

CATION SIEVE PROPERTIES OF THE OPEN ZEOLITES
CHABAZITE, MORDENITE, ERIONITE AND
CLINOPTILOLITE

L. L. AMES, JR., *General Electric Company, Richland, Washington.*

ABSTRACT

The partial cation sieve properties of the "open" zeolites chabazite, mordenite, erionite and clinoptilolite were studied in an effort to determine the mechanism responsible for the type and intensity of the observed cation replacement series. It was found that neither the hydration state of the cations before entering the zeolite structure nor relative loading rates had any significant effect on the type or intensity of alkali metal or alkaline earth metal cation replacement series. Molten salt experiments with Cs₁₃₇-containing zeolites demonstrated that at higher temperatures the normal hydrated type replacement series could be reversed to a coulombic replacement series without destruction of the aluminosilicate framework. The above results were interpreted as being caused by the presence or absence of structural water. Additional stereochemical studies are necessary to determine the details of the mechanism.

INTRODUCTION

There are at least three mechanisms responsible for the cation sieve properties exhibited by natural zeolites. One such mechanism is the positive exclusion of certain cations due to the inability of these larger cations to enter the zeolite lattice in significant amounts. The sieve effect shown by analcite for Cs⁺ is an example of such an exclusion based on cation size (Barrer, 1950).

A second mechanism for a cation sieve effect is the inability of the negative charge distribution on the zeolite structure to accommodate a given cation. An example of this mechanism is given in the difficulty of obtaining calcium or barium-rich analcites (Barrer, 1950) or sodium-rich heulandites (Mumpton, 1960) by cation exchange. Determination of a third mechanism constitutes the object of this paper. Only the so-called "open" zeolites, or those zeolites that can accept any of the alkali metal or alkaline earth metal cations, will concern us here. Examples of such zeolites are chabazite, mordenite, erionite and clinoptilolite. Knowledge of the mechanism that causes the cation sieve effects shown by these open zeolites may also assist in understanding the extreme cation selectivity of clinoptilolite.

To ascertain the cause or causes of the partial cation sieve action, the exchange kinetics of chabazite, mordenite and erionite were investigated. The cation sieve effects shown by clinoptilolite were reported previously (Ames, 1960).

PREVIOUS WORK

Barrer has done the bulk of the research on cation exchange properties of zeolites. General references concerning the cation exchange properties

of chabazite and mordenite include Barrer (1948, 1950), Barrer and Sammon (1955), and Barrer and Brook (1953). Dent and Smith (1958) reported on the crystal structure of chabazite. Barrer (1950) discussed the hydration factor in cation exchange in relation to ease of entry of the cation into the zeolite crystal, and mentioned that replacement order was the same from melts and aqueous solutions. Barrer (1958) also pointed out the unsolved problem of cation selectivity shown by the "open" zeolites that theoretically can accept all cations of the alkali metal and alkaline earth metal series. This same reference also reported the replacement series $Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2}$ for near sodium-based faujasite. Barrer and Raitt (1954) reported the replacement series $Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$ and $Mg^{+2} > Ca^{+2} > Ba^{+2}$ for silver-based ultramarine. Barrer and Falconer (1956) reported the replacement series $Na^{+} > K^{+} > Rb^{+} > Cs^{+}$ for silver-based cancrinite. Milligan and Weiser (1937) reported the dehydration characteristics of chabazite and several other zeolites.

METHODS OF INVESTIGATION

The exchange kinetics of chabazite, mordenite and erionite were investigated using methods previously described (Ames, 1960). Figure 1 is a diagram of the experimental apparatus used to determine cesium diffusion rates in sodium-based clinoptilolite and erionite particles and the effect of sodium on their cesium loading rates.

A half-gram sample of zeolite was placed into a coarse fritted glass

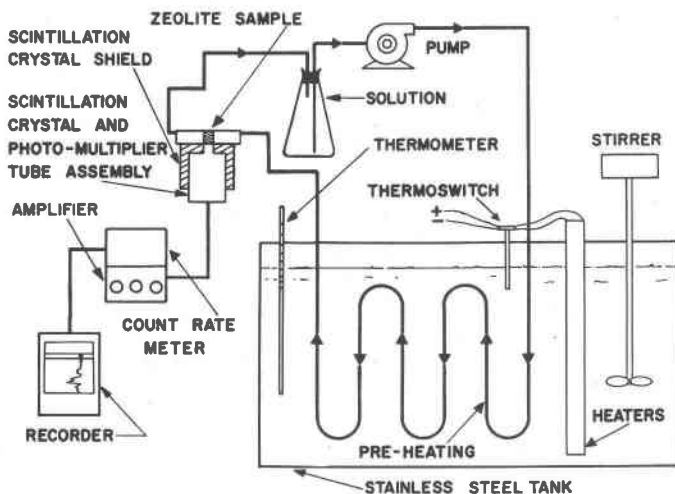


FIG. 1. Experimental apparatus used to obtain zeolite loading curves.

filter tube and held in position with Pyrex wool. This tube was then clamped in position over the top of the opening in the lead-lined crystal shield, connected onto the influent and effluent lines, and the pump started to circulate the solution through the zeolite sample at 7000 ml per hour. In addition to being 0.2 M CsCl, this influent solution contained sufficient Cs¹³⁷ to allow full cesium loading of the one-half gram zeolite sample while removing less than two per cent of the Cs¹³⁷ from solution. This solution was allowed to circulate through the zeolite overnight to obtain an equilibrium cesium capacity. Since these zeolites reached greater than 90 per cent capacity in 15 to 20 minutes, the assumption that equilibrium was reached in 10 to 15 hours is a valid one.

The count rate meter was adjusted to assure that equilibrium was reached for the highest capacity zeolite while the recorder remained on-scale. The apparatus was checked frequently with a standard Cs¹³⁷ source to insure that the recorder returned to the same relative position between experiments. Knowing the amount of CsCl corresponding to a given Cs¹³⁷ count, the loading curves per half gram of zeolite could be compared.

To study the diffusion of a cation pair within the zeolite particle or grain, three conditions are assumed to prevail: (1) that within the limits of experimental error (plus or minus two per cent), the concentration of the radioactivity in the influent equals that in the effluent, and that this condition does not change with increases in flow rate or concentration of exchanging cation, (2) that the zeolite particles are spherical and of known radius or surface area, and (3) that the specific diffusion rates of each cation of the pair are the same, a condition that is strictly valid only in the case of the exchange of one isotope for that of another isotope of the same element (Helfferich and Plesset, 1958). Boyd, *et al.* (1947) showed that the following expression should hold, given the above conditions,

$$F = \frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{e^{-n^2 B t}}{n^2}$$

where

F = the fractional approach to equilibrium loading,

$B = \frac{\pi^2 D_i}{r^2}$ = a specific reaction rate,

where

D_i = effective diffusion coefficient,

Q_t = particle loading at time t ,

Q_∞ = particle loading at time infinity, and

r = particle radius.

Reichenberg (1953) published values of Bt for corresponding F values. Plotting Bt vs. t yields a straight line of slope B . From B , the effective diffusion coefficient D_i may be computed. Given values of B at two different temperatures, the Arrhenius activation energy Ea , can be calculated from the modified Arrhenius equation,

$$\ln \frac{k_2}{k_1} = \frac{Ea(T_2 - T_1)}{RT_2T_1} \quad (\text{Daniels and Alberty, 1955}),$$

where

k_1 = a specific reaction rate at T_1 ,

k_2 = a specific reaction rate at T_2 and

R = the gas constant.

The effect of higher temperatures on the Cs^{137} distribution between zeolites and anhydrous melts was studied utilizing LiNO_3 and KNO_3 .

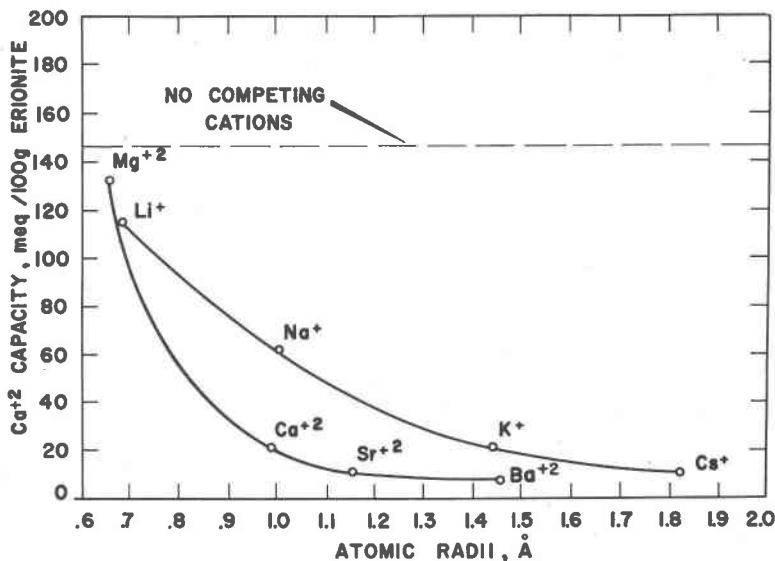


FIG. 2. The effect of competing cations on the calcium capacity of erionite. The point for calcium was obtained by adding sufficient Ca^{+2} to the original $0.01N$ Ca^{+2} to total $0.06N$ Ca^{+2} and computing the final 50 per cent breakthrough capacity on the basis of $0.01N$ Ca^{+2} . A similar procedure was followed when Cs^{137} rather than Ca^{45} was used as the tracing radioisotope.

Common influent solution $0.05N$ competing cations as indicated, $0.01N$ Ca^{+2} , $10,000$ Ca^{45} d/m/ml.

Common temperature 25°C .

Common influent pH 7.0

Common flow rate 473 ml./cm.²/hr.

Common column 25 g., 0.25 to 1.0 mm., sodium-based erionite

Initially, ten grams of the zeolite (1.0 mm. diameter grain size) were saturated with 0.01 *M* CsCl plus 5.0×10^{-8} *M* Cs¹³⁷, washed thoroughly with several volumes of distilled water, and dried at 105 C. One gram of this material was then placed in a platinum crucible with four grams of LiNO₃ or KNO₃ respectively. These crucibles were placed in a furnace for at least 24 hours at within plus or minus five degrees of the desired temperature. Upon termination of the experiment, a small portion of the molten salt was separated from the 1.0 mm. zeolite by decantation onto a cold, clean surface. This salt bead was then immediately weighed, dis-

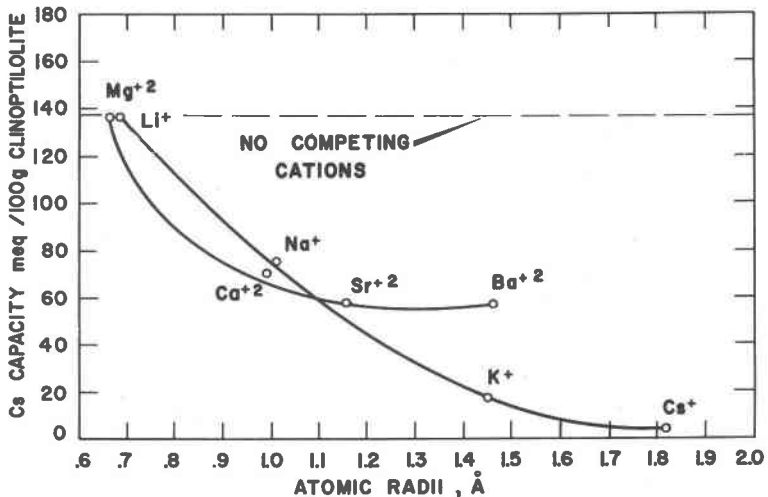


FIG. 3. The effect of competing cations on the cesium capacity of clinoptilolite.

Common influent solution	1.0 <i>N</i> competing cations as indicated, 0.01 <i>N</i> Cs ⁺ , 1.74×10^{-8} <i>N</i> Cs ¹³⁷
Common temperature	25° C.
Common influent pH	5.0
Common flow rate	294 ml./cm. ² /hr.
Common column	50 g., 0.25 to 1.0 mm., sodium-based clinoptilolite.

solved in a known volume of water and counted for Cs¹³⁷ on a gamma spectrometer. These results were reported as Cs¹³⁷ per gram of LiNO₃ or KNO₃ after correction for salt volatility at that temperature and length of heating time. The procedure followed in studies with Na²² was similar to that for Cs¹³⁷ except the zeolites were saturated with 0.01 *M* NaNO₃ plus 12.0×10^{-8} *M* Na²² after initial rinse with 3.0 *M* CaCl₂ solution. The zeolite samples were then washed from the remaining salt in the platinum crucible and an *x*-ray diffraction pattern obtained to be certain that the zeolite had remained structurally intact.

The clinoptilolite used in this study was obtained from the National Lead Company's Hector, California, deposits. The erionite was from Nevada, and the chabazite and mordenite were obtained from Ward's Natural Science Establishment. Both the mordenite and chabazite were originally from Nova Scotia. The purity of the erionite and clinoptilolite, as closely as could be ascertained, varied from 85 to 90 per cent. The chabazite and mordenite were hand-picked to greater than 95 per cent purity.

RESULTS

Figures 2, 3, 4 and 5 show the cesium capacities of erionite, clinoptilolite, mordenite and chabazite respectively, plotted vs. the atomic radii of

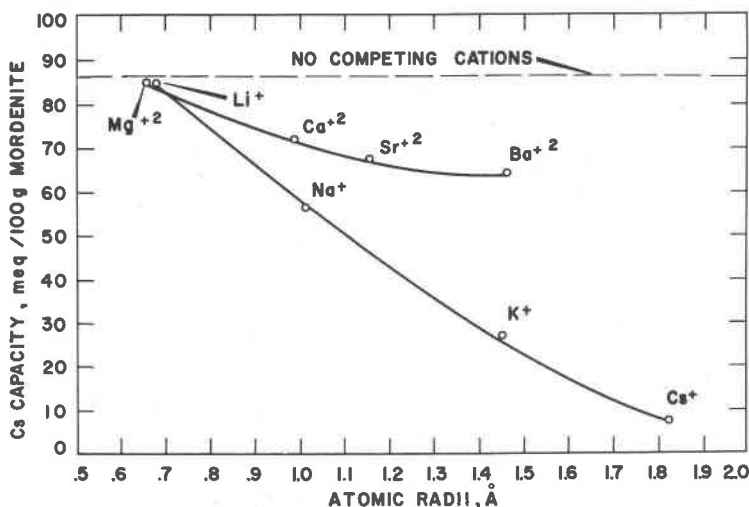


FIG. 4. The effect of competing cations on the cesium capacity of mordenite.

Common influent solution	0.01 <i>N</i> competing cations as indicated, 0.01 <i>N</i> Cs ⁺ , 1.74 × 10 ⁻⁸ <i>N</i> Cs ¹³⁷
Common temperature	25° C.
Common influent pH	7.0
Common flow rate	473 ml./cm. ² /hr.
Common column	50 g., 0.25 to 1.0 mm., sodium-based mordenite.

competing cations according to Green (1959). Two aspects of these data are noteworthy; first, the replacement series of all these open zeolites are quite similar, and second, the cation selectivities of these zeolites are highlighted by varying the amounts of competing cations from one to one hundred times the concentration of cesium.

Cesium loading curves were obtained both with and without the addi-

tion of competing sodium, utilizing the apparatus shown in Fig. 1. Figure 6 gives cesium loading curves for clinoptilolite with sodium concentrations of 0, 5, and 10 times that of cesium. Figure 7 represents comparable information for erionite. The curves of Figs. 6 and 7 cannot be used to compute specific reaction rates because the fractions of loading are not indicated. Figures 6 and 7 are useful, however, in showing that clino-

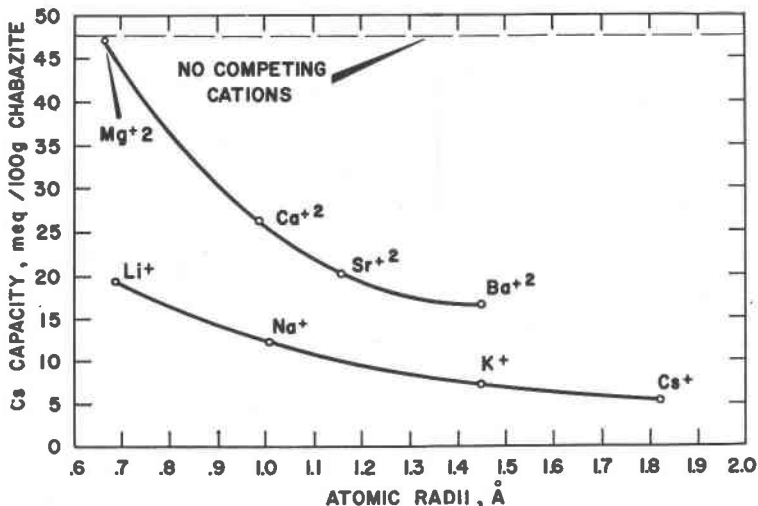


FIG. 5. The effect of competing cations on the cesium capacity of chabazite.

Common influent solution	0.01 <i>N</i> competing cations as indicated, 0.01 <i>N</i> Cs ⁺ , 1.74 × 10 ⁻⁸ <i>N</i> Cs ¹³⁷
Common temperature	25° C.
Common influent pH	7.0
Common flow rate	473 ml./cm. ² /hr.
Common column	50 g., 0.25 to 1.0 mm., sodium-based chabazite.

ptilolite tends to maintain a given cesium distribution between zeolite and solution despite an increasing sodium concentration.

Curves indicating fraction of loading may be used to compute specific reaction rates and diffusion coefficients for the cation exchange $\text{Na}^+ \rightleftharpoons \text{Cs}^+$. The specific reaction rates are determined from loading fraction values by plotting corresponding Bt values vs. t . The diffusion coefficients computed from the specific reaction rates are given in Table I. Differences in the cation selectivities between erionite and clinoptilolite are not caused by differences in diffusion coefficients.

For comparative purposes, most organic cation exchange resins yield D_i values of about 1×10^{-5} cm.²/sec., essentially aqueous diffusion (Boyd, Adamson and Myers, 1947). Diffusion through a solid would yield a

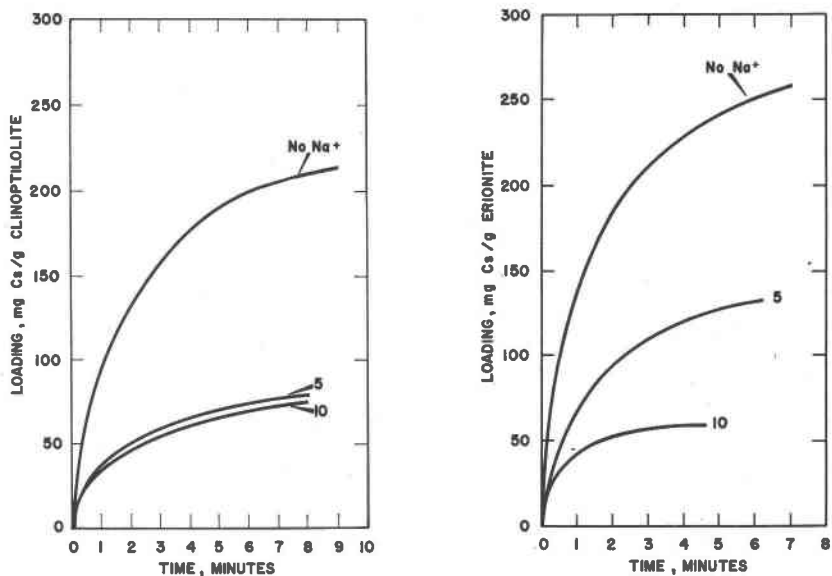


FIG. 6 (left). Cesium loading curves for clinoptilolite.

Common influent solution $0.2N$ Cs^+ , sodium to cesium concentration ratios as indicated
 $5.0 \times 10^{-8}N$ Cs^{137} .
 Common temperature $25^\circ C$.
 Common flow rate 7000 ml./cm.²/hr.
 Common influent pH 7.0
 Common column 0.5 g., 0.0134 cm. avg. diam., sodium-based clinoptilolite.

FIG. 7 (right). Cesium loading curves for erionite.

Common influent solution $0.2N$ Cs^+ , sodium to cesium concentration ratios as indicated,
 $5.0 \times 10^{-8}N$ Cs^{137} .
 Common temperature $25^\circ C$.
 Common flow rate 7000 ml./cm.²/hr.
 Common influent pH 7.0
 Common column 0.5 g., 0.0134 cm. avg. diam., sodium-based erionite.

TABLE I. KINETICS OF THE EXCHANGE SYSTEM $Na^+ \rightleftharpoons Cs^+$ IN CLINOPTILOLITE AND ERIONITE

Zeolite	Temperature $^\circ C$.	B , sec. ⁻¹	D_i , cm. ² /sec.	E_a Kcal/mole
Erionite	25	3.3×10^{-2}	1.55×10^{-7}	2.2
Erionite	50	4.4×10^{-2}	2.06×10^{-7}	
Clinoptilolite	25	3.5×10^{-2}	1.66×10^{-7}	4.7
Clinoptilolite	50	6.6×10^{-2}	3.07×10^{-7}	

D_i of 1×10^{-11} or less (Barrer, 1958). Barrer (1958) also reported very small ΔH values for the open zeolite chabazite.

The cation exchange characteristics of the open zeolites in fused salt solutions were studied. Table II gives a portion of the results of the molten salt experiments.

It is quite likely that equilibrium was not attained in any of the examples given in Table II because ionic migration is relatively slow through fused salts. However, there was apparently little difference in the total amount of Cs^{137} displaced in one day or five days of contact time.

TABLE II. THE EFFECT OF TEMPERATURE ON CESIUM AND SODIUM DISTRIBUTIONS IN MORDENITE, ERIONITE AND CLINOPTILOLITE

Zeolite	Salt	Temperature ° C.	Counts/min/g salt	Distribution	Contact time hours
				ratio, $\frac{\text{LiNO}_3}{\text{KNO}_3}$	
Cs^{137}					
Mordenite	LiNO_3	350	7,377		40
Mordenite	KNO_3	350	10,540	0.70	40
Mordenite	LiNO_3	460	16,723		25
Mordenite	KNO_3	460	8,928	1.87	25
Erionite	LiNO_3	360	37,678		24
Erionite	KNO_3	360	81,029	0.47	24
Erionite	LiNO_3	460	108,232		24
Erionite	KNO_3	460	81,174	1.33	24
Clinoptilolite	LiNO_3	340	31,165		130
Clinoptilolite	KNO_3	340	30,488	1.02	130
Clinoptilolite	LiNO_3	360	42,689		65
Clinoptilolite	KNO_3	360	33,449	1.28	65
Na^{22}					
Erionite	LiNO_3	345	9,320		24
Erionite	KNO_3	345	13,994	0.67	24
Erionite	LiNO_3	420	11,125		24
Erionite	KNO_3	420	7,539	1.48	24
Clinoptilolite	LiNO_3	345	4,815		24
Clinoptilolite	KNO_3	345	4,383	1.10	24
Clinoptilolite	LiNO_3	420	6,213		24
Clinoptilolite	KNO_3	420	3,588	1.73	24

Note the reversal of the cesium replacement series with rising temperature by lithium and potassium respectively. The melting point of 334° C. for KNO₃ prevented experiments at temperatures lower than 340° C., since results on the Cs¹³⁷ displaced by Li⁺ alone would be meaningless.

CONCLUSIONS

The replacement series Cs⁺ > K⁺ > Na⁺ > Li⁺ and Ba⁺² > Sr⁺² > Ca⁺² > Mg⁺² of Figures 2, 3, 4 and 5 are typical of hydrated series where the affinity of a given cation for a polar molecule such as water is directly proportional to its field strength (Grimm, 1953). It is unlikely, however, that Li⁺ is entering the zeolite while surrounded with 10 to 15 molecules of water. The dimensions of most of the openings for chabazite, erionite and mordenite are known with some degree of accuracy (Barrer and Kerr, 1959), and would not permit the entry of such a 10 angstrom hydrated cation as Li⁺. The structure of clinoptilolite is largely unknown so that no statement can be made concerning its channel dimensions except to say that they are greater than the diameter of Cs⁺.

If cation hydration state before entering the zeolite resulted in a hydrated type replacement series, then cation exchange from an anhydrous molten salt should yield a normal coulombic replacement series under all circumstances. The results of Table II show that, except for clinoptilolite, it was still possible to obtain a hydrated type of replacement series at 340° C. Further evidence that the hydration state of the entering cation does not significantly affect the type of replacement series is seen in the reported replacement series for anhydrous feldspathoids (Barrer and Raitt, 1954, and Barrer and Falconer, 1956). Normal coulombic replacement series prevailed at low temperatures with the feldspathoids.

Thus cationic hydration state before entry into the zeolite was not a significant causal factor, but the hydrated type replacement series at low temperatures remained to be explained. The data of Table II at the higher temperatures suggested that the hydrated series was a function of the structural water rather than external water. At higher temperatures the molten salt-zeolite experiments yielded a coulombic type replacement series, suggesting that the partial cation sieve properties of open zeolites are a result of interactions between the presence or absence of structural water and cations of the alkali metal and alkaline earth replacement series (Taylor, 1934). The enhanced cation selectivity of clinoptilolite is probably due to unusually favorable steric factors involving the exchanging cations, the exchange sites and structural water. The results of the molten salt-clinoptilolite experiments shown in Table II, and the D.T.A. pattern of clinoptilolite given by Mumpton (1960),

suggest that the structural water of clinoptilolite is not as firmly bonded to the aluminosilicate framework as is water to the other, less cation-selective, open zeolites. At least part of the structural water of clinoptilolite is relatively loosely held and free to exert a more intense sieving effect on the cations entering the aluminosilicate framework.

A high field strength cation such as Li^+ would tend to block its own diffusion path to an exchange site and to approach exchange sites less closely in clinoptilolite than the same cation in an open zeolite in which the structural waters are more firmly bonded to the aluminosilicate framework. A low field strength cation such as Cs^+ is relatively free to migrate and becomes fixed on an exchange site more readily under the same circumstances. Removal of most of the structural water would, of course, tend to favor the high field strength cation. Thus a situation normally present in these open zeolites is intensified in the case of clinoptilolite.

Understanding of the details of the mechanism awaits determination of steric relationships between structural water and exchangeable cations in clinoptilolite, along with more detailed structural work on the other open zeolites. Such an understanding could lead to the synthesis of zeolites with even more intense cation selectivities.

ACKNOWLEDGMENTS

The author wishes to acknowledge the able assistance and helpful suggestions of Mrs. Olevia C. Sterner in the laboratory work. The samples of erionite were collected by Dr. Richard H. Olson of the Nevada State Bureau of Mines at Reno, Nevada.

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Manuscript received January 26, 1961.