

SYNTHESIS OF SILICEOUS MORDENITES

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ABSTRACT

The zeolite mordenite has been synthesized in a siliceous form containing up to nearly twice the normal silica content. Synthesis appears dependent on use of aluminosilicate gel prepared by reacting sodium silicate with aluminum chloride solutions. The $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of the resultant mordenite depends systematically on the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of the reacting mixture.

Zeolites are hydrated aluminosilicates with open, wide-meshed frameworks composed of SiO_4 and AlO_4 tetrahedra. To balance the negative charge of the framework, cations (usually alkalis or alkaline earths) are contained. Because of their highly adsorbent nature, much interest in these materials has developed in the past two decades as desiccants, catalysts, adsorbents, and ion exchangers. Excellent reviews have been written by Barrer (1964) and Breck (1964). Two volumes have been recently published containing 77 papers on these silicates (Gould, 1971).

Many have studied the synthesis of zeolites to the extent that most of the natural forms have been made. In addition, a number of new synthetic zeolites have been discovered, some which have no similar form in nature.

The stoichiometry of most zeolites, both natural and synthetic, has been found to be within narrow limits with regard to the $\text{SiO}_2:\text{Al}_2\text{O}_3$ molecular ratio of the framework. The composition of the exchangeable cations and the adsorbed water can vary considerably depending on the chemical and thermal history of the sample. Variations in the patent references have shown the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios for several of the synthetic zeolites as: type X: 2.0-3.0; type Y: 3-6; type A: 1.35-2.35; type O: 12.15-12.25; type ZK-4: 2.5-4.0. Of these, type Y shows the greatest range, and Breck (1964) and Jenkins (1970) describe methods for preparation of this faujasite-type zeolite with $\text{SiO}_2:\text{Al}_2\text{O}_3$ molecular ratios above 4.5.

Saha (1959) synthesized analcime with $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratios from 3 to 6 from glasses of a wide range of composition. Later, Coombs and Whetten (1967) studied many analcime samples throughout the world and determined $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios varying from 4 to 5.6. These works illustrate the coupling of laboratory syntheses with studies of natural minerals to obtain knowledge of geochemical processes.

The zeolite mordenite is mainly constructed of parallel tubes or channels enclosed by 8- and 12-membered rings of SiO_4 and AlO_4 tetrahedra. The structure was determined by Meier (1961) and is represented in Figure 1. The unit cell content is $\text{Na}_8 (\text{AlO}_2)_8 (\text{SiO}_2)_{40} \cdot 24 \text{H}_2\text{O}$. Mordenite was first synthesized by Barrer (1948) who later found (1959) that, using gels as starting material, temperatures of at least 250°C and $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios of at least 12 were required. He used rather high relative water contents, with the $\text{H}_2\text{O}:\text{Al}_2\text{O}_3$ ratio estimated to be several hundred. Ames and Sand (1958) synthesized sodium mordenite in 1 to 2 days at 200 to 300°C from gels. These earlier studies resulted in zeolites with openings of only about 4 Å, which are about the same size as are present in natural mordenites. In 1961, Sand (1961) succeeded in synthesizing mordenite with openings of about 8 Å, thus conforming to Meier's structure. It has been proposed that the smaller pore openings in natural and previously prepared mordenites are due to stacking faults in the structure (Meier, 1961) or to amorphous material clogging the long tubular pores (Sand, 1967). All of these previous methods of preparation resulted in mordenites with $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios ranging from about 9 to 11.

This paper describes methods by which mordenites with $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratios of from 12 to 19.5 have been prepared. These are not to be confused with aluminum-deficient mordenites prepared by subsequent acid-leaching such as described by Kranich *et al.* (1971).

The synthetic zeolites were prepared by heating various mixtures at 184°C for 16 hours in small silver lined autoclaves. The principal part of each mixture was a hydrous aluminum silicate gel prepared by reacting dilute sodium silicate solution with dilute aluminum chloride solution which had additional hydrochloric acid added to provide about 10 percent excess chlorine over that required by the sodium. The gels were washed thoroughly with water and dried and analyzed on a mole basis, as follows:

Gel A — $0.06 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 13.1 \text{SiO}_2 \cdot 4.3 \text{H}_2\text{O}$

Gel B — $0.11 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 10.1 \text{SiO}_2 \cdot 15.3 \text{H}_2\text{O}$

Gel C — $0.03 \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 15.5 \text{SiO}_2 \cdot 45.2 \text{H}_2\text{O}$

Mixtures for autoclaving were prepared from the gels together with sodium silicate solution, sodium hydroxide and water to provide an increasing $\text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio as shown in Table 1. After autoclaving, the mixtures were washed thoroughly with water, dried, chemically analyzed, and crystallographically analyzed by X-ray diffraction.

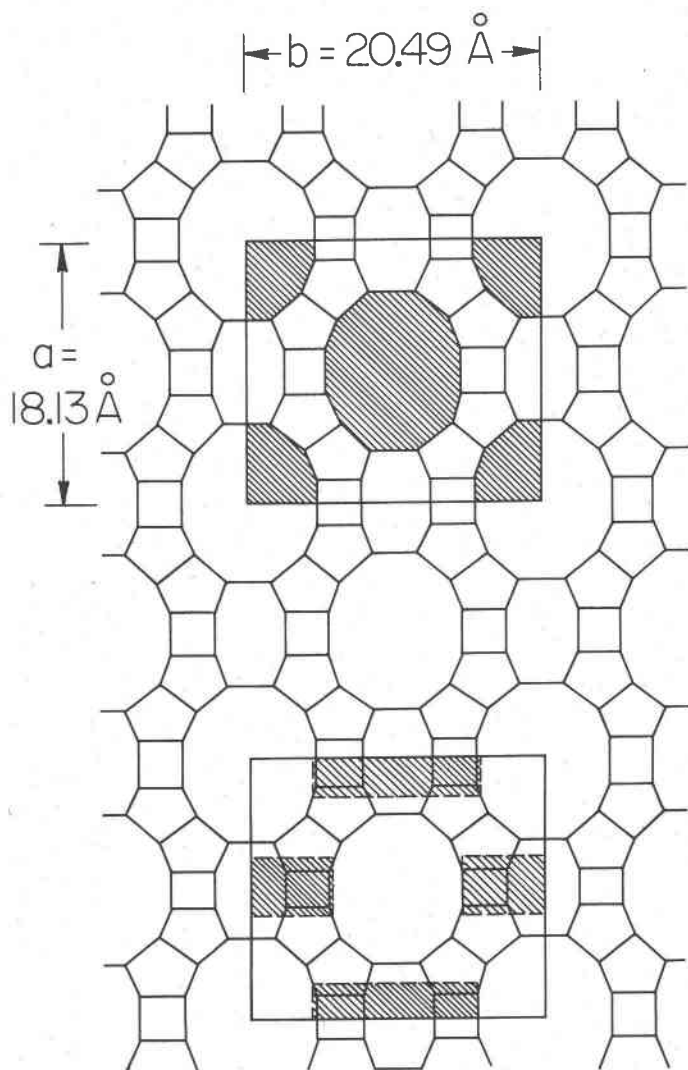


FIG. 1. Mordenite cross section diagram. The lines represent oxygen atoms and the points of intersection represent silicon or aluminum atoms. The cross hatching in the upper unit cell represents the major tubular pores. The cross hatching in the lower unit cell represents smaller cavities normal to the tubes and occurring at intervals.

Since the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of both natural mordenite and previously synthesized forms had always been near 10, the possibility of these samples being mixtures of mordenite with amorphous silica was investigated. The net intensities of six reflections, (150), (241), (002), (202), (060), and (530), obtained by Geiger counter scans of copper X-radiation, were summed for each sample and compared with the average of two well-crystallized samples of $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio of 10. Using the latter as unity, the summed relative net intensities of the samples were: (1) 1.10, (2) 1.08, (3) 1.08, (4) 1.14, and (5) 1.34. In all cases, the crystallinity of these samples was superior as judged by X-ray diffraction. Unlabelled samples were submitted to a skilled petrographer who stated that the high silica samples appeared more crystalline than those of the 10 mole ratio.

Crystallinity did diminish when higher $\text{SiO}_2:\text{Al}_2\text{O}_3$ mixtures were reacted, indicating a maximum product mole ratio of 20 $\text{SiO}_2:\text{Al}_2\text{O}_3$.

The species of zeolite which will appear in this type of synthesis is dependent on the chemical composition including water content, temperature, time, impurities, and type of reactant. Breck (1964) discusses these parameters and shows a quaternary reaction diagram for $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ at 100°C and at 90 to 98 mole percent H_2O . These show that the compositions of the zeolites *A*, *B*, and *X* which form in this system are only on the corners of the reactant composition areas. Regis *et al.* (1960) showed in a phase study at 100°C that under certain conditions some zeolites are transitory, converting to other species in time.

In this study the water content was held at about 77 mole percent, the temperature at 184°C and the time at 16 hours. The reaction mixtures were in the range of $(10 + a)\text{Na}_2\text{O} \cdot (3 + a)\text{Al}_2\text{O}_3 \cdot (87 - a)\text{SiO}_2$ where $0 < a < 3$, which defines a line paralleling the zeolite composition line projected on the anhydrous ternary diagram. The resultant zeolite compositions followed the relationship $p = 2.8 + 0.62 r$ where $p = \text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio of the zeolite product and $r = \text{SiO}_2:\text{Al}_2\text{O}_3$ mole ratio of the reaction mixture. No special significance is claimed for these relationships except to show that zeolite synthesis does obey systematic but complex parameters.

It is difficult to visualize the crystallization of these complex minerals as compared with the one to one deposition of Na and Cl during the formation of halite. Barrer (1959) said "The development of elaborate and continued space patterns by progressive additions of single (Al, Si) O_4 tetrahedra is difficult to imagine, particularly in the case of very open zeolite structures. The formation of these frameworks is, however, much more easily visualized if the aqueous crystal-

Table 1.
Stoichiometry of Reacting Mixtures and Resultant Zeolites

Sample	Gel	Reactant Mixture			Zeolite Product	
		SiO ₂ :Al ₂ O ₃	Na ₂ O:SiO ₂	H ₂ O:SiO ₂	SiO ₂ :Al ₂ O ₃	Na ₂ O:SiO ₂
1	A	15.1	0.16	4.1	12.0	0.09
2	B	18.4	0.14	4.0	14.4	0.07
3	C	18.4	0.14	4.0	14.8	0.06
4	C	21.3	0.12	4.1	16.0	0.06
5	C	25.6	0.12	4.6	18.1	0.05
6	C	25.6	0.12	4.6	19.5	0.05

lizing magma there are secondary building blocks in the form of rings of tetrahedra, or polyhedra. These may pack in various simple coordinations to yield different aluminosilicates."

The smallest polyhedra in the mordenite structure (see Figure 1) are four- and five-membered rings of tetrahedra. These link to enclose eight-membered and twelve-membered rings. In normal mordenite, only one AlO₄ tetrahedron could occur in a trio of two five-membered rings and one four-membered ring. In the twelve-membered ring only two AlO₄ tetrahedra could occur. It appears that in the zeolites of this work that the twelve-membered ring may contain only one AlO₄ tetrahedron. However, this is the minimum since higher SiO₂:Al₂O₃ ratios could not be achieved.

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Manuscript received, February 14, 1972; accepted for publication, April 9, 1972.