

CATION-EXCHANGE REACTIONS OF SILICEOUS AND ALUMINOUS PHILLIPSITES

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Abstract—Exchange isotherms for the pairs Na-K and Na-Ca were measured by use of 0.1 N solutions at 5°, 35°, and 70°C in phillipsite from Tecopa, California (3.63 Al/32 oxygen unit cell), and Oki Islands, Shimane Prefecture, Japan (6.31 Al/32 oxygen unit cell). All isotherms except those for Na-Ca at 5°C were reversible. Free energy was evaluated for all reversible exchanges. The thermodynamic affinity sequences were $K > Na > Ca$ in both phillipsites. The selectivity for K in competition with Na and that for Na competing with Ca became larger at the lower temperatures. The siliceous phillipsite preferred the larger cation more strongly for the Na-K system, and Na more strongly for the Na-Ca system than the aluminous phillipsite.

Key Words—Cation exchange, Cation selectivity, Chemical composition, Phillipsite, Zeolite.

INTRODUCTION

The influence of framework charge density on the cation-exchange property of a zeolite was discussed by Barrer and Klinowski (1972) who indicated that a larger cation is preferred by the siliceous form and a smaller cation by the aluminous form for univalent-univalent exchanges. Their discussion was based on studies of siliceous and aluminous forms of faujasite-type zeolite (Barrer *et al.*, 1969a) and of chabazite (Barrer *et al.*, 1969b; Barrer and Klinowski, 1972). More experimental studies of other zeolites are required. Furthermore, Ca is preferred more strongly in the Na-Ca exchange system by the aluminous forms of the zeolites mentioned above. This behavior should also be examined in other zeolites.

Because phillipsites vary widely in Si/Al ratio (Galli and Ghittoni, 1972), cation-exchange properties can be compared between the siliceous form and the aluminous form of this zeolite. Ames (1964a, 1964b) and Barrer and Munday (1971) studied the cation-exchange reactions of siliceous phillipsites at 25°C; however, the cation-exchange properties of aluminous phillipsite have not been examined. Phillipsite is abundant in deep-sea deposits (Stoncipher, 1978), and cation-exchange experiments at different temperatures are therefore of considerable interest in the distribution of cations between phillipsite and sea water.

The present paper compares the exchange properties of phillipsites having various Si/Al ratios and clarifies the behavior of sodium, potassium, and calcium ions in phillipsite and in solution at different temperatures.

MATERIALS AND METHODS

Materials

The phillipsites used in the present study were from a zeolite tuff near Tecopa, California (Sheppard and Gude, 1968), and from Oki Islands, Shimane Prefecture, Japan. Both samples were free of impurities as estimated from their X-ray powder diffraction patterns. Chemical analyses (Table 1) of the phillipsites were carried out by the following methods: SiO₂ and Al₂O₃ by gravimetry; Na₂O and K₂O by flame photometry; MgO, CaO, and Fe₂O₃ by atomic absorption spectroscopy; TiO₂ by spectrophotometry; and H₂O by thermogravimetry. The phillipsite from Tecopa is more siliceous than that from Oki. The former is called Si-rich phillipsite and the latter, Si-poor phillipsite in this paper.

Experimental procedures

The materials were ground to pass a 115-mesh sieve. For cation-exchange experiments, homoionic zeolites are required as starting materials. Na-, K-, and Ca-exchanged phillipsites were therefore prepared by several successive treatments of the zeolites with saturated solutions of NaCl, KCl, and CaCl₂, respectively. Each treatment was carried out for one week at 80°C. The products were filtered and washed with distilled water until they were free of Cl⁻. The exchanged products were dried for one day. The cation contents of the exchanged products are given in Table 2. All samples are nearly homoionic. The small amount of cations that remained after the treatments were assumed to be non-exchangeable, and are neglected in the calculation of the results.

Cation-exchange isotherms were measured by the static method (Barrer and Munday, 1971). About 0.1 g of the nearly homoionic zeolites was equilibrated in

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Table 1. Chemical analyses of untreated phillipsites from Tecopa, California, and Oki, Japan.

	Tecopa	Oki
SiO ₂	54.68	43.65
Al ₂ O ₃	14.60	24.08
Fe ₂ O ₃ ¹	0.79	0.01
TiO ₂	0.16	0.01
MgO	0.39	0.17
CaO	0.00	8.05
Na ₂ O	4.56	2.57
K ₂ O	6.52	3.53
H ₂ O(±)	15.24	17.80
Total	99.94%	100.30%

Numbers of ions on the basis of 32 oxygens

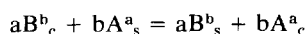
	Tecopa	Oki
Si	12.19	9.70
Al	3.63	6.31
Fe	0.12	0.07
Mg	0.12	0.06
Ca	0.00	1.92
Na	1.87	1.11
K	1.76	1.00
H ₂ O	10.74	13.20
Si/Al	3.35	1.54

¹ Total iron given as Fe₂O₃.

polyethylene bottles with 50 ml of solution. The total normality of the metal chloride solution was 0.1 N, and the initial composition of the solution was adjusted appropriately. In this paper, the term Na-K system denotes the reaction of the Na-exchanged phillipsite with mixed NaCl-KCl solution and that of the K-exchanged phillipsite with mixed NaCl-KCl solution, and the term Na-Ca system denotes the reaction of the Na-exchanged phillipsite with mixed NaCl-CaCl₂ solution and that of the Ca-exchanged phillipsite with mixed NaCl-CaCl₂ solution. The polyethylene bottles were shaken in a water bath at 70° and 35°C and for one week for the Na-K system and for two weeks for the Na-Ca system; at 5°C for two weeks for the Na-K system, and for four weeks for the Na-Ca system. The zeolite was separated from the solution with use of a filter paper. It took less than one minute to filter the zeolite. After filtration it was washed with distilled water and dried for one day. Chemical analyses of the exchanged zeolites and the solutions were performed by the same methods as the untreated materials.

Calculation of thermodynamic functions

The cation-exchange reaction may be written as follows:



for two cations B^b and A^a with valences b and a, respectively. The subscripts c and s refer to the crystal

Table 2. Cationic compositions of the exchange phillipsites (wt. %).

Tecopa	Na-ex.	K-ex.	Ca-ex.
MgO	0.26	0.40	0.44
CaO	0.00	0.00	7.85
Na ₂ O	9.36	0.20	0.27
K ₂ O	0.44	11.20	0.40

Oki	Na-ex.	K-ex.	Ca-ex.
MgO	0.03	0.05	0.09
CaO	0.20	0.52	11.54
Na ₂ O	12.99	0.12	0.28
K ₂ O	0.05	16.21	0.33

and the solution. The thermodynamic equilibrium constant, K, and the corrected selectivity coefficient, K_c, become:

$$K = A_c^b f_A^b m_B^a \gamma_B^a / B_c^a f_B^a m_A^b \gamma_A^b,$$

or

$$K_c = A_c^b m_B^a \gamma_B^a / B_c^a m_A^b \gamma_A^b,$$

where A_c and B_c denote the equivalent fractions of cations in crystals. The values f_A and f_B are the activity coefficients for the ions in crystals when their concentrations were expressed as equivalent fractions, m_A and m_B are the molalities of ions in solutions, and γ_A and γ_B are the activity coefficients for the ions in the solutions.

K is evaluated by the following equation (Gaines and Thomas, 1953):

$$\ln K = (b - a) + \int_0^1 \ln K_c(dB_c),$$

assuming that the changes in the activity of water in zeolite and solution phases are negligible.

For dilute solutions, the difference between molality and molarity is so small that it can be neglected. Thus, m_A and m_B can be obtained from the experimental results. The mean activity coefficient, γ_±, can be calculated from the concentration of a dilute solution with the extended Debye-Hückel equation (Lewis and Randall, 1961), and the ionic activity coefficient, γ, can be obtained by the mean salt method (Garrels and Christ, 1965). The corrected selectivity coefficients were calculated from the results of the chemical analyses of the zeolites and the solutions. For all exchanges, the starting materials in the forward direction are Na-exchanged phillipsites.

The logarithmic values of K_c were fitted as a function of Na_c by the least-squares method to a second degree polynomial to facilitate the calculation. The standard

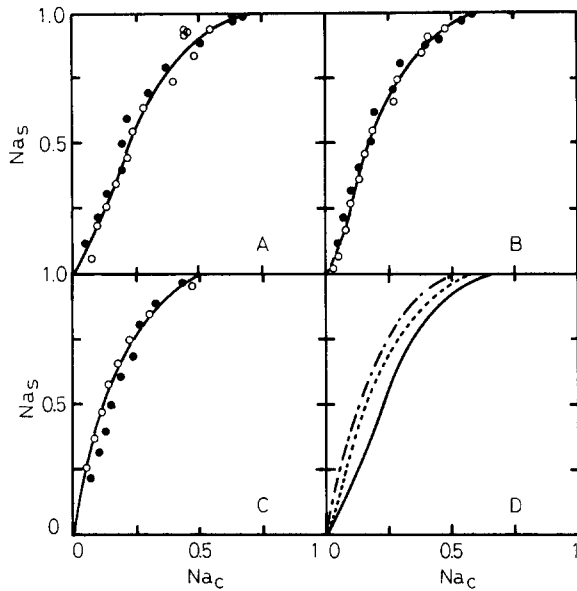


Figure 1. Exchange isotherms for the Na-K system in the Si-rich phillipsite at (A) 70°C, (B) 35°C, and (C) 5°C. (D) shows the comparison of the isotherms. — = 70°C; - - - = 35°C; - · - = 5°C. Open circles = Na displacement; solid circles = K displacement.

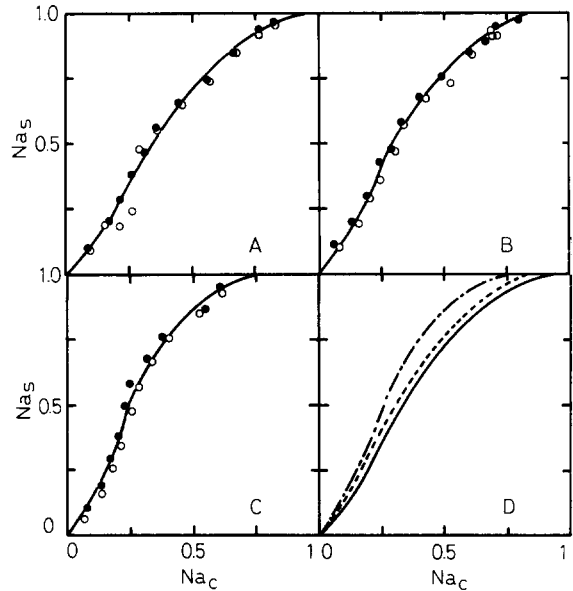


Figure 2. Exchange isotherms for the Na-K system in the Si-poor phillipsite at (A) 70°C, (B) 35°C, and (C) 5°C. (D) shows the comparison of the isotherms. — = 70°C; - - - = 35°C; - · - = 5°C. Open circles = Na displacement; solid circles = K displacement.

free energy, ΔG^* , per gram-equivalent of exchange is given by the equation:

$$\Delta G^* = -RT \ln K/(ab).$$

The equilibrium constant at 25°C can be calculated from the values at the different temperatures by:

$$\ln K(T_1) = \ln K(T_2) - ab\Delta H^* (1/T_1 - 1/T_2)/R,$$

in which $\ln K(T_1)$ and $\ln K(T_2)$ are the values of $\ln K$ at T_1K and T_2K , respectively, and ΔH^* is the standard enthalpy of exchange. ΔH^* was obtained from the other sets of temperatures.

RESULTS AND DISCUSSION

Isotherms

Figures 1 and 2 show the cation-exchange isotherms for the Na-K system in the Si-rich phillipsite and the Si-poor phillipsite, respectively. Both phillipsites in 0.1 N solutions show a preference for K over Na at all temperatures; however, the selectivity for K over Na is smaller in the higher charged zeolite than in the lower charged one. At lower temperatures, the selectivity for Na in competition with K becomes smaller in both phillipsites. Phillipsite in deep-sea deposits is rich in potassium (Stonecipher, 1978). Therefore, the strong preference for K shown in the isotherms at 5°C agrees with the chemistry of deep-sea phillipsite. The exchange isotherms for the Na-Ca system are shown in

Figures 3 and 4. The irreversibility of the exchanges at 5°C may be due to the low reaction rate. The Si-poor phillipsite prefers Ca over Na at 35° and 70°C, whereas the Si-rich phillipsite prefers Na over Ca at 35°C. The

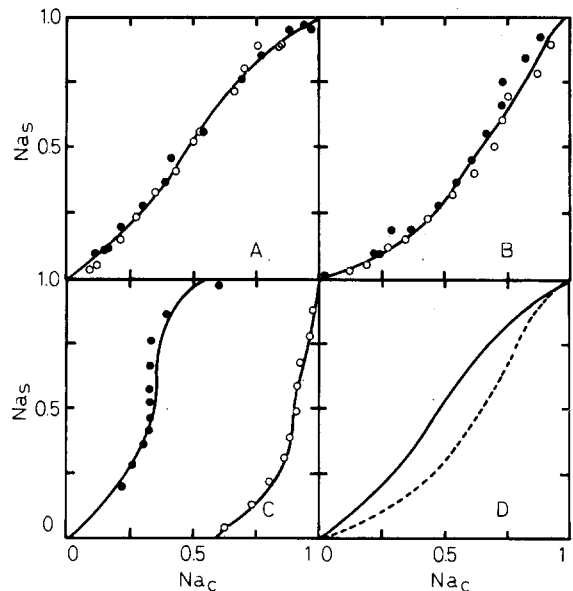


Figure 3. Exchange isotherms for the Na-Ca system in the Si-rich phillipsite at (A) 70°C, (B) 35°C, and (C) 5°C. (D) shows the comparison of the reversible isotherms. — = 70°C; - - - = 35°C. Open circles = Na displacement; solid circles = Ca displacement.

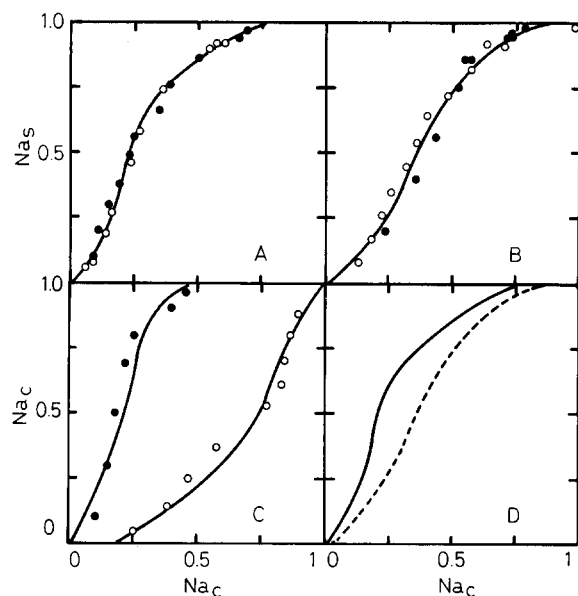


Figure 4. Exchange isotherms for the Na-Ca system in the Si-poor phillipsite at (A) 70°C, (B) 35°C, and (C) 5°C. (D) shows the comparison of the reversible isotherms. — = 70°C; - - - - = 35°C. Open circles = Na displacement; solid circles = Ca displacement.

selectivity for Na over Ca is smaller in the higher charged zeolite. With increasing temperature, the selectivity for Na becomes much less.

Thermodynamic properties

The equilibrium constant, K , the standard free energy, ΔG° , and the calculated enthalpy, ΔH° , are given in Table 3. The thermodynamic affinity sequences are $K > Na > Ca$ in both phillipsites. The changes of ΔG°

Table 3. Thermodynamic functions of exchanges.

System ¹	Temperature (°C)	Equilibrium constant	ΔG° (kJ per equiv.)	ΔH° (kJ per equiv.)
Si-rich phillipsite				
Na-K*	70	14.040	-7.538	-9.435
	35	23.479	-8.086	
	5	34.928	-8.218	
Na-Ca*	70	0.108	3.183	16.955
	35	0.028	4.606	
Si-poor phillipsite				
Na-K*	70	2.947	-3.083	-6.617
	35	3.378	-3.119	
	5	4.352	-3.401	
Na-Ca*	70	0.693	0.524	13.858
	35	0.230	1.884	

¹ The asterisks denote entering cations.

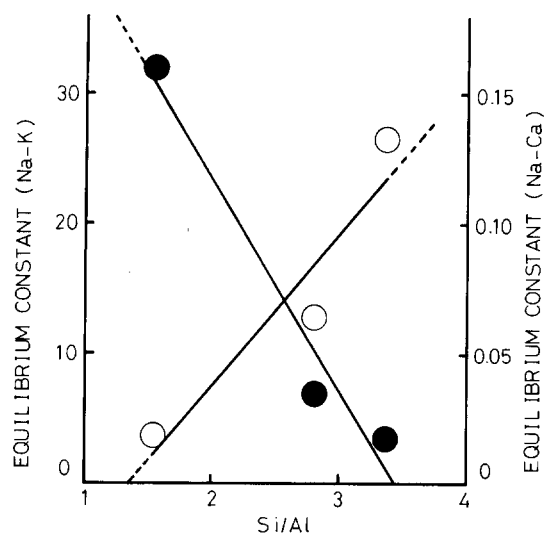


Figure 5. Plot showing the equilibrium constants for the Na-K system and the Na-Ca system at 25°C against the Si/Al atomic ratios in phillipsite. Open circles = the Na-K system; solid circles = the Na-Ca system.

with increasing temperatures agrees with those in the isotherms for the Na-K system and the Na-Ca system. For the Na-K system, ΔG° in the Si-poor phillipsite is considerably larger than in the Si-rich material. For the Na-Ca system, ΔG° in the Si-poor phillipsite is smaller. The influence of framework charge density on the exchange property is confirmed, and the behavior in phillipsite agrees with that found in faujasite-type zeolites (Barrer *et al.*, 1969a) and chabazite (Barrer *et al.*, 1969b; Barrer and Klinowski, 1972).

The phillipsite used in the experiments by Barrer and Munday (1971) is intermediate in Si/Al atomic ratio (2.8) between the material from Tecopa (3.35) and that from Oki (1.54). The equilibrium constant obtained in their study for the Na-K system at 25°C is 12.9; the values calculated here for the Si-rich and Si-poor phillipsites are 26.6 and 3.7, respectively. For the Na-Ca system, the value found by Barrer and Munday (1971) is 0.035, whereas the values calculated here for the equilibrium constants are 0.018 and 0.160 for the Si-rich and the Si-poor forms, respectively. Figure 5 shows the relationship between the equilibrium constant and the Si/Al atomic ratio. If a linear relation is assumed between the equilibrium constant, K , and the Si/Al atomic ratio, the regression equation for the Na-K system becomes:

$$K = -15.6 + 11.7(\text{Si/Al}), \text{ and}$$

for the Na-Ca system, the regression equation becomes:

$$K = 0.281 - 0.0821(\text{Si/Al}).$$

According to Rinaldi *et al.* (1974), two sets of channels are present in the crystal structure of phillipsite,

and the cations are located in the channels. Considering the amount of void space per exchangeable cation, the repulsive force between cations is more significant in higher charged phillipsite for the location of cations. From this point of view, the preference for the larger cation diminished as the Si/Al ratio decreased for univalent-univalent exchange, and the substitution of one calcium atom for two sodium atoms is more preferable in more aluminous phillipsite.

CONCLUSIONS

From the experimental results, the thermodynamic affinity sequences are $K > Na > Ca$ in both Si-rich and Al-rich phillipsites. The selectivity for K in competition with Na and that for Na competing with Ca become larger at lower temperatures. The Si-rich phillipsite prefers the larger cation more strongly in the Na-K system, and Na more strongly in the Na-Ca system than the Al-rich phillipsite. The influence of framework charge density on the exchange property of phillipsite is similar to that found by Barrer *et al.* (1969a) for faujasite-type zeolites and by Barrer *et al.* (1969b) and Barrer and Klinowski (1972) for chabazite. From regression equations calculated for the Na-K and the Na-Ca exchange systems, the equilibrium constant correlates with the atomic ratio of the phillipsite.

More experiments with phillipsites having various Si/Al ratios are needed to derive the empirical regression equation, and the crystal structure analyses of Na-, K-, and Ca-exchanged phillipsites are required. From these data the contribution from the repulsive forces between cations to the cation-exchange reactions in phillipsite might be estimated.

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Резюме—Изоэри обмен для пар Na-K и Na-Ca измерялись при использовании 0,1 N растворов при 5°, 35°, и 70°C в филлипситах из Озера Текопа в Калифорнии (3,63 Al/32 O элементарная ячейка) и островов Оки, в префектуре Шимане, Япония (6,31 Al/32 O элементарная ячейка). Все изотермы, за исключением этих для Na-Ca при 5°C, были обратимы. Свободная энергия была определена для всех обратимых обменов. Для обоих Филлипситов порядок термодинамического сродства был: K > Na > Ca. Селективность для K, соревнующегося с Na, и селективность для Na, соревнующегося с Ca, увеличивалась при более низких температурах. Кремнеземный филлипсит предпочитал больший катион для системы Na-K и Na ион для системы Na-Ca более, чем глиноземный филлипсит. [E.C.]

Resümee—Es wurden die Austauschisotherme für die Paare Na-K und Na-Ca für die Phillipsite von Lake Tecopa, Kalifornien (3,63 Al/32 O Elementarzelle) und Oki Islands, Simane Prefecture, Japan, gemessen, wobei 0,1 N Lösungen bei 5°, 35°, und 70°C verwendet wurden. Alle Isotherme mit Ausnahme derer für Na-Ca bei 5°C waren reversibel. Die freie Energie wurde für alle reversiblen Austauschreaktionen berechnet. Die thermodynamische Affinitäts-abfolge war in beiden Phillipsiten K > Na > Ca. Die Selektivität für K gegenüber Na und die für Na gegenüber Ca wurde bei niedrigen Temperaturen größer. Der Silizium-reiche Phillipsit bevorzugt im Fall des Na-K-Systems das größere Kation stärker und im Fall des Na-Ca-Systems das Na stärker als der Al-reiche Phillipsit. [U.W.]

Résumé—Les isothermes d'échange pour les paires Na-K et Na-Ca ont été mesurées par l'emploi de 0,1 N solutions à 5°, 35°, et 70°C dans des phillipsites de Lake Tecopa, Californie (maille 3,63 Al/32 O) et des îles Oki, Préfecture Shimane, Japon (maille 6,31 Al/32 O). Tous les isothermes étaient réversibles sauf ceux pour Na-Ca à 5°C. L'énergie libre a été évaluée pour tous les échanges réversibles. Les séquences d'affinité thermodynamique étaient K > Na > Ca dans les deux phillipsites. La sélectivité pour K en compétition avec Na et celle pour Na en compétition avec Ca est devenue plus grandes à de basses températures. La phillipsite silice montrait une plus forte préférence que la phillipsite aluminium pour le plus grand cation pour le système Na-K et pour Na pour le système Na-Ca. [D.J.]