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A Model of Crystal Defects in Calcite by Sodium and Potassium Uptake

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Crystal defects in calcite containing Na and K ions were investigated by means of a model based on statistical thermodynamics and measurements of thermoelectric power. The varying amount of Na and K ions in the crystal was interpreted on an assumption of ideal solution of the ions as $Ca_{1-x-y}\square_{x+y}[Na_{2x}, K_{2y}]CO_3$, where $\square$ and [ ] means Ca-vacancy and interstitial ion, respectively. In the model, the excess charge of Na and K ions is balanced with Ca-vacancy to form interstitial-vacancy pairs ($[Na, K]_2\square$). Measurements of thermoelectric power in calcite showed the cationic transport which resulted from Na and K interstitials and/or Ca-vacancies. From the ideal mixing of Na and K ions at interstitial sites, the K/Na molar ratio in calcite was correlated with that in aqueous solution at 20 °C and pH 8.5 by the formula,

$$\frac{K_S}{Na_S} = 0.20\frac{K_L}{Na_L},$$

where S and L refer to solid- and aqueous-phase, respectively.

The study of sodium and potassium partitioning between carbonate minerals and aqueous solution has suggested the incorporation of these monovalent ions into the carbonate lattice rather than their presence as solid non-carbonate impurities or liquid inclusions.[1,2] In the partitioning of an ion with different valence from that of host carbonate ion, electroneutrality must be maintained in the crystal. The incorporation of such ions is usually accompanied with the formation of crystal defects, such as vacancies, interstitial ions, and substitutional ions.[3] The identification of crystal defects associated with impurity ions is needed to establish the partition theory of carbonate minerals. Although defect in calcite has been considered in the partitioning process of Na and K, the identification of defects has not fully been performed.

Electrical properties, such as ionic conductivity, dielectric loss and thermoelectric power, of calcium carbonate have been studied to characterize the crystal defects in the crystals.[4–6] These transport properties depend on the concentration and mobility of defects in the crystal and give direct information concerning the defect characteristics. However, it is difficult to assign the type of defect to each impurity ion, because natural and synthetic calcium carbonates contain different amounts of impurity ions. The nature of defect induced by impurity ions needs to be better understood. For the study of electrical properties, it is necessary to use samples having controlled impurity content. Further difficulty arises from the polycrystalline nature of samples. It is pointed out that the measurement of thermoelectric power of ionic crystals is not affected by the state of aggregation of samples.[7] The method, therefore, seems to be practical when we use substances not in a single-crystal form.

Statistical thermodynamics has been applied to the theoretical investigation of crystal defects in ionic crystals.[8–11] Assuming random distribution of defects in a crystal, configurational entropy is calculated to derive the equation which satisfies the condition of minimum free energy. The equation describes the equilibrium concentration of defect with respect to impurity concentration and temperature. This method requires a defect model which makes us calculate the configurational entropy and is useful for identifying the type of crystal defects.

Ishikawa and Ichikuni[2] suggested the interstitial incorporation of sodium and potassium in calcite, and assumed that the position between the carbonate ion and CaO_6 octahedron would be a possible interstitial site. Formation of Ca-vacancy in calcite was also assumed in order to explain compensation for the excess charge due to sodium and potassium. The purpose of this paper is to verify the above model based on the statistical thermodynamic calculation of sodium and potassium doping in calcite and the measurement of thermoelectric power. The model gives the formula expressing the relationship between K/Na ratio in calcite and that in aqueous phase.

Experimental

Calcite was precipitated from $Ca(OH)_2$ solution containing different amounts of NaCl and KCl by adding CO_2-saturated water. The solution was constantly stirred at 20 °C in a closed reaction vessel until an equilibrium after about 40 h. Precipitated calcite was about 1 μm in size and rhombohedral in shape. The uniform distribution of Na and K in calcite crystals was confirmed by fractional leaching in dilute HCl solution.[2] Synthetic calcite contained Cl of about 0.001 $mol\,kg^{-1}$. The content was 10^2 times lower than Na and K contents. The effect of Cl on the Na and K uptake by calcite was, therefore, disregarded in the discussion.

The measurement of thermoelectric power was made on calcite samples containing 0.13 $mol\,kg^{-1}$ of Na and 0.073 $mol\,kg^{-1}$ of K. The thermoelectric cell used was made of pyrophyllite preheated at 800 °C for 3 h. The arrangement of the cell was similar to that of Parravano.[7] Calcite

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Table 1. Data on Sodium and Potassium Uptake by Calcite at pH 8.5 and 20 °C. For all Experiments, $\mathrm{Ca^{2+}}$ = 0.6 mM; $\mathrm{HCO_3^-}$ = 1.2 mM

No.	$a_{\mathrm{Na}}^{\mathrm{L}}$	$a_{\mathrm{K}}^{\mathrm{L}}$	$\mathrm{K_L}$	$\mathrm{Na_S}$	$\mathrm{K_S}$	$\mathrm{K_S}$
			$\mathrm{Na_L}$	mol/kg^{-1}	mol/kg^{-1}	$\mathrm{Na_S}$
1	0.0016	0.058	40	0.00983	0.0235	2.39
2	0.0078	0.058	8.0	0.0186	0.0246	1.32
3	0.015	0.058	4.0	0.0276	0.0224	0.812
4	0.017	0.017	1.0	0.034	0.00824	0.242
5	0.023	0.058	2.7	0.0398	0.0221	0.555
6	0.030	0.058	2.0	0.0497	0.0211	0.425
7	0.037	0.058	1.6	0.0626	0.0208	0.332
8	0.038	0.038	1.0	0.0632	0.0151	0.239
9	0.059	0.058	1.0	0.0830	0.0157	0.189
10	0.072	0.069	1.0	0.0985	0.0184	0.187
11	0.086	0.058	0.67	0.0936	0.0142	0.152
12	0.11	0.058	0.50	0.100	0.0118	0.118
13	0.14	0.058	0.43	0.105	0.0095	0.0905

a) $a_{\mathrm{Na}}^{\mathrm{L}}$ and $a_{\mathrm{K}}^{\mathrm{L}}$ represent activity values of Na and K in solution, and $\mathrm{Na_S}$ and $\mathrm{K_S}$ are contents of Na and K in precipitated $\mathrm{CaCO_3}$.

sample was pressed at about 0.5 GPa to form a pellet of 5 mm in diameter and 7 mm thick, and was set between two platinum electrodes inside the cell. The electrodes were tightly pressed against the sample by two pyrophyllite supports, which contain chromel-alumel thermocouples and nichrome heaters near the sample. In order to reduce thermal convection current, the cell was mounted horizontally in the furnace. Supplementary heating was provided with nichrome heater to establish a temperature gradient between the electrodes.

Results

Coprecipitation of Na and K with calcite was carried out under controlled conditions where aqueous concentration of $\mathrm{Ca^{2+}}$ and $\mathrm{HCO_3^-}$ was fixed at 0.6 and 1.2 mM, respectively, at pH 8.5. Table 1 gives the amounts of coprecipitated Na and K with respect to various Na and K compositions of aqueous solutions. To investigate the relationship between contents of Na and K in calcite, the amount of coprecipitated K was determined as a function of that of Na as shown in Fig. 1, where aqueous K activity was fixed at a constant value ($a_{\mathrm{K}}^{\mathrm{L}}$=0.058). The result shows that K incorporation into calcite decreases with increasing Na content. The relationship between Na content and K content in calcite will be quantitatively examined in Discussion.

The thermoelectric voltage (ΔV) in samples was reversibly changed with increasing and decreasing temperature gradient (ΔT) between two electrodes. Figure 2 shows the thermoelectric power ($\Delta V/\Delta T$) as a function of temperature when ΔT was maintained at 10—15 °C. Bars in Fig. 2 show the range of the thermoelectric power of increasing and decreasing temperature. For all the samples the colder side of the sample was found to be positive in the temperature range between 360 and 570 °C and thermoelectric power showed a maximum and a minimum.

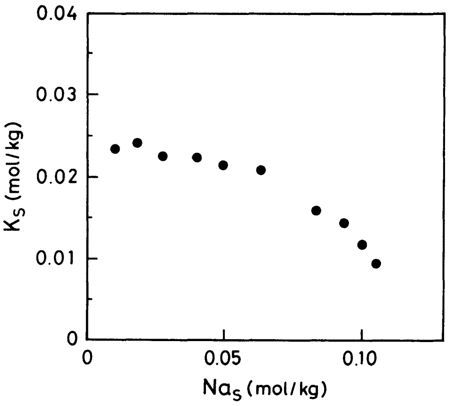

Fig. 1. Sodium and potassium uptake by calcite at pH 8.5 and 20°C. Aqueous activity of potassium is fixed at 0.058 and that of sodium ranges from 0.0016 to 0.14.

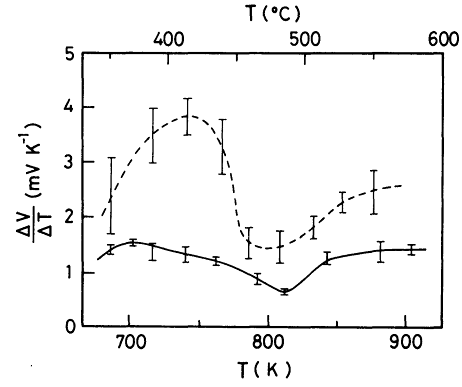

Fig. 2. Thermoelectric voltage per degree of calcite as a function of temperature. —: $\mathrm{Na_S}$=0.13 mol kg^{-1}, ---: $\mathrm{K_S}$=0.073 mol kg^{-1}.

Discussion

Interstitial-Vacancy Type Solid Solution. A mech-

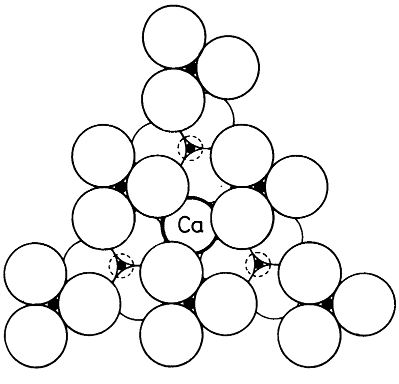

Fig. 3. Interstitial positions in the calcite lattice. The symbol ○ represents equivalent interstitial sites around a Ca ion. Another set of three sites, found at inversion points with respect to the Ca ion, are omitted for the sake of simplicity.

anism of Na and K uptake by calcite was suggested by the present authors,[2] who assumed that Na and K are incorporated into interstitial positions in the calcite lattice. The total numbers of available interstitial sites for Na and K were 0.15 and 0.12 mol kg^{-1}, respectively, and Ca-vacancy (net charge is −2) balances with the positive charge of the ions. The interstitial sites in the calcite crystal are indicated in Fig. 3. The calculated size of the sites is about 0.89 A in radius (see Appendix), and a site is surrounded by six O^{2-} ions. Oxide ions cause a negative atmosphere around the sites.

According to the mechanism, solid solution of Na_2CO_3 and K_2CO_3 in $CaCO_3$ is formulated as,

$$(1-x-y)\mathrm{CaCO_3(S)} + x\mathrm{Na_2CO_3(L)} + y\mathrm{K_2CO_3(L)} = \mathrm{Ca}_{1-x-y}\square_{x+y}[\mathrm{Na}_{2x},\mathrm{K}_{2y}]\mathrm{CO_3(S)}, \tag{1}$$

where □ and [ ] means Ca-vacancy and interstitial ion, respectively.

In order to deduce the equilibrium relationship between x and y in reaction (1), we assume as follows:

(i) Formation of interstitial-vacancy pairs ([Na, K]$_2$□), to maintain electroneutrality in calcite.

(ii) Random distribution of the interstitial-vacancy pairs in the crystal, where dimer or trimer aggregations of the pairs are disregarded.

(iii) Ideal mixing of Na and K on the interstitial sites.

Assumptions (ii) and (iii) are introduced to simplify a calculation. As to assumption (ii), formation of dimer and trimer complexes of impurities and vacancies has been known in alkali halides at low temperature and high impurity contents.[12–14] Although this phenomenon may occur in the present case, simplicity of the model would be preferable, because any such treatments to produce an aggregation of impurity-vacancy complexes had not been done.

The dependence of K composition (y) on Na composition (x) in calcite at a constant temperature is determined by minimizing the free energy of $\mathrm{Ca}_{1-x-y}\square_{x+y}[\mathrm{Na}_{2x},\mathrm{K}_{2y}]\mathrm{CO_3}$. To calculate the Gibbs free energy, $G=U+pV-TS$, of the solid solution, it is necessary to know the entropy term. The entropy of crystalline solids is the combination of the entropy due to thermal vibration of lattice ions (S^t) and the configurational entropy (S^c) due to mixing of ions in the crystal.

The configurational entropy among degenerate configurations is defined by the formula,

$$S^c = k\ln\Omega, \tag{2}$$

where Ω, multiplicity of thermodynamic probability of the system, is the number of distinguishable configurations that the system can adopt, and k is Boltzmann's constant. Using Eq. 2, the configurational entropy of $\mathrm{Ca}_{1-x-y}\square_{x+y}[\mathrm{Na}_{2x},\mathrm{K}_{2y}]\mathrm{CO_3}$ is calculated as,

$$\begin{aligned} S^c &= k\ln\Omega^{\mathrm{i-v\ pair}} \\ &= k\ln\Bigg[\Bigg(\frac{N_0!}{\left(N_0-\frac{n^T}{2}N_0\right)!\left(\frac{n^T}{2}N_0\right)!} \\ &\quad\times\frac{\left(\frac{n^T}{2}N_0\right)!}{\left(\frac{n^T}{2}N_0-xN_0-yN_0\right)!\,(xN_0+yN_0)!}\Bigg)_{\mathrm{v}} \\ &\quad\times\left(\frac{(2xN_0+2yN_0)!}{(2xN_0)!\,(2xN_0)!}\right)_{\mathrm{i}}\times 3^{(xN_0+yN_0)}\Bigg)\Bigg], \end{aligned} \tag{3}$$

where i and v denotes interstitial and vacancy, respectively, and N_0 is Avogadro's number and n^T the total number of available interstitial sites in calcite. In Fig. 3, there are six equivalent interstitial sites (only three of such sites are shown) around a Ca ion just above and below the same cationic layer of the lattice. Since it results in three equivalent inversion-related [Na, K]$_2$ □ pairs with respect to one Ca-vacancy, the multiplicity increases by a factor of 3 over each interstitial-vacancy pair of a configuration. By use of Stirling's approximation, $\ln N! \simeq N\ln N-N$, Eq. 3 is transformed,

$$\begin{aligned} S^c = -\,kN_0\ln\Bigg[&\left(1-\frac{n^T}{2}\right)\ln\left(1-\frac{n^T}{2}\right) \\ &+\left(\frac{n^T}{2}-x-v\right)\ln\left(\frac{n^T}{2}-x-y\right)+(x+y)\ln(x+v) \\ &+2x\ln 2x+2y\ln 2y-(2x+2y)\ln(2x+2y) \\ &-(x+y)\ln 3\Bigg]. \end{aligned} \tag{4}$$

The difference in the free energy (ΔG) of reaction (1) is then formulated as Eq. 5, using the molar free energy of species i, $g_i=u_i+pv_i-Ts_i^t$, where u_i is the molar internal energy, v_i the molar volume, and s_i^t the molar vibrational entropy.

$$\begin{aligned} \Delta G &= [(1-x-y)g_{\mathrm{Ca}}+(x+y)g_{\square}+2xg_{\mathrm{Na}} \\ &\quad+2yg_{\mathrm{K}}+g_{\mathrm{CO_3}}-TS^c]-[(1-x-y)g_{\mathrm{Ca}} \\ &\quad+(1-x-y)g_{\mathrm{CO_3}}+x\mu^{\mathrm{L}}_{\mathrm{Na_2CO_3}}+y\mu^{\mathrm{L}}_{\mathrm{K_2CO_3}}] \\ &= x(2g_{\mathrm{Na}}+g_{\square}+g_{\mathrm{CO_3}}-\mu^{\mathrm{L}}_{\mathrm{Na_2CO_3}}) \\ &\quad+y(2g_{\mathrm{K}}+g_{\square}+g_{\mathrm{CO_3}}-\mu^{\mathrm{L}}_{\mathrm{K_2CO_3}})-TS^c, \end{aligned} \tag{5}$$

where μ^{L} is the chemical potential of Na_2CO_3 and K_2CO_3 in aqueous solution. Thus, the relationship between x and y is obtained from Eqs. 4 and 5, with the condition that at the equilibrium $\partial\Delta G/\partial y=0$ at constant x and constant temperature,

$$\begin{aligned}\left(\frac{\partial\Delta G}{\partial y}\right)_{x,T} &= (2g_{\mathrm{K}}+g_{\square}+g_{\mathrm{CO_3}}-\mu^{\mathrm{L}}_{\mathrm{K_2CO_3}}) - T\left(\frac{\partial S^{\mathrm{c}}}{\partial y}\right)_{x,T} \\ &= (2g_{\mathrm{K}}+g_{\square}+g_{\mathrm{CO_3}}-\mu^{\mathrm{L}}_{\mathrm{K_2CO_3}}) \\ &\quad + kN_0T\ln\left[\frac{(x+y)(2y)^2}{3\left(\frac{n^{\mathrm{T}}}{2}-x-y)(2x+2y\right)^2}\right]=0. \quad (6)\end{aligned}$$

Replacing x and y by Na composition Na_S, and K composition K_S, respectively, Eq. 6 is rewritten as,

$$\begin{aligned}\ln\frac{K_S}{Na_S+K_S} &= -\ 0.5\ln\frac{Na_S+K_S}{n^{\mathrm{T}}-Na_S-K_S} \\ &\quad -0.5\left(\frac{2g_{\mathrm{K}}+g_{\square}+g_{\mathrm{CO_3}}-\mu^{\mathrm{L}}_{\mathrm{K_2CO_3}}}{kN_0T}-\ln 3\right). \quad (7)\end{aligned}$$

If aqueous activity of K_2CO_3 is fixed at a constant value, then $\mu^{\mathrm{L}}_{\mathrm{K_2CO_3}}$ becomes constant and Eq. 7 shows a linear relationship between Na_S and K_S in calcite with an inclination of -0.5.

To examine the validity of the interstitial-vacancy model described above, $\ln(K_S/[Na_S+K_S])$ is plotted against $\ln([Na_S+K_S]/[n^{\mathrm{T}}-Na_S-K_S])$ in Fig. 4. As to n^{T}, different values of 0.15 and 0.12 mol kg^{-1} were obtained for Na and K, respectively. Since interstitial-vacancy pairs should be defined with respect to the sites available for both Na and K, 0.12 mol kg^{-1} was adopted as n^{T}. Other data used are given in Table 1. The empirical equation was formulated by the least-squares fit as,

$$\ln\frac{K_S}{Na_S+K_S}=-\ 0.51\ln\frac{Na_S+K_S}{0.12-Na_S-K_S}-0.94. \quad (8)$$

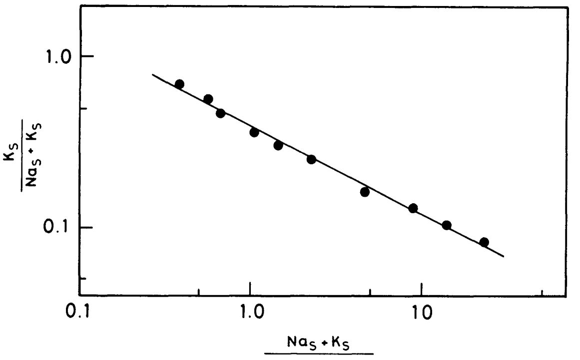

Fig. 4. Logarithmic relationship between sodium and potassium contents of calcite at 20°C and a constant activity of K_2CO_3 in aqueous solution.

The inclination of Eq. 8 (−0.51) is identical with the theoretical value in Eq. 7 (−0.5), showing that the interstitial-vacancy model gives an adequate explanation for Na and K mixing in calcite.

Defects associated with Na and K in calcite were investigated by measuring the thermoelectric power of the doped calcite crystal. The sign of thermoelectric power relates with the sign of dominant charge carriers in the crystal. Since charge carriers move along the temperature gradient toward the colder electrode, the positive sign indicates that the charge carrier is a cation. As shown in Fig. 2, the sign of thermoelectric power was positive in the temperature range of 360—570 °C, where defects induced by impurities dominate in calcite.[5] This result indicates the presence of charged defects which cause the transportation of cations and are attributed to interstitial cations or cation vacancies, that is, Na and K interstitials or Ca-vacancies. It has been observed in the measurements of ionic conductivity in alkali halides that the concentration of free interstitials or vacancies is increased by the dissociation of impurity-vacancy pairs in the similar temperature range.[15] The maximum and the minimum of thermoelectric power in Fig. 2 may correspond to the change in transportation mechanism induced by the dissociation of the interstitials-vacancy pairs. These results support the interstitial incorporation of Na and K, when the electroneutrality is maintained by formation of Ca-vacancies in calcite.

K/Na in Calcite as a Function of Aqueous K/Na. Natural calcites contain different amounts of Na and K depending on the origin. Table 2 summarizes the difference in K/Na molar ratio in various natural calcites. Some studies have reported a correlation of K/Na in calcites with chemical composition of natural waters from which precipitation took place.[16,17] In spite of considerable scattering of K/Na in natural calcites, however, the applicability of K/Na value as a geochemical indicator has not been established. Our study strongly suggests that K/Na in calsites can be formulated as a function of K/Na in aqueous solutions based on the mechanism of ion incorporation into the crystal.

Equilibrium partitioning of the ions between calcite

Table 2. Potassium/Sodium Molar Ratio in Marine and Freshwater Calcite

	Salinity	K_L	K_S	Na_S	K_S/Na_S	
	‰	Na_L	ppm	ppm	Obsd	Calcd
Marine calcite						
Shells[20]	35	0.0218	18—280	2160—6580	0.0040—0.037	0.0044
Freshwater calcite						
Travertines[17,21]	0.8—4.7	0.013—0.044	16—282	220—1410	0.034—0.40	0.0026—0.0088
Limestones[18]	0.23—0.25	0.017—0.063	3—33	19—47	0.099—0.50	0.0034—0.013

and aqueous solution is represented by Eqs. 9 and 10 for Na and K, respectively, where Na and K incorporation into the crystal is assumed to be independent of aqueous Ca and pH.[2)]

$$K_{Na} = \frac{Na_S}{\gamma_{Na} Na_L [*]_S} \quad \text{and} \tag{9}$$

$$K_K = \frac{K_S}{\gamma_K K_L [*]_S}, \tag{10}$$

in which K is the equilibrium constant of Na and K partitioning, γ is the activity coefficient of aqueous Na and K, and $[*]_S$ means the number of vacant interstitial sites in calcite. On the assumption of ideal mixing of Na and K, the activity coefficient of each ion in the crystal is unity and Eq. 11 is obtained from Eqs. 9 and 10.

$$\frac{K_S}{Na_S} = \frac{K_K \gamma_K K_L [*]_S}{K_{Na} \gamma_{Na} Na_L [*]_S} \simeq \frac{K_K}{K_{Na}} \times \frac{K_L}{Na_L}. \tag{11}$$

The proportional relationship of K/Na between calcite and aqueous solution was confirmed by the result in Fig. 5 by use of data in Table 1. The empirical equation was obtained as,

$$\frac{K_S}{Na_S} = 0.20 \frac{K_L}{Na_L}. \tag{12}$$

The K/Na ratios in marine shells, travertines, and limestones are estimated by Eq. 12 and given in Table 2. Observed values of K/Na differ by 1—2 orders of magnitude from those of marine shells to those of fresh water limestones. Calculated K/Na ratio in marine biogenic calcite (0.0044) is in the same range of observed K/Na values (0.0040—0.037). The wide range of observed values will be due to variations in physiological conditions of marine invertebrates as explained by the present authors.[2)] Travertines and freshwater limestones, however, have higher K/Na ratios (0.034—0.5) than the calculated values (0.0026—0.013). It is known that K in limestones correlates with acid-insoluble residues and is attributed to contamination from clay minerals.[18,19)] The discrepancy described above may be due to the increase in K content by the contamination.

Conclusions

The distribution of Na and K ions in calcite was formulated on an assumption of ideal mixing of the ions at interstitial sites which are associated with Ca-vacancies. The presence of the pairs composed of Na and K interstitials and Ca-vacancy was confirmed by measuring the thermoelectric power of calcites containing Na and K ions.

A model for Na and K uptake by calcite was presented to treat the partition mechanism of monovalent ions and the mechanism of formation of interstitials and vacancies. Although the theory of elemental partitioning between carbonates and natural waters has asserted the simple substitution of host ions by divalent impurities, most natural carbonates contain some mono- and trivalent ions, such as F^- an PO_4^{3-}. The partitioning of such ions has been qualitatively estimated with respect to ionic charge and radius. It should be noted that the role of crystal defects during the diagenesis of carbonate minerals is poorly understood. An extensive characterization of defects associated with various impurity ions will be fruitful in clarifying geochemical properties of sedimentary minerals.

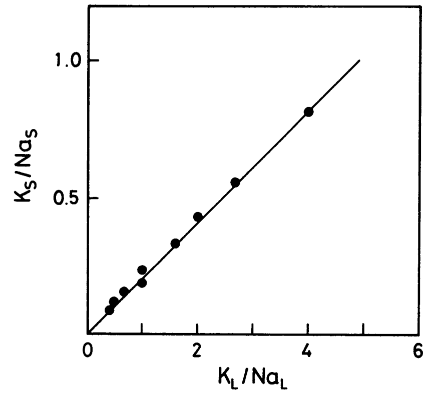

Fig. 5. Potassium/sodium molar ratio in calcite as a function of that in aqueous solution at 20°C.

The authors wish to thank Dr. Takaaki. Kobayashi for his critical comments on the study, and Dr. Kenichi Kondo for his technical assistance in the measurements of thermoelectric power.

Appendix

The calculated size of the coordination polyhedron of the presumed interstitial sites.

The interstitial site is surrounded by six oxygens. In the hexagonal system, the crystallographic coordinates of the four neighboring carbons in calcite are given by C_1 (0, 0, 1/4), C_2 (1, 1, 1/4), C_3 (0, 1, 1/4), and C_4 (1/3, 2/3, 1/12). Then those of the six oxygens will be O_1 (d, d, 1/4), O_2 (1$-d$, 1, 1/4), O_3 (0, 1$-d$, 1/4), O_4 (1/3$-d$, 2/3$-d$, 1/12), $O_{4'}$ (1/3, 2/3+d, 1/12), and $O_{4''}$ (1/3+d, 2/3, 1/12), where d corresponds to the C-O distance in CO_3^{2-} divided by the lattice parameter a, and O_4, $O_{4'}$, and $O_{4''}$ belong to the same CO_3^{2-}. The d value is calculated as 0.2568 based on the crystallographic data by Effenberger et al.[22)]

The co-ordinates of the interstitial site are given by i (1/3, 2/3, 0.1863), which is equidistant from the six oxygens. The distance r between two points (x_1, y_1, z_1) and (x_2, y_2, z_2) can be calculated by,

$$r^2 = a^2[(x_1-x_2)^2 + (y_1-y_2)^2 - (x_1-x_2)(y_1-y_2)] + c^2(z_1-z_2)^2,$$

where a and c are the lattice parameters for calcite. The distance between i and any O is then 2.1744 Å. Assuming that the O radius is equal to the C-O distance in CO_3^{2-}, we get 0.8929 Å as the radius of the interstitial site.

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