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Fractionation of Strontium Isotopes in Cation-Exchange Chromatography

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Abstract

Strontium isotope fractionation has been observed in cation-exchange chromatography of strontium salts. The heavier isotopes have been found enriched at the front parts of displacement-type chromatograms, which means that the heavier isotopes are preferentially fractionated into the solution phase. The average values of the single-stage separation factor (S) minus one per unit mass difference between isotopes have been 1.0×10^{-6} for the strontium chloride system, 2.9×10^{-6} for the strontium acetate system, and 3.1×10^{-6} for the strontium lactate system at 25°C. No evidence of the odd-even anomalous isotope effects has been observed. The isotopic reduced partition function ratios (RPFRs) of the strontium species involved in the present study have been estimated; the RPFRs of the complex species have been found to be larger than that of the simple hydrated strontium ion, which accounts for the experimental results that the S values of the strontium lactate and strontium acetate systems are larger than that of the strontium chloride system.

INTRODUCTION

Strontium is the fifteenth most abundant element in the earth's crust (*1*), and the number of naturally occurring isotopes is four: ^{84}Sr (isotopic abundance = 0.56%), ^{86}Sr (9.86), ^{87}Sr (7.02), and ^{88}Sr (82.56) (*2*). It has very limited practical uses such as in alloys, getters, and light-emitting materials, but the abundance ratio of its isotopes has a specific application in the ^{87}Rb–^{87}Sr method for age determination in geoscience.

The present work deals with fractionation of strontium isotopes in ion-exchange chromatography. This topic is interesting in two respects. One concerns anomalous isotope effects. Fujii et al. (*3*) demonstrated that the uranium isotope effect in the U(IV)–U(VI) chemical exchange system is proportional to the mass difference for the isotopes ^{234}U, ^{236}U, and ^{238}U, whereas ^{235}U behaves as if it has a mass of 234.5, thus suggesting an anomalous isotope effect which could be attributable to the odd-even difference in the mass number of isotopes. Strontium isotopes could offer another example of anomalous isotope effects and could provide a means to detect the origin of such effects. Another interest is in the direction of the strontium isotope effect in ion-exchange chromatography. Heavier isotopes of magnesium, the second lightest member of Group II in the periodic table, to which strontium belongs, are enriched in the front parts of magnesium adsorption bands formed in chromatographic separation columns packed with strongly acidic cation-exchange resins (*4*, *5*). That is, the heavier isotopes (^{25}Mg, ^{26}Mg) are preferentially fractionated into the solution phase while the lighter isotope, ^{24}Mg, is preferentially retained in the resin phase. Seemingly conflicting observations have been reported on isotope fractionation of calcium, another member of Group II, in ion-exchange systems. Klinskii et al. (*6*) reported that the heavier isotopes were enriched in the resin phase of cation-exchange chromatography. On the other hand, Heumann and Lieser (*7*), Aaltonen (*4*), Russell and Papanastassiou (*8*), Kobayashi et al. (*9*), and Jepson and Shockey (*10*) stated that the heavier isotopes were preferentially fractionated into the solution phase of chromatography when using strongly acidic cation exchangers. The direction of the isotope fractionation effect of rubidium, the element that precedes strontium in the periodic table, is opposite to that of magnesium; the heavier isotope, ^{87}Rb, is enriched in the rear parts of rubidium adsorption bands (*11*, *12*). Thus, accurate determinations of the direction of isotope fractionation of strontium and of its magnitude are important for the systematization of isotope effects of the alkali metals and the alkaline earth metals in aqueous ion-exchange systems.

There seems to be only one previous work that dealt with separation of strontium isotopes by ion-exchange chromatography. Aaltonen (*13*) carried out an elution chromatographic experiment with a strongly acidic cation-exchange resin and reported that the heavier isotopes were enriched in the solution phase. The value of the single-stage separation factor, *S*, for the ^{84}Sr/^{88}Sr isotopic pair was 1.000097.

EXPERIMENTAL

Reagents

The ion-exchange resin used was a highly porous strongly acidic cation-exchange resin, Asahi LS-6, in the H^+ form, 100–200 mesh, having sulfo groups as the exchange group. All reagents used were of analytical-reagent grade and were used without further purification.

Chromatographic Process

Three experiments were carried out, one in the breakthrough operation and two in the band displacement operation. Experimental conditions are summarized in Table 1. For each experiment, two chromatographic columns (210 cm in length × 10 mm in inner diameter, made of Pyrex glass, with a water jacket) were connected in series with a Teflon tube (1 mm in inner diameter), so that the total resin bed height was ca. 400 cm. In the breakthrough experiment (Sr8901), a strontium feed solution was fed to the first column packed with the resin in the H^+ form at a constant rate by a peristaltic pump, and the effluent from the second column was collected and portioned into fractions of 4 cm^3. In the band displacement

TABLE 1
Experimental Conditions[a]

	Run		
	Sr8901	Sr8903	Sr8904
Operating manner	Breakthrough	Band	Band
Sr feed solution	0.093 M $SrCl_2$	0.10 M $Sr(CH_3COO)_2$ + 0.30 M CH_3COOH (pH = 4.34)	0.11 M $Sr(OH)_2$ + 0.50 M $CH_3CHOHCOOH$ (pH = 3.37)
Eluent	—	0.10 M $Ba(CH_3COO)_2$ + 0.30 M CH_3COOH (pH = 4.36)	0.10 M $Ba(OH)_2$ + 0.50 M $CH_3CHOHCOOH$ (pH = 3.42)
Resin bed height (cm)	413.5	395.0	355.0
Sr band length (cm)	—	36.5	28.9
Flow rate ($cm^3 \cdot cm^{-2} \cdot h^{-1}$)	11.5	13.0	11.8
Band velocity (cm/h)	1.91	2.04	1.86

[a] 1 M = 1 mol/dm^3; temperature = 25.0 ± 0.2°C; resin = strongly acidic cation-exchange resin, Asahi LS-6, H^+ form, 100–200 mesh.

experiments (Sr8903, Sr8904), strontium adsorption bands formed on the resin in the H^+ form were eluted by appropriate eluents containing barium ions as the replacement ion for Sr^{2+}. Effluents from the second columns were collected and portioned into fractions of 5 cm^3.

The temperature of the columns was kept at 25.0 ± 0.2°C throughout an experiment by passing temperature-controlled water through water jackets attached to the columns.

Analysis

For each of the fractions of the effluents, the pH was measured and the strontium concentration was determined by atomic absorption spectroscopy after appropriate dilution with pure water. For the feed solutions and several fractions in the front parts of the strontium adsorption bands, the isotopic ratios $^{88}Sr/^{86}Sr$, $^{87}Sr/^{86}Sr$, and $^{84}Sr/^{86}Sr$ were measured. The procedure follows.

In Sr8901, an aliquot of a fraction containing about 50 μmol strontium was treated to prepare the sample for mass spectrometry (mass sample). The aliquot was passed through a chromatographic column packed with an anion-exchange resin (Muromac 1-x8, 200–400 mesh, ca. 1 g) in the OH^- form. To the effluent from the column, which was in fact an aqueous strontium hydroxide solution, nitric acid was added, yielding a strontium nitrate solution. This solution was evaporated to dryness, and then pure water was added so that the final strontium concentration was 0.05 *M* (1 *M* = 1 mol/dm^3).

In Sr8903 and Sr8904, an aliquot of a fraction containing 30 μmol strontium was treated. After the aliquot was passed through a Muromac 1-x8 resin-packed column, the effluent was evaporated to dryness in a platinum crucible and was incinerated at 1000°C for 10 h in an electric furnace, yielding strontium oxide. The strontium oxide obtained was dissolved in a nitric acid solution and was evaporated to dryness. The resultant strontium nitrate was dissolved with pure water and its concentration was adjusted to 0.03 *M*.

The strontium isotopic ratios of a mass sample were measured with the double-filament surface ionization technique by using a Finnigan MAT 261 mass spectrometer at the National Defense Academy. The filament unit for the strontium isotopic ratio measurements consisted of two filaments, one a vaporizing filament and the other an ionization filament, both made of rhenium ribbon. An aliquot of the mass sample (strontium nitrate) containing 2 μg strontium was loaded on the vaporizing filament, dried, and further heated, yielding strontium oxide. Ionization was performed by passing a heating electric current through the ionization filament and a much smaller current through the vaporizing filament (about one-tenth of the current through the ionization filament). When the ion beam intensities of $^{84}Sr^+$, $^{86}Sr^+$, $^{87}Sr^+$, and $^{88}Sr^+$ became sufficiently high about 1 h after initiation of heating, the ^{84}Sr–^{88}Sr mass peaks were repeatedly recorded. The mass scanning was repeated eight times in a block, and in most cases 10 blocks were recorded as one measurement. The measuring time was about 2 h, and hence the total time spent for one measurement was about 3 h. The strontium isotopic ratios of a block were calculated by averaging all the peak-height ratios in the block, and those of the mass sample were calculated as the averages of the isotopic ratios of the 10 blocks. The relative standard deviation of a measurement was typically 0.04% for the $^{84}Sr/^{86}Sr$ isotopic pair, 0.01% for the $^{87}Sr/^{86}Sr$ pair, and 0.01% for the $^{88}Sr/^{86}Sr$ pair.

RESULTS AND DISCUSSION

Chromatograms and isotopic ratios of the three experiments are shown in Figs. 1, 2, and 3. In the lower half of each figure are drawn the strontium concentration profile and the pH of the effluent. In the upper part are

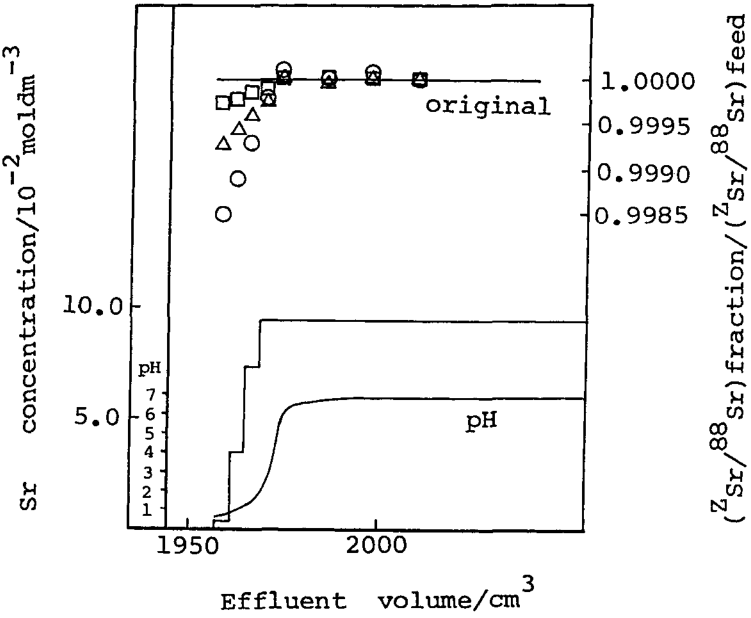

FIG. 1. Chromatogram and the strontium isotopic ratios in the effluent fractions relative to the corresponding isotopic ratios in the feed solution for the strontium–chloride system (Run Sr8901). The circles (○) represent the $^{84}Sr/^{88}Sr$ isotopic ratios, the triangles (△) the $^{86}Sr/^{88}Sr$ isotopic ratios, and the squares (□) the $^{87}Sr/^{88}Sr$ isotopic ratios. Experimental conditions are given in Table 1.

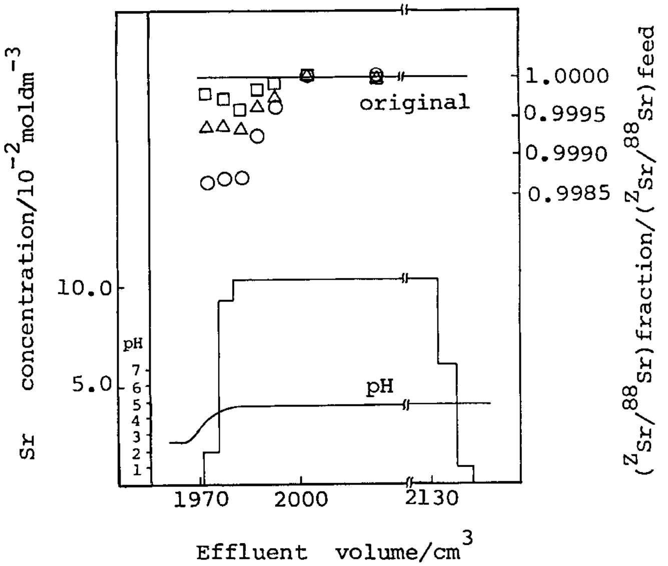

FIG. 2. Chromatogram and the strontium isotopic ratios in the effluent fractions relative to the corresponding isotopic ratios in the feed solution for the strontium–acetate system (Run Sr8903). The circles (○) represent the $^{84}Sr/^{88}Sr$ isotopic ratios, the triangles (△) the $^{86}Sr/^{88}Sr$ isotopic ratios, and the squares (□) the $^{87}Sr/^{88}Sr$ isotopic ratios. Experimental conditions are given in Table 1.

shown the isotopic ratios $^{84}Sr/^{88}Sr$, $^{86}Sr/^{88}Sr$, and $^{87}Sr/^{88}Sr$ in the fractions divided by the corresponding quantities in the feed solution.

It is seen that in every experiment the heavier isotopes are enriched in the front part of the strontium adsorption band. That is, they are preferentially fractionated into the solution phase. Although economic reasons prevented us from measuring the isotopic ratios in the rear parts of the strontium bands of the two band experiments (Sr8903 and Sr8904), we can expect that the rear parts are enriched in the lighter isotopes. The direction of the strontium isotope fractionation observed in the present study is the same as that reported by Aaltonen (*13*), those observed for the magnesium isotopes (*4*, *5*) and those of the calcium isotopes reported in Ref *4*, *7–10*, but is opposite to the direction of rubidium isotope fractionation (*11*, *12*).

It is also seen in the figures that the deviation of the value of $^{z}Sr/^{88}Sr)_{fraction}/(^{z}Sr/^{88}Sr)_{feed}$ (z = 84, 86, or 87) from unity is larger for smaller z, meaning that the strontium isotope effect is larger for the larger mass difference between isotopes.

The single-stage separation factors, $S(84/88)$ for the $^{84}Sr/^{88}Sr$ isotopic

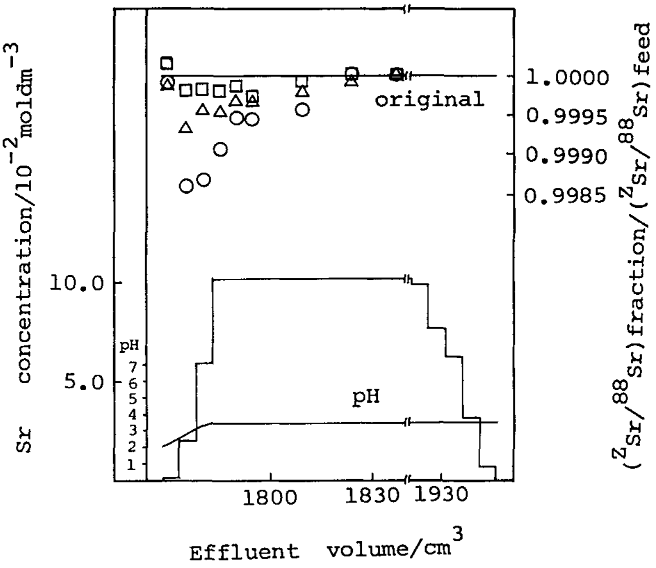

FIG. 3. Chromatogram and the strontium isotopic ratios in the effluent fractions relative to the corresponding isotopic ratios in the feed solution for the strontium–lactate system (Run Sr8904). The circles (○) represent the ^{84}Sr/^{88}Sr isotopic ratios, the triangles (△) the ^{86}Sr/^{88}Sr isotopic ratios, and the squares (□) the ^{87}Sr/^{88}Sr isotopic ratios. Experimental conditions are given in Table 1.

pair, $S(86/88)$ for the ^{86}Sr/^{88}Sr pair and $S(87/88)$ for the ^{87}Sr/^{88}Sr pair, were calculated by using the equation (*14*),

$$S = 1 + \Sigma \mid R_i - R_o \mid f_i/[QR_o(1 - R_o)] \qquad (1)$$

where, assuming a two-isotope system (^{88}Sr and ^{z}Sr with $z = 84$, 86, or 87), R_o is the isotopic molar fraction of the lighter isotope in the feed solution, R_i is that in the ith fraction of the effluent, f_i is the amount of strontium in the ith fraction, Q is the total exchange capacity of the column, and the summation is taken over all fractions that were depleted in the lighter isotope. The calculated results are summarized in Table 2. Data are given in two forms, ϵ ($= S - 1$) and ϵ per unit mass difference between the two isotopes, $\epsilon/\Delta M$. The ϵ values obtained are on the order of 10^{-6} as a whole. For comparison, the results by Aaltonen (*13*) are also given. The following may be extracted from the table:

1. For a given system, a larger ϵ value is obtained for the isotopic pair with a larger mass difference. However, ϵ per unit mass difference is

TABLE 2
Separation Factors Obtained[a]

Run	System	Isotopic pair	ϵ[b]	$\epsilon/\Delta M$	Av $\epsilon/\Delta M$
Sr8901	Strontium chloride	$^{84}Sr/^{88}Sr$	3.6×10^{-6}	9.0×10^{-7}	1.0×10^{-6}
		$^{86}Sr/^{88}Sr$	2.3×10^{-6}	1.1×10^{-6}	
		$^{87}Sr/^{88}Sr$	9.7×10^{-7}	9.7×10^{-7}	
Sr8903	Strontium acetate	$^{84}Sr/^{88}Sr$	1.1×10^{-5}	2.8×10^{-6}	2.9×10^{-6}
		$^{86}Sr/^{88}Sr$	6.6×10^{-6}	3.3×10^{-6}	
		$^{87}Sr/^{88}Sr$	2.7×10^{-6}	2.7×10^{-6}	
Sr8904	Strontium lactate	$^{84}Sr/^{88}Sr$	1.2×10^{-5}	3.1×10^{-6}	3.1×10^{-6}
		$^{86}Sr/^{88}Sr$	6.8×10^{-6}	3.4×10^{-6}	
		$^{87}Sr/^{88}Sr$	2.9×10^{-6}	2.9×10^{-6}	
Aaltonen[c]	Strontium α-hydroxyisobutyrate	$^{84}Sr/^{88}Sr$	9.7×10^{-5}	2.4×10^{-5}	2.3×10^{-5}
		$^{87}Sr/^{88}Sr$	2.1×10^{-5}	2.1×10^{-5}	

[a] Temperature = 25.0 ± 0.2°C.

[b] $\epsilon = S - 1$.

[c] Taken from Ref. *13*.

the same for all the isotopic pairs examined within experimental errors. (The experimental errors were typically about 10%.) This is consistent with what is predicted by the classical Bigeleisen–Mayer theory on isotope effects (*15*), and no evidence of the odd-even anomaly in isotope effects (*3*) was found. Nevertheless, the present results do not necessarily deny totally the existence of anomalous strontium isotope effects in ion-exchange systems. Ten percent errors on ϵ values are too large to detect expectedly small anomalous isotope effects, if any. Much longer chromatographic developments will be necessary to give a decisive conclusion on this subject.

2. For a given isotopic pair, the strontium–acetate ion (Sr–Ac) system (Sr8903) yielded a larger ϵ value than the strontium–chloride ion (Sr–Cl) system (Sr8901). The strontium–lactate ion (Sr–La) system (Sr8904) showed an ϵ value equivalent to or slightly larger than that of the Sr–Ac system. Thus, ϵ (Sr–La) $\geqq$ ϵ (Sr–Ac) $>$ ϵ (Sr–Cl). The result that the Sr–La and Sr–Ac systems had larger ϵ values than the Sr–Cl system corresponds to the fact that the complex formations of the strontium ion with the lactate and acetate ions in the external solution phase make positive contributions to the overall isotope effects in ion-exchange systems. This point will be discussed in more detail in the next section.

3. Aaltonen (*13*) reported ϵ values one order of magnitude larger than those obtained in this work. The difference in a ϵ value between Aaltonen and the present authors may be attributable to the kind of complexing partner anions used; he used the α-hydroxyisobutyrate ion while we utilized lactate, acetate, or chloride ion. Temperature may be another factor. Our experiments were carried out at 25°C. Unfortunately, the temperature of Aaltonen's experiment was not specified.

Estimation of the Reduced Partition Function Ratios of the Strontium Species Involved in the Present Work

The heavier isotope to lighter isotope isotopic reduced partition function ratios (RPFRs) of the strontium species involved in the present systems can be estimated by using the separation factor data obtained, the Bigeleisen–Mayer simplifying formula of the RPFR (*15*), data on the hydration number of the strontium and of the Sr^{2+}–H_2O symmetric stretching frequency in aqueous solutions, and the theory of isotope distribution between two phases (*16*) under some appropriate assumptions. Application of the theory (*16*) to the Sr–La and Sr–Ac systems yields the following expression of S in terms of the RPFRs and molar fractions of the strontium species involved in the systems:

$$\ln S = \ln (x_{Sr}f_{Sr} + x_{SrL}f_{SrL}) - \ln (y_{Sr}g_{Sr} + y_{SrL}g_{SrL}) \qquad (2)$$

In Eq. (2), x_{Sr} and f_{Sr} are the molar fraction and the RPFR of Sr^{2+} in the solution phase, x_{SrL} and f_{SrL} are those of SrL^+ [L = lactate ion (La^-) or acetate ion (Ac^-)] in the solution phase, and y and g are, respectively, the quantities corresponding to x and f in the resin phase. Under the present experimental conditions, there are no appreciable amounts of higher-order complexes between Sr^{2+} and La^- or Ac^- (*17*). (That is, $x_{Sr} + x_{SrL} = 1$ and $y_{Sr} + y_{SrL} = 1$.) Although the degree of hydration occurring is not indicated in Eq. (2) and in following equations for simplicity, it should be noted that all the strontium species are hydrated both in the solution phase and in the resin phase and that hydration plays an important role in isotope effects in aqueous systems (*18*).

For the Sr–Cl system, there occurs no appreciable complex formation between the strontium ions and the chloride ions under the present experimental conditions. Thus, $x_{SrL} = y_{SrL} = 0$ ($L = Cl^-$) and Eq. (2) is simplified to

$$\ln S = \ln (f_{Sr}/g_{Sr}) \qquad (3)$$

Equation (3) shows that the separation factors of the Sr–Cl system are nothing but the equilibrium constants of the following strontium isotope exchange reaction between the solution and the resin phases,

$$\mathrm{Sr}'^{2+}_{(s)} + \mathrm{Sr}^{2+}_{(r)} = \mathrm{Sr}^{2+}_{(s)} + \mathrm{Sr}'^{2+}_{(r)} \tag{4}$$

where the primed quantities are those of the lighter isotope and the nonprimed quantities are those of the heavier isotope, and the subscripts (*s*) and (*r*) refer to the solution phase and the resin phase, respectively.

The RPFR of the simple hydrated strontium ion in the solution phase, f_{Sr}, is calculable by using the Bigeleisen–Mayer formula (*15*):

$$\ln f = [nm\Delta M/(24MM')](hc\omega/kT)^2 \tag{5}$$

where n is the hydration number, m is the mass of a hydrating water molecule, M and M' are the masses of the heavier and lighter strontium isotopes, $\Delta M = M - M'$, h is Planck's constant, c is the velocity of light, ω is the Sr^{2+}–$\mathrm{H_2O}$ totally symmetric stretching frequency in cm^{-1} in aqueous solutions, k is Boltzmann's constant, T is the temperature, and the symmetry numbers are omitted in the expression. A molecular dynamics calculation (*19*) showed that the hydration number in the primary hydration sphere around a strontium ion is 9.8 and ω is 250 cm^{-1}. Thus, all the quantities in Eq. (5) are assigned certain values, and consequently, f_{Sr} can be calculated. In the above, only the hydration in the primary hydration sphere was taken into consideration. The RPFRs of Sr^{2+} in the resin phase, g_{Sr}, are obtainable from the f_{Sr} values and the separation factor data in the Sr–Cl system.

In order to estimate the RPFRs of the complex species of strontium, SrLa^+ and SrAc^+, in and outside the resin phase of the Sr–La and Sr–Ac systems, knowledge of the molar fractions of these species is required. Their molar fractions in the solution phase can be estimated by using the data of stability constants of SrLa^+ (*20*) and SrAc^+ (*21*) and of the dissociation constants of lactic acid (*22*) and acetic acid (*23*). Molar fractions of the complex species in the resin phase may be calculable from knowledge of the strontium band velocities in the Sr–La and Sr–Ac systems relative to the velocity in the Sr–Cl system. Values of x_{SrL} and y_{SrL} thus obtained are listed in Table 3, together with those of x_{Sr} and y_{Sr}. By using these values and a simplifying relation,

$$f_{\mathrm{SrL}}/f_{\mathrm{Sr}} = g_{\mathrm{SrL}}/g_{\mathrm{Sr}} \tag{6}$$

TABLE 3
Calculated Molar Fractions of the Strontium Species in and outside the Resin Phase

Run	System	x_{Sr}	y_{Sr}	x_{SrL}	y_{SrL}
Sr8901	Sr–Cl	1.000	1.000	0.000	0.000
Sr8903	Sr–Ac	0.347	0.702	0.653	0.298
Sr8904	Sr–La	0.486	0.719	0.514	0.281

The RPFRs of all the strontium species viable in the present systems were calculated, and the results are summarized in Table 4.

It is seen in Table 4 that $f > g$ for any isotopic pair of any strontium species examined. $f_{Sr} > g_{Sr}$ is equivalent to the experimental fact that S in the Sr–Cl system is larger than unity. $f_{SrL} > g_{SrL}$ is a consequence of this fact and a reasonably assumed Relation (6).

It is also seen in Table 4 that the RPFR of the complex species is larger than that of the simple hydrated strontium ion ($f_{SrL} > f_{Sr}$ and $g_{SrL} > g_{Sr}$) for any isotopic pair. Based on the consideration of uranium isotope effects in the previous paper (*18*), this result indicates that strontium ions form outer sphere complexes both with lactate ions and with acetate ions in aqueous systems. The experimental result that the separation factors in the Sr–La and Sr–Ac systems are larger than the corresponding separation factors in the Sr–Cl system is attributable to the fact that $x_{SrL} > y_{SrL}$ and $f_{SrL}/f_{Sr} = g_{SrL}/g_{Sr} > 1$. The complex formations in the solution phase increase the overall separation factor values.

The accuracy of the RPFR values in Table 4 is questionable due to approximations employed and uncertainties in parameter values used in our RPFR calculations. However, the relative order of the magnitudes of

TABLE 4
Values of the Reduced Partition Function Ratios of the Strontium Species at 25°C

		Isotopic pair		
Species[a]	Phase	$^{84}Sr/^{88}Sr$	$^{86}Sr/^{88}Sr$	$^{87}Sr/^{88}Sr$
Sr^{2+}	Solution (f)	1.0058113	1.0028341	1.0013978
	Resin (g)	1.0058077	1.0028318	1.0013968
$SrAc^+$	Solution (f)	1.0058323	1.0028463	1.0014027
	Resin (g)	1.0058287	1.0028440	1.0014017
$SrLa^+$	Solution (f)	1.0058489	1.0028534	1.0014060
	Resin (g)	1.0058451	1.0028511	1.0014050

[a] Hydration is ignored in the expressions.

the RPFR values in Table 4 will be unchanged even if some other approximations are adopted and/or different values of the stability constants, dissociation constants, hydration numbers, etc. are used. The approximation of the RPFR of the simple hydrated strontium ion, Eq. (5), will be improved by an application of the finite orthogonal polynomial method (*24*) and probably further improved by the use of the WINIMAX weighting factor (*25*).

CONCLUSION

Major findings of the present study on cation-exchange chromatographic separation of strontium isotopes are summarized as follows.

1. Heavier isotopes were preferentially fractionated into the solution phase in all the chromatographic experiments conducted.
2. Anomalous isotope effects which could be attributable to the odd-even difference in mass number of isotopes were not identified within experimental errors. The values of ϵ per unit mass difference were 1.0×10^{-6} for the strontium chloride system, 2.9×10^{-6} for the strontium acetate system, and 3.1×10^{-6} for the strontium lactate system at 25°C.
3. The RPFRs of the complex species ($SrLa^+$ and $SrAc^+$) were larger than that of the simple hydrated strontium ion. The complex formation (probably outer sphere type complex formation) in the solution phase increased the overall separation factor.

REFERENCES

1. N. N. Greenwood and A. Earshaw, *Chemistry of the Elements,* Pergamon Press, Oxford, 1984.
2. C. M. Lederer, J. M. Hollander, and I. Perlman, *Table of Isotopes,* 6th ed., Wiley, New York, 1967.
3. Y. Fujii, M. Nomura, M. Okamoto, H. Onitsuka, F. Kawakami, and K. Takeda, *Z. Naturforsch., 44a,* 395 (1989).
4. J. Aaltonen, *Suom. Kem., B, 44,* 1 (1972).
5. T. Oi, S. Yanase, and H. Kakihana, *Sep. Sci. Technol., 22,* 2203 (1987).
6. G. D. Klinskii, D. A. Knyazev, and G. I. Viasova, *Zh. Fiz. Khim., 48,* 659 (1974).
7. K. G. Heumann and K. H. Lieser, *Z. Naturforsch., 27b,* 126 (1972).
8. W. A. Russell and D. A. Papanastassiou, *Anal. Chem., 50,* 1151 (1978).
9. N. Kobayashi, Y. Fujii, M. Okamoto, and H. Kakihana, *Bull. Res. Lab. Nucl. Reactors, 5,* 19 (1980).
10. B. E. Jepson and G. C. Shockey, *Sep. Sci. Technol., 19,* 173 (1984).
11. M. Hosoe, T. Oi, K. Kawada, and H. Kakihana, *J. Chromatogr., 435,* 253 (1988).
12. M. Hosoe, T. Oi, K. Kawada, and H. Kakihana, *Ibid., 438,* 225 (1988).
13. J. Aaltonen, *Suom. Kem., B, 45,* 141 (1972).
14. H. Kakihana and T. Kanzaki, *Bull. Tokyo Inst. Technol., 90,* 77 (1969).
15. J. Bigeleisen and M. G. Mayer, *J. Chem. Phys., 15,* 261 (1947).

16. H. Kakihana and M. Aida, *Bull. Tokyo Inst. Technol., 116,* 39 (1973).
17. L. G. Sillen and E. A. Martell, *Stability Constants of Metal–Ion Complexes. Supplement No. 1,* Special Publication No. 25, Chemical Society, London, 1971.
18. T. Oi and H. Kakihana, *Z. Naturforsch., 44a,* 399 (1989).
19. E. Spohr, G. Palinkas, K. Heinzinger, P. Bopp, and M. M. Probst. *J. Phys. Chem., 92,* 6754 (1988).
20. A. E. Martell and R. M. Smith, *Critical Stability Constants,* Vol. 3, Plenum Press, New York, 1977.
21. G. N. Nancoras, *J. Chem. Soc.,* p. 744 (1956).
22. A. W. Martin and H. V. Tartar, *J. Am. Chem. Soc., 59,* 2672 (1937).
23. H. S. Harned and R. W. Ehlers, *Ibid., 55,* 65 (1933).
24. T. Ishida, W. Spindel, and J. Bigeleisen, *Adv. Chem. Ser., 89,* 192 (1969).
25. M. W. Lee and J. Bigeleisen, *J. Chem. Phys., 72,* 4661 (1979).

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