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Cation-Exchange Properties of Phillipsite (a Zeolite Mineral): The Differences between Si-Rich and Si-Poor Phillipsites

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ABSTRACT

Cation-exchange experiments on Si-rich and Si-poor phillipsites with a 0.1 N NaCl + KCl or a 0.1 N NaCl + $CaCl_2$ solution at 70 and 35°C are analyzed to obtain the equilibrium constants and Margules parameters for their solid solutions. The Si-rich phillipsite shows a larger preference for K^+ over Na^+ than the Si-poor one at 70 and 35°C. While the Si-rich phillipsite shows no preference for Na^+ over Ca^{2+} at 70°C and prefers Na^+ over Ca^{2+} at 35°C, the Si-poor phillipsite prefers Ca^{2+} over Na^+ at both temperatures. Based on the experimental results, equilibrium constants for the cation-exchange reactions and Margules parameters for the phillipsite solid solutions are computed. The equilibrium constants for Na–K and Na–Ca exchange reactions depend strongly on the Si content in the phillipsite. The Si-rich phillipsite shows the large nonidealities in the Na–K series compared with the Si-poor phillipsite. For Na–Ca series phillipsites, the activity coefficient versus composition relations at 70°C do not differ between these phillipsites but those relations at 35°C do show differences.

Key Words. Phillipsite; Si content; Cation-exchange reaction

INTRODUCTION

An important property of zeolite minerals is their ability to undergo ion-exchange reactions. Thus, there have been many studies on the ion-exchange properties of zeolites for industrial applications (1). Phillipsite, one of the zeolite minerals, has the ideal chemical formula $K_2(Ca_{0.5}, Na)_4(Al_6, Si_{10})O_{32} \cdot 12H_2O$ (2). In natural phillipsite, the substitution of Al for Si or vice versa occurs to a considerable degree. The number of Si atoms on the basis of the chemical formula varies from 12 to 9 (2). The cation-exchange properties of siliceous phillipsite were studied by Ames (3, 4) and Barrer and Munday (5) at 25°C. Later, Shibue (6) obtained Na–K and Na–Ca exchange isotherms of siliceous and aluminous phillipsites by reacting the phillipsites with an aqueous NaCl + KCl or NaCl + $CaCl_2$ solution at 70 and 35°C. Shibue (6) showed that the cation-exchange properties of siliceous and aluminous phillipsites differ in regard to their selectivities for Na^+ over K^+ and Na^+ over Ca^{2+}. The differences in the cation selectivities reflect the equilibrium constants or mixing properties of the phillipsite solid solutions or both.

Shibue (6) obtained the activity coefficients of aqueous ions by the mean salt method (7) based on an extended Debye–Hückel equation (8). Since then, there have been many studies on the thermodynamic properties of aqueous electrolyte solutions. Activity coefficients of Na^+, K^+, or Ca^{2+} in an NaCl + KCl or NaCl + $CaCl_2$ solution at elevated temperatures were derived by Greenberg and Møller (9). Recalculation of the activity coefficients of individual cations in mixed electrolyte solutions will result in more accurate derived thermodynamic quantities.

This study aims to show the differences in the equilibrium constants as well as the mixing properties of the phillipsite solid solutions by reanalyzing the experimental results. Based on the recalculation, this study derives Margules equations for the solid solutions by using a nonlinear least-square regression technique.

EXPERIMENTAL

Materials

Two natural phillipsites, one from Lake Tecopa in California and the other from the Oki Islands in Japan, were separated by handpicking. No contaminated minerals were found by the x-ray powder diffraction method.

The chemical compositions of the phillipsites were analyzed by the following methods: SiO_2 and Al_2O_3 by gravimetry; Na_2O and K_2O by flame photometry; MgO, CaO, and Fe_2O_3 by atomic absorption spectroscopy; H_2O by thermogravimetry. The analytical results, together with the chemical formulas of the phillipsites, are listed in Table 1. The numbers of Si atoms per unit formula are 12.21 for Tecopa phillipsite and 9.70 for Oki phillipsite. Hereafter, phillipsite from Tecopa will be designated as Si-rich phillipsite and phillipsite from Oki as Si-poor phillipsite.

TABLE 1
Chemical Compositions of Phillipsites from Lake Tecopa and Oki

	Tecopa	Oki
SiO_2	57.68	43.65
Al_2O_3	14.60	24.08
Fe_2O_3	0.79	0.44
MgO	0.39	0.17
CaO	0.00	8.05
Na_2O	4.56	2.57
K_2O	6.52	3.53
H_2O (±)	15.24	17.80
Total	99.78	100.29

Chemical formula	
Tecopa	$(K_{1.76}, Na_{1.87}, Mg_{0.12})$ $\times(Al_{3.64}, Fe^{3+}_{0.13}, Si_{12.21})O_{32}\cdot 10.75H_2O$
Oki	$(K_{1.00}, Na_{1.11}, Ca_{1.92}, Mg_{0.06})$ $\times(Al_{6.31}, Fe^{3+}_{0.07}, Si_{9.70})O_{32}\cdot 13.19H_2O$

The natural phillipsites were ground in an agate mortar to pass a 115-mesh sieve. Na-, K-, and Ca-exchanged phillipsites were prepared by several successive treatments of the zeolites in NaCl-, KCl-, or $CaCl_2$-saturated solutions at 80°C. The exchanged phillipsites were separated by filtration and were washed with distilled water. Na-, K-, and Ca-exchanged phillipsites are almost homoionic in regard to exchangeable cations (Table 2). These phillipsites were used as the starting materials for the cation-exchange experiments.

Cation-Exchange Experiments

The experiments were carried out for Na–K and Na–Ca exchange reactions. The pretreated phillipsite (100 mg) was equilibrated with 0.1000 N chloride solutions (50 mL) of various cation compositions in polyethylene bottles. The compositions of the initial solutions were converted into the molal scale by using the equation of Krumgalz et al. (10) at 25°C and 1 bar. In some experimental runs the weight of the starting solid, the volume of the solution, or both were changed. Runs were carried out at 70 ± 2°C and 35 ± 2°C in a water bath. The duration time was 1 week for the Na–K exchange reaction and 2 weeks for the Na–Ca exchange reaction.

TABLE 2
Na_2O, K_2O, and CaO Contents (wt%) in Starting Materials for Cation-Exchange Experiments

Tecopa phillipsite	Na-exchanged	K-exchanged	Ca-exchanged
Na_2O	9.36	0.20	0.27
K_2O	0.44	11.10	1.40
CaO	0.00	0.00	6.85
MgO	0.26	0.40	0.44
Oki phillipsite	**Na-exchanged**	**K-exchanged**	**Ca-exchanged**
Na_2O	12.99	0.12	0.28
K_2O	0.05	14.71	1.83
CaO	0.20	0.52	10.04
MgO	0.03	0.05	0.09

After the experimental run the treated phillipsite was separated from the solution within 1 minute by filtration. Then the solid phase was washed with distilled water and dried for 1 day. Cationic compositions of the solid phase and the coexisting aqueous solution were analyzed by atomic absorption spectroscopy. Water contents in the phillipsites were assumed to be constant during the experiments and were not analyzed.

The analytical results of solution compositions obtained as the molar unit were converted into the molal scale. The compositions of the solid phase were expressed as equivalent fractions of Na (X_{Na}) and K (X_K) for the Na–K exchange reaction or as equivalent fractions of Na and Ca (X_{Ca}) for the Na–Ca exchange reaction. These quantities are related to the moles of cations in phillipsite (n_{Na}, n_K, and n_{Ca}) by the following equations.

$$X_{Na} = \frac{n_{Na}}{n_{Na} + n_K} \tag{1}$$

$$X_K = \frac{n_K}{n_{Na} + n_K} \tag{2}$$

for the Na–K exchange reaction, and

$$X_{Na} = \frac{n_{Na}}{n_{Na} + 2n_{Ca}} \tag{3}$$

$$X_{\mathrm{Ca}} = \frac{2n_{\mathrm{Ca}}}{n_{\mathrm{Na}} + 2n_{\mathrm{Ca}}} \tag{4}$$

for the Na–Ca exchange reaction.

THERMODYNAMICS OF CATION-EXCHANGE REACTIONS

The cation-exchange reactions of concern here can be written as

$$\mathrm{NaX} + \mathrm{K}^+ = \mathrm{KX} + \mathrm{Na}^+ \tag{5}$$

$$\mathrm{NaX} + 0.5\mathrm{Ca}^{2+} = \mathrm{Ca}_{0.5}\mathrm{X} + \mathrm{Na}^+ \tag{6}$$

where X stands for the zeolite framework with a unit negative charge. Trace amounts of the other cation oxides are not considered for the analyses of the experimental results. Then the thermodynamic equilibrium constant for the Na–K exchange reaction ($K_{\mathrm{Na\text{-}K}}$) and the Na–Ca exchange reaction ($K_{\mathrm{Na\text{-}Ca}}$) can be expressed as

$$K_{\mathrm{Na\text{-}K}} = \frac{X_{\mathrm{K}} f_{\mathrm{K}} m_{\mathrm{Na}} \gamma_{\mathrm{Na}}}{X_{\mathrm{Na}} f_{\mathrm{Na}} m_{\mathrm{K}} \gamma_{\mathrm{K}}} \tag{7}$$

$$K_{\mathrm{Na\text{-}Ca}} = \frac{X_{\mathrm{Ca}} f_{\mathrm{Ca}} m_{\mathrm{Na}} \gamma_{\mathrm{Na}}}{X_{\mathrm{Na}} f_{\mathrm{Na}} m_{\mathrm{Ca}}^{0.5} \gamma_{\mathrm{Ca}}^{0.5}} \tag{8}$$

where f_{Na}, f_{K}, and f_{Ca} denote the activity coefficients of NaX, KX, and $\mathrm{Ca}_{0.5}\mathrm{X}$, respectively, in phillipsite solid solutions. The molalities of cations in the aqueous phase are expressed as m_{Na}, m_{K}, and m_{Ca}, and their activity coefficients are expressed as γ_{Na}, γ_{K}, and γ_{Ca}.

Activity coefficients of the components in phillipsite solid solutions are expressed by a Margules equation based on the asymmetric regular solution model. By this formulation, f_{Na} and f_{K} in Na–K series phillipsite can be expressed as

$$RT \ln f_{\mathrm{Na}} = [W_{\mathrm{NaK}} + 2(W_{\mathrm{KNa}} - W_{\mathrm{NaK}})X_{\mathrm{Na}}]X_{\mathrm{K}}^2 \tag{9}$$

$$RT \ln f_{\mathrm{K}} = [W_{\mathrm{KNa}} + 2(W_{\mathrm{NaK}} - W_{\mathrm{KNa}})X_{\mathrm{K}}]X_{\mathrm{Na}}^2 \tag{10}$$

where W_{NaK} and W_{KNa} stand for Margules parameters, R stands for the universal gas constant, and T is the absolute temperature. For Na–Ca series phillipsite, f_{Na} and f_{Ca} can be expressed as

$$RT \ln f_{\mathrm{Na}} = [W_{\mathrm{NaCa}} + 2(W_{\mathrm{CaNa}} - W_{\mathrm{NaCa}})X_{\mathrm{Na}}]X_{\mathrm{Ca}}^2 \tag{11}$$

$$RT \ln f_{\mathrm{Ca}} = [W_{\mathrm{CaNa}} + 2(W_{\mathrm{NaCa}} - W_{\mathrm{CaNa}})X_{\mathrm{Ca}}]X_{\mathrm{Na}}^2 \tag{12}$$

Margules parameters for this binary are expressed as W_{NaCa} and W_{CaNa}.

Activity Coefficient of Aqueous Species

The activity coefficients of aqueous cations, M (=Na$^+$, K$^+$, or Ca^{2+}), are calculated by the equations of Greenberg and Møller (9). Their equation can be written as follows.

$$\begin{aligned}
\ln \gamma_M = {} & Z_M^2\Bigg(-A^{\Phi}\left[\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \left(\frac{2}{1.2}\right)\ln(1 + 1.2\sqrt{I})\right] \\
& + m_{Cl}(m_{Na}B^*_{NaCl} + m_K B^*_{KCl} + m_{Ca}B^*_{CaCl_2})\Bigg) \\
& + Z_M^2(m_{Na}m_K\Phi^*_{Na\text{-}K} + m_{Na}m_{Ca}\Phi^*_{Na\text{-}Ca} + m_K m_{Ca}\Phi^*_{Na\text{-}Ca} + m_{Cl}^2\Phi^*_{Cl\text{-}Cl}) \\
& + m_{Cl}\left[2B_{MCl} + (m_{Na} + m_K + 2m_{Ca} + m_{Cl})\frac{C^{\Phi}_{MCl}}{2\sqrt{Z_M}}\right] \\
& + m_{Na}(2\Phi_{M\text{-}Na} + m_{Cl}\Psi_{M\text{-}Na\text{-}Cl}) + m_K(2\Phi_{M\text{-}K} + m_{Cl}\Psi_{M\text{-}K\text{-}Cl}) \\
& + m_{Ca}(2\Phi_{M\text{-}Ca} + m_{Cl}\Psi_{M\text{-}Ca\text{-}Cl}) + m_{Cl}^2\Phi_{M\text{-}Cl\text{-}Cl} \\
& + |Z_M|\left[m_{Cl}\left(\frac{m_{Na}C^{\Phi}_{NaCl}}{2} + \frac{m_K C^{\Phi}_{KCl}}{2} + \frac{m_{Ca}C^{\Phi}_{CaCl_2}}{2\sqrt{2}}\right)\right] \qquad (13)
\end{aligned}$$

where Z_M stands for the charge of cation M, A^{Φ} is one-third the Debye–Hückel limiting slope, and I stands for ionic strength. The terms B and B^* are dependent on temperature and ionic strength, and are expressed by the following equations:

$$B = \beta^{(0)} + \beta^{(1)}\left(\frac{1 - (1 + 2\sqrt{I})e^{-2\sqrt{I}}}{2I}\right) \qquad (14)$$

$$B^* = -\beta^{(1)}\left(\frac{1 - (1 + 2\sqrt{I} + 2I)e^{-2\sqrt{I}}}{2I^2}\right) \qquad (15)$$

Functions $\beta^{(0)}$, $\beta^{(1)}$, and C^{Φ} for each chloride are expressed in the following form:

$$a_1 + a_2T + \frac{a_3}{T} + a_4 \ln T + \frac{a_5}{T - 263} + a_6T^2 + \frac{a_7}{680 - T} + \frac{a_8}{T - 227} \qquad (16)$$

A^{Φ} and Ψ were also expressed as the polynomial form of Eq. (16). The numerical values of the coefficients a_1 to a_7 for the computation of $\beta^{(0)}$, $\beta^{(1)}$, C^{Φ}, A^{Φ}, and Ψ are given in Greenberg and Møller (9). The terms Φ

and Φ^* are computed by the functions of Pitzer (11). The effects of neutral species interactions were set to zero in Eq. (13) according to Greenberg and Møller (9).

CALCULATION METHOD OF EQUILIBRIUM CONSTANTS AND MARGULES PARAMETERS

Calculations of the equilibrium constants and Margules parameters for phillipsite solid solutions are carried out by the nonlinear least-square regression method. We define function F as

$$F \equiv -\ln K_{\text{Na-K}} + \ln \frac{1 - X_{\text{Na}}}{X_{\text{Na}}} + \ln \frac{f_{\text{K}}}{f_{\text{Na}}} - \ln \frac{m_{\text{K}}\gamma_{\text{K}}}{m_{\text{Na}}\gamma_{\text{Na}}} \tag{17}$$

for the Na–K exchange reaction and

$$F \equiv -\ln K_{\text{Na-Ca}} + \ln \frac{1 - X_{\text{Na}}}{X_{\text{Na}}} + \ln \frac{f_{\text{Ca}}}{f_{\text{Na}}} - \ln \frac{m_{\text{Ca}}^{0.5}\gamma_{\text{Ca}}^{0.5}}{m_{\text{Na}}\gamma_{\text{Na}}} \tag{18}$$

for the Na–Ca exchange reaction. Substitutions of Eqs. (9) and (10) into Eq. (17) and rearrangement of the right-hand side of the equation gives

$$\begin{aligned} F = {} & -\ln K_{\text{Na-K}} + \ln \frac{1 - X_{\text{Na}}}{X_{\text{Na}}} \\ & + \frac{W_{\text{KNa}}X_{\text{Na}}(3X_{\text{Na}} - 2) - W_{\text{NaK}}(1 - 4X_{\text{Na}} + 3X_{\text{Na}}^2)}{RT} - \ln \frac{m_{\text{K}}\gamma_{\text{K}}}{m_{\text{Na}}\gamma_{\text{Na}}} \end{aligned} \tag{19}$$

From Eqs. (11), (12), and (18), we obtain

$$\begin{aligned} F = {} & -\ln K_{\text{Na-Ca}} + \ln \frac{1 - X_{\text{Na}}}{X_{\text{Na}}} \\ & + \frac{W_{\text{CaNa}}X_{\text{Na}}(3X_{\text{Na}} - 2) - W_{\text{NaCa}}(1 - 4X_{\text{Na}} + 3X_{\text{Na}}^2)}{RT} - \ln \frac{m_{\text{Ca}}^{0.5}\gamma_{\text{Ca}}^{0.5}}{m_{\text{Na}}\gamma_{\text{Na}}} \end{aligned} \tag{20}$$

Solid compositions are assumed to have certain errors, and solution compositions are assumed to be free of errors. Substitutions of the true Margules parameters and equilibrium constant and the calculated solid compositions into Eq. (19) or (20) should give $F = 0$ for all the experimental runs. Then this study minimizes the objective function (Q) as follows:

$$Q = \sum_i \frac{(X_{\text{Na}}^{(i)} - x_{\text{Na}}^{(i)})^2}{(\sigma^{(i)})^2} \tag{21}$$

where $\sigma^{(i)}$ designates the standard deviation of the analyses of the solid phase, and $X^{(i)}_{\mathrm{Na}}$ and $x^{(i)}_{\mathrm{Na}}$ stand for the measured and calculated solid compositions, respectively, for the ith experimental run. This study assigns 10^{-4} for all the $\sigma^{(i)}$ values.

Calculations of parameters and solid compositions follow the method of Britt and Luecke (12). The approximate parameters are designated as $\hat{K}$, $\hat{W}_{ij}$, and $\hat{W}_{ji}$, and the true parameters are designated as K, W_{ij}, and W_{ji}. The subscripts ij and ji stand for the cation pairs (Na–K and Na–Ca). For the ith experimental run, we denote the value of F as $F^{(i)}$. By solving the following equation, we obtain new estimates of the parameters and solid-phase compositions.

$$\begin{vmatrix} \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\frac{1}{L^{(i)}} & \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\frac{1}{L^{(i)}} & \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\frac{1}{L^{(i)}} \\ \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\frac{1}{L^{(i)}} & \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\frac{1}{L^{(i)}} & \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\frac{1}{L^{(i)}} \\ \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\frac{1}{L^{(i)}} & \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\frac{1}{L^{(i)}} & \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\frac{1}{L^{(i)}} \end{vmatrix}$$

$$\begin{vmatrix} \hat{K} - K \\ \hat{W}_{ij} - W_{ij} \\ \hat{W}_{ji} - W_{ji} \end{vmatrix} \quad \begin{vmatrix} \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{K}}\right)\left(\frac{F^{(i)} + \frac{\partial F^{(i)}}{\partial x^{(i)}_{\mathrm{Na}}}(X^{(i)}_{\mathrm{Na}} - x^{(i)}_{\mathrm{Na}})}{L^{(i)}}\right) \\ \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ij}}\right)\left(\frac{F^{(i)} + \frac{\partial F^{(i)}}{\partial x^{(i)}_{\mathrm{Na}}}(X^{(i)}_{\mathrm{Na}} - x^{(i)}_{\mathrm{Na}})}{L^{(i)}}\right) \\ \sum_i \left(\frac{\partial F^{(i)}}{\partial \hat{W}_{ji}}\right)\left(\frac{F^{(i)} + \frac{\partial F^{(i)}}{\partial x^{(i)}_{\mathrm{Na}}}(X^{i}_{\mathrm{Na}} - x^{(i)}_{\mathrm{Na}})}{L^{(i)}}\right) \end{vmatrix} \tag{22}$$

In Eq. (22), $L^{(i)}$ is defined as follows:

$$L^{(i)} = (\sigma^{(i)})^2 \left(\frac{\partial F^{(i)}}{\partial x^{(i)}_{\mathrm{Na}}}\right)^2 \tag{23}$$

The iteration is repeated until the parameters and $x^{(i)}_{\mathrm{Na}}$ values converged.

RESULTS AND DISCUSSION

Equilibrium Constants and Margules Parameters

The equilibrium constants for the cation-exchange reactions and Margules parameters for phillipsite solid solutions are listed in Table 3.

TABLE 3
Equilibrium Constants for the Na–K Exchange Reaction ($K_{\text{Na-K}}$) and the Na–Ca Exchange Reaction ($K_{\text{Na-Ca}}$) and Margules Parameters (kJ/mol) for Phillipsite Solid Solutions[a]

	Si-rich phillipsite	
	70°C	35°C
Na–K exchange:		
$K_{\text{Na-K}}$	16.88 (2.20)	28.26 (2.40)
W_{NaK}	−7.195 (0.465)	−5.492 (0.322)
W_{KNa}	−7.229 (1.532)	−8.286 (0.839)
Na–Ca exchange:		
$K_{\text{Na-Ca}}$	0.3756 (0.0173)	0.2114 (0.0175)
W_{NaCa}	−0.9434 (0.4779)	−0.5429 (0.7178)
W_{CaNa}	1.532 (0.348)	−0.3381 (0.6233)
	Si-poor phillipsite	
	70°C	35°C
Na–K exchange:		
$K_{\text{Na-K}}$	3.083 (0.194)	3.220 (0.283)
W_{NaK}	−2.445 (0.456)	−2.636 (0.521)
W_{KNa}	−4.125 (0.648)	−2.823 (0.851)
Na–Ca exchange:		
$K_{\text{Na-Ca}}$	1.164 (0.062)	0.6984 (0.0655)
W_{NaCa}	−0.8989 (0.3078)	−2.664 (0.750)
W_{CaNa}	1.318 (0.580)	−0.1034 (0.7342)

[a] Values in parentheses indicate standard errors.

The equilibrium constants for the Na–K exchange reaction ($K_{\text{Na-K}}$) involving the Si-rich phillipsite are larger than those involving the Si-poor phillipsite at both 70 and 35°C. The $K_{\text{Na-K}}$ values at 35°C are larger than those at 70°C for both phillipsites. The equilibrium constants for the Na–Ca exchange reaction ($K_{\text{Na-Ca}}$) involving the Si-rich phillipsite is smaller than those involving the Si-poor phillipsite at both temperatures. The $K_{\text{Na-Ca}}$ values at 70°C are larger than those at 35°C for both phillipsites. From the equilibrium constants, the Si-rich phillipsite shows the affinity sequence K > Na > Ca while the Si-poor phillipsite shows the sequence K > Ca > Na at 70°C and K > Na > Ca at 35°C.

Cation-Exchange Isotherms

Cation-exchange isotherms and the experimental data points for the Na–K exchange reaction are shown in Fig. 1. The data points are obtained

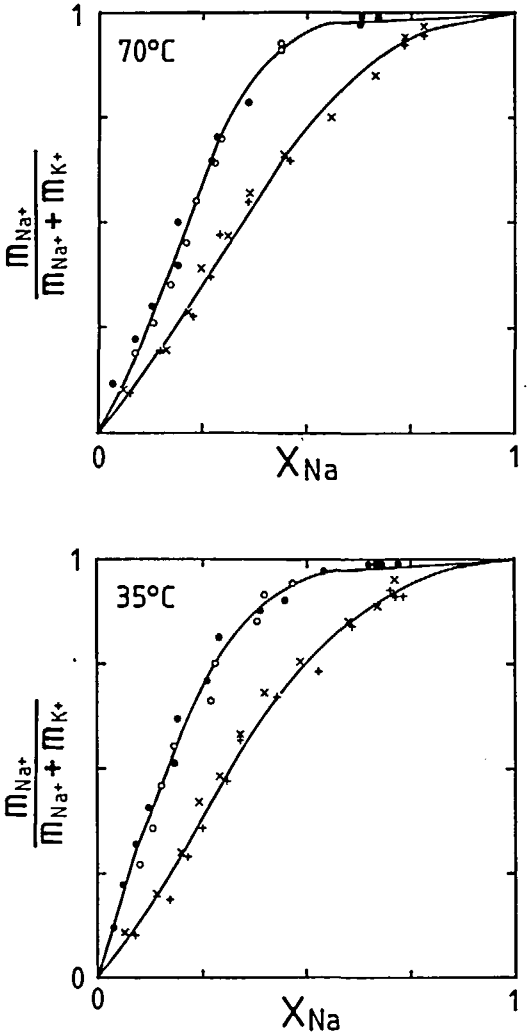

FIG. 1 Na–K exchange isotherms at 70 and 35°C. Open and filled circles show the results for Na release and K release from Si-rich phillipsite, respectively. Pluses and crosses show the results for Na release and K release from Si-poor phillipsite, respectively.

from the analytical results of both solid and solution compositions (Tables 4 to 7). At a specific solution composition, X_{Na} can be computed from Eq. (19) by substituting the computed γ_{Na} and γ_{K} values and the obtained $K_{\mathrm{Na\text{-}K}}$, W_{NaK}, and W_{KNa} values. Setting $F = 0$, X_{Na} is computed by successive iterations. The results of the calculations are shown as isotherms in Fig. 1.

TABLE 4

Na–K Exchange Reaction of Si-Rich Phillipsite with Aqueous Solution at 70°C

	Initial solution		Final solution			
Run[a]	m_{K}	m_{Na}	m_{K}	m_{Na}	Initial solid	Final solid,[b] X_{Na}
1[c]	0.0100	0.0902	0.0065	0.0961	Na-ex	0.5464
2[c]	0.0100	0.0902	0.0053	0.0914	Na-ex	0.4359
3[c]	0.0201	0.0802	0.0158	0.0805	Na-ex	0.4749
4[c]	0.0301	0.0702	0.0254	0.0739	Na-ex	0.3937
5	0.0401	0.0602	0.0351	0.0623	Na-ex	0.2774
6	0.0501	0.0501	0.0437	0.0543	Na-ex	0.2289
7	0.0602	0.0401	0.0542	0.0445	Na-ex	0.2127
8	0.0702	0.0301	0.0654	0.0357	Na-ex	0.1722
9	0.0802	0.0201	0.0740	0.0267	Na-ex	0.1267
10	0.0903	0.0100	0.0830	0.0194	Na-ex	0.0906
11[c]	0.1003	0.0000	0.0914	0.0060	Na-ex	0.0652
12	0.0100	0.0902	0.0084	0.0943	Na-ex	0.4448
13	0.0100	0.0902	0.0077	0.0918	Na-ex	0.4399
14	0.0100	0.0902	0.0066	0.0909	Na-ex	0.4525
15	0.0000	0.1002	0.0025	0.0991	K-ex	0.6298
16[c]	0.0100	0.0902	0.0110	0.0859	K-ex	0.4965
17	0.0201	0.0802	0.0209	0.0782	K-ex	0.3605
18	0.0301	0.0702	0.0300	0.0686	K-ex	0.2872
19[c]	0.0401	0.0602	0.0394	0.0592	K-ex	0.2119
20	0.0501	0.0501	0.0488	0.0493	K-ex	0.1904
21	0.0602	0.0401	0.0583	0.0394	K-ex	0.1893
22	0.0702	0.0301	0.0684	0.0303	K-ex	0.1340
23	0.0802	0.0201	0.0787	0.0220	K-ex	0.0894
24	0.0903	0.0100	0.0877	0.0117	K-ex	0.0432
25	0.0000	0.1002	0.0015	0.0996	K-ex	0.6288
26	0.0000	0.1002	0.0014	0.0960	K-ex	0.6714

[a] Composition. Runs 1, 3–10, 12, 15–24: 100 mg in 50 mL. Run 2: 75 mg in 100 mL. Run 11: 50 mg in 100 mL. Runs 14, 25: 40 mg in 100 mL. Runs 13, 26: 100 mg in 100 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and K in phillipsite.

[c] *These data are not included in the final regression and the cation-exchange isotherm.*

TABLE 5

Na–K Exchange Reaction of Si-Rich Phillipsite with Aqueous Solution at 35°C

Run[a]	Initial solution		Final solution		Initial solid	Final solid,[b]
	m_K	m_{Na}	m_K	m_{Na}		X_{Na}
1	0.0100	0.0902	0.0060	0.0920	Na-ex	0.4737
2	0.0201	0.0802	0.0156	0.0880	Na-ex	0.3766
3	0.0301	0.0702	0.0253	0.0745	Na-ex	0.2836
4	0.0401	0.0602	0.0340	0.0671	Na-ex	0.2655
5	0.0501	0.0501	0.0452	0.0542	Na-ex	0.1793
6	0.0602	0.0401	0.0541	0.0457	Na-ex	0.1500
7	0.0702	0.0301	0.0640	0.0364	Na-ex	0.1283
8	0.0802	0.0201	0.0727	0.0273	Na-ex	0.0994
9[c]	0.0903	0.0100	0.0821	0.0174	Na-ex	0.0816
10[c]	0.1003	0.0000	0.0916	0.0065	Na-ex	0.0476
11[c]	0.1003	0.0000	0.1000	0.0017	Na-ex	0.0329
12	0.0100	0.0902	0.0087	0.0908	Na-ex	0.3992
13	0.0100	0.0902	0.0091	0.0894	Na-ex	0.3976
14	0.0000	0.1002	0.0025	0.0934	K-ex	0.5419
15	0.0100	0.0902	0.0115	0.0855	K-ex	0.3902
16	0.0201	0.0802	0.0195	0.0803	K-ex	0.2868
17	0.0301	0.0702	0.0293	0.0701	K-ex	0.2554
18	0.0401	0.0602	0.0388	0.0621	K-ex	0.1870
19	0.0501	0.0501	0.0493	0.0510	K-ex	0.1793
20	0.0602	0.0401	0.0583	0.0408	K-ex	0.1183
21	0.0702	0.0301	0.0691	0.0323	K-ex	0.0862
22	0.0802	0.0201	0.0764	0.0218	K-ex	0.0598
23	0.0903	0.0100	0.0868	0.0114	K-ex	0.0392
24	0.0000	0.1002	0.0008	0.0962	K-ex	0.6820
25	0.0100	0.0902	0.0095	0.0901	K-ex	0.4463
26	0.0000	0.1002	0.0006	0.0975	K-ex	0.7186
27	0.0000	0.1002	0.0007	0.1003	K-ex	0.6748
28	0.0000	0.1002	0.0009	0.1006	K-ex	0.6537

[a] Composition. Runs 1–10, 14–23: 100 mg in 100 mL. Runs 11, 24, 25: 100 mg in 200 mL. Runs 12, 13, 28: 50 mg in 100 mL. Run 26: 30 mg in 100 mL. Run 27: 40 mg in 100 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and K in phillipsite.

[c] These data are not included in the final regression and the cation-exchange isotherm.

Most of the experimental results of the reverse exchange reactions (Na uptake from solution) agree with those of the forward exchange reactions (Na release from phillipsite) lying close to the computed isotherms. Therefore, the exchange isotherms obtained are considered to be the equilibrium

TABLE 6
Na–K Exchange Reaction of Si-Poor Phillipsite with Aqueous Solution at 70°C

	Initial solution		Final solution			
Run[a]	m_K	m_{Na}	m_K	m_{Na}	Initial solid	Final solid,[b] X_{Na}
1	0.1003	0.0000	0.0908	0.0091	Na-ex	0.0756
2	0.0903	0.0100	0.0795	0.0187	Na-ex	0.1512
3	0.0802	0.0201	0.0699	0.0278	Na-ex	0.2202
4	0.0702	0.0301	0.0610	0.0365	Na-ex	0.2664
5	0.0602	0.0401	0.0510	0.0465	Na-ex	0.2932
6	0.0501	0.0501	0.0428	0.0551	Na-ex	0.3603
7	0.0401	0.0602	0.0342	0.0649	Na-ex	0.4598
8[c]	0.0301	0.0702	0.0264	0.0748	Na-ex	0.5703
9[c]	0.0201	0.0802	0.0148	0.0826	Na-ex	0.6649
10	0.0050	0.0952	0.0042	0.0965	Na-ex	0.7800
11	0.0100	0.0902	0.0084	0.0925	Na-ex	0.7291
12	0.0903	0.0100	0.0888	0.0101	K-ex	0.0721
13	0.0802	0.0201	0.0798	0.0196	K-ex	0.1651
14	0.0702	0.0301	0.0727	0.0291	K-ex	0.2142
15	0.0602	0.0401	0.0604	0.0380	K-ex	0.2541
16	0.0501	0.0501	0.0513	0.0461	K-ex	0.3095
17	0.0401	0.0602	0.0426	0.0556	K-ex	0.3621
18	0.0301	0.0702	0.0328	0.0647	K-ex	0.4522
19	0.0201	0.0802	0.0245	0.0753	K-ex	0.5649
20	0.0100	0.0902	0.0150	0.0820	K-ex	0.6554
21	0.0000	0.1002	0.0058	0.0908	K-ex	0.7336
22	0.0000	0.1002	0.0034	0.0937	K-ex	0.7820

[a] Composition. Runs 1–9, 12–21: 100 mg in 50 mL. Runs 10, 22: 100 mg in 200 mL. Run 11: 100 mg in 100 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and K in phillipsite.

[c] These data are not included in the final regression and the cation-exchange isotherm.

ones. Both Si-rich and Si-poor phillipsites prefer K^+ over Na^+ at 70 and 35°C. The selectivity for K^+ over Na^+ is larger in the Si-rich phillipsite than in the Si-poor one.

Cation-exchange isotherms and experimental data points for Na–Ca exchange reaction are shown in Fig. 2. The data points are obtained from the analytical results of both solid and solution compositions (Tables 8 to 11). The isotherms are obtained from Eq. (20) by the method of the isotherm calculation for the Na–K exchange reaction. Most of the experi-

TABLE 7
Na–K Exchange Reaction of Si-Poor Phillipsite with Aqueous Solution at 35°C

	Initial solution		Final solution		Initial solid	Final solid,[b]
Run[a]	m_K	m_{Na}	m_K	m_{Na}		X_{Na}
1	0.1003	0.0000	0.0890	0.0098	Na-ex	0.0887
2	0.0903	0.0100	0.0821	0.0192	Na-ex	0.1742
3	0.0802	0.0201	0.0715	0.0289	Na-ex	0.2143
4	0.0702	0.0301	0.0654	0.0364	Na-ex	0.2505
5	0.0602	0.0401	0.0508	0.0458	Na-ex	0.3104
6	0.0501	0.0501	0.0434	0.0572	Na-ex	0.3401
7	0.0401	0.0602	0.0323	0.0644	Na-ex	0.4261
8	0.0301	0.0702	0.0271	0.0741	Na-ex	0.5342
9	0.0201	0.0802	0.0163	0.0827	Na-ex	0.6136
10	0.0100	0.0902	0.0067	0.0928	Na-ex	0.6963
11	0.0100	0.0902	0.0093	0.0907	Na-ex	0.7079
12	0.0100	0.0902	0.0092	0.0882	Na-ex	0.7213
13	0.0903	0.0100	0.0891	0.0106	K-ex	0.0725
14	0.0802	0.0201	0.0786	0.0201	K-ex	0.1421
15	0.0702	0.0301	0.0692	0.0290	K-ex	0.2010
16	0.0602	0.0401	0.0584	0.0432	K-ex	0.2410
17	0.0501	0.0501	0.0504	0.0471	K-ex	0.2871
18	0.0401	0.0602	0.0406	0.0563	K-ex	0.3350
19	0.0301	0.0702	0.0306	0.0663	K-ex	0.4047
20	0.0201	0.0802	0.0233	0.0731	K-ex	0.4876
21	0.0100	0.0902	0.0143	0.0843	K-ex	0.6007
22	0.0000	0.1002	0.0050	0.0925	K-ex	0.7094
23[c]	0.0000	0.1002	0.0020	0.1004	K-ex	0.8239
24	0.0100	0.0902	0.0111	0.0908	K-ex	0.6707

[a] Composition. Runs 1–10, 13–22: 100 mg in 50 mL. Run 11: 100 mgin 250 mL. Runs 12, 23, 24: 100 mg in 200 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and K in phillipsite.

[c] This data is not included in the final regression and the cation-exchange isotherm.

mental results of the reverse exchange reactions (Na uptake from solution) agree with those of the forward exchange reactions (Na release from phillipsite) lying close to the computed isotherms. Therefore, the calculated isotherms are considered to be the equilibrium ones. The Si-poor phillipsite prefers Ca^{2+} over Na^+ at both temperatures while the Si-rich one

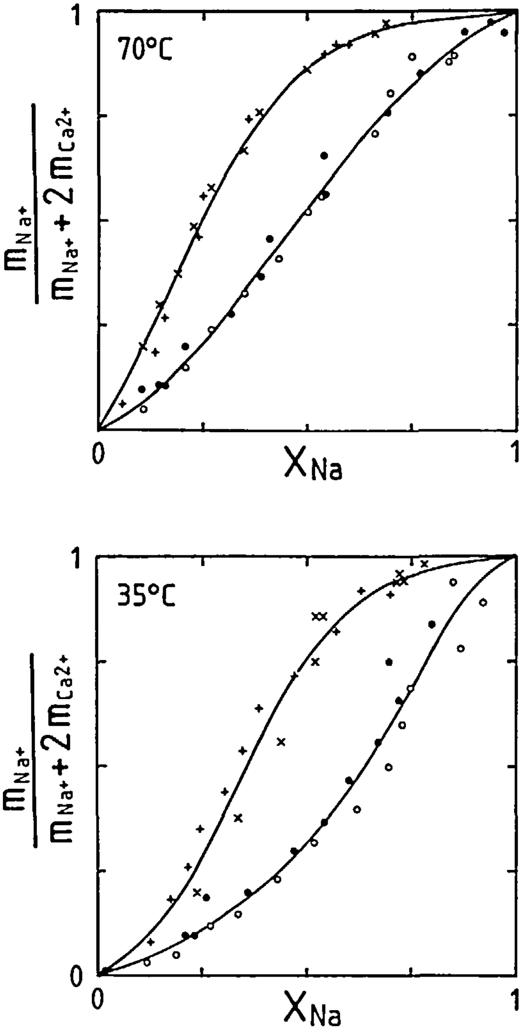

FIG. 2 Na-Ca exchange isotherms at 70 and 35°C. Open and solid circles show the results for Na release and Ca release from the Si-rich phillipsite, respectively. Pluses and crosses show the results for Na release and Ca release from Si-poor phillipsite, respectively.

TABLE 8

Na–Ca Exchange Reaction of Si-Rich Phillipsite with Aqueous Solution at 70°C

Run[a]	Initial solution m_{Ca}	Initial solution m_{Na}	Final solution m_{Ca}	Final solution m_{Na}	Initial solid	Final solid,[b] X_{Na}
1	0.0502	0.0000	0.0481	0.0055	Na-ex	0.1180
2	0.0452	0.0100	0.0438	0.0154	Na-ex	0.2065
3	0.0402	0.0200	0.0388	0.0245	Na-ex	0.2749
4	0.0352	0.0301	0.0346	0.0335	Na-ex	0.3519
5	0.0302	0.0401	0.0297	0.0414	Na-ex	0.4295
6	0.0251	0.0501	0.0236	0.0511	Na-ex	0.4984
7	0.0201	0.0601	0.0217	0.0562	Na-ex	0.5334
8	0.0151	0.0702	0.0148	0.0709	Na-ex	0.6633
9	0.0101	0.0802	0.0101	0.0790	Na-ex	0.6994
10	0.0050	0.0902	0.0056	0.0884	Na-ex	0.7537
11	0.0050	0.0902	0.0058	0.0856	Na-ex	0.8445
12	0.0050	0.0902	0.0052	0.0863	Na-ex	0.8498
13[c]	0.0502	0.0000	0.0474	0.0025	Na-ex	0.0939
14	0.0452	0.0100	0.0437	0.0101	Ca-ex	0.1095
15	0.0402	0.0200	0.0403	0.0196	Ca-ex	0.2068
16	0.0352	0.0301	0.0367	0.0290	Ca-ex	0.3204
17	0.0301	0.0401	0.0319	0.0373	Ca-ex	0.3866
18	0.0251	0.0501	0.0269	0.0456	Ca-ex	0.4065
19	0.0201	0.0601	0.0221	0.0558	Ca-ex	0.5397
20	0.0151	0.0702	0.0171	0.0656	Ca-ex	0.5407
21	0.0101	0.0802	0.0123	0.0754	Ca-ex	0.6857
22	0.0050	0.0902	0.0075	0.0841	Ca-ex	0.7690
23	0.0000	0.1002	0.0027	0.0924	Ca-ex	0.8751
24	0.0000	0.1002	0.0021	0.0866	Ca-ex	0.9668
25	0.0000	0.1002	0.0014	0.1007	Ca-ex	0.9408
26	0.0452	0.0100	0.0443	0.0113	Ca-ex	0.1485
27	0.0452	0.0100	0.0434	0.0107	Ca-ex	0.1589

[a] Composition. Runs 1–10, 14–23: 100 mg in 50 mL. Runs 11, 13, 24, 27: 50 mg in 100 mL. Runs 12, 25, 26: 100 mg in 100 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and Ca in phillipsite.

[c] These data are not included in the final regression and the cation-exchange isotherm.

prefers Na^+ over Ca^{2+} at 35°C and shows no preference for Na^+ over Ca^{2+} at 70°C.

Activity Coefficients Versus Composition

Using the obtained Margules parameters, activity coefficients of components in phillipsite solid solutions were computed against X_{Na} at 70 and

TABLE 9
Na–Ca Exchange Reaction of Si-Rich Phillipsite with Aqueous Solution at 35°C

	Initial solution		Final solution		Initial solid	Final solid,[b]
Run[a]	m_{Ca}	m_{Na}	m_{Ca}	m_{Na}		X_{Na}
1	0.0050	0.0902	0.0057	0.0879	Na-ex	0.9160
2	0.0101	0.0802	0.0109	0.0764	Na-ex	0.8685
3	0.0151	0.0702	0.0154	0.0689	Na-ex	0.7479
4	0.0201	0.0601	0.0199	0.0597	Na-ex	0.7315
5	0.0251	0.0501	0.0248	0.0491	Na-ex	0.7029
6	0.0301	0.0401	0.0306	0.0403	Na-ex	0.6230
7	0.0352	0.0301	0.0342	0.0319	Na-ex	0.5272
8	0.0402	0.0200	0.0396	0.0240	Na-ex	0.4292
9	0.0452	0.0100	0.0437	0.0150	Na-ex	0.3421
10	0.0452	0.0100	0.0458	0.0121	Na-ex	0.2668
11	0.0502	0.0000	0.0483	0.0049	Na-ex	0.1897
12	0.0000	0.1002	0.0506	0.0028	Na-ex	0.1242
13	0.0000	0.1002	0.0028	0.0919	Na-ex	0.8542
14	0.0050	0.0902	0.0078	0.0847	Ca-ex	0.7977
15	0.0101	0.0802	0.0244	0.0744	Ca-ex	0.6957
16	0.0151	0.0702	0.0166	0.0646	Ca-ex	0.7224
17	0.0201	0.0601	0.0212	0.0549	Ca-ex	0.6724
18	0.0251	0.0501	0.0262	0.0465	Ca-ex	0.6021
19	0.0301	0.0401	0.0304	0.0361	Ca-ex	0.5360
20	0.0352	0.0301	0.0351	0.0278	Ca-ex	0.4749
21	0.0402	0.0200	0.0395	0.0189	Ca-ex	0.3622
22	0.0452	0.0100	0.0435	0.0097	Ca-ex	0.2318
23	0.0452	0.0100	0.0464	0.0098	Ca-ex	0.2078
24	0.0452	0.0100	0.0481	0.0013	Ca-ex	0.0205
25	0.0402	0.0200	0.0409	0.0193	Ca-ex	0.2651

[a] Composition. Runs 1–9, 11, 13–22, 24: 100 mg in 50 mL. Runs 10, 12, 23, 25: 100 mg in 100 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and Ca in phillipsite.

35°C (Figs. 3 and 4) by using Eqs. (9) and (10) or Eqs. (11) and (12). For the Na–K series, the Si-rich phillipsite shows larger nonideality (deviations of f_{Na} and f_K from 1) than the Si-poor phillipsite at both temperatures. The relations between the activity coefficient and composition show little temperature dependence. For the Na–Ca series phillipsites, activity coefficients versus composition relations at 70° C show little differences of f_{Na}

TABLE 10
Na–Ca Exchange Reaction of Si-Poor Phillipsite with Aqueous Solution at 70°C

Run[a]	Initial solution m_{Ca}	Initial solution m_{Na}	Final solution m_{Ca}	Final solution m_{Na}	Initial solid	Final solid,[b] X_{Na}
1	0.0050	0.0902	0.0040	0.0941	Na-ex	0.5971
2	0.0151	0.0702	0.0132	0.0742	Na-ex	0.3627
3	0.0251	0.0501	0.0217	0.0550	Na-ex	0.2510
4	0.0301	0.0401	0.0265	0.0455	Na-ex	0.2357
5	0.0402	0.0200	0.0390	0.0290	Na-ex	0.1581
6	0.0452	0.0100	0.0414	0.0189	Na-ex	0.1373
7[c]	0.0502	0.0000	0.0460	0.0085	Na-ex	0.0857
8	0.0050	0.0902	0.0041	0.0903	Na-ex	0.5651
9	0.0050	0.0902	0.0052	0.0928	Na-ex	0.5363
10	0.0502	0.0000	0.0486	0.0060	Na-ex	0.0566
11	0.0000	0.1002	0.0026	0.0872	Ca-ex	0.6633
12	0.0050	0.0902	0.0069	0.0842	Ca-ex	0.5027
13	0.0101	0.0802	0.0124	0.0786	Ca-ex	0.3946
14	0.0151	0.0702	0.0166	0.0656	Ca-ex	0.3467
15	0.0201	0.0601	0.0212	0.0575	Ca-ex	0.2707
16	0.0251	0.0501	0.0264	0.0506	Ca-ex	0.2310
17	0.0301	0.0401	0.0318	0.0388	Ca-ex	0.1882
18	0.0352	0.0301	0.0358	0.0300	Ca-ex	0.1528
19	0.0402	0.0200	0.0409	0.0207	Ca-ex	0.1057
20[c]	0.0452	0.0100	0.0463	0.0098	Ca-ex	0.0992
21	0.0000	0.1002	0.0016	0.0954	Ca-ex	0.6927

[a] Composition. Runs 1–7, 11–20: 100 mg in 50 mL. Run 8: 100 mg in 100 mL. Runs 9, 10, 21: 150 mg in 100 mL.

[b] *Solid-phase compositions are obtained from the analyses of Na and Ca in phillipsite.*

[c] These data are not included in the final regression and the cation-exchange isotherm.

and f_{Ca} between the Si-rich and the Si-poor phillipsites. This arises because the W_{NaCa} and W_{CaNa} values are almost the same. However, the differences in f_{Na} and f_{Ca} between the Si-rich phillipsite and the Si-poor phillipsite are large at 35°C. For almost the entire composition range the Si-poor phillipsite shows larger nonideality than the Si-rich phillipsite.

Calculations of Na–Ca Exchange Isotherms

When the exchanging cations have different charges, the cation-exchange isotherms depend strongly on the total normality in the coexisting

TABLE 11
Na–Ca Exchange Reaction of Si-Poor Phillipsite with Aqueous Solution at 35°C

Run[a]	Initial solution		Final solution		Initial solid	Final solid,[b] X_{Na}
	m_{Ca}	m_{Na}	m_{Ca}	m_{Na}		
1	0.0050	0.0902	0.0040	0.0948	Na-ex	0.6281
2	0.0101	0.0802	0.0092	0.0827	Na-ex	0.5748
3	0.0151	0.0702	0.0140	0.0729	Na-ex	0.4723
4	0.0201	0.0601	0.0179	0.0635	Na-ex	0.3884
5	0.0251	0.0501	0.0224	0.0532	Na-ex	0.3509
6	0.0301	0.0401	0.0274	0.0439	Na-ex	0.3056
7	0.0352	0.0301	0.0332	0.0356	Na-ex	0.2482
8	0.0402	0.0200	0.0363	0.0257	Na-ex	0.2186
9	0.0452	0.0100	0.0410	0.0174	Na-ex	0.1773
10	0.0502	0.0000	0.0463	0.0083	Na-ex	0.1279
11	0.0050	0.0902	0.0047	0.0910	Na-ex	0.7046
12[c]	0.0025	0.0952	0.0005	0.0973	Na-ex	0.9792
13	0.0000	0.1002	0.0025	0.0925	Ca-ex	0.7340
14	0.0050	0.0902	0.0071	0.0842	Ca-ex	0.5379
15	0.0101	0.0802	0.0123	0.0727	Ca-ex	0.5231
16	0.0201	0.0601	0.0218	0.0554	Ca-ex	0.4413
17	0.0301	0.0401	0.0310	0.0378	Ca-ex	0.3354
18	0.0402	0.0200	0.0412	0.0202	Ca-ex	0.2414
19	0.0000	0.1002	0.0024	0.0921	Ca-ex	0.7184
20	0.0050	0.0902	0.0070	0.0846	Ca-ex	0.5323
21	0.0000	0.1002	0.0018	0.0970	Ca-ex	0.7270
22	0.0000	0.1002	0.0025	0.0985	Ca-ex	0.7812

[a] Composition. Runs 1–10, 13–19: 100 mg in 50 mL. Runs 11, 12, 20, 21: 100 mg in 100 mL. Runs 22: 60 mg in 100 mL.

[b] Solid-phase compositions are obtained from the analyses of Na and Ca in phillipsite.

[c] These data are not included in the final regression and the cation-exchange isotherm.

solution (13). Calculations were carried out for total normalities of 0.01, 0.1, and 1 N. The computed isotherms at 70 and 35°C are shown in Figs. 5 and 6, respectively. When the total normality of the coexisting solution is 0.01 N, both phillipsites prefer Na^+ to Ca^{2+} at both temperatures. On the other hand, the exchange isotherms at the total normality = 1 N show that both phillipsites prefer Ca^{2+} to Na^+ at 70 and 35°C. Therefore, dilution of the solution makes both phillipsites prefer Na^+ to Ca^{2+}.

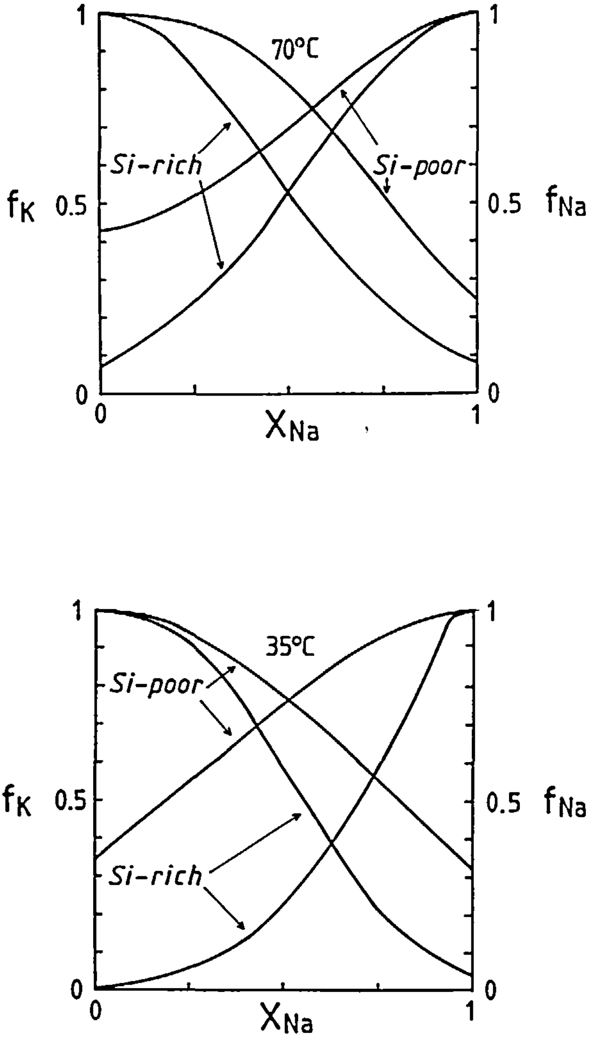

FIG. 3 Activity coefficients versus composition relations in Na–K series phillipsites at 70 and 35°C.

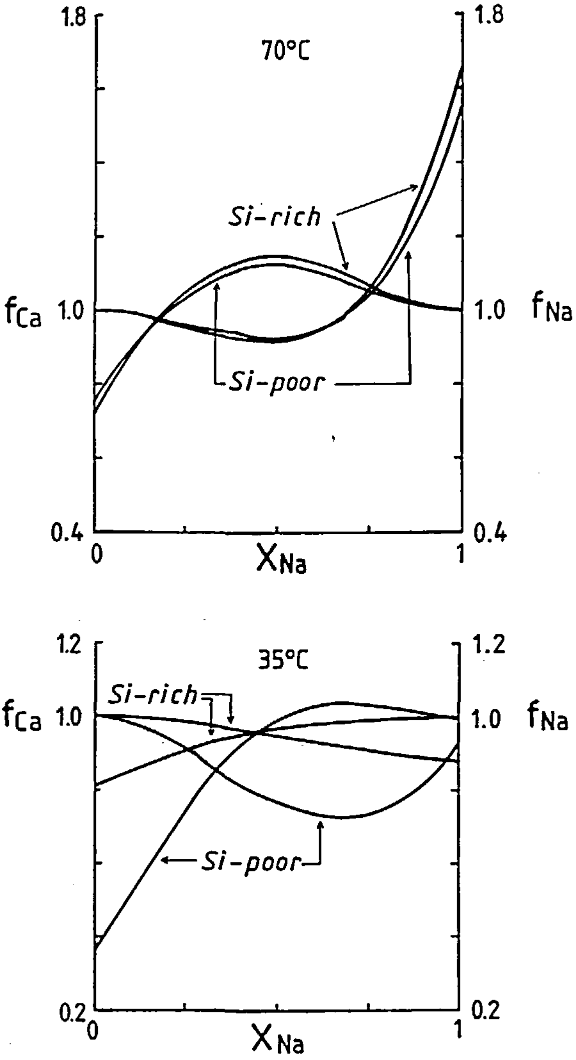

FIG. 4 Activity coefficients versus composition relations in Na–Ca series phillipsites at 70 and 35°C.

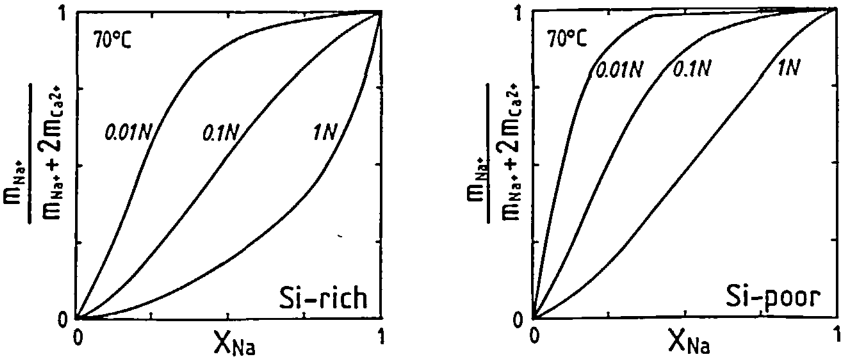

FIG. 5 Na–Ca exchange isotherms at 70°C when the total normalities are 1, 0.1, and 0.01 N.

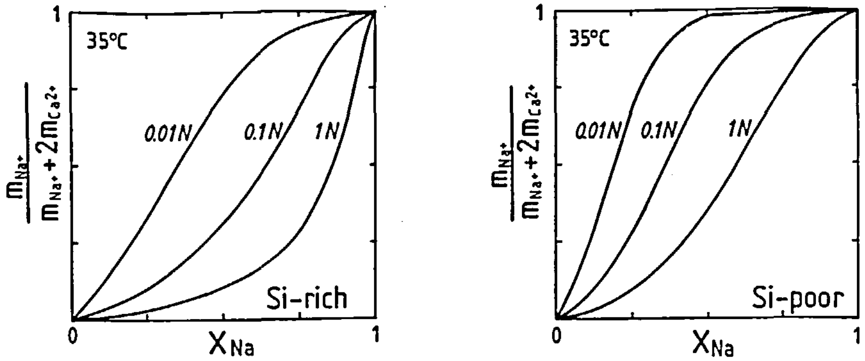

FIG. 6 Na–Ca exchange isotherms at 35°C when the total normalities are 1, 0.1, and 0.01 N.

CONCLUSIONS

Cation-exchange properties of the Si-rich and Si-poor phillipsites with a 0.1 N NaCl + KCl or 0.1 N NaCl + $CaCl_2$ solution were obtained at 70 and 35°C and are compared. The equilibrium constants for the cation-exchange reactions depend on the Si content in phillipsite. The activity coefficients of the components in Na–K series phillipsites depend on the Si content with a small temperature dependence. Although Na–Ca series phillipsites show little differences in the activity coefficient versus composition relations at 70°C, the activity coefficients of the components at 35°C depend on the Si-content.

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