

## SYNTHESIS AND CHARACTERIZATION OF ZEOLITES IN THE SYSTEM $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$

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**Abstract**—Zeolites having the structures of phillipsite, merlinoite, and gobbinsite were synthesized from clear solutions at 80°C in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and their morphologies, cell parameters, and compositions determined. At 3.5 M silica concentration, the formation of merlinoite (synthetic zeolite W) is favored over the formation of phillipsite (synthetic zeolite ZK-19) by solution conditions of high pH (> 13.6) and low Na/(Na + K) ratios (< 0.5).

Using the information obtained from the synthesis experiments, the presence of merlinoite was predicted in sediments from Searles Lake, a saline, alkaline lake in California with ideal physiochemical conditions for its formation. Merlinoite was subsequently discovered to occur in tuffaceous sediments as part of an authigenic silicate zonation pattern from phillipsite → phillipsite + merlinoite → merlinoite → K-feldspar with increasing depth. Because of the close similarities in the physical properties of phillipsite and merlinoite, merlinoite may be much more common as an authigenic mineral than is currently realized.

**Key Words**—Gobbinsite, Merlinoite, Phillipsite, Saline, Alkaline lake, Synthesis, Zeolite P<sub>i</sub>, Zeolite W, Zeolite ZK-19.

### INTRODUCTION

Interpretation of zeolite syntheses in the  $(\text{Na}_2\text{O}, \text{K}_2\text{O})-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system has been somewhat confused because of name duplications and the misidentification of synthesis products. Detailed comparisons of X-ray powder diffraction patterns for synthetic phases in the  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system by Taylor and Roy (1964) and for those in the  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system by Sherman (1977) have greatly clarified the relations among synthetic Na- and K-zeolites. Little effort has been made, however, to clarify phase relations for zeolites in the combined  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system. In this paper, we report the synthesis and characterization of zeolite ZK-19, zeolite W, and zeolite P<sub>i</sub> in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ .

Zeolite ZK-19 has the phillipsite framework structure and was synthesized and described by Kühl (1968, 1969, 1971). Zeolite W was first synthesized by D. W. Breck in 1953 (Sherman, 1977), and subsequently by many investigators (e.g., Barrer and Baynham, 1956; Milton, 1961; Taylor and Roy, 1964; Breck and Flanigen, 1968; Bosmans *et al.*, 1973; Colella *et al.*, 1977). Until 1977, zeolite W was thought to have the phillipsite structure. Based on differences in the X-ray powder diffraction patterns, Breck (1974) and Sherman (1977)

suggested that zeolite W has a structure related to, but different from, that of phillipsite. It was not until the natural equivalent of zeolite W, merlinoite, was discovered by Passaglia *et al.* (1977) and its crystal structure refined by Galli *et al.* (1979), that it was recognized that merlinoite corresponds to one of the 17 theoretical zeolite frameworks based on linkages of 8- and 4-membered rings proposed by Smith and Rinaldi (1962). The P group of zeolites have variable composition and exhibit different space group symmetries. The tetragonal sodium-form (designated as Na-P<sub>i</sub>) was first synthesized by Barrer *et al.* (1959a), and was recently discovered to occur naturally as the zeolite gobbinsite by Nawaz and Malone (1982). The crystal structure originally proposed for the P zeolites by Barrer *et al.* (1959b) was later disproved by Baerlocher and Meier (1972), who showed the framework to be an isotype of gismondine.

The present experimental study was undertaken to clarify the crystallization relations among these structurally related zeolites in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and to apply the observations to natural parageneses. The following problems were examined: (1) the effect of solution Na/(Na + K) ratio and solution pH on the structure of the precipitated zeolite, (2) the effect of solution Na/(Na + K) ratio on zeolite Na/(Na + K) ratio, and (3) the determination of the morphologies, compositions, and X-ray powder diffraction

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patterns of the synthetic zeolites. The results of the synthesis experiments were then used to explain and predict natural occurrences of these zeolites.

### EXPERIMENTAL

At present, the most commonly used method of zeolite synthesis involves the crystallization of zeolites from alkali hydroxide-hydrous aluminosilicate gel mixtures in closed hydrothermal systems at temperatures varying from room temperature to 175°C. Under these conditions, however, widely different zeolite species have been obtained from systems having the same chemical composition, but differing in the nature of the starting materials, in the type of nucleation process, or in the length of reaction time (e.g., see Schwachow and Heinze, 1971). In an effort to avoid such reproducibility problems, the zeolites in the present study were synthesized from clear solutions using the method described by Dibble *et al.* (1980).

Solutions with bulk compositions 0–5.1 M Na + 0–5.4 M K + 0.038–0.062 M Al + 3.5 M Si were prepared from appropriate mixtures of Baker Analyzed Reagents: aluminum chloride hexahydrate, silicic acid, sodium hydroxide, and potassium hydroxide. Aluminum chloride hexahydrate, sodium hydroxide, and potassium hydroxide were dissolved in distilled, deionized water and held at about 85°C while being mechanically stirred. Silicic acid was then added with vigorous stirring until a clear solution was obtained in 5–10 min. The solutions were then immediately stored in 250-ml polypropylene bottles in ovens maintained at  $80 \pm 1^\circ\text{C}$ . The pH of the solutions was measured at 21°C by combination pH electrode, and the compositions of the solutions were determined by d.c. plasma emission spectroscopy. The composition and pH of the solutions are given in Table 1. Trace element analyses were also performed on several solutions to verify that the only cations present were Na, K, Al, and Si. The solution chemistries in Table 1 are for the initial experimental conditions; however, solution pH was continuously monitored before and after nucleation, and solution composition was analyzed again after zeolite precipitation for experiments P-1 through P-4. No variation in solution chemistry was found during zeolite nucleation and growth, which is to be expected because the experimental solutions are essentially highly concentrated buffer solutions, and the volume of precipitate is very small compared with the solution volume.

In 4 to 7 days, depending on the composition of the solution, a milky turbidity appeared which signaled nucleation. After 1–4 months, the zeolite crystals were centrifuged from solution, washed with distilled, deionized water until the pH of the wash water fell below 7, and allowed to dry at room temperature over a 76-hr period to insure complete hydration. The zeolites were characterized by X-ray powder diffraction

(XRD), scanning electron microscopy (SEM), and electron microprobe analysis.

XRD data were obtained for water-smear mounts of these synthetic zeolites at  $\frac{1}{2}^\circ 2\theta/\text{min}$  with a Philips diffractometer using Ni-filtered  $\text{CuK}\alpha$  radiation. The XRD data were indexed and refined using the Job 9214 computer program of Appleman *et al.* (1972). The compositions of the synthetic zeolites were determined by electron microprobe analysis using feldspar standards, 15 kV accelerating potential, a sample current of 0.01  $\mu\text{A}$ , and a beam size of 40  $\mu\text{m}$ . The zeolite mounts were prepared by grinding each sample by hand to approximately  $\leq 1 \mu\text{m}$  in size, packing the powder into a sample holder against a polished surface with 2000-lb pressure, and then carbon coating the packed surface. Four to six spots were analyzed for each sample using 10-sec counting times. The analyses were reproducible to  $\geq 3\%$  between spots, and alkali migration problems were minimized by the large spot size and short counting times. The water content of each zeolite was determined by heating a fully hydrated sample to 800°C for 12 hr and measuring the weight loss. The analyses were normalized to total 100%, and unit-cell compositions were calculated on a 32-oxygen basis for phillipsite and gobbinsite and on a 64-oxygen basis for merlinoite.

### RESULTS

Representative XRD data for the synthetic zeolites are given in Table 2. Samples P-6, P-10 through P-12, P-19, and P-20 were identified as zeolite ZK-19 (phillipsite) by their XRD patterns which closely correspond to the data listed for P-5 phillipsite in Table 2A. The XRD patterns for samples P-1 through P-4, P-8, P-9, P-21, and P-22 closely correspond to the data for sample P-7 (Table 2B) and identify them as zeolite W (merlinoite). Zeolite Na-P, (gobbinsite) was identified in only one sample, P-18, whose XRD data are given in Table 2C. For a given zeolite structure, peak intensities and d-spacings vary with composition. In the following, the synthetic zeolites will be referred to by structure (phillipsite, merlinoite, and gobbinsite), rather than by synthesis nomenclature (ZK-19, W, and Na-P).

Scanning electron micrographs of the synthetic phillipsite, merlinoite, and gobbinsite are shown in Figure 1. The phillipsite crystals shown in Figure 1a are pseudo-orthorhombic and are elongated along *b*. The merlinoite crystals in Figure 1b were crystallized in 6 days and exhibit the “wheatseaf” morphology typical of zeolite W. When crystallized under slower growth conditions (74 days), the merlinoite crystals showed orthorhombic morphology and were elongated along *c* (see Figure 1c). Natural merlinoite crystals exhibit the latter morphology, but may display cruciform-like growth zones such as that shown in Figure 1b (see Passaglia *et al.*, 1977). Figure 1d shows orthorhombic

Table 1. Initial solution compositions for zeolite precipitation experiments.<sup>1</sup>

|                       | P-1      |            | P-2      |            | P-3      |            | P-4      |            |          |            |
|-----------------------|----------|------------|----------|------------|----------|------------|----------|------------|----------|------------|
|                       | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter |          |            |
| Si                    | 97,800   | 3.48       | 97,500   | 3.47       | 99,400   | 3.54       | 98,300   | 3.50       |          |            |
| Al                    | 1020     | 0.38       | 1190     | 0.044      | 1370     | 0.051      | 1360     | 0.051      |          |            |
| Na                    | 80,800   | 3.52       | 81,900   | 3.56       | 84,000   | 3.66       | 82,200   | 3.58       |          |            |
| K                     | 138,000  | 3.52       | 141,000  | 3.61       | 145,000  | 3.71       | 142,000  | 3.64       |          |            |
| Si/Al                 |          | 91.6       |          | 78.9       |          | 69.4       |          | 68.6       |          |            |
| (Na + K)/Si           |          | 2.02       |          | 2.07       |          | 2.08       |          | 2.06       |          |            |
| (Na + K)/Al           |          | 185        |          | 163        |          | 145        |          | 142        |          |            |
| Na/(Na + K)           |          | 0.50       |          | 0.50       |          | 0.50       |          | 0.50       |          |            |
| pH                    |          | 13.66      |          | 13.67      |          | 13.68      |          | 13.67      |          |            |
| Duration <sup>2</sup> |          | 211        |          | 150        |          | 150        |          | 150        |          |            |
|                       | P-5      |            | P-6      |            | P-7      |            | P-8      |            |          |            |
|                       | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter |          |            |
| Si                    | 94,700   | 3.37       | 98,300   | 3.50       | 104,000  | 3.70       | 96,200   | 3.43       |          |            |
| Al                    | 1490     | 0.055      | 1430     | 0.053      | 1380     | 0.051      | 1410     | 0.052      |          |            |
| Na                    | 55,000   | 2.39       | 63,500   | 2.76       | 77,800   | 3.39       | 86,300   | 3.35       |          |            |
| K                     | 94,800   | 2.42       | 109,000  | 2.80       | 135,000  | 3.46       | 150,000  | 3.85       |          |            |
| Si/Al                 |          | 61.3       |          | 66.0       |          | 72.5       |          | 66.0       |          |            |
| (Na + K)/Si           |          | 1.43       |          | 1.59       |          | 1.85       |          | 2.20       |          |            |
| (Na + K)/Al           |          | 87.5       |          | 105        |          | 134        |          | 146        |          |            |
| Na/(Na + K)           |          | 0.50       |          | 0.50       |          | 0.50       |          | 0.49       |          |            |
| pH                    |          | 13.35      |          | 13.55      |          | 13.64      |          | 13.71      |          |            |
| Duration <sup>2</sup> |          | 74         |          | 74         |          | 74         |          | 74         |          |            |
|                       | P-9      |            | P-10     |            | P-11     |            | P-12     |            |          |            |
|                       | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter |          |            |
| Si                    | 98,800   | 3.52       | 95,400   | 3.40       | 95,300   | 3.39       | 95,400   | 3.40       |          |            |
| Al                    | 1560     | 0.059      | 1410     | 0.053      | 1410     | 0.052      | 1410     | 0.053      |          |            |
| Na                    | 110,000  | 3.13       | 64,100   | 2.79       | 71,400   | 3.11       | 77,100   | 3.35       |          |            |
| K                     | 71,900   | 2.82       | 105,000  | 2.68       | 115,000  | 2.95       | 126,000  | 3.23       |          |            |
| Si/Al                 |          | 63.3       |          | 64.2       |          | 64.8       |          | 64.2       |          |            |
| (Na + K)/Si           |          | 1.69       |          | 1.61       |          | 1.79       |          | 1.94       |          |            |
| (Na + K)/Al           |          | 101        |          | 103        |          | 116        |          | 124        |          |            |
| Na/(Na + K)           |          | 0.53       |          | 0.51       |          | 0.51       |          | 0.51       |          |            |
| pH                    |          | 13.59      |          | 13.34      |          | 13.36      |          | 13.37      |          |            |
| Duration <sup>2</sup> |          | 150        |          | 40         |          | 40         |          | 40         |          |            |
|                       | P-18     |            | P-19     |            | P-20     |            | P-21     |            | P-22     |            |
|                       | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter | mg/liter | mole/liter |
| Si                    | 96,500   | 3.43       | 96,600   | 3.44       | 96,500   | 3.44       | 96,600   | 3.44       | 96,300   | 3.43       |
| Al                    | 1120     | 0.042      | 1680     | 0.062      | 1150     | 0.043      | 1580     | 0.059      | 1520     | 0.056      |
| Na                    | 117,000  | 5.09       | 110,000  | 4.79       | 94,800   | 4.12       | 41,000   | 1.78       | <2000    | 0.00       |
| K                     | <3000    | 0.00       | 40,400   | 1.03       | 48,500   | 1.24       | 144,000  | 3.68       | 210,000  | 5.38       |
| Si/Al                 |          | 83.7       |          | 53.8       |          | 80.0       |          | 58.3       |          | 61.2       |
| (Na + K)/Si           |          | 1.48       |          | 1.69       |          | 1.56       |          | 1.59       |          | 1.57       |
| (Na + K)/Al           |          | 121        |          | 93.9       |          | 125        |          | 92.5       |          | 96.1       |
| Na/(Na + K)           |          | 1.00       |          | 0.82       |          | 0.77       |          | 0.33       |          | 0.00       |
| pH                    |          | 13.56      |          | 13.59      |          | 13.57      |          | 13.58      |          | 13.57      |
| Duration <sup>2</sup> |          | 42         |          | 42         |          | 42         |          | 42         |          | 42         |

<sup>1</sup> Determined by d.c. plasma emission spectroscopy.<sup>2</sup> Duration of experiment in days.

crystals of gobbinsite which are commonly capped by the two-sided "domes" typical of natural phillipsite crystals. To the authors' knowledge, no photographs of gobbinsite or garronite ( $\text{Ca-P}_1$ ) have been published. By analogy with phillipsite, the true symmetry of gobbinsite is probably lower than tetragonal, perhaps orthorhombic or even monoclinic.

The compositions of the synthetic zeolites are given in Table 3. By systematically varying the pH and Na/(Na + K) ratio of the initial solutions, the synthesis fields for phillipsite and merlinoite were roughly determined at 80°C (Figure 2). Much more work remains to delineate the synthesis fields for these phases completely, but general conclusions can be drawn from the

Table 2. X-ray powder diffraction data for P-5 type ZK-19 synthetic phillipsite (A), P-7 type W synthetic merlinoite (B), and P-18 Na-P<sub>1</sub> synthetic gobbinsite (C).

| (A)   |       |                  | (B)  |       |                  | (C)   |       |                  |
|---|-------|------------------|--|-------|------------------|---|-------|------------------|
| hkl   | d(Å)  | I/I <sub>0</sub> | hkl  | d(Å)  | I/I <sub>0</sub> | hkl   | d(Å)  | I/I <sub>0</sub> |
| 100   | 8.169 | 6                | 110  | 9.926 | 6                | 110   | 7.056 | 15               |
| 002   | 7.121 | 35               | 011  | 8.170 | 10               | 111   | 5.594 | <5               |
| 011   | 6.389 | <5               | 200  | 7.071 | 25               | 200   | 5.041 | 15               |
| 120   | 5.366 | 5                | 121  | 5.331 | 20               | 002   | 4.892 | 7                |
| 021   | 5.034 | 5                | 002  | 5.010 | 20               | 102   | 4.402 | <5               |
| -201  | 4.969 | 15               | 310  | 4.442 | 20               | 211   | 4.095 | 35               |
| 101   | 4.283 | 10               | 031  | 4.281 | 20               | 202   | 3.431 | 8                |
| -131  | 4.100 | 20               | 311  | 4.083 | 5                | 212   | 3.325 | 10               |
| -221  | 4.070 | 15               | 310  | 3.645 | 20               | 310   | 3.188 | 100              |
| 212   | 3.940 | <5               | 222  | 3.549 | 7                | 103   | 3.109 | 60               |
| 121   | 3.672 | 5                | 401  | 3.512 | <5               | 311   | 3.046 | 5                |
| 012   | 3.470 | <5               | 141  | 3.259 | 85               | 113   | 2.973 | <5               |
| 140   | 3.257 | 45               | 420  | 3.170 | 100              | 302   | 2.776 | 5                |
| -132  | 3.190 | 100              | 123  | 2.959 | 55               | 203   | 2.745 | <5               |
| -312  | 3.155 | 30               | 341  | 2.754 | 55               | 321   | 2.692 | 50               |
| 230   | 3.091 | <5               | 242  | 2.667 | 20               | 213   | 2.650 | 15               |
| -322  | 2.944 | 35               | 521  | 2.545 | 30               | 400   | 2.528 | 5                |
| -142  | 2.749 | 25               | 152  | 2.436 | 10               | 322   | 2.436 | 5                |
| -242  | 2.686 | 40               |  |       |                  |   |       |                  |
| 122   | 2.563 | 7                |  |       |                  |   |       |                  |
| 042   | 2.521 | 5                |  |       |                  |   |       |                  |
| -342  | 2.392 | 4                |  |       |                  |   |       |                  |
| Monoclinic, <i>P2<sub>1</sub>/m</i><br><i>a</i> = 9.920 (2) Å<br><i>b</i> = 14.234 (3) Å<br><i>c</i> = 8.751 (2) Å<br>$\beta$ = 125.17° (2)<br><i>V</i> = 1010 (1) Å <sup>3</sup> |       |                  | Orthorhombic, <i>Immm</i><br><i>a</i> = 14.043 (4) Å<br><i>b</i> = 14.209 (4) Å<br><i>c</i> = 10.033 (4) Å<br><i>V</i> = 2002 (1) Å <sup>3</sup> |       |                  | Tetragonal, <i>P4<sub>2</sub>2<sub>1</sub>2</i><br><i>a</i> = 10.106 (6) Å<br><i>b</i> = 10.106 (6) Å<br><i>c</i> = 9.805 (7) Å<br><i>V</i> = 1001 (1) Å <sup>3</sup> |       |                  |

available data. At total dissolved silica concentrations of 3.5 M, the precipitation of phillipsite is favored by solution conditions of pH < 13.6 and by mole fraction Na > 0.5. The precipitation of merlinoite is favored by solution conditions of pH > 13.6 and by mole fraction Na < 0.5. Gobbinsite was found to precipitate from a sodium aluminosilicate solution (P-18) having a pH = 13.56. The gobbinsite synthesis field was not explored further, although the topology of the field is depicted in Figure 2.

Using rhyolitic pumices as starting materials, Colella *et al.* (1977) found that the synthesis of merlinoite was favored by high concentrations of potassium in the contact solutions. Merlinoite formation was also favored by temperatures > 100°C. Similar experiments were carried out in the present study at different pHs, and no differences were found in the synthesis fields of phillipsite and merlinoite between 60 and 100°C. Colella *et al.* (1977) reported the synthesis of zeolite M from pure sodium solutions, but their XRD data much more closely correspond to a type P zeolite rather than zeolite M.

Figure 3 is a plot of zeolite Na/(Na + K) ratio vs. solution Na/(Na + K) ratio. A smooth curve can be drawn through several of the points, but this may be fortuitous. For solutions having a Na/(Na + K) ratio

of 0.5, the zeolite Na/(Na + K) ratio ranges from about 0.1 to 0.25, and most of the points lie above the curve. This scatter in zeolite Na/(Na + K) ratio could be the result of a 3% analytical standard deviation, which seems nominal considering the fact that electron microprobe count rates for alkali elements in zeolites are known to drift with time (R. Rinaldi, Istituto di Mineralogia, Università di Modena, Modena, Italy, personal communication, 1983). It is clear from Figure 3 that the solution Na/(Na + K) ratio determines both the zeolite Na/(Na + K) ratio and zeolite structure for a fixed solution pH and silica concentration. The phillipsites precipitated at solution Na/(Na + K) = 0.5 were obtained by decreasing the pH of the initial solutions. The relationship between the composition of the solution and the composition of the zeolite that precipitates from it is shown in Figure 4. A tie-line connects the solution-zeolite pairs. For clarity, clustered lines with duplicate slopes were omitted from the illustration. For all of the experiments, the zeolite Si/Al ratio was markedly lower than the Si/Al ratio of the parent solution. No correlation between the Si/Al ratio of the solution and the Si/Al ratio of the resultant zeolite was noted. For all mixed Na-K solutions, however, the phillipsites and merlinoites selectively incorporated K into their structure over Na so that the zeolite Na/(Na

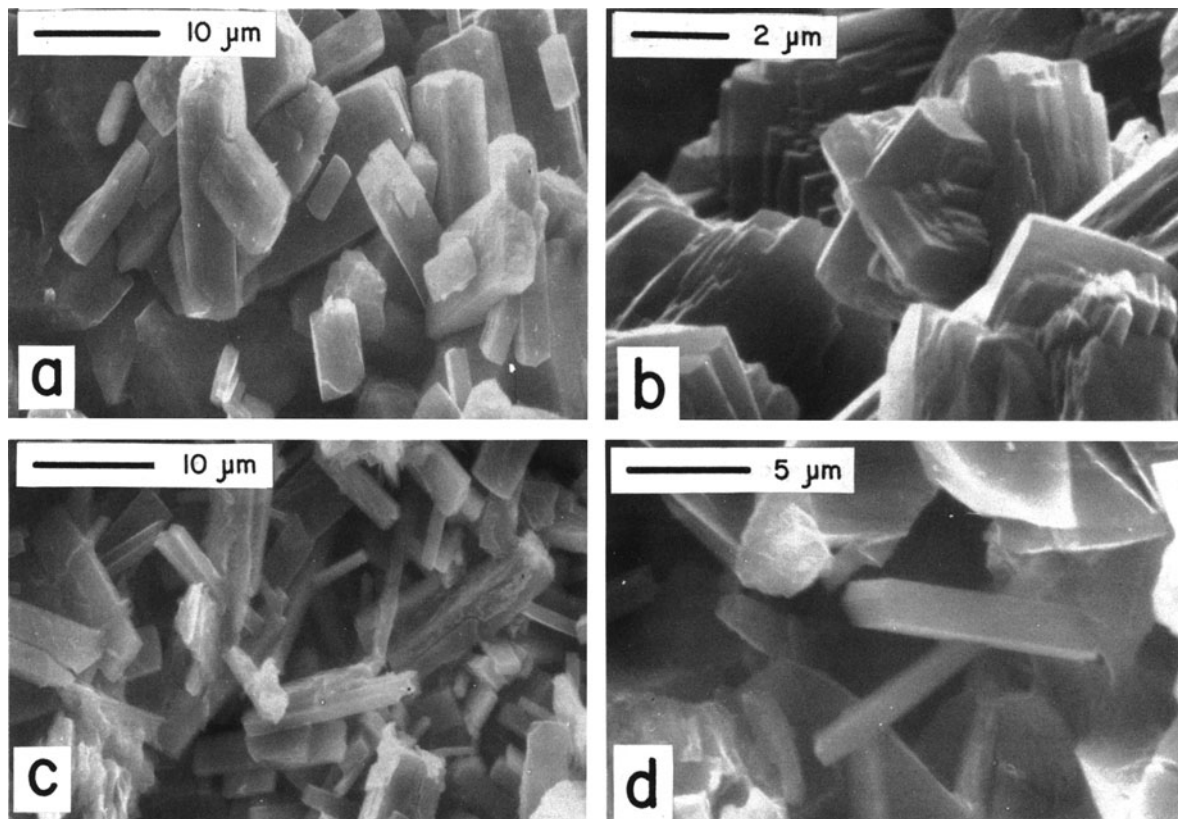


Figure 1. Scanning electron micrographs of synthetic zeolites: (a) type ZK-19 phillipsite (P-5), (b) type W merlinoite (P-2) showing fast growth morphology (note cruciform-like growth zone), (c) type W merlinoite (P-7) showing slow growth morphology, and (d) type P, Na-gismondine (P-18).

+ K) ratio was significantly lower than the solution  $\text{Na}/(\text{Na} + \text{K})$  ratio. This preference for potassium was also noted by Barrer and Munday (1971), Stonecipher

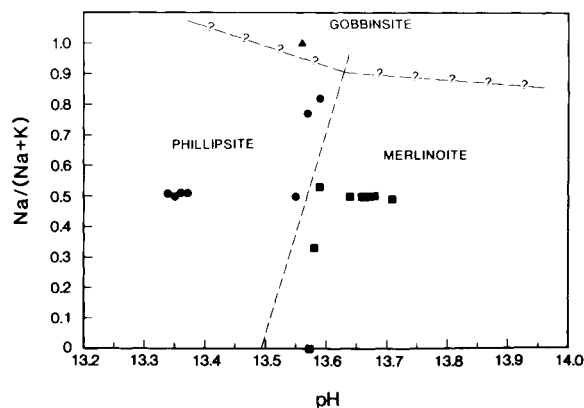


Figure 2. Synthesis fields of zeolites in the system  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  as a function of solution  $\text{Na}/(\text{Na} + \text{K})$  ratio and pH ( $[\text{Si}] = 3.5 \text{ M}$ ,  $T = 80^\circ\text{C}$ ).

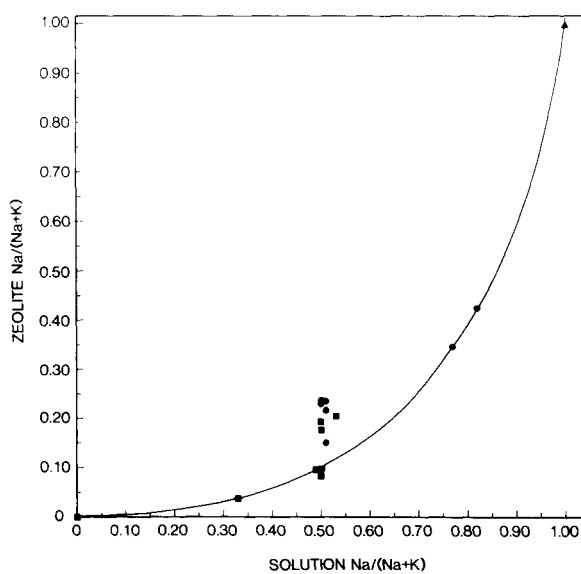


Figure 3. Plot of zeolite  $\text{Na}/(\text{Na} + \text{K})$  ratio vs. solution  $\text{Na}/(\text{Na} + \text{K})$  ratio.  $\blacktriangle$  = gobbinsite;  $\bullet$  = phillipsite; and  $\blacksquare$  = merlinoite.

Table 3. Electron microprobe analyses of synthetic zeolites.

|                                    | P-1   | P-2   | P-3   | P-4   | P-5   | P-6   | P-7   | P-8   | P-9   |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Weight percent oxide               |       |       |       |       |       |       |       |       |       |
| SiO <sub>2</sub>                   | 49.1  | 49.8  | 47.1  | 45.8  | 50.2  | 47.2  | 49.5  | 46.8  | 48.8  |
| Al <sub>2</sub> O <sub>3</sub>     | 22.4  | 22.6  | 21.5  | 21.0  | 19.4  | 20.2  | 22.3  | 21.9  | 21.4  |
| K <sub>2</sub> O                   | 16.7  | 15.2  | 16.7  | 15.5  | 12.7  | 14.3  | 15.3  | 16.3  | 13.8  |
| Na <sub>2</sub> O                  | 1.24  | 0.91  | 1.19  | 2.45  | 2.61  | 2.83  | 2.16  | 1.14  | 2.32  |
| H <sub>2</sub> O <sup>2</sup>      | 10.6  | 11.5  | 13.5  | 15.2  | 15.1  | 15.5  | 10.8  | 13.9  | 13.7  |
| Total                              | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Unit-cell composition <sup>1</sup> |       |       |       |       |       |       |       |       |       |
| Si                                 | 20.99 | 21.23 | 20.94 | 20.78 | 11.05 | 10.64 | 21.09 | 20.82 | 21.33 |
| Al                                 | 11.30 | 11.36 | 11.24 | 11.24 | 5.04  | 5.37  | 11.18 | 11.50 | 11.00 |
| K                                  | 9.11  | 8.24  | 9.48  | 8.99  | 3.56  | 4.11  | 8.31  | 9.24  | 7.70  |
| Na                                 | 1.03  | 0.75  | 1.03  | 2.16  | 1.11  | 1.24  | 1.79  | 0.99  | 1.97  |
| H <sub>2</sub> O                   | 15.19 | 16.33 | 20.06 | 22.96 | 11.13 | 11.64 | 15.41 | 20.63 | 19.93 |
| Si/Al                              | 1.86  | 1.87  | 1.86  | 1.85  | 2.19  | 1.98  | 1.89  | 1.81  | 1.94  |
| <sup>3</sup> Mineral               | M     | M     | M     | M     | P     | P     | M     | M     | M     |
|                                    | P-10  | P-11  | P-12  | P-18  | P-19  | P-20  | P-21  | P-22  |       |
| Weight percent oxide               |       |       |       |       |       |       |       |       |       |
| SiO <sub>2</sub>                   | 50.9  | 50.8  | 50.6  | 52.7  | 46.7  | 46.1  | 46.6  | 45.9  |       |
| Al <sub>2</sub> O <sub>3</sub>     | 19.6  | 19.8  | 19.6  | 23.0  | 20.5  | 20.4  | 20.4  | 20.0  |       |
| K <sub>2</sub> O                   | 12.7  | 11.8  | 13.8  | 0.06  | 11.6  | 13.4  | 21.7  | 23.1  |       |
| Na <sub>2</sub> O                  | 2.29  | 2.38  | 1.59  | 7.55  | 5.68  | 4.65  | 0.57  | 0.00  |       |
| H <sub>2</sub> O <sup>2</sup>      | 14.5  | 15.2  | 14.4  | 16.7  | 15.5  | 15.5  | 10.9  | 11.0  |       |
| Total                              | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |       |
| Unit-cell composition <sup>1</sup> |       |       |       |       |       |       |       |       |       |
| Si                                 | 11.10 | 11.11 | 11.07 | 10.99 | 10.49 | 10.44 | 20.76 | 20.69 |       |
| Al                                 | 5.04  | 5.10  | 5.06  | 5.66  | 5.41  | 5.45  | 10.71 | 10.64 |       |
| K                                  | 3.51  | 3.28  | 3.86  | 0.02  | 3.33  | 3.88  | 12.33 | 13.30 |       |
| Na                                 | 0.97  | 1.01  | 0.68  | 3.05  | 2.47  | 2.04  | 0.49  | 0.00  |       |
| H <sub>2</sub> O                   | 10.51 | 11.10 | 10.55 | 11.61 | 11.59 | 11.68 | 16.14 | 16.53 |       |
| Si/Al                              | 2.20  | 2.18  | 2.19  | 1.94  | 1.94  | 1.92  | 1.94  | 1.94  |       |
| <sup>3</sup> Mineral               | P     | P     | P     | G     | P     | P     | M     | M     |       |

<sup>1</sup> Basis: 32 oxygen/cell for phillipsite and gobbinsite, 64 oxygen/cell for merlinoite.

<sup>2</sup> Determined by gravimetric methods.

<sup>3</sup> P = phillipsite, M = merlinoite, G = gobbinsite.

(1978), and Shibue (1981) for phillipsite and by Colella *et al.* (1977) for merlinoite. The solution-zeolite tie-lines shown in Figure 4 are nearly parallel, suggesting that the selectivity of phillipsite for potassium is identical to that of merlinoite. A relationship also exists between the zeolite Si/Al ratio and the solution pH. This relationship will be discussed in detail elsewhere.

#### DISCUSSION AND GEOLOGIC APPLICATION

Phillipsite was discovered in 1824 as a vug-filling mineral in volcanic rocks. Today, phillipsite is thought to be one of the most abundant mineral species on earth owing to its extensive occurrence in deep-sea sediments and in lacustrine sediments of the western United States and Africa. Merlinoite, on the other hand, was first discovered in 1977 and has been reported only from localities in Italy and Russia (Passaglia *et al.*, 1977; Khomyakov *et al.*, 1981). Its apparent rarity is

in contrast with the relative ease of synthesizing merlinoite compared to phillipsite from mixed Na-K aluminosilicate gels and solutions.

The synthetic merlinoite grown under slow growth conditions in the present study has a lath-shaped morphology similar to that of synthetic phillipsite (see Figure 1). Passaglia *et al.* (1977) noted the similar morphologies of natural phillipsite and merlinoite and emphasized that the unequivocal distinction between the two can only be achieved by XRD analysis. The XRD patterns for phillipsite and merlinoite are quite similar, differing only in the presence or absence of a few lines (see Table 4). The most obvious difference is the presence of 10-Å and 4.5-Å peaks in merlinoite patterns and their absence in phillipsite patterns, and the presence of 6.4-Å, 4.13-Å, and 3.15-Å peaks for phillipsite which are absent in patterns for merlinoite. If the 10-Å peak of merlinoite was discounted by the analyst as being due to the presence of illite in the

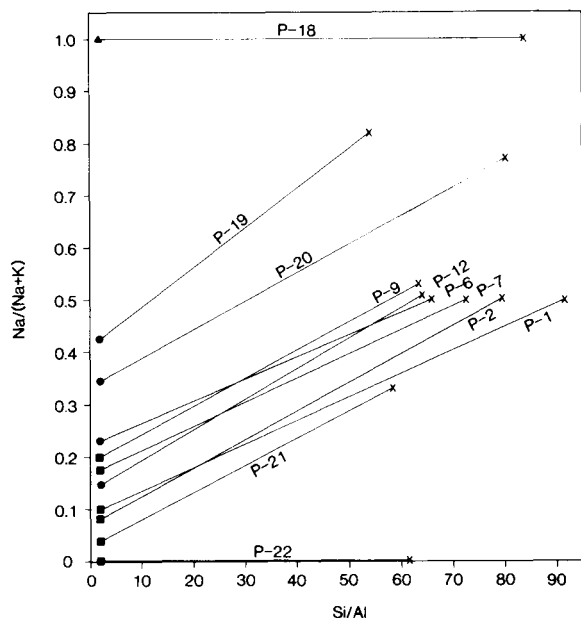


Figure 4. Synthesis experiment solution/zeolite pair compositions. X designates solution composition.  $\blacktriangle$  = gobbinsite;  $\bullet$  = phillipsite; and  $\blacksquare$  = merlinoite compositions.

mineral assemblage, it is possible that merlinoite could easily be misidentified as phillipsite.

The present data show the formation of merlinoite to be favored by solution conditions of  $\text{pH} > 13.6$  and  $\text{Na}/(\text{Na} + \text{K}) < 0.5$ . The delineated synthesis fields, of course, are only valid for the experimental conditions used (i.e., 3.5 M silica solutions having  $\text{pH} > 13.2$ ). Natural waters, in contrast, do not have pHs much above 10 or silica concentrations much above 0.03 M (Livingstone, 1963; White *et al.*, 1963). To predict the formation conditions of merlinoite in nature, these experiments must be extrapolated to conditions which are more geologically reasonable. This extrapolation can be made qualitatively by examining the solubility of silica as a function of pH (Figure 5). The short horizontal line brackets the experimental conditions used in the present study. If these conditions are extrapolated to lower silica concentrations, maintaining the relative position across the multimeric/monomeric boundary, the required pH of the solutions also drops. Therefore, a  $\text{pH} > 10$  is not necessarily required for merlinoite formation, provided that the solutions have a low enough Na/K ratio. Relative to phillipsite, merlinoite precipitation requires a higher solution pH and/or higher potassium concentrations.

Most natural waters have Na/K ratios greater than 45 (the value for seawater) and pHs below 9 (Livingstone, 1963; White *et al.*, 1963). These solution conditions would be expected to favor the formation of phillipsite. For merlinoite formation, it can be antic-

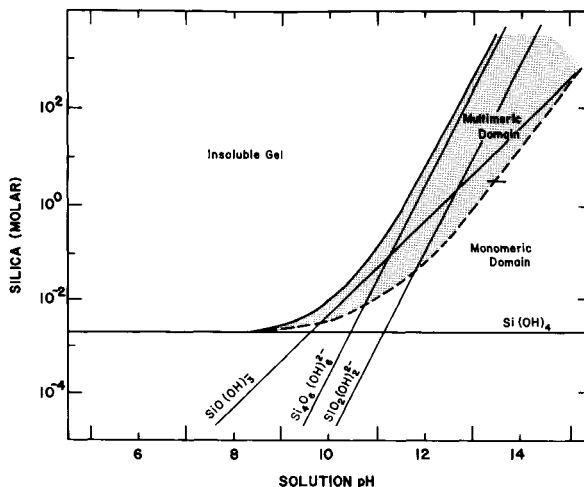


Figure 5. Silica solubility as a function of solution pH. (After Stumm and Morgan, 1981, pg. 541.)

ipated that solutions with pHs of about 9–10 and Na/K ratios  $< 45$  are required. These solution conditions are found in some saline, alkaline lakes in the western United States; however, only phillipsite has been reported from these sediments (e.g., Hay, 1964).

The saline, alkaline lakes and lake beds of the Owens Valley area in California represent a progressive downstream concentration of salts from the Waucoba lake beds and Owens Lake through China Lake to Searles Lake. Phillipsite has been reported in all of these lake sediments (Hay and Moiola, 1963; Hay, 1964; Hay, 1966), but the exceptionally high potassium concentration ( $\text{Na}/\text{K} = 7.2\text{--}13.1$ ) and high pH (9.1–9.5) of the Searles Lake brines has led to the formation of K-feldspar as the dominant authigenic silicate at Searles Lake. Based on the above discussion, the chemistry of the Searles Lake brines would seem likely to favor the formation of merlinoite.

Samples of "phillipsite"-bearing tuffs from Searles Lake in drill core KM-3 were therefore obtained from G. I. Smith of the U.S. Geological Survey, and the authigenic zeolites were examined. In general, the mineral assemblage of the tuffaceous sediments changes from an upper phillipsite-bearing zone to a lower K-feldspar-bearing zone. The reaction phillipsite  $\rightarrow$  K-feldspar could represent changing pore fluid chemistry toward higher potassium concentrations and/or higher pH with depth, conditions that also favor the reaction phillipsite  $\rightarrow$  merlinoite. Our study of the drill core was therefore concentrated at the base of the phillipsite-bearing zone; in particular, the 134.5-ft and 138-ft samples.

Hand-picked, zeolite-rich portions of these two samples were suspended in a bromoform-acetone solution (S.G. = 2.3) to remove any clay that might be present.

Table 4. A comparison of the X-ray powder diffraction data for natural merlinoite, phillipsite and gobbinsite.

| Merlinoite <sup>1</sup> |       |                  | Phillipsite <sup>2</sup> |       |                  | Gobbinsite <sup>3</sup> |       |                  |
|-------------------------|-------|------------------|--------------------------|-------|------------------|-------------------------|-------|------------------|
| hkl                     | d     | I/I <sub>0</sub> | hkl                      | d     | I/I <sub>0</sub> | hkl                     | d     | I/I <sub>0</sub> |
| 110                     | 10.02 | 12               | —                        | —     | —                | —                       | —     | —                |
| 011, 101                | 8.15  | 12               | 101                      | 8.192 | w                | —                       | —     | —                |
| 020                     | 7.12  | 90               | 002                      | 7.189 | s                | —                       | —     | —                |
| 200                     | 7.08  | 88               | 020                      | 7.150 | s                | 110, 101                | 7.11  | 100              |
| —                       | —     | —                | 012                      | 6.430 | mw               | —                       | —     | —                |
| 121, 211                | 5.36  | 40               | 121                      | 5.391 | m                | 111                     | 5.78  | 20               |
| 220                     | 5.03  | 35               | 022                      | 5.082 | mw               | 200                     | 5.056 | 50               |
| 002                     | 4.98  | 20               | 200                      | 4.970 | m                | 002                     | 4.893 | 30               |
| 130, 310, 112           | 4.48  | 37               | —                        | —     | —                | 102                     | 4.409 | 25               |
| 031                     | 4.29  | 28               | 103                      | 4.327 | mw               | —                       | —     | —                |
| —                       | —     | —                | 113, 131                 | 4.136 | s                | 211                     | 4.116 | 100              |
| 022, 202                | 4.07  | 8                | 202, 220                 | 4.089 | mw               | —                       | —     | —                |
| —                       | —     | —                | 032                      | 3.979 | w                | 112                     | 4.027 | 20               |
| 231, 321                | 3.66  | 18               | —                        | —     | —                | —                       | —     | —                |
| 040                     | 3.56  | 5                | —                        | —     | —                | —                       | —     | —                |
| 222, 400                | 3.53  | 4                | 014                      | 3.494 | w                | 202                     | 3.515 | 10               |
| 330, 132, 312           | 3.34  | 2                | —                        | —     | —                | 212                     | 3.326 | 30               |
| 141                     | 3.26  | 44               | 141                      | 3.282 | s                | —                       | —     | —                |
| 411                     | 3.24  | 41               | —                        | —     | —                | —                       | —     | —                |
| 013, 103                | 3.23  | 38               | 301, 024 }<br>042, 133 } | 3.211 | vs               | 310, 301                | 3.201 | 100              |
| 240, 420                | 3.18  | 100              | 311                      | 3.148 | s                | —                       | —     | —                |
| —                       | —     | —                | 232                      | 3.106 | w                | 103                     | 3.106 | 80               |
| —                       | —     | —                | —                        | —     | —                | 311                     | 3.040 | 10               |
| 123, 213                | 2.935 | 34               | 321                      | 2.942 | s                | 113                     | 2.968 | 10               |
| —                       | —     | —                | 204, 240                 | 2.912 | m                | —                       | —     | —                |
| —                       | —     | —                | 034                      | 2.875 | m                | 222                     | 2.887 | 5                |
| 332, 510                | 2.770 | 16               | 105, 143                 | 2.764 | s                | 302, 203                | 2.757 | 5                |
| 051, 341                | 2.730 | 27               | —                        | —     | —                | —                       | —     | —                |
| 431, 033, 501           | 2.720 | 30               | 115                      | 2.718 | s                | —                       | —     | —                |
| —                       | —     | —                | 151, 224                 | 2.703 | vs               | 321, 312                | 2.699 | 80               |
| —                       | —     | —                | 242                      | 2.694 | s                | —                       | —     | —                |
| —                       | —     | —                | 313                      | 2.679 | s                | —                       | —     | —                |
| 242, 422                | 2.670 | 11               | 331                      | 2.673 | s                | 213                     | 2.651 | 40               |
| 251                     | 2.552 | 16               | 125                      | 2.581 | m                | 400                     | 2.539 | 25               |

<sup>1</sup> Passaglia *et al.* (1977). w = weak, s = strong, vs = very strong, m = medium, mw = medium weak.

<sup>2</sup> Sample 11, Galli and Ghittoni (1972), orthorhombic indexing.

<sup>3</sup> Nawaz and Malone (1982).

The XRD patterns of the two purified samples and of natural phillipsite and merlinoite are shown in Figure 6. Both phillipsite and merlinoite are present as authigenic silicates in the 134.5-ft sample (diagnostic peaks for merlinoite = 10 and 4.5 Å; diagnostic peaks for phillipsite = 6.4, 4.13, and 3.15 Å). Merlinoite is the only authigenic silicate present in the 138-ft sample. The major illite peaks at 4.46, 3.88, and 3.10 Å are absent from these patterns. Only phillipsite is present in the 65.3-ft sample.

Scanning electron microscopy confirms the XRD analyses. The scanning electron micrograph of the purified zeolites from the 134.5-ft sample (Figure 7a) shows pristine, 10–20-μm size phillipsite with coexisting merlinoite crystals. Figure 7b (the purified 138-ft sample) shows only merlinoite crystals and minor amounts (<10%) of an unidentified substance which might be a clay mineral. The merlinoite crystals are 10 μm in length and exhibit the “wheat sheaf bundle” morphol-

ogy typical of zeolite W synthetic merlinoite (see Sherman, 1977).

An authigenic silicate zonation pattern which may correspond to increasing pH and/or increasing concentration of K<sup>+</sup> in the pore waters is therefore established, from phillipsite → phillipsite + merlinoite → merlinoite → K-feldspar, with increasing depth. KEV-EX energy dispersive spectra show the phillipsite and merlinoite crystals to be composed of only K, Na, Al, and Si. Spectra of the coexisting phillipsite and merlinoite in the 134.5-ft sample indicate that their Si/Al ratios are approximately the same, but that the merlinoite has a higher potassium content and a lower sodium content than the phillipsite. The merlinoite in the 138-ft sample is more potassium-rich than that in the 134.5-ft sample, supporting the hypothesis that the authigenic silicate zonation pattern may be partly the result of increasing K<sup>+</sup> concentration in the pore waters with depth.



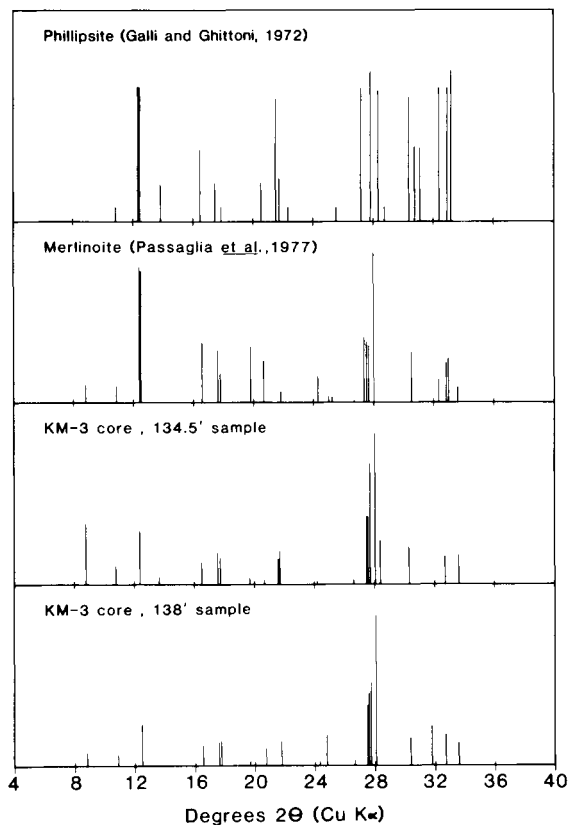


Figure 6. X-ray powder diffraction patterns of KM-3 core samples and natural phillipsite and merlinoite.

It is important to note that most of the major studies of zeolites in sedimentary rocks were conducted before the existence of merlinoite was discovered. Based on the discovery of merlinoite in the tuffaceous sediments of Searles Lake, it is suggested that a second look at other reported phillipsite occurrences is warranted. Merlinoite and phillipsite form under similar, but distinct physiochemical conditions. The presence or absence of these minerals may help to decipher the chemical evolution of the pore waters from which they precipitated.

#### ACKNOWLEDGMENTS

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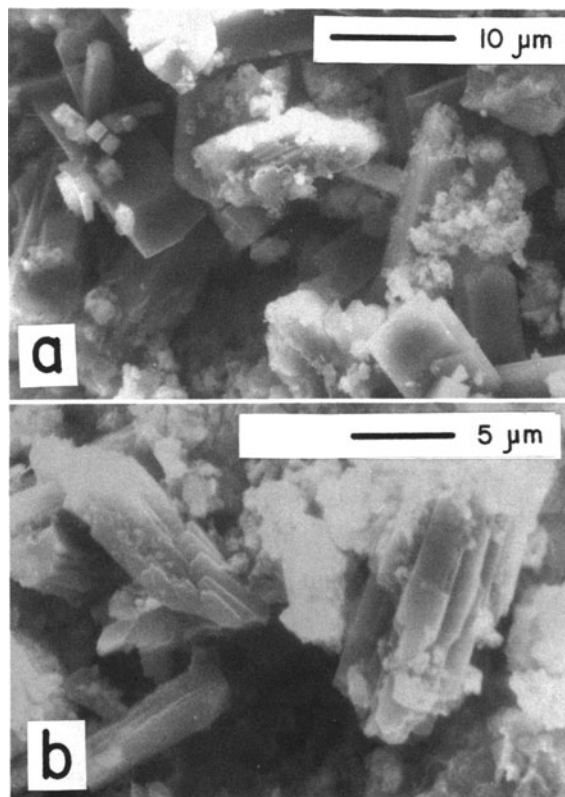


Figure 7. Electron micrographs showing (a) phillipsite with coexisting merlinoite crystals from 134.5-ft sample, and (b) merlinoite crystals from 138-ft sample, drill core KM-3.

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**Резюме**—Цеоциты, имеющие структуры филлипсита, мерлиноита и гоббинсита, синтезировались из чистых растворов при 80°C в системе  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ . Определялись морфологии, параметры ячейки и состав этих материалов. При концентрации кремнезема равной 3,5 М, образование мерлиноита (синтетического филлипсита W) происходило легче, чем образование филлипсита (синтетического цеолита ZK-19) в условиях раствора при высоком pH (>13,6) и низких (<0,5) отношениях  $\text{Na}/(\text{Na} + \text{K})$ .

На основании информации, полученной из экспериментов синтеза, предсказывалось присутствие мерлиноита в осадках из озера Сирлез, соленого, щелочного озера в Калифорнии, имеющего идеальные физико-химические условия для формирования мерлиноита. Впоследствии мерлиноит образовался в туфовых осадках как составляющая аутогенного порядка кремнеземных зон с увеличивающейся глубиной: филлипсит → филлипсит + мерлиноит → мерлиноит → K-фельдшпат. В результате подобия физических свойств филлипсита и мерлиноита, мерлиноит может быть более общим аутогенным минералом, чем представлено в настоящее время. [E.G.]

**Resümee**—Zeolithe mit den Strukturen von Phillipsit, Merlinoit, und Gobbinsit wurden aus klaren Lösungen bei 80°C im System  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  synthetisiert, und ihre Morphologie sowie ihre Zellparameter und ihre chemische Zusammensetzung bestimmt. Bei einer 3,5 m  $\text{SiO}_2$ -Konzentration wird die Bildung von Merlinoit (synthetisch Zeolith W) im Vergleich zur Zildung von Phillipsit (synthetisch Zeolith ZK-19) bevorzugt, wenn der pH-Wert der Lösung hoch ist (>13,6) und die  $\text{Na}/(\text{Na} + \text{K})$ -Verhältnisse niedrig sind (<0,5).

Aufgrund der aus den Syntheseexperimenten gewonnenen Ergebnisse wurde das Auftreten von Merlinoit in den Sedimenten vom Searles Lake, einem salinen, alkalihaltigen See in Kalifornien, vorausgesagt, der ideale physikochemische Bedingungen für die Bildung von Merlinoit aufweist. Daraufhin zeigte sich, daß Merlinoit in tuffhaltigen Sedimenten als ein Teil einer authigenen zonalen Verteilung der Silikate auftritt und zwar mit zunehmender Tiefe: Phillipsit → Phillipsit + Merlinoit → Merlinoit → K-Feldspat. Wegen der sehr ähnlichen physikalischen Eigenschaften von Phillipsit und Merlinoit dürfte Merlinoit als authigenes Mineral weitaus verbreiteter sein als man bisher annimmt. [U.W.]

**Résumé**—On a synthétisé des zéolites ayant les structures de la phillipsite, la merlinoite et la gobbsite à partir de solutions claires à 80°C dans le système  $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  et on a déterminé leurs morphologies, leurs paramètres de maille, et leurs compositions. A une concentration de silice de 3,5 M, la formation de merlinoite (zéolite synthétique W) est favorisée vis à vis de la formation de phillipsite (zéolite synthétique ZK-19) sous des conditions de solutions de pH élevé (> 13,6) et des proportions Na/(Na + K) basses (< 0,5).

En employant l'information obtenue des expériences de synthèse, on a prédit la présence de merlinoite dans des sédiments de Searles Lake, un lac salin, alcalin, en Californie avec des conditions physicochimiques idéales pour sa formation. On a subséquentement découvert que la merlinoite se trouvait dans des sédiments tuffacés en tant que partie d'une séquence de zone silicate authigénique de la phillipsite → phillipsite + merlinoite → merlinoite → feldspar K, en proportion avec la profondeur. A cause des similarités très proches des propriétés physiques de la phillipsite et de la merlinoite, la merlinoite pourrait être beaucoup plus commune en tant que minéral authigénique que l'on ne se rendait compte jusqu'à présent. [D. J.]