



# Oxygen and hydrogen isotope analysis of experimentally generated magmatic and metamorphic aqueous fluids using laser spectroscopy (WS-CRDS)

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## ABSTRACT

We report a new procedure for the analysis of oxygen and hydrogen isotopes in water that is experimentally produced in high-temperature high-pressure experiments via wavelength-scanned cavity ring down spectroscopy (WS-CRDS). This work builds on a recently developed method by Affolter et al. (2014) for the analysis of fluid inclusions in cave carbonate deposits. We show that a simple modification of the setup allows extraction and analysis of experimentally produced fluids from their noble metal capsules in an online water extraction line, and analyse them without further treatment of the water molecule prior to isotope determination. We tested this method on standard water reference samples and water experimentally generated during thermal decomposition of hydrous minerals in hydrothermally altered rocks. Preliminary results indicate that fluids released from hydrothermally altered rocks at conditions of 640 °C and 100 MPa maintain isotopic compositions close to those of the meteoric water involved in their alteration. Further development and application of this method will offer great insights into the origin and evolution of water in magmatic and metamorphic systems, and be a valuable tool in the determination of experimentally derived fluid-melt and fluid-mineral isotope fractionation.

## 1. Introduction

Stable isotope analysis is an important tool for tracking the origin and evolution of fluids present at different depth levels in the Earth's atmosphere, crust and mantle, ranging from water condensate preserved in cave carbonates and meteoric and seawater at the Earth's surface, over shallow groundwater to deeper aqueous magmatic and metamorphic fluids and brines and COH-fluids at mantle depths. These fluids can either be measured directly as water samples (Pärn et al., 2018) or as fluid inclusions preserved in speleothems (Affolter et al., 2019), marine carbonates (Dassié et al., 2018), or magmatic and metamorphic minerals (Jenkin et al., 1994; Wilkinson et al., 1995). More commonly these fluids are measured indirectly through the analysis and recalculation from

stable isotope compositions of rocks and minerals that these fluids exchanged with (Criss and Taylor, 1983; Fekete et al., 2016). These recalculations rely on fluid-mineral isotope fractionation factors determined from theory (e.g. Zhao and Zheng, 2003) or from experiments conducted over a suitable range of pressure and temperature conditions (Clayton et al., 1972; Kueter et al., 2020; Matsuhisa et al., 1979). However, due to the limited volumes, these experimentally generated fluids are rarely analysed directly and their isotopic compositions are usually inferred from mass-balance of the starting material and mineral products.

Traditionally, direct analysis of water and fluid inclusion samples has been conducted via isotope ratio mass spectrometry (IRMS) techniques by equilibration with CO<sub>2</sub> (Epstein and Mayeda, 1953) or conversion to

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a suitable gas (Dennis et al., 2001; Sharp et al., 2001). Over the past decade, laser spectroscopy has evolved into a reliable and precise alternative method for the analysis of stable isotope compositions of pure water (e.g. Brand et al., 2009; de Graaf et al., 2020). For bulk fluid inclusion analysis, both IRMS and laser spectroscopic techniques have been used as online methods (Affolter et al., 2014; Dassié et al., 2018; Uemura et al., 2016; Vonhof et al., 2006), whereby a crushing or extraction device is coupled directly to the analytical instrument, allowing more accurate and precise results. So far, however, these online techniques have not yet been commonly applied to the extraction and analysis of fluids or gases from experimental capsules (one notable exception being COH-fluids analysed by Kueter et al., 2019; Kueter et al., 2020), where small fluid volumes and the need for an opening and extraction mechanism pose similar analytical challenges. In this study, we introduce an analytical setup for the extraction of water from experimental capsules and subsequent online analysis for O and H isotope ratios via wavelength-scanned cavity ring-down laser spectroscopy (WS-CRDS), further developed from an online laser spectroscopic method for bulk fluid inclusion analysis of speleothems by Affolter et al. (2014). We evaluate this method by various tests with isotopically characterised reference water samples and apply this technique to experiments involving near-solidus heating of hydrothermally altered low- $\delta^{18}\text{O}$  rock. Finally, we compare our new method to other commonly used techniques, and assess its potential in tracing the source and evolution of these fluids by their stable isotope compositions.

## 2. Methods

### 2.1. Preparation of test capsules

To test the extraction of fluids from experimental capsules, a total of 14 capsules (4 mm outer diameter, 22 mm length) were prepared from Au tubes. The capsules were subdivided into three “test-water” capsules (designated TW) containing standard water of known isotopic composition only, nine “test-sand” capsules (TS) containing standard water and analytical-grade quartz sand, and one capsule with hydrothermally altered material (D-005-10) that had been experimentally heated (see Section 2.2). Both TW and TS capsules were loaded with ca. 6  $\mu\text{l}$  of one of the water samples listed in Table 1. All  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in this study are given relative to Vienna Standard Mean Ocean Water (V-SMOW). The TS capsules were additionally loaded with analytical grade quartz sand in order to simulate a simple rock-fluid system. After being crimped close and welded shut with an arc welder, all capsules were tested for leakages by weighing, heating them to 110 °C overnight and reweighing; only capsules remaining within 0.05 mg of the original weight were used for further analytical tests.

**Table 1**  
Deionised water samples used for extraction tests.

Water sample	n	$\delta^{18}\text{O}$ (‰)	$\delta\text{D}$ (‰)
<b>Std 1</b>			
CO <sub>2</sub> equilibration (ETHZ)	1	-11.4	
Picarro autosampler (Uni Bern)	1	-11.4	-83.0
Picarro injection (Uni Bern)	5	-11.1	-79.5
Avg $\pm$ 2 SD		-11.3 $\pm$ 0.3	-81.3 $\pm$ 5.0
<b>Std 2</b>			
CO <sub>2</sub> equilibration (ETHZ)	1	-4.6	
Picarro autosampler (Uni Bern)	1	-4.6	-60.9
Picarro injection (Uni Bern)	2	-4.4	-60.8
Avg $\pm$ 2 SD		-4.5 $\pm$ 0.2	-60.8 $\pm$ 0.1
<b>Std 3</b>			
CO <sub>2</sub> equilibration (ETHZ)	1	35.7	
Picarro autosampler (Uni Bern)	1	33.4	70.5
Picarro injection (Uni Bern)	3	34.1	70.8
Avg $\pm$ 2 SD		34.4 $\pm$ 2.4	70.7 $\pm$ 0.4

### 2.2. Dehydration experiment

To test our setup with a realistic experimentally generated fluid, a dehydration experiment was run on a sample of hydrothermally altered dacitic tuff (sample CH 14005 from Troch et al. (2020)). Sample CH 14005 has a whole-rock  $\delta^{18}\text{O}$  value of -3.8 ‰ and a bulk water content of 2.5 wt%. It contains the mineral assemblage quartz ( $\delta^{18}\text{O}$  +9.1 ‰), plagioclase and alkali feldspar ( $\delta^{18}\text{O}$  +0.6 ‰) and chloritised biotite (no  $\delta^{18}\text{O}$  data available) in devitrified groundmass. The powdered and homogenised starting material was loaded into an Au capsule of 4 mm outer diameter and 22 mm length. The open capsule was dried overnight at 110 °C in air before being crimped closed and welded shut with an arc welder. The capsule was tested for leaks the same way as previous test capsules. The dehydration experiment was run in an Ar-pressurised fast-quench externally heated pressure vessel (MHC) at ETH Zurich, at conditions of 640 °C and 100 MPa for 24 h. Exposure to run temperature and rapid cooling to room temperature occurred within seconds by tilting the apparatus vertically, so that the capsule fell from the water-cooled cold end of the rod into the hot zone or vice versa. During the experiment, the vessel was kept quasi-horizontally (10°).

### 2.3. Water extraction and analysis

The setup for water extraction and analysis consists of a simple extraction cell coupled to a Picarro L2140-i analyser, as outlined in detail in (Affolter et al., 2014; Affolter et al., 2015) and shown in Fig. 1. The entire line (Swagelok 1/8" stainless steel) is flushed with dry nitrogen and is kept at a constant temperature of 140 °C and pressure of 0.58 bar above atmospheric pressure (1.58 bar) in order to prevent oxygen and hydrogen isotopic fractionation during water condensation. A stable water background is generated by constant injection and mixing of internal standard water (ST-08) with known  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values. A stainless-steel capillary purge reduces the incoming water signal by releasing a dry nitrogen/water vapour mixture. A syringe injection unit located in front of the extraction cell allows different standard reference water samples to be added for calibration and quality control. Reference water samples used in the course of this study were also analysed using this interface and are referred to as “Picarro injection” in Table 1.

Connected to the line, the extraction cell consists of a copper tube, which holds the sample and deforms in a ductile manner without breaking when squeezed by a hydraulic press (in this case a Power Team P12 hydraulic press exerting a pressure of ca. 200 bar or force of 10,000 N on the Cu-tube). A 7  $\mu\text{m}$  Swagelok online filter placed after the Cu-tube prevents sample pieces from travelling through the line and damaging the laser spectrometer. Compared to the original setup, a few modifications were made for the extraction of water from experimental capsules. In order to efficiently open the experimental capsule, the capsule is mantled with multiple stainless-steel retaining rings (here we use three to four Seeger rings of an inner diameter of 3.5 mm, Fig. 1). When squeezed within the copper tube, these rings easily cut through the soft and easily deformable noble metal capsule material, so that water vapour from the capsule can efficiently be extracted. One run was conducted by inserting a rock fragment of sample CH 14005 into the Cu-tube without a confining capsule, in order to test whether this sample contained any pore water. The copper tube is squeezed by applying a pressure of ca. 200 bar on the tube via a hydraulic press.

### 2.4. Additional isotope analyses

In order to characterise the three water samples used in this study for their oxygen and hydrogen isotope compositions, they were additionally analysed via the Picarro L2140-i coupled to an autosampler at the University of Bern and by traditional CO<sub>2</sub> equilibration in the Climate Geology Stable Isotope Laboratory at ETH Zurich.

For liquid water analysis via Picarro autosampler mode, aliquots of 2 ml of water are filled in glass vials and sealed with aluminium caps

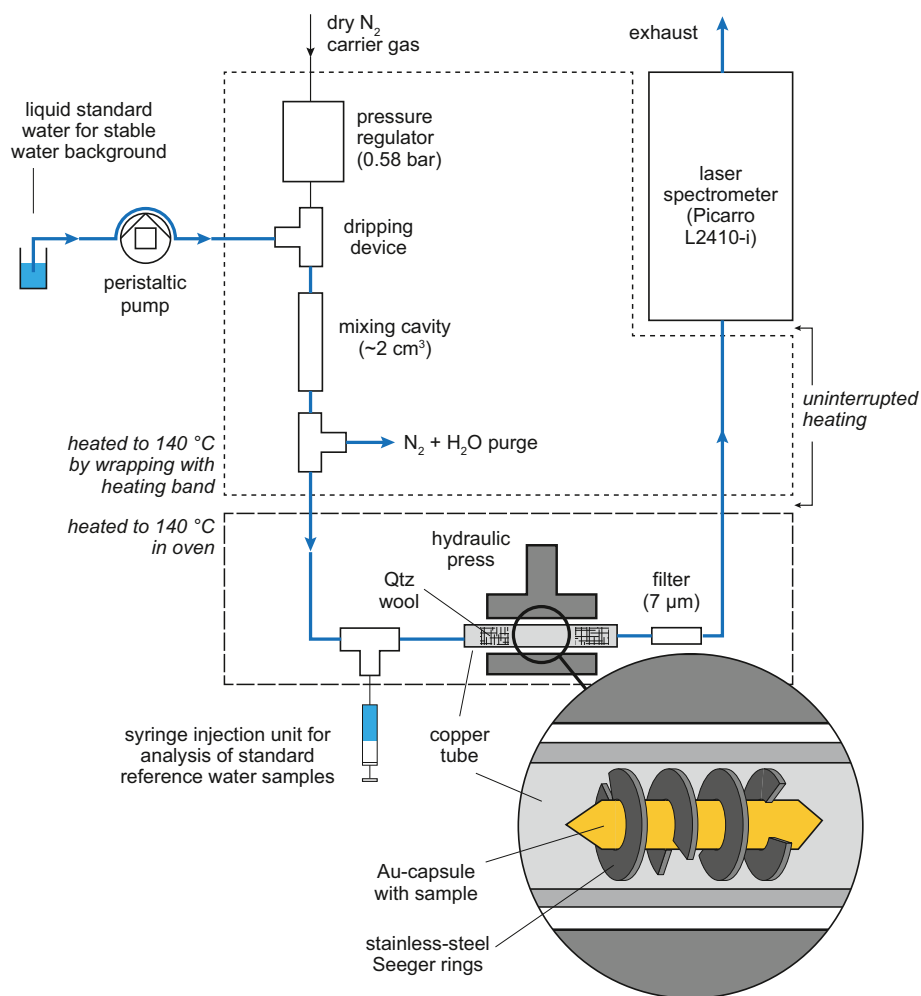


Fig. 1. Schematic setup of online extraction line coupled to laser spectrometer (modified after Affolter et al., 2014).

including inner rubber. The vials are then placed in a PAL COMBI-xt autosampler (CTC Analytics AG, Zwingen/Switzerland), which is connected to the analyser. Following the analysis, a syringe pumps and injects six times directly into the vapourisation unit of the analyser. Due to memory effects, the first three values are discarded. Reproducibility of measurements is  $\pm 0.1$  ‰ for  $\delta^{18}\text{O}$  and  $\pm 0.5$ – $1.0$  ‰ for  $\delta\text{D}$ . These values are referred to as “Picarro autosampler” in Table 1.

For the  $\text{CO}_2$  equilibration method at ETH Zurich, 200  $\mu\text{l}$  of water were pipetted in 12 ml septum-capped vials, which were subsequently filled with a mixture of 0.3 %  $\text{CO}_2$  and He. After equilibration at 25 °C for at least 18 h, the  $\text{CO}_2/\text{He}$  mixture was measured using a Gas Bench II connected to a Delta V plus isotope ratio mass spectrometer (both ThermoFisher Scientific, Bremen, Germany). The system is calibrated with the international standards SMOW, SLAP and GISP. Within the range of these standards, reproducibility of the measurements based on repeated measurements of an internal standard was better than 0.06 ‰. We note that the maximum  $\delta^{18}\text{O}$  value of these reference waters is 1.6 ‰, leading to a larger uncertainty for the isotopically heavy Std 3 due to stretching of the scale.

Additionally, whole-rock oxygen and hydrogen isotope compositions of the hydrothermally altered starting material for the dehydration experiment were analysed via conventional silicate fluorination and hydrogen extraction in the Stable Isotope laboratory at the University of Cape Town, following the procedures outlined in Curtis et al. (2013). The typical precision for  $\delta^{18}\text{O}$  is  $\pm 0.2$  ‰, for  $\delta\text{D}$   $\pm 4$  ‰, and for  $\text{H}_2\text{O}$  contents  $\pm 0.2$  wt% (all 2 SD).

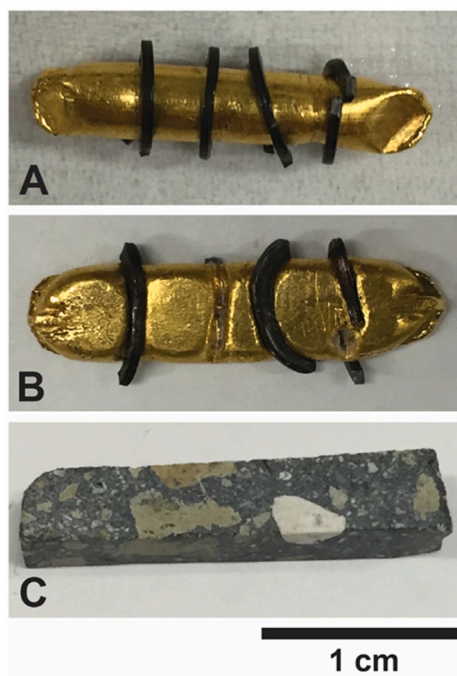
### 3. Results

#### 3.1. Capsule opening

In all but one case, the stainless-steel Seeger rings successfully lacerated the noble metal capsules. The cutting was sharp and opened the capsule in multiple locations along the sample (Fig. 2B), allowing to recover water from the test capsules. One of the TW capsules deformed without being lacerated when squeezed in the copper tube and thus did not allow water recovery (Table 3), possibly due to the large air volume in the TW capsules. The necessity for the Seeger rings was demonstrated by one test run, whereby one of the TS capsules was squeezed without Seeger rings, resulting in deformation and considerable flattening of the capsule without opening.

#### 3.2. Oxygen and hydrogen isotopic compositions of extracted water

Analysis of water samples extracted from noble metal capsules containing only water results in  $\delta^{18}\text{O}$  values of  $-11.0$  ‰,  $-3.5$  ‰, and  $+33.8$  ‰, and  $\delta\text{D}$  values of  $-78.4$  ‰,  $-59.4$  ‰, and  $+71.5$  ‰ (Table 3) for the three different water samples with average reference  $\delta^{18}\text{O}$  values of  $-11.3$  ‰,  $-4.5$  ‰, and  $34.4$  ‰, and  $\delta\text{D}$  values of  $-81.3$  ‰,  $-60.8$  ‰, and  $+70.7$  ‰ (Table 1), respectively. Analysis of water samples extracted from noble metal capsules containing both water and quartz sand results in average  $\delta^{18}\text{O}$  values of  $-10.5$  ‰,  $-3.1$  ‰, and  $+33.1$  ‰, and average  $\delta\text{D}$  values of  $-78.8$  ‰,  $-57.4$  ‰, and  $+69.0$  ‰ (Table 3). A comparison of oxygen and hydrogen isotope compositions of the



**Fig. 2.** (A) initial Au-capsule filled with water and quartz sand and mantled with four stainless-steel Seeger rings, (B) the same capsule after being squeezed within the copper tube by the hydraulic press at 200 bar. Note the deformation of the noble metal underneath the harder Seeger ring. The sand is hard to see in the photo due to the limited colour contrast but is visible through holes in the Au-capsule. Most capsules are cut completely into separate pieces during this process. (C) Rock fragment of sample CH 14005 prior to being crushed in the copper tube without confining capsule in order to test for pore water. Scale refers to all three images.

extracted water with independently analysed water samples suggests that the deviation from reference values is slightly larger for capsules containing both water and quartz sand (TS) compared to capsules containing only water (TW) (deviations for  $\delta^{18}\text{O} \pm 1.4\text{‰}$  (TS) compared to  $\pm 1.0\text{‰}$  (TW), for  $\delta\text{D} \pm 3.4\text{‰}$  (TS) compared to  $\pm 2.9\text{‰}$  (TW)). However, overall the results agree well with average reference values, and both isotope systems do not reveal significant bias towards higher or lower  $\delta^{18}\text{O}$  or  $\delta\text{D}$  values.

Water extracted following the experimental dehydration of sample CH 14005 has a  $\delta^{18}\text{O}$  value of  $-11.6\text{‰}$ , significantly lower than its whole-rock  $\delta^{18}\text{O}$  value ( $\delta^{18}\text{O} = -3.8\text{‰}$ , Table 2). The  $\delta\text{D}$  value of the extracted water is  $-141.6\text{‰}$ , similar to the whole-rock  $\delta\text{D}$  value of the hydrothermally altered starting material ( $\delta\text{D} = -130\text{‰}$ , Table 2).

### 3.3. Extracted water contents

WS-CRDS laser spectroscopy is primarily designed for the determination of isotope ratios, but the total amount of extracted  $\text{H}_2\text{O}$  can be

**Table 2**  
Stable isotope composition of hydrothermally altered experimental starting material.

Sample	$\delta^{18}\text{O}$ (‰)	$\delta\text{D}$ (‰)	wt% $\text{H}_2\text{O}$	Ref
<i>Whole-rock analyses</i>				
Bulk	$-3.8 \pm 0.3$		$2.6 \pm 0.3$	Troch et al. (2020) this study
Bulk		$-130 \pm 4$	$2.5 \pm 0.2$	
<i>Mineral analyses</i>				
Feldspar	0.61			Troch et al. (2020)
Quartz	9.09			Troch et al. (2020)

all uncertainties are 2 SD.

estimated from integration of the bulk  $\text{H}_2\text{O}$  signal during analysis. For standard injection with syringes and crushing of speleothems, we usually achieve a precision better than  $0.1\ \mu\text{l}$  (Affolter et al., 2014). Although extracted water volumes in this study are generally similar to those originally added to the capsule, they sometimes show large deviations, with average gains of  $0.3\ \mu\text{l}$  ( $n = 8$ ) and average losses of  $1.7\ \mu\text{l}$  ( $n = 3$ ) compared the original value. It is difficult to explain why in some cases, seemingly more water was extracted from the capsules than was originally added. The general reproducibility of the isotopic compositions argues against large-scale loss or evaporation of water during capsule preparation, and deviations generally exceed the uncertainty of analytical-grade scales (repeatability  $\pm 0.015\ \text{mg}$ , linearity  $\pm 0.08\ \text{mg}$  for Mettler Toledo AX205 laboratory scale). Until further investigation, we therefore interpret the scatter as representing the general uncertainty for water contents determined through this method. From the capsule of the dehydration experiment,  $3.8\ \mu\text{l}$   $\text{H}_2\text{O}$  were extracted, corresponding to  $\sim 70\%$  of the total mineral-bound water in the hydrothermally altered rock sample as determined from Karl-Fischer titration (Troch et al., 2020; Troch et al., 2018) and during hydrogen isotope analysis (Table 2).

## 4. Discussion

### 4.1. Method validation through test capsules

We show that a simple modification of the online extraction line through the use of retaining rings allows water to be extracted from experimental noble metal capsules, without significant isotope fractionation. The combination of gold capsules and stainless-steel rings seems to be particularly efficient for capsule laceration due to the great contrast in hardness, however, other soft noble metals commonly used in experiments, such as silver or gold and silver alloys (AgPd, AuPd etc.) may be similarly suitable. Key for effective capsule opening is the use of tightly fitted rings and sufficient inner capsule pressure, in order to avoid deformation of the capsule without opening. Enough inner capsule pressure can be generated by sufficient filling of the capsule with solid or liquid sample material.

Comparison between the initially added and subsequently extracted water volumes (Table 3, see Section 3.2) suggests near-complete extraction of water for most TW and TS capsules ( $\pm 0.2\ \mu\text{l}$ , corresponding to a recovery of 97%). Incomplete extraction or kinetic effects during gas transport would be expected to result in lower oxygen and hydrogen isotope ratios in the extracted water compared to reference compositions (Table 1), however, we do not observe significant deviations of analysed water compositions towards systematically higher or lower  $\delta^{18}\text{O}$  or  $\delta\text{D}$  values (Table 3). Oxygen isotopic compositions of water extracted from capsules containing water only (TW) are generally closer to the reference  $\delta^{18}\text{O}$  value compared to water extracted from capsules containing both water and quartz sand (TS; Fig. 3), which could indicate some exchange between water and quartz ( $\delta^{18}\text{O}_{\text{Qtz}}$  ca.  $+9\text{‰}$ ). However, the extremely slow diffusion rates for oxygen in quartz (e.g. Gilletti and Yund, 1984) and the fact that prior to extraction, the capsules were never exposed to temperatures  $>110\text{ °C}$  make such an exchange unlikely. The general correlation between the deviations of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  towards either isotopically lighter or heavier compositions also rules out such an effect (e.g. analysis of Std 2 water + sand experiments result in higher values for both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  compared to reference value, analysis of Std 3 water + sand experiments results in lower values for both  $\delta\text{D}$  and  $\delta^{18}\text{O}$  (Fig. 3)), as exchange between  $\text{H}_2\text{O}$  and anhydrous  $\text{SiO}_2$  should only affect  $\delta^{18}\text{O}$  values. The correlation between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  rather suggests that these small deviations from reference values are the result of limited evaporation during the filling of the capsule and/or imperfect extraction due to adsorption on quartz and capsule surfaces, although we note that these variations do not correlate with the quantified amounts of water extracted from the capsules. We therefore interpret any deviation of single analytical runs from reference  $\delta^{18}\text{O}$  and



**Table 3**  
Results water extraction from capsules.

Sample	Name	Added H <sub>2</sub> O (μl)	δ <sup>18</sup> O (‰)	δD (‰)	H <sub>2</sub> O (μl)
<i>Capsules with reference water Std 1</i>					
<i>Target values</i>					
Std 1 only	TW-1	4.2	-11.3 ± 0.3	-81.3 ± 5.0	2.4
Sand + Std 1	TS-9	4.2	-11.0 ± 0.4	-78.4 ± 1.5	4.9
<i>Capsules with reference water Std 2</i>					
<i>Target values</i>					
Std 2 only	TW-3	4.2	-4.5 ± 0.2	-60.8 ± 0.1	1.3
Sand + Std 2	TS-1	6.0	-3.5 ± 0.4	-59.4 ± 1.5	6.0
Sand + Std 2	TS-2	5.9	-2.9 ± 0.4	-57.1 ± 1.5	5.9
Sand + Std 2	TS-3	5.8	-3.0 ± 0.4	-57.5 ± 1.5	5.9
Sand + Std 2	TS-3	5.8	-2.8 ± 0.4	-57.3 ± 1.5	5.9
Sand + Std 2	TS-6	4.6	-3.3 ± 0.4	-57.4 ± 1.5	5.3
Sand + Std 2	TS-7	4.7	-3.4 ± 0.4	-57.5 ± 1.5	5.2
Avg. Sand + Std 2	TS		-3.1 ± 0.2	-57.4 ± 0.7	
<i>Capsules with reference water Std 3</i>					
<i>Target values</i>					
Std 3 only	TW-4	4.6	34.4 ± 2.4	70.7 ± 0.4	5.5
Sand + Std 3	TS-10	4.5	33.8 ± 0.4	71.5 ± 1.5	4.8
Sand + Std 3	TS-11	3.9	32.9 ± 0.4	68.3 ± 1.5	4.8
Sand + Std 3	TS-11	3.9	33.2 ± 0.4	69.6 ± 1.5	4.8
Avg. Sand + Std 3	TS		33.1 ± 0.3	69.0 ± 1.1	
<i>Other experiments</i>					
Dehydration experiment (cap)		5.4*	-11.6	-141.6	3.8
Rock sample (w/o cap)			no water released		

\* based on a bulk water content in the sample of 2.5 wt% H<sub>2</sub>O; no additional water was added to this experiment. Target values based on average ± 2 SD from Table 1.

δD values as reflecting the general uncertainty of the method, including both the uncertainty during the preparation and extraction process and the analytical uncertainty of the Picarro instrument.

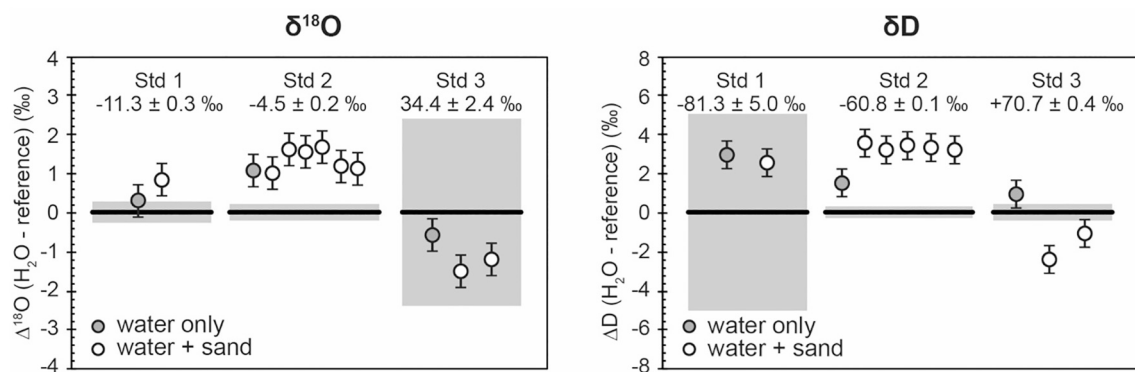
#### 4.2. Extraction and isotopic fingerprints of experimentally generated fluid

Below, we discuss results from our dehydration experiment on natural, hydrothermally altered dacite in regard to (1) the amount of fluid extracted from the experiment and variable parameters that could affect this, and (2) the isotopic composition of water released in the experiment and its source.

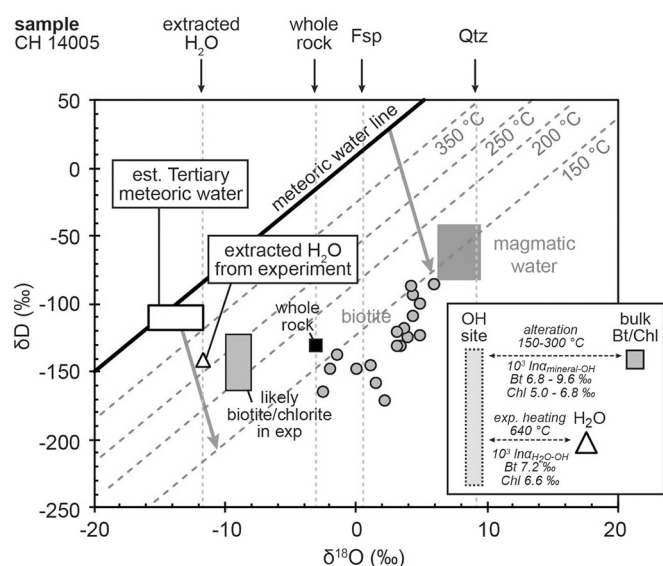
In experimental samples exposed to elevated temperatures and pressures, complete water removal from the capsule may be hindered by lower permeability compared to our test charges containing equigranular and thus highly permeable quartz sand. The bulk water concentration in the sample analysed via Karl-Fischer titration (2.62 wt%, Troch et al., 2020) suggests a total water content of 5.7 μl in the capsule, most of which is structurally bound in minerals. Detailed petrological and isotopic investigation of the natural hydrothermally altered sample used in this study and similarly hydrothermally altered rocks from the same setting suggest that most water in these rocks is bound in partially chloritised biotite (Troch et al., 2020), and more water-rich clay and

zeolite minerals make up less than 1 % of the modal mineral assemblage. Partial melting experiments at conditions of 750–1000 °C and 100–200 MPa in the same study suggest that chloritised biotite rapidly breaks down to form spinel and magnetite, a process that is likely to begin already at lower temperature. Extraction of 3.8 μl H<sub>2</sub>O (Table 3) suggests that ~70 % of total H<sub>2</sub>O were released during experimental heating to 640 °C and subsequently extracted from the sample, which agrees well with the amount of water expected from partial breakdown of chloritised biotite in our experiment. While we cannot rule out that the lower permeability of common experimental charges leads to slightly reduced extraction efficiencies compared to our test samples with quartz sand, the use of multiple perforating Seeger rings seems to be an effective means for sufficient laceration of the capsule and pathway generation within the sample during water extraction.

Hydrogen isotopes also indicate that a sufficient amount of H<sub>2</sub>O was extracted without isotopic fractionation. The δD value is in the same range as biotite data from hydrothermally altered rocks in the Challis volcanic field and Idaho batholith area (Fig. 4, Criss and Taylor (1983)), and slightly lower than Tertiary meteoric water involved in hydrothermal alteration as estimated by Criss and Taylor (1983). Both the biotite data and the isotopic composition for the extracted fluid are consistent with these samples having undergone high-temperature propylitic



**Fig. 3.** Average oxygen (left) and hydrogen (right) isotope compositions between extracted water from capsules containing either one three water standards only (TW) or water and quartz sand (TS). The results are shown as deviation from the reference values of these water samples as noted in the figure and given in Table 1.



**Fig. 4.** Oxygen and hydrogen isotopic compositions of fluid (white triangle) experimentally generated from hydrothermally altered rock (sample CH 14005) with whole rock and mineral  $\delta^{18}\text{O}$  values (Troch et al., 2020) indicated by dotted grey lines and black square. Grey circles indicate data by Criss and Taylor (1983) for biotite in hydrothermally altered rocks in the same setting, square with same colour shows likely composition of chloritised biotite in our experiment. Dashed grey lines mark isotope compositions of biotite in equilibrium with meteoric water (thick black line) at different alteration temperatures based on isotope fractionation factors by Zheng (1993) and Suzuoki and Epstein (1976); thick grey arrows mark direction of this exchange. White square symbol marks the composition of meteoric water involved in Tertiary hydrothermal fluid circulation in the Challis volcanic field and Idaho batholith area (USA), as estimated by Criss and Taylor (1983) and Chamberlain et al. (2020). Inset box shows direction and extent of oxygen isotope fractionation during alteration and experimental heating between whole biotite/chlorite and its hydroxyl site, as well as between hydroxyl site and water, based on fractionation factors by Zheng (1993).

alteration (150–350 °C, Criss and Taylor (1983)) by meteoric water that had experienced variable rock exchange towards isotopically heavier compositions. If hydrogen isotope fractionation or kinetic effects occurred during incomplete water extraction, it would result in lower  $\delta\text{D}$  values in the extracted water, because at extraction temperatures below 220 °C, protium concentrates in the vapour phase (Horita and Wesolowski, 1994). The observation that the hydrogen isotope composition of the extracted fluid matches the hydrogen isotope range in biotite from the area therefore suggests that fractionation and kinetic effects during extraction were limited.

In terms of oxygen isotopic compositions, the extracted water is significantly lower in  $\delta^{18}\text{O}$  value than biotite from Criss and Taylor (1983) and close to the estimated Tertiary meteoric water composition (Fig. 4). Biotite  $\delta^{18}\text{O}$  data from Troch et al. (2020) extend to  $\delta^{18}\text{O}$  values as low as  $-11.1$  ‰, but are not shown in Fig. 4 as they do not have any associated  $\delta\text{D}$  values. These lowest values are within error of the  $\delta^{18}\text{O}$  value of extracted water. Unfortunately, biotite  $\delta^{18}\text{O}$  values are not available for our experimental starting material, however, it is likely that biotite in sample CH 14005 had a  $\delta^{18}\text{O}$  value between  $-8$  and  $-10$ ‰, based on a general correlation between whole-rock  $\delta^{18}\text{O}$  values and biotite  $\delta^{18}\text{O}$  values in samples from the same setting (Troch et al., 2020). At an experimental temperature of 640 °C, equilibrium isotope fractionation factors for sheet silicate-water pairs would be negative ( $\Delta^{18}\text{O}(\text{biotite-H}_2\text{O}) = -2.5$  ‰ and  $\Delta^{18}\text{O}(\text{chlorite-H}_2\text{O}) = -1.9$  ‰ at 640 °C (Zheng, 1993)). Since known  $\delta^{18}\text{O}$  values of chloritised biotite are all higher than that of extracted water, the oxygen isotope composition of extracted water cannot be explained by equilibrium isotope fractionation between biotite/chlorite and  $\text{H}_2\text{O}$ .

Significant differences in oxygen isotope ratios exist between hydroxyl and non-hydroxyl oxygen in hydrous sheet silicates (Girard and Savin, 1996; Zheng, 1993). At alteration temperatures of 150–300 °C, this intra-crystal fractionation between hydroxyl oxygen and bulk mineral  $10^3\ln\alpha_{\text{mineral-OH}} (\approx \Delta^{18}\text{O}(\text{mineral-OH}))$  varies between 5.0 and 6.8 ‰ for chlorite and 6.8 to 9.6 ‰ for biotite (Zheng, 1993).  $\text{OH}^-$  hosted in the hydroxyl site of chloritised biotite should, therefore, have  $\delta^{18}\text{O}$  values that are 5–10 ‰ lower than the bulk mineral, so  $\delta^{18}\text{O}(\text{OH})$  would be between  $-13$  and  $-20$  ‰ for bulk biotite/chlorite  $\delta^{18}\text{O}$  values between  $-8$  and  $-10$  ‰. During the experimental heating, biotite-chlorite undergoes dehydroxylation ( $2 \text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2} \text{O}_2$ ), which means that only half of the original hydroxyl oxygen is included in the extracted and analysed water (Seligman and Bindeman, 2019). Combining  $\Delta^{18}\text{O}(\text{mineral-OH})$  and  $\Delta^{18}\text{O}(\text{mineral-H}_2\text{O})$  values from Zheng (1993) for experimental temperatures of 640 °C, we calculate  $\Delta^{18}\text{O}(\text{H}_2\text{O-OH})$  values of 6.6 and 7.2 ‰ for chlorite and biotite, respectively. Water released from chloritised biotite in our experiment at 640 °C should therefore have a  $\delta^{18}\text{O}$  value between  $-5.8$  and  $-14.4$  ‰, which is consistent with the oxygen isotopic composition of fluid extracted from our experiment. Due to the uncertainty in the initial sheet silicate oxygen isotope composition and the difference in fractionation factors between biotite and chlorite, these calculations only provide a rough estimate for the  $\delta^{18}\text{O}$  value of released  $\text{H}_2\text{O}$ . However, they support our conclusion that both oxygen and hydrogen isotope compositions are consistent with extracted  $\text{H}_2\text{O}$  originating from the breakdown of chloritised biotite during the experiment, and can be analysed without significant isotopic fractionation during the extraction process.

#### 4.3. Isotopic fingerprinting of experimental fluids and additional applications

Due to the large relative mass difference of light stable isotopes and associated strong isotopic fractionation, crustal fluids exhibit a wide spectrum of stable isotope compositions, ranging from meteoric water with  $\delta^{18}\text{O}$  values  $< -25$  ‰ during widespread glaciation (e.g. Bindeman et al., 2010) over present-day sea water ( $\delta^{18}\text{O} = 0$  ‰) to metamorphic fluids with  $\delta^{18}\text{O}$  values that may exceed  $+10$  ‰ (e.g. Wilkinson et al., 1995). The preliminary data from our dehydration experiments (Section 4.2) may be too limited for any general conclusions on the isotopic compositions of crustal fluids released during thermal metamorphism. However, compared to this range, the small uncertainties of this method (average uncertainties  $\delta^{18}\text{O} \pm 1.1$  ‰,  $\delta\text{D} \pm 2.9$  ‰) clearly illustrate its enormous potential in deciphering the origin of these fluids, including linking them to specific breakdown reactions.

High-Temperature Conversion/Elemental Analyser systems (TC/EA) similarly allow hydrogen isotope analysis of water released from hydrous minerals or glasses (e.g. Bindeman and Lowenstern, 2016; Martin et al., 2017; Seligman and Bindeman, 2019; Seligman et al., 2016). However, during the analysis samples are usually heated to temperatures of  $\sim 1450$  °C for complete water extraction, which makes it impossible to analyse experimentally produced fluids in samples that contain residual hydrous minerals. Coupling a thermal gravimeter to a laser spectrometer allows isotopic analysis during step-heating of a sample (Bauska et al., 2018; Mering and Barker, 2018), however, these analyses are limited to atmospheric pressures. With our new method presented here, aqueous fluids can be analysed that were generated over a wide pressure range, e.g. in experiments simulating fluid release from subducting slabs (e.g. Kessel et al., 2005; Tenthorey and Hermann, 2004) and various crustal and upper mantle fluids on Earth (e.g. Fu et al., 2001) or in extraterrestrial systems (e.g. Baker et al., 2000; Yurimoto et al., 2014).

Rather than relying on the mineral record or mass-balance calculations, isotope analysis of water released from experimental capsules allows to trace fluid compositions directly. The opportunity to extract and analyse minute volumes of water enclosed in a sealed container makes this method ideal for both analysis of experimental fluids and

bulk fluid inclusion analysis, such as the speleothem inclusions this method was originally designed for (Affolter et al., 2014) or bulk fluid inclusion analysis in host minerals such as quartz or topaz (Wilkinson et al., 1995), which are commonly investigated in order to characterise magmatic, metamorphic and ore-forming fluids.

## 5. Conclusions

We present a new method for the stable isotope analysis of water extracted from experimental capsules by coupling a Picarro L2410-i laser spectrometer to an online extraction device consisting of a copper tube and steel rings. A series of tests with reference water and quartz sand samples suggests an average uncertainty of  $\pm 1.1$  ‰ for  $\delta^{18}\text{O}$  and  $\pm 2.9$  ‰ for  $\delta\text{D}$ , including both uncertainty during the preparation and extraction process and analytical uncertainty of the instrument. We apply this method to the extraction of fluid that was experimentally generated by heating a low- $\delta^{18}\text{O}$  hydrothermally altered rock sample to 640 °C under pressure, leading to partial thermal decomposition of chloritised biotite in the sample. Oxygen and hydrogen isotope compositions of the extracted water are significantly lighter than the bulk rock stable isotope composition and reflect the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  value of meteoric water involved in the alteration process. This illustrates the potential of using stable isotope exchange experiments in the investigation and simulation of the behaviour of aqueous crustal fluids and associated magmatic-hydrothermal systems.

## Declaration of Competing Interest

We declare that we have no competing interests.

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