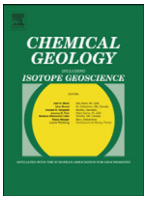
Chemical Geology 412 (2015) 99–106

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo



Sulfate and sulfide sulfur isotopes ($\delta^{34}S$ and $\delta^{33}S$) measured by solution and laser ablation MC-ICP-MS: An enhanced approach using external correction

Michael J. Pribil *, W. Ian Ridley, Poul Emsbo

U.S. Geological Survey, MS 973, Denver Federal Center, Denver, CO 80225, United States

ARTICLE INFO

Article history:
Received 6 February 2015
Received in revised form 4 July 2015
Accepted 8 July 2015
Available online 11 July 2015

Editor: Michael E. Böttcher

Keywords:
Sulfur isotope
MC-ICP-MS
LA-MC-ICP-MS
Plasma induced fractionation
δ34Ssulfide and δ33Ssulfide measurements

ABSTRACT

Isotope ratio measurements using a multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) commonly use standard-sample bracketing with a single isotope standard for mass bias correction for elements with narrow-range isotope systems measured by MC-ICP-MS, e.g. Cu, Fe, Zn, and Hg. However, sulfur (S) isotopic composition ($\delta^{34}S$) in nature can range from at least −40 to +40‰, potentially exceeding the ability of standard-sample bracketing using a single sulfur isotope standard to accurately correct for mass bias. Isotopic fractionation via solution and laser ablation introduction was determined during sulfate sulfur ($S_{sulfate}$) isotope measurements. An external isotope calibration curve was constructed using in-house and National Institute of Standards and Technology (NIST) $S_{sulfate}$ isotope reference materials (RM) in an attempt to correct for the difference. The ability of external isotope correction for $S_{sulfate}$ isotope measurements was evaluated by analyzing NIST and United States Geological Survey (USGS) $S_{sulfate}$ isotope reference materials as unknowns. Differences in $\delta^{34}S_{sulfate}$ between standard-sample bracketing and standard-sample bracketing with external isotope correction for sulfate samples ranged from 0.72‰ to 2.35‰ over a $\delta^{34}S$ range of 1.40‰ to 21.17‰. No isotopic differences were observed when analyzing $S_{sulfide}$ reference materials over a $\delta^{34}S_{sulfide}$ range of −32.1‰ to 17.3‰ and a $\delta^{33}S$ range of −16.5‰ to 8.9‰ via laser ablation (LA)-MC-ICP-MS. Here, we identify a possible plasma induced fractionation for $S_{sulfate}$ and describe a new method using external isotope calibration corrections using solution and LA-MC-ICP-MS.

Published by Elsevier B.V.

1. Introduction

Isotope ratios of sulfur (^{32}S, ^{33}S, and ^{34}S) are commonly used to trace this allotropic and abundant element through complex abiotic and biotic cycling and redox processes (Thode et al., 1961; Rees et al., 1978; Bühn et al., 2012). Many analytical methods exist for measuring sulfur isotope ratios including secondary ion mass spectrometry (SIMS) (Deloule et al., 1986; Chaussidon et al., 1989), gas source isotope ratio mass spectrometry (GS-IRMS or GS-MS) (Thode et al., 1961; Rees et al., 1978), elemental analyzer isotope ratios mass spectrometry (EA-IRMS) (Giesemann et al., 1994; Studley et al., 2002; Grassineau, 2006), and more recently multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (Mason et al., 2006; Craddock et al., 2008; Bühn et al., 2012; Paris et al., 2013). Generally, GS-MS is considered the "gold standard" for precise and accurate sulfur isotope measurements. However, more recently $\delta^{34}S$ measurements for solution and solid samples by MC-ICP-MS have achieved similar precision (Mason et al., 2006; Craddock et al., 2008; Bühn et al., 2012; Paris et al., 2013) as other conventional instruments (Thode et al., 1961; Rees et al., 1978; Deloule et al., 1986; Chaussidon et al., 1989; Giesemann et al., 1994; Studley et al., 2002; Grassineau, 2006). Additionally, the low detection limits of MC-ICP-MS provide the ability to analyze isotope ratios of samples with only trace amounts of sulfur (Paris et al., 2013; Bern et al., 2015). Furthermore, complementing these new methods for $\delta^{34}S$ measurements are the recent advancements for measuring $\delta^{33}S$ by LA-MC-ICP-MS and SIMS (Whitehouse et al., 2005; Mason et al., 2006; Bühn et al., 2012).

Spectral and non-spectral matrix effects present challenges to obtaining high-precision isotope ratio measurements using MC-ICP-MS. For example, matrix elements can affect the vaporization and ionization efficiency in the plasma of the element of interest resulting in instrumental-induced isotopic fractionation (Carlson and Hauri, 2001; Zhu et al., 2002; Albarède and Beard, 2004). For solution sulfur samples, these artifacts can be largely eliminated by appropriate preparation and chemical purification of the samples (e.g., Mason et al., 2006; Craddock et al., 2008; Paris et al., 2013). Recent advances in LA-MC-ICP-MS have provided the potential to analyze samples (i.e., anhydrite, pyrite, chalcopyrite, pyrrhotite, and barite) at a high spatial resolution for both $\delta^{34}S$ and $\delta^{33}S$ (Mason et al., 2006; Craddock et al., 2008; Bühn et al., 2012). However, a limited number of matrix-matched solid sulfur isotope

---

* Corresponding author.
E-mail address: mpribil@usgs.gov (M.J. Pribil).

http://dx.doi.org/10.1016/j.chemgeo.2015.07.014
0009-2541/Published by Elsevier B.V.

reference materials exist for LA-MC-ICP-MS analyses, thus making the determination of matrix effects difficult to assess and correct during isotope ratio analysis.

Recently, differences have been identified between the reported $\delta^{34}S_{sulfate}$ of well-characterized sulfate reference materials measured by both solution and LA-MC-ICP-MS and their accepted sulfur isotopic compositions. For example, Bühn et al. (2012) measured and reported the $\delta^{34}S_{sulfate}$ of National Institute of Standards and Technology (NIST) RM 8557 by LA-MC-ICP-MS using both International Atomic Energy Agency (IAEA) S-1 and IAEA S-3 as bracketing standards to correct for instrumental isotopic mass fractionation. Their reported $\delta^{34}S_{sulfate}$ for NIST RM 8557 (22.59‰) were consistently heavier than the accepted $\delta^{34}S_{sulfate}$ for this reference material (21.17‰). Mason et al. (2006) reported $\delta^{34}S_{sulfate}$ for NIST RM 8557 and NIST RM 8553 of 18.4‰ and 11.4‰, respectively, when measured using IAEA S-1 as a bracketing standard combined with internal Si isotope correction. These measured values were lighter by 2.77‰ and 5.46‰ relative to their accepted $\delta^{34}S_{sulfate}$. Further, the $\delta^{34}S_{sulfate}$ for NIST RM 8557 reported by Mason et al. (2006) using only standard-sample bracketing to correct for instrumental mass fractionation was 23.0‰, nearly 2‰ heavier than the accepted value. These differences persisted even in the instance when a sulfate reference material was used to bracket the isotopic measurement of another sulfate reference material analyzed as an unknown. We have observed at the U.S. Geological Survey (USGS) similar differences between measured and accepted $\delta^{34}S_{sulfate}$ for sulfate reference materials measured by solution MC-ICP-MS. The reported data clearly indicate that standard-sample bracketing and Si-doping methods may be inadequate for the correction of instrumental mass bias for sulfate sulfur isotope measurements. These observations, as well as similar offsets determined when conducting $S_{sulfate}$ isotope measurements at the USGS provided the rationale for the present study.

No attempt was made to cross calibrate $S_{sulfate}$ to $S_{sulfide}$ reference material because: (1) solutions of sulfide are expected to exist as the oxidized form of sulfur ($S_{sulfate}$) in nitric acid solutions, and (2) modern laser ablation system sample chambers are capable of housing numerous reference materials that can generally allow some degree of sulfate or sulfide matrix matching of a reference material to the sample. The goals of this study were thus to: (1) determine if isotopic differences from accepted values using standard-sample bracketing method were observed for both liquid and solid $S_{sulfate}$ sample introduction; (2) determine if the isotopic differences formed a linear array that would allow for external isotope correction to the standard-sample bracketed data; (3) determine if sulfide reference materials exhibit isotopic difference as do sulfate reference materials over a broad isotopic range; and (4) identify the possible source of the induced $S_{sulfate}$ isotopic fractionation.

2. Experimental

2.1. Sulfur isotope ratio calculations

Multiple sulfur isotope reference material from NIST and IAEA, and USGS in-house reference materials that were well characterized by GS–MS were used in this study (Table 1). Here, we assume that these materials represent the closest approach to “true” sulfur isotopic compositions, i.e., benchmarks against which other values for the same materials can be evaluated, and are referred to here as “accepted” values. The isotope ratio data ($\delta^{34}S$ and $\delta^{33}S$) for reference material and samples are reported relative to the Vienna Cañon Diablo troilite (VCDT) scale defined by the assignment of $\delta^{34}S$ of −0.30‰ to the IAEA S-1 Ag_2S reference material (Krouse and Coplen, 1997) using the expression:

$$\delta^{34\text{ or }33}S_{V-CDT} = \left[\frac{\dfrac{34\text{ or }33}{32}S_{sample}}{\dfrac{34\text{ or }33}{32}S_{reference\ V-CDT}} - 1\right] \times 1000 \tag{1}$$

Mass independent fractionation (MIF) is evaluated by $\delta^{34}S$ and $\delta^{33}S$ deviation from the theoretical mass-dependent fractionation (MDF) line determined using a first-order mass-dependent fractionation law (Young et al., 2002):

$$\beta = \left(\frac{\dfrac{1}{m_1} - \dfrac{1}{m_2}}{\dfrac{1}{m_1} - \dfrac{1}{m_3}}\right) \tag{2}$$

Where $m_1 = {}^{34}S$, $m_2 = {}^{33}S$ and $m_3 = {}^{32}S$ resulting with a β for $\delta^{34}S$ and $\delta^{33}S$ of 0.515. The deviation from the theoretical MDF, defined by $\Delta^{33}S$ (Johnson, 2011) is:

$$\Delta^{33}S = \delta^{33}S - 0.515 \times \delta^{34}S \tag{3}$$

2.2. Sample preparation

Powdered reference materials for LA-MC-ICP-MS were pressed into pellets (15 mm in diameter) using a hydraulic press without binder at approximately 15,000 lb per square inch. The pressed pellets demonstrated stable ablation characteristics determined by steady and reproducible sulfur signal during analyses, as well as preserving the integrity of the pellet. Samples were pressed without binder to reduce possible contamination from the binder material. Reference material samples were prepared for solution introduction by dissolving a precise amount of powdered material in 2% HNO_3 in pre-cleaned 250 ml vials to

Table 1
NIST and IAEA reference materials and USGS in-house reference sulfur isotope materials used for this study.

Reference material	Sulfur material	Accepted value ($\delta^{34}S$ ‰,V-CDT)	2σ (‰)
NIST RM 8554 (IAEA S-1)	Silver Sulfide	−0.30[a]	n/a
NIST RM 8529 (IAEA S-3)	Silver Sulfide	−32.3[b]	0.20
NIST RM 8553 (IAEA S-4)	Elemental sulfur	16.86[a]	0.03
NIST RM 8556 (NBS 123)	Sphalerite (sulfide)	17.09[a]	0.19
NIST RM 8557 (NBS 127)	Barium sulfate	21.17[a]	0.09
USGS M-158	Fresh water (sulfate)	1.40[c]	0.30
USGS Na_2SO_4	Sodium sulfate	1.10[c]	0.30
USGS THEN	Sodium sulfate	4.03[c]	0.30
USGS GYP	Calcium sulfate	10.00[c]	0.30
USGS TECH	Calcium sulfate	15.36[c]	0.30
USGS phosphate	Sulfur rich phosphate (sulfate)	19.30[c]	0.30
CASS-4	Seawater (sulfate)	20.99	0.06

[a] Information from the NIST reference material certificates.
[b] Information from the IAEA reference material certificates.
[c] In-house reference material characterized by the USGS Stable Isotope Laboratory in Denver, CO.