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A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reagent

T.W. Vennemann and J.R. O'Neil

Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA

ABSTRACT

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A new method based on Zn reagent for the quantitative conversion H_2O to H_2 for the hydrogen isotope analysis of hydrous minerals and whole rocks has been developed. Analyses by this method are of comparable accuracy and precision (~ 1‰; ≤0.1 wt% error for determination of H_2O) to those of conventional extraction methods based on uranium reagent and is significantly simpler, faster and less expensive.

1. Introduction

Zinc has been used successfully as an alternative reductant to uranium for the quantitative conversion of H_2O to H_2 for D/H determinations of water samples (e.g., Coleman et al., 1982; Kendall and Coplen, 1985) but not for hydrous minerals. In this paper we describe a new method for the hydrogen isotope and water analysis of hydrous minerals using Zn reagent. This method, which has been used successfully for the last two years at the University of Michigan, is largely a combination of the conventional technique using uranium reagent (e.g., Bigeleisen et al., 1952; Godfrey, 1962; Kyser and O'Neil, 1984) and those for water analyses based on Zn (e.g., Coleman et al., 1982). The technique described herein is an attractive alternative to the conventional reduction of H_2O by uranium as it is fast, simple, relatively inexpensive and allows for precise and accurate analyses of small sample sizes. A large number of inquiries prompted us to publish the details of the technique.

The development of the method described below is an outgrowth of our detailed research performed to test the feasibility of a closed tube technique for the hydrogen isotope analysis of hydrous minerals as first suggested to us by P. Agrinier and M. Javoy (pers. commun., 1990). This closed tube technique involves quantitative reduction of the H_2O in hydrous minerals or rocks by Zn reagent where sample and Zn are inserted into quartz tubes and, after evacuation, are heated to 1200°C in a resistance furnace. Unfortunately, rapid back-reaction between the H_2 produced and the residual mineral/melt, in combination with hydrogen diffusion through the glass walls at these high temperatures results in inaccurate, variably shifted δD-values for a range of minerals. Even though the measured values for a given mineral separate were very precise (better than ± 1‰), shifts in δD of up to +20‰ from the

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Correspondence to: T.W. Vennemann, Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, USA.

true value appeared to be a critical function of the nature of the mineral (e.g., Fe content), necessitating variable correction factors and a detailed knowledge of the mineral chemistry prior to isotopic analysis.

2. Description and results

Since the technique currently used in the Stable Isotope Laboratory of the University of Michigan for the hydrogen isotope analysis of water forms the basis for our mass-spectrometer calibration and hence the basis for the mineral D/H analyses, it is briefly described below. All values are reported in the familiar δ-notation relative to SMOW (Vienna Standard Mean Ocean Water).

2.1. D/H analysis of water and volume calibration

Microliter quantities of water of between 0.5–5 μl ($\sim$2 μl is the routine amount) are injected by a gas-tight microsyringe into evacuated Pyrex® tubes ($\sim$25 cm in length) containing Zn granules or shavings (Fig. 1). About 30–50 mg Zn, or simply an excess amount, are used per expected μl of H_2O. Prior to use, the Pyrex® tubes are roasted at 500°C for a minimum of 1 hr and then stored at 110°C. For the analyses reported below, both AnalaR® Zn shot (0.5–2 mm) and Zn laths supplied by the Biogeochemical Laboratory of the University of Indiana were used. No significant difference in results were observed between these two types of Zn. Injection is made through a Silicone® septum held in place by a small neck in the glass. The water is transferred with gentle heating of the glass apparatus to the lower portion of the tube which is at liquid-nitrogen temperature. Any non-condensible gases are then pumped off and the tube is sealed off with a gas–oxygen flame. Sealed tubes containing water and Zn are then placed in a muffle furnace for 10 min at 480°C. Under these conditions the reaction between Zn and H_2O goes to
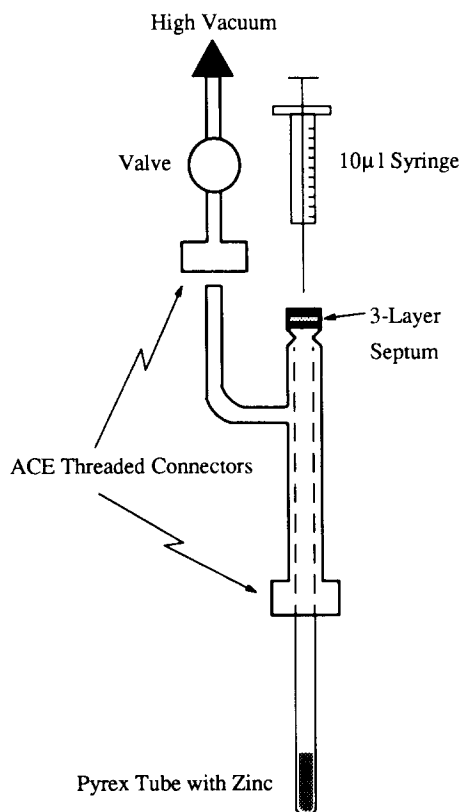

Fig. 1. Schematic representation of the apparatus used for the hydrogen isotope analysis of water samples.

completion, producing ZnO and a quantitative yield of H_2. Subsequently the cooled tubes are cracked in vacuum on the mass spectrometer and the product H_2 is analyzed for its hydrogen isotope composition. Results of some routine analyses of our in-house reference water and several standards are given in Table 1. The reference gas was calibrated using SMOW and SLAP (Standard Light Antarctic Precipitation), analyzed in the same fashion. We have stored reacted tubes at room temperature for up to 2 months without noticing any change in δD-value of the contained gas. This technique can also be used for accurate D/H measurements of brines but, unlike for samples of pure water, it requires occasional cleaning of the plugs and the interior walls of the glass apparatus to remove any residual salts. If the same syringe is used for a set of different

TABLE 1

D/H analyses of water

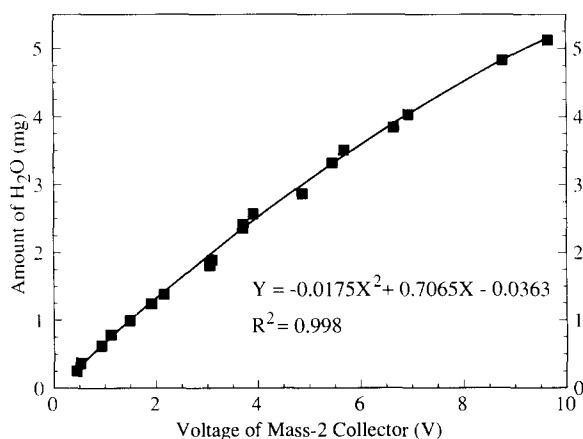| Sample	δD (‰ vs. SMOW)		1σ	n
	expected	measured		
MDIW (in-house standard)	−58	−58	0.5	18
Inter-1	−96	−96	0.8	2
Inter-2	−127	−128	−	1
Inter-4	−85	−86	0.5	2
Inter-5 (brine)	−80	−81	0.7	2
Inter-6 (brine)	−33	−33	0.6	2

n = number of analyses.

Fig. 2. Typical volume calibration curve of the inlet of the mass spectrometer (Finnigan® Mat-Delta S).

samples, it is advisable to purge the syringe with water from the next sample to be injected.

For the volume calibration of the inlet of our mass spectrometer (Finnigan® Mat-Delta S), weighed amounts of distilled water are reacted with Zn by the method just described and the H_2 produced is expanded into a constant volume of the mass spectrometer sample inlet (Pyrex® tube length = 20 ± 1 cm). For a fixed volume, the voltage on the mass-2 collector is proportional to the quantity of H_2O. This procedure is repeated for different amounts of water to establish a calibration curve (Fig. 2). The quantity of H_2O from unknown samples is determined directly from the calibration curve with a precision of better than ± 0.1 wt%.

The calibration curve is checked periodically to assure that source conditions of the mass spectrometer remain constant.

2.2. Pyrex® vs. quartz or Vycor® tubing

Experiments conducted to test for hydrogen isotope exchange between possible hydrogen-bearing phases in the glass and hydrogen produced by the reduction of water within the glass tubes are summarized in Table 2. In agreement with the observations by Kendall and Coplen (1985), a change of 1–2‰ in the δD-values of hydrogen gas within Pyrex® tubes is noticeable for reaction times exceeding 1 hr. A similar change in δD-value is also observed for very small samples (< 0.5 mg H_2O) heated for 10–20 min at 480°C. For Pyrex® tubes containing H_2, Zn and ZnO and held at 300°C, a decrease in δD of up to ∼20‰ was observed after 65–86 hr. However, no change in yield is observed, suggesting that no hydrogen has been lost by diffusion through the glass. In contrast to the behaviour in Pyrex®, δD-values of hydrogen in quartz and Vycor® tubes are not significantly changed after 1 hr at 480°C and only a small change (∼2–4‰) is observed for extended periods at 350°C (Table 2). However, significant loss of hydrogen by diffusion through quartz and Vycor® glass is indicated by low yields. It is possible that the small shift towards more positive δD-values for hydrogen held in quartz and Vycor® tubes for extended periods at temperatures of 300°C is a result of the preferential diffusion of protium relative to deuterium. Furthermore, even for reaction periods of only 10 min, there appears to be a 1–2‰ shift between δD-values of hydrogen produced in Pyrex® relative to quartz and Vycor® tubes. It is likely that this difference may be a function of borosilicate glass containing significant amounts of hydrogen which is available for exchange with the hydrogen gas produced by reduction of H_2O (Kendall and Coplen, 1985). Effects of this hydrogen isotope exchange can be minimized or effectively

TABLE 2

D/H exchange and diffusion of H_2 in Pyrex®, quartz and Vycor® tubes (all using MDIW = $-58‰$)

Sample	Amount of H_2O (mg)	Reaction time (^{h} ^{m})	Temperature (°C)	δD (‰) (‰ vs. SMOW)	Yield (%)
(A) Pyrex® tubes:					
1	~2	0:30	480	−58	−
2	~2	1:00	480	−61	−
3	1.63	24:15	300	−73	99
4	~2	40:45	300	−74	−
5	2.16	49:00	300	−77	101
6	~2	65:50	300	−81	−
7	2.27	86:50	300	−75	101
(B) Quartz tubes:					
1	~2	0:30	480	−56	−
2	~2	1:00	480	−56	−
3	2.26	26:00	350	−54	95
4	1.45	69:00	350	−52	82
5	2.19	86:50	300	−46	94
(C) Vycor® tubes:					
1	2.81	0:30	480	−57	99
2	2.75	88:50	350	−55	77
3	2.80	133:50	350	−52	65

eliminated by using samples with $\gtrsim 1$ mg H_2O, or alternatively using quartz or Vycor® tubes.

2.3. D/H analyses of minerals and whole rocks

The extraction line used for the D/H analysis of minerals is illustrated in Fig. 3. Weighed amounts of hydrous minerals are loaded into ~12-cm-long quartz tubes (6-mm o.d., 4-mm i.d.) which have been roasted at 800°C and stored at 110°C prior to use. A sufficient amount of mineral is loaded to obtain $\gtrsim 1$ mg H_2O. As a first approximation, the amount of water can be estimated from stoichiometry. We have run samples providing as little as 0.5 mg H_2O (e.g. ~15 mg of NBS-*30* @3.5 wt% H_2O) and obtained accuracy and precision similar to those for larger samples (see Table 3). About 100–200 mg of coarse-grained (~800 μm) quartz, which was previously decrepitated in a vacuum at 1100°C, are then loaded above the

sample followed by a small wad of quartz wool (pre-roasted at 800°C). Addition of the quartz grains is a key aspect of the method. Most importantly it prevents collapse of the tube on heating, but also helps retain powders in the bottom of the tube during initial stages of degassing and can aid in lowering the temperature of water release by chemical reaction with the sample. In our system four samples thus loaded are attached to the extraction line via ACE®,* threaded glass connectors and evacuated simultaneously at 150°C by use of a pre-drilled aluminium heating block and a heating plate. At the same time, four Pyrex® tubes (20 cm long; 6-mm o.d.; 4-mm i.d.; pre-roasted at 500°C) containing weighed amounts of Zn are also evacuated, as is the cupric oxide (CuO wire), which is packed into a quartz glass tube joined to the system via waxed ball and socket

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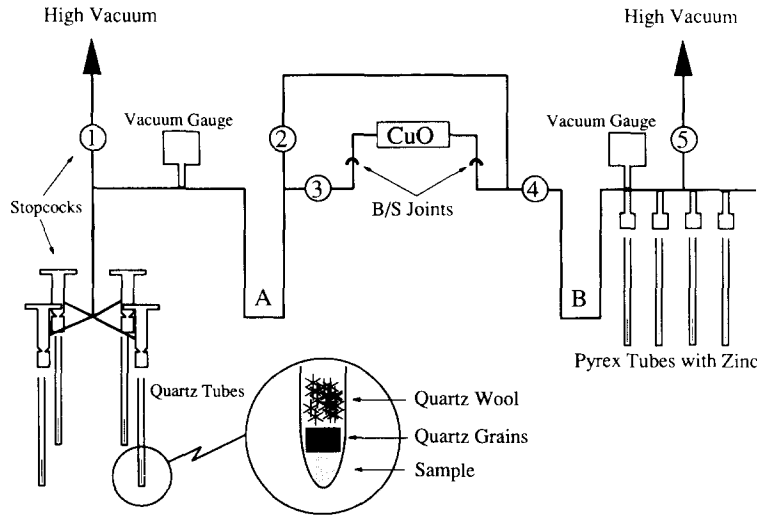*ACE Glass, Inc., Vineland, New Jersey, U.S.A.

Fig. 3. Schematic representation of the vacuum extraction line used for the quantitative conversion of H_2O to H_2 for hydrogen isotope analysis of hydrous minerals and rocks. Overall horizontal distance is ~ 80 cm. All glass tubing consists of borosilicate glass (12-mm o.d.; traps A and B 10-mm o.d.) except for the section containing the CuO, which is made from 12-mm (o.d.) quartz tubing. Stopcocks are high-vacuum O-ring types with a Teflon® plug (0–5-mm orifice; ACE Glass, Inc., Vineland, New Jersey, U.S.A.).

ground glass joints (*18/9* type). The CuO is held in place by quartz-wool plugs and heated to 700°C by a high-temperature heating tape. Once the samples are completely degassed (commonly ~ 2 hr in our system), all stopcocks to the sample tubes are closed except for that of the tube containing the sample to be extracted. The line is closed off from the pumping system (stopcocks *1* and *5*), the bypass is isolated (stopcock *2*) and liquid nitrogen is added to the bottom 1/3 of traps A and B. The sample contained in the quartz tube is then heated using a fuel–gas–oxygen torch (we have measured temperatures of $> 1400°C$ inside the tube). To avoid heating the other samples and any background items, a graphite plate is held behind the sample tube during heating. Water released during heating is collected in trap A while hydrogen, which may be formed by reaction of released water with Fe in the sample, is oxidized by CuO held at 700°C and condensed in trap B as H_2O. Production of small amounts of hydrogen are particularly common for mafic samples (e.g., Kyser and O'Neil, 1984). Samples are heated until no further

change in pressure is indicated by the vacuum gauge in front of trap A. Reaction times are commonly ~ 3–4 min, or ~ 10 min in the case of large samples and/or whole rocks. While the quartz grains placed above the sample will prevent the quartz tube from collapsing, care must be taken to avoid heating above the quartz grains as the tube will readily collapse under vacuum.

Once the sample is completely dehydrated as evidenced by the reading on the vacuum gauge, traps A and B are topped-off and any non-condensible gases remaining are pumped out via stopcock *5*. After evacuation of the non-condensible gases, stopcock *5* is closed, the stopcock to the first sample tube is closed and the liquid-nitrogen trap at A is replaced by an acetone–dry ice (or similar temperature) slush trap and the non-condensibles are passed through the CuO and frozen at liquid-nitrogen temperatures in trap B. Thereafter, stopcock *3* is closed, *2* is opened and the slush removed. The released H_2O is then transferred into trap B, bypassing the CuO. During transfer the line is heated with a heat gun. The by-pass reduces

TABLE 3

D/H analyses of minerals

Mineral	Source*	Expected		Measured					
		δD (‰ vs. SMOW)	H_2O (wt%)	δD (‰ vs. SMOW)	1σ	n	H_2O (wt%)	1σ	n
Biotite-1 (NBS-30)		−65	3.50	−64	1.4	10	3.49	0.06	10
Biotite-2	[1]	−84	2.48	−82	1.8	3	2.53	0.01	3
Biotite-3	[2]	−62	3.53	−60	−	1	3.62	−	1
Muscovite-1	[2]	−46	?	−46	1.2	4	4.24	0.08	4
Muscovite-2	[3]	−64	2.70	−57	0.6	2	3.32	0.04	2
Hornblende-1	[4]	−84	2.02	−81	0.5	3	2.06	0.08	3
Hornblende-2	[4]	−102	1.46	−108	1.5	3	1.45	0.02	3
Hornblende-3	[4]	−62	1.86	−55	−	1	1.77	−	1
Hornblende-4	[4]	−85	1.69	−79	−	1	−	−	−
Chlorite	[3]	−83	10.10	−66	0.7	3	11.20	0.02	3
Kaolinite/quartz	[5]	−46	?	−47	1.6	2	7.08	0.01	2
Kaolinite	[5]	−45	?	−42	0.8	2	13.38	0.15	2
Tourmaline	[3]	−36	2.40	−58	2.0	2	2.92	0.06	2
Alunite-1	[5]	−23	?	−21	1.0	2	13.21	0.50	2
Alunite-2	[5]	−25	?	−25	2.0	2	11.90	0.01	2

n = number of samples; ? = wt% H_2O unknown; − = not determined.
*Sources: see text.

the time taken for the extraction, as passing H_2O through the CuO heated to 700°C is relatively slow. For all of our work so far, no difference in yield nor δD-value has been observed between H_2O that is bypassed and H_2O that is moved through the CuO. After complete transfer of H_2O into trap B (~5 min), stopcock 4 is closed, the Dewar containing liquid nitrogen is exchanged by one containing a dry ice–acetone slush and any non-condensible gases are pumped out via stopcock 5 (or may be collected, for example, CO_2 released from crystallographic sites of the mineral). The H_2O is subsequently transferred into a labelled Pyrex® tube containing Zn.

The above procedure is then repeated for the other three samples. The extraction of four degassed samples takes ~2–2.5 hr. Once sealed in the Pyrex® tubes containing Zn, the tubes are inserted into a muffle furnace at 480°C for 10 min and are then ready for mass-spectro-

metric analysis, including measurements of water contents as described above.

Typical results for a number of different minerals analyzed during the past year with this procedure are given in Table 3. The reported δD-values and water contents in Table 3 were obtained for different splits of the same mineral separates that were analyzed in other laboratories within the last few years by a conventional uranium procedure. These laboratories include the Stable Isotope Laboratories of the California Institute of Technology, United States Geological Survey (Menlo Park and Denver), University of Utah, and the University of Saskatoon. These laboratories are not identified in the table. In general, the method described here provides results for δD and water contents that are in good agreement with, and of comparable precision (±1–2‰) to those obtained by the conventional uranium technique. Where differences exist, the sam-

ples analyzed by our method, provide higher concentrations of H_2O for all minerals analyzed (chlorite, muscovite and tourmaline). As most of these samples were analyzed in parallel with at least one NBS-*30*, whose δD and wt% H_2O duplicated well, any significant differences in δD or H_2O content are likely to be a function of incomplete H_2O extraction in other laboratories or, alternatively, a function of different laboratory volume and δD calibrations.

2.4. Special cases and some problems

Over the last two years, the method described in this paper has been used successfully by a large number of researchers on a wide spectrum of minerals including muscovite, biotite, phlogopite, chlorite, epidote, tourmaline, hornblende, actinolite, pyrophyllite, kaolinite, montmorillonite, smectites, axinite, ilvaite ($CaFe_{2+}3Fe^{3+}O(Si_2O_7)(OH)$) and basaltic and granitic–granodioritic whole-rock samples. In only two cases, ilvaite and occasional mixed smectite–montmorillonite samples, the latter apparently containing minor Fe- and Ti-oxides, did we encounter the problem of substantial reaction between the sample and the quartz tube, which can cause a break in the vacuum. In the case of ilvaite, a low-temperature (low oxygen) flame was found to release all the water and eliminate severe reaction with the quartz tube. In the case of the mixed smectite–montmorillonite samples $\sim 2/3$ sample were ground with $\sim 1/3$ quartz grains (degassed at $1100°C$) to provide excess reagent silica and then reacted in the normal way, producing results identical to those of similar samples not containing the Fe- and Ti-oxides. This procedure prevents the quartz tube from cracking.

For some whole rocks or mineral separates where large amounts of material are required ($\geqslant 70$ mg), the partially melted quartz tube may develop fractures upon cooling. To avoid atmospheric contamination which may result from fracturing of the reagent tube, the stop-cock directly above the sample should be closed shortly after fusing the sample. As all H_2O will have been removed from the small quartz tube, isolation of this part will not in any way affect the results.

Alunite, which produces significant quantities of acid (sulfurous?) upon rapid heating as a result of the simultaneous release of H_2O and SO_2, is also treated in a special way. This treatment is commonly off-line to the extraction system shown in Fig. 3 as H_2SO_4 is not volatile in a vacuum system and once added has to be washed out with water. Furthermore, the released acid also reacts with the FETFE®,* O-rings used on the Teflon® stopcocks. Slow but gradual step-heating of alunite from 300° to 650°C over a period of ~ 1 hr, using a small resistance furnace, will maximize the release of H_2O and minimize release of SO_2. The water thus extracted is then distilled into Pyrex® tubes containing Zn.

Fluid inclusion water can be extracted on the same system but the large amounts of material commonly required will necessitate the use of large quartz tubes ($\geqslant 10$ mm) and should be heated with resistance furnaces (maximum temperatures $\sim 1150°C$).

3. Conclusions

The method for the quantitative extraction and conversion of H_2O from minerals using zinc reagent as described in this paper is an attractive alternative to the conventional techniques based on uranium (e.g., Bigeleisen et al., 1952). It provides comparable precision and accuracy relative to the conventional technique and is also relatively inexpensive and simple as it eliminates the need for an induction furnace, Toepler® pump, manometer, expensive metal foil and crucibles and complex cleaning procedures of the equipment involving dangerous acids. The technique described in this paper can be performed in almost any

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*ACE Glass, Inc., Vineland, New Jersey, U.S.A.

laboratory where a vacuum system, a torch and a muffle furnace are available. Furthermore, the hydrogen extracted from minerals and rocks can be stored for significant lengths of time and sent to other laboratories for mass-spectrometric analysis of the H_2.

Acknowledgements

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