Measurement of the hydrogen and oxygen isotopic compositions of concentrated chloride brines and brines from fluid inclusions in halite

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ABSTRACT


Solutions of 1-5 m NaCl, KCl, CaCl₂ and MgCl₂, and synthetic brines were analyzed for hydrogen and oxygen isotopic compositions by vacuum distillation-microequilibration techniques. No effect on the hydrogen isotopic composition was observed for any of the solutions within the precision of the technique of ± 0.1% determined from analyses of distilled water. Oxygen isotopic compositions of solutions measured by vacuum distillation-microequilibration indicate that oxygen isotopes are not fractionated during analysis in NaCl, KCl and CaCl₂ solutions. Vacuum distillation-microequilibration analyses of MgCl₂ solutions show depletions in δ¹⁸O relative to pure water that can be related to the concentration of Mg²⁺ in the solution. The greatest depletion in δ¹⁸O occurs in the 4 m MgCl₂ solutions which have δ¹⁸O-values 6% lower than that measured for pure water. Corrections based on the measurement of the δ¹⁸O-values of the pure MgCl₂ solutions can also be applied to mixed chloride brines. Both melting and crushing of halite grown in solutions of known isotopic composition followed by microequilibration to determine the stable isotopic composition of fluid inclusions give results within the precision determined from analyses of distilled water.

1. Introduction

Many of the techniques used for analysis of the isotopic composition of brines are slight modifications of the techniques used to analyze dilute waters. The validity of these techniques commonly used to determine the hydrogen and oxygen isotopic compositions of brines have been questioned because of the effect of cations on the structure of water (Sofer and Gat, 1972, 1975; Stewart and Friedman, 1975; Iorita and Matsuo, 1986; Iorita and Gat, 1988; Horita, 1989). Brines of a few millilitres are usually analyzed for oxygen isotopic ratios by CO₂-brine equilibration (Epstein and Mayeda, 1953) and corrections are made for the effect of various ions on the activities of the isotopic species (Sofer and Gat, 1972). Hydrogen isotope ratios are usually determined by vacuum distillation of the water from 1-5 µl of brine and decomposition of the water on hot uranium (Bigeleisen et al., 1952). Smaller brine samples, of < 1 ml, can be analyzed by vacuum distillation of the pure water from the brine, followed by CO₂-H₂O microequilibration and decomposition of the water for simultaneous hydrogen and oxygen isotope ratio determinations although the chemical compositions of the brines may affect the results (Kishima and Sakai, 1980).

Since the pioneering work of Taube (1954) on the effect of ions in solution on the ¹⁸O/¹⁶O ratio of CO₂ in equilibrium with chloride and other electrolyte solutions, many studies have
demonstrated that water molecules are selectively incorporated into the hydration spheres of ions in solution resulting in a change in the activity of $^{18}O$ and D relative to $^{16}O$ and H in the remaining water (e.g., Sofer and Gat, 1972, 1975; Stewart and Friedman, 1975). Therefore, the stable isotope ratios of hydrogen and oxygen in brines by gas-liquid equilibration usually reflect the isotope activity ratios, and these ratios are difficult to compare to the more informative isotope concentration ratios measured by water decomposition. Various correction factors that depend on the type and concentration of ions in solution have been derived to adjust hydrogen and oxygen isotope activity ratios to isotope concentrations ratios for chloride brines (Sofer and Gat, 1972, 1975; Stewart and Friedman, 1975). However, for very small samples of brine such as those obtained from fluid inclusions in minerals, it is difficult to measure the concentrations of ions required to correct isotope values from activity ratios to concentration ratios. Also, these correction factors, particularly in concentrated Mg- or Ca-chloride solutions, are not well defined as demonstrated by conflicting hydrogen correction values obtained by different studies (e.g., Sofer and Gat, 1975; Stewart and Friedman, 1975). To avoid corrections for ions in solution and allow analysis of hydrogen and oxygen isotope ratios on the same small sample of brine, the water can be removed from the brine by vacuum distillation and the pure water analyzed by $^{18}O$-H$_2$O equilibration for oxygen isotope concentration ratios and decomposition on hot uranium ($750^\circ$C) for hydrogen isotope concentration ratios (Kishima and Sakai, 1980). However, based on limited data, Horita and Matsuo (1986) and Horita (1989) suggest that significant fractionations of hydrogen and oxygen isotopes occur during vacuum distillation of brines due to precipitation of hydrated phases or hydroxides. They have proposed alternative analytical procedures that require large volumes of brine and complex distillation procedures that are not only labo-

rious, but cannot be applied to small samples.

The purpose of this study is to present a technique that allows simple and accurate measurement of the stable isotopic compositions of water from chloride brines of even the limited volume in fluid inclusions. Fractionation corrections are not necessary using this technique except for Mg-rich brines which require a minimal correction for oxygen isotope ratios only. This lack of corrections needed to determine directly the concentration ratios of hydrogen and oxygen isotopes from chloride brines using this technique suggests that extraction and vacuum distillation of water from fluid inclusions in chloride minerals will not involve significant isotopic fractionations.

2. Methods, techniques, and material studied

2.1. Hydrogen isotope analyses

The hydrogen isotopic composition of small samples of water and brine are routinely determined using vacuum distillation followed by quantitative decomposition of the water over hot uranium (Fig. 1) as described by Bigeleisen et al. (1952). Small samples (1–5 µl) of water or brine are introduced into the vacuum line by injection with a micro-syringe through a rubber septum in the injection port. All the water is distilled from the brine into a cold trap at $-196^\circ$C by heating the injection port to $250^\circ$C for 3–5 min. with a heat gun. Small amounts of non-condensible gasses remaining after vacuum distillation, which may represent dissolved atmospheric gasses or leakage through the injection port, are evacuated from the system. The sample is then exposed to uranium at $750^\circ$C and the isotopic composition of the resultant H$_2$ measured on the mass spectrometer. Replicate analyses of pure water standards indicate a reproducibility of $\delta$D-values of ±1‰ using this vacuum distillation method.
2.2. Hydrogen and oxygen isotope analyses by microequilibration

Determination of the hydrogen and oxygen isotopic composition of small samples (< 1 ml) of water or brine is accomplished using the vacuum distillation-microequilibration technique of Kishima and Sakai (1980). A brine or water sample of 1–5 µl is distilled in vacuum using the same procedure as for hydrogen isotope analysis described in Section 2.1 and the resulting pure water is frozen into a small volume (1–2 ml) equilibration vessel (Fig. 1) along with a known quantity (60–70 pmol) of pure CO₂ of known isotopic composition. The equilibration vessels are then immersed in a water bath regulated to 25 ± 0.1°C for 48 hr.

After equilibration, the CO₂ and the water are separated by differential freezing using a dry-ice slush (−78°C). Both the quantity and stable isotopic composition of the CO₂ are measured. The remaining water is quantitatively decomposed to H₂ by reaction with hot uranium to obtain its hydrogen isotopic composition. The amount of hydrogen gas produced, which represents the quantity of water in the equilibration vessels, is measured manometrically (Fig. 1).

\[ \delta^{18}O_{\text{H}_2O} = \delta^{18}O_{\text{H}_2O}^{f} + (\delta^{18}O_{\text{CO}_2} / 2n_{\text{CO}_2}) \]

where \( \delta^{f} \) and \( \delta^{i} \) represent the isotopic compositions of the H₂O and CO₂ before and after equilibration, respectively; and \( n \) represents the number of moles of H₂O and CO₂. \( \delta^{18}O_{\text{H}_2O} \) is calculated from \( \delta^{18}O_{\text{CO}_2} \) assuming equilibrium fractionation at 25°C, and a CO₂–H₂O fractionation factor of 1.0412 (O'Neil et al., 1975). The effect of both water vapour and liquid water, which are present in the equilibration vessels, on the calculated \( \delta^{18}O \) of the water was found...
to be small (\(<0.1\%_\text{oo}\)). Because this effect is small compared to the error in the method, it was omitted from the calculation of the $\delta^{18}\text{O}$-value of the water.

Samples that differ by > 1 $\mu$mol in the amount of, or by 0.5\%\text{oo} in the $\delta^{13}\text{C}$-value of, the CO$_2$ introduced and extracted from the sample vessels are discarded. Differences in the amount or carbon isotopic composition of the CO$_2$ before and after equilibration result from leakage of CO$_2$ during equilibration or loss and fractionation of CO$_2$ during the loading or extraction process. Samples that have a large amount of non-condensible gasses at any stage during the loading or extraction procedure are also discarded, as again leakage is suspected.

The reproducibility of values using this method was determined from repeat analyses of NBS standards and an in-house distilled water standard, designated UofS (for University of Saskatchewan) Standard, which has $\delta$D- and $\delta^{18}\text{O}$-values of $-136$ and $-16.7\%_\text{oo}$, respectively. Repeat analyses of UofS Standard by vacuum distillation–microequilibration indicate reproducibilities for the method of $\pm 5\%_\text{oo}$ for hydrogen and $\pm 1\%_\text{oo}$ for oxygen (Fig. 2).

A modification of the microequilibration technique of Kishima and Sakai (1980) resulted in a reduction in the number of samples lost due to leakage of the microequilibration vessels. Water produced from vacuum distillation of brines or extracted from fluid inclusions in halite was frozen into a length of 4-mm-ID Pyrex$^\text{®}$ tubing which serves as a microequilibration vessel. A measured quantity of CO$_2$ of known isotopic composition is frozen into the tubing, and the tube sealed at an appropriate length (~8 cm) with a torch. Extraction consists of breaking the sealed tube in vacuum and separation of the CO$_2$ and water for analysis. This modification produces similar precision of $\delta$D- and $\delta^{18}\text{O}$-values (Fig. 2), but is simpler, faster, and more reliable than microequilibration using the reusable microequilibration vessels.

**Fig. 2. Differences between the hydrogen and oxygen isotopic compositions of UofS (University of Saskatchewan) Standard water analyzed by standard vacuum distillation for hydrogen and CO$_2$–H$_2$O equilibration for oxygen and those obtained by the vacuum distillation–microequilibration technique. $\delta$D and $\delta^{18}\text{O}$ are the $\delta$D$_\text{known} - \delta$D$_\text{microequilibration}$ and $\delta^{18}\text{O}_{known} - \delta^{18}\text{O}_{microequilibration}$, respectively, and the cross represents the values determined from repeat analyses using vacuum distillation for hydrogen isotope analysis and CO$_2$–H$_2$O equilibration for oxygen isotope analysis. Errors for the vacuum distillation–microequilibration technique as indicated by UofS Standard are $\pm 5\%_\text{oo}$ for $\delta$D-values and $\pm 1\%_\text{oo}$ for $\delta^{18}\text{O}$-values. Circles represent analyses using reusable valved microequilibration vessels and triangles represent analyses using sealed glass tubes.**

### 2.3. Fluid inclusions in halite

Brines trapped as fluid inclusions in halite are extracted by melting or crushing the halite in vacuum. In the melting method, ~0.5 g of clean halite is placed into a molybdenum boat and preheated at 110°C for 1 hr. in vacuum to drive off any adherent water. The temperature of the molybdenum boat is then raised slowly to ~800°C using an induction furnace to melt the halite and release the water from fluid inclusions (Knauth and Beeunas, 1986). In the crushing method, ~0.5 g of clean halite is placed in a stainless-steel pipe, which is closed at one end and connected to the vacuum system at the other. After preheating for 1 hr. at 110°C to remove any adherent water, the halite is crushed by squeezing the pipe in a vice. The pipe is reconnected to the vacuum line and heated to 350°C for ~30 min. to collect the water liberated by crushing (O’Neil et al., 1986). The water collected using both these methods is analyzed for its stable isotopic composition.
composition using the microequilibration technique described in Section 2.2.

2.4. Preparation and analysis of materials

Solutions of 1–5 m NaCl, KCl, CaCl₂ and MgCl₂ were prepared by dissolving appropriate quantities of anhydrous reagent grade MgCl₂ (1–3 wt.
% H₂O), and anhydrous analytical grade NaCl, KCl and CaCl₂ in water of known isotopic composition (Table I). Anhydrous MgCl₂ and CaCl₂ react exothermically when mixed with water. To minimize changes in the isotopic composition of the solutions due to evaporation caused by this reaction, the mixing flasks were immersed in an ice–salt–water bath.

In addition to these solutions, artificial brines were prepared. These brines have chemical compositions similar to brines derived from the evaporation of seawater to halite precipitation, sylvite precipitation (McCaffery et al., 1987), and carnallite precipitation (Braitsch, 1962). A brine chemically similar to brines encountered in potash mines in Saskatchewan was also prepared (Wittrup and Kyser, 1990) (Table II).

Halite was precipitated from a pure NaCl supersaturated solution by lowering the temperature of the solution from 80° to 25°C over a period of 3 days. In addition, samples of halite and brine were collected from a natural brine pool at the PCS Rocanville potash mine in Saskatchewan (Table II). Microscopic examination of natural and synthetic halite crystals revealed many small fluid inclusions. Samples of natural halite to be used for isotope analysis are hand-picked and cleaned of foreign minerals and then washed with carbon tetrachloride to remove any organic material and surface oils from the mineral.

The D/H ratios of hydrogen and the ¹⁸O/¹⁶O ratios of CO₂ were determined with a Finnigan® Mat Delta and a Finnigan® Mat 25I stable isotope ratio mass spectrometer, respectively. Stable isotopic compositions are reported in the familiar delta notation defined as:

\[ \delta (\text{o}) = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000 \]  

where R is the ¹⁸O/¹⁶O or D/H of the sample or the standard, SMOW. All results were normalized to the stable isotopic composition of the pure water used to mix the solutions, \( \delta = \delta_{\text{solution}} - \delta_{\text{water}} \). The \( \delta \) and \( \delta^{18}O \)-value of the pure water is \(-141\) and \(-17.0\)\%o, respectively.
3. Results and discussion

Measurements of the $\delta D$-values of the NaCl, KCl, CaCl$_2$, and MgCl$_2$ solutions by the vacuum distillation method (Bigeleisen et al., 1952) differ from the $\delta D$-value of pure water by up to 5%, but there is no consistent relationship between $\delta D$-values and the molality of any of the solutions (Fig. 3). The decreased precision of the $\delta D$-values from $\pm 1\%$ for pure water to $\pm 5\%$ for the brine samples (Fig. 3) may be attributed to trapping of water as inclusions or adsorption of water on residual salts during evaporation. Reaction of the water with the salt during distillation to produce stable hydroxides which result in significant fractionations of hydrogen isotopes as proposed by Horita (1989) is not evident from our data.

$\delta D$-values measured by vacuum distillation–microequilibration for each solution (Kishima and Sakai, 1980) are also usually within the $\pm 5\%$ error indicated by measurement of UofS Standard water (Fig. 4a). Those values that deviate by amounts greater than the $\pm 5\%$ error show no consistent correlation with molality.

Except for a few values, the $\delta ^{18}O$-values of the NaCl, KCl and CaCl$_2$ solutions measured by vacuum distillation–microequilibration agree to within 1% of the $\delta ^{18}O$-value of the water from which the solutions were prepared, suggesting that no fractionation of oxygen isotopes occurs (Fig. 4b). Similar results were found previously by Zuber et al. (1978) for solutions of NaCl, KCl and CaCl$_2$ up to 5 m and MgCl$_2$ solutions up to 1.25 m. MgCl$_2$ solutions show a depletion of $^{18}O$ that can be related to the concentration of Mg$^{2+}$ in solution (Fig. 4b). This trend reaches a maximum depletion of 6% at 4 m MgCl$_2$, but then reverses so that 5 m solutions are only depleted by 3–4%. It is unlikely that these depletions are due to processes that may have occurred during preparation of the 4 or 5 m MgCl$_2$ solutions because this would be reflected by a similar trend in the hydrogen isotopic compositions. CO$_2$ equilibrated with the MgCl$_2$ solutions using the

![Fig. 3. Effect of the molality of: (a) CaCl$_2$; (b) MgCl$_2$; (c) KCl; and (d) NaCl, on the hydrogen isotopic composition of solutions analyzed using vacuum distillation. The dashed line corresponds to no effect on the $\delta D$-value of the pure water from which the solutions were prepared. The symbols represent average values obtained by at least 4 analyses of each solution and the range in values is indicated by the bars for each solution.](image-url)

![Fig. 4. Differences between the: (a) relative $\delta D$-values; and (b) relative $\delta ^{18}O$-values, of various solutions of CaCl$_2$ ( ), MgCl$_2$ (▲), KCl (●) and NaCl (■) obtained by vacuum distillation–microequilibration. Dashed lines represent the error obtained from repeat analyses of UofS Standard (Fig. 2). Only MgCl$_2$ solutions show a decrease in the $\delta ^{18}O$-values that correspond to MgCl$_2$ concentrations relative to the $\delta ^{18}O$-values of the water from which the solutions were prepared.](image-url)
method of Epstein and Mayeda (1953) gives oxygen isotope activities that can be related to the known oxygen isotope concentration ratios of these solutions by the corrections of Sofer and Gat (1972). This further suggests that fractionation of oxygen isotopes were minimal during preparation of the solutions.

During preparation of the MgCl₂ solutions a black precipitate was noticed and subsequent pH measurements revealed that pH-values decrease with increasing molality (Table I). Electron microprobe analysis of the solid revealed a Mg–O–Cl phase and Zr, the latter of which is probably a contaminant in the MgCl₂ reagent and possibly served as a nucleation site for precipitation of the Mg–O–Cl phase. Precipitation of the Mg–O–Cl phase, which has a δ¹⁸O-value of +8‰, caused some fractionation of the oxygen isotopes in the brine and released H⁺, which resulted in low pH-values (Table I). However, mass-balance calculations indicate that incorporation of ¹⁸O into the solid phase cannot account for the observed depletion of ¹⁸O in the water because the quantity of Mg–O–Cl that precipitated would only result in a depletion of 0.1‰ in the most concentrated MgCl₂ solution.

Results from vacuum distillation and hydrogen isotope analyses of synthetic brines are similar to those found for the single-salt solutions (Fig. 5a). No systematic hydrogen isotope fractionations occur during vacuum distillation followed by hydrogen isotope analysis; however, the δD-values determined for these brines are more variable than those obtained from pure water. This variability is probably attributable to the same processes that occur in the single-salt solutions. Similarly, δD-values obtained from vacuum distillation–microequilibration of synthetic brines are within the ±5‰ precision of the method, and indicate that no substantial hydrogen isotope fractionations occur for any of the synthetic brines (Fig. 5b). Depletions of ¹⁸O in the synthetic brines obtained using vacuum distillation–microequilibration (Fig. 5b) correlate with the molality of Mg²⁺ in the brines and tend to follow the trend observed in the MgCl₂ solutions (Fig. 6). It is likely that of all the cations in solution, only Mg causes fractionation of oxygen isotopes during vacuum distillation, as would be predicted from the results of the single-salt solutions (Fig. 4).

The stable isotopic compositions of water from fluid inclusions in halite, analyzed by both crushing and melting methods, agree well with those of the respective brines from which the halites were precipitated (Fig. 7). Some scatter is expected for natural halites because these samples were collected from a brine pool in a potash mine which is fed by leaks into the
Fig. 6. Relationship between the oxygen isotopic compositions of Synthetic Potash Leak Brine (□); Synthetic Halite Brine (Δ); Sylivite Facies Brine (○); and Carnallite Facies Brine (●), and the concentration of MgCl₂ in the solution. The dashed line represents the trend observed in the pure MgCl₂ solutions (Fig. 4b) and the bar represents the uncertainty in each measurement.

Fig. 7. Stable isotopic compositions of fluid inclusions in halite analyzed by the crushing method (Δ) and melting method (○) and the corresponding brines from a brine pool at PCS Rocanville 405-00-23 (●).

mine. The stable isotopic composition of the pool varies either through evaporation or changes in the stable isotopic composition of the inflowing brine as is demonstrated by different isotopic compositions of the pool sampled two years apart (Fig. 7). Synthetic halites were precipitated from a pure NaCl brine with δD- and δ¹⁸O-values of -140±5 and -16.9±1‰, respectively, and the isotopic composition of water released from fluid inclusions by melting the synthetic halite agree with those of the parent brine (δD=-135‰, δ¹⁸O=-15.9‰).

The precision in the measurement of the isotopic composition of water in inclusions released by crushing halite followed by heating to moderate temperature (350°C) to distill the water from the salt is similar to that of vacuum distillation–microequilibration of concentrated chloride brines. Further, water released by melting of synthetic halite at high temperature (800°C) followed by microequilibration also yields δD- and δ¹⁸O-values to within 5 and 1‰, respectively, of the parent brine. These results support the findings of Knauth and Beeunas (1986) that both the melting and crushing methods can be used to determine the stable isotopic composition of water from fluid inclusions in halite.

Chemical compositions of fluid inclusions in halite can be measured directly (Lazar and Holland, 1988) or estimated from freezing-point depression measurements (Roedder, 1984). Because Mg²⁺ in solution results in fractionation of δ¹⁸O of solutions during distillation, a good estimate of the Mg²⁺ concentration in fluid inclusion brines is a necessary prerequisite to stable isotope determinations of fluids in inclusions in halite. Because the halite pool has a low Mg²⁺ concentration (Table II), no correction of the oxygen isotopic compositions of water from fluid inclusions are necessary. Synthetic halites, precipitated from a pure NaCl solution, also do not require any corrections. However, natural samples of halite may contain varying concentrations of Mg²⁺ in their fluid inclusions and therefore will require small corrections for oxygen isotopic compositions only, providing that the MgCl₂ concentration can be estimated.

Significant fractionation of hydrogen and oxygen isotopes by the formation of NaOH during melting of halite, as proposed by Horita and Matsuo (1986), is not indicated by our data. Melting of NaCl in moist air will only produce 1–2.5 μmol NaOH/g NaCl (Johnson, 1934; Otterson, 1960) and yields of water from fluid inclusions in halite are usually 600–800 μmol H₂O/g NaCl. From mass-balance considerations, the small amount of NaOH produced by reaction of fluid inclusion waters with halite during melting in vacuum could not pro-
duce any significant variations in the stable isotopic composition of fluid inclusion brines.

4. Conclusions

The vacuum distillation-microequilibration technique allows hydrogen and oxygen isotopic analysis of up to 5 m Na-K-Ca chloride solutions with a precision of ± 5% for hydrogen and ± 1% for oxygen. Pure MgCl₂ solutions and chloride brines containing Mg²⁺ also yield δD-values within ± 5% of the true value of the water but require a correction to the δ¹⁸O-values measured to a maximum of + 6% for 4 m MgCl₂ and smaller corrections for less concentrated and more concentrated Mg-brines. This behaviour suggests that fractionation of oxygen isotopes by reaction with MgCl₂ during vacuum distillation is a result of complex processes.

No fractionation of hydrogen or oxygen isotopes occur during melting or crushing of halite for stable isotope analysis of fluid inclusion brines. Corrections of the oxygen isotopic composition of fluid inclusion brines in halite can be estimated if the concentration of Mg in fluid inclusion brines can be measured directly or estimated by typical fluid inclusion methods.

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