



PII S0016-7037(01)00611-1

Calibrated sulfur isotope abundance ratios of three IAEA sulfur isotope reference materials and V-CDT with a reassessment of the atomic weight of sulfur

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(Received December 11, 1999; accepted in revised form February 10, 2001)

Abstract—Calibrated values have been obtained for sulfur isotope abundance ratios of sulfur isotope reference materials distributed by the IAEA (Vienna). For the calibration of the measurements, a set of synthetic isotope mixtures were prepared gravimetrically from high purity Ag₂S materials enriched in ³²S, ³³S, and ³⁴S. All materials were converted into SF₆ gas and subsequently, their sulfur isotope ratios were measured on the SF₅⁺ species using a special gas source mass spectrometer equipped with a molecular flow inlet system (IRMM's Avogadro II amount comparator). Values for the ³²S/³⁴S abundance ratios are 22.650 4(20), 22.142 4(20), and 23.393 3(17) for IAEA-S-1, IAEA-S-2, and IAEA-S-3, respectively. The calculated ³²S/³⁴S abundance ratio for V-CDT is 22.643 6(20), which is very close to the calibrated ratio obtained by Ding et al. (1999). In this way, the zero point of the VCDT scale is anchored firmly to the international system of units SI. The ³²S/³³S abundance ratios are 126.942(47), 125.473(55), 129.072(32), and 126.948(47) for IAEA-S-1, IAEA-S-2, IAEA-S-3, and V-CDT, respectively. In this way, the linearity of the V-CDT scale is improved over this range. The values of the sulfur molar mass for IAEA-S-1 and V-CDT were calculated to be 32.063 877(56) and 32.063 911(56), respectively, the values with the smallest combined uncertainty ever reported for the sulfur molar masses (atomic weights). Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

The isotope composition of sulfur in terrestrial materials varies over a wide range, whereas the isotope composition of sulfur in meteorites is rather constant and close to the average composition of terrestrial samples. For this reason, troilite (FeS) from the Cañon Diablo meteorite (CDT) has been used as an international reference for sulfur isotopic composition since 1962 (McNamara and Thode, 1950; Jensen and Nakai, 1962). Its sulfur isotope composition has been taken as the basis for the calculation of the atomic weight of sulfur (IUPAC-CAWIA, 1984). After more than 30 years of use, unfortunately, CDT is no longer easily obtainable, and furthermore, it has been proven that CDT is slightly inhomogeneous in its sulfur isotopic composition (Beaudoin et al., 1994; Gonfiantini et al., 1993; Robinson, 1993). To establish continuity of data acquisition, the IAEA advisory group on reference materials for stable isotope measurements (Vienna, 1993) proposed a V-CDT scale, defined by a new reference material, IAEA-S-1 (Ag₂S), having a δ³⁴S_{V-CDT} of −0.3‰ (Robinson, 1993). This proposal was accepted by CAWIA in 1995 (IUPAC-CAWIA, 1997, 1998). It was recommended that since then all data for sulfur isotope composition should be reported as δ values related to V-CDT, i.e.,

$$\delta^i S_{V-CDT}(\text{‰}) = [(\delta^i S)_{\text{sample}} / (\delta^i S)_{V-CDT} - 1] \times 10^3$$

where $i = 32$ and $j = 33, 34$, and 36 .

A special effort was made to have the isotope composition of

V-CDT be identical to that of CDT (Robinson, 1993). However, in practice there are some differences between the current V-CDT scale and the previous CDT scale for the following reasons: the isotopic inhomogeneity of the old CDT material and the differences in instruments, chemical procedures, and working standards used by the laboratories participating in intercomparison measurements.

This will cause some shift (it may be very small, but cannot be quantified exactly) of the zero point of the sulfur isotope scale. This situation is not very satisfactory for the community of isotope geochemistry. Furthermore, if we do not solve it beforehand, similar problems may appear again when IAEA-S-1 is exhausted and a new reference sample is established. Therefore, at the 7th IAEA Consultants Meeting on Reference Materials for Stable Isotope Measurements in Groningen in 1998, it was recommended to initiate the linking of δ-scale to the calibrated isotopic ratios of reference materials. The latter has demonstrated traceability to actual ratios of amounts of the isotopes concerned within a specified, proven, and small uncertainty.

For this reason, the absolute isotope abundance ratios of the IAEA sulfur isotope reference materials were measured. Preliminary work on calibrated the ³²S/³⁴S abundance ratio of IAEA-S-1 and V-CDT was done previously by Ding et al. (1999). The absolute ³²S/³⁴S abundance ratio of V-CDT resulting from that study is 22.649 6(60), ~1.9% higher than the currently assigned ratio of 22.22 for CDT (Jensen and Nakai, 1962). Thus, further work was undertaken at IRMM to measure the absolute ³²S/³³S and ³²S/³⁴S abundance ratios of these IAEA sulfur isotope reference materials. In a previous paper, the chemical procedure for preparing synthetic isotope mixtures was described (Ding et al., 2000). Here, the calibration

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Table 1. Impurities by ICP-MS (Vanhaecke et al., 1996) in the isotopically enriched Ag₂S materials used in the preparation of the isotope mixtures.

Impurities (in μg/g)	Ag ₂ S-32 ^a	Ag ₂ S-33 ^b	Ag ₂ S-34 ^c
Mg	2.9 (1.1)	2.6 (1.0)	2.4 (0.9)
Al	4.1 (2.1)	3.9 (2.0)	3.9 (2.0)
Ti	2.1 (0.8)	2.1 (0.8)	2.2 (0.8)
Cr	0.34 (13)	0.34 (13)	0.30 (12)
Ni	4.5 (1.8)	4.6 (1.9)	4.1 (1.7)
Cu	0.22 (08)	1.08 (40)	0.41 (10)
Zn	27 (10)	1.7 (0.7)	21.7 (8.6)
As	0.87 (35)	3.0 (1.2)	5.6 (2.2)
Zr	0.65 (26)	1.5 (0.5)	1.0 (0.4)
Ba	0.43 (17)	0.45 (19)	0.43 (19)
Ir	0.43 (17)	0.68 (21)	0.66 (22)
Hg	1.0 (0.4)	0.87 (40)	1.1 (0.4)

* The uncertainties are given in brackets and apply to the last two digits; $U = k \cdot u_c$ ($k = 2$).

^a Ag₂S-32 = Ag₂S enriched in ³²S; ^b Ag₂S-33 = Ag₂S enriched in ³³S; ^c Ag₂S-34 = Ag₂S enriched in ³⁴S.

results of absolute ³²S/³³S as well as the ³²S/³⁴S ratios of IAEA-S-1, IAEA-S-2 and IAEA-S-3 reference materials are reported. Also the isotopic composition and atomic weight corresponding to V-CDT are calculated from the new experimental data.

2. EXPERIMENTAL

2.1. Preparation of Synthetic Isotope Mixtures

Two synthetic S isotope mixtures (M-1 and M-2) close to the predetermined values for sulfur isotope abundance ratios were gravimetrically prepared from sulfur isotope-enriched materials in the form of Ag₂S (Ding et al., 2000). These sulfur isotope-enriched Ag₂S compounds were prepared from isotopically enriched elemental sulfur, purchased from JSC JV ISOFLEX, Russia. M-1 is close to V-CDT, but M-2 is significantly enriched in ³²S and very much depleted in ³³S.

2.2. The Isotopic Measurements

All isotopic measurements were carried out on SF₆ (Ding et al., 1989). Careful contamination-free conversion of all compounds to SF₆ was of paramount importance.

2.2.1. Preparation of SF₆

Subsamples of all Ag₂S materials were converted to SF₆ by reaction with BrF₅ in a vacuum at 320 ± 20°C:



The amount of Ag₂S used in each fluorination was 20 to 30 μmol. Ag₂S was weighed (5–8 mg) in a small box made from Al foil, then placed in a nickel reaction vessel and brought

under vacuum. BrF₅ was admitted to the reactor. The reactor was heated to 320 ± 20°C for ~14 h. After completing the reaction, the product SF₆ gas was purified by two-fold fractional distillation (liquid nitrogen and dry ice-acetone), followed by a last purification via gas chromatography (Ding et al., 1989).

2.2.2. Mass Spectrometry

All sulfur isotope abundance ratio measurements were carried out at IRMM on the Avogadro II amount comparator (a special MAT-271 mass spectrometer with a molecular flow inlet system and single collector, which was modified at IRMM). This instrument has been used successfully for calibrated measurements of isotope abundance ratios of Si, Xe, and Kr (De Bièvre et al., 1994, 1995, 1996; Valkiers et al., 1998, 1999, 2001). Recently developed adsorption models (Gonfiantini et al., 1997a, 1997b) have been applied to reduce the combined uncertainty of the measurements. The precision (as standard uncertainty) for isotope ratio measurements was 0.005% for ³³S/³²S and ³⁴S/³²S ratios, and up to 0.1% for the ³⁶S/³²S ratio. See tables 1-3.

2.3. The Conversion of the Measured Ion Current Ratios Into Abundance Ratios (*K* Factors)

The *K* factors for converting the measured ion current ratio I_{32}/I_i into abundance ratio ³²S/ⁱS, were determined from M-1 and M-2 and are given in Tables 4 and 5:

$$K = [f(^{32}\text{S})/f(^i\text{S})]/[I(^{32}\text{SF}_5^+)/I(^i\text{SF}_5^+)] \text{ where } i \text{ refers to } ^{33}\text{S}, ^{34}\text{S} \text{ and } ^{36}\text{S}.$$

The observed ion current ratios $[I(^{32}\text{SF}_5^+)/I(^i\text{SF}_5^+)]$ were obtained directly from mass-spectrometry measurements. The $[f(^{32}\text{S})/f(^i\text{S})]$ values for M-1 and M-2 were calculated from the mass (corrected for impurities) and isotopic compositions of the isotopically enriched components and atomic masses.

The *K* factor of the ³²S/³⁴S conversion from the ion current ratios to amount or abundance ratios for M-1 is almost identical to that for M-2 (see Table 5). Therefore, the average of these two values (1.000 234) is taken to be the *K* factor.

However, for the ³²S/³³S conversion, the situation is slightly different. The value derived for M-1 is very close to unity, whereas the value derived from M-2 deviates from unity by ~1% (Table 4). It should be noted that the amount of Ag₂S-33 used to make M-2 is ~4 times less than that to make M-1 (see Table 3), and that the δ³³S value of M-2 is about –680‰, far from the values of normal terrestrial materials. Taking into account these conditions, the agreement between these two *K* factors is quite good. However, for the same

Table 2. The abundance *g* of Ag₂³²S, Ag₂³³S, Ag₂³⁴S, and Ag₂³⁶S (in %) in the different Ag₂S starting materials.

Material	<i>g</i> (Ag ₂ ³² S)	<i>g</i> (Ag ₂ ³³ S)	<i>g</i> (Ag ₂ ³⁴ S)	<i>g</i> (Ag ₂ ³⁶ S)
Ag ₂ S-32 ^a	99.909 97 (18)	0.048 354 (14)	0.041 280 (81)	0.000 393 (79)
Ag ₂ S-33 ^b	4.631 61 (17)	94.952 16 (22)	0.415 21 (11)	0.001 024 (24)
Ag ₂ S-34 ^c	3.659 98 (14)	0.045 161 (10)	96.293 11 (23)	0.001 75 (19)

* The combined uncertainties are given in brackets and apply to the last two digits.

^a Ag₂S-32 = Ag₂S enriched in ³²S; ^b Ag₂S-33 = Ag₂S enriched in ³³S; ^c Ag₂S-34 = Ag₂S enriched in ³⁴S.

Table 3. The mass m of different Ag_2S starting materials used for the preparation of the isotope mixtures.

Material	M-1 (Mixture 1) m/mg	M-2 (Mixture 2) m/mg
$\text{Ag}_2\text{S-32}^a$	17 374.7 (5)	18 635.9 (5)
$\text{Ag}_2\text{S-33}^b$	135.395 (5)	39.790 (5)
$\text{Ag}_2\text{S-34}^c$	796.16 (2)	797.94 (2)

* The combined uncertainties are given in brackets and apply to the last digit.

^a $\text{Ag}_2\text{S-32}$ = Ag_2S enriched in ^{32}S ; ^b $\text{Ag}_2\text{S-33}$ = Ag_2S enriched in ^{33}S ; ^c $\text{Ag}_2\text{S-34}$ = Ag_2S enriched in ^{34}S .

reasons, the value derived from M-1 would have smaller uncertainty and higher weight than that derived from M-2. Therefore, the value derived from M-1 (0.999 96) is taken to be the K factor for the $^{32}\text{S}/^{33}\text{S}$ conversion.

3. THE $^{32}\text{S}/^{33}\text{S}$ AND $^{32}\text{S}/^{34}\text{S}$ ISOTOPE RATIOS IN IAEA-S-1, IAEA-S-2, IAEA-S-3

Subsamples of the three IAEA reference materials were converted to SF_6 via the BrF_5 route, and the ion current ratios for $^{32}\text{S}/^{33}\text{S}$ and $^{32}\text{S}/^{34}\text{S}$ were measured as described in Table 6.

From the measured ion current ratios I_{32}/I_{33} and I_{32}/I_{34} of IAEA-S-1, IAEA-S-2, and IAEA-S-3 with their respective K factors (Tables 4, 5), absolute $^{32}\text{S}/^{33}\text{S}$ and $^{32}\text{S}/^{34}\text{S}$ isotope abundance ratios can be calculated (Table 7). The derived $^{32}\text{S}/^{33}\text{S}$ and $^{32}\text{S}/^{34}\text{S}$ isotope abundance ratios of V-CDT are also included in Table 7.

From these results, it can be seen that the $^{32}\text{S}/^{34}\text{S}$ isotope amount ratio of V-CDT is $\sim 1.9\%$ higher than the currently accepted ratio of 22.22 and is very close to the ratio of 22.649 6(60) reported by Ding et al. (1999).

For checking the precision of these data, the $\delta^{33}\text{S}_{\text{V-CDT}}$ and $\delta^{34}\text{S}_{\text{V-CDT}}$ values calculated from the above-calibrated $^{32}\text{S}/^{33}\text{S}$ and $^{32}\text{S}/^{34}\text{S}$ ratios are compared with those determined in the Institute of Mineral Deposits (IMD), CAGS, Beijing (Table 8) by differential measurements. The agreement between the two sets of data is quite good despite the fact that different instruments and different sample conversion lines were used (MAT-251 in IMD vs. IRMM amount comparator at IRMM).

The uncertainties in Table 8 are combined uncertainties (not repeatabilities) and very small. Deriving δ values from the ratios of two absolute ratios has the advantage of anchoring the δ scale.

Table 4. The observed and prepared isotope abundance ratio $^{32}\text{S}/^{33}\text{S}$ in M-1 and M-2 with the resulting conversion K factors.

Ratio	$^{32}\text{S}/^{33}\text{S}$	
	M-1	M-2
Measured I_{32}/I_{33}	127.186 (19)	397.488 (95)
Prepared $^{32}\text{S}/^{33}\text{S}$	127.181 (71)	397.13 (22)
Conversion factor K	0.999 96 (28)	0.999 087 (62)

* The uncertainties are given in brackets and apply to the last two digits; $U = k.u_c$ ($k = 1$).

Table 5. The observed and prepared isotope ratio $^{32}\text{S}/^{34}\text{S}$ in M-1 and M-2 with the resulting K factors.

Ratio	$^{32}\text{S}/^{34}\text{S}$	
	M-1	M-2
Measured I_{32}/I_{34}	22.638 47 (51)	24.214 36 (64)
Prepared $^{32}\text{S}/^{34}\text{S}$	22.643 34 (92)	24.220 5 (11)
Conversion factor K	1.000 214 (46)	1.000 253 (48)

* The uncertainties are given in brackets and apply to the last two digits; $U = k.u_c$ ($k = 1$).

4. THE MOLAR MASS (ATOMIC WEIGHT) OF SULFUR

The current molar mass (atomic weight) of sulfur $A_r(\text{S}) = 32.066(6)$ was recommended by IUPAC-CAWIA in 1983 (IUPAC-CAWIA, 1984). This value is based on the sulfur isotope abundance of CDT reported by McNamara and Thode (1950). Since the $^{32}\text{S}/^{34}\text{S}$ isotope abundance ratio of V-CDT obtained in this study is $\sim 1.9\%$ higher than the consensus ratio, the atomic weight of sulfur based on these new data is significantly different. For determining $A_r(\text{S})$ of IAEA-S-1, the $^{32}\text{S}/^{36}\text{S}$ ratio of IAEA-S-1 was also measured, and the value 6 519(20) was obtained. Assuming that IAEA-S-1 has a $\delta^{36}\text{S}_{\text{V-CDT}}$ of ~ -0.6 ($2 \times \delta^{34}\text{S}_{\text{V-CDT}}$), the $^{32}\text{S}/^{36}\text{S}$ ratio of V-CDT was calculated to be 6 515(20). Based on the sulfur isotope abundance values obtained in this study for IAEA-S-1 and V-CDT, their atomic weights can be calculated using available atomic data (Wapstra and Audi, 1993) and, for example, software for atomic weight and uncertainty calculation (Schaefer et al., 1994; ISO, 1992). The results are in Table 9.

These data were taken into consideration for the revision of the sulfur standard atomic weight by IUPAC-CAWIA (2000).

5. CONCLUSIONS

Measuring absolute or calibrated isotope abundance ratios is a measurement capability which exists at very few places worldwide. This work demonstrates that it is very relevant for anchoring delta isotopic measurement scales to the international system of units SI and for establishing the linearity of such scales (i.e., problem of scale contraction). In the past, they were available at NBS (now called NIST) and CEA (e.g., Hagemann et al., 1970; Baertschi, 1976); today they are available only at the Institute of Mineral Deposits, CAGS (Beijing) and at IRMM (Geel). In the latter location, they have been used extensively to prepare absolute isotopic reference materials (e.g., for B, Li, Mg, Fe, Cr, Rb, Sr, Pt, U, and Pu) and primary

Table 6. The measured sulfur ion current ratios of IAEA-S-1, IAEA-S-2, and IAEA-S-3.

Sample	I_{32}/I_{33}	I_{32}/I_{34}	Number of preparations
IAEA-S-1	126.947 (37)	22.645 1 (17)	9
IAEA-S-2	125.478 (46)	22.137 2 (17)	9
IAEA-S-3	129.077 3 (85)	23.388 1 (14)	9

* The uncertainties are given in brackets and apply to the last two digits; $U = k.u_c$ ($k = 1$).

Table 7. The derived $^{32}\text{S}/^{33}\text{S}$ and $^{32}\text{S}/^{34}\text{S}$ isotope abundance ratios of IAEA-S-1, IAEA-S-2, IAEA-S-3, and V-CDT.

Sample	$^{32}\text{S}/^{33}\text{S}$	$^{32}\text{S}/^{34}\text{S}$
IAEA-S-1	126.942 (47)	22.650 4 (20)
IAEA-S-2	125.473 (55)	22.142 4 (20)
IAEA-S-3	129.072 (32)	23.393 3 (17)
V-CDT	126.948 (47)	22.643 6 (20)

* The uncertainties are given in brackets and apply to the last two digits; $U = k.u_c$ ($k = 1$).

isotopic gas standards (PIGS, e.g., for Xe, Kr, SF_6 , and SiF_4). The gas isotopic work is based on expertise developed in the context of IRMM's Avogadro project.

This paper presents calibrated $^{32}\text{S}/^{34}\text{S}$ ratios for IAEA-S-1, IAEA-S-2, IAEA-S-3, and V-CDT at 22.650 4, 22.142 4, 23.393 3, and 22.643 6, respectively. The calibrated $^{32}\text{S}/^{33}\text{S}$ ratios for IAEA-S-1, IAEA-S-2, IAEA-S-3, and V-CDT are 126.942, 125.473, 129.072, and 126.948, respectively. These results can serve as anchors to connect the V-CDT relative δ scale to a fixed absolute sulfur isotope scale. Relative sulfur isotope composition (δ scale) can be measured easily with a precision of 0.1‰ (Ding et al., 1989). However, it is a floating system until it is connected to the absolute sulfur isotope scale. Therefore, these new calibrated data can improve the reliability and comparability of sulfur isotope data in V-CDT scale.

At the 8th IAEA Consultants Meeting on Reference Materials for Stable Isotope Measurements (Vienna, 2000), the data presented in this work contributed to the new assigned values for $\delta^{34}\text{S}_{\text{V-CDT}}$ values of IAEA-S-1, IAEA-S-2, and IAEA-S-3. It was recommended that each laboratory normalize its sulfur isotope data to the V-CDT scale by calibrating its working standards against IAEA-S-1 and IAEA-S-2 or IAEA-S-3. The detailed method for doing this will be given in the working group report of the 8th IAEA Consultants Meeting (Vienna, 2000).

The work presented also solves the long-standing discrepancy regarding the $^{32}\text{S}/^{34}\text{S}$ ratio of CDT. The previously assigned $^{32}\text{S}/^{34}\text{S}$ ratio of CDT was 22.22 (Jensen and Nakai, 1962), but a ratio of 22.57 can be calculated from abundance values for ^{32}S (95.02%) and ^{34}S (4.21%) (McNamara and Thode, 1950). This discrepancy has been puzzling the sulfur isotope community for a long period. A new absolute value of 22.6436 is now available to resolve this discrepancy.

The values of molar mass (atomic weight) of sulfur in IAEA-S-1 and V-CDT are determined to be 32.063 877(56)

Table 8. A comparison of $\delta^{33}\text{S}_{\text{V-CDT}}$ and $\delta^{34}\text{S}_{\text{V-CDT}}$ values in various samples measured at IRMM, Geel and at IMD, Beijing.

Sample	$\delta^{33}\text{S}_{\text{V-CDT}}$ (‰)		$\delta^{34}\text{S}_{\text{V-CDT}}$ (‰)	
	IRMM-Geel	IMD-Beijing	IRMM-Geel	IMD-Beijing
IAEA-S-1	-0.05 (52)	-0.05 (17)	-0.30 (12)	-0.30 (16)
IAEA-S-2	11.65 (11)	11.48 (33)	22.64 (11)	22.67 (15)
IAEA-S-3	-16.56 (31)	-16.65 (31)	-32.06 (11)	-32.55 (12)

* The uncertainties are given in brackets and apply to the last two digits; $U = k.u_c$ ($k = 1$).

Table 9. Atomic weights of sulfur for IAEA-S-1 reference materials and V-CDT.

Sample	$A_r(\text{S})$
IAEA-S-1	32.063 877 (56)
V-CDT	32.063 911 (56)

* The uncertainties are given in brackets and apply to the last two digits; $U = k.u_c$ ($k = 1$).

and 32.063 911(56), respectively, with the smallest combined uncertainty of all sulfur molar masses reported. These data were taken into consideration for the 1999 revision of atomic weights by IUPAC-CAWIA (2000), and a better value was decided for the standard atomic weight of sulfur.

Acknowledgments—We thank the International Atomic Energy Agency (IAEA) for providing T. Ding an IAEA fellowship to participate in this project at IRMM. We thank Paul Vercammen (Belgian Valve and Fittings, Zaventem, Belgium) for his professional help; we warmly acknowledge D. Vendelbo, P. Hansen, P. Damen, and G. Van Baelen for constructing the sample preparation line for SF_6 conversion and for maintaining the Avogadro II amount comparator. We thank the reviewers for their constructive comments.

Associate editor: H. Ohmoto

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