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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 (RMs). A strategy of two-point calibrations spanning δ^2H range of the unknowns using two RMs is recommended. Unfortunately, the supply of the previously widely used isotopic RM, 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 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, which are urgently needed. The U.S. Geological Survey (USGS) has prepared two such RMs, USGS57 biotite and USGS58 muscovite. The δ^2H 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 HTC 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)
$\delta^2H_{VSMOW\text{-}SLAP}$ = −91.5 ± 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)
$\delta^2H_{VSMOW\text{-}SLAP}$ = −28.4 ± 1.6 mUr (n = 24)
Mass fraction hydrogen = 0.448 ± 0.002% (n = 4)
Mass fraction water = 4.03 ± 0.02% (n = 4).

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

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

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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 of water with uranium or zinc metal to liberate molecular hydrogen 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 HTC 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 δ^2H_{VSMOW}, which is defined by the relation (Coplen, 2011):

$$\delta^2H_{VSMOW} = \frac{R(^2H/^1H)_P - R(^2H/^1H)_{VSMOW}}{R(^2H/^1H)_{VSMOW}}$$

where $R(^2H/^1H)_P$ is the ratio $N(^2H)_P / N(^1H)_P$ and $N(^2H)_P$ and $N(^1H)_P$ are the numbers of the two isotopes of hydrogen, ^2H and ^1H, 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 $\delta^2H_{VSMOW\text{-}SLAP}$ values.

Accurate hydrogen isotope analysis by on-line or off-line techniques requires appropriate isotopic reference materials (RMs). A strategy of two-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 RM, 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 $\delta^2H_{VSMOW\text{-}SLAP}$ 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 ($\delta^2H_{VSMOW\text{-}SLAP}$ = − 99.2 mUr; Schimmelmann et al., 2016), NBS 22 oil ($\delta^2H_{VSMOW\text{-}SLAP}$ = − 117.2 mUr; Schimmelmann et al., 2016), USGS42 Tibetan human hair ($\delta^2H_{VSMOW\text{-}SLAP}$ = − 72.9 mUr; Coplen and Qi, 2016), and USGS43 Indian human hair ($\delta^2H_{VSMOW\text{-}SLAP}$ = − 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 $\delta^2H_{VSMOW\text{-}SLAP}$ 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., 2014a). The $\delta^2H_{VSMOW\text{-}SLAP}$ 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 $\delta^2H_{VSMOW\text{-}SLAP}$ of NBS 30 biotite, but not of biotites with lower iron content. Moreover, the $\delta^2H_{VSMOW\text{-}SLAP}$ 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., 2014a). In 2016, 19 new organic RMs for hydrogen, carbon, and nitrogen stable isotope-ratio measurements were prepared (Schimmelmann et al., 2016), and these enabled more accurate determinations of relative stable isotope ratios of hydrogen (δ^2H), carbon (δ^{13}C), and nitrogen (δ^{15}N) measurements using at least two isotopic RMs to anchor the isotope-delta scale 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 HTC 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 (Armbruster et al., 2006; Hunsinger et al., 2013; Qi et al., 2014a; Gehre et al., 2015; Nair et al., 2015; Gehre et al., 2017). 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 HTC (Hunsinger et al., 2013; Gehre et al., 2015; Nair et al., 2015; Gehre et al., 2017). 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 HTC method that uses a glassy, carbon-filled reactor. 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) enabling quantitative conversion to molecular hydrogen. Gehre et al. (2017) later improved the Cr-EA method and extended the investigation of δ^2H analysis to substances containing fluorine, chlorine, bromine, iodine, and sulfur. The optimized the EA-Cr/HTC-IRMS technique, which 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 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 laboratories participated in this study. Sample preparation methods and methods to determine $\delta^2H_{VSMOW\text{-}SLAP}$ values are described in this article.