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New biotite and muscovite isotopic reference materials, USGS57 and USGS58, for δ^2H measurements–a replacement for NBS 30

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ABSTRACT

The advent of continuous-flow isotope-ratio mass spectrometry (CF-IRMS) coupled with a high temperature conversion (HTC) system enabled faster, more cost effective, and more precise δ^2H analysis of hydrogen-bearing solids. Accurate hydrogen isotopic analysis by on-line or off-line techniques requires appropriate isotopic reference materials (RM). A strategy of 2-point calibrations spanning δ^2H range of the unknowns using two RMs is recommended. Unfortunately, the supply of the previously widely used isotopic reference material, NBS 30 biotite, is exhausted. In addition, recent measurements have shown that the determination of δ^2H values of NBS 30 biotite on the VSMOW-SLAP isotope-delta scale by on-line HTC systems with CF-IRMS may be unreliable because hydrogen in this biotite may not be converted quantitatively to molecular hydrogen. The $\delta^2H_{VSMOW\text{-}SLAP}$ values of NBS 30 biotite analyzed by

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on-line HTC systems can be as much as 21 mUr (or ‰) too positive compared to the accepted value of –65.7 mUr, determined by only a few conventional off-line measurements. To ensure accurate and traceable on-line hydrogen isotope-ratio determinations in mineral samples, we here propose two isotopically homogeneous, hydrous mineral RMs with well-characterized isotope ratio values are urgently needed. The U.S. Geological Survey (USGS) has prepared two such RMs, USGS57 biotite and USGS58 muscovite. The δ^{2}H values were determined by both glassy carbon-based on-line conversion and chromium-based on-line conversion, and results were confirmed by off-line conversion. The quantitative conversion of hydrogen from the two RMs using the on-line TC/EA method was carefully evaluated in this study. The isotopic compositions of these new RMs with 1-σ uncertainties and mass fractions of hydrogen are:

USGS57 (biotite)
$\delta^{2}\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -91.5 \pm 2.4$ mUr (n = 24)
Mass fraction hydrogen = 0.416 ± 0.002 % (n = 4)
Mass fraction water = 3.74 ± 0.02 % (n = 4)

USGS58 (muscovite)
$\delta^{2}\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -28.4 \pm 1.6$ mUr (n = 24)
Mass fraction hydrogen = 0.448 ± 0.002 % (n = 4)
Mass fraction water = 4.03 ± 0.02 % (n = 4)

These $\delta^{2}\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}}$ values encompass typical ranges for solid unknowns of crustal and mantle origin and are available to users for recommended two point calibration.

Keywords: TC/EA, hydrogen isotopes, isotope standards

1. Introduction

Hydrogen-isotope information obtained from hydrogen liberated from hydroxyl bearing minerals has been widely used to answer scientific questions on the petrogenesis of minerals and their host rocks (Suzuoki and Epstein, 1976), investigating topics in sedimentary geology and geochemistry (Savin and Epstein, 1970), tracking the origin of hydrous fluids at seismogenic depths (Mittempergher et al., 2014) and water in volcanic glass (Seligman et al., 2016), evaluating fluid fluxes in silicic magmas (Deering et al., 2012), investigating ancient climate and hydrologic regimes (Abruzzese et al., 2005), or classifying CM and CR chondrites (Alexander et al., 2013). Before continuous-flow high temperature conversion (HTC) techniques (also called the on-line TC/EA method) were developed, off-line reduction with uranium or zinc metal of water liberated by microwave or other means of heating hydrogen-bearing silicates served as the conventional method for hydrogen isotopic analysis of solids (Bigeleisen et al., 1952; Friedman, 1953; Godfrey, 1962; Coleman et al., 1982; Kendall and Coplen, 1985; Suzuoki and Epstein, 1976; Vennemann and O'Neil, 1993). Since the late 1990s, the advent of continuous-flow isotope-ratio mass spectrometry (CF-IRMS) coupled with a HTC system enabled faster, more cost effective, and sometimes also more precise δ^2H analysis of hydrogen-bearing solids, gases, and water samples (Begley and Scrimgeour, 1996; Burgoyne and Hayes, 1998; Hilkert et al., 1999). This method benefits from the fact that only 1–20 mg of material is required, which is 50–200 mg less than that for the conventional off-line method, enabling (1) replication and triplication of measurements for improved precision, and (2) analysis of alteration-free specimens. Sharp *et al.* (2001) applied the CF-IRMS technique to hydrous minerals and developed a rapid method for δ^2H measurements. Since then, many researchers have adapted and improved on-line TC/EA methods for hydrogen-isotope analysis of closed-system fluids, freshwater chert, silicic magmas, and various hydrous minerals (Marks et al., 2004; Abruzzese et al., 2005; Gong et al., 2007; Deering et al., 2012; Underwood et al., 2012; Bindeman et al., 2012; VanDeVelde and Bowen, 2013; Bauer and Vennemann, 2014; Mittempergher et al., 2014; Seligman et al., 2016).

Stable hydrogen isotopic compositions are expressed as delta values denoted as $\delta^2\mathrm{H}_{\mathrm{VSMOW}}$, which is defined by the relation (Coplen, 2011):

$$\delta^2\mathrm{H}_{\mathrm{VSMOW}} = \frac{R\left({}^2\mathrm{H}/{}^1\mathrm{H}\right)_{\mathrm{P}} - R\left({}^2\mathrm{H}/{}^1\mathrm{H}\right)_{\mathrm{VSMOW}}}{R\left({}^2\mathrm{H}/{}^1\mathrm{H}\right)_{\mathrm{VSMOW}}}$$

where $R({}^2\mathrm{H}/{}^1\mathrm{H})_\mathrm{P}$ is the ratio $N({}^2\mathrm{H})_\mathrm{P}$ / $N({}^1\mathrm{H})_\mathrm{P}$ and $N({}^2\mathrm{H})_\mathrm{P}$ and $N({}^1\mathrm{H})_\mathrm{P}$ are the numbers of the two isotopes of hydrogen, ^{2}H and ^{1}H, respectively, in a sample P, and similarly for the reference VSMOW (Vienna Standard Mean Ocean Water). The International Union of Pure and Applied

Chemistry (IUPAC) recommends that use of the per mil symbol (‰) be avoided (Cohen et al., 2007). Therefore, we follow the suggestion of Brand and Coplen (2012) and use the term urey (symbol Ur), which is suited for diverse isotope scales of all elements. One milliurey = 0.001 = 1 ‰. A delta value in the traditional form of –25 ‰ can be expressed as –25 mUr. The δ^2H_{VSMOW} values herein are normalized on an isotope scale such that the δ^2H value of SLAP (Standard Light Antarctic Precipitation) is –428 mUr (Gonfiantini, 1978; Coplen, 1994), and they are identified as $\delta^2H_{VSMOW-SLAP}$ values.

Accurate hydrogen isotope analysis by on-line or off-line techniques requires appropriate isotopic reference materials (RM). A strategy of 2-point calibrations (Coplen, 1988; Coplen, 1994; Werner and Brand, 2001; Paul et al., 2007; Brand et al., 2014; Schimmelmann et al., 2009; Bindeman et al 2012; Schimmelmann et al., 2016) using two RMs is recommended. However, only one internationally distributed mineral isotopic reference material, NBS 30 biotite, exists. NBS 30 was prepared by I. Friedman, J. R. O'Neil, and G. Cebula (U.S. Geological Survey) from a sample of the Lakeview tonalite (Southern California batholith) provided by L. Silver (California Institute of Technology, Pasadena, California) (Gonfiantini, 1984), and its particle size ranges between 200 and 300 μm. This material is intended for calibration of oxygen and hydrogen isotopic measurements of silicates and hydrous solids. The assigned $\delta^2H_{VSMOW-SLAP}$ value of –65.7 mUr for NBS 30 biotite is the average value obtained from measurements reported by Gonfiantini (1984) and Hut (1987). Prior to 2016, only a few other international RMs existed for hydrogen isotopic analysis of solids, including IAEA-CH-7 polyethylene foil ($\delta^2H_{VSMOW-SLAP}$ = –99.2 mUr; Schimmelmann et al., 2016), NBS 22 oil ($\delta^2H_{VSMOW-SLAP}$ = –117.2 mUr; Schimmelmann et al., 2016), USGS42 Tibetan human hair ($\delta^2H_{VSMOW-SLAP}$ = – 72.9 mUr; Coplen and Qi, 2016), and USGS43 Indian human hair ($\delta^2H_{VSMOW-SLAP}$ = –44.4 mUr; Coplen and Qi, 2016). The supplies of NBS 30 biotite and NBS 22 oil are exhausted, and polyethylene and human hair RMs are not suitable for δ^2H measurements of hydrous minerals. Furthermore, determination of $\delta^2H_{VSMOW-SLAP}$ values of NBS 30 biotite by established on-line HTC techniques was found to be unreliable because hydrogen conversion from this biotite proved to be non-quantitative (Qi et al., 2014). The $\delta^2H_{VSMOW-SLAP}$ values of NBS 30 by three laboratories were as much as 21 mUr higher than the accepted value of –65.7 mUr, determined by conventional off-line measurements. Further experiments revealed a strong correlation between grain size and $\delta^2H_{VSMOW-SLAP}$ of NBS 30 biotite, but not of biotites with lower iron content. Moreover, the $\delta^2H_{VSMOW-SLAP}$ values of NBS 30 as a function of particle size showed a clear trend toward –65.7 mUr with finer grain size (Qi et al., 2014). In 2016, 19 new organic reference materials (RMs) for hydrogen, carbon, and nitrogen stable isotope-ratio measurements were prepared (Schimmelmann et al., 2016), and these enable more accurate determinations of relative stable isotope ratios of hydrogen (δ^2H), carbon ($\delta^{13}C$), and nitrogen ($\delta^{15}N$) using at least two isotopic reference materials to anchor the isotope-delta scales with RMs having strongly contrasting isotopic compositions (Coplen, 1988; Coplen, 1996; Paul et al., 2007; Brand et al., 2014). However, none of the 19 RMs is suitable for hydrogen isotopic analysis of minerals because of differences in the material matrix.

Although a conventional on-line TC/EA method using a glassy carbon-filled reactor (C-EA) has enabled faster, more cost-effective measurements of hydrogen and oxygen isotopes in a wide range of solid materials, accurate δ^2H measurements of many materials have been found to be problematic (Hunsinger et al., 2013; Qi et al., 2014; Gehre et al., 2015; Nair et al., 2015; Gehre et al., 2016). Besides the problem exemplified by NBS 30 biotite mentioned above, the formation of hydrogen-bearing by-products, such as HCN and HCl (HX), was verified when nitrogen-, chlorine-, and sulfur-bearing organic materials were analyzed by conventional on-line TC/EA (Hunsinger et al., 2013; Gehre et al., 2015; Nair et al., 2015; Gehre et al., 2016). The formation of hydrogen-bearing by-products prevents a quantitative conversion of organically bound hydrogen in samples to the analyte H_2. Thus, δ^2H results are seriously compromised because of isotopic fractionation. To overcome this problem, Gehre et al. (2015) have modified the conventional on-line TC/EA method that uses a glassy, carbon-filled reactor. Instead, they developed a method employing a chromium-filled, high-temperature reactor (Cr-EA). This method minimizes the production of intermediately formed hydrogen-bearing by-products (HCN, HCl) leading to quantitative conversion to molecular hydrogen. Gehre et al. (2016) later improved the Cr-EA method of δ^2H analysis and extended the investigation of δ^2H analysis to substances containing fluorine, chlorine, bromine, iodine, and sulfur. The optimized EA-Cr/HTC-IRMS technique offers more accurate δ^2H analysis of fluorine-, chlorine-, bromine-, iodine-, and sulfur-bearing substances.

To ensure accurate and traceable on-line δ^2H determination of mineral samples, two isotopically homogeneous hydrous mineral RMs with well-characterized δ^2H values are needed. The U.S. Geological Survey (USGS) has prepared two such RMs, USGS57 biotite and USGS58 muscovite, both from China. At the same time, the quantitative conversion of hydrogen from these two RMs was carefully evaluated using on-line C-EA and Cr-EA methods, as well as off-line conversion (Kokubu et al., 1961). Seven isotope laboratories participated in this study. Sample preparation methods and methods to determine $\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}}$ values are described in this article.

2. Selection of two mineral isotopic reference materials

Two phyllosilicate RMs having $\delta^2\mathrm{H}$ values sufficiently different to encompass most natural hydrous minerals were sought. Five powdered biotites and four muscovites with different particle sizes ranging from 74 to 250 µm (200 to 60 mesh) were purchased from Antai Mining Co., Ltd. (Lingshou County, Shijiazhuang, Hebei Province, China). The biotite and muscovite were separated from natural rocks in China and crushed in an industrial scale factory. The biotite with particle size of 177 µm (80 mesh) and the muscovite with particle size of 149 µm (100 mesh) were found to be suitable RMs, and they were designated as USGS57 and USGS58, respectively. About 2 kg of each material was tumbled in a large glass jar for seven days to ensure homogeneity of the different mineral grains and hence isotopic compositions.

3. Experimental methods

3.1. The isotopic reference materials

The isotopic reference materials VSMOW, VSMOW2, SLAP2, GISP, NBS 22 oil ($\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -117.2$ mUr; Schimmelmann et al., 2016) and USGS47 ($\delta^2\mathrm{H}_{\mathrm{VSMOW}} = -150.2$ mUr; Qi et al., 2014) were sealed in silver tubes using a semi-automated sealing technique (Qi et al., 2010). The selected reference samples were distributed to the other participating laboratories. All laboratories used combinations of primary and secondary international measurement standards for two-point calibrations. Each laboratory also analyzed their in-house references to ensure the quality of $\delta^2\mathrm{H}$ measurements. USGS62 caffeine ($\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -156.1$ mUr; Schimmelmann et al., 2016) was used to quantify the mass fraction of hydrogen.

3.2. The $\delta^2H_{VSMOW\text{-}SLAP}$ determination

Six of the laboratories used a variety of analytical approaches for measuring δ^2H using on-line conversion with EA-C/HTC or EA-Cr/HTC methods, and one laboratory analyzed δ^2H with an off-line method.

At the RSIL, the δ^2H measurements were made with a HTC (TCEA, Thermo-Finnigan, Bremen, Germany) reduction unit equipped with a Costech Zero-Blank 100-position Autosampler (Costech, Valencia, California), a ConFlo IV gas introduction system (Thermo Fisher, Bremen, Germany), and a Delta^{plus} XP isotope-ratio mass spectrometer (Thermo, Bremen, Germany). The details of the method using a glassy carbon-filled reactor were described by Qi et al. (2014). For samples analyzed with a Cr-filled reactor, the glassy carbon tube inside the ceramic tube that is normally filled with glassy carbon chips was packed with a mixture of chromium and glassy carbon chips. The mix ratio of chromium chips to glassy carbon chips was about 1:1 by volume. The bottom 35 mm of the ceramic tube was filled with chromium and glassy carbon chips and was supported by silver wool. The helium carrier gas (100 mL/min) was fed from the top, as originally supplied. The reactor temperature was set to values between 1050 to 1450 °C, and the GC temperature was maintained at 80 °C.

Solid mineral samples were weighed into silver capsules. Reference waters and oil contained the same amount of hydrogen as found in mineral samples, and these liquids were crimp-sealed into segments of silver tubes and interspersed with unknown samples and analyzed as solid samples (Qi et al., 2010). The use of reference waters in silver tubes made it possible to directly measure δ^2H values of mineral materials against reference waters with known δ^2H values (Coplen and Qi, 2010) following the principle of identical treatment (Werner and Brand, 2001). For the other laboratories the on-line methodologies based on a variety of high temperature conversion elemental analyzer (TC/EA) and gas chromatographic (GC) interfaces, as well as mass spectrometers from different manufacturers, are summarized in Table 1.

For off-line analysis, structural hydrogen was extracted from the RMs using a method modified after Godfrey (1962), Kyser and O'Neil (1984) and Vennemann and O’Neil (1993). Briefly, ~70 mg of muscovite or biotite were loaded into a quartz tube and outgassed for 12 h at 200 °C to remove adsorbed water. The sample was then heated using a fuel-gas-oxygen torch for ~10 min during which released H_2O was trapped at –196 °C. Gas initially released as H_2 was oxidized over copper oxide (CuO) at 550 °C to form H_2O, which was also collected in the –196 °C trap. The total water collected was then reacted with powdered chromium at 900 °C to produce H_2, which was collected on charcoal at –196 °C and the yield of H_2 measured. The H_2 was analyzed using a Thermo Scientific Delta^{plus} XL dual-inlet IRMS. Values of δ^2H were calibrated to VSMOW-SLAP using 3-mL volumes of VSMOW and USGS47. The water standards were treated in an identical fashion to the total water released from the RMs.

Table 1

Stable isotope analytical methods and equipment of participating laboratories

Laboratory	Instruments	Method and condition
University of Chicago, Chicago, USA	On-line, Thermo Scientific DELTA V PLUS, Thermo Scientific TC/EA connected *via* Thermo ConFlo IV interface	Glassy carbon tube filled with glassy carbon chips without graphite crucible. Reactor 1450 ºC, GC 90 ºC, helium flow 100 mL min^{-1}
Stable Isotope Laboratory, University of Lausanne, Switzerland	On-line, Thermo Scientific Delta^{plus} XL, Thermo Scientific TC/EA connected *via* Thermo ConFlo III interface	Glassy carbon tube filled with glassy carbon chips with graphite crucible. Reactor 1450 ºC, GC 85 ºC, helium flow ~90 mL min^{-1}
University of Oregon, Eugene, Oregon, USA	Online Thermo Scientific MAT253-TC/EA system	Glassy carbon chips and oven, 1450 °C, GC at 70 °C during run, 300 °C overnight prior to analytical session. Helium flow 80 mL min^{-1} (Martin et al., 2017)
UFZ, Helmholtz-Centre for Environmental Research, Leipzig, Germany	On-line Euro 3000 Elemental Analyzer (Eurovector, Italy), Connected *via* Thermo ConFlo IV to a Thermo Scientific MAT 253™	Quartz oven filled with chromium, one-oven system, 1150–1270 °C, helium flow ~100 mL min^{-1} (Gehre et al. 2015)
MPI-BGC, Max Planck Institute for Biogeochemistry, Jena, Germany	On-line, Hekatech HTO connected *via* Thermo ConFlo III interface to Thermo Scientific Delta^{plus} XL	Oven filled with a mixture of chromium and glassy carbon chips, one-oven system, 1400-1450 °C, helium carrier gas ~80 mL min^{-1} with reversed flow (Gehre et al., 2004, Nair et al., 2015)
RSIL, U.S Geological Survey, Reston, Virginia, USA	On-line, Thermo Scientific Delta^{plus} XP, Thermo Scientific TC/EA connected *via* Thermo ConFlo IV interface	*Method #1:* Glassy carbon tube filled with glassy carbon chips without graphite crucible. Reactor 1450 ºC, GC 80 ºC, helium flow 120 mL min^{-1}. *Method #2:* Removed glassy carbon tube. Filled ceramic tube from bottom

		to top with glassy carbon chips, quartz wool and 3 cm of chromium powder. Reactor 1150 ºC, GC 80 ºC, helium flow 120 mL min^{-1}
Laboratory for Stable Isotope Science, The University of Western Ontario, London, Ontario, Canada	Manual dual-inlet measurements using a Thermo Scientific Delta^{plus} XL dual-inlet IRMS	Off-line heating in evacuated quartz tubes using a fuel-gas oxygen torch (Vennemann and O'Neil, 1993); released water trapped at –196 °C, and released H_2 oxidized over CuO at 550 °C and combined with released water; reduction of H_2O to H_2 with chromium at 900 ºC; collection of analyte H_2 on charcoal at –196 °C and measurement of yield (Godfrey, 1962; Kyser and O'Neil, 1984). All performed using a vacuum line.

4. Results and discussion

4.1. Isotopic homogeneity and evaluation of chemical purity of the two RMs

To test for isotopic homogeneity, fifteen vials of each RM were selected randomly, labeled as vial #1 vial through vial #15. The δ^2H values of three aliquots from each vial of USGS57 and USGS58 were determined (Table 2). Two different sample amounts were analyzed in the Cr-filled reactor and the glassy carbon-filled reactor (Table 2). The sample masses for the Cr-filled reactors were ~1.8 mg (equivalent to 0.07 µL of water or 8.3 µg of hydrogen). The sample masses of USGS57 and USGS58 for the glassy carbon-filled reactor were 3.56 and 3.25 mg, respectively (both equivalent to 0.15 µL of water or 16.7 µg of hydrogen). To account for δ^2H drift resulting from residue buildup over time, each analysis run was controlled by analyzing two or more aliquots of the RM from the vial #1 at the beginning, the middle, and the end of the run. No drift in δ^2H values was observed from any of the four runs. The standard deviations of the larger-sample masses (for the glassy carbon-filled reactor) were better than those of the smaller-sample masses (for the Cr-filled reactor). For example, the mean values of the 15 standard deviations of USGS57 and USGS58 analyzed using the glassy carbon-filled reactor were 0.7 and 0.5 mUr, respectively. The mean values of the 15 standard deviations of USGS57 and USGS58 analyzed using the Cr-filled reactor were 1.3 and 1.2 mUr, respectively. There are a few vials that appeared to have higher standard deviations for δ^2H values in Table 2, for example, between 2.6 and 3.4 mUr when small amounts of material were analyzed. It is not clear whether this higher standard deviation only reflects material homogeneity inside the respective vial or whether it was the result of using a smaller amount of sample. Because these two mineral materials were produced in an industry-scale factory, we cannot rule out that small particles with substantially different δ^2H values may be mixed in the RMs. To be cautious, it is recommended that at least two or three of the same RM be analyzed at the beginning, the middle, and the end of a run with an amount of hydrogen no less than 16.7 µg. Nevertheless, the average standard deviations of the averages of the 15 measurements of USGS57 and USGS58 shown in Table 2 are 1.1 and 0.6 mUr, respectively, demonstrating that the two RMs are isotopically homogeneous above the tested aliquot-size level.

The mineralogical purity of USGS57 and USGS58 was evaluated by X-ray diffraction at USGS, Reston. USGS57 contains 98 % biotite by mass and USGS58 contains 97 % muscovite by mass (Table 3).

Table 2

Hydrogen isotopic homogeneity of USGS57 biotite and USGS58 muscovite

[The δ^2H values are measured, not scale-normalized values.]

Sample	USGS57 biotite		USGS58 muscovite	
	Cr-packed reactor[a] δ^2H (mUr)	Glassy carbon-packed reactor[b] δ^2H (mUr)	Cr-packed reactor[a] δ^2H (mUr)	Glassy carbon-packed reactor[b] δ^2H (mUr)
#1	−90.1 ± 1.3	−94.3 ± 0.8	−28.4 ± 1.4	−29.5 ± 0.3
#2	−90.0 ± 1.3	−94.3 ± 1.4	−29.2 ± 0.4	−29.6 ± 0.7
#3	−89.2 ± 0.7	−94.3 ± 0.7	−27.9 ± 1.3	−29.6 ± 0.6
#4	−90.8 ± 0.9	−93.8 ± 0.3	−28.0 ± 1.4	−29.7 ± 0.7
#5	−91.1 ± 1.1	−94.3 ± 0.2	−27.9 ± 0.6	−30.2 ± 0.7
#6	−89.9 ± 2.6	−93.8 ± 0.2	−28.2 ± 0.9	−29.8 ± 0.4
#7	−91.1 ± 1.3	−94.3 ± 0.2	−27.1 ± 3.4	−30.0 ± 0.3
#8	−91.5 ± 0.4	−94.3 ± 0.6	−28.0 ± 1.1	−30.1 ± 0.3
#9	−90.1 ± 3.3	−93.9 ± 0.9	−28.8 ± 0.3	−29.7 ± 0.6
#10	−90.2 ± 0.8	−94.8 ± 1.0	−27.0 ± 0.5	−29.4 ± 0.8
#11	−91.0 ± 1.9	−94.1 ± 0.5	−27.0 ± 3.1	−28.8 ± 0.5
#12	−91.4 ± 2.0	−94.0 ± 0.8	−28.4 ± 1.1	−30.1 ± 0.7
#13	−92.9 ± 0.4	−92.1 ± 2.6	−28.2 ± 1.9	−29.3 ± 0.5
#14	−92.0 ± 1.3	−89.7 ± 0.5	−28.2 ± 1.1	−29.3 ± 0.4
#15	−92.3 ± 0.9	−93.0 ± 0.5	−27.1 ± 0.2	−28.9 ± 0.3
average	−91.0 ± 0.9	−93.8 ± 1.2	−28.0 ± 0.7	−29.6 ± 0.4

[a] The amount of material used for these analyses contain hydrogen equivalent to hydrogen in 0.07 μL of water

[b] The amount of material used for these analyses contains hydrogen extracted from the equivalent of 0.15 µL of water

Table 3

The mass fractions of biotite, muscovite, and other minerals in USGS57 and USGS58 [ideal formulae: biotite, $K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$; muscovite, $KAl_2(AlSi_3O_{10})(OH)_2$; K-feldspar, $KAlSi_3O_8$; quartz, SiO_2; plagioclase, solid solution of $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$; chlorite, $Mg_3(Si_4O_{10})(OH)_2 \cdot Mg_3(OH)_6$.]

Name	Material	Mass Fraction					
		Biotite	Muscovite	K-feldspar	Quartz	Plagioclase	Chlorite
USGS57	Biotite 80 mesh	0.98		trace	trace	0.01	0.01
USGS58	Muscovite 100 mesh		0.97	0.01	trace	0.02	trace

4.2. Particle size, chromium- and glassy carbon-filled reactors, and drying test

Work by Qi et al. (2014) demonstrated that determination of $\delta^2H_{VSMOW\text{-}SLAP}$ values of NBS 30 biotite with on-line TC/EA systems with glassy carbon-filled reactors was unreliable because hydrogen conversion from this specific biotite RM is not quantitative. Experiments have shown that the $\delta^2H_{VSMOW\text{-}SLAP}$ values of NBS 30 demonstrate a clear trend toward –65.7 mUr with finer grain size. The difference in $\delta^2H_{VSMOW\text{-}SLAP}$ values obtained from NBS 30 with original particle size and that with a finer particle size can be as high as 21 mUr (Qi et al., 2014). In addition, Hunsinger et al. (2013), Gehre et al.(2015) and Nair et al. (2015) established that hydrogen isotopic results can be seriously compromised when N-, Cl-, S-bearing organic materials are analyzed by conventional on-line TC/EA method (with glassy carbon-filled reactor) because of isotopic fractionation caused by the formation of hydrogen-bearing by-products, such as HCN and HCl. To overcome this problem, Gehre et al. (2015) have modified the conventional glassy-carbon only on-line TC/EA method using elemental chromium (Cr-EA). This method prevents hydrogen-bearing by-products (HCN and HCl) from surviving in the reactor and enables quantitative conversion of hydrogen from organic matter to molecular hydrogen. Gehre et al. (2016) further improved the Cr-EA method of hydrogen isotopic analysis and extended the investigation of hydrogen isotopic analysis to substances containing fluorine, chlorine, bromine, iodine, and sulfur. The optimized EA-Cr/HTC-IRMS technique offers more accurate hydrogen isotopic analysis of fluorine-, chlorine-, bromine-, iodine-, and sulfur-bearing substances.

To test for particle-size effects using the on-line TCEA systems, different size fractions of the two new RMs were analyzed with both the Cr-filled and glassy carbon-filled reactors. Samples of USGS57 biotite and USGS58 muscovite (original particle sizes of 177 μm and 149 μm, respectively) were ground, and different size fractions collected. Four aliquots from each size fraction of each material were weighed as the first set for evaluation. Another set of samples identical to the first set was also weighed. Half of samples from each size fraction from the second set were dried in a vacuum oven at 70 °C overnight, and half remained undried. The first set of samples was analyzed by conventional TC/EA with the glassy carbon-filled reactor method (Qi et al., 2014). The second set with dried and undried samples was analyzed by TC/EA with the Cr-filled reactor. The measured δ^2H values (not scale-normalized values) and ratios of relative peak area to mass from the different particle size fractions are summarized in Table 4. There are no measurable differences in δ^2H values or in relative hydrogen yields (relative peak area to mass) between dried and undried USGS57 and USGS58 for the same particle size (Table 4), as determined with the Cr-filled reactor. This demonstrates that USGS57 biotite and USGS58 muscovite do not absorb detectable amounts of moisture under normal laboratory conditions. However, measured δ^2H values and relative hydrogen yields vary with particle size for both USGS57 biotite (Fig. 1a) and USGS58 muscovite (Fig. 1b). This indicates that the two materials behaved differently in the HTC system, presumably because of the different chemical compositions of USGS57 and USGS58. For USGS57 biotite, Figure 1a shows that the amount of hydrogen released from the same amount of material increased and the δ^2H value decreased with finer particle size in the range of 74−177 μm. This pattern is similar to the pattern shown by NBS 30 biotite (Qi et al., 2014). Interestingly, when the particle size of USGS57 is smaller than 74 μm, the relative hydrogen yield decreased from the highest value of 17.91 to 17.08, and the lowest δ^2H value of −98.4 mUr is obtained. For USGS58 muscovite, the highest relative hydrogen yield and most positive δ^2H values were measured for the particle size between 105−149 μm (Fig. 1b). Like USGS57, when particle size of USGS58 was smaller than 74 μm, the relative hydrogen yield also decreased from the highest value of 20.51 (dried) and 20.37 (undried) to 18.64 (dried) and 18.62 (undried), respectively, and the lowest δ^2H values of −34.4 mUr (dried) and −33.4 mUr (undried) were obtained. When undried samples from different particle sizes were analyzed using the glassy carbon-filled reactor, the patterns of δ^2H values and relative hydrogen yields are very similar to those determined with the Cr-filled reactor for both USGS57 (Fig. 1c) and USGS58 (Fig. 1d). The δ^2H values of USGS57 biotite analyzed with the glassy carbon-filled reactor may be more consistent with an average value of −94.3 ± 0.3 mUr compared to the value of −96.5 ± 1.2 mUr (dried) or −97.2 ± 1.1 mUr (undried) for the Cr-filled reactors. The variation of the relative hydrogen yields with particle was similar for both types of reactors (Table 4).

Table 4

Variation in measured δ^2H values and relative hydrogen yields (relative peak area / mass) of USGS57 biotite and USGS58 muscovite having different particle sizes and drying conditions

[Standard deviations are one sigma; δ^2H values are measured, not scale normalized.]

			USGS57 biotite		USGS58 muscovite	
Method	Treatment	Particle size (μm)	δ^2H (mUr)	Relative hydrogen yield	δ^2H (mUr)	Relative hydrogen yield
Cr	dried	Original	−95.5 ± 0.2	17.47 ± 0.12	−31.8 ± 0.9	19.72 ± 0.05
	dried	>149	−95.6 ± 1.3	17.70 ± 0.19	−28.3 ± 0.3	20.34 ± 0.05
	dried	105−149	−96.2 ± 1.4	17.84 ± 0.02	−27.6 ± 1.3	20.51 ± 0.34
	dried	74−105	−96.9 ± 1.3	17.91 ± 0.02	−30.3 ± 0.0	19.74 ± 0.02
	dried	<74	−98.4 ± 0.6	17.08 ± 0.00	−34.4 ± 0.2	18.64 ± 0.05
		Average	**−96.5 ± 1.2**	**17.60 ± 0.34**	**−30.5 ± 2.7**	**19.79 ± 0.73**
	undried	Original	−96.4 ± 0.3	17.41 ± 0.01	−30.6 ± 1.4	19.54 ± 0.09
	undried	>149	−96.2 ± 0.3	17.73 ± 0.08	−28.7 ± 0.3	20.37 ± 0.08
	undried	105−149	−97.3 ± 0.2	17.83 ± 0.13	−27.9 ± 0.1	20.25 ± 0.09
	undried	74−105	−97.3 ± 1.6	17.99 ± 0.01	−28.8 ± 1.1	19.81 ± 0.07
	undried	<74	−99.0 ± 0.5	17.11 ± 0.05	−33.4 ± 0.9	18.62 ± 0.09
		Average	**−97.2 ± 1.1**	**17.62 ± 0.36**	**−29.9 ± 2.2**	**19.72 ± 0.70**
Glassy carbon	undried	Original	−93.9 ± 1.0	16.01 ± 0.17	−31.2 ± 1.1	18.05 ± 0.12
	undried	>149	−94.3 ± 0.3	16.22 ± 0.06	−28.1 ± 0.4	18.94 ± 0.04
	undried	105−149	−94.5 ± 0.3	16.43 ± 0.09	−28.0 ± 0.4	18.79 ± 0.07
	undried	74−105	−94.2 ± 0.5	16.51 ± 0.10	−28.8 ± 1.2	18.43 ± 0.11
	undried	<74	−94.6 ± 0.5	15.67 ± 0.08	−32.1 ± 0.3	17.46 ± 0.11
		Average	**−94.3 ± 0.3**	**16.17 ± 0.34**	**−29.6 ± 1.9**	**18.33 ± 0.60**

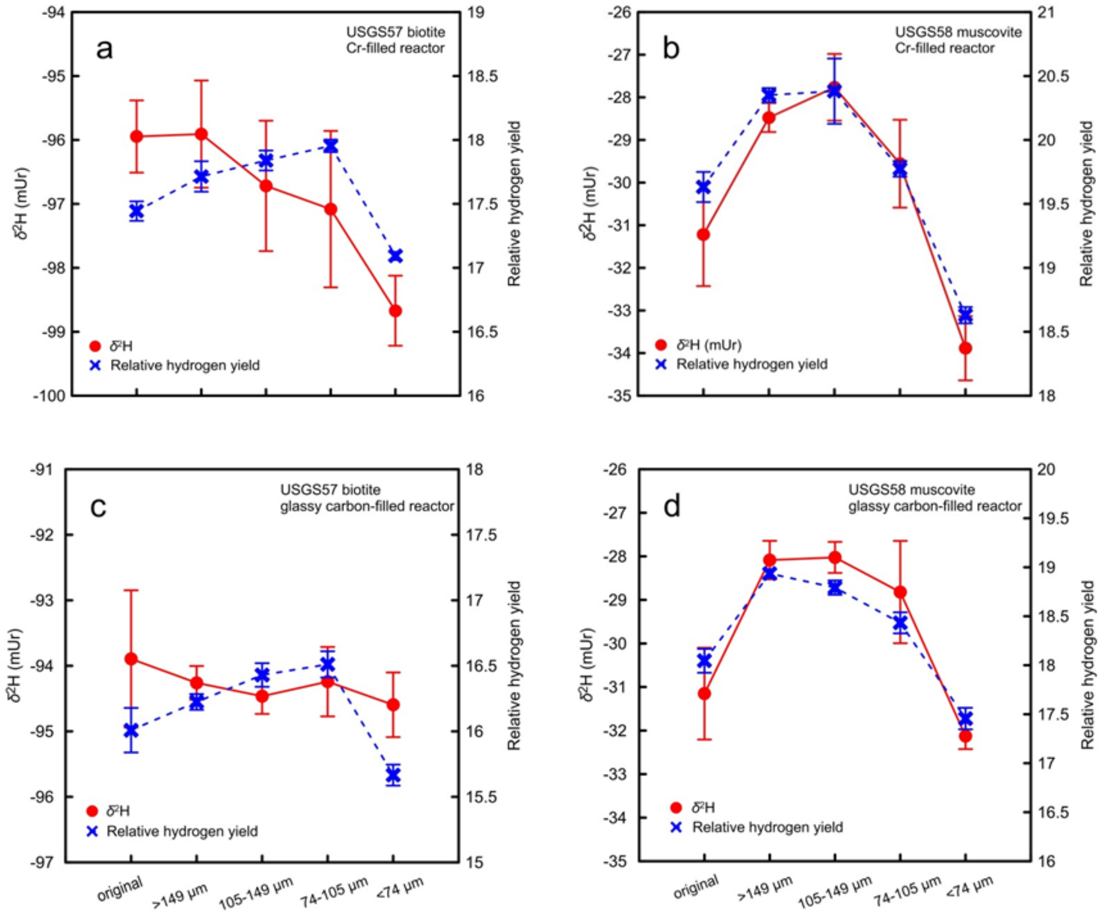

Fig. 1. Variation in δ^2H value and relative hydrogen yield with a Cr-filled reactor of USGS57 biotite (a) and USGS58 muscovite (b) as a function of particle size; variation in δ^2H value and relative hydrogen yield with a glassy carbon-filled reactor of USGS57 biotite (c) and USGS58 muscovite (d) as a function of particle size. Each data point is an average value of 4 analyses. The data in figure (a) and figure (b) are the combined results for analyses obtained in two dried samples and two undried samples. The δ^2H values are measured, not scale normalized values.

4.3. Determination of mass fraction of hydrogen

Two independent analysis runs with different reactor filling (Cr-filled or glassy carbon-filled) were carried out to quantify the mass fractions of hydrogen in the two RMs. With the run that used Cr-filled reactor, we evaluated (1) the molecular hydrogen yields from different particle-size fractions of each material, and (2) the potential fraction of absorbed water by comparing the mass fraction of hydrogen in dried and undried USGS57 and USGS58. Several aliquots of caffeine with precisely determined masses were analyzed to quantify the mass of hydrogen in the RMs. USGS62 caffeine samples were also analyzed at the beginning, the middle, and the end of a run to account for drift in the measurement of hydrogen yield. Samples of USGS57 biotite (original size 177μm) and USGS58 muscovite (original size 147 μm) were ground, and size fractions ranging from 177 μm to ≤ 74 μm were collected and analyzed. Two sets of samples with two aliquots of each size fraction of each RM were prepared. One set of samples was dried in a vacuum oven at 70 °C overnight with caffeine samples. The two sets of samples were analyzed in the same run with a Cr-filled reactor. The results (Table 5) indicate that there is no difference in mass fraction of hydrogen determined with dried or with undried samples of USGS57 and USGS58. These results demonstrate that USGS57 biotite and USGS58 muscovite do not absorb detectable amount of moisture under normal laboratory conditions. However, the hydrogen yield varied with different particle-size fractions. For USGS57 biotite, with the results from both dried and undried samples, the hydrogen yield increased from 0.42 % (3.82 % as H_2O) to 0.44 % (3.92 % as H_2O) as the particle fraction decreased from the original size of 177 μm to 74 μm. For USGS58 muscovite, the highest hydrogen yield was obtained from samples with particle-size fraction between 105 μm and 149 μm, from both dried and undried samples. It is interesting that hydrogen yield (as hydrogen) substantially decreased for particle-size fractions smaller than 74 μm for both USGS57 and USGS58. The reason is unclear. We speculate that a chemical reaction occurred when very fine mineral powders were in contact with the chromium or glassy carbon reactor. Alternatively, it is possible that hydrogen in the fine-grained minerals, exposed at high temperature (>1250 °C) under reducing conditions is not released as molecular hydrogen because a small fraction of this hydrogen is strongly bonded to other elements in the mineral. In a second run in which a glassy carbon-filled reactor was used, we only analyzed original materials and the fraction with particle size smaller than 74 μm of

USGS57, USGS58 and NBS 30 of dried materials. In this run, several aliquots of polyethylene powder, USGS77 with precisely determined masses, were analyzed to quantify the mass of hydrogen in the RMs. The calculated values of the mass fraction of hydrogen were lower than the values obtained in the Cr-filled reactor run calculated by caffeine for both USGS57 and USGS58 (Table 5). We suspect that quantitative conversion of hydrogen from caffeine in the Cr-filled reactor was not completed. Thus, higher values of mass fraction of hydrogen in USGS57 and USGS58 were derived. Although the issues of quantitative conversion of hydrogen from caffeine by the on-line TC/EA method have been investigated by Gehre et al. (2015) and Nair et al. (2015) recently, further studies are required based on the results of the present study. Another observation from the data in Table 5 is that the pattern of mass fraction of hydrogen is different: (1) between USGS57 and USGS58 when analyzing in the same run, and (2) the same material with different particle size analyzed by different reactor filling (Cr or glassy carbon). With the assumption that polyethylene does not suffer from hydrogen quantitative conversion issues either in glassy a carbon-filled reactor or in a Cr-filled reactor, we decided to use the values of mass fraction of hydrogen for USGS57 and USGS58 derived by polyethylene reaction. The recommended mass fractions of hydrogen in USGS57 and USGS58 are 0.416 % (3.74 % as H_2O) and 0.448 % (4.03 % as H_2O), respectively (Table 5). These values agree well with the empirical mass fractions of hydrogen of 0.404% (3.64 % as H_2O) in biotite ($KMg_{2.5}Fe^{2+}_{0.5}AlSi_3O_{10}(OH)_{1.75}F_{0.25}$), and 0.451 % (4.06 % as H_2O) in muscovite ($KAl_3Si_3O_{10}(OH)_{1.8}F_{0.2}$).

The mass fractions of hydrogen were also determined in the original material (200 to 300 μm) and the fine material (smaller than 74 μm) of NBS 30 by reaction of polyethylene in the same run with a glassy carbon reactor (Table 5). The mass fraction of hydrogen of 0.475 % (4.27 % as H_2O) from the fine fraction is about 17 % higher than that of 0.398 % (3.55 % as H_2O) determined on the original material. This observation agrees well with the findings by Qi et al. (2014). However, the water content of 4.27 % in NBS 30 biotite is much too high compared to the empirical water content of 3.64 % in pure biotite. We speculate that NBS 30 contains some impurities, such as lamellae of chlorite, with about 10–12 % water by mass. This water cannot be released from the material having the original, relatively-large particle size by the on-line TC/EA method, but it can be released from the material with smaller particle size. The hydrogen yields from different particle sizes of NBS 30 demonstrated a clear trend toward higher yield with finer grain size (Qi et al. 2014). It is unclear how the assigned water content of 3.5 % was obtained. We would assume that the manometry method would be used to determine the water content. Further study may be useful for investigating methods for accurate water content measurement.

Table 5

Hydrogen mass fractions of USGS57, USGS58, and NBS 30 as a function of particle size and drying conditions

[Measurements determined with both a Cr-filled reactor (NBS 30 was not included) and a glassy carbon-filled reactor; uncertainties are 1-sigma standard deviations.]

Reactor	Particle size (µm)	USGS57 biotite				USGS58 muscovite				NBS 30 biotite	
		Dried		Undried		Dried		Undried		Dried	
		As H (%)	As H_2O (%)	As H (%)	As H_2O (%)	As H (%)	As H_2O (%)	As H (%)	As H_2O (%)	As H (%)	As H_2O (%)
Cr-filled[c]	Original	0.425	3.82	0.423	3.81	0.479	4.31	0.475	4.27	_	_
	149−177 or 149	0.430	3.87	0.431	3.88	0.494	4.44	0.494	4.45	_	_
	105−149	0.434	3.90	0.433	3.90	0.498	4.48	0.491	4.42	_	_
	74−105	0.435	3.92	0.437	3.93	0.479	4.31	0.481	4.33	_	_
	<74	0.416	3.74	0.416	3.75	0.454	4.08	0.453	4.08	_	_
Glassy carbon-filled[d]	Original	0.416	3.74	_	_	0.432	3.89	_	_	0.395	3.55
	<74	0.409	3.68			0.448	4.03			0.475	4.27
Recommended mass fraction H[c]		**0.416 ± 0.002 %, n = 4**				**0.448 ± 0.002 %, n = 4**				**0.475 ± 0.015 %, n = 4**	
Recommended mass fraction H_2O		**3.74 ± 0.02 %, n = 4**				**4.03 ± 0.02 %, n = 4**				**4.27 ± 0.14 %, n = 4**	

[c] Measurements determined with a Cr-filled reactor; calculations were based on the yield of hydrogen from caffeine.

[d] Measurements determined with a glassy carbon-filled reactor; calculations were based on the yield of hydrogen from polyethylene.

[e] The recommended mass fractions of hydrogen (H) and water (H_2O) were based on the assumption that the highest yield should provide most accurate values.

4.4. Moisture absorption and removal

To test the efficiency of water removal by drying samples of RMs in a vacuum oven at 45 °C for few hours, a dual-water equilibration experiment was conducted. This test was presented in Table 4 of Qi et al. (2014). The sample named Biotite-1 (177 µm) is the same material as USGS57 and the sample named Muscovite-2 (149 µm) is USGS58. The two RMs were divided into three groups. The first group was analyzed without any treatment. The second group of samples was allowed to exchange with water vapor enriched in ^{2}H (UC04 with $\delta^{2}\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = +113$ mUr). The third group of samples was allowed to exchange with water depleted in ^{2}H (W-63333 with $\delta^{2}\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -399.5$ mUr). The exchange experiment was conducted in a closed container at ambient temperature for 11 days. Samples were dried in a vacuum oven at 45 °C for 5 h prior to analysis. The δ^{2}H values summarized in Table 6 indicate that neither the amount of water adsorbed on mineral surfaces, nor hydrogen isotopic exchange, are substantial at ambient temperature. The finer material, USGS58 muscovite, which was exposed to W-63333 had slightly more negative δ^{2}H values, but values were within two sigma of the original material. The results in Table 6 confirm that there is little to no hydrogen exchange between hydrogen in two RMs and water at ambient temperature, and adsorbed moisture on both RMs can be removed effectively by drying in a vacuum oven at 45 °C for 5 h. The samples analyzed at the University of Oregon were all dried in vacuum at 130 °C for 14 h inside silver cups, immediately loaded (5 min exposure to air while in silver cups), and analyzed.

Table 6

The δ^2H values of USGS57 biotite and USGS58 muscovite

[Each sample was divided into three groups. One group was analyzed without any treatment (labelled "Original"). The second group of samples was equilibrated in water enriched in ^{2}H, UC04. The third group was equilibrated in water depleted in ^{2}H, W-63333. The δ^2H values are not normalized to VSMOW-SLAP, but are measured δ^2H values expressed relative to the same laboratory reference. Uncertainties are one standard deviation.]

Description	δ^2H (mUr)	
	USGS57 biotite 177 µm	USGS58 muscovite 149 µm
Original	−87.8	−29.0
	−89.1	−27.1
	−90.0	−28.0
Mean	**−89.0 ± 1.1**	**−28.0 ± 1.0**
Equilibrated with UC04	−90.7	−30.8
	−92.1	−28.8
	−90.9	−28.6
Mean	**−91.2 ± 0.8**	**−29.4 ± 1.2**
Equilibrated with W-63333	−89.8	−31.2
	−89.1	−30.1
	−92.8	−30.2
Mean	**−90.6 ± 2.0**	**−30.5 ± 0.6**

4.5. The $\delta^2H_{VSMOW\text{-}SLAP}$ results

Six laboratories used on-line methods based on a variety of high temperature conversion elemental analyzers (TC/EA, with Cr-filled reactor or glassy carbon-filled reactors) and gas chromatographic (GC) interfaces, as well as mass spectrometers from different manufacturers (Table 1). The results presented in Table 7 are all normalized to the VSMOW-SLAP scale using

2-point calibration schemes. The average $\delta^2H_{VSMOW\text{-}SLAP}$ values of –91.5 ± 2.4 mUr for USGS57 biotite and –28.4 ± 1.7 mUr for USGS58 muscovite analyzed by six laboratories using on-line TC/EA methods (both glassy carbon-filled reactors and Cr-filled reactors) were confirmed by the results obtained using the off-line method (–92.9 ± 2.8 mUr for USGS57 and –28.1 ± 0.8 mUr for USGS58). The final mean $\delta^2H_{VSMOW\text{-}SLAP}$ values of –91.5 ± 2.4 mUr for USGS57 biotite and –28.4 ± 1.6 mUr for USGS58 muscovite were calculated from 23 on-line results and one off-line result. The uncertainties are given as 1-σ standard deviation.

The UFZ, MPI-BGC, and RSIL performed measurements at different temperatures using Cr-filled reactors, with temperatures ranging between 1050 °C and 1430 °C; no systematic difference was observed within analytical uncertainty. A typical $\delta^2H_{VSMOW\text{-}SLAP}$ measurement uncertainty was ~1 to 2 mUr. Although variations in δ^2H values and hydrogen yields from samples with different particle sizes of USGS57 and USGS58 were observed by using both glassy carbon-filled reactor and Cr-filled reactor (as discussed early), one would assume that the measured δ^2H values with highest hydrogen yields should be considered as the most reliable values. However, the overall uncertainties of δ^2H values from all size fractions (Table 4) are insignificant compare to the measurement shown in Table 7. The average uncertainties of δ^2H values from all size fractions are in the range of 0.3 to 1.2 mUr for USGS57 and 1.9 to 2.7 mUr for USGS58, respectively (Table 4).

Table 7

The $\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}}$ values of USGS57 biotite, USGS58 muscovite, and NBS 30 biotite isotopic reference materials analyzed by on-line high temperature conversion/elemental analyzer and an off-line method by seven isotope laboratories

[Uncertainties are one-sigma standard deviations.]

Laboratory	Run #	Reactor used	condition	USGS57 biotite $\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}}$	n	USGS58 muscovite $\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}}$	n	NBS 30 biotite $\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}}$	n
UC	1	Glassy carbon	1450 °C	−94.7 ± 1.0	11	−29.9 ± 1.3	12	−54.0 ± 1.7	4
UL	1	Glassy carbon	1450 °C	−89.4 ± 1.0	10	−25.7 ± 1.0	10	−47.7 ± 3.5	7
UO	1	Glassy carbon	1450 °C	−92.3 ± 1.3	3	−30.6 ± 0.6	3	−57.0 ± 1.0	3
UO	2	Glassy carbon	1450 °C	−91.0 ± 0.6	3	−28.0 ± 0.5	3	−54.3 ± 1.6	3
UO	3	Glassy carbon	1450 °C	−91.0 ± 1.2	4	−28.0 ± 1.8	4	−54.0 ± 1.7	4
UO	4	Glassy carbon	1450 °C	−95.2 ± 0.4	3	−31.2 ± 0.1	3	−54.0 ± 1.7	3
UO	5	Glassy carbon	1450 °C	−95.6 ± 0.1	2	−32.7 ± 0.7	2	−54.0 ± 1.7	3
UO	6	Glassy carbon	1450 °C	−91.0 ± 1.2	4	−28.1 ± 1.4	4	−54.0 ± 1.7	4
UFZ	1	Cr	1150 °C	−86.8 ± 1.7	5	−27.8 ± 0.1	5	−53.1 ± 0.5	5
UFZ	2	Cr	1150 °C	−86.5 ± 2.1	5	−27.8 ± 0.5	5	−53.0 ± 0.4	5
UFZ	3	Cr	1270 °C	−91.9 ± 1.3	5	−29.9 ± 0.6	5	−54.1 ± 0.8	5
UFZ	4	Cr	1270 °C	−93.4 ± 0.9	4	−30.0 ± 0.8	4	−54.1 ± 0.7	4
UFZ	5	Cr	1270 °C with V_2O_5	−89.0 ± 0.7	4	−27.3 ± 0.9	4	−51.9 ± 1.3	5
UFZ	6	Cr	1270 °C with V_2O_5	−90.1 ± 1.5	5	−27.2 ± 2.6	4	−51.0 ± 1.0	5
UFZ	7	Cr	1270 °C with $V_2O_5 + O_2$	−89.6 ± 1.3	5	−28.4 ± 1.0	5	−52.3 ± 0.9	5
MPI-BGC	1	Cr	1430 °C	−91.1 ± 0.5	4	−27.4 ± 0.6	4	−52.3 ± 0.4	4
MPI-BGC	2	Cr	1400 °C	−91.2 ± 0.7	4	−26.5 ± 0.5	4	−52.3 ± 1.3	4
MPI-BGC	3	Cr	1400 °C	−93.7 ± 0.7	4	−28.2 ± 0.4	4	−53.8 ± 0.8	4
RSIL	1	Glassy carbon	1450 °C	−89.5 ± 0.7	7	−26.2 ± 1.5	7	−49.5 ± 1.2	7
RSIL	2	Cr	1050 °C	−91.9 ± 1.1	6	−28.8 ± 0.3	6	−53.8 ± 0.6	6
RSIL	3	Cr	1050 °C to 1350 °C[f]	−92.4 ± 0.9	7	−27.6 ± 0.6	7	−54.2 ± 1.1	7
RSIL	4	Cr	1050 °C	−92.5 ± 0.6	7	−28.0 ± 0.8	5	−54.9 ± 1.2	6
RSIL	5	Cr	1150 °C	−94.2 ± 2.0	3	−27.5 ± 0.3	3	−55.1 ± 1.2	3
			Average on-line data	−91.5 ± 2.4, n = 23		−28.4 ± 1.7, n = 23		−53.4 ± 2.5, n = 23	

UWO	Off-line[g]	−92.9 ± 2.8	5	−28.1 ± 0.8	5
	Average all	−91.5 ± 2.4, n = 24		−28.4 ± 1.6, n = 24	

[f] Each sample was analyzed at different temperatures between 1050 °C and 1350 °C during the same run.

[g] The $\delta^{2}H_{VSMOW-SLAP}$ measurements determined with the off-line method were performed on different days.

The mean $\delta^2H_{\text{VSMOW-SLAP}}$ value of –53.4 ± 2.5 mUr for NBS 30 biotite obtained from 9 analyses using a glassy carbon-filled reactor and 14 analyses using a Cr-filled reactor (at different temperatures) by five laboratories confirmed Qi et al. (2014)'s finding that the $\delta^2H_{\text{VSMOW-SLAP}}$ values of NBS 30 biotite (having an original particle size between 200 and 300 µm) analyzed by on-line HTC systems can be substantially too positive compared to the accepted value of –65.7 mUr (Gonfiantini and Rozanski, 1995). Although USGS57 is biotite, it behaves differently in the HTC systems compare to NBS 30 biotite. This is because the USGS57 biotite contains less impurities relative to NBS 30, and unlike NBS 30, USGS57 is homogeneous among the size fractions analyzed and does not contain an alteration product (chlorite) in its final fractions. The conversion of hydroxyl ions in USGS58 muscovite to molecular hydrogen is hypothesized to be quantitative. Users should be cautious in analyzing hydrous minerals using on-line HTC systems. Conversion of hydrogen in minerals to molecular hydrogen may not be quantitative, depending upon their chemical composition and particle size, even for the same phase (e.g. biotite) with the result that $\delta^2H_{\text{VSMOW-SLAP}}$ values may be unreliable.

4.6. Additional observation with caffeine

To quantify accurately the mass fraction of hydrogen in the two RMs, several aliquots of USGS62 caffeine with precisely determined (and different) masses were analyzed at the beginning, middle, and end of a run to monitor and adjust for apparent changes in the hydrogen yield during a run for both the glassy carbon-filled reactor and the Cr-filled reactor. Caffeine samples placed at the beginning of a sequence were analyzed with a newly packed glassy carbon reactor. As one might expect, formation of hydrogen-bearing by-products (HCN) from the caffeine reaction prevents quantitative conversion of organic hydrogen to molecular hydrogen when a conventional on-line TC/EA method with a glassy carbon-filled reactor is used. Thus, $\delta^2H_{\text{VSMOW-SLAP}}$ results are seriously compromised due to non-quantitative conversion of hydrogen to molecular hydrogen (Gehre et al., 2015). This is demonstrated in Figure 2a with data obtained from a newly packed reactor. The caffeine samples at the middle of the sequence were analyzed after 20 biotite samples having 3.5-mg in each sample. The $\delta^2H_{\text{VSMOW-SLAP}}$ values and relative hydrogen yields from caffeine changed from −175.2 mUr (analyzed in fresh reactor) to −166.5 mUr (analyzed after biotite), and 132 (analyzed in fresh reactor) to 156 (analyzed after biotite), respectively (Fig. 2a). The $\delta^2H_{VSMOW-SLAP}$ values of −158.4 ± 2.2 mUr from caffeine analyzed at end of the sequence of 20 muscovite samples is almost identical to the assigned value of −156.1 ± 2.1 mUr (Schimmelmann et al., 2016). The relative hydrogen yield also increased significantly. This observation indicates that the mineral residue generated from high temperature conversion can prevent the formation of HCN from caffeine and can improve the quantitative conversion of hydrogen. The analysis with an identical arrangement of samples in the sequence was carried out with a Cr-filled reactor. Both $\delta^2H_{VSMOW-SLAP}$ values and relative hydrogen yields (as relative peak area/mass) from caffeine were approximately the same through the sequence (Fig. 2b). From these observations, one needs to be cautious in deciding whether glassy carbon-filled or Cr-filled reactors should be used when different materials are intend to be analyzed in the same analytical sequence.

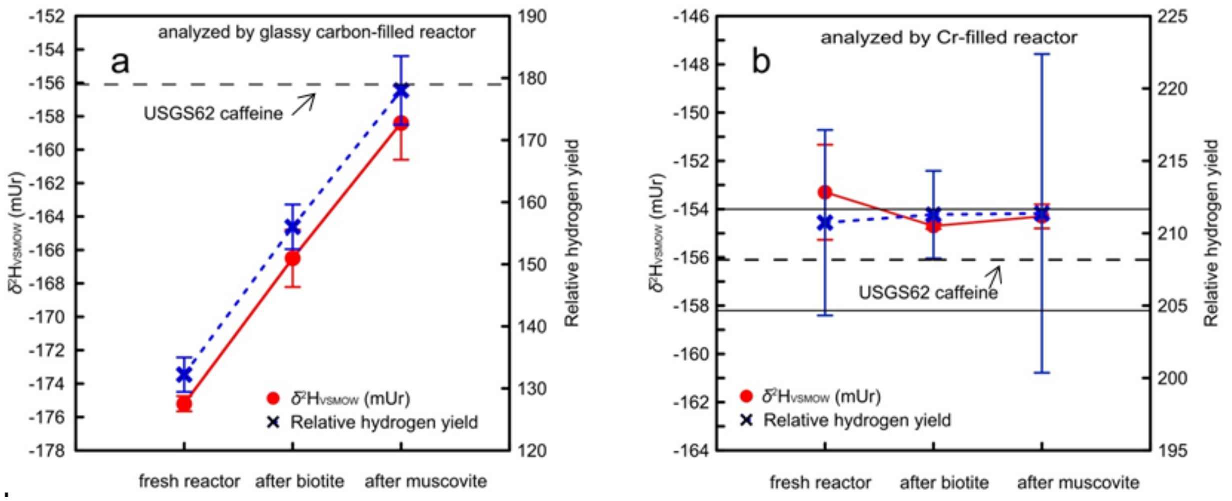

Fig. 2. The $\delta^2H_{VSMOW-SLAP}$ values and relative hydrogen yields (relative peak areas / mass) of USGS62 caffeine analyzed at the beginning (fresh reactor), middle (after biotite), and end (after muscovite) of a sequence using a glassy carbon-filled reactor (a) and a Cr-filled reactor (b).

5. Conclusion

The supply of the internationally distributed isotopic reference material NBS 30 biotite is exhausted. To ensure accurate and traceable on-line hydrogen isotope-ratio determinations of mineral samples, two isotopically homogeneous hydrous mineral RMs, USGS57 biotite and USGS58 muscovite, have been prepared by the U.S. Geological Survey (USGS). The δ^2H values were determined by both glassy carbon-based on-line conversion and chromium-based on-line conversion by six international isotope laboratories, and results were verified by the classic off-line conversion method. The isotopic compositions with 1-σ uncertainty and mass fractions of hydrogen in these materials are:

USGS57 (biotite)
$\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -91.5 \pm 2.4$ mUr (n = 24)
Hydrogen mass fraction = 0.416 ± 0.002 % (n = 4)
Fraction of water = 3.74 ± 0.02 % (n = 4)

USGS58 (muscovite)
$\delta^2\mathrm{H}_{\mathrm{VSMOW\text{-}SLAP}} = -28.4 \pm 1.6$ mUr (n = 24)
Hydrogen mass fraction = 0.448 ± 0.002 % (n = 4)
Fraction of water = 4.03 ± 0.02 % (n = 4)

The use of these RMs will promote high quality and standardized stable isotope measurements of hydrogen in hydrous mineral samples. Analyzing a mineral sample with a particle size ≤ 74 µm and ≥ 177 µm is not recommended based on this study. Users should be cautious in analyzing hydrous minerals using these RMs with on-line HTC systems because conversion of hydrogen in minerals to molecular hydrogen may not be quantitative, depending upon mineral chemical composition and particle size. There is no significant difference in results for these two RMs between samples analyzed using the glassy carbon-filled reactor method or the Cr-filled reactor method. The glassy carbon-based conversion method yields more consistent δ^2H values than the Cr-based conversion for the two RMs, especially for USGS57 biotite. Further study may be needed for investigating the accurate water content of NBS 30 biotite.

6. Source for USGS57 and USGS58

USGS57 biotite and USGS58 muscovite isotopic reference materials are available from:
U.S. Geological Survey
Reston Stable Isotope Laboratory
431 National Center
12201 Sunrise Valley Drive
Reston, Virginia 20192
USA
http://isotopes.usgs.gov/
Fax: +1 703 648 5889

Each distribution unit contains 0.5 g of mineral powder.

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