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INFLUENCE OF NaCl AQUEOUS SOLUTIONS ON ISOTOPIC EQUILIBRIA
AND RATES OF EXCHANGE IN MINERAL-FLUID SYSTEMS

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ABSTRACT

The effect of NaCl aqueous solutions on the rates of isotopic exchange and fractionation factors between minerals and fluids has been evaluated at elevated temperatures using the available experimental data. Rates of oxygen isotopic exchange are significantly increased by interaction of a solid with NaCl solutions. For example, the rate of granite-H₂O oxygen isotopic exchange is $10^{-9.45}$ moles O m⁻² sec⁻¹ at 200°C, but $10^{-7.75}$ for granite-0.5 m NaCl interaction. The durations required to attain 90% isotopic exchange in the granite-fluid system have been calculated using a modified surface-exchange rate model (Cole et al., 1983). These calculations indicate that granite-pure water interaction requires approximately 3700 years to reach 90% exchange, but only 74 years for reaction with 0.5 m NaCl at 200°C [grain radius = 0.1 cm, (W/R)_{mass} = 1].

Isotopic fractionation factors between minerals and aqueous NaCl solutions can differ significantly from the mineral-pure water values. The salt effect can be as large as 2 to 3.5 permil for oxygen and 12 permil for hydrogen at temperatures above 150°C. If ignored, the salt effect associated with 4 m NaCl solution can lead to maximum error in geothermometer estimates for oxygen of 35°C in the quartz-fluid system, and 50°C for hydrogen in the kaolinite-fluid system. The magnitude of these salinity effects is far too great to be ignored, and must be accounted for when modeling isotopic exchange in hydrothermal systems.

INTRODUCTION

The evidence of large-scale transport of fluids through the crust is clearly present in the rock record. Weathering zones, hydrothermal ore deposits, geothermal systems, and altered oceanic crust exemplify the kinds of fluid-rock interaction expected in relatively shallow settings where temperatures and pressures generally do not exceed 400°C and 1 kb, respectively. Based on oxygen and hydrogen isotope studies, it has been demonstrated that certain igneous intrusives have interacted on a very large scale with meteoric groundwaters (e.g., Taylor, 1979;

Criss and Taylor, 1986). At greater depths, various lines of evidence (e.g., fluid inclusions, secondary hydrous phases, etc.) point to the existence of a fluid phase in rocks undergoing metamorphism at temperatures to 600°C and pressures to 3-4 kb (see Ferry and Burt, 1982). As a consequence of these fluid-rock interactions, both chemical and isotopic exchange occur in response to changes in temperature, pressure, fluid and rock composition, time and permeability. With regard to chemical changes, crustal fluids exhibit a wide range in salinities from nearly pure water in some shallow groundwater systems to as much as 60 wt. % dissolved solids in high temperature hydrothermal systems associated with magmatic activity. The chemistry of these fluids is highly variable, but most naturally occurring waters contain varying proportions of Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻, H₂S, and aqueous CO₂ as the dominant dissolved species.

It has long been appreciated that dissolved ions exert a major influence on both the fractionation factors and rates of oxygen and hydrogen isotope exchange between liquid water and other phases (e.g., minerals, H₂O vapor, CO₂). Taube (1954) observed that the oxygen isotope properties of saline solutions differed from those of water at room temperature. More recently, experiments have been carried out at elevated temperatures to determine the magnitude of the oxygen and hydrogen salinity-isotope effects (Truesdell, 1974; Graham and Sheppard, 1980; Kazahaya, 1986; Wesolowski and Cole, unpub.) Experimental mineral-water isotopic fractionation studies commonly employed the use of electrolyte-bearing solutions to enhance the isotopic reaction rates by increasing the solubilities of the reactant phases (e.g., calcite-NH₄Cl: O'Neil et al., 1969; feldspar-NaCl, KCl: O'Neil and Taylor, 1967; quartz-NaF: Clayton et al., 1972).

Critical to the interpretation of isotope effects in mineral-fluid systems is a knowledge of (1) equilibrium isotope relations among minerals, and between minerals and fluids, (2) rates of the isotopic exchange reactions, and (3) factors that influence the equilibrium and kinetic isotopic properties of minerals, such as the fluid composition ("salt effect"). The purpose

of this communication is twofold: first, to demonstrate that rates of isotopic exchange between minerals (rocks) and fluid are significantly increased when electrolytes are present, and thus the duration of isotopic equilibration will depend directly on the fluid composition during interaction; and second, to show that the "salt effect" on the equilibrium isotope partitioning between minerals and fluids is substantial, particularly for hydrogen, and cannot be ignored when performing geothermometer calculations, or estimating the fluid isotopic composition in natural systems.

RATES OF ISOTOPIIC EXCHANGE

Oxygen and hydrogen isotopic exchange between minerals (rocks) and fluids has been attributed to two major processes, diffusion and dissolution-precipitation (Cole et al., 1983). When minerals and fluids are in chemical equilibrium, isotopic exchange occurs primarily through a diffusion mechanism. Diffusion coefficients for oxygen and hydrogen have been summarized for a variety of mineral-fluid systems by Cole and Ohmoto (1986). In contrast, isotopic exchange in mineral-fluid systems that are initially far from chemical equilibrium is controlled chiefly by surface reactions, such as dissolution-recrystallization or transformation of one mineral to another. Oxygen isotopic shifts observed in geothermal systems and hydrothermal ore deposits have resulted from surface exchange or alteration reactions during water-rock interaction at elevated temperatures. The final products of the alteration process depend on (1) temperature, (2) pressure, (3) solution composition, (4) original rock composition, (5) duration of interaction, and (6) permeability (or availability of exposed surfaces).

Cole et al. (1983) proposed a rate model based on the addition and removal of oxygen atoms from the mineral surface such that

$$r = \frac{-2n(1-F)(W)(S)}{(W+S)(A)(t)} \quad (1)$$

where W and S are the moles of oxygen in water and solid, respectively, A is the surface area (m²), t is time (sec), F is the degree of equilibration (F = 1 at equilibrium), and r is the rate constant, expressed as mole of O m⁻² sec⁻¹. This expression has been used to evaluate the rates of experimental oxygen isotopic exchange between (1) basalt-seawater (Cole et al., 1987), (2) granite-H₂O-NaCl (Cole, 1980; Cole and Ohmoto, in prep.), and (3) a variety of isotopic exchange reactions involving new mineral growth or recrystallization described in the literature. These rate data have been summarized recently by Cole and Ohmoto (1986). Rate constants were found to range from 10⁻⁹ to 10⁻⁴ moles O m⁻² sec⁻¹ over the temperature range of 200 to 800°C, respectively, and activation energies average between 9 and 22 kcal mole⁻¹. These activation energies are similar to those reported for chemical reactions involving fluids and mineral surfaces (Berner, 1978).

Figure 1 shows representative rate curves estimated from the model described above. These

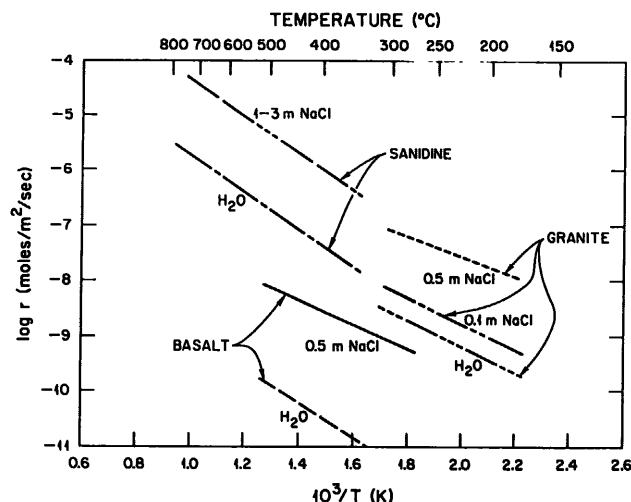


Figure 1. Arrhenius plot of experimentally determined oxygen isotope rate constants, r, in units of moles of O/m² of solid surface/sec. Data are from Cole and Ohmoto (1986) and Cole, et al. (1987).

examples show clearly that rates of oxygen isotope exchange are significantly increased by interaction of a solid with NaCl solutions. The cation exchange reaction between sanidine and 1 to 3 M NaCl forming albite resulted in a 30-fold increase in the isotopic exchange rate compared to the sanidine-H₂O reaction. A similar magnitude of increase was observed for the granite-0.5 m NaCl interaction. Although the salinity was less in these experiments compared to O'Neil and Taylor's (1967) feldspar study, a number of rapid alteration reactions affected the granite (e.g., formation of zeolites, chlorite after biotite), enhancing the rates even more. A similar situation is also observed for the experimental basalt-seawater system (Cole et al., 1987). With regard to the granite data, an empirical expression relating salinity (up to 0.5m NaCl) and rate is given by

$$\log r(\text{NaCl}) \approx \log r(\text{H}_2\text{O}) / (1 + 0.445(m_{\text{NaCl}})) \quad (2)$$

where

$$\log r(\text{H}_2\text{O}) = -4.307 - 2.404 (10^3/T) \quad (3)$$

DURATIONS OF FLUID-ROCK ISOTOPIIC EXCHANGE

It has been shown that several geothermal (e.g., Roosevelt, Wairakei) and epithermal ore deposit systems (e.g., Sunnyside, Goldfield, Tonopah) exhibit varying degrees of bulk rock-water oxygen isotopic disequilibrium, even though in many instances vein minerals have isotopically

equilibrated with the fluid (Cole, 1983). The isotopic disequilibrium data on these natural systems may be used with the appropriate rate model to estimate the minimum duration of fluid interaction with the rock, provided the effect of the salinity is accounted for by use of the proper rate constants. A fundamental relationship has been proposed that quantitatively evaluates the important parameters influencing isotopic exchange in an alteration environment (Cole et al., 1983). This relationship, for a closed system, is given as

$$t(\text{sec}) = \frac{-\ln(1-F)(W/R)(a)(\rho)(X)}{3(1+(W/R))(r)(10^{-4})} \quad (4)$$

where F is the degree of equilibration, (W/R) is the mole ratio of oxygen in water to rock, a is the spherical grain radius (cm), ρ is the grain density, X is the number of moles of oxygen per gram of rock, and r is the rate constant.

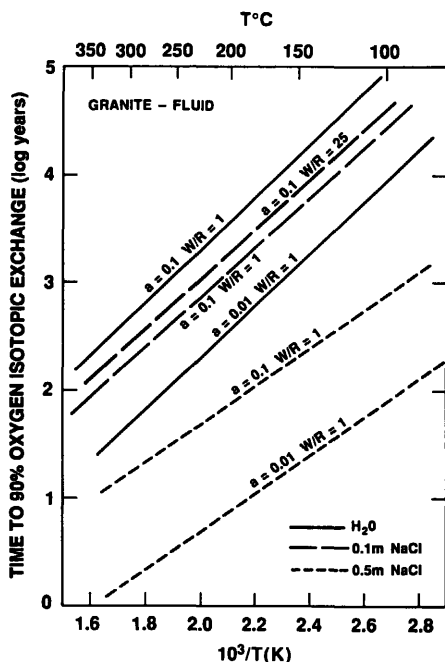


Figure 2. Time to 90% oxygen isotopic exchange versus temperature for the granite-fluid system. The curves are calculated from Equation (4) described in text. Rate constants are taken from Fig. 1. The a refers to grain radius (in cm), and (W/R) in the water to rock mass ratio.

Using the rate data from the granite-fluid system (Fig. 1), we have calculated the time required to attain 90 % isotopic exchange as a function of temperature, grain size, and (W/R) ratio. Figure 2 indicates, for example, that granite-pure water interaction with a = 0.1 cm and (W/R)_{mass} = 1 requires approximately 3700 years to reach 90% exchange at 200°C, but only 74 years for reaction with 0.5 m NaCl (2.84 wt. % NaCl). For the same conditions of grain size,

(W/R) ratio, and temperature, an increase in salinity to only 0.1 m results in a time for 90% exchange of 1480 years. An increase in the salinity from pure water to 0.5 m NaCl has a much larger effect on decreasing rates of rock-fluid exchange than a 10-fold decrease in grain size. For example, a decrease in grain radius by one order of magnitude (0.1 to 0.01 cm) leads to a decrease in the time needed for 90% isotopic equilibration of one order of magnitude. An increase in temperature results in an obvious decrease in the equilibration time--e.g., 1480 years at 200°C, a = 0.1 cm, (W/R)_{mass} = 1 to only 186 years for 300°C interaction. The magnitudes of these salt effects are clearly not small, and must be accounted for when modeling isotopic exchange rates in hydrothermal systems.

SUMMARY OF EXPERIMENTAL NaCl AQUEOUS SOLUTION-H₂O ISOTOPIC FRACTIONATION

One of the most fundamental, and yet at the same time most poorly understood, aspects of stable isotope geochemistry of hydrothermal fluids is the effect of dissolved electrolytes (e.g., NaCl, CaCl₂) on the equilibrium partitioning of oxygen and hydrogen isotopes between brines and other phases (vapor, gases, minerals) during boiling and water-rock interaction. Experimental measurements of the effect of salt on oxygen and hydrogen isotope partitioning at room temperature, measured both by direct sampling of vapor over brines (D/H and ¹⁸O/¹⁶O) and by sampling CO₂ gas equilibrated with the brines (¹⁸O/¹⁶O only), have been reported by Taube (1954), Sofer and Gat (1972, 1975), Stewart and Friedman (1975), Truesdell (1974), and Bopp et al. (1977). For both hydrogen and oxygen isotopes, the salinity effects in solutions of pure salts (NaCl, CaCl₂, etc.) are large (i.e., several permil in oxygen and up to 20 permil in hydrogen) and linearly proportional to the molality of the dissolved salt. The effect on oxygen isotope partitioning is more strongly controlled by the nature of the cation, whereas anion properties more strongly influence hydrogen isotope fractionation. These observations have been interpreted as being a consequence of hydration of ions in aqueous solutions with concomitant partitioning of isotopes between the hydration waters and "free" solvent molecules (Taube, 1954, Bopp et al., 1977). This interpretation implies that the isotopic activity ratios, a_{H₂¹⁸O}/a_{H₂¹⁶O} and a_{HDO}/a_{H₂O} differ from the isotopic concentration ratios of the solution and that it is the isotopic activity ratio which determines the partitioning of isotopes between the solution and other phases (vapor, gases, minerals).

One might intuitively expect these salinity effects on the isotopic activity ratios to vary systematically with salt concentration at elevated temperatures and to decrease in magnitude with increasing temperature due to (1) the usual decrease in isotope separation between coexisting phases as temperature increases, and (2) the decrease in ion hydration with increasing temperature as a result of ion pair formation. Experi-

mental results for NaCl solutions summarized in Fig. 3 and Tables 1 and 2 indicate that such is

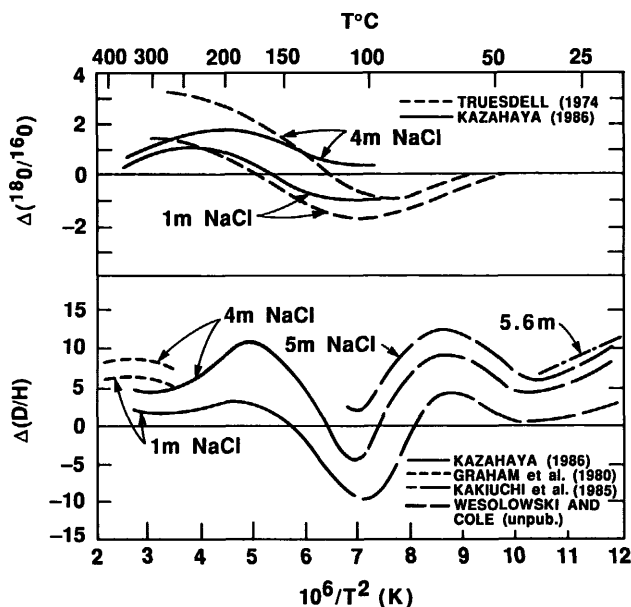


Figure 3. Differences between oxygen (top half) isotopic composition of CO₂ (Truesdell) or vapor (Kazahaya) in equilibrium with NaCl aqueous solutions and CO₂ or vapor in equilibrium with pure water. Differences between hydrogen (bottom half) isotopic composition of either vapor (Kazahaya; Wesolowski and Cole), H₂ (Kakiuchi, et al.), or epidote (Graham and Sheppard) in equilibrium with NaCl aqueous solutions and these same phases in equilibrium with pure water. Data of Wesolowski and Cole, (100°, 70°C, unpub.) have been extrapolated to 20° [data of Stewart and Friedman (1975)].

Table 1. The Δ(¹⁸O/¹⁶O) values for NaCl aqueous solutions taken from the experimental studies of Truesdell (1974) and Kazahaya (1986).

T°C	Kazahaya (1986)		Truesdell (1974)	
	Δ(1 m)	Δ(4 m)	Δ(1 m)	Δ(4 m)
100	-1.14	0.28	-1.54	-0.82
150	-0.32	1.12	-0.45	1.47
200	0.69	1.73	0.60	2.52
250	0.96	1.51	0.85	3.0
300	0.84	1.09	--	(3.25)
350	0.35	0.7	--	--

(Parentheses refer to extrapolated values beyond limits of experimental data.)
For a definition of Δ used in Tables 1-5, see Equation (5).

Table 2. The Δ(D/H) values for NaCl aqueous solutions taken from experimental studies by Stewart and Friedman (1975-a), Wesolowski and Cole (unpub.-b), Kazahaya (1986-c), and Graham and Sheppard (1980-*).

T°C	Δ(1 m)	Δ(4 m)	Source
20	2.3	9.2	a
70	3.9	10.0	b
100	-10.0	-1.25	b
109	-8.5	-4.25	c
150	0.4	7.64	c
179	3.21	10.90	c
200	3.35	9.75	c
250	1.65 (5.1)*	5.54 (6.72)*	c
300	1.68 (6.6)*	4.39 (8.5)*	c
350	2.19 (6.8)*	5.17 (8.7)*	c

not the case, but rather that salinity effects exhibit a complex temperature and compositional dependence. Because less is known about the salt effects for other electrolyte systems (e.g., KCl, CaCl₂, MgCl₂), particularly for hydrogen isotope exchange, we have focused our attention on the NaCl solutions, assuming they are a reasonable analogue for the salt effects in natural systems. The curves in Fig. 3 represent the average trends through data derived from a variety of sources. Maximum scatter in the oxygen isotope fractionation data is on the order of 0.5 to 1.0 permil (Truesdell, 1974; Kazahaya, 1986), and can be as much as 2 permil for hydrogen (Kazahaya, 1986).

In Fig. 3, Δ equals the difference in the isotopic activity ratios of the isotopic molecules between pure water and NaCl aqueous solution, determined using a separate phase; i.e., CO₂ gas in Truesdell's (1974) experiments, vapor for Kazahaya (1986), Stewart and Friedman (1975), and Wesolowski and Cole (unpub.); H₂ gas for Kakiuchi et al. (1985); and epidote in the work of Graham and Sheppard (1980), as the monitor of the isotopic activity ratios. Thus,

$$\Delta = 10^3 \ln((a'/a)_{\text{NaCl}} / (a'/a)_{\text{pure water}}) \quad (5)$$

where a' = activity of HDO or H₂¹⁸O and a = activity of H₂O (with "normal" ¹⁸O/¹⁶O ratio) and H₂¹⁶O, respectively. In the case of Truesdell's oxygen isotope exchange experiments, this equation becomes

$$\Delta = 10^3 \ln(\alpha_{\text{CO}_2\text{-NaCl}} / \alpha_{\text{CO}_2\text{-pure water}}) \quad (6)$$

For pure water, the isotopic activities are presumably equal to their concentrations.

Experimental results reported by Truesdell (1974), who compared the oxygen isotopic composition of CO₂ gas equilibrated with pure water with its composition in equilibrium with NaCl aqueous solution of identical oxygen isotopic composition, exhibit similar patterns compared with the data of Kazahaya (1986) except for results from 4 m NaCl solutions above 200°C. Perhaps at high salinities and temperatures, the nature of CO₂

in aqueous solution has a markedly different effect on the structure of water compared to the lower concentration-temperature conditions. Truesdell (1974) assumed that the role of CO₂ was identical whether it exchanged with pure water or salt solution, and that the isotope effects were due solely to changes in the water structure upon addition of electrolyte. In any event, the trends are certainly non-linear with respect to temperature. ¹⁸O/¹⁶O enrichments on the order of 1.5 to 3.0 permil are expected for a phase equilibrated with an NaCl solution compared to pure water at 200°C, and depletions in ¹⁸O/¹⁶O in an equilibrated phase of 1 to 1.5 permil at 125°C. A Δ value of 0.0 permil (cross-over) is observed at approximately 164°C for the 1 m NaCl data of Kazahaya (1986).

Large hydrogen isotope salinity effects [Δ(D/H)] in NaCl solutions are observed in data summarized in Fig. 3 and Table 2. Between 25 and 300°C, the data take on the appearance of a sine wave. D/H enrichments in phases equilibrated with NaCl solutions (1-4 m) compared to pure water are expected for the temperature intervals of approximately 150 to 300°C and 25 to 80°C. These enrichments may be as large as 12 permil (4 to 5 m NaCl). The 100°C, 1 m NaCl data of Wesolowski and Cole (unpub.) for liquid-vapor isotope exchange agree closely with data of Kazahaya (1986; Table 2, 109°C). Graham and Sheppard (1980) determined Δ values using the systems epidote-NaCl-H₂O and epidote-H₂O. These data differ considerably from the high temperature results of Kazahaya (1986). The disagreement may be attributed to the difference in the experimental pressure conditions--i.e., saturated vapor pressure for Kazahaya's (1986) study and 2 to 4 kb pressure for Graham and Sheppard's work--wherein the chemical properties of the solute and the structure of the solution should be different to a certain extent.

SALT EFFECT ON MINERAL-SOLUTION ISOTOPE FRACTIONATIONS

The magnitudes of the salinity isotope effects shown in Fig. 3 and listed in Tables 1 and 2 are far too large to be ignored and must be taken into account in interpretation of isotopic data for hydrothermal systems. The salt effect can modify the D/H and ¹⁸O/¹⁶O fractionation factors between a vapor, a gas, or a mineral equilibrated with a NaCl aqueous solution (Truesdell, 1974). At present, the salt effect should only be applied in cases where pressures are at or near vapor-saturated conditions (Kazahaya, 1986). With this in mind, we have used the data summarized in Tables 1 and 2 to modify the oxygen isotope fractionation factors between quartz-water (Fig. 4; after Matsuhisa, et al., 1979) and kaolinite-water (Fig. 4; after Kulla, 1979), and hydrogen isotope fractionation factors between kaolinite and water (Fig. 5; after Liu and Epstein, 1984). To obtain these modified curves and the data from which they are derived, given in Tables 3, 4, and 5, we simply added the Δ values from Table 1 or 2 to the fractionation factors at the appropriate temperatures.

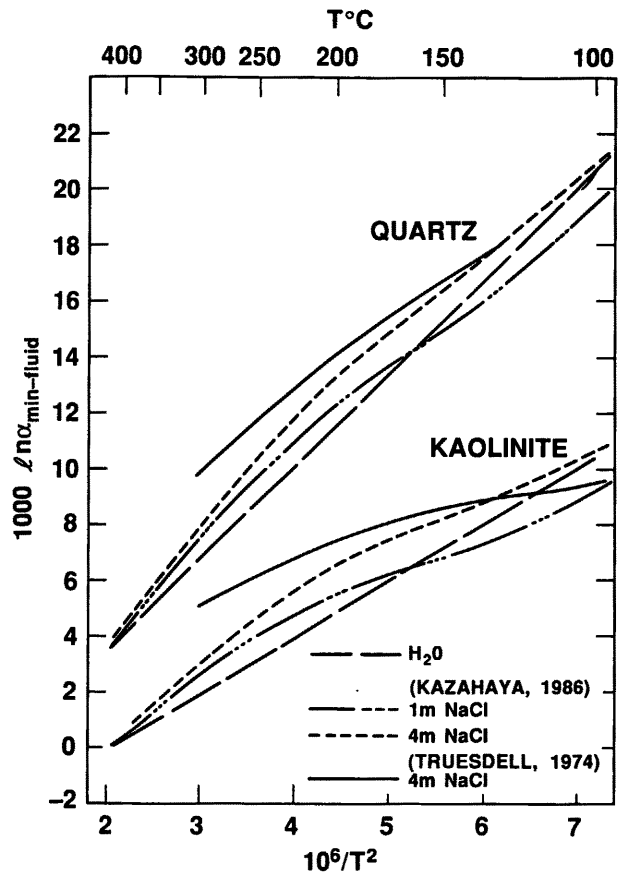


Figure 4. Modifications of the oxygen isotopic fractionation factors for quartz-water (after Matsuhisa, et al. (1979) and kaolinite-water (after Kulla, 1979) for the "salt effect." Data are given in Tables 3 and 4.

Table 3. Comparison of the oxygen isotope fractionation factors for the system quartz-H₂O-NaCl (1, 4 m).

T°C	Δ _{qtz-H₂O}	Kazahaya (1986)		Truesdell (1974)	
		Δ(1 m)	Δ(4 m)	Δ(1 m)	Δ(4 m)
100	20.67	19.53	20.95	19.14	19.85
150	15.33	15.01	16.45	14.88	16.80
200	11.62	12.31	13.35	12.22	14.14
250	8.88	9.84	10.39	10.39	11.88
300	6.84	7.68	7.93	---	(10.09)
350	5.27	5.62	5.97	---	---

1000 ln α_{qtz-H₂O} = Δ_{qtz-H₂O} - 3.34 (10⁶/T²) - 3.31 after Matsuhisa, et al. (1979).

Table 4. Comparison of the oxygen isotope fractionation factors for the system kaolinite-H₂O-NaCl (1, 4 m).

T°C	Δ_{kaol-H_2O}	Kazahaya (1986)		Truesdell (1974)	
		$\Delta(1\text{ m})$	$\Delta(4\text{ m})$	$\Delta(1\text{ m})$	$\Delta(4\text{ m})$
100	10.39	9.25	10.67	8.86	9.57
150	7.13	6.81	8.25	6.68	8.60
200	4.87	5.56	6.60	5.47	7.39
250	3.20	4.16	4.71	4.05	6.20
300	1.95	2.79	3.04	--	(5.20)
350	0.99	1.34	1.69	--	

$$1000 \ln \alpha_{kaol-H_2O} = \Delta_{kaol-H_2O} = 2.39 (10^6/T^2) - 2.51 \text{ after Kullia (1979).}$$

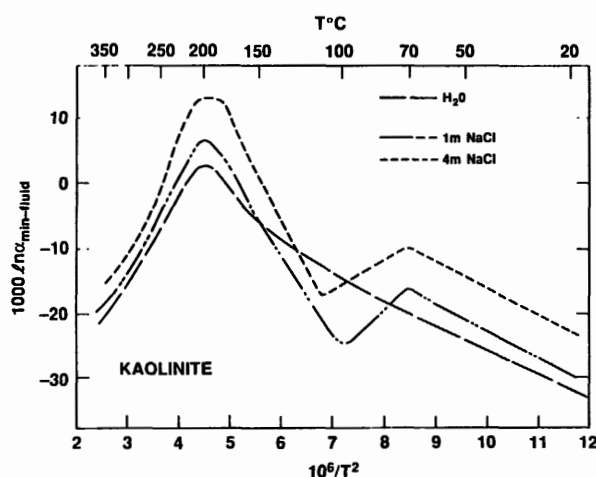


Figure 5. Modification of the hydrogen isotopic fractionation factors for kaolinite-water (after Liu and Epstein, 1984) for the "salt effect." Data are given in Table 5.

Table 5. Estimation of the hydrogen isotope fractionation factors for the system kaolinite-H₂O-NaCl (1, 4 m).

T°C	Δ_{kaol-H_2O}	$\Delta(1\text{ m})$	$\Delta(4\text{ m})$
20	-31.45	-29.15	-22.25
70	-19.93	-16.03	-9.93
100	-14.37	-24.37	-15.62
109	-12.87	-21.37	-17.32
150	-6.18	-5.78	-1.46
179	0.75	3.96	11.65
200	3.0	6.35	12.75
250	-6.4	-4.75	-0.86
300	-15.1	-13.42	-10.71
350	-20.2	-18.01	-15.03

$$1000 \ln \alpha_{kaol-H_2O} = \Delta_{kaol-H_2O} \text{ (data taken from Table II and Fig. 9 of Liu and Epstein, 1984).}$$

As anticipated, compared to the pure water curves, maximum values (positive deviations) for oxygen isotope fractionation occur at approximately 225 and 200°C for 1 m and 4 m NaCl, respectively, using the data of Kazahaya (1986). Maximum positive deviations using Truesdell's (1974) data occur at approximately 300°C for both 1 and 4 m NaCl. The 1 m NaCl curves for both quartz and kaolinite are extrapolated to approach the pure water curves because the salt effects determined by Kazahaya (1986) appear to diminish with increasing temperature. For a fractionation of 6 permil, a temperature of 215°C is estimated for the system, kaolinite-4m NaCl (using Kazahaya's data), but only 170°C for the pure water system; a potential error of nearly 50°C if the wrong curve is used. Because quartz-water has a steeper fractionation slope (Fig. 4), the potential temperature errors are less pronounced, more on the order of 25 to 35°C. Attempts to predict the fluid isotopic composition in equilibrium with kaolinite assuming no salt effect may be in error by as much as 2 permil (4 m vs. pure water) when applying Kazahaya's (1986) data, or 3.5 permil if one uses Truesdell's (1974) 4 m results.

The salt effect on hydrogen isotope fractionation is illustrated through the use of Liu and Epstein's (1984) kaolinite-water curve (Fig. 5 and Table 5). At temperatures above 125 to 150°C, the 1 m and 4 m NaCl-corrected curves exhibit higher fractionations compared with the pure water curve. A maximum deviation of approximately 12 permil is observed for the 4 m data at 200°C. Between approximately 80 and 120°C, the salt effect produces lower fractionation factors compared to the pure water curve, with a value of -24 permil predicted at 100°C for 1 m NaCl versus -14 permil for pure water. Between 100°C and 80°C, the 4 m and 1 m-NaCl curves, respectively, cross-over and exhibit a positive deviation from the pure water trend. Errors in the estimated isotopic composition of fluids in equilibrium with kaolinite may be as large as 11 to 12 permil (either too heavy or too light, depending on the temperature). Measured fractionations between kaolinite and fluids from natural systems may yield geothermometer estimates in error by as much as 50°C for a salinity of 4 m if the salt effect is disregarded.

SUMMARY

Experimental data indicate that aqueous electrolytes have a profound effect on both the rates of isotopic exchange and the equilibrium fractionation factors between minerals and fluids. Using rate data from the system: granite-H₂O-NaCl, we have calculated the times required to achieve 90% oxygen isotope exchange over the temperature interval of 150 to 300°C. These calculations indicate that for an increase in salinity from 0.0 to 0.1 m (NaCl), the time required to reach 90% exchange decreases by a factor of between 2.5 and 3.0--e.g., 3700 years (pure water) versus 1480 years (0.1 m) at 200°C for a (W/R)_{mass} = 1 and a grain radius of 0.1 cm. The effect of electrolytes on the mineral-fluid

fractionation factors may cause deviations from the pure water fractionations by as much as 2 to 3.5 permil for oxygen and 12 permil for hydrogen at temperatures above 150°C. If unaccounted for, the salt effect at 4 m NaCl can lead to maximum errors in the geothermometer estimates for oxygen and hydrogen of nearly 35 and 50°C, respectively. This same effect translates into a maximum error in the estimation of the fluid isotopic composition of over 2 permil for oxygen and 12 permil for hydrogen. The magnitude of the salinity isotope effects summarized in this communication are far too large to be ignored, and must be accounted for when modeling isotopic exchange in hydrothermal systems.

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