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SALT EFFECTS ON STABLE ISOTOPE PARTITIONING AND THEIR GEOCHEMICAL IMPLICATIONS FOR GEOTHERMAL BRINES

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ABSTRACT

The effects of dissolved salts ($NaCl$, KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, $MgSO_4$, and their mixtures) on oxygen and hydrogen isotope partitioning between brines and coexisting phases (vapor and calcite) were experimentally determined at 50-350°C and 300°C, respectively. In liquid-vapor equilibration experiments, for all of the salts studied, the hydrogen isotope fractionation factors between the salt solutions and vapor decreased appreciably (up to 20‰) compared to pure water-vapor. Except for KCl solutions at 50°C, the oxygen isotope fractionation factors between salt solutions and vapor were higher (up to 4‰) than, or very close to, that of pure water. The observed isotope salt effects are all linear with the molalities of the solutions. Mixed salt solutions mimicking natural geothermal brines exhibit salt effects additive of those of individual salts. The isotope exchange experiments of calcite-water at 300°C and 1 kbar yielded a fractionation factor of 5.9±0.3‰ for pure water and effects of $NaCl$ consistent with those obtained from the liquid-vapor equilibration experiments.

The isotope salt effects observed in this study are too large to be ignored, and must be taken into account for isotopic studies of geothermal systems (i.e., estimation of isotope ratios and temperatures of deep-seated geothermal brines).

INTRODUCTION

It has long been recognized that dissolved salts in water can change oxygen and hydrogen isotope partitioning between water and other phases (i.e., vapor, minerals) due to the hydration of ions upon the dissolution of salts in water. However, their effects have not been well determined at elevated temperatures (cf. Truesdell, 1974). We are currently conducting a series of hydrothermal experiments of the system brine-vapor or minerals to 350°C, in order to determine precisely the effects of dissolved salts abundant in brines on isotope partitioning at temperatures encountered in geothermal systems.

The so-called "isotope salt effect" has important implications for the interpretation and modeling of isotopic data of brines and rocks obtained from geothermal fields. We will show how to use our new results of isotopic partitioning to help better evaluate energy resources of many geothermal fields.

EXPERIMENTAL

We can determine the salt effect on oxygen and hydrogen isotope partitioning between liquid water and a coexisting phase A (vapor, minerals) from,

$$10^3 \ln\Gamma = 10^3 \ln\alpha_{A\text{-brine}} - 10^3 \ln\alpha_{A\text{-pure water}} \qquad (1)$$

where α is an equilibrium isotope fractionation factor between a phase A and liquid water. The isotope salt effect (Γ), which is caused by the dissolution of salts in water, can be more rigorously defined as follows,

$$\Gamma = \frac{a(HDO)/a(H_2O)}{X(HDO)/X(H_2O)} \text{ or } \frac{a(H_2^{18}O)/a(H_2^{16}O)}{X(H_2^{18}O)/X(H_2^{16}O)}$$

$$= \gamma(HDO)/\gamma(H_2O) \text{ or } \gamma(H_2^{18}O)/\gamma(H_2^{16}O), \qquad (2)$$

where a, X, and γ denote activity, mole fraction, and activity coefficient, respectively.

In order to examine the effects of dissolved salts on isotope partition, a series of vapor-liquid water equilibration experiments were carried out for $NaCl$ solutions from 50 to 350°C, $CaCl_2$ solutions from 50 to 200°C, and for KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ solutions from 50 to 100°C. Several mixed salt solutions mimicking natural geothermal brines (Salton Sea brine) were also studied at 50 to 100°C. In order to cover the wide range of temperature, three different liquid-vapor equilibration apparatus were employed, using both static and dynamic sampling techniques of water vapor. The overall errors in values of $10^3 \ln\Gamma$ are ±0.1 to 0.15‰ (1σ) and ±1.0 to 1.5‰ (1σ) for oxygen and hydrogen isotopes, respectively.

The effect of dissolved $NaCl$ on oxygen isotope

partitioning between calcite ($CaCO_3$) and water was also studied at 300°C and 1 kbar. Since complete isotope exchange of this reaction is not expected during the experiments, the partial isotope exchange method of Northrop and Clayton (1966) was used to calculate the equilibrium isotope fractionation factor. This technique gives errors of about ±0.2 to 0.3‰ (1σ).

RESULTS AND DISCUSSION
(1) Liquid-Vapor Equilibration Method
We first determined precisely liquid-vapor isotope fractionation factors of pure water from 25 to 350°C, because there are few precise data available in the literature above 100°C. All of our results and most of the literature data were then regressed to single equations valid from the freezing temperature (0°C) to the critical temperature of water (374.1°C),

$$10^3 \ln\alpha_{l-v}(D) = 1159(T^3/10^9) - 1620(T^2/T^6) + 794.8(T/10^3)$$
$$-161.0 + 2.999(10^9/T^3) \qquad (3)$$

within ±1.2‰ (1σ), and

$$10^3 \ln\alpha_{l-v}(^{18}O) = -7.69 + 6.712(10^3/T) - 1.666(10^6/T^2)$$
$$+0.3504(10^9/T^3) \qquad (4)$$

within ±0.11‰ (1σ) (Horita and Wesolowski, in review).

Liquid-vapor isotope fractionation factors of the single salt solutions ($NaCl$, KCl, $MgCl_2$, $CaCl_2$, Na_2SO_4, and $MgSO_4$) with different molalities were determined in order to calculate the isotope salt effects from the following equation,

$$10^3 \ln\Gamma = 10^3 \ln\alpha_{l-v(pure\ water)} - 10^3 \ln\alpha_{l-v(brine)}. \qquad (5)$$

Values of $10^3 \ln\Gamma(D)$ for 0-6 molal $NaCl$ solutions at 50 to 350°C, 0-5 molal $CaCl_2$ solutions at 50 to 200°C, and for 0-4 molal KCl, 0-5 molal $MgCl_2$, 0-2 molal Na_2SO_4, and 0-2 molal $MgSO_4$ solutions at 50 to 100°C were all positive and linear with their molalities within analytical errors. In other words, hydrogen isotope fractionation factors, $10^3 \ln\alpha(D)$, between the salt solutions and vapor are always smaller (up to 20‰) than those of pure water. The magnitude of values of $10^3 \ln\Gamma(D)$ is in the order $CaCl_2 \geq MgCl_2 > MgSO_4 > NaCl \approx KCl > Na_2SO_4$ at the same molalities at 50 to 100°C (see Fig. 1 for 100°C). Our results of NaCl solutions from 50 to 350°C together with those in the literature near and below room temperature show that values of $10^3 \ln\Gamma(D)$ of NaCl solutions decrease from 2.6‰/molal at 10°C to 1.0‰/molal at 130°C, and are nearly constant from 130 to 300°C. Then, the values appear to increase to 2.0‰/molal at 350°C. The values of $10^3 \ln\Gamma(D)$/molal for $CaCl_2$ solutions from 50

to 200°C, and of KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ solutions from 50 to 100°C decrease slightly with increasing temperature.

Except for KCl solutions at 50°C, oxygen isotope salt effects, $10^3 \ln\Gamma(^{18}O)$, in all of the salt solutions are negative or very close to zero; namely oxygen isotope fractionation factors, $10^3 \ln\alpha(^{18}O)$, between the salt solutions and vapor are larger (up to 4‰) than, or very close to, that of pure water. Divalent cation salts (Mg^{2+} and Ca^{2+}) exhibit oxygen isotope salt effects much larger than monovalent cation salts (Na^+ and K^+) (see Fig. 1 for 100°C). Values of $10^3 \ln\Gamma(^{18}O)$ in $MgCl_2$ and $MgSO_4$ solutions are indistinguishable between 50 and 100°C, suggesting that cations determine oxygen isotope salt effects. Our results for the oxygen isotope salt effect of 0-6 molal NaCl solutions from 50 to 350°C show that NaCl has
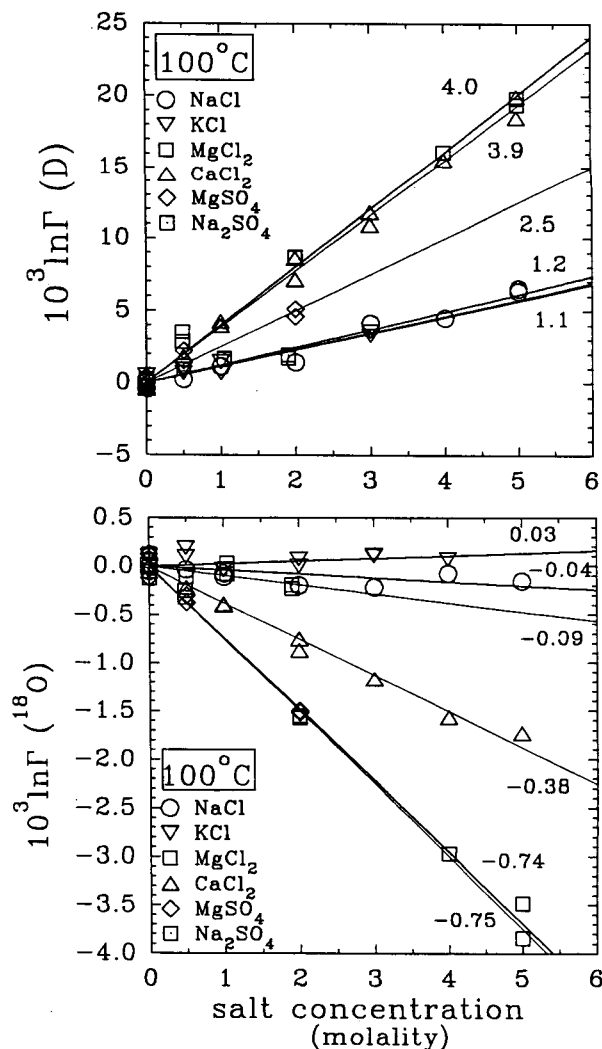

Fig. 1. Salt effect on liquid-vapor partitioning of oxygen and hydrogen isotopes at 100°C.

almost no effect on oxygen isotope partitioning to 200°C, but that values of $10^3 \ln\Gamma(^{18}O)$ start to deviate to negative values at higher temperatures (Fig. 2). Our results for NaCl solutions clearly contradict those of Truesdell (1974) and Kazahaya (1986), who observed complex temperature and molality dependence (Fig. 2). Kazahaya (1986) employed a liquid-vapor equilibration method similar to ours, while Truesdell (1974) used a CO_2-brine equilibration method.

All of the results of the oxygen and hydrogen isotope salt effects in the single salt solutions determined between 50 to 100°C were satisfactorily regressed to an equation with a simple form,

$$10^3 \ln\Gamma = m(a + b/T), \tag{6}$$

where a (molality^{-1}) and b (K.molality^{-1}) are parameters, m molality of a salt solution, and T(K). The results of the fitting are shown in Table 1.

The oxygen and hydrogen isotope salt effects in mixed salt solutions of the system Na-K-Mg-Ca-Cl-SO_4, some of which mimic natural geothermal brines (Salton Sea), were measured using the liquid-vapor equilibration methods between 50 and 100°C. Then, we examined whether the measured isotope salt effects in the mixed salt solutions can be described as an additive property of the isotope salt effects of

individual single salts contained in the mixed salt solutions; namely (Horita et al., 1993b)

$$10^3 \ln\Gamma_{\text{mixed salt soln}} = \Sigma(10^3 \ln\Gamma_{\text{single salt soln}})$$
$$= \Sigma\{m_i(a_i + b_i/T)\}, \tag{7}$$

where i is the ith single salt in mixed salt solutions. Figs. 3a and 3b show that the measured oxygen and hydrogen isotope salt effects in the mixed salt solutions agree well with the calculated values using parameter values in Table 1 and Eqn (7) within analytical errors and uncertainty in the calculations. This is true even for the mixed salt solutions of chloride and sulfate anions with very high ionic strengths. Sofer and Gat (1972; 1975) and Horita and Gat (1989) also observed that this simple mixing rule applies to synthetic and natural chloride-mixed solutions at room temperature. Thus, Eqn (7) can be used to calculate oxygen and hydrogen isotope salt effects in complex natural brines, at least to 100°C.

(2) Calcite-Water Isotope Exchange Method
Hydrothermal experiments of partial isotope exchange were carried out on calcite-pure water at 300°C and 1 kbar for a duration of 126 days. A calculated equilibrium oxygen isotope fractionation factor, $10^3 \ln\alpha_{\text{calcite-pure water}}$ was 5.9±0.3‰. From the experiments of calcite-1, 3, and 5 molal NaCl solutions, we obtained $10^3 \ln\alpha_{\text{calcite-NaCl soln}}$ values of 5.6±0.2, 5.0±0.15, and 4.9±0.2 ‰ for 1, 3, and 5 molal NaCl solutions, respectively (Table 2). Oxygen isotope salt effects can be calculated from,
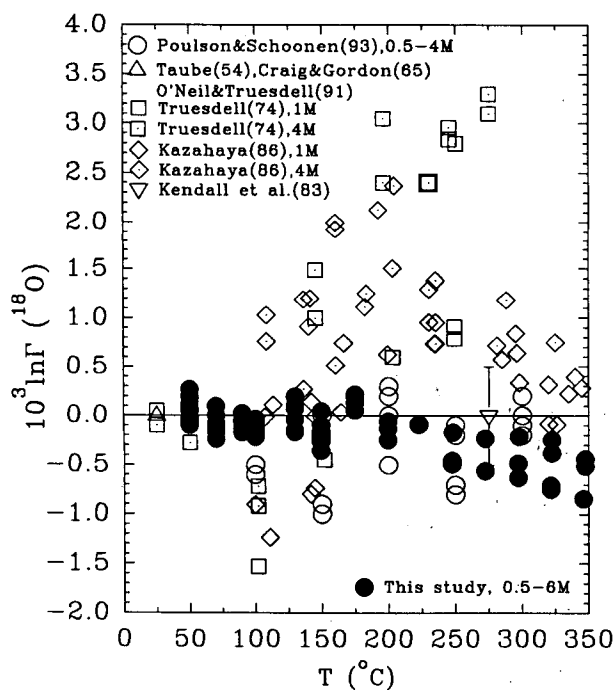

Fig. 2. Effect of NaCl on oxygen isotope partitioning.

Table 1. Results of least-squares fitting of the isotope salt effect in single salt solutions (Horita et al.1993a)

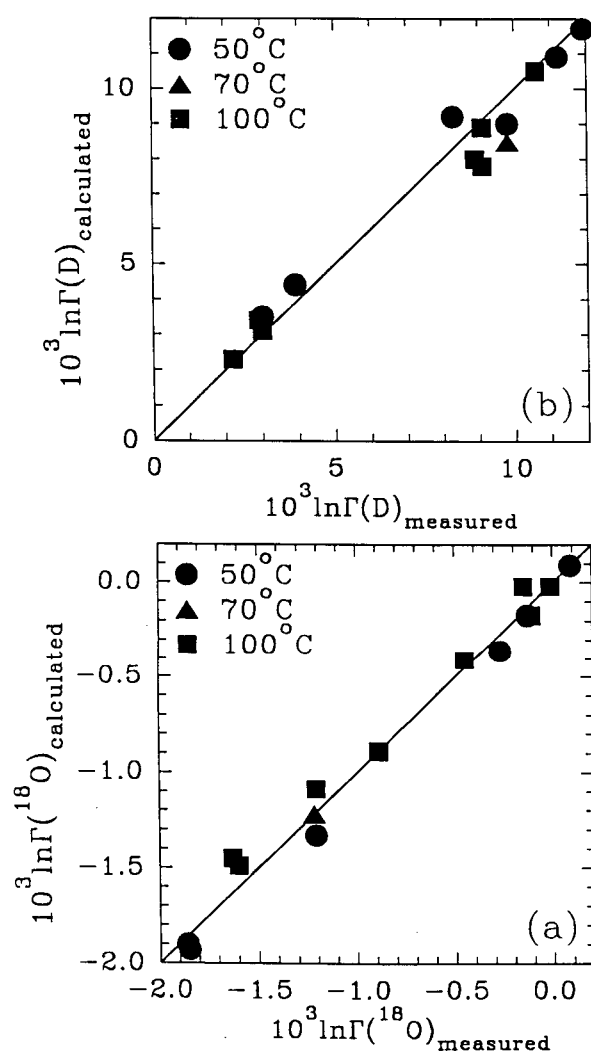| salt | $10^3 \ln\Gamma$ | parameter | | T(°C) |
		a	b	
NaCl	(D)	-2.89	1503.1	10-100
	(^{18}O)	-0.015	0	25-100
KCl	(D)	-5.10	2278.4	20-100
	(^{18}O)	-0.612	230.83	25-100
$MgCl_2$	(D)	+4.14	0	50-100
	(^{18}O)	+0.841	-582.73	25-100
$CaCl_2$	(D)	-2.34	2318.2	50-100
	(^{18}O)	-0.368	0	50-100
Na_2SO_4	(D)	+0.86	0	50-100
	(^{18}O)	-0.143	0	50-100
$MgSO_4$	(D)	+8.45	-2221.8	50-100
	(^{18}O)	+0.414	-432.33	0-100

Fig. 3. Effects of mixed salt solutions on oxygen and hydrogen isotope partitioning at 50-100°C.

Table 2. Results of the isotope exchange experiments of calcite-water at 300°C and 1 kbar.

NaCl	F(%)	$10^3\ln\alpha$	$10^3\ln\Gamma(^{18}O)$
pure water	7.4	5.9±0.3	
1 molal	19.0	5.6±0.2	-0.3
3 molal	22.7	5.0±0.15	-0.9
5 molal	25.0	4.9±0.2	-1.0

F=fraction of isotope exchange

$$10^3\ln\Gamma(^{18}O)=10^3\ln\alpha_{calcite-NaClsoln}-10^3\ln\alpha_{calcite-purewater} \quad (8)$$

yielding $10^3\ln\Gamma(^{18}O)$ values of -0.3 to -1.0‰ (Table 2). The magnitude of these oxygen isotope salt effects obtained from the calcite-water experiments is consistent with those obtained from the liquid-vapor equilibration method at 300°C (-0.2 to -0.6‰ for 1 and 5 molal NaCl solutions) (Fig. 2).

A previous study on oxygen isotope fractionation in the system calcite-0.7 molal NH_4Cl solution gave a $10^3\ln\alpha$ value of about 5.6‰ at 300°C (O'Neil et al., 1969, corrected in Friedman and O'Neil, 1977). Kendall et al. (1983) also carried out experiments for oxygen isotope fractionation factor of the system calcite-0.5 molal $NH_4Cl\pm1$ or 4 molal NaCl solution at 275°C. They found that the average oxygen isotope fractionation factors were 6.8±0.5‰ regardless of the presence of NaCl; the equation by O'Neil et al. (1969) yields 6.4‰ at 275°C. Thus, our results and those of O'Neil et al. (1969) and Kendall et al. (1983) are generally consistent with each other, although the effect of NH_4Cl is not well determined.

IMPLICATIONS FOR GEOTHERMAL STUDIES

In some geothermal fields, both steam and liquid water can be collected, and their oxygen and hydrogen isotopic compositions can be used as the water-steam isotope geothermometer, using Eqns (3) and (4). However, incomplete separation of steam and water, and partial condensation of steam after the phase separation often result in discordant, unreasonable temperatures for the phase separation. A third water-steam isotope geothermometer employs the slope in the δD-$\delta^{18}O$ diagram, given by the ratio of differences in oxygen and hydrogen isotopic compositions of water and steam samples,

$$\text{slope}=\Delta\delta D/\Delta\delta^{18}O=(\delta D_l-\delta D_v)/(\delta^{18}O_l-\delta^{18}O_v)$$
$$\approx(1-\alpha_{l-v}(D)^{-1})/(1-\alpha_{l-v}(^{18}O)^{-1}) \quad (9)$$

Values of the slope were calculated from Eqns (3), (4), and (9) from 0 to 372°C, and shown in Fig. 4. The value of the slope decreases from about 8 near room temperature with increasing temperature, due to a rapid decrease in the value of the hydrogen isotope fractionation factor. The sign of the slope changes at about 229°C because of the cross-over of the hydrogen isotope fractionation factor. The effects of incomplete separation of water and steam, and partial condensation of steam on calculated temperatures of the phase separation using Eqn (9) are much smaller than those obtained from values of $\Delta\delta D$ and $\Delta\delta^{18}O$, alone. However, the water-steam isotope geothermometer using the value of $\Delta\delta D/\Delta\delta^{18}O$ should be limited to temperatures less than 250°C, due to large errors in the calculations above that temperature. Since dissolved salts in water

change both oxygen and hydrogen isotope fractionations factor between liquid water and steam, their effects must be taken into account for the evaluation of temperatures of the phase separation.

The importance of the isotope salt effect for evaluating reservoir temperatures of geothermal systems can be illustrated using a mineral-water isotope geothermometer. In active geothermal fields, isotopic compositions of brines and rocks obtained from bore holes have been used to estimate reservoir temperatures, assuming the attainment of isotope equilibrium. For example, samples of kaolinite and water obtained from a bore hole in a geothermal field give a measured $10^3 \ln\alpha(D)_{kaol-water}$ value of -15‰. In order to calculate the underground reservoir temperature, the isotope salt effect of the water sample must be taken into account. The effects of 1 and 3 molal NaCl solutions and Salton Sea brine on the hydrogen isotope fractionation factor are shown in Fig. 5 as examples. The composition of Salton Sea brine is 3.14 molal Na^+, 0.882 molal Ca^{2+}, 0.588 molal K^+, and 5.76 molal Cl^- (Williams and McKibben, 1989). The fractionation factor between kaolinite and pure water is taken from Liu and Epstein (1984). If the fractionation factor for pure water was inadvertently used for 1 and 3 molal NaCl solutions, and Salton Sea brine, the calculated isotope temperatures will be approximately 7, 24, and 59°C higher than the correct one, respectively.
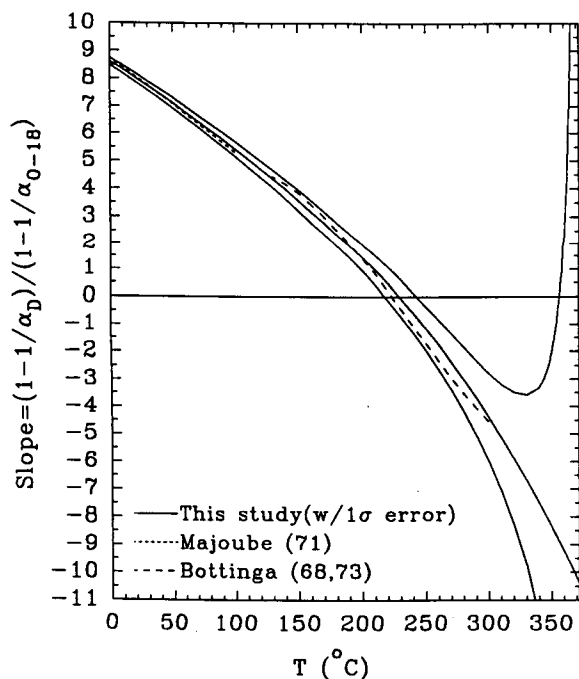
Discrepancies reported in the literature between temperatures obtained from mineral-water isotope geothermometers and measured bore hole temperatures, homogenization temperatures of fluid inclusions, and other chemical geothermometers could be due to the disregard of possible isotope salt effect in waters in the calculations. The same principle should be applied to isotope geothermometers between brines and dissolved species (e.g., SO_4^{2-}), but isotope geothermometers using coexisting minerals or gaseous species (e.g., CO_2, CH_4) are independent of the isotope salt effect in brines.

Another important example is the estimation of isotopic compositions of fluids from which mineral assemblages were precipitated in geothermal fields. Isotopic data of minerals together with estimated temperatures of the precipitation of the minerals obtained from fluid inclusion microthermometry and/or other types of geothermometers can give the isotope ratios of the parental fluids, using mineral-water isotope fractionation factors. Alternatively, fluid inclusions in minerals can be extracted and their isotopic compositions can be determined, thus providing directly isotope ratios of the mineral-forming fluids. When fluids precipitating minerals in geothermal fields are brines, the isotope ratios of the fluids obtained by the above two approaches could be different due to the isotope salt effect in the brines (Truesdell, 1974).
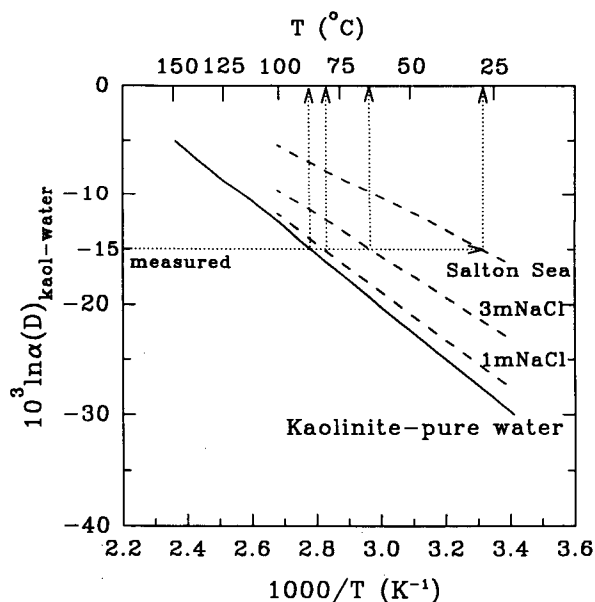

Fig. 4. Ratio of $\Delta\delta D/\Delta\delta^{18}O$ of water and steam samples as a function of temperature.

Fig. 5. Salt effect on kaolinite-water hydrogen isotope geothermometer.

CONCLUSIONS

Our hydrothermal experimental studies demonstrate that salt effects on stable isotope partitioning between brines and other phases (vapor and minerals) indeed persist up to at least 350°C, but that the complex temperature and composition dependence reported in the literature is almost certainly an experimental artifact. Our new, precise results on isotope partitioning and salt effects permit a improved quantitative evaluation of the geochemical characteristics of geothermal systems.

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