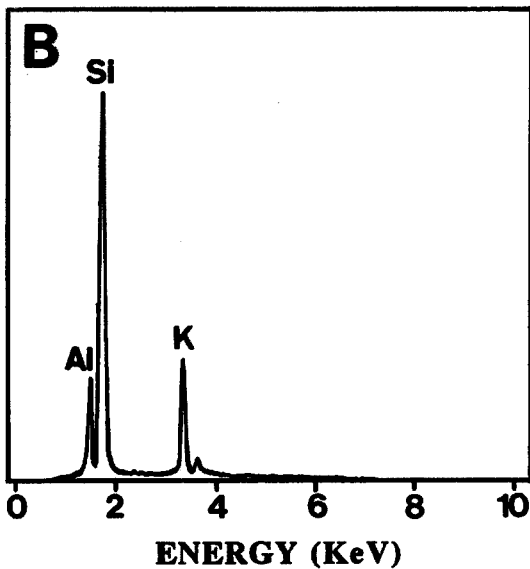
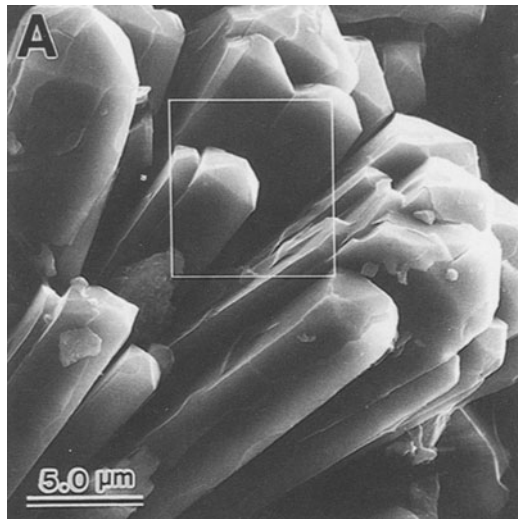


Figure 7. SEM and EDX spectrum of prismatic crystals of sanidine formed by reaction at 200 °C for 30 d in 0.5 *N* NaOH solution.

tion products of smectite, phillipsite and rhodesite crystallized progressively with increasing pH of NaOH solutions, and smectite, merlinoite and sanidine grew successively in KOH solutions as pH increased. Generally, the dissolution rate of rock-forming minerals and glasses tends to increase with increasing pH in alkaline condition; then solution compositions change as dissolution proceeds. Figure 8 shows the relationship between Na or K concentrations and pH of the NaOH or KOH solutions, in which a good correlation between log Na and pH, and between log K and pH, can be observed. Similarly, Si concentrations of both NaOH and KOH solutions increased with increasing pH, indicating that dissolution of obsidian was apparently extended in higher alkaline conditions

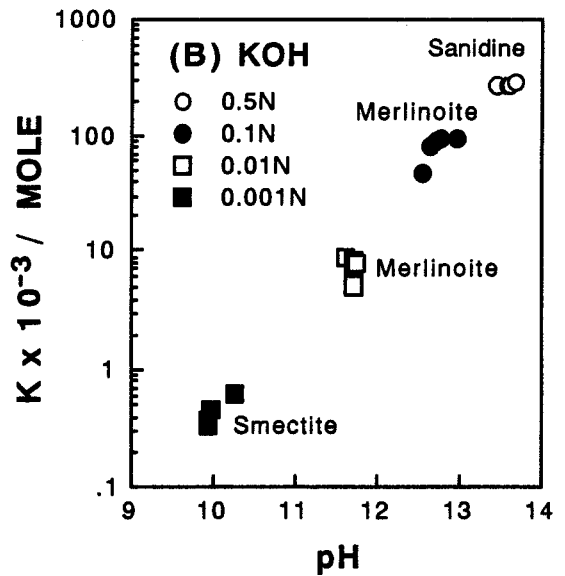
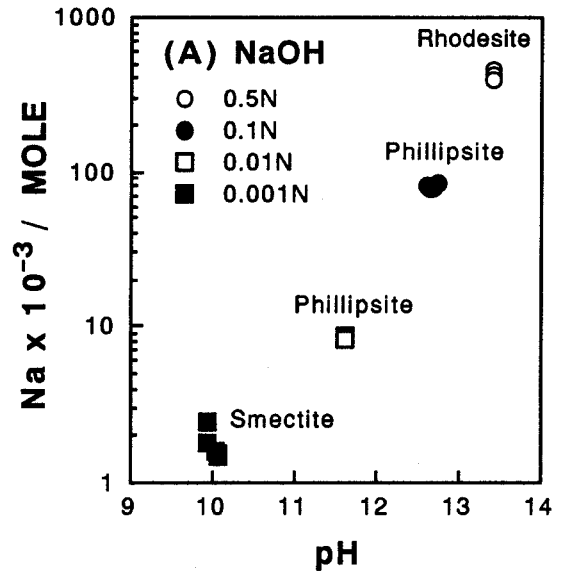


Figure 8. Plot of: A) Na concentration as a function of pH in 0.001 to 0.5 *N* NaOH solutions after reactions at 200 °C for 1 to 30 d, and B) K concentration in 0.001 to 0.5 *N* KOH solutions plotted similarly.

(Figure 9). Alternatively, the Si/Al ratio of 0.001 and 0.01 *N* NaOH solutions was retained below about Si/Al = 60; however, that of 0.1 and 0.5 *N* NaOH solutions increased successively up to about Si/Al = 3500 as the reaction proceeded (Figure 10a). Similar behaviors of the Si/Al ratio were recognized in KOH solutions (Figure 10b). The Na/K ratio of both 0.001 *N* NaOH and KOH solutions ranged from approximately Na/K = 1 to 20; however, the ratio increased progressively in NaOH solutions and decreased rapidly in KOH solutions with increasing pH (Figure 11). Thus, smectite mainly appeared in high pH, Si/Al and



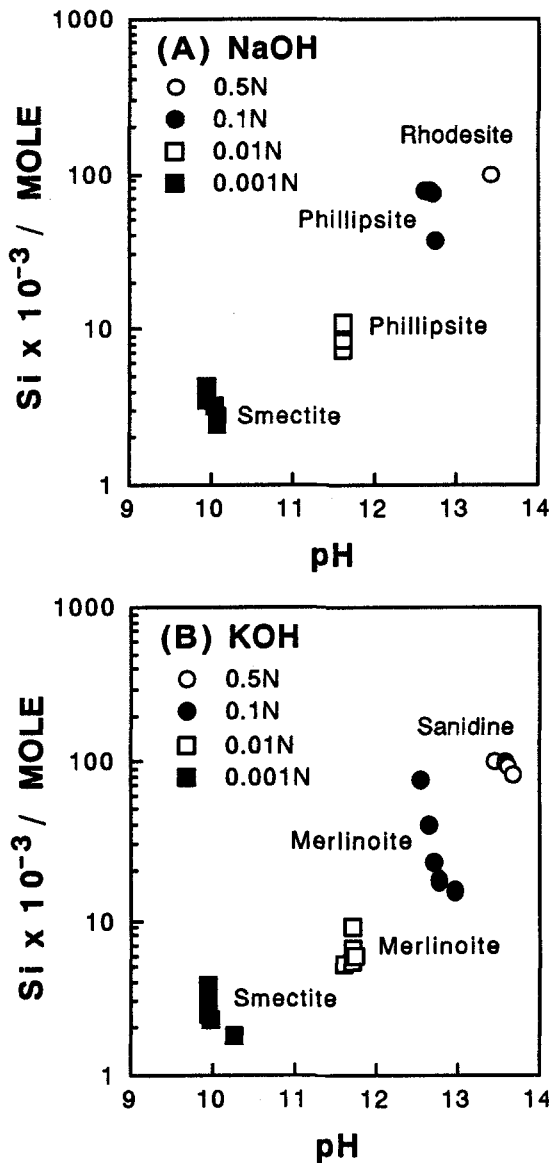


Figure 9. Plot of Si concentration as a function of pH in 0.001 to 0.5 N A) NaOH and B) KOH solutions after reactions at 200 °C for 1 to 30 d.

Na/K conditions, whereas rhodesite should be produced in higher pH, Si/Al and Na/K conditions, and sanidine was also formed in conditions of very high pH and Si/Al, and very low Na/K. In intermediate conditions of pH and Si/Al, however, crystallization of phillipsite was stimulated in solutions of Na/K > 10, but formation of merlinoite was favored in conditions of Na/K < 1.

#### DISCUSSION

The pH value, Si/Al, and Na/K ratios of the reacting solution are important factors determining the kind of products formed from obsidian by hydrothermal re-

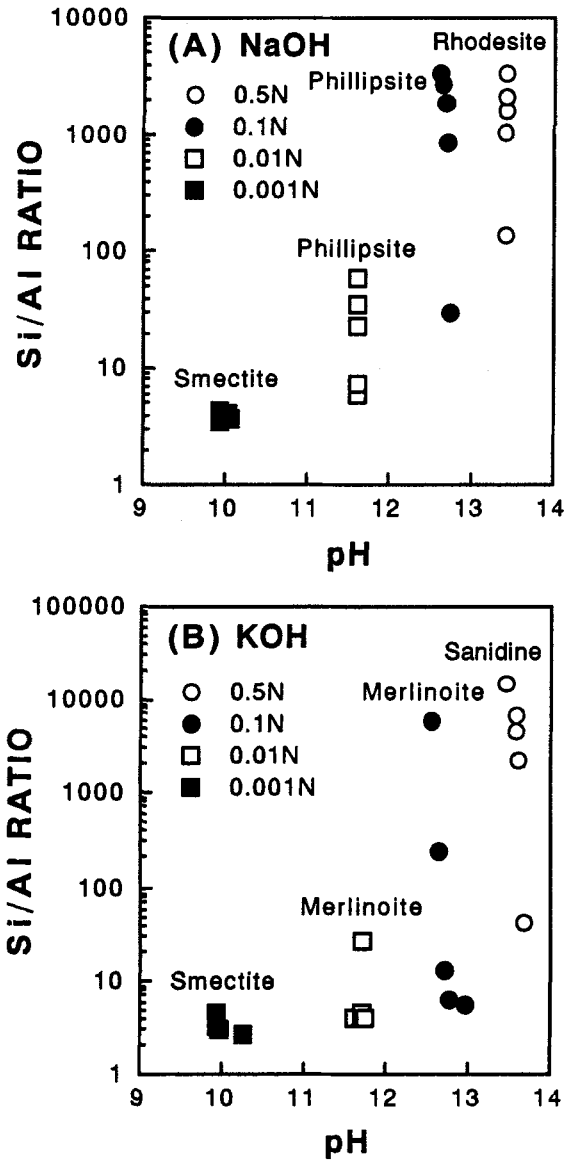


Figure 10. Plot of Si/Al ratio as a function of pH in 0.001 to 0.5 N A) NaOH and B) KOH solutions after reactions at 200 °C for 1 to 30 d.

action with alkaline solutions of NaOH and KOH at approximately 9.9–13.8 pH range. The present study demonstrated that smectite, phillipsite and rhodesite were progressively formed in NaOH solution with increasing pH, and that smectite, merlinoite and sanidine were successively produced in KOH solution as pH increased. Smectite was formed in both 0.001 N NaOH and KOH solutions under conditions of slightly high pH, Si/Al and Na/K. When deionized water is used, smectite can be easily synthesized from obsidian by hydrothermal reaction at 200 °C as a stable phase. The solution composition is developed to the stability field of smectite due to the incongruent dissolution of ob-

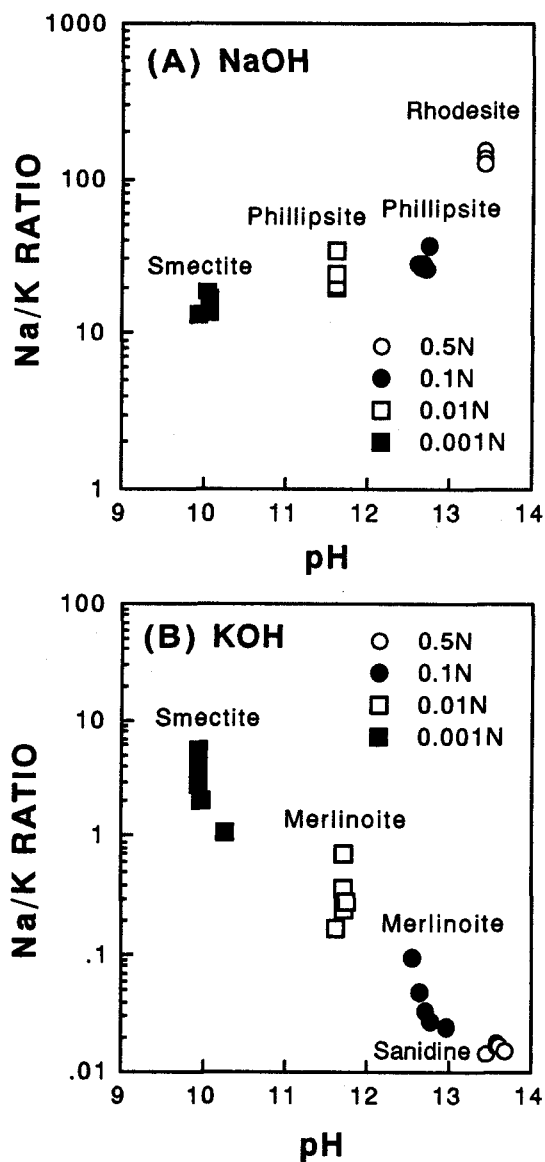


Figure 11. Plot of Na/K ratio as a function of pH in 0.001 to 0.5 *N* A) NaOH and B) KOH solutions after reactions at 200 °C for 1 to 30 d.

sidian (Kawano et al. 1993). The present smectite seems to be formed by the same mechanism, but the effect of NaOH and KOH on the formation reaction of smectite may be small or negligible because their concentrations are very low. In extremely high pH, Si/Al and Na/K conditions, rhodesite was formed, while sanidine was produced in very high pH and Si/Al and very low Na/K conditions. In intermediate conditions of pH and Si/Al, phillipsite crystallized in solutions of Na/K > 10, while merlinoite appeared in conditions of Na/K < 1. Thus, essential products of obsidian in the high-alkaline solutions must be phillip-

site and rhodesite for NaOH but merlinoite and sanidine for KOH.

Formation of the products would occur as the following processes: 1st, dissolution of obsidian; 2nd, increase in concentration of elements in solutions; and finally, precipitation of products from the saturated solutions. The concentration of Si quickly reached the approximate solubility limits of silica at the initial stages of each experiment for both NaOH and KOH solutions. The value also increased significantly with increasing pH, as illustrated by Stumm and Morgan (1981). The Si/Al ratio of obsidian used in this study is approximately 5.53, which is slightly greater than that of the precipitated products except with rhodesite, and thus formation of the products causes an increase in the Si/Al ratio of solutions. Moreover, a small amount of less-soluble fibrous boehmite existed in the products of all experiments in spite of high-alkali conditions, which is also a reason for the increase in Si/Al ratio. Consequently, the Si/Al ratio of solutions showed a tendency to increase with increasing pH. Similarly, such relation was apparently observed between the Si/Al ratio of reaction products and the pH of solutions in which they formed. Donahoe and Liou (1985) obtained synthetic phillipsite and merlinoite from solutions containing Si, Al, Na and K in the pH range 13.34–13.71 at 80 °C, and confirmed that Si/Al ratio of each product decreased linearly with increasing pH. They explained that increasing pH shifts the solution aluminosilicate species distribution toward less polymerized ones, which causes a decrease in the Si/Al ratio of the species. In the present study, however, smectite, phillipsite and rhodesite were progressively formed in NaOH solutions as pH increased, and the Si/Al ratio of the products increased as follows: smectite > phillipsite > rhodesite. In KOH solutions, the Si/Al ratio of the products increases in the following order: smectite > merlinoite > sanidine. These observations suggest that increasing pH favors crystallization of products having a higher Si/Al ratio.

The many experimental syntheses of zeolites related to phillipsite and merlinoite, using various starting materials involving natural rhyolitic glass by hydrothermal reaction in alkaline condition, are listed in Table 4. According to these results, zeolite species formed were greatly influenced by reaction conditions such as composition of starting material, pH and composition of reacting solution, solid/liquid ratio, temperature and time. Donahoe et al. (1984) synthesized phillipsite, merlinoite and gobbinsite in the system Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O using solutions containing Si, Al, Na and K in high-alkali conditions of pH 13.34–13.71, and found that phillipsite was crystallized in solutions of pH < 13.6 and Na/(Na+K) > 0.5, while formation of merlinoite was favored in solutions of pH > 13.6 and Na/(Na+K) ratio < 0.5. Later, Barth-Wirsching and Höller (1989) confirmed that formation of phillip-

Table 4. List of previous investigations on the syntheses of zeolites related to phillipsite and merlinoite.

Major product	Starting material	Solution	Temp. (°C)	Reference
Merlinoite	Silica-alumina gel	NaOH, KOH	250	Barrer et al. (1959)
Phillipsite	Alumino-silicate glass	NaOH, KOH	~250	Coombs et al. (1959)
Phillipsite	Metasilicate, waterglass	NaOH, KOH	~100	Kühl (1969)
Phillipsite	Rhyolitic glass	NaOH	80	Mariner and Surdam (1970)
Phillipsite	Rhyolitic pumice	NaOH, KOH	~80	Colella and Aiello (1975)
Zeolite S, Zeolite P	Silica-alumina gel	NaOH	130–175	De Kimpe (1976)
Phillipsite, Analcime, Mordenite, Alkali feldspar	Rhyolitic glass	NaOH	150–250	Wirsching (1976)
Merlinoite	Rhyolitic pumice	NaOH, KOH	140	Colella et al. (1977)
Phillipsite	Rhyolitic glass	Na <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub>	130–150	Hawkins et al. (1978)
Phillipsite, Analcime	Volcanic glass	NaOH	150, 200, 250	Höller and Wirsching (1978)
Mordenite, Phillipsite, Wairakite, Analcime, Heulandite, Thomsonite	Rhyolitic glass, Basaltic glass, Oligoclase, Nepheline	CaCl <sub>2</sub> , NaOH	100–250	Wirsching (1981)
Phillipsite, Clinoptilolite, Mordenite	Volcanic glass	Na <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub>	115–150	Hawkins (1981)
Phillipsite, Hydroxysodalite, Faujasite	Pumice, Perlite, Tuff	NaOH	85, 95	Burriesci et al. (1984)
Phillipsite, Merlinoite	Chemical reagents		80	Donahoe et al. (1984)
Phillipsite, Merlinoite	Chemical reagents		80	Donahoe and Liou (1985)
Phillipsite, Analcime, Merlinoite, Chabazite	Rhyolitic glass, Basaltic glass	NaOH, KOH	50–250	Barth-Wirsching and Höller (1989)
Analcime	Opalinus shale	NaOH	150–200	Chermak (1992)
Phillipsite, K-feldspar	Opalinus shale	KOH	150–200	Chermak (1993)
Phillipsite	Fly ash	NaOH	105	Park and Choi (1995)

site and merlinoite from rhyolitic glass was favored in NaOH and KOH solutions, respectively. Although numerous experiments have been conducted as mentioned above, rhodesite has not yet been synthesized.

Rhodesite was first discovered in 1957 from the Bultfontein diamond mine located in Kimberley, South Africa (Mountain 1957). Since then, only 1 locality—Trinity County, California—has reported the mineral (Sheppard and Gude 1969). No experimental study of the formation of rhodesite nor study of its crystallographic structure using single crystal XRD has been reported. Thus, the formation conditions of rhodesite and its crystal structure remain obscure. The present rhodesite was crystallized in extremely high-alkaline conditions of pH 13.4, while phillipsite was produced at pH 12.7. The result suggests that rhodesite is stable at higher alkalinity than phillipsite, and thus it occurs rarely in nature. In contrast, phillipsite, merlinoite and sanidine were obtained in relatively lower pH conditions compared with rhodesite (see Tables 1 and 2), and these minerals commonly occur in nature, especially in saline, alkaline lake deposits (Hay 1966). The mineralogical assemblage in Searles Lakes, California, which is one of the saline, alkaline lake deposits, changed from an upper phillipsite + merlinoite zone to a lower K-feldspar zone as alteration proceeded (Hay and Moiola 1963; Hay 1986). Further detailed

study on the mineralogical changes of the Searles Lake deposit revealed the following sequence with increasing depth: phillipsite → phillipsite + merlinoite → merlinoite → K-feldspar, which may correspond to increasing pH and/or increasing concentration of K in the pore water (Donahoe et al. 1984). The results of the present study agree well with such an observation of natural occurrence.

It is important to accurately identify the formation condition of rhodesite and its crystal structure. Synthetic rhodesite is easily produced from obsidian in conditions of higher pH than that of the stability field of phillipsite, but the natural occurrence of the minerals has been identified in only 2 localities: Kimberley in 1957 and California in 1969. The XRD pattern of rhodesite is close to that of K-feldspar with the exception of a few reflections, especially at 11.97 and 5.063 Å peaks of rhodesite. It is thus very difficult to identify rhodesite from a mixture of K-feldspar and small amount of rhodesite, so in this case the presence of rhodesite tends to be ignored. Although the exact formation condition is not clear, it is expected that the formation condition of rhodesite is distinct from that of K-feldspar. Consequently, more detailed information on the formation of natural zeolite may be obtained to apply the exact formation condition for natural geological environments.

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