

ION-EXCHANGE PROPERTIES OF THE NATURAL ZEOLITE ERIONITE¹

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Abstract—Natural erionite was exhaustively ion exchanged with Na⁺ to give the anhydrous unit-cell composition (K_{1.9}Na_{5.4}Ca_{0.1}Mg_{0.1})[(AlO₂)_{7.4}(SiO₂)_{28.6}]. A thermodynamic study of alkali and alkaline earth metal ion exchange in this zeolite was made and the selectivity series found to be Rb > Cs ≥ K > Ba > Sr > Ca > Na > Li. In all cases approximately two K⁺ ions per unit cell (probably those in the cancrinite cages) could not be replaced by conventional ion exchange. It was also found that two Na⁺ ions per unit cell are extremely difficult to replace with alkaline earth ions. It is believed that complete replacement of the approximately six Na⁺ cations in the two large cages per unit cell of erionite would result in a non-uniform, divalent cation population in these cages. A more stable anhydrous composition is (K₂Ca₂Na₂)[(AlO₂)₈(SiO₂)₂₈] in which each large cage contains one Ca²⁺ or other alkaline earth cation and one Na⁺ ion.

Key Words—Erionite, Ion exchange, Offretite, Selectivity, Zeolite, Zeolite T.

INTRODUCTION

The structure of the aluminosilicate framework erionite was worked out in 1959 by Staples and Gard. In 1967, Bennett and Gard showed by electron diffraction that although offretite and erionite are two distinctly different minerals, their framework structures are sufficiently similar to permit intergrowth of the two zeolites. They also concluded that the synthetic zeolite T has the offretite structure with some disordering due to intergrowth of erionite. In 1970, Sherry reported ion-exchange data for a sample of zeolite T prepared according to the Union Carbide Corporation patent (Breck and Acara, 1960). From the very low intensity of the X-ray powder diffraction peaks for lines with odd ℓ indices, which Bennett and Gard had pointed out are absent from the X-ray powder diffraction pattern of offretite, it was concluded that this sample of zeolite T was a disordered offretite.

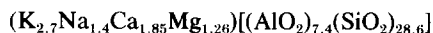
Gard and Tait (1971) later reported that a sample of synthetic zeolite T prepared for them by Sherry contained significantly more erionite than the 2–3% that he had estimated in the 1970 work and that erionite present in this sample existed as ordered domains less than a few hundred Ångstrom units thick. Based on these data, it appears that the earlier ion-exchange work (Sherry, 1970) with zeolite T was a study of ion-exchange equilibria in what is chiefly the offretite framework. The presence of intergrown erionite, however, could seriously affect the rates of exchange in this material because of random termination of the large channels that are parallel to the c axis in offretite (Gard and Tait, 1972).

A study of ion exchange in the erionite-offretite family of zeolites affords the opportunity to investigate how ion-exchange properties vary with subtle changes in zeolite crystal structure, while holding the chemical composition essentially constant. The purpose of this paper is to compare the ion-exchange properties of the erionite and offretite frameworks.

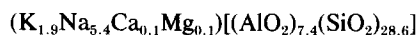
EXPERIMENTAL

The erionite used for this work was obtained from Jersey Valley, Nevada, and contained only traces of clinoptilolite according to the X-ray diffraction analysis.³ A chemical analysis of the untreated sample is given in Table 1. This material was ground to less than 300 mesh and then ion-exchanged by column elution techniques at room temperature using 1.00 N NaCl. The product still contained some Ca and Mg, and elution was continued at 90°C removing most of the remaining Ca and Mg. The analysis of the final product which was used for all of the reactions reported herein is listed in Table 1.

The anhydrous unit-cell composition of the untreated erionite is



and of the Na-erionite is



Ion-exchange isotherms were determined at 0.1 normality by equilibrating appropriate quantities of chloride solution with zeolite that had been stored over saturated NH₄Cl solution. Equilibration was done in polyethylene bottles that were shaken for 24 hr or more

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³ Ed. note. See Deffeyes, K. S. (1959) Erionite from Cenozoic tuffaceous sediments, central Nevada: *Am. Mineral.* **44**, 501–509; Papke, K. G. (1972) Erionite and other associated zeolites in Nevada: *Nev. Bur. Mines Geol. Bull.* **79**, 32 pp.

Table 1. Chemical analysis of natural and sodium-exchanged erionite.

	Natural Erionite		Na-Erionite	
	Wt %	Moles/ Mole Al	Wt %	Moles/ Mole Al
K	4.5	0.37	3.00	0.25
Na	1.4	0.19	5.10	0.73
Ca	1.58	0.25	0.11	0.018
Mg	0.64	0.17	0.05	0.015
SiO ₂	72.4	3.84	70.5	3.86
Al ₂ O ₃	16.0	1.00	15.5	1.00
Fe	1.7	—	1.7	—
Cl	—	—	<0.2	—

in a water bath in which the temperature was controlled to within $\pm 0.5^\circ\text{C}$. Kokatailo *et al.* (1972) demonstrated that natural erionite can have stacking faults. Gard and Tait (1971) reported that 12 samples of natural erionite examined by them had such stacking faults. The presence or absence of stacking faults resulting in a small amount of intergrown offretite should not measurably affect the ion-exchange equilibria for the erionite sample studied.

The equilibrium ion distribution was followed by tracing the solutions with Na²² and/or Cs¹³⁷, Ca⁴⁵, Sr⁸⁹, and Ba¹³³. The appropriate beta or gamma radiation was detected using a Packard Tricarb Model 3375 scintillation spectrometer with the autogamma attachment. Additional experimental details are given by Sherry (1970).

RESULTS AND DISCUSSION

The column elution results verify those obtained on natural erionite by N. Y. Chen, E. J. Rosinski, and J. R. Wilson of Mobil Research and Development Corporation, Paulsboro, New Jersey, showing that roughly 25% of the cations in this zeolite are nonexchangeable using conventional ion-exchange techniques and that these are K⁺ ions. The same result was obtained using zeolite T (Sherry, 1970) and a synthetic offretite (Aiello *et al.*, 1970). The erionite ion-exchange results are consistent with the structural study of natural erionite by Kawahara and Curien (1969) who placed one K⁺ ion in each of the two cancrinite cages that are in each erionite unit cell. Diffusion of a K⁺ ion out of a cancrinite cage should be very difficult because the diffusion path is through a nonplanar ring of six oxygens with a limiting diameter of 0.74 Å (Sherry, 1970). Erionite exhaustively ion exchanged with Na⁺ and having an Si/Al atom ratio of 3.5 should have the following anhydrous unit-cell formula:



The sample of natural erionite used in this study has a Si/Al atom ratio of 3.86 and consequently has 7.5 cations per unit cell, of which two should be nonexchange-

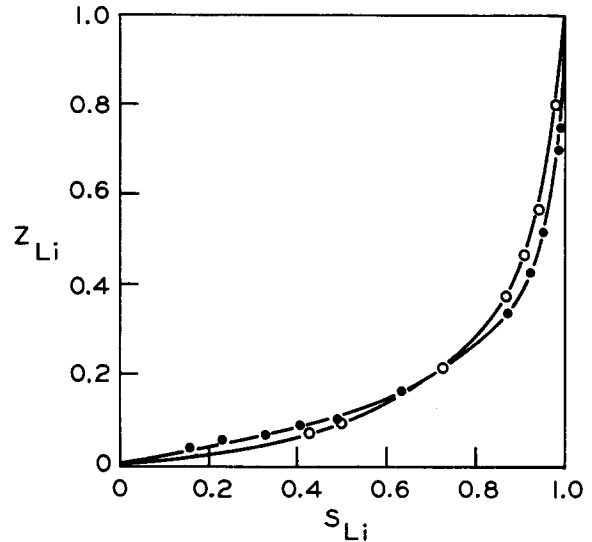


Figure 1. Ion-exchange isotherms for the Li-Na-erionite system at 0.100 total normality. \circ = 25°C , \bullet = 5°C .

able K⁺ ions. Thus, the theoretical fraction of nonexchangeable ions is 26.6%. It was found that 1.9 ions of 7.5 ions per unit cell (25.4%) were K⁺ ions that could not be replaced.

The structural determination of a natural offretite by Gard and Tait (1972) shows that offretite has 18 (SiO₂ + AlO₂) groups per unit cell compared to 36 for erionite and that a K⁺ ion is in the one cancrinite cage in each unit cell. Thus, one of the four cations that are in the "idealized" unit having a Si/Al atom ratio of 3.5 should be nonexchangeable in agreement with earlier experimental results (Sherry, 1970).

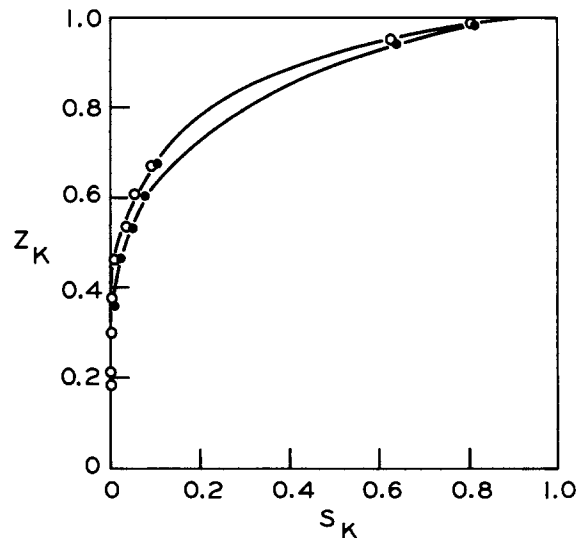


Figure 2. Ion-exchange isotherms for the K-Na-erionite system at 0.100 total normality. \circ = 25°C , \bullet = 5°C .

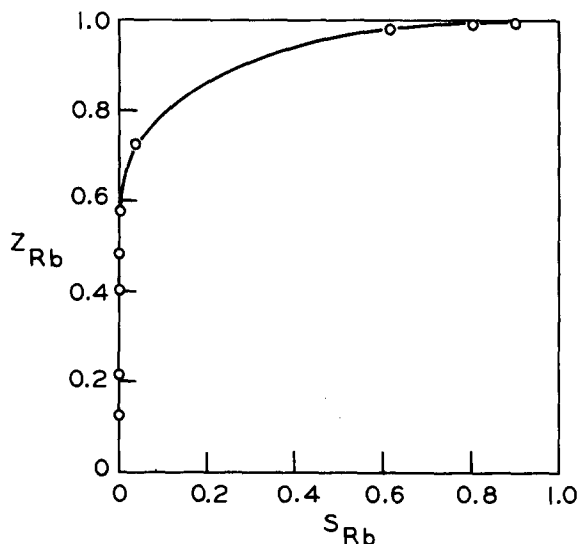


Figure 3. Ion-exchange isotherms for the Rb-Na-erionite system at 25°C and 0.100 total normality. \circ = 25°C.

Because K^+ ions left in an erionite that had been exhaustively ion exchanged with Na^+ are not exchangeable, this zeolite is defined in this work as the Na^+ form and is designated as NaE. Alkali metal and alkaline earth ion exchange has been studied in NaE, and the data are plotted in the form of ion-exchange isotherms in Figures 1-7. In these figures 100% ion exchange represents complete replacement of the Na^+ ions initially present in NaE. Reversibility was demonstrated by complete replacement of all of the Na^+ ions in NaE by K^+ , Rb^+ , and Cs^+ ions. The shapes of the K^+ , Rb^+ , and Cs^+ -NaE ion-exchange isotherms in Figures 2-4 indicate

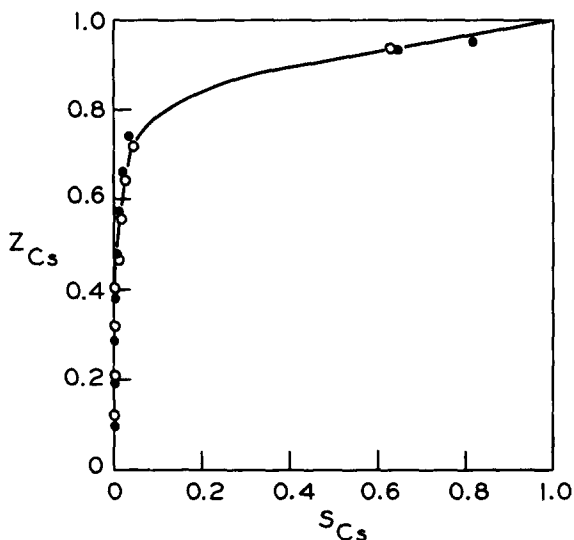


Figure 4. Ion-exchange isotherms for the Cs-Na-erionite system at 0.100 total normality. \circ = 25°C, \bullet = 5°C.

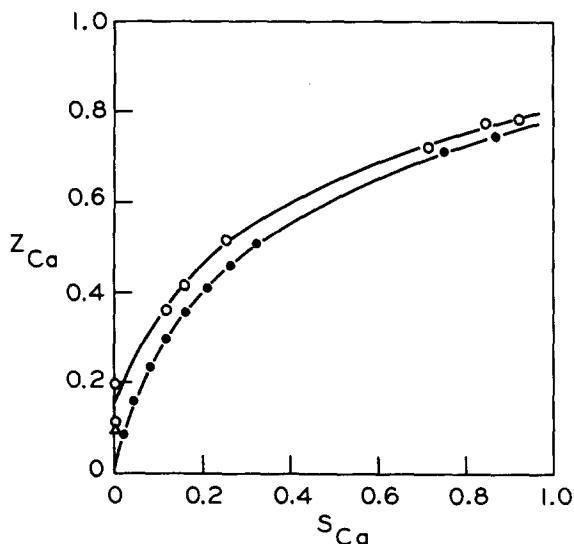


Figure 5. Ion-exchange isotherms for the Ca-Na-erionite system at 0.100 total normality. \circ = 25°C, \bullet = 5°C.

the strong preference of erionite for K^+ , Rb^+ , and Cs^+ ions over Na^+ ions. These isotherms also show that NaE prefers Ca^{2+} , Sr^{2+} , and Ba^{2+} ions over Na^+ ions at low levels of divalent ion loadings and that this divalent ion specificity drastically decreases with increasing divalent ion loading, even reversing at high loadings. The selectivity series exhibited by erionite at low loadings is



The same ion-selectivity pattern is exhibited by zeolite T (Sherry, 1970). Thus, the generalization still appears

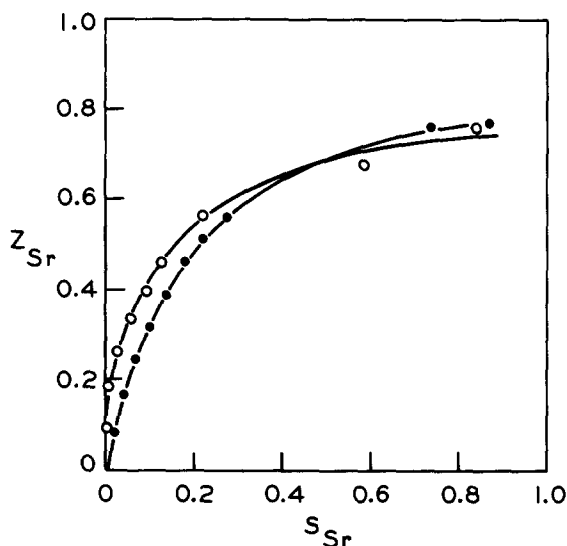


Figure 6. Ion-exchange isotherms for the Sr-Na-erionite system at 0.100 total normality. \circ = 25°C, \bullet = 5°C.

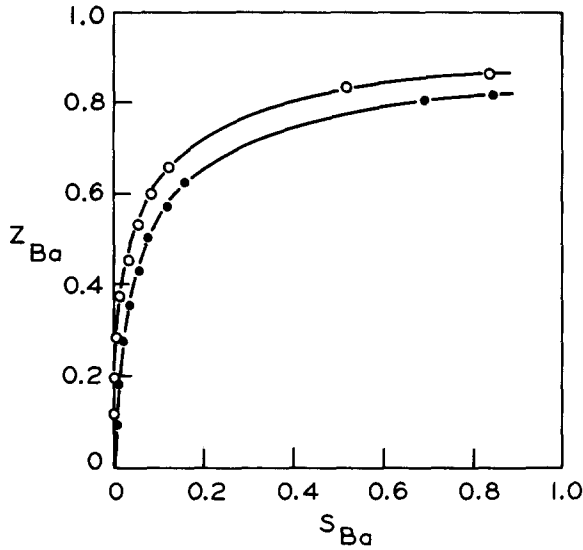


Figure 7. Ion-exchange isotherms for the Ba-Na-erionite system at 0.1 total normality. \circ = 25°C, \bullet = 5°C.

to be valid that the more siliceous zeolites prefer some monovalent cations to some divalent ones (Sherry, 1969).

As another example Barrer *et al.* (1969) found that natural chabazite also prefers K^+ ions to the alkaline earth cations at low ionic strength. This K^+ -ion specificity is probably the explanation for the high potassium content of natural erionites and chabazites.

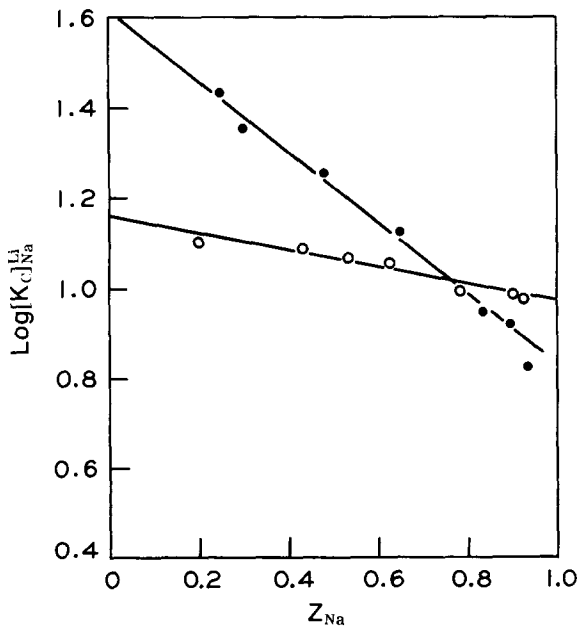


Figure 8. Corrected selectivity coefficient for the exchange of Li^+ into Na-erionite as a function of zeolite composition at 0.1 total normality. \circ = 25°C, \bullet = 5°C.

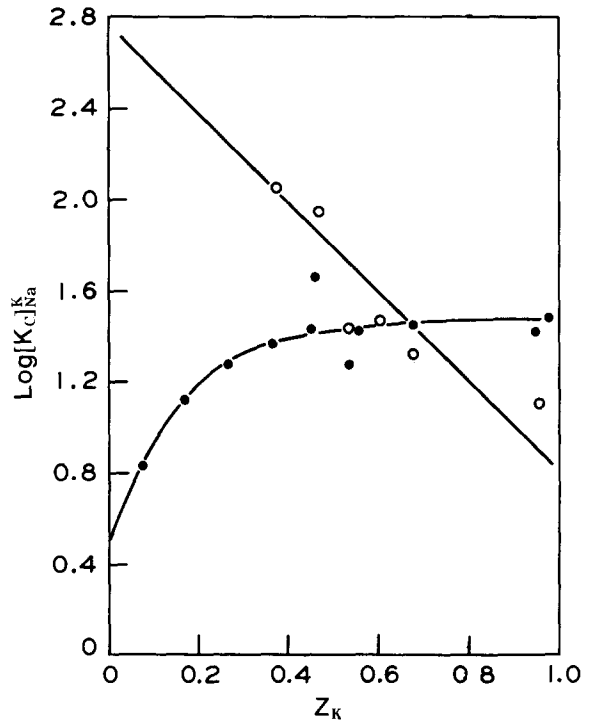


Figure 9. Corrected selectivity coefficient for the exchange of K^+ into Na-erionite as a function of zeolite composition at 0.1 total normality. \circ = 25°C, \bullet = 5°C.

The preference for K^+ ions over other alkali metal ions only involves the exchangeable cations in erionite and cannot be explained by siting in different kinds of cages. The six exchangeable cations that are in a unit cell must all be located in the large erionite cages because the hexagonal prisms of hydrated erionite are empty, and the cancrinite cages are filled with K^+ ions that do not exchange using conventional ion-exchange techniques (Kawahara and Curien, 1969). Thus, three exchangeable univalent ions are located in each of the two large erionite cages in a unit cell. On the other hand, alkaline earth ion exchange for univalent ions is structure related. Replacement of four Na^+ ions in each unit cell by two divalent ions results in a uniform cation population in these cavities, each cavity containing one divalent and one univalent cation. Replacement of the last two univalent ions in the unit cell must result in a nonuniform cation population of the large erionite cages. In a completely Ca^{2+} exchanged erionite half the large cages should contain two Ca^{2+} ion and half should contain one.

In Figures 8–12 the corrected selectivity coefficient is plotted as a function of loading of the ingoing ion. This coefficient, which is simply the mass action coefficient describing the ion-exchange reaction with a correction for the solution-phase activity coefficients, is defined by the equations

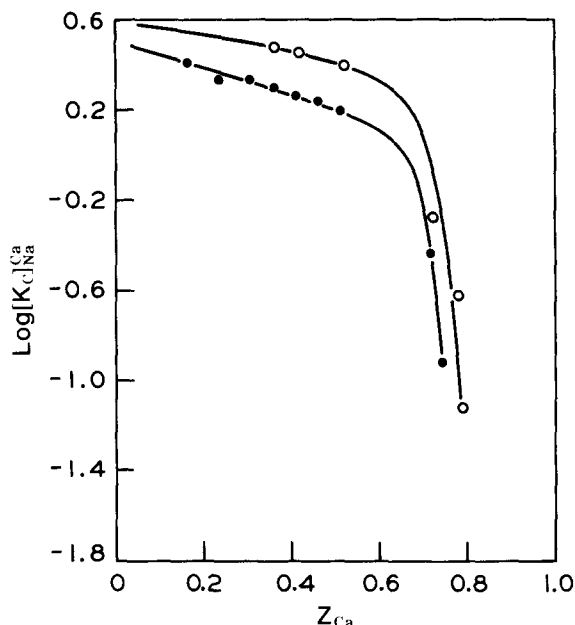


Figure 10. Corrected selectivity coefficient for the exchange of Ca^{2+} into Na-erionite as a function of zeolite composition at 0.1 total normality. $\circ = 25^\circ\text{C}$, $\bullet = 5^\circ\text{C}$.

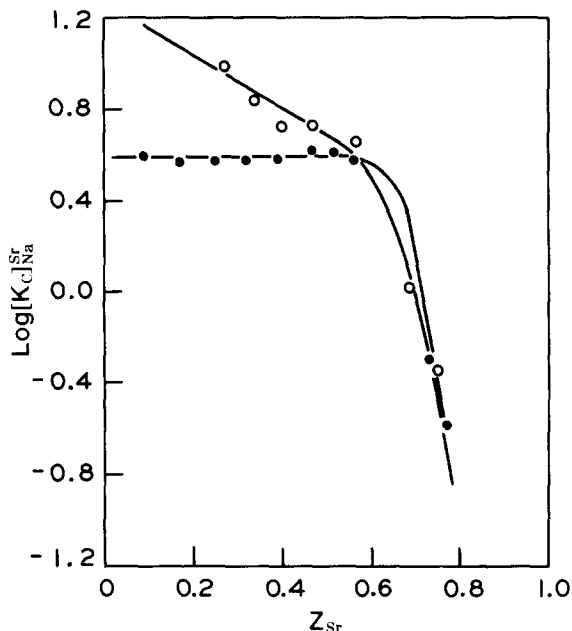
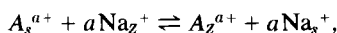


Figure 11. Corrected selectivity coefficient for the exchange of Sr^{2+} into Na-erionite as a function of zeolite composition at 0.1 total normality. $\circ = 25^\circ\text{C}$, $\bullet = 5^\circ\text{C}$.



$$K = \frac{X_A \cdot f_A \cdot m_{\text{Na}}^a \cdot \gamma_{\pm \text{NaCl}}^{2a}}{X_{\text{Na}}^a \cdot f_{\text{Na}}^a \cdot m_A \cdot \gamma_{\pm A}^{a+1}},$$

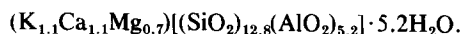
$$K = K_C \cdot f_A / f_{\text{Na}}^a.$$

In these equations A^{a+} is the ingoing cation, K is the thermodynamic equilibrium constant, X denotes equivalent fractions in the zeolite phase, m denotes molalities in the solution phase, f denotes activity coefficients in the zeolite phase, and γ_{\pm} denotes mean molal activity coefficients in the solution phase. The mean molal activity coefficients have been substituted for single ion activity coefficients and evaluated as described by Sherry (1970). Thus, variation in K_C is caused by variation in activity coefficients in the zeolite phase.

The selectivity plots for alkaline earth ion exchange of Na^+ ions have very unusual shapes. The corrected selectivity coefficient is not too dependent on zeolite composition up to about 65–75% loading, but then decreases in value precipitously as attempts are made to load alkaline earth ions onto the exchanger. If the natural erionite used in this study is unfaulted, *i.e.*, it does not contain intergrown offretite, the 5.5–6 exchangeable Na^+ ions initially present in each unit cell before alkaline earth ion exchange are located in the large erionite cages—three in each of the two erionite cages per unit cell. Replacement of the first four Na^+ ions per unit cell with two alkali earth cations results in the same cation population in each large cage—one divalent and one Na^+ ion. Replacement of the last two Na^+ ions in

each unit cell by one alkaline earth cation results in one half of the large cages containing two divalent cations and the other half containing one. This nonuniform cation population is thermodynamically less stable than one in which a uniform cation population is achieved (Sherry, 1969). It can be concluded from the present ion-exchange isotherms and selectivity plots that it is extremely difficult to replace all of the exchangeable cations (those in the large erionite cages) in natural erionite with divalent ones by simple ion exchange because K_C rapidly approaches zero when attempts are made to load the zeolite with more than about 70% alkaline earth cations.

Alkaline earth ion exchange in zeolite T is somewhat different. This zeolite is essentially the offretite structure with some intergrown erionite (Sherry, 1970; Gard and Tait, 1972). Presuming the presence of less than 10% intergrown erionite, the equilibrium ion-exchange properties of zeolite T can be discussed in terms of the offretite framework structure. Gard and Tait (1972) determined by X-ray diffraction techniques the structure of a hydrated natural offretite having the unit-cell contents



They found about one K^+ ion in each cancrinite cage and about one Mg^{2+} in each gmelinite cage. The remaining Ca^{2+} ions are sited in the large channels along with water molecules in a way which leaves the unit-

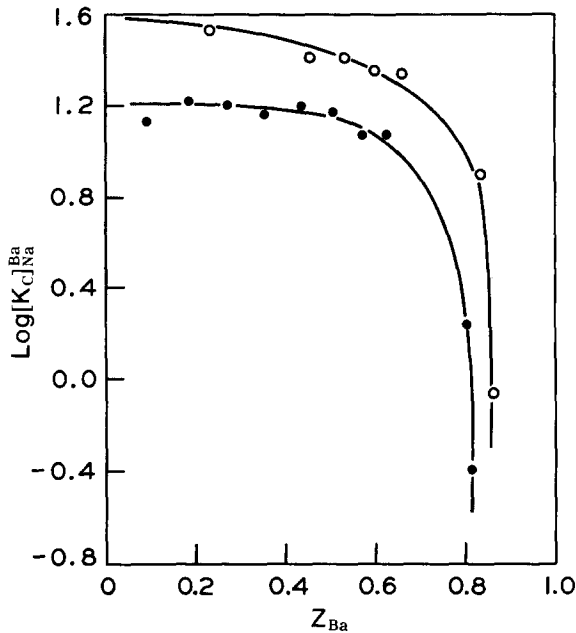


Figure 12. Corrected selectivity coefficient for the exchange of Ba^{2+} into Na-erionite as a function of zeolite composition at 0.1 total normality. ○ = 25°C, ● = 5°C.

cell composition nonuniform with respect to Ca^{2+} ions. This cation distribution should have lowered the symmetry and changed the unit-cell size, but this was not observed, probably because the ions and water in the large channels do not contribute greatly to the coherent scattering of X-rays. The long channel in offretite connects a large number of unit cells, and it is possible for the divalent ions and water molecules present in these channels to occupy positions of lowest energy without regard to the apparent unit-cell boundaries. Thus, it is not difficult to replace all of the univalent cations with divalent ones (Sherry, 1970).

These results account for the finding that natural offretite seems to occur only with exchangeable ions that are alkaline earth cations (Gard and Tait, 1971) and that natural erionite contains both alkali metal and alkaline earth exchangeable cations (see Table 1 and Peterson *et al.*, 1965; Eberly, 1964).

Free energies of exchange from the selectivity data have not been calculated because in the case of K^+ , Rb^+ , and Cs^+ ion exchange, the high selectivity for

these ions results in only a few of the data points being known with sufficient accuracy. In the case of divalent ion exchange the difficulty in replacing two of the six Na^+ ions in a unit cell of NaE leads to a difficult decision as to choice of standard states. If one chooses as standard states the zeolite $(\text{Na}_6\text{K}_2)[(\text{AlO}_2)_8(\text{SiO}_2)_{28}]$ and $(\text{Ca}_2\text{Na}_2\text{K}_2)[(\text{AlO}_2)_8(\text{SiO}_2)_{28}]$, the difference in the free energy of these two standard states and the equilibrium constant for the ion-exchange reaction may be simply calculated. However, due to the uniqueness of this ion-exchange system, calculation of the free energies of exchange is not instructive because they cannot be meaningful compared to any others.

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Резюме—После интенсивного ионного обмена натурального эрионита с Na^+ было получено безводное соединение элементарной ячейки $\text{K}_{1,9}\text{Na}_{5,4}\text{Ca}_{0,1}\text{Mg}_{0,1}((\text{AlO}_2)_{7,4}(\text{SiO}_2)_{28,6})$. Было проведено термодинамическое изучение ионного обмена щелочных и щелочноземельных металлов в этом цеолите и обнаружены следующие селективные серии $\text{Rb} > \text{Cs} \cong \text{K} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Na} > \text{Li}$. Во всех случаях примерно два иона K^+ на элементарную ячейку (возможно в канкринитовых полостях) не могли быть замещены в результате обычного ионного обмена. Было также обнаружено, что два иона Na^+ на элементарную ячейку замещаются щелочноземельными ионами с большими трудностями. Можно полагать, что полное замещение приблизительно 6 катионов в двух больших полостях на элементарную ячейку эрионита даст неоднородную двухвалентную совокупность катионов в этих полостях. Более стабильным безводным соединением является $\text{K}_2\text{Ca}_2\text{Na}_2((\text{AlO}_2)_8(\text{SiO}_2)_{28})$, в котором каждая большая полость содержит один Ca^{2+} или другой щелочноземельный катион и один ион Na^+ .

Resümee—Natürlich vorkommendes Erionit wurde völlig mit Na^+ ausgetauscht, um die folgende wasserfreie einzellige Zusammensetzung zu ergeben $\text{K}_{1,9}\text{Na}_{5,4}\text{Ca}_{0,1}\text{Mg}_{0,1}((\text{AlO}_2)_{7,4}(\text{SiO}_2)_{28,6})$. Eine thermodynamische Untersuchung von Alkali- und Erdalkalimetall Ionenaustausch in diesem Zeolithen wurde unternommen und die Reihenfolge der Selektivität war $\text{Rb} > \text{Cs} \cong \text{K} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Na} > \text{Li}$. In allen Fällen konnten ungefähr zwei K^+ Ionen per Einzelle (wahrscheinlich diejenigen in den Cancrinit Körben) nicht durch üblichen Ionenaustausch ausgetauscht werden. Es wurde auch herausgefunden, daß es äußerst schwierig war, zwei Na^+ Ionen per Einzelle durch Erdalkalitionen auszutauschen. Man glaubt, daß vollständiger Austausch der ungefähr 6 Na^+ Kationen in den zwei großen Körben per Erionit Einzelle zu einer nicht einheitlichen, zweiwertigen Kationenbevölkerung in diesen Körben führen würde. Eine stabilere, wasserfreie Zusammensetzung ist $\text{K}_2\text{Ca}_2\text{Na}_2((\text{AlO}_2)_8(\text{SiO}_2)_{28})$, in welcher jeder große Korb ein Ca^{2+} oder anderes Erdalkaliation und ein Na^+ Ion enthält.

Résumé—De l'erionite naturelle a subi un échange complet d'ions avec du Na^+ pour donner la maille anhydre de composition $\text{K}_{1,9}\text{Na}_{5,4}\text{Ca}_{0,1}\text{Mg}_{0,1}((\text{AlO}_2)_{7,4}(\text{SiO}_2)_{28,6})$. Une étude thermodynamique de l'échange d'ions d'alcalins et de métaux alcalino-terreux dans cette zéolite a été faite et la série de sélectivité s'est montrée être $\text{Rb} > \text{Cs} \cong \text{K} > \text{Ba} > \text{Sr} > \text{Ca} > \text{Na} > \text{Li}$. Dans tous les cas, environ 2 ions K^+ dans chaque maille (probablement ceux dans les cages de cancrinite) ne pouvaient pas être remplacés par échange traditionnel d'ions. Il a aussi été trouvé que dans chaque maille il était très difficile de remplacer 2 ions Na^+ par 2 ions alcalino-terreux. On croit que le remplacement des approximativement 6 cations Na^+ dans les 2 grandes cages dans chaque maille d'erionite produirait une population non-uniforme de cations divalents dans ces cages. Une composition anhydre plus stable est $\text{K}_2\text{Ca}_2\text{Na}_2((\text{AlO}_2)_8(\text{SiO}_2)_{28})$ dans laquelle chaque grande cage contient un Ca^{2+} ou un autre cation alcalino-terreux et un ion Na^+ .