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Influence of dissolved ions on determination of oxygen isotope composition of aqueous solutions using the CO₂-H₂O equilibration method

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RATIONALE: Stable isotope compositions of natural waters, such as seawater, glaciers and basinal brines, can provide valuable information about Earth's hydrological cycle and its evolutionary history. However, a high concentration of dissolved ions in some natural waters hinders an accurate analysis of their oxygen isotope composition. A laboratory study was carried out in order to provide guidelines on how to resolve this analytical difficulty.

METHODS: CO₂ gas was equilibrated with saline aqueous solutions of various chemical compositions at 25 °C. Subsequently, the oxygen isotope composition of the CO₂ was determined at different equilibration times using a dual-inlet isotope ratio mass spectrometer in order to evaluate the oxygen isotope salt effect and the rate of oxygen isotope exchange between CO₂ and the saline solution.

RESULTS: Using the experimentally determined oxygen isotope salt effects of aqueous chloride and sulfate solutions, an empirical method for the prediction of the oxygen isotope salt effect of a 1.0 molal chloride or sulfate solution was proposed. The rates of oxygen isotope exchange between CO₂ and saline solutions were also examined. Our experimental data indicates that the sequence of the oxygen isotope exchange time is as: MgSO₄ > CaCl₂ ≈ Na₂SO₄ > NaCl > MgCl₂ > KCl > H₂O.

CONCLUSIONS: The isotope salt effect and the kinetics of isotope exchange must be taken into account when the oxygen isotope composition of a saline aqueous solution is determined using the CO₂-H₂O equilibration method. Our experimental data and the proposed prediction method provide essential guidelines for the accurate δ¹⁸O analysis of saline aqueous solutions. Copyright © 2012 John Wiley & Sons, Ltd.

Water is essential for life and therefore it has played a critical role in the creation and proliferation of the biosphere on Earth. Water is also a key player in the evolution and chemical change of the lithosphere. Furthermore, water in the ocean covers approximately three-quarters of the Earth's surface and its circulation is tightly connected with Earth's climate system. For these reasons, the study of water has been one of the most important fields of research in Earth sciences. Recently, attention has been drawn to the physical, chemical, and biological characteristics of extreme environments in order to gain a basic understanding of the origin of life on Earth. Accordingly, numerous studies of saline systems, such as Mono Lake in the United States and the Dead Sea between Jordan and Israel, are underway and therefore more isotopic analyses of saline aqueous solutions can be expected.

The field of stable isotope geochemistry was born after Harold Urey's discovery of deuterium in 1931. Since then, numerous geological materials have been examined by stable isotope geochemists to better understand the Earth as a system and therefore to tackle various complex geological

problems. In particular, stable isotope geochemists have long investigated the oxygen isotope properties of various geo-fluids in order to (1) identify the source of water that may originate from different geological settings,^[1,2] (2) estimate the temperature of mineral formation using stable isotope thermometry,^[3–5] and (3) understand the hydrological cycle and its associated biogeochemical processes in and near the Earth's surface.^[6–8]

The oxygen isotope compositions of aqueous solutions have been typically determined by using one of the two methods or slightly modified versions of them.^[9–11] The first method is the so-called 'classic CO₂-H₂O equilibration method'. In this method, a sample of water is equilibrated with CO₂ gas at a constant temperature and the oxygen isotope composition of the isotopically equilibrated CO₂ is then analyzed to determine the oxygen isotope composition of the water sample. The second method, which is typically used for small-size samples (<0.01 mL), involves a quantitative conversion of water into a gas form (CO, CO₂, or O₂), followed by an isotopic analysis of the gas by stable isotope ratio mass spectrometry.^[12,13] Due to its analytical simplicity and ease of operation, most stable isotope laboratories around the world use the classic CO₂-H₂O equilibration method for their routine δ¹⁸O analysis of aqueous solution samples. Recently, the classic CO₂-H₂O equilibration method has gained more popularity following the introduction of an

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automated on-line CO₂-H₂O equilibration system that is specifically designed for continuous-flow isotope ratio mass spectrometry (CF-IRMS).^[14] This relatively new but innovative technique requires a considerably smaller amount of aqueous solution than the conventional off-line or on-line CO₂-H₂O equilibration method for a dual-inlet isotope ratio mass spectrometry (DI-IRMS) system.^[15]

Regardless of the sample preparation method (on-line vs. off-line) or the type of the stable isotope ratio mass spectrometry (DI-IRMS vs. CF-IRMS), the rate of oxygen isotope exchange for a given CO₂-solution system has to be evaluated carefully in order to accurately determine the oxygen isotope composition of the aqueous solution when the classic CO₂-H₂O equilibration method is employed. It should be noted that the oxygen isotope exchange kinetics between CO₂ and high ionic strength (*I*) or saline aqueous solutions, such as brines or seawater (*I* = ~0.7 mol/kg), are not the same as those for low ionic strength solutions, such as freshwater or meteoric water, although the CO₂-H₂O equilibration method is performed under the same experimental conditions. Furthermore, the oxygen isotope salt effect has also to be considered when the oxygen isotope compositions (activity vs. concentration) of saline aqueous solutions are determined.^[16–20] In this study, a simple method to estimate the oxygen isotope salt effect of 1.0 molal chloride- or sulfate-bearing aqueous solutions is proposed. In addition, as very little data is available regarding the kinetics of oxygen isotope exchange between CO₂ and saline aqueous solutions,^[16,17] several saline aqueous solutions of geochemical importance were tested to provide guidelines for the accurate δ¹⁸O analysis of saline solutions when the CO₂-H₂O equilibration method is used.

EXPERIMENTAL

Preparation of saline aqueous solutions

A suite of chloride or sulfate solutions of at least two different ionic strengths was prepared gravimetrically by dissolving an ACS-grade anhydrous chemical (KCl, NaCl, CaCl₂, MgCl₂, Na₂SO₄, or MgSO₄) in deionized water (18 MΩ cm). Typically, the individual solution was stored in a closed 1 L glass bottle at 25 °C (±0.01°C) prior to its first use for the experiment. No traces of precipitation of chloride or sulfate salt were observed

on the wall or the bottom of the glass bottle. Three different batches of deionized water (KUDIW-1, KUDIW-2, and KUDIW-3) were used throughout the study and their oxygen isotope compositions of water-equilibrated CO₂ were 30.32 ± 0.05‰, 30.20 ± 0.07‰, and 30.43 ± 0.06‰, respectively, relative to the oxygen isotope composition of a laboratory standard CO₂ at Korea University. Table 1 shows the range of ionic strengths of all the saline aqueous solutions tested in this study.

Oxygen isotope analysis

Water-equilibrated CO₂ (δ¹⁸O_{CO₂-water) or solution-equilibrated CO₂ (δ¹⁸O_{CO₂-solution)}}

All the saline aqueous solutions were analyzed at 25 °C using an automated CO₂-H₂O equilibration device, together with a Finnigan MAT 252 stable isotope mass spectrometer (ThermoFinnigan, Bremen, Germany), at Korea University (Fig. 1). Typically, 5 mL of deionized water or saline aqueous solutions were transferred, by using a pre-cleaned plastic syringe, into a small custom-made glass reaction bottle that was designed for the automated CO₂-H₂O equilibration device at Korea University. Thereafter, the water or the saline aqueous solution in the glass reaction bottle was degassed through a capillary tube and a set amount of pure CO₂ gas was then introduced into the glass reaction bottle. The glass reaction bottle was then shaken at a constant rate of 2.0 Hz to promote oxygen isotope exchange reaction between CO₂ and the solution until the end of the isotopic analysis. The automated CO₂-H₂O equilibration device accommodated 24 glass reaction bottles simultaneously and thus a maximum of 24 aqueous solution samples could be analyzed sequentially in a single batch. In this paper, δ¹⁸O_{CO₂-solution represents the oxygen isotope composition of CO₂ that was equilibrated with an aqueous solution. For example, δ¹⁸O_{CO₂-water or δ¹⁸O_{CO₂-NaCl denotes the oxygen isotope composition of CO₂ that was equilibrated with deionized water or NaCl solution, respectively. All the experimentally determined oxygen isotope compositions, such as the δ¹⁸O_{CO₂-water, δ¹⁸O_{CO₂-solution, and δ¹⁸O_{CO₂ⁱⁿⁱ values, are reported in permil (‰) with respect to the oxygen isotope composition of a laboratory standard CO₂ at Korea University, not to the international standard SMOW. The precision (1σ) of most of the δ¹⁸O_{CO₂-solution analyses, on the basis of replicate}}}}}}}

Table 1. Ionic strengths of saline aqueous solutions examined in this study

Solution	Cation	Anion	Ionic strength (mol/kg)			
			0.5 molal	1.0 molal	2.0 molal	3.0 molal
Chloride solutions						
KCl	K ⁺	Cl ⁻	0.50	0.99	1.96	n/a
NaCl	Na ⁺	Cl ⁻	n/a	0.99	n/a	2.91
CaCl ₂	Ca ²⁺	Cl ⁻	1.05	1.85	n/a	n/a
MgCl ₂	Mg ²⁺	Cl ⁻	1.25	2.24	n/a	n/a
Sulfate solutions						
Na ₂ SO ₄	Na ⁺	SO ₄ ²⁻	1.14	2.06	n/a	n/a
MgSO ₄	Mg ²⁺	SO ₄ ²⁻	0.77	1.28	n/a	n/a

n/a = not applicable.

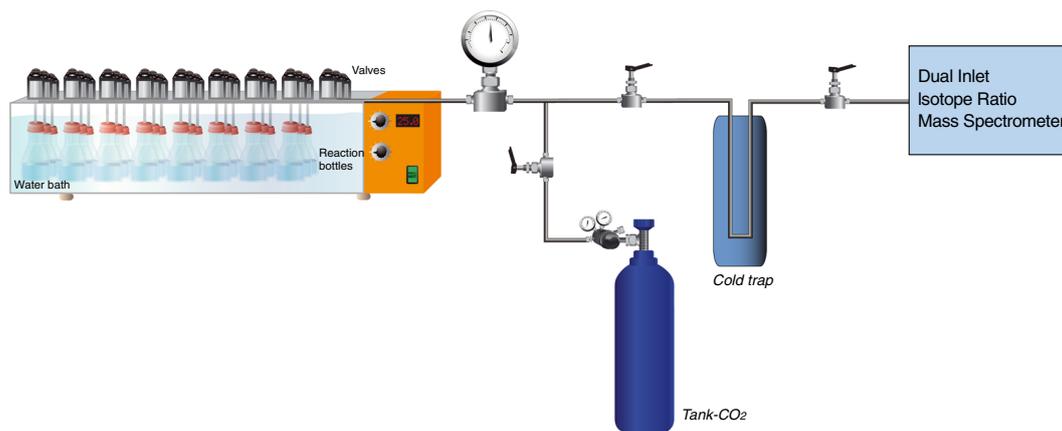


Figure 1. Schematics of an automated $\text{CO}_2\text{-H}_2\text{O}$ equilibration device, coupled with a Finnigan MAT 252 dual-inlet stable isotope mass spectrometer, at Korea University.

analyses of saline aqueous solutions, was better than $\pm 0.1\%$. The *oxygen isotope salt effect* in a saline aqueous solution ($\text{OISE}_{\text{solution}}$) at 25°C is reported by the permil fractionation ($1000\ln\alpha_{\text{solution-water}}$) in this study, where

$$\alpha_{\text{solution-water}} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{solution}}}{(^{18}\text{O}/^{16}\text{O})_{\text{water}}} = \frac{\delta^{18}\text{O}_{\text{CO}_2\text{-solution}} + 1000}{\delta^{18}\text{O}_{\text{CO}_2\text{-water}} + 1000}$$

Oxygen isotope equilibrium in the $\text{CO}_2\text{-solution}$ system ($\delta^{18}\text{O}_{\text{CO}_2\text{-solution}}^{\text{eq}}$) was assumed to have been achieved when $\delta^{18}\text{O}_{\text{CO}_2\text{-solution}}$ value became constant (typically $< 0.1\%$). The kinetics of oxygen isotope exchange in the various $\text{CO}_2\text{-solution}$ systems were also evaluated on the basis of their rate constant (k) or the half-time of oxygen isotope exchange ($t_{1/2} = \frac{\ln 2}{k}$). The value of k is defined as:

$$\frac{\delta^{18}\text{O}_{\text{CO}_2\text{-solution}}^t - \delta^{18}\text{O}_{\text{CO}_2\text{-solution}}^{\text{eq}}}{\delta^{18}\text{O}_{\text{CO}_2}^{\text{ini}} - \delta^{18}\text{O}_{\text{CO}_2\text{-solution}}^{\text{eq}}} = (1 - F) = e^{-kt}$$

where F is the fraction of isotope exchange, $\delta^{18}\text{O}_{\text{CO}_2\text{-solution}}^t$ is the oxygen isotope composition of solution-equilibrated CO_2 at time t , and $\delta^{18}\text{O}_{\text{CO}_2}^{\text{ini}}$ is the initial oxygen isotope composition of the CO_2 gas used for the $\text{CO}_2\text{-solution}$ equilibration. Note that $F=1$ at isotopic equilibrium and there has been no isotope exchange when $F=0$.

Initial oxygen isotope composition of CO_2 ($\delta^{18}\text{O}_{\text{CO}_2}^{\text{ini}}$)

The initial oxygen isotope composition of CO_2 for each $\text{CO}_2\text{-solution}$ equilibration experiment was determined by placing two or three glass reaction bottles in the $\text{CO}_2\text{-H}_2\text{O}$ equilibration device without a solution sample. Since there was no water phase with which the introduced CO_2 gas could have undergone oxygen isotope exchange, the oxygen isotope composition of the CO_2 measured from the empty reaction bottles basically represented the initial oxygen isotope composition of the CO_2 ($\delta^{18}\text{O}_{\text{CO}_2}^{\text{ini}}$ value). Appendix 1 (see Supporting Information) shows the exact positions of the empty glass reaction bottles for each trial in the automated $\text{CO}_2\text{-H}_2\text{O}$ equilibration device. Because the first tank- CO_2 was exhausted while the study was underway, the second tank- CO_2 was used for the remainder of the study. The

average initial oxygen isotope compositions ($\delta^{18}\text{O}_{\text{CO}_2}^{\text{ini}}$) of the two tank- CO_2 gases (Tank- $\text{CO}_2\text{-1}$ and Tank $\text{CO}_2\text{-2}$) were 16.4% and 14.0% , respectively.

RESULTS AND DISCUSSION

CO_2 equilibration time

The most important observation from Fig. 2 was that the $\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$ values, collected from a different trial, but at the same CO_2 equilibration time, were rather scattered and not uniform when the oxygen isotope equilibrium in the $\text{CO}_2\text{-H}_2\text{O}$ system (~ 4.4 h) was not established. In other words, the degree of $\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$ variability at any CO_2 equilibration time prior to oxygen isotope equilibrium in the $\text{CO}_2\text{-H}_2\text{O}$ system was significantly large. For example, the $\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$ values collected after 0.53 h of CO_2 equilibration varied from $+21.9\%$ to $+27.4\%$, whereas the $\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$ values determined after 11.65 h of CO_2 equilibration only ranged from $+30.1\%$ to 30.6% .

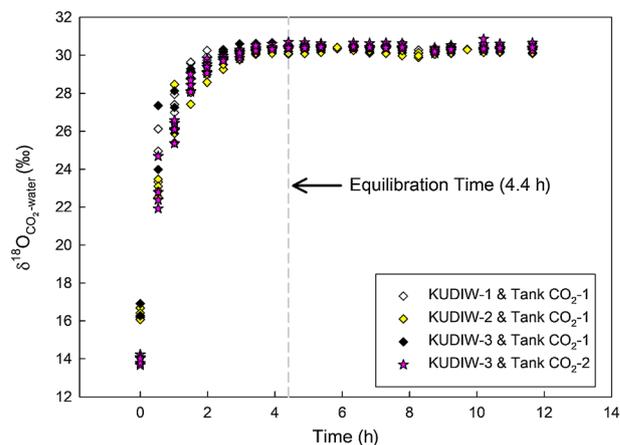


Figure 2. Changes in the oxygen isotope composition of water-equilibrated CO_2 as a function of CO_2 equilibration time under four different experimental conditions. Note that the oxygen isotope compositions are reported relative to the oxygen isotope composition of a laboratory standard CO_2 at Korea University.

The implication of this experimental observation was that the CO₂ equilibration time of oxygen isotope exchange in the CO₂-H₂O system must be carefully evaluated under each laboratory's experimental conditions. This basic practice is essential prior to a routine analysis of aqueous solution samples of any concentration in order to *precisely* determine the oxygen isotope compositions of aqueous solutions. Figure 2 clearly demonstrates that incomplete CO₂-H₂O equilibration significantly decreased the analytical *precision* of the CO₂-H₂O equilibration technique and thus reduced the reproducibility of the overall isotopic analysis, whether or not the oxygen isotope analysis of aqueous solutions was performed under identical experimental conditions. As a result, an evaluation of the CO₂-H₂O equilibration time under each laboratory's specific experimental conditions is a critical step for the *precise* oxygen isotope analysis of aqueous solutions when the CO₂-H₂O equilibration method is employed.

Figure 2 also shows how the oxygen isotope composition of water-equilibrated CO₂ ($\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$) changed as a function of CO₂ equilibration time when two isotopically distinct CO₂ gases were used for the CO₂-H₂O equilibration method. The difference in the initial oxygen isotope composition of the two tank-CO₂ gases was approximately +2.4‰. However, the time required for the attainment of oxygen isotope equilibrium in the CO₂-H₂O system was almost identical under our experimental conditions regardless of the initial oxygen isotope composition of CO₂ ($\delta^{18}\text{O}_{\text{CO}_2}^{\text{ini}}$). As the analytical reproducibility of a typical oxygen isotope analysis of a saline aqueous solution was approximately $\pm 0.1\%$ in this study, a minimum of 4.4 h appeared to be required for the establishment of the oxygen isotope equilibrium (a steady-state $\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$ value) in the CO₂-H₂O system under the experimental conditions employed in this study (Fig. 2).

Oxygen isotope salt effect (OISE)

The oxygen isotope salt effects ($1000\ln\alpha_{\text{solution-water}}$ or $\text{OISE}_{\text{solution}}$) determined in this study are listed in Table 2 along with experimental data published in other key studies.^[18–20] It was found that the $\delta^{18}\text{O}_{\text{CO}_2\text{-solution}}$ values from most saline aqueous solutions examined in this study were at or very near oxygen isotope equilibrium within the time frame of the routine CO₂-solution equilibration method. For example, the maximum equilibration time of our routine CO₂-solution equilibration was 11.65 h. However, the oxygen isotope equilibria had been established within 3.4 to 7.3 h for most saline aqueous solutions tested in this study regardless of their solution composition and concentration at 25 °C. As a result, the oxygen isotope salt effects of chloride as well as sulfate solutions were determined in this study. Overall, the oxygen isotope salt effects obtained in this study were consistent with the existing experimental data with regards to their direction and magnitude (Table 2).

Chloride solutions

No oxygen isotope salt effect was observed from NaCl solutions of up to 3.0 molal concentration under the experimental conditions tested in this study. In contrast, KCl solutions showed a positive effect, whereas a MgCl₂ solution and a CaCl₂ solution yielded a negative isotope salt effect. In particular, the measured oxygen isotope salt effect of a 0.5,

1.0, or 2.0 molal solution of KCl was 0.11‰, 0.24‰, or 0.36‰, respectively. Meanwhile, the oxygen isotope salt effect of a MgCl₂ solution varied from –0.50‰ to –1.14‰ and the isotope salt effect for a CaCl₂ solution ranged from –0.22‰ to –0.49‰ as a function of the ionic strength of the aqueous solution.

Sulfate solutions

Two sulfate solutions were examined in this study to assess their oxygen isotope salt effect when their concentration varied from 0.0 to 1.0 molal. The oxygen isotope salt effect was more significant in the case of a MgSO₄ solution than for a Na₂SO₄ solution (Table 2). For a 1.0 molal solution, the oxygen isotope salt effect was –1.12‰ for a MgSO₄ solution, but the effect was only –0.14‰ for a Na₂SO₄ solution. To the best of our knowledge, the oxygen isotope salt effect of a Na₂SO₄ solution has never been reported by using the CO₂-solution equilibration technique. However, it was not clear whether the oxygen isotope equilibria had been attained between CO₂ and the MgSO₄ solutions (see Trials 28–30 in Appendix 1, Supporting Information) because $\delta^{18}\text{O}_{\text{CO}_2\text{-MgSO}_4}$ values collected after 9 h of CO₂ equilibration were not still reproducible (>0.1‰).

Oxygen isotope ion effect (OIE_{ion})

Chloride solutions

A special effort was made in this study to empirically quantify the oxygen isotope effect of individual ions (e.g., Li⁺, Na⁺, Ca²⁺, Mg²⁺, and SO₄²⁻) in order to develop a simple, yet reliable, method for the prediction of the oxygen isotope salt effect in a 1.0 molal aqueous solution of any chemical composition. First, the oxygen isotope salt effects ($1000\ln\alpha_{\text{solution-water}}$ or $\text{OISE}_{\text{solution}}$) from 1.0 molal solutions in O'Neil and Truesdell^[18] as well as this study were used to *calculate* the oxygen isotope effect of individual cations or anions (OIE_{ion}). All the experimental data used for this empirical quantification are noted in Table 2. Second, for the sake of simplicity, the oxygen isotope effect of 1.0 molal Cl[–] ions (OIE_{Cl[–]}) was assigned as 1.00‰ in order to disentangle the oxygen isotope salt effect of 1.0 molal cations in a saline aqueous solution. It should be remembered that the oxygen isotope salt effect of a NaCl solution was 'nil' regardless of its concentration (see Table 2). Given this unique isotopic property of the NaCl solution and the assigned oxygen isotope effect of 1.00‰ for 1.0 molal Cl[–] (OIE_{Cl[–]}), the oxygen isotope effect of 1 molal Na⁺ (OIE_{Na⁺}) was determined to be –1.00‰ on the basis of the following approximations and calculations:

$$\begin{aligned} 1000\ln\alpha_{\text{NaCl-H}_2\text{O}} &= \text{OISE}_{\text{NaCl}} = \text{OIE}_{\text{Na}^+} + \text{OIE}_{\text{Cl}^-} = 0.00\text{‰} \\ \text{OIE}_{\text{Na}^+} &= \text{OISE}_{\text{NaCl}} - \text{OIE}_{\text{Cl}^-} = (0.00\text{‰}) - (1.00\text{‰}) \\ &= -1.00\text{‰} \end{aligned}$$

where $\text{OIE}_{\text{Cl}^-} = 1.00\text{‰}$.

Likewise, the oxygen isotope effects of other monovalent cations of 1.0 molal concentration were also calculated and these are listed in Table 3. For divalent and trivalent cations, the oxygen isotope effects of the ions were calculated by taking into account the number of moles of Cl[–] ions in the given solutions. For example, the calculated oxygen isotope effect of 1.0 molal Mg²⁺ was decoupled from the experimentally determined oxygen isotope salt effect of a 1.0 molal MgCl₂ solution ($1000\ln\alpha_{\text{MgCl}_2\text{-H}_2\text{O}} = -1.14\text{‰}$, see Table 2) as follows:

Table 2. Experimentally determined oxygen isotope salt effects at 25°C from previous and current studies

Solution	Conc. (molal)	Oxygen isotope salt effect (‰)			
		O'Neil and Truesdell ^[18]	Horita and Kendall ^[20]	This study* (experimental)	This study (estimation)
Chloride solutions					
NaCl	1.0	0.00 ^b	0.00	0.03 ± 0.02	−0.02
	3.0			0.00 ± 0.02	
	6.0	0.00			
LiCl	1.0	−0.10 ^b			−0.40
MgCl ₂	0.5	−0.12 ^a	−0.56 ^a	−0.52 ± 0.02, −0.50 ± 0.02	−1.01
	1.0	−0.71 ^a	−1.11	−1.14 ^b ± 0.02	
	2.0	−1.80			
	3.0	−3.00			
	3.5	−3.65			
	4.0	−4.50			
CaCl ₂	0.5	−0.20 ^a	−0.23 ^a	−0.22 ± 0.02, −0.23 ± 0.04	−0.15
	1.0	−0.41 ^a	−0.45	−0.49 ^b ± 0.03	
	4.0	−1.63			
CdCl ₂	1.0	−0.28 ^{a,b}			−0.27
	4.0	−1.10			
AlCl ₃	1.0	−3.01 ^b			−3.13
	2.0	−6.30			
	3.0	−9.05			
KCl	0.5	0.14 ^a	0.08 ^a	0.11 ± 0.02	0.26
	1.0	0.28 ^a	0.16	0.24 ^b ± 0.02	
	2.0	0.56		0.36 ± 0.03	
CsCl	1.0	0.48 ^{a,b}			0.40
	5.0	1.13			
	8.0	1.62			
Sulfate solutions					
Na ₂ SO ₄	0.5			−0.09 ± 0.02	−0.18
	1.0			−0.14 ^b ± 0.04	
MgSO ₄	0.5	−0.67 ^a	−0.52 ^a	−0.57 ± 0.02, −0.61 ± 0.06	−1.15
	1.0	−1.05	−1.04	−1.12 ^b ± 0.15	
	2.0	−1.82			
Al ₂ (SO ₄) ₃	1.0	−6.19 ^b			−6.67

Conc. = Concentration.
 *Standard error ($s_e = \sigma_p / \sqrt{n}$) was calculated based on the propagated standard deviation (σ_p) and the corresponding number of isotopic analyses (n) for a given solution.
^aDenotes an estimated value from the same study, but different concentrations.
^bDenotes a value used to calculate the oxygen isotope effect of individual ions.

$$1000\ln\alpha_{\text{MgCl}_2-\text{H}_2\text{O}} = \text{OISE}_{\text{MgCl}_2} = \text{OIE}_{\text{Mg}^{2+}} + 2\text{OIE}_{\text{Cl}^-} = -1.14\text{‰}$$

$$\text{OIE}_{\text{Mg}^{2+}} = \text{OISE}_{\text{MgCl}_2} - 2\text{OIE}_{\text{Cl}^-} = (-1.14\text{‰}) - 2 \times (1.00\text{‰}) = -3.14\text{‰}$$

where $\text{OIE}_{\text{Cl}^-} = 1.00\text{‰}$ by default.

Table 3 summarizes the calculated oxygen isotope effects of mono-, di-, and trivalent cations, which varied from -0.52‰ for Cs^+ to -6.01‰ for Al^{3+} .

Sulfate solutions

As a first step, the oxygen isotope effect of 1.0 molal SO_4^{2-} was calculated based on the same approximations used for the chloride solutions in the previous section. Given that the experimentally determined oxygen isotope salt effect of a 1.0 molal Na_2SO_4 solution is -0.14‰ (Table 2) and the

pre-assigned oxygen isotope effect for 1.0 molal Na^+ (OIE_{Na^+}) is -1.00‰ , a value of 1.86‰ was obtained for the oxygen isotope effect of 1.0 molal SO_4^{2-} ($\text{OIE}_{\text{SO}_4^{2-}}$). Subsequently, by assigning 1.86‰ as an oxygen isotope effect of 1.0 molal SO_4^{2-} , the oxygen isotope effect of Mg^{2+} as well as that of Al^{3+} could also be calculated based on the experimentally determined oxygen isotope salt effects indicated in Table 2.^[18–20] The calculated oxygen isotope effects for 1.0 molal Mg^{2+} and 1.0 molal Al^{3+} were -2.98‰ and -5.89‰ , respectively.

Estimation of the oxygen isotope salt effect (OISE)

It should be noted that the oxygen isotope effect of 1.0 molal Mg^{2+} is -3.14‰ when the effect is calculated on the basis of the oxygen isotope salt effect of a 1.0 molal MgCl_2 solution. The same oxygen isotope effect, however, becomes -2.98‰ when the calculation is made based on the oxygen isotope salt

Table 3. Calculated oxygen isotope effects of mono-, di-, and trivalent ions and other physiochemical parameters

Solution	Conc. (molal)	Anion/Cation*	Cation	Cal. Ion Effect (%)	Ionic Potential	E.N.	D.-H.	Anion	Cal. Ion Effect (%)
Chloride solutions									
NaCl	1.0	1	Na ⁺	-1.00	0.98	0.93	4	Cl ⁻	1.00 ^a
LiCl	1.0	1	Li ⁺	-1.10	1.32	0.98	6	Cl ⁻	1.00 ^a
MgCl ₂	1.0	2	Mg ²⁺	-3.14	2.78	1.31	8	Cl ⁻	1.00 ^a
CaCl ₂	1.0	2	Ca ²⁺	-2.49	2.00	1.00	6	Cl ⁻	1.00 ^a
CdCl ₂	1.0	2	Cd ²⁺	-2.28	2.11	1.69	5	Cl ⁻	1.00 ^a
AlCl ₃	1.0	3	Al ³⁺	-6.01	5.61	1.61	9	Cl ⁻	1.00 ^a
KCl	1.0	1	K ⁺	-0.76	0.72	0.82	3	Cl ⁻	1.00 ^a
CsCl	1.0	1	Cs ⁺	-0.52	0.60	0.79	2.5	Cl ⁻	1.00 ^a
Sulfate solutions									
Na ₂ SO ₄	1.0	0.5	Na ⁺	-1.00 ^b	0.98	0.93	4	SO ₄ ²⁻	1.86
MgSO ₄	1.0	1	Mg ²⁺	-2.98	2.78	1.31	8	SO ₄ ²⁻	1.86
Al ₂ (SO ₄) ₃	1.0	1.5	Al ³⁺	-5.89	5.61	1.61	9	SO ₄ ²⁻	1.86

Conc. = Concentration; E.N. = Electronegativity; D.-H. = Debye-Hückel ion size parameter; Cal. Ion Effect = Calculated oxygen isotope effect of ions.

*A ratio of the number of moles of anions to the number of moles of cations.

^aDenotes a pre-assigned value (See the text).

^bDenotes a calculated value on the basis of a 1.0 molal NaCl solution.

effect of a 1.0 molal MgSO₄ solution (see Table 3). Similarly, the oxygen isotope effect of 1.0 molal Al³⁺ is -6.01‰ when employing the chloride solution-based calculations, whereas the same oxygen isotope effect becomes -5.89‰ when the sulfate solution-based calculations are used. Nonetheless, the differences in the oxygen isotope effect of cations (0.16‰ for Mg²⁺ and 0.12‰ for Al³⁺) between the two types of calculations are not significant, considering the analytical error associated with the measurement of the oxygen isotope salt effect and the discrepancy among the existing experimental data used for these calculations (Table 2). In this study, the chloride solution-based oxygen isotope effects of cations were used to *estimate* the oxygen isotope salt effects of saline aqueous solutions.

Relation between *calculated* oxygen isotope ion effect and ionic potential (Ip)

An interesting feature of the *calculated* oxygen isotope effects of cations shown in Table 3 is that the absolute value of each ion's *calculated* oxygen isotope effect was highly comparable in size with the ionic potential of the corresponding cation. More specifically, the *calculated* oxygen isotope effects of cations are negatively proportional to the corresponding ionic potentials (Fig. 3(A)), where the ionic potential is defined as the ratio of the electric charge to the radius of an ion.^[21] A strong correlation between the *calculated* oxygen isotope ion effect and ionic potential was not unexpected because (1) the oxygen isotope salt effect is believed to be directly related to the bonding between water molecules and dissolved ions in the solution,^[18] and (2) the bond of inner-sphere complexes, such as calcium aquocomplexes, tends to be stronger as the ionic potential of a cation for a given ligand (or of a ligand for a given cation) increases. O'Neil and Truesdell^[18] considered the oxygen isotope salt effects as an individual electrolyte's 'structure-making' or 'structure-breaking' capacity, which again can be related to the ionic potentials of free ions in the electrolyte. Furthermore, the authors^[18]

proposed that water molecules bonded to a structure-making cation would have a high δ¹⁸O value relative to those bonded to other water molecules, elaborating the origin of the oxygen isotope salt effect. On the basis of their experimental results, they further hypothesized that approximately 54% of water molecules in a 5.0 molal MgCl₂ solution were bonded to Mg²⁺.

Electronegativities^[21] and Debye-Hückel ion size parameters^[21] of several cations also correlated with the *calculated* oxygen isotope effects of cations predicted in this study (Figs. 3(B) and 3(C)). However, the strongest correlation existed between the ionic potential and the *calculated* oxygen isotope effect of cations. Accordingly, a linear regression derived from the correlation between these two variables was used to *estimate* the oxygen isotope effects of cations that were not experimentally determined in this study.

Estimation of the oxygen isotope salt effect

The oxygen isotope ion effects of 1.0 molal Cu²⁺ and 1.0 molal Zn²⁺ were *estimated* on the basis of the linear regression relationship proposed in the previous section (see Fig. 3(A) and Table 4). Furthermore, the oxygen isotope effects of saline aqueous solutions, such as CuCl₂, CuSO₄, and ZnSO₄, which were not examined in the previous key studies,^[18,19] were *estimated* by using the *calculated* oxygen isotope effects of ions (Table 3). For example, in the case of a 1.0 molal CuCl₂ solution, the *estimated* oxygen isotope salt effect is -0.96‰, as shown in the following two equations:

$$\begin{aligned}
 1000\ln\alpha_{\text{CuCl}_2-\text{H}_2\text{O}} &= \text{OISE}_{\text{CuCl}_2} \\
 \text{OISE}_{\text{CuCl}_2} &= \text{OIE}_{\text{Cu}^{2+}} + 2\text{OIE}_{\text{Cl}^-} \\
 &= (-2.96\text{‰}) + 2 \times (1.00\text{‰}) \\
 &= -0.96\text{‰}
 \end{aligned}$$

Similarly, the oxygen isotope salt effects of a 1.0 molal CuSO₄ and a 1.0 molal ZnSO₄ solution are *estimated* to be -1.10‰ and -1.06‰, respectively. Table 4 shows that these *estimated* oxygen isotope salt effects, obtained using the

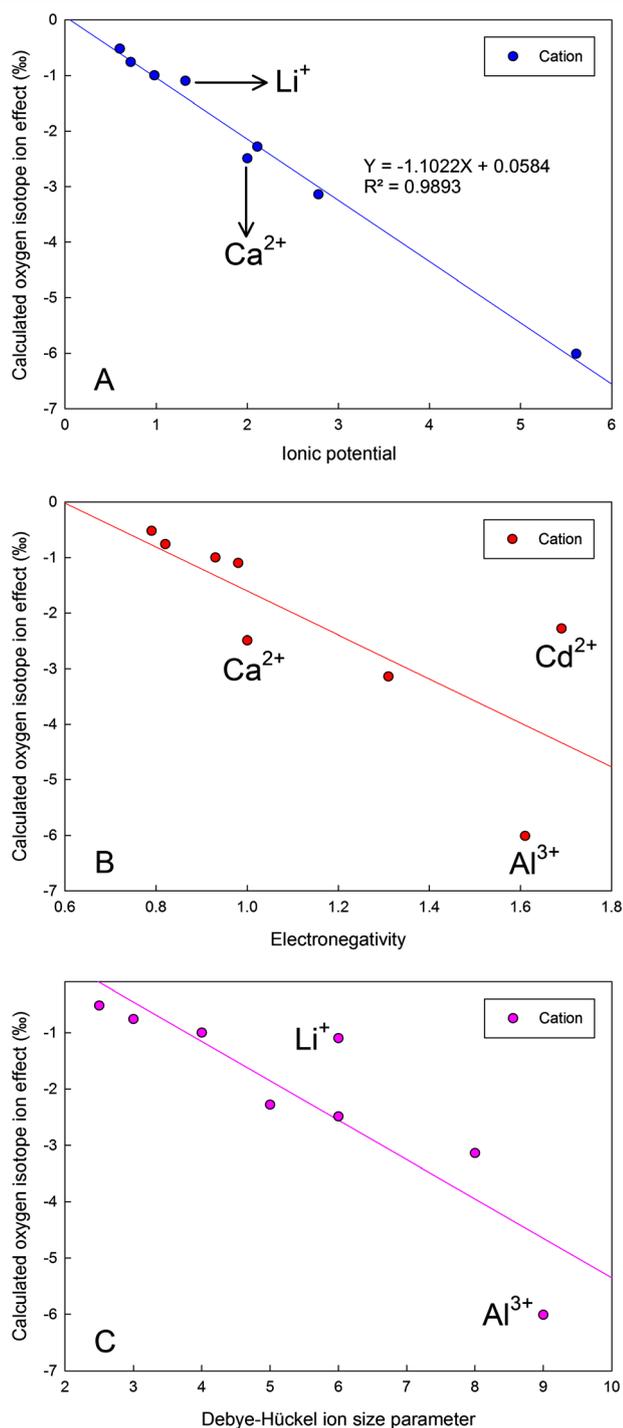


Figure 3. Relationship between calculated oxygen isotope ion effect and (A) ionic potential, (B) electronegativity, and (C) Debye-Hückel ion size parameter for cations listed in Table 3.

empirical prediction method proposed in this study, are more or less consistent with the best estimates from existing experimental observations,^(e.g.,¹²²) thus supporting the reliability of using the proposed method for predicting the oxygen isotope salt effects of saline aqueous solutions.

This study clearly illustrates that ionic potentials of cations are highly correlated with the oxygen isotope effects of cations. Furthermore, it was demonstrated that our proposed prediction method could be used to *estimate* the oxygen

isotope salt effects of any saline aqueous solutions. Although all the examples shown here were chosen to demonstrate the estimation of the oxygen isotope salt effects of 1.0 molal aqueous solutions, the proposed method can be expanded to any aqueous solutions of lower or higher concentrations, such as 0.5 or 2.0 molal solutions, as long as reliable experimental data for a given concentration is available.

Kinetics of oxygen isotope exchange

Effect of solution composition: chloride solutions

The rates of oxygen isotope exchange between CO_2 and four different types of 1.0 molal chloride solutions were experimentally determined at 25 °C. The oxygen isotope exchange rate in the CO_2 -water system, shown by a gray dashed line in Fig. 4, was derived using $\delta^{18}\text{O}_{\text{CO}_2\text{-water}}$ values determined from 14 individual trials (Trials 1–14 in Appendix 1, see Supporting Information). As a result, these kinetic data from the 14-time repeated experiments were more scattered than those based on a single experiment for chloride solutions. Nevertheless, the oxygen isotope exchange rate in the CO_2 -water system was clearly faster than those in any other systems containing 1.0 molal chloride solutions (Fig. 4(A)). Another important observation made in this study was that there was a certain order to the oxygen isotope exchange kinetics among the four CO_2 -chloride solution systems examined: $\text{CaCl}_2 > \text{NaCl} > \text{MgCl}_2 > \text{KCl}$. The half-time of isotope exchange ($t_{1/2}$) of the 1.0 molal KCl solution was 0.61 h while that of the 1.0 molal CaCl_2 solution was 0.99 h (Table 5). It appears that there was no direct relationship between the order of the reaction kinetics and the magnitude of the oxygen isotope salt effect among the chloride solutions examined in this study. Additional experimental tests and theoretical considerations are required to elucidate these experimental observations.

Effect of solution composition: sulfate solutions

The experimentally determined oxygen isotope kinetic data collected from CO_2 equilibration experiments using two types of sulfate solutions were more scattered than those obtained from the chloride solutions of the same concentration (Fig. 4(B)). In particular, a time-series analysis of $\delta^{18}\text{O}_{\text{CO}_2\text{-MgSO}_4}$ values collected from the CO_2 equilibration experiments were not as reproducible ($<0.1\%$) as those from Na_2SO_4 as well as those from the chloride solutions (Appendix 1, see Supporting Information). However, the rate of oxygen isotope exchange between CO_2 and 1.0 molal Na_2SO_4 or 1.0 molal MgSO_4 solution was obviously slower than that of the CO_2 -water system. More specifically, the half-times of oxygen isotope exchange ($t_{1/2}$) were 0.98 h for the 1.0 molal Na_2SO_4 solution and 1.39 h for the 1.0 molal MgSO_4 solution (Table 5).

Effect of solution concentration

Figure 5 illustrates that the rates of oxygen isotope exchange in the CO_2 -solution system were directly proportional to the concentrations of the saline aqueous solutions. For example, the half-time ($t_{1/2}$) of oxygen isotope exchange for a CaCl_2 solution increased from 0.64 to 0.99 h as the concentration of the CaCl_2 solution changed from 0.5 to 1.0 molal. Therefore, our experimental data clearly demonstrated that a longer

Table 4. Comparison of the estimated and the measured oxygen isotope salt effects of Cu- or Zn-bearing aqueous solutions

Ion/solution	Conc. (molal)	Ionic potential	Estimated effect* (%)	Measured effect** (%)
Cu ²⁺	1.0	2.74	-2.96	n/a
Zn ²⁺	1.0	2.70	-2.92	n/a
CuCl ₂	1.0	n/a	-0.96	-1.20
CuSO ₄	1.0	n/a	-1.10	-1.55 ^a
ZnSO ₄	1.0	n/a	-1.06	-1.00 ^a

n/a = not applicable.

*An estimated oxygen isotope effect of cations or an estimated oxygen isotope salt effect from this study.

**An experimentally determined oxygen isotope salt effect. Taken from Appendix in Horita *et al.*^[19]

^aDenotes an estimated value based on experimentally determined oxygen isotope salt effects from other concentrations.

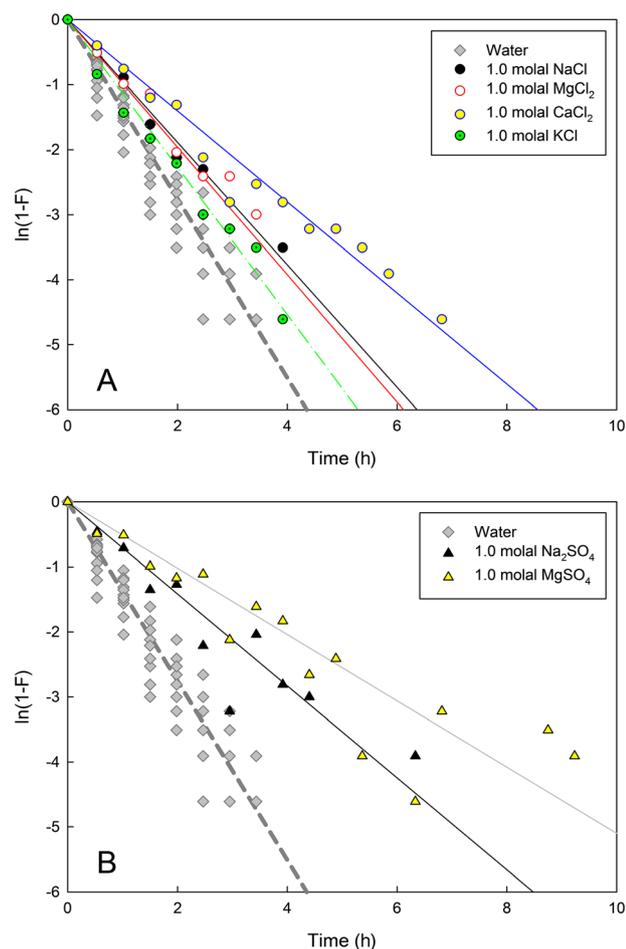


Figure 4. Rates of oxygen isotope exchange between CO₂ and (A) 1.0 molal chloride solutions (CaCl₂, NaCl, MgCl₂, and KCl) and (B) 1.0 molal sulfate solutions (Na₂SO₄ and MgSO₄) at 25 °C.

CO₂ equilibration time was required to establish oxygen isotope equilibrium between CO₂ and a saline aqueous solution as the solution concentration increased. However, the rate of change in the half-time of the oxygen isotope exchange was not uniform as a function of solution concentration among the saline aqueous solutions examined in this study.

Another notable observation was that the oxygen isotope exchange rate for a 0.5 molal KCl solution was faster than that for water. The half-time of oxygen isotope exchange ($t_{1/2}$) was

Table 5. Rate constants (k) and half-times ($t_{1/2}$) of oxygen isotope exchange for the CO₂-solution systems

Solution	Conc. (molal)	Oxygen isotope exchange kinetics	
		k (h ⁻¹)	$t_{1/2}$ (h)
Water		1.38	0.50
Chloride solutions			
NaCl	1.0	0.94	0.74
	3.0	0.72	0.96
MgCl ₂	0.5	1.15	0.60
	1.0	0.98	0.71
CaCl ₂	0.5	1.08	0.64
	1.0	0.70	0.99
KCl	0.5	1.56	0.44
	1.0	1.13	0.61
	2.0	1.04	0.67
Sulfate solutions			
Na ₂ SO ₄	0.5	1.02	0.68
	1.0	0.71	0.98
MgSO ₄	0.5	0.93	0.75
	1.0	0.50	1.39

Conc. = Concentration.

0.44 h for the 0.5 molal KCl solution whereas that for water was 0.50 h. It should be noted that KCl is the only electrolyte that shows a positive oxygen isotope salt effect in this study and thus the 'structure-breaking' nature of KCl might increase the oxygen isotope exchange kinetic in the CO₂-solution system.

Guidelines for accurate and precise $\delta^{18}\text{O}$ measurement of saline aqueous solutions

First, CO₂ equilibration time with water or a laboratory working standard has to be identified under each laboratory's routine experimental conditions. This is a critical step to increase the precision of the oxygen isotope analysis of aqueous solution samples when the classic CO₂-H₂O equilibration method is employed because most stable isotope laboratories have unique laboratory settings and environments. Re-evaluation of a predefined CO₂ equilibration time is also essential when

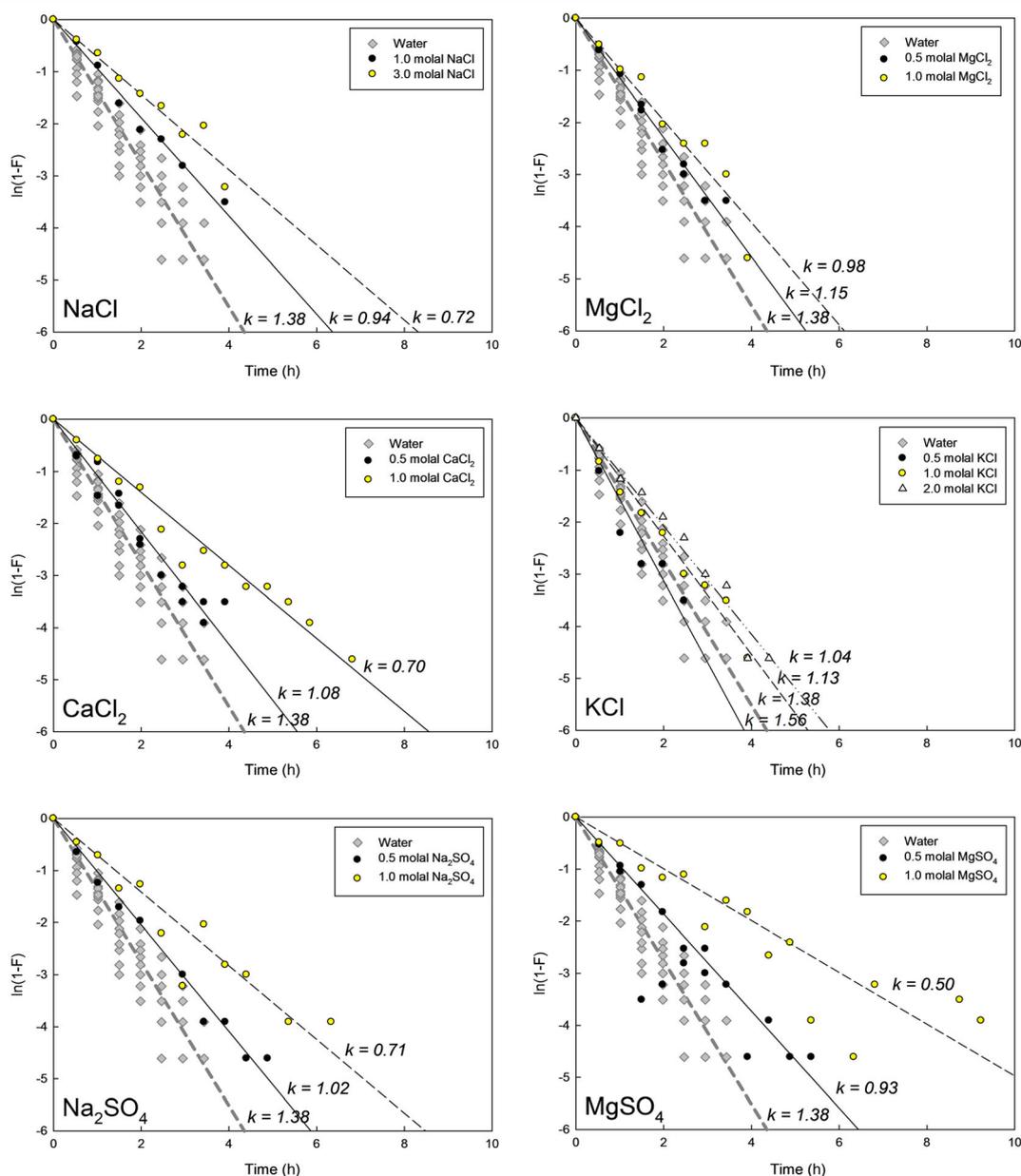


Figure 5. Oxygen isotope exchange kinetics in various CO_2 -solution systems as a function of solution concentration at 25 °C.

any modifications of the existing experimental protocols or settings are expected. Second, the use of pure CO_2 gas whose oxygen isotope composition is extremely higher or lower than the typical $\delta^{18}\text{O}$ range of natural water is not recommended. Since the oxygen isotope fractionation between CO_2 and water is 1.0412 at 25 °C,^[23] it would be ideal to use pure CO_2 gas whose oxygen isotope composition is approximately 40‰ higher than the oxygen isotope compositions of each individual laboratory's typical aqueous solution samples, particularly when the CO_2 - H_2O equilibration is carried out at 25 °C. This practice will increase the precision of the overall oxygen isotope analysis. Third, the CO_2 equilibration time for saline aqueous solutions has to be determined (or at least estimated) under each laboratory's specific experimental conditions. Our experimental data demonstrated that a longer

CO_2 equilibration time is required for most saline aqueous solutions (Figs. 4 and 5). The kinetic data presented in Table 5 will provide basic guidelines for the determination, or at least estimation, of the CO_2 equilibration times for most common chloride and sulfate solutions of geological interest. Finally, the oxygen isotope salt effect must be taken into account when the $\delta^{18}\text{O}$ value of a saline aqueous solution is ultimately reported (isotope activity ratio vs. isotope concentration ratio).^[19,20] The direction and the magnitude of the oxygen isotope salt effect are basically determined by (1) the reaction temperature of CO_2 -solution equilibration and (2) the solution chemistry of the aqueous solution. Published^[16–18,20,24] and current experimental observations as well as the proposed prediction method described in this study are useful resources for the correction of the oxygen isotope salt effect.

CONCLUSIONS

The effects of dissolved ions on the equilibrium and kinetics of oxygen isotope exchange in various CO₂-solution systems were examined in order to provide practical guidelines for the accurate and precise oxygen isotope analysis of saline aqueous solutions when the classic CO₂-H₂O equilibration method is employed. Here we reported the experimentally determined oxygen isotope salt effects and the kinetics of oxygen isotope exchange between CO₂ and KCl, NaCl, CaCl₂, MgCl₂, Na₂SO₄, and MgSO₄ solutions at 25 °C. Furthermore, an empirical prediction method, based on the ionic potential of a cation and the existing experimental data, was developed in order to estimate the oxygen isotope salt effect of any chloride or sulfate solution of 1.0 molal concentration, especially for saline aqueous solutions without any existing experimental data.

Finally, four guidelines were proposed for the accurate and precise δ¹⁸O analysis of high (e.g., seawater or hypersaline lake water) or low ionic strength solutions (e.g., rain or glaciers). We recommend that each stable isotope laboratory should optimize its own analytical protocols based on its experimental environments prior to the routine isotopic analysis of aqueous solutions.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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