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# Method for Simultaneous Oxygen and Hydrogen Isotope Analysis of Water of Crystallization in Hydrated Minerals

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**The isotopic composition of water in hydrated minerals, such as gypsum and jarosite, has numerous applications in studies of recent climate change, ore formation, and soil development. However, oxygen and hydrogen isotope analysis of water of crystallization is currently a complex procedure. Commonly used techniques involve offline extraction of water from hydrated minerals and subsequent isotope analysis. Such methods are time-consuming, require relatively large sample sizes, and the stepwise procedure has to be carried out with extreme caution to avoid erroneous results. We present a novel online method for the oxygen and hydrogen isotope analysis of water of crystallization in hydrous minerals. Gypsum ($CaSO_4 \cdot 2H_2O$) samples, 2 mg in size, are reacted in a simply modified carbon reducing furnace connected to a continuous-flow mass spectrometer system. Analysis time is less than 10 min/sample. The precision (2 std dev mean) of our method for 2-mg gypsum (30 $\mu$mol of $H_2O$) samples is 0.3‰ for oxygen and less than 1.4‰ for hydrogen isotope measurements. For oxygen isotope analysis alone, samples as small as 0.2 mg of gypsum can be analyzed with a precision of 0.3‰.**

The $\delta^2$H and $\delta^{18}$O of water of crystallization in gypsum have defined mineral–water fractionation factors ($\alpha_{b\text{-}wc}$ $^{18}O = 1.004$, $\alpha_{b\text{-}wc}$ $^{2}H = 0.980$)[1] that can reflect whether the mineral precipitated from a marine or a meteoric water body, through hydration of anhydrite, or sulfide oxidation in groundwater.[1−3] Although dehydration, rehydration, and re-equilibration may alter the isotopic composition of water of crystallization, particularly in samples from older or wetter locations, several studies have utilized water of crystallization in gypsum and other hydrous minerals. Halas and Krouse used water of crystallization in gypsum deposits of the Miocene Carpathian Foredeep to develop hypotheses regarding paleoclimate,[4] while Duwuona et al. observed that water of crystallization in gypsum and jarosite from soils accurately reflected local precipitation.[5] Matsubaya and Sakai provided evidence that the gypsum of the Kuroko-type ore deposits formed through several different mechanisms, including fractional hydration of anhydrite, rather than entirely from marine hydrothermal fluids as previously thought.[3] Bath et al. were able to infer gypsification mechanisms in a large anhydrite deposit through their work with minor element contents and the isotopic composition of water of hydration.[6] Finally, Khademi et al. showed that the isotopic composition of water of crystallization in gypsosols, and therefore the gypsum formation process, is related to local geomorphology.[7]

While potentially very informative, use of combined hydrogen and oxygen analysis of water of crystallization in hydrous minerals is currently limited by sample size and analytical complexity. Previous techniques have measured the isotopic composition of water of crystallization either by quantitatively extracting water of crystallization from the mineral[2,8] or by decomposing the mineral at high temperature to release hydrogen and oxygen.[9,10]

Early methods for analysis of isotopes in water of crystallization relied upon quantitative extraction of ~5 mL of water from ~25-g gypsum samples by heating to 400 °C under vacuum and equilibration of the extracted water with $CO_2$, at an overall precision of 0.3‰ for oxygen.[2] Subsequent studies reduced sample sizes to those which will produce 2−3 mL of crystallization water[5] and improved precision to approximately that of normal $CO_2$ equilibration and reduction on uranium or zinc by refining sample preparation and dehydration specifications.[1,4,7] Studies of natural samples often include a purification step intended to remove contaminants from the extracted liquid.[1,4,6,7] More recently, Khademi et al. extracted and analyzed water of hydration from 7-g gypsum samples with a precision of <0.14‰ for oxygen and 0.5‰ for hydrogen.[7] The measurement of oxygen isotopes in water of crystallization was significantly refined by Playa et al.,[8] who adapted the extraction process to suit the guanadine hydrochloride reaction, previously used for isotopic analysis of small amounts

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(1) Sofer, Z. *Geochim. Cosmochim. Acta* **1978**, *42*, 1141–1149.
(2) Gonfiantini, R.; Fontes, J. C. *Nature* **1963**, *200*, 644–646.
(3) Matsubaya, O.; Sakai, H,. *Geochem. J.* **1973**, *7*, 153–165.
(4) Halas, S.; Krouse, H. R. *Geochim. Cosmochim. Acta* **1982**, *46*, 293–296.
(5) Duwuona, G. N.; Mermu, A. R.; Krouse, H. R. *Soil Sci. Soc. Am. J.* **1992**, *56*, 309–313.
(6) Bath, A. H.; Darling, W. G.; George, I. A.; Milodowski, A. E. *Geochim. Cosmochim. Acta* **1987**, *51*, 3113–3118.
(7) Khademi, H.; Mermut, A. R.; Krouse, H. R. *Chem. Geol.* **1997**, *138*, 245–255.
(8) Playà, E.; Recio, C.; Mitchell, J. *Chem. Geol.* **2005**, *217*, 89–96.
(9) Sharp, Z. D.; Atudorei, V.; Durakiewicz, T. *Chem. Geol.* **2001**, *178*, 197–210.
(10) Gong, B.; Zheng, Y. F.; Chen, R. X. *Rapid Commun. Mass Spectrom.* **2007**, *21*, 1386–1392.



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of water.[11,12] Despite such improvements, extraction remains a tedious method that requires 45 min of heating per sample, plus additional time for equilibration and oxygen and hydrogen isotope analyses. Thus, extraction methods may yield excellent precision and reproducibility; however, they are time-consuming, can be technically difficult, and require relatively large amounts of sample.

The recent growth in continuous-flow, online techniques, including the analysis of hydrogen and oxygen in water through high-temperature reduction, e.g., ref 13, has led to new methods for studying the isotopic composition of water of crystallization in both hydrated and nominally anhydrous minerals. Bulk thermal conversion, as described by Sharp and Gong et al., allows for continuous-flow measurement of $\delta^2$H for water of crystallization in small amounts of hydrated and nominally anhydrous minerals.[9,10] A sample bearing as little as 0.01 $\mu$L of $H_2O$ is dropped into a carbon furnace at 1450 °C where the sample decomposes, releasing hydrogen—among other gases—which is carried in a He flow to the mass spectrometer. Provided water release is complete; bulk thermal conversion reduces the risk of analysis-associated fractionation and allows for far smaller sample sizes than extraction. However, such conversion cannot be used for oxygen isotope analyses because complete reductive thermal conversion releases structural oxygen along with oxygen from water of crystallization. A further concern, when studying nominally anhydrous minerals, is the potential of release of nonstoichiometric hydrogen.[14]

Here, we present a method that is based on a modification of the thermochemical reduction reactor for oxygen and hydrogen isotope analysis of liquid samples by continuous-flow IRMS.[e.g.15] Our method provides both hydrogen and oxygen isotope measurements while reducing sample size. Furthermore, the method requires only the conventional thermal reduction apparatus, is quick (49 complete hydrogen and oxygen measurements in under 7 h), and requires only minimal sample preparation. The method has been tested on gypsum and epsomite ($MgSO_4 \cdot 7H_2O$), but is potentially applicable to all hydrated minerals and possibly to fluid inclusions in minerals such as halite (NaCl).

## EXPERIMENTAL SECTION

**Reactor Setup.** Our method for online simultaneous measurement of hydrogen and oxygen from water of crystallization could be set up using any continuous-flow, isotope ratio mass spectrometer, equipped with a thermal reduction furnace. In developing the method, we used a Finnigan thermal conversion elemental analyzer with a Costech Zero-blank autosampler coupled to a Finnigan MAT 253 isotope ratio mass spectrometer via a Finnigan ConfloIII open split.

The reduction furnace is a modification of an arrangement for oxygen and hydrogen isotope analysis of liquid samples that consists of a ceramic tube containing a 470-mm-long glassy carbon tube with an inner diameter of 9 mm in redirected flow setup.[15]

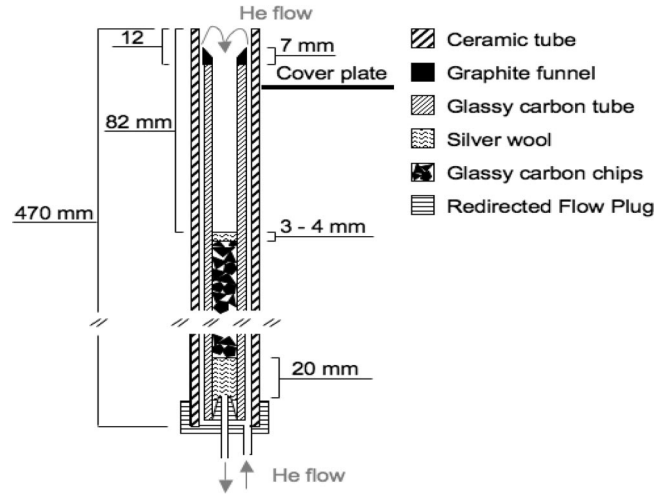


**Figure 1.** Reactor arrangement for the new method. Samples enter at the top and dehydrate on the Ag wool plug; the water is then entrained in the helium carrier gas, which enters from the bottom of the furnace, flows upward between the glassy carbon and ceramic tubes, then downward, and out through the glassy carbon to a gas chromatography column.

A small graphite funnel (Figure 1) was introduced at the top of the glassy carbon tube to ensure that samples dropped into the reactor. We extended the glassy carbon chip filling well above the hottest point in the reactor (Figure 1) up to 82 mm below the top of the ceramic tube. The top of the fill was covered by a 3-mm silver wool plug. Temperature measurements at sample depth were carried out with an S-type thermocouple inserted into the reduction furnace through a modified injection port while maintaining the carrier gas flow at the same rate as during sample analysis (87.0 sccm). Benzoic acid samples (IAEA 601 and IAEA 602) were used to establish whether the samples dehydrated completely. The degassed water, entrained in the redirected He flow, quantitatively reduces in the 1450 °C reactor to form $H_2$ and CO[16] before continuing to the gas chromatography column.

The gas chromatography column (Varian, molecular sieve 5 Å, 80−100 mesh, 0.5-m length) was kept at 90 °C to separate $H_2$ and CO such that there would be sufficient time between elution of $H_2$ and CO gases for the peak jump feature of the Finnigan Isodat software package to switch the tuning of the magnetic field of the mass spectrometer from $H_2$ ($m/z$ 2 and 3) to CO ($m/z$ 28, 29, 30). Overnight and during maintenance breaks, the temperature of the GC column oven was raised to 280 °C to help maintain peak separation of $H_2$ and CO and reduce peak tailing and memory effects. We compensated for hydrogen memory effects by running samples in sets of five and discounting the first of each set. We included standards at the beginning and end of each run to account for possible drift and to establish precision. We applied a standard $H_3^+$-factor correction, obtained by calibrating over a stepwise increase in hydrogen flow, to account for $H_3^+$ ions created in the source of the mass spectrometer.

We tested samples with water contents of 30 $\mu$mol of$H_2O$ and 3 $\mu$mol of $H_2O$. The greater volume of water removed from the larger (30 $\mu$mol of $H_2O$) samples required the addition of helium dilution to avoid overwhelming the mass spectrometer.


(11) Boyer, P. D.; Grawec, D. Y.; Sueltera, S. I.; Densey, D. E. *J. Anal. Khim. (Akad. Nauk SSSR)* **1961**, *12*, 1906–1910.

(12) Dugan, J. P.; Borthwick, J.; Harmon, R. S.; Gagnier, M. A.; Glahn, J. E.; Kinsel, E. P.; MacLeod, S.; Viglino, J. A.; Hess, J. W. *Anal. Chem.* **1985**, *57*, 1734–1736.

(13) Begley, I. S.; Scrimgeour, C. M. *Anal. Chem.* **1997**, *69*, 1530–1535.

(14) Baatartsogt, B.; Wagner, T.; Taubald, H.; Mierdel, K.; Markl, G. *Chem. Geol.* **2007**, *244*, 474–482.

(15) Gehre, M.; Geilmann, H.; Richter, J.; Werner, R. A.; Brand, W. A. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 2650–2660.

(16) Leuenberger, M. C.; Filot, M. S. *Rapid Commun. Mass Spectrom.* **2007**, *21*, 1587–1598.

**Sample Preparation and Thermal Conversion.** Powdered, crushed, or crystalline samples on the milligram scale were dried and weighed according to water content into small silver capsules (i.d. 3 mm, Costech), which were then trimmed, flattened, and introduced into the reduction furnace through the autosampler. A measure of the water released from a sample, its yield, was calculated through the time-integrated intensity of the collected ions, the amount of sample, and its calculated water content, calibrated by running IAEA benzoic acid.

**Preparation of Laboratory Standards.** Ideally, standards should be of the same material as the samples and bracket the samples' isotopic composition,[17] as is the case with calibrating extracted waters against water standards such as VSMOW, SLAP, and GISP; however, no such standards exist for water of crystallization in hydrated minerals. We precipitated one gypsum laboratory standard ("gypsum 2") from a NaCl and $CaSO_4$ brine labeled with $^{18}O$-enriched water through the addition of $CaCl_2$. A second gypsum laboratory standard ("gypsum 3") was precipitated from previously evaporated water through titration of $Na_2SO_4$ with $CaCl_2$. We filtered and dried the gypsum standards at room temperature before drying in a room-temperature vacuum oven.[8] We selected a commercially available crystalline magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$, J. T. Baker, Inc.) for a third standard ("CEpsomite"). Water of crystallization was extracted from 2.4 g of gypsum or 1 g of epsomite following the method of Gonfiantini and Fontes to yield 0.5 mL of water of crystallization.[2] Reduction on chromium[18] and $CO_2$ equilibration,[19] respectively, provided the $\delta^2H$ and $\delta^{18}O$ of the extracted water of crystallization as well as the $\delta^2H$ and $\delta^{18}O$ of the gypsum precipitation brines.

**Experimental Setup.** With the reactor temperature set at 1450 °C, we measured a temperature of 460 °C ± 30 °C at 8 cm below and 400 °C ± 30 °C at 6.5 cm below the top of the ceramic tube. Thus, samples dropped into the reactor dehydrate at temperatures around 430 °C. Our temperature measurements from 8 and 6.5 cm into the reactor imply that sample accumulation of ≤1.5 cm should not raise the samples out of the dehydration temperature zone. Trimming and folding the sample-bearing capsules significantly reduces the volume of sample accumulation in the reactor such that we could analyze ~90 2-mg tightly folded samples before observing the decreased yields associated with sample accumulation above the 1.5-cm dehydration zone. Because sample materials remain contained within the silver capsules, it is not necessary to completely disassemble the reduction furnace between sets of samples provided the capsules are removed before extensive accumulation. We found that a small tube attached to a household vacuum cleaner made for a simple used-capsule retrieval device. The reduction furnace need only be disassembled when the glassy carbon chips, glassy carbon tube, and ceramic tube begin to degrade, producing higher backgrounds and poor reproducibility. The glassy carbon chips within the hot zone degrade most quickly and need to be replaced regularly.

## RESULTS

**Conversion Efficiency.** We calculated the measured yields either relative to benzoic acid, which was assumed to be 100%, or as a percentage of the average time-integrated intensity for all samples of that composition within the set of samples. Once we established consistent, near 100% yields with respect to benzoic acid, we could switch to using the average time-integrated intensity of the samples. This average yield system allows us to track changes in yield such as those that accompany sample buildup in the reduction furnace without consuming large quantities of reference material or taking up space that could be dedicated to samples. Yields versus benzoic acid for 0.2-mg gypsum samples without He dilution were 101 ± 3% for hydrogen and 101 ± 4% for oxygen. Yields relative to sample type were 101 ± 6% for both hydrogen and oxygen at 2-mg sample size with helium dilution.

**Table 1. Isotopic Composition of Extractions of Water of Crystallization and Measurements Obtained through the Dehydration/Conversion Method of This Paper[a]**

| sample | average $\delta^2H$ | average $\delta^{18}O$ |
|---|---|---|
| gypsum 2 extractions, $n = 3$ | −87.8 ± 3.5 | 24.0 ± 0.3 |
| 2 mg of gypsum 2, $n = 46$ | −92.5 ± 1.1 | 24.2 ± 0.3 |
| 0.2 mg of gypsum 2, $n = 7$ | −59.1 ± 13.4 | 22.6 ± 0.3 |
| gypsum 3 extractions, $n = 3$ | 14.3 ± 0.6 | 17.1 ± 0.2 |
| 2 mg of gypsum 3, $n = 37$ | 9.5 ± 1.5 | 16.4 ± 0.5 |
| 0.2 mg of gypsum 3, $n = 6$ | 20.4 ± 26.7 | 16.7 ± 1.2 |
| CEpsomite extractions, $n = 3$ | −61.2 ± 0.7 | −1.6 ± 0.2 |
| CEpsomite, $n = 41$ | −51.5 ± 1.3 | −1.2 ± 0.3 |

[a] Helium dilution was used with 2-mg samples; 0.2-mg samples were analyzed without helium dilution. The number of replicates analyzed ($n$) is indicated. Error is given as 2 × standard deviation/square root ($n$). Average yield for all extractions is 98.4 ± 0.01%.

**Analytical Precision.** We found in preliminary runs using 0.2-mg gypsum samples that precision (2 × standard deviation of the mean) was 1.2‰ or better for oxygen while hydrogen was 27‰. With further experimentation, we discovered that the first measurement in a replicate analysis set was usually an outlier. We also found that although 0.2-mg samples gave satisfactory oxygen isotope analyses, there was a memory effect with the hydrogen isotope analyses that could be eliminated by increasing the sample size to 2 mg. For 2-mg samples and with the first sample measurement discarded, hydrogen isotopes were measured with an average precision of 2.3‰, while oxygen isotope measurements were precise to 0.7‰ or better (both 2 × standard deviation of the mean). The oxygen and hydrogen isotope values for extracted water of crystallization and water of crystallization measured through our method are presented in Table 1 and Figure 2.

**Standards.** Our synthetic gypsum contains virtually no organic or volatile contaminants, obviating the additional distillation step adopted by many groups for use with natural samples. The gypsum precipitates were filtered from the brine, rinsed, and left to dry under atmospheric conditions for several days before drying at room temperature and high vacuum for 10 min.[8] Upon the observation of high yields in conventional extractions (>100%) and in 0.2-mg samples relative to benzoic acid, the standards were dried an additional 10 min at room temperature under high vacuum. Subsequently lower yields (~98% in conventional extractions) prompted XRD analysis, which revealed the presence of minor amounts of bassanite ($2CaSO_4 \cdot H_2O$) in both gypsum standards, potentially the result of excessive vacuum drying. Replicate analyses conducted over a number of weeks show that

(17) Coplen, T. B. *Pure Appl. Chem.* **1994**, *66*, 273–276.
(18) Gehre, M.; Horfling, R.; Kowski, P.; Straugh, G. *Anal. Chem.* **1996**, *68*, 4414–4417.
(19) Epstein, S.; Mayeda, T. K. *Geochim. Cosmochim. Acta* **1953**, *4*, 213–224.

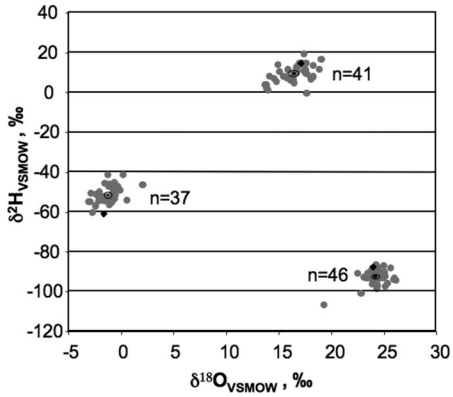


**Figure 2.** Oxygen and hydrogen isotope measurements of 2-mg gypsum and 1-mg epsomite standards analyzed through the dehydration/reduction method of this paper. Solid black circles and black ellipses represent the average and 2 standard deviations of mean, respectively, for analyses of the three standards. Each shaded circle represents a single anaysis calibrated by reference to the known hydration water compositions of the three standards (black diamonds), including correction for measurement drift.

the isotopic composition of water of crystallization in gypsum is conserved on that time scale.

## DISCUSSION

**Precision and Sample Size.** Oxygen from water of crystallization in gypsum could be measured in samples bearing 0.05 $\mu$L of water (0.2 mg of gypsum). At the 0.05-$\mu$L water sample size, hydrogen measurements deviated strongly from the measurements obtained from extracted water of crystallization. Samples of 0.5 $\mu$L of water (2 mg of gypsum), with the corresponding addition of helium dilution at the Conflow III interface, saw improvements in the precision and accuracy of hydrogen measurements but some deterioration in the precision of our oxygen measurements (Table 1). There is no definitive explanation for the improved precision for hydrogen measurements and poorer precision for oxygen measurements exhibited by larger samples (2 mg, as opposed to 0.2 mg), but it might result from nonquantitative conversion to $H_2$ and CO, such that additional hydrogen overwhelms the memory effect but increases scatter. However, the yield data do not unambiguously support this hypothesis, and furthermore scattered outliers generally do not show correlation of hydrogen and oxygen isotope data as expected from partial conversion. (The two highly visible outliers in the G2 data in Figure 2 clearly correlate but equally clearly are exceptions).

Our high standard deviation for hydrogen measurements at the 0.2-mg sample size results from a combination of factors, including machine drift, compression/extension in the hydrogen scale, and sample memory. The observed hydrogen memory effect was independent of the number of samples already in the reactor and reactor age, implying that the hydrogen memory does not come from the samples or furnace but may, as others have suspected, be related to adsorption on the stainless steel lines or another part of the system,[20] or to the GC column.[21] Adjusting the GC column oven temperature and replacing the column improved elution time and peak shape but did not remove the memory effect. Memory effects in hydrogen are still present in 2-mg gypsum samples but are less severe and can be further reduced by running several consecutive replicates (Table 2).

Some of the scatter in hydrogen and oxygen isotope measurements (Figure 2) may also be attributable to isotopic or mineralogical heterogeneity in the samples due to precipitation or drying technique. However, the gypsum standards were thoroughly mixed and slightly ground for further homogenization. We have not observed trends that resemble Rayleigh fractionation of crystal precipitation. Therefore, sample heterogeneity is unlikely to cause the observed scatter.

**Accuracy of Results.** It is apparent from Figure 1 and from the arguments above that there may be a problem of accuracy of data even if they are of sufficiently high precision. As with all other stable isotope methods, it is usual to measure differences of sample isotope compositions relative to reference or standard materials of similar chemical composition with known or accepted isotope values. In the absence of a suitable isotope reference material, the quality of the isotope data for a new method or a previously unanalyzed material can be ascertained if blanks are negligible and if yields are near to 100%, e.g., ref 22. In that case, all of the isotopic material analyzed is that of the sample and the results should be valid. For hydrated sulfate minerals, there are no accepted standards and it is not immediately apparent whether extraction from materials we used for calibration is an acceptably accurate process.

The gypsum standards we precipitated lack the complications of natural or coarser grained samples, which may contain organic matter or fluid inclusions. The effect of fluid inclusion water on water of crystallization isotope analysis depends on the history and mineralogy of the sample but would be drawn out of a crushed sample during vacuum drying.

Significant fractionations of oxygen have been observed in the dehydration of brines and salts, particularly those bearing alkalai earth metals.[23−25] The new method described in this paper avoids fractionation due to formation of, or exchange with, other minerals by completely dehydrating the sample and removing all of the water from the system. Hydrogen isotope fractionation associated with the production of HCl in a dehydrated chloride-bearing brine[23] is prevented by analysis of solid calcium sulfate and magnesium sulfate samples alone. Since our new technique dehydrates at a higher temperature than that used for the large samples, we consider it more likely to give accurate results; however, both methods give full yields. It is not possible to judge which method gives more accurate results. A possible future approach might be preparation of a range of hydrated salt reference materials not containing hydrogen or oxygen other than water of hydration; these could be analyzed by methods other than thermal release of water (e.g., fluorination for oxygen isotope values).

The organic content of natural samples may have a complicating affect on hydrogen isotope measurements from this method; however, additional sample preparation steps to remove organic

(20) Olsen, J.; Seierstad, I.; Vinther, B.; Johnsen, S.; Heinemeier, J. *Int. J. Mass Spectrom.* **2006**, *254*, 44–52.
(21) Morse, A. D.; Wright, I. P.; Pillinger, C. T. *Chem. Geol.* **1993**, *107*, 147–158.
(22) Ader, M.; Coleman, M.; Doyle, S. P.; Stroud, M. S.; Wakelin, D. *Anal. Chem.* **2001**, *73*, 4946–4950.
(23) Horita, J. *Chem. Geol.* **1989**, *79*, 107–112.
(24) Koehler, G.; Chipley, D.; Kyser, T. K. *Chem. Geol.* **1991**, *94*, 45–54.
(25) Koehler, G.; Kyser, T. K. *Geochim. Cosmochim. Acta* **1996**, *60*, 2721–2726.

**Table 2. Example Set of 30 μmol of $H_2O$-Bearing Samples Analyzed through the Dehydration/Conversion Method of This Paper[a]**

| time | sample | raw $\delta^2H$ | calibrated $\delta^2H$ | H yield | raw $\delta^{18}O$ | calibrated $\delta^{18}O$ | O Y=yield |
|---|---|---|---|---|---|---|---|
| 12:00:52 | G3−1 | 15.832 | 13.1 | 101 | 32.907 | 18.9 | 101 |
| 12:09:19 | G3−2 | 19.025 | 16.8 | 100 | 32.596 | 18.7 | 101 |
| 12:17:44 | G3−3 | 14.812 | 11.7 | 100 | 32.319 | 18.4 | 101 |
| 12:26:13 | G3−4 | 16.465 | 13.6 | 101 | 31.737 | 17.9 | 101 |
| 12:34:43 | G3−5 | 14.804 | 11.6 | 101 | 31.037 | 17.2 | 101 |
| 12:43:12 | CE−1 | −38.596 | −51.2 | 107 | 12.711 | −3.1 | 107 |
| 12:51:42 | CE−2 | −37.899 | −50.4 | 102 | 13.181 | −2.5 | 103 |
| 13:00:11 | CE−3 | −39.17 | −52.0 | 102 | 13.429 | −2.1 | 101 |
| 13:08:41 | CE−4 | −40.88 | −54.0 | 104 | 12.394 | −3.2 | 103 |
| 13:17:12 | CE−5 | −38.514 | −51.3 | 100 | 13.645 | −1.7 | 100 |
| 13:25:42 | G2−1 | −63.673 | −80.9 | 100 | 35.23 | 22.4 | 101 |
| 13:34:17 | G2−2 | −72.639 | −91.5 | 100 | 35.348 | 22.6 | 100 |
| 13:42:48 | G2−3 | −72.905 | −91.9 | 101 | 35.456 | 22.9 | 100 |
| 13:51:18 | G2−4 | −69.193 | −87.6 | 100 | 35.954 | 23.5 | 100 |
| 13:59:48 | G2−5 | −72.121 | −91.1 | 100 | 35.806 | 23.4 | 100 |
| 16:58:23 | G3−6 | 12.843 | 7.6 | 101 | 26.553 | 15.1 | 100 |
| 17:06:53 | G3−7 | 12.449 | 7.1 | 100 | 28.792 | 17.7 | 100 |
| 17:15:24 | G3−8 | 13.704 | 8.5 | 101 | 26.416 | 15.1 | 100 |
| 17:23:54 | G3−9 | 16.512 | 11.7 | 100 | 26.722 | 15.5 | 100 |
| 17:32:25 | G3−10 | 16.022 | 11.1 | 99 | 27.383 | 16.4 | 100 |
| 17:40:56 | CE−6 | −29.443 | −42.4 | 91 | 11.852 | −0.8 | 91 |
| 17:49:27 | CE−7 | −34.435 | −48.3 | 91 | 12.299 | −0.2 | 91 |
| 17:57:58 | CE−8 | −33.291 | −47.0 | 89 | 11.739 | −0.8 | 90 |
| 18:06:30 | G2−6 | −66.621 | −86.2 | 100 | 32.444 | 22.4 | 99 |
| 18:15:02 | G2−7 | −69.683 | −89.9 | 100 | 32.934 | 23.0 | 100 |
| 18:23:33 | G2−8 | −71.404 | −92.0 | 100 | 32.886 | 23.0 | 100 |
| 18:32:05 | G2−9 | −70.649 | −91.1 | 99 | 32.94 | 23.2 | 100 |
| 18:40:36 | G2−10 | −72.178 | −93.0 | 100 | 33.154 | 23.5 | 99 |

[a] Samples are 2-mg replicates of the gypsum standards (G2 and G3) and 1-mg replicates of the epsomite standard (CE), respectively. The final digits of the sample numbers are the successive run numbers for each sample. All samples were run without helium dilution. Yields are given relative to sample type.

matter or separate isotopic analysis of the organic matter may help to resolve this challenge.

The high yield for both hydrogen and oxygen in 0.2-mg gypsum samples relative to benzoic acid suggests that the samples were not completely dry after 10 min in high vacuum, rather than that more oxygen is being released than hydrogen, as would be the case if sulfate were decomposing in the reactor. Because the samples are kept above their dehydration temperature, it is unlikely that they will be rehydrated by subsequent samples. Consistently complete hydrogen and oxygen yields relative to benzoic acid at 0.2-mg sample size allowed us to assume that dehydration was similarly effective for the larger samples.

**Operational Details.** The throughput of the method is highly dependent on minimizing hydrogen memory. At four or five replicates of three standards at the beginning and end of a run, standards alone would constitute more than half the available slots, leaving room for only five sets of replicates. We ran samples in sets of five to show that a steady value had been attained; using the final sample of three or the last two of four would likely be an acceptable way to increase throughput. Sets of four replicates would provide two complete hydrogen and oxygen measurements for six samples in less than 9 h. With five replicates, even the larger sample size is still well under the 2 g of gypsum needed for conventional extraction.

Sample depth in the reduction furnace has an important impact on both ensuring complete dehydration and preventing memory effects. Anomalous isotope measurements would result if a portion of the sample either enters the hot zone of the reactor or dehydrates incompletely. We observed that samples occasionally burst the silver capsules; however, loose powder was infrequently observed in the reduction furnace. Samples that did burst through the silver capsule tended to form a solid crust attached to the silver without spreading through the furnace. Thus, provided the dehydration zone is maintained and a funnel used to guide samples into the furnace, sample location is unlikely to cause errors.

## CONCLUSIONS

An essential benefit of this method is that we avoid releasing structural oxygen along with the water of crystallization. With bulk conversion techniques, the oxygen isotope composition of water of hydration could be calculated from a mass balance equation with the bulk oxygen isotope value, the oxygen from sulfate value (from barium sulfate precipitated from the material or from a dehydrated sample), and the calculated contribution from each. However, making two measurements to calculate one value increases uncertainty and may complicate the analytical procedure if sulfate measurements are not needed. Analyses of water of crystallization by our method are particularly appealing for sulfates, such as the gypsum in this study, because sulfate is very stable under most conditions[26] and will not exchange oxygen with the water of crystallization during vacuum drying or dehydration in the reactor. Complete dehydration ensures that only the water of crystallization from the sample is measured, without the formation of new minerals. Thus, the hydrogen and oxygen from water of crystallization measured through the method of this paper may readily be combined with analyses of hydrogen and oxygen from brine and the sulfur and oxygen from sulfate to provide measurements for the entire system.

(26) Chiba, H.; Sakai, H. *Geochim. Cosmochim. Acta* **1985**, *49*, 993–1000.

We observed high yields for conventional extraction (>100%) and through our method in gypsum samples dried for 10 min under high vacuum at room temperature, and yet lower extraction yields (~98%) and the presence of bassanite ($2CaSO_4 \cdot H_2O$) in samples that had undergone further vacuum drying at room temperature. Therefore, vacuum and temperature conditions during drying must be tailored to specific sample types (e.g., titrated gypsum vs crystalline epsomite vs natural gypsum) to remove adsorbed water without releasing or fractionating the water of crystallization.[8] Epsomite samples occasionally showed decreased yields and heavier isotopic values over the course of several hours in a zero-blank autosampler, suggesting that samples should be arranged such that the isotopic composition of the water of crystallization in minerals that dehydrate more readily is measured early in the set of analyses.

Although we chose to use the peak jump feature as the setting for our mass spectrometer for measurements of both oxygen and hydrogen from one sample, the method would be equally effective as a combination of oxygen measurements on smaller samples (without He dilution) with replicate larger samples for hydrogen measurements (with He dilution). Samples for this study that were run in sets of five consecutive replicates demonstrate the diminishing effect of previous samples of different hydrogen isotope composition. The number of replicates can be reduced to three or four with only the last sample(s) accepted, thereby increasing throughput without sacrificing precision.

The high-temperature dehydration and reduction method is a rapid, simple technique for analyzing the isotopic composition of water of crystallization in gypsum with a precision of 4‰ for hydrogen and 1.4‰ for oxygen. Samples need only produce 28 $\mu$mol (0.5 $\mu$L) of water for analysis with helium dilution at the above precision. With greater and successful efforts to reduce hydrogen memory effects, the sample size could be reduced by a factor of 10 to samples containing only 0.05 $\mu$L of water (equivalent to 180 $\mu$g of gypsum).

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