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MINERALOGICAL NOTES

SYNTHESIS OF A CLINOPTILOLITE-LIKE ZEOLITE[1]

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INTRODUCTION

Much hydrothermal work has already been done in systems that produce zeolitic phases. Barrer and White (1951) previously investigated the system lithia-alumina-silica-water between the silica-to-alumina ratios of 1 to 10 at temperatures of 150° C. to 450° C. Aluminum hydroxide, lithium hydroxide and silicic acid were used as starting materials. All experiments were performed with an excess of lithium hydroxide. Barrer and Baynham (1956) reported results of an investigation into the high-silica portion of the system potash-alumina-silica-water. Barrer (1948) also reported results of his investigations into the high-silica portion of the system soda-alumina-silica-water, and noted that a pH of 8 to 10 was associated with the higher mordenite yields.

The purpose of the present study was to investigate portions of the high-silica, zeolitic or relatively low temperature region of several base cation systems. During the course of this study, a clinoptilolite-like phase was synthesized. The data pertinent to the synthesis of the clinoptilolite-like phase are presented here.

METHODS OF INVESTIGATION

Starting materials used in the hydrothermal syntheses included Davison Silica Gel, silicic acid, lithium hydroxide, sodium hydroxide, potassium hydroxide, dried aluminum hydroxide and silica and alumina gels co-precipitated from mixed solutions of sodium metasilicate and sodium aluminate. The Davison Silica Gel, hereafter referred to as silica gel, was supplied for use as a drying agent in a 14 to 40 mesh size range. Consequently, the 14 to 40 mesh gel was ball-milled to pass through a minus 325 mesh sieve prior to use. A chemical analysis of a typical sample of silica gel is given in Table 1, and a photomicrograph of the sieved gel is shown in Fig. 1. The state of hydration of the lithium hydroxide was determined by *x*-ray diffraction.

The constituents were added in the desired mole ratios and thoroughly mixed in a blender. The mixed starting material was placed in a 20 ml, silver-lined, Morey-type reactor and raised to the desired temperature in a furnace. The reactor was immediately quenched in cold water upon removal from the furnace. The pH of the remaining water soluble contents

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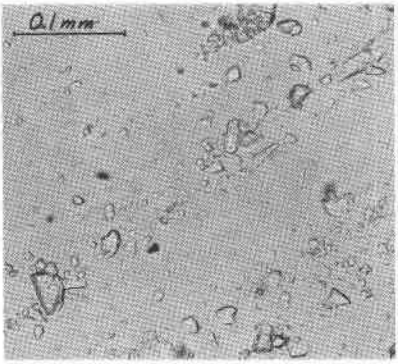
TABLE 1. TYPICAL CHEMICAL ANALYSIS OF DAVIDSON SILICA GEL

Constituent	Weight %
SiO_2	99.71
Fe_2O_3	0.03
Al_2O_3	0.10
TiO_2	0.09
CaO	0.01
Na_2O	0.02
ZrO_2	0.01
	99.97

was determined at 25° C. Readings higher than pH 10 were of little interest and were recorded as merely greater than 10. Insoluble final products were washed with distilled water, air-dried, and examined by *x*-ray diffraction and with the petrographic microscope. Photomicrographs were taken of some of the final products.

RESULTS AND DISCUSSION

Table 2 summarizes the hydrothermal experiments used to define the conditions of formation of the clinoptilolite-like phase in the system lithia-alumina-silica-water. Three starting mixtures were used with similar results, although reaction rates were not comparable. The silica gel-



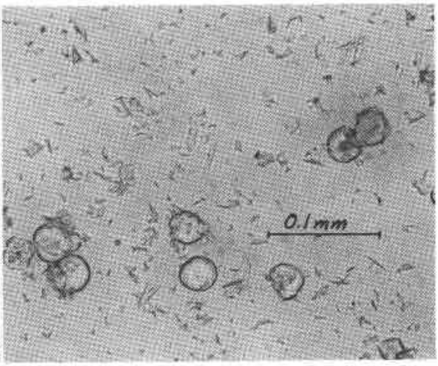


FIG. 1. *Left:* Photomicrograph of Davison Silica Gel used as a starting material for many of the hydrothermal syntheses.

FIG. 2. *Right:* Photomicrograph of mordenite (bladed crystals) and analcime (spheroids) grown from the starting composition $8SiO_2\cdot Al_2O_3\cdot Na_2O\cdot 8.5H_2O$. Silica gel, dried $Al(OH)_3$ and NaOH were used as starting materials at 293° C. for 2 days. Final pH of the equilibrium solution was 7.8 at 25° C.

TABLE 2. HYDROTHERMAL DATA FOR THE HIGH-SILICA PORTION OF THE LITHIA-ALUMINA-SILICA WATER SYSTEM

Composition of Starting Materials. (Silica Gel, dried $Al(OH)_3$, $LiOH \cdot H_2O$)$SiO_2/Al_2O_3/Li_2O/H_2O$	Temp., ° C.	Estimated Pressure, psi	Duration, days	Final Products	Final pH 25° C.
6/1/0.5/8.5	293	1150	3	Little crystallization	>10
8/1/0.6/8.5	293	1150	2	Clinoptilolite-like phase	7.6
8/1/1/8.5	285	1000	5	Clinoptilolite-like phase	7.1
8/1/1.5/8.5	270	800	3	Clinoptilolite-like phase	8.6
8/1/2/8.5	254	625	3	Clinoptilolite-like phase	7.5
8/1/3/8.5	254	625	2	"Species A" plus quartz	10.0
10/1/1/8.5	285	1000	5	Clinoptilolite-like phase	8.7
10/1/1/8.5	304	1350	3	Clinoptilolite-like phase	8.2
10/1/1/8.5	357	2500	2	Some petalite	10.0
14/1/1/8.5	298	1200	2	Little crystallization	>10
14/1/1.5/8.5	298	1200	2	Clinoptilolite-like phase plus quartz	8.4
18/1/1/8.5	298	1200	2	Little crystallization	>10
18/1/1.5/8.5	298	1200	2	Clinoptilolite-like phase plus quartz	7.7
(Ethyl orthosilicate, calcined nitrates) $SiO_2/Al_2O_3/Li_2O/H_2O$					
8/1/1/8.5	295	1160	3	Clinoptilolite-like phase	7.4
(Silicic acid, dried $Al(OH)_3$, $LiOH \cdot H_2O$) $SiO_2/Al_2O_3/Li_2O/H_2O$					
8/1/1/8.5	300	1250	4	Clinoptilolite-like phase	7.5
8/1/1/8.5	260	700	3	Little crystallization	9.0

dried aluminum hydroxide-lithium hydroxide mixture reacted most rapidly, calcined nitrates and ethyl orthosilicate were next, and silicic acid-dried aluminum hydroxide-lithium hydroxide mixture was the slowest to react. Compositions containing silica to alumina ratios as high as 18 yielded the clinoptilolite-like phase with the silica gel-dried aluminum hydroxide-lithium hydroxide starting mixture. Note that the final pH of the water soluble contents of the reactor is generally indicative of the degree of the reaction that has occurred; *i.e.*, if the lithium hydroxide has reacted, lithium cations are removed from the equilibrium solution and the pH is lowered.

Other experiments with various starting mixtures and compositions are listed in Table 3. Starting with sodium-or potassium-containing systems, no clinoptilolite-like phases were synthesized. Products included mordenite, analcime, quartz and chabazite. Chabazite was previously reported in the system potash-alumina-silica-water by Barrer and Baynham (1956). Figure 2 shows mordenite and analcime crystals synthesized from the silica gel-dried aluminum hydroxide-lithium hydroxide starting mixture. The appearance of the mordenite crystals is similar to that reported by Barrer (1948). Several hydrothermal experiments with mixed-base starting materials consisting of silica gel, dried aluminum hydroxide, lithium hydroxide and NaOH yielded only mordenite. The clinoptilolite-like phase was not stable in a system containing both lithium and sodium. The mordenite crystals synthesized in the above lithium-and sodium-containing system exhibited an unusual growth habit of radial clusters as shown in Fig. 3. The clinoptilolite-like phase was examined further to establish that it was a clinoptilolite-like phase, and not a heulandite-like or mordenite-like phase. Figure 4 compares the *x*-ray diffraction pattern tracings of an Oregon clinoptilolite (Fisher, 1962), the clinoptilolite-like phase of this study, a natural heulandite and a synthetic mordenite. There are many similarities and differences in the four *x*-ray diffraction tracings. The Oregon clinoptilolite and synthetic clinoptilolite-like phase are, for all practical purposes, the same pattern. The differences between the position of the reflections for heulandite and clinoptilolite are nil, but the differences in reflection intensities are marked, as previously reported by Ames, *et al.* (1958) and Mumpton (1960). However, preferred orientation of the heulandite causes much of the intensity difference. Mordenite can be distinguished from clinoptilolite rather easily on the basis of differences in their *x*-ray diffraction patterns (Ames *et al.*, 1958). Shepard (1961) has reported on the results of a heat-treatment method for distinguishing clinoptilolite, which is stable to about 750° C. in air (Mumpton, 1960), and heulandite-like zeolites. Heating heulandite or heulandite-like minerals to 400° C. for 10 minutes resulted

TABLE 3. HYDROTHERMAL DATA FOR THE HIGH-SILICA PORTION OF SEVERAL RELATED SYSTEMS

Composition of Starting Materials (Co-precipitated gels, NaOH) $SiO_2/Al_2O_3/Na_2O/H_2O$	Temp., ° C.	Estimated Pressure, psi	Duration, days	Final Products	Final pH 25° C.
8/1/0.5/8.5	245	520	2	Little crystallization	>10
8/1/1/8.5	254	625	2	Mordenite plus analcime	8.8
8/1/1.5/8.5	293	1150	2	Analcime	>10
(Silica gel, dried $Al(OH)_3$, NaOH) $SiO_2/Al_2O_3/Na_2O/H_2O$					
8/1/0.5/8.5	245	560	2	Little crystallization	>10
8/1/1/8.5	293	1150	2	Mordenite plus analcime	7.8
8/1/1.5/8.5	293	1150	2	Analcime	>10
10/1/1/8.5	293	1150	2	Mordenite	8.5
(Silica gel, dried $Al(OH)_3$, NaOH, $LiOH \cdot H_2O$) $SiO_2/Al_2O_3/Na_2O/Li_2O/H_2O$					
10/1/0.5/0.5/8.5	295	1160	3	Little crystallization	9.5
10/1/1/1/8.5	295	1160	2	Mordenite	7.7
(Silica gel, dried $Al(OH)_3$, KOH) $SiO_2/Al_2O_3/K_2O/H_2O$					
8/1/1/8.5	293	1150	3	Quartz plus chabazite	6.7
10/1/1/8.5	227	400	3	Little crystallization	>10

in the appearance of an x-ray diffraction peak at 8.35 Å, typical of heulandite "B" (Mumpton, 1960). Shepard's results were duplicated in this laboratory with clinoptilolite and heulandite.

Heat-treatment of the clinoptilolite-like phase of this study for as long as one hour failed to produce an 8.35 Å heulandite B diffraction peak. No structural changes were noted on x-ray diffraction patterns when the clinoptilolite-like phase was heated to 600° C. It is concluded from these results that the presumed clinoptilolite-like phase is not a heulandite-like phase.

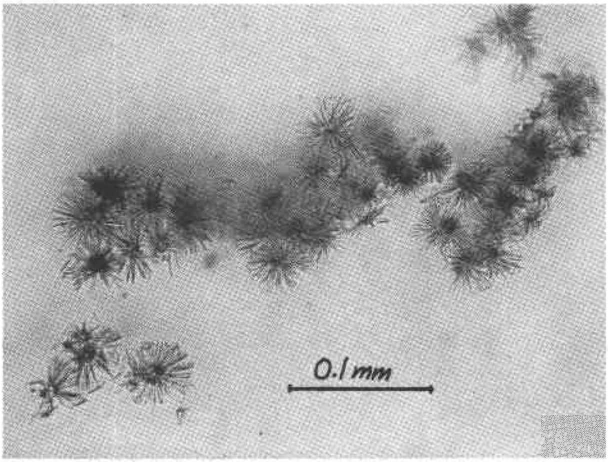


FIG. 3. Photomicrograph of mordenite in an unusual crystal habit (radiating groups) grown from the starting composition $10SiO_2 \cdot Al_2O_3 \cdot Na_2O \cdot Li_2O \cdot 8.5H_2O$. Co-precipitated alumina and silica gels, $LiOH \cdot H_2O$ and NaOH were used as starting materials at 254° C. for 2 days. Final pH was 8.5 at 25° C.

The acid stability of a synthetic mordenite (Norton Zeolon), natural clinoptilolite and the synthetic clinoptilolite-like phase were compared by placing samples of each, at 25° C., in 50 per cent HCl for 24 hours. Aluminum was detected in the HCl from all samples, but the x-ray diffraction pattern of the synthetic mordenite was essentially unchanged. The x-ray diffraction patterns of the natural clinoptilolite and synthetic, clinoptilolite-like phase showed that in both cases degradation was slowly occurring. From a consideration of differences in the x-ray diffraction patterns, and in acid stabilities, the synthetic, clinoptilolite-like phase of this study is not a mordenite. All physical and chemical characteristics identify the phase as clinoptilolite-like.

Caution is always indicated when attempting to extrapolate laboratory

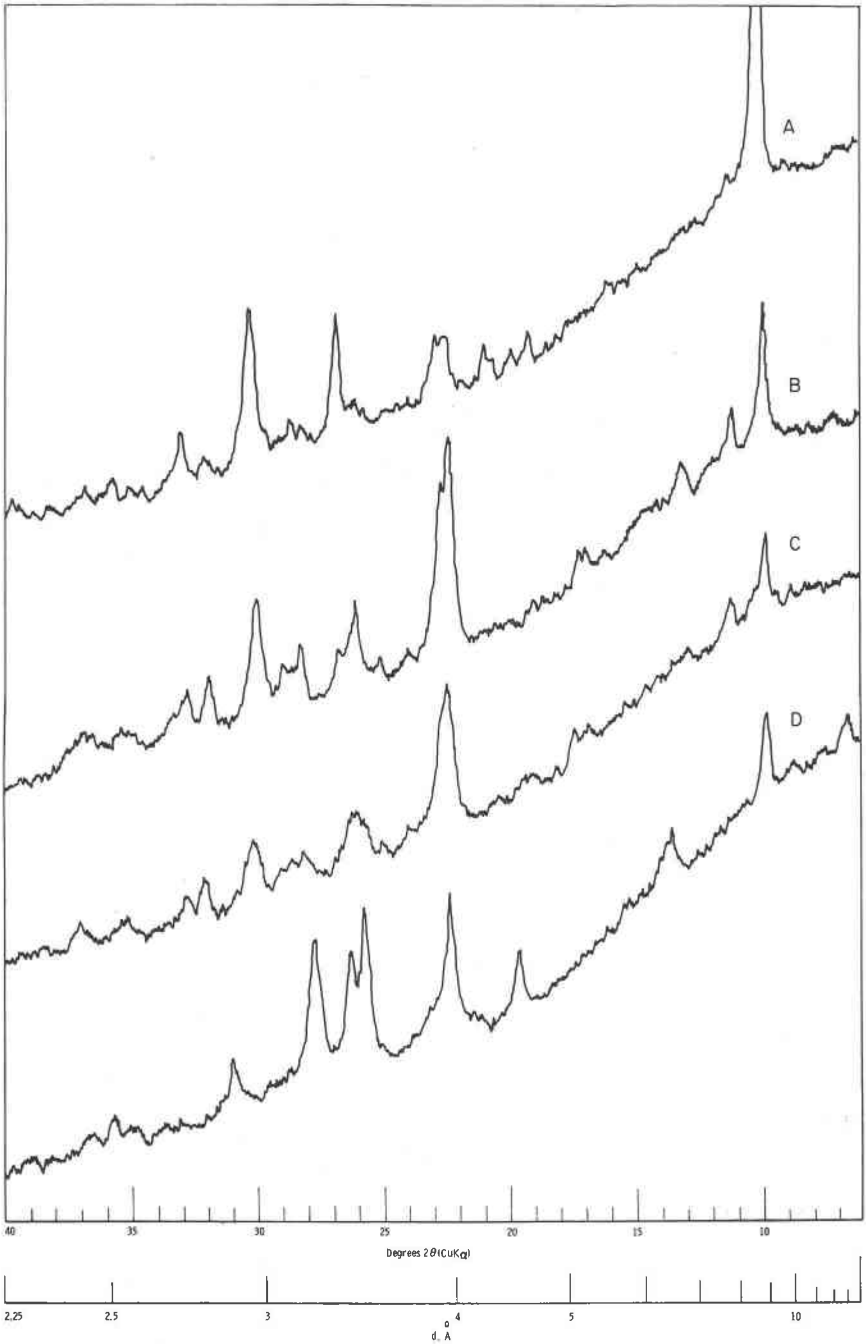


FIG. 4. *X*-ray diffraction pattern tracings of (A) natural heulandite, (B) sodium-based Oregon clinoptilolite, (C) the synthetic, sodium-based, clinoptilolite-like phase, and (D) a synthetic, sodium-based mordenite.

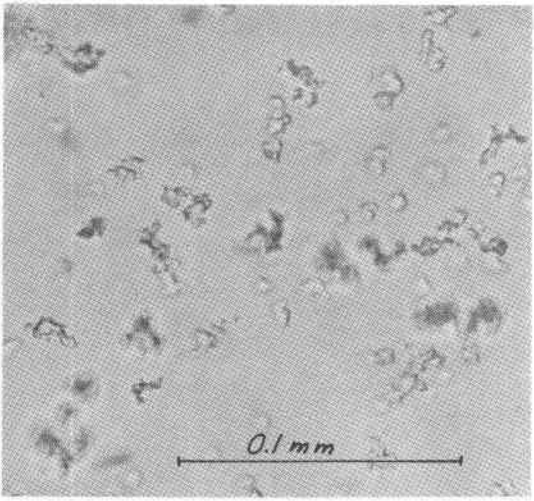


FIG. 5. Photomicrograph of the synthetic, clinoptilolite-like phase grown from the starting composition $8SiO_2 \cdot Al_2O_3 \cdot Li_2O \cdot 8.5H_2O$. Silica gel, dried $Al(OH)_3$ and $LiOH \cdot H_2O$ were used as starting materials at 285° C. for 5 days. Final pH of the equilibrium solution was 7.1 at 25° C.

hydrothermal results to natural systems (Coombs *et al.*, 1959). Perhaps we may conclude, however, that if clinoptilolite and mordenite co-exist, the natural assemblage has not reached equilibrium. Mordenite is apparently the stable phase in sodium-containing systems.

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THE CLEAVAGES OF BeO AND OTHER MINERALS HAVING THE WURTZITE STRUCTURE[1]

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In the course of studies on the mechanical properties of minerals having the wurtzite structure, cleavages were encountered which were in disagreement with those described by Palache *et al.* (1944, Vol. I) and more recently by Wolff and Broder (1959, 1960). A re-examination of the cleavage behavior was undertaken on single crystals of five wurtzite-type compounds by orienting and embedding them in Canada balsam and subjecting them to percussion normal to the base and again normal to the prism. In each case the pattern of cracks radiating outwards from the point of impact was examined under the microscope at magnifications up to 1000×. In general, a particular crack was found to follow a curving path with discontinuities in course which indicated preferred directions of fracture. The angular bearings of these preferred directions were tabulated and plotted together with the traces of the crystal faces indexed by *x*-ray diffraction. The cleavages inferred from such data for the several compounds are listed in Table 1 together with published data for comparison.

The most striking result centers around the $\{11\bar{2}0\}$ cleavage which appeared in all of the crystals examined. In ZnS(H) it is the dominant cleavage, as Palache *et al.* also note, without, however, observing the second prismatic cleavage $\{10\bar{1}0\}$. Wolff and Broder, on the other hand, finding only one of the prismatic cleavages in ZnS(H), described it as $\{10\bar{1}0\}$, but did not explain how they indexed it. In all of the other minerals, the order of the prismatic cleavages is reversed, the $\{10\bar{1}0\}$ being much easier than the $\{11\bar{2}0\}$, which Palache *et al.* do not mention at all, but which Wolff and Broder observe in every case but that of zincite.

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[1] Work was performed under the auspices of the U. S. Atomic Energy Commission.