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Revised δ^{34}S reference values for IAEA sulfur isotope reference materials S-2 and S-3[†]

Jacqueline L. Mann*, Robert D. Vocke, Jr. and W. Robert Kelly

Inorganic Chemical Metrology Group, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, MS8391, Gaithersburg, MD 20899, USA

Revised δ^{34}S reference values with associated expanded uncertainties (95% confidence interval (C.I.)) are presented for the sulfur isotope reference materials IAEA-S-2 (22.62 ± 0.16‰) and IAEA-S-3 (−32.49 ± 0.16‰). These revised values are determined using two relative-difference measurement techniques, gas source isotope ratio mass spectrometry (GIRMS) and double-spike multi-collector thermal ionization mass spectrometry (MC-TIMS). Gas analyses have traditionally been considered the most robust for relative isotopic difference measurements of sulfur. The double-spike MC-TIMS technique provides an independent method for value-assignment validation and produces revised values that are both unbiased and more precise than previous value assignments. Unbiased δ^{34}S values are required to anchor the positive and negative end members of the sulfur delta (δ) scale because they are the basis for reporting both δ^{34}S values and the derived mass-independent Δ^{33}S and Δ^{36}S values. Published in 2009 by John Wiley & Sons, Ltd.

Sulfur (S) has four stable isotopes: ^{32}S, ^{33}S, ^{34}S and ^{36}S, with approximate relative isotopic abundances of 95, 0.75, 4.2 and 0.15%, respectively. The abundances of these isotopes change in response to atmospheric, geologic, biologic, and hydrologic processes and consequently they are powerful tracers of the sources, transport mechanisms, and reactions involving S in these environments. These changes are measured as variations in sulfur isotope amount ratios. Because the mass-dependent variations in sulfur isotope amount ratios are small, the isotope-amount ratio variations are expressed as differences between a sample and a standard. The differences in measured isotope-amount ratios [$n(^{34}S)/n(^{32}S)$] for a given sample are reported, for example, as δ^{34}S values defined in Eqn. (1):

$$\delta^{34}S_{VCDT} = \frac{\left[\frac{n(^{34}S)}{n(^{32}S)}\right]_{SAMPLE} - \left[\frac{n(^{34}S)}{n(^{32}S)}\right]_{VCDT}}{\left[\frac{n(^{34}S)}{n(^{32}S)}\right]_{VCDT}} \quad (1)$$

where $[n(^{34}S)/n(^{32}S)]_{SAMPLE}$ is the measured $(^{34}S)/(^{32}S)$ ratio in the sample and $[n(^{34}S)/n(^{32}S)]_{VCDT}$ is the measured $(^{34}S)/(^{32}S)$ ratio in the standard IAEA-S-1. The primary isotope reference material for the δ^{34}S isotopic scale is the International Atomic Energy Agency's IAEA-S-1, which has a consensus value of −0.3‰ to bring the scale in line with older δ^{34}S measurements made on the Canyon Diablo Troilite (CDT) scale. IAEA-S-1 defines the Vienna Canyon Diablo Troilite (VCDT) scale.[1]

Correspondence to: J. L. Mann, Inorganic Chemical Metrology Group, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, MS8391, Gaithersburg, MD 20899, USA.
E-mail: jmann@nist.gov
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Traditionally, geological or mineral samples have been used as sulfur isotope standards, but many of these turned out to be isotopically inhomogeneous. Laboratory inter-comparison exercises on these materials commonly showed variability that was larger than the typical analytical precisions of isotope ratio mass spectrometers, thus raising concerns regarding the calibration of sulfur isotope measurements. Originally, δ^{34}S values were reported relative to the CDT standard, which was given the value of 0‰. As instrumental precision improved, it was suggested that CDT was inhomogeneous at the 0.4‰ level.[2] Thus, in the 1990s, three new chemically pure and homogenous silver sulfide calibration/reference materials were synthesized: IAEA-S-1, IAEA-S-2, and IAEA-S-3 (formerly NZ1, NZ2, and NZ3).[3] The starting materials for IAEA-S-1 and IAEA-S-3 were sphalerites with $\delta^{34}S_{CDT}$ values close to 0 and −30‰, respectively. IAEA-S-2 was produced from a gypsum with a $\delta^{34}S_{CDT}$ value close to +21‰.[3] These reference materials are distributed by the IAEA and NIST as IAEA-S-1 (NIST – RM 8554), IAEA-S-2 (NIST – RM 8555), and IAEA-S-3 (NIST – RM 8529). The $\delta^{34}S_{VCDT}$ values reported for these reference materials, given in Table 1, vary in some cases by more than the stated analytical precisions, suggesting that the corrections applied for biases in the sample preparation and gas source mass spectrometry procedures are questionable.[3,4–7] In 2000, the 8th IAEA Advisory Working Group on sulfur isotopes presented a consensus calibration of the VCDT scale using these new IAEA reference materials.[4,5] The measurements used for the value assignment of IAEA-S-2 (−22.66 ± 0.13‰ (1$\hat{\sigma}$)) and IAEA-S-3 (−32.30 ± 0.12‰ (1$\hat{\sigma}$))[5,6] were based on absolute ratio measurements performed by Ding *et al.*[6,8,9] at the Institute for Reference Materials and Measurement (IRMM) Geel, Belgium, and isotope ratio difference measurements performed at the Institute of

Table 1. Published sulfur isotope-ratio data for the three IAEA sulfur reference materials used to set historical consensus values

	$\delta^{34}S \times 10^3$ (‰) $\pm 1\hat{\sigma}$	$\delta^{34}S(i/VCDT)$ or $\delta^{34}S(i/CDT)$	Value type	Method	Source of data
IAEA-S-1 (Ag$_2$S)	-0.30 ± 0.03 (n = 3)	CDT	Consensus value	G-IRMS-SF$_6$	Robinson[3]
(defines VCDT)	-0.26 ± 0.09 (n = 15)	CDT	Consensus value	G-IRMS-SO$_2$	Robinson[3]
IAEA-S-2 (Ag$_2$S)	21.7 ± 0.3 (n = 4)	VCDT	Consensus value	G-IRMS-SO$_2$	Robinson[3]
	21.5 ± 0.07 (n = 4)	VCDT	Consensus value	G-IRMS-SO$_2$	Robinson[3]
	22.66	VCDT	Consensus value	G-IRMS-SF$_6$	Taylor et al.[4]
	22.67 ± 0.15	VCDT	Discrete value	G-IRMS-SF$_6$	Taylor et al.[4] and Ding et al.[6]
	22.64 ± 0.11	VCDT	Discrete value	G-IRMS-SF$_6$	Taylor et al.[4] and Ding et al.[6]
	22.66 ± 0.81	VCDT	Discrete value	G-IRMS-SF$_6$	Taylor et al.[4]
	22.66 ± 0.13	VCDT	Consensus value	G-IRMS-SF$_6$	Taylor et al.[5]
	22.7 ± 0.2	VCDT	Consensus value	G-IRMS-SF$_6$	IAEA[7]
IAEA-S-3 (Ag$_2$S)	-32.30	VCDT	Consensus value	G-IRMS-SF$_6$	Taylor et al.[4]
	-32.55 ± 0.12	VCDT	Discrete value	G-IRMS-SF$_6$	Taylor et al.[4] and Ding et al.[6]
	-32.06 ± 0.11	VCDT	Discrete value	G-IRMS-SF$_6$	Taylor et al.[4] and Ding et al.[6]
	-32.24 ± 0.38	VCDT	Discrete value	G-IRMS-SF$_6$	Taylor et al.[4]
	-32.30 ± 0.12	VCDT	Consensus value	G-IRMS-SF$_6$	Taylor et al.[5]
	-32.3 ± 0.2	VCDT	Consensus value	G-IRMS-SF$_6$	IAEA[7]

Mineral Deposits (IMD) Beijing, China (now Institute of Mineral Resources, CAGS) and the Geological Survey of Canada (GSC) Ottawa, Canada (Table 2 and Figs. 1(a) and 1(b)). Although the values reported for IAEA-S-2 appear to be consistent among laboratories, those for IAEA-S-3 appear to be inconsistent showing a 0.5‰ difference between IRMM and IMD, which is well outside their stated precisions.

Recently, a multi-collector thermal ionization mass spectrometry technique was used to measure $\delta^{34}S_{VCDT}$ in the same three international reference materials.[10] The technique is based on the production of arsenic sulfide molecular ions (AsS$^+$) by thermal ionization using silica gel/phosphoric acid as an emitter and combines MC-TIMS with a ^{33}S-^{36}S double spike. This is an internal correction method that is well understood and the only known potential bias is in the fractionation law (linear, power, or exponential) used to model and correct for instrumental (Rayleigh-like) fractionation during thermal ionization. The MC-TIMS technique can be used as a relative-difference method thereby providing an independent way to assess the differing values going into the δ value-assignment for the IAEA-S-2 and IAEA-S-3 standards. Using these new data together with aforementioned data from IMD, we offer a re-evaluation of the values put forward by the 8th IAEA

Advisory Working Group and suggest new unbiased values and associated uncertainties for IAEA-S-2 and S-3 relative to VCDT.

MEASUREMENT TECHNIQUES EMPLOYED FOR SULFUR ISOTOPE ANALYSIS

Numerous analytical methods have been developed for S isotope composition analysis, each for a specific purpose. Lists of these methods, including traditional and non-traditional measurement techniques, are provided in Tables 3(a) and 3(b), respectively. The type of procedure and the instrument used for isotopic measurements are given in columns 1 and 2, the species measured in column 3, the purpose for which the techniques were developed in column 4, and the final two columns list the typical precisions obtained using these techniques and the principal biases associated with each.

Traditional measurement methods

Traditionally, $\delta^{34}S$ measurements are performed using relative-difference dual-inlet[11–18] or continuous-flow[19–21] gas source isotope ratio mass spectrometry (G-IRMS, CF-IRMS), where sulfur is introduced as gaseous sulfur dioxide

Table 2. $\delta^{34}S$ data results for IAEA-S-2 and IAEA-S-3

IAEA standard	Laboratory	Sulfur isotope composition value $\delta^{34}S \times 10^3$ (‰)	$1\hat{\sigma}$
IAEA-S-2	GSC	22.66[a]	0.81
	IRMM	22.64[a,b]	0.11
	IMD	22.67[a,b]	0.15
Previous mean estimate		**22.66**[a,b]	**0.13**[c]
IAEA-S-3	GSC	-32.24[a]	0.38
	IRMM	-32.06[a,b]	0.11
	IMD	-32.55[a,b]	0.12
Previous mean estimate		**-32.30**[a,b]	**0.12**[c]

[a] Taylor et al.;[4] Taylor et al.[5]
[b] Ding et al.[6]
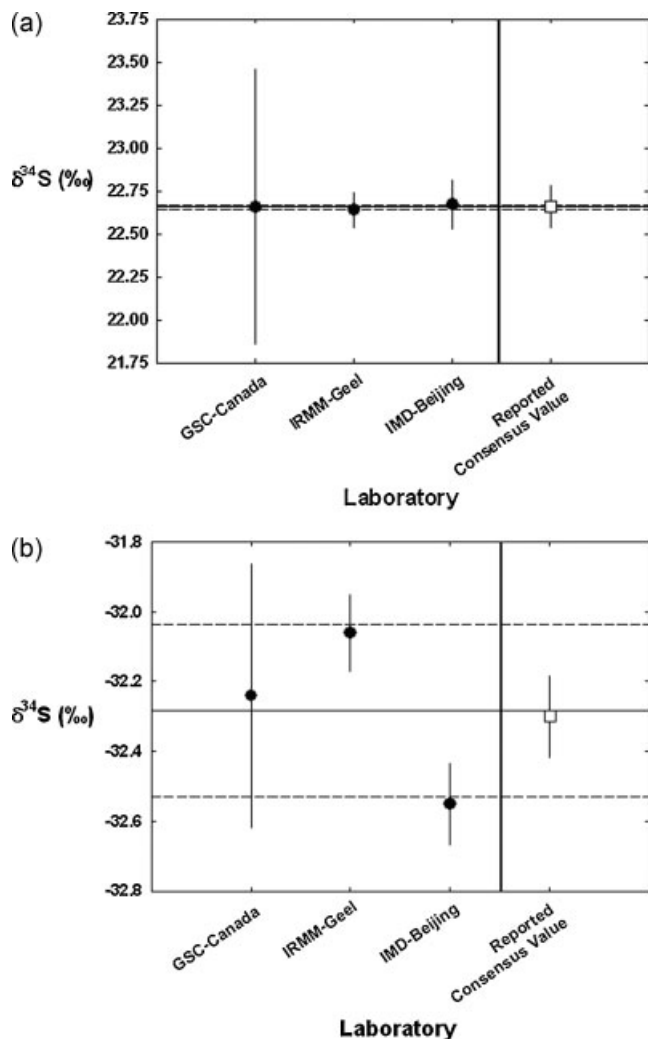[c] Excludes uncertainty from GSC.

Figure 1. The individual laboratory results for IAEA reference materials IAEA-S-2 (a) and IAEA-S-3 (b) and the consensus value identified by the 8th Working Group. The error bars for the individual laboratory results are $1\hat{\sigma}$ as are those to the right. The reported consensus values exclude the uncertainty from GSC-Canada. See text for details.

(SO_2) or sulfur hexafluoride (SF_6). These external standard techniques are commonly used with various on-line hyphenated instruments including elemental analyzers and gas chromatographs to automate the combustion and purification processes. For SO_2 analysis, samples are commonly converted into either barium sulfate or silver sulfide and combusted to SO_2 gas for mass spectrometric determination. Isotopic ratio determinations are made on the SO_2^+ species with precisions generally in the 0.1 to 0.25‰ range.[11,12,14,15,19–21] For SF_6 analysis samples may be converted into silver sulfide, or analyzed directly as natural sulfide minerals, by fluorination to produce SF_6 gas for mass spectrometric determination.[13,16–18] Sulfate samples require additional chemical reduction steps to convert the sample into the sulfide form for processing. The isotopic ratios are measured using the SF_5^+ species. The SF_6 technique is the preferred technique for high-precision sulfur isotope analysis (<0.1‰) because SF_6 gas is much less 'sticky'

than SO_2 gas, reducing the memory as well as scale contraction/expansion effects associated with SO_2 gas, and because interferences from the isotopomers of oxygen do not exist. In cases where the amount of available sample is limited, continuous-flow methods are preferred over dual-inlet approaches because smaller sample sizes (1 μmol S or 33 μg S) are required; however, measurement precisions are typically degraded (≈0.25‰).

Non-traditional measurement methods

During the last decade, many additional techniques have become available for S isotope composition measurements. For instance, on-line sulfur monoxide (SO) CF-IRMS and laser-assisted SF_6 techniques have been developed that build on existing IRMS methods. Sulfur samples analyzed using the SO CF-IRMS technique are combusted to produce SO_2^+ ions and SO^+ ions are then generated via unimolecular dissociation. The method was developed to accommodate smaller sample sizes and the limited mass range of smaller IRMS instruments, and to reduce the interferences from oxygen isotopomers as well as decrease the sample processing required for analysis.[22,23] This method is less precise (<0.3‰) than the SO_2 and SF_6 techniques due to the greater degree of scale contraction/expansion and linearity difficulties associated with the SO^+ ion. Ono et al.[24] developed an in situ laser-assisted method for S isotope analysis that is capable of measuring small sample sizes, ≈5 μg S, and providing data with high enough spatial resolution to investigate biogeochemical processes that are difficult to evaluate using conventional bulk analysis methods. The technique takes advantage of the benefits realized by the SF_6 technique; however, due to significant instrumental mass bias from ion scattering and incomplete transfer of sample in the vacuum line, and potentially large blank effects, in addition to peak tailing, linearity and scale contraction/expansion effects, the precisions (≈0.2–0.3‰) obtained using this procedure are also degraded relative to those from conventional SF_6 methods.[24,25]

Several other independent techniques have also been employed for S isotope measurements including multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS),[26–34] secondary ion mass spectrometry (SIMS),[35–37] tunable laser spectroscopy,[38] the Avogadro technique,[6,8,9] and double-spike MC-TIMS.[10] MC-ICPMS has been increasingly used for precise isotope measurements of the non-traditional stable isotopes as well as sulfur.[26–34] The primary advantages of this method are the reduction in required sample size (<10 μg S) and the reduction in preparation steps which reduce the potential blank. Combining MC-ICPMS with laser ablation further allows for in situ or high-resolution spatial analysis. The major drawbacks of this technique are instrumental mass bias and the matrix effects, which are particularly pronounced for laser ablation measurements. As a consequence, the precisions are typically not better than 0.2‰, and are more commonly around 0.5‰. Similar to the laser ablation techniques, SIMS has also been employed for in situ sulfur isotope analysis.[35–37] A primary beam of cesium (Cs) is used to sputter the sample to enhance negative secondary ion yields. Ratio measurements are made on negatively charged

Table 3a. Traditional measurement techniques for S isotope composition analysis

Procedure	Instrument	Species measured	Purpose	Typical precisions ($1\hat{\sigma}$)	Principal biases
Off-line combustion SO_2	Multi-collector gas isotope ratio mass spectrometry (G-IRMS) or continuous flow isotope ratio mass spectrometry (CF-IRMS)	SO_2^+	Measure sulfur isotope composition with high precision (size required > 1 mg S)	≈0.10–0.2‰[a]	Linearity, scale contraction/expansion, mass interferences from the isotopes of oxygen
On-line combustion SO_2		SO_2^+	Measure sulfur isotope composition with high precision on smaller samples (≈33 μg S) compared with off-line SO_2 procedures	≈0.1–0.25‰[b]	Linearity, scale contraction/expansion, mass interferences from the isotopes of oxygen
SF_6	Multi-collector gas isotope ratio mass spectrometry (G-IRMS)	SF_5^+ F is mononuclidic	No interference from isotopomers of oxygen, less 'sticky' gas	<0.1‰[c]	Linearity, scale contraction/expansion, peak tailing (although minimal compared with the SO_2 technique)

[a] Thode et al.;[11] Fritz et al.;[12] Robinson and Kusakabe;[14] Rees.[15]
[b] Giesemann et al.;[19] Grassineau et al.;[20] Studley et al.[21]
[c] Ding et al.;[8] Leskovsek et al.;[13] Rees;[16] Hoering and Prewitt;[17] Gao and Thiemens.[18]

elemental sulfur (S⁻). The method is quite complex and large-scale fractionation effects occur associated with ion emission and sample sputtering as well as fractionation during transport from the sample surface to the detectors. In addition, there can be quite significant matrix effects on the instrumental mass bias.[35–37,39,40] The precisions obtained by this technique are ultimately similar to those obtained using other *in situ* techniques, approximately 0.25‰. Another technique, based on tunable laser spectroscopy, has been developed as a potential field instrument for *in situ* S isotope analysis.[38] SO_2 is produced via on-line combustion techniques and then expanded into the laser spectrometer. Once enough gas is entrained, $\delta^{34}S$ measurements are taken. The precisions of this technique are ca. ±4‰ due to the extensive fractionation from sequestration of SO_2 and other factors such as measurement drift, memory effects, susceptibility to temperature fluctuations, and optical fringe noise.

The majority of the non-traditional techniques mentioned produce less precise measurements relative to the traditional SO_2 and SF_6 techniques. However, two additional non-traditional methods for S isotope analysis developed within the last decade, the Avogadro and double-spike MC-TIMS techniques, have achieved precisions that are comparable with those achieved by the best traditional measurement methods (<0.15‰).[6,8–10] The Avogadro method, using synthetic isotope mixtures prepared gravimetrically from high-purity Ag_2S enriched in ^{32}S, ^{33}S, and ^{34}S, for calibration, has been used to determine absolute S isotope ratios with reported precisions approaching 0.10‰. All materials are converted into SF_6 gas and isotopic ratios are measured as the SF_5^+ species on a modified single-collector gas source instrument (IRMM's Avogadro II amount comparator, a modified MAT 271 mass spectrometer; FinniganMAT, Bremen, Germany) equipped with a molecular flow inlet system.[6,8,9] The synthetic mixtures of the enriched isotopes are used to correct the measured ratios

to an absolute value. These mixtures are measured following a rigidly defined protocol specifying the sample form, amount, and loading parameters among other factors. From these measurements, simple correction factors (c.f. = True/Experimental) for the measured isotope ratios are obtained.

Sulfur isotope ratio measurements have also been determined with very high precision (<0.10‰) using double-spike MC-TIMS. This technique uses a high-purity ^{33}S-^{36}S double spike calibrated relative to the internationally accepted absolute value for VCDT reported by Ding et al.[6] ($\delta^{34}S_{VCDT} = -0.3‰$, $^{32}S/^{34}S = 22.6436$) to calculate an instrumental fractionation factor (α) which corrects for the instrumental fractionation inherent to the TIMS technique.[10] The major advantage of this technique is that its principal known bias is the law used to correct for instrumental fractionation. The accuracy of the three fractionation laws (linear, power, and exponential) has been checked with deterministic data as well by simulated data containing random errors by Mann and Kelly.[10] It was shown that sulfur isotope fractionation during thermal ionization is similar to the fractionation of calcium (Ca), selenium (Se), and magnesium (Mg)[10,41–43] and closely follows the exponential law. This is a better choice for instrumental fractionation correction as the drift in this value over the depletion of the reservoir is smaller than for the other laws. For all MC-TIMS data reported here, the exponential law was used for fractionation correction. An additional benefit realized by the double-spike internal standard technique is that it introduces no new biases because only isotopic ratios need to be measured; therefore, complete recovery of the sample is not required for unbiased results, unlike techniques that use external standards.[10] By adding the double spike prior to sample processing, any mass fractionation that may result from sample loss during drying and/or chemical reduction of the sample is accounted for by assuming that equilibration is achieved between the sample and the spike. This is a major

Table 3b. Non-traditional measurement techniques for S isotope composition analysis

Procedure	Instrument	Species measured	Purpose	Typical precisions $(1\hat{\sigma})$	Principal biases
On-line combustion SO	Multi-collector CF-IRMS	SO^+	Reduced sample processing, less interference from isotopomers of oxygen	<0.3‰[a]	Linearity, scale contraction/expansion, peak tailing
Laser-assisted SF_6	Multi-collector G-IRMS	SF_5^+, F is mononuclidic	*In situ* determination for spatial analysis, smaller sample sizes ($\approx$5 μg if combined with GCMS)	0.2–0.3‰[b]	Linearity, scale contraction/expansion, peak tailing due to fluorocarbons, incomplete transfer of sample in vacuum line, blank
Solution/gas	Multi-collector ICPMS		Reduce sample preparation steps and time, smaller samples (<10 μg), blank reduction	0.1–0.5‰[c]	Correction procedure/law employed to model and correct for instrumental mass bias, matrix effects, extensive isobaric interferences, blank
Laser ablation	Multi-collector ICPMS		*In situ* determination for spatial analysis	0.2–0.5‰[d]	Correction procedure/law employed to model and correct for instrumental mass bias, matrix and laser produced fractionation, blank, background
Cs^+ beam	SIMS	Secondary ions of S^-	*In situ* determination for spatial analysis	$\approx$0.25‰[e]	Large-scale instrumental fractionation during ion emission and sputtering, fractionation during transport from sample surface to detectors, marked matrix effects on instrumental mass bias, correction law employed to model and correct for instrumental mass bias, sample voltage
SO_2	Tunable laser spectroscopy	SO_2	Potential field instrumentation for *in situ* sulfur isotope analysis	$\approx$4‰[f]	Measurement drift, memory effects, temperature fluctuations, optical fringe noise
Avogadro	Modified single-collector gas source instrument	SF_5^+, F is mononuclidic	Determine absolute values for three IAEA standards (IAEA-S-1, S-2, S-3)	$\approx$0.1–0.15‰[g]	Linearity, assumptions regarding the kinetic gas law, effusion, and adsorption/desorption for mass fractionation correction, T/E fractionation correction, ionization probabilities
^{33}S-^{36}S double spike	MC-TIMS	AsS^+, As is mononuclidic	Measure small (<1 μg S) sample sizes, determine concentration and composition simultaneously, evaluate blank concentration and composition	<0.1‰[h]	Correction law employed to model and correct for instrumental (Rayleigh-like) fractionation in MC-TIMS

[a] Baublys *et al.*;[22] Kaufman *et al.*[23]
[b] Beaudoin and Taylor;[2] Ono *et al.*;[24] Hu *et al.*[26]
[c] Mason *et al.*;[26] Prohaska *et al.*;[27] Krupp *et al.*;[28] You and Li;[29] Clough *et al.*;[30] Sanamaria-Fernandez and Hearn;[31] Craddock *et al.*[32]
[d] Craddock *et al.*;[32] Mason *et al.*;[33] Bendall *et al.*[34]
[e] Riciputi;[35] Paterson *et al.*;[36] Riciputi.[37]
[f] Christensen *et al.*[38]
[g] Ding *et al.*;[6] Ding *et al.*[9]
[h] Mann and Kelly.[10]

advantage for small sample sizes (<1 μmol S) where losses could potentially produce changes in isotopic ratios which would produce unknown biases in $\delta^{34}S$. In addition, biases due to interferences or scale contraction/expansion associated with G-IRMS do not exist because the technique is based on solid source analysis on S as AsS^+. Finally, the double-spike method allows the isotopic composition and concentration of the blank to be determined by direct measurement by isotope dilution. Because of the significant advantages realized by the MC-TIMS internal standard technique, it provides an independent approach for the measurement of $\delta^{34}S$ and it is thus an ideal method for the independent validation of $\delta^{34}S$ measurements by traditional high-precision gas IRMS.

IMPLICATIONS OF BIAS-FREE REFERENCE MATERIALS

Most stable isotope applications employ the relative differences in the isotope-amount ratios to assess changes in the system of interest. This relative measurement scale, or delta scale, is defined relative to the isotope-amount ratio in a primary reference material where isotope-amount ratios are reported as deviations from the isotope-amount ratio of the chosen reference material (see Eqn. (1)). Determinations of differences in $^{34}S/^{32}S$ between two samples are typically more accurate than the independent determination of their absolute isotope-amount ratio values[44] as biases are factored out and instrumental biases are minimized. It has repeatedly been observed, however, that laboratories measuring the same sample often disagree outside their reported 'uncertainty' of measurement,[45,46] and this situation has not improved substantially in the last two decades, except in a few cases.[47] The various techniques now employed for S isotope analysis all have associated biases (Table 3) that, if not corrected for properly, can cause potential offsets (e.g. Fig. 1(b) – IAEA-S-3). To address these biases, end-member reference materials that have accurate values are required in order to appropriately correct the sample raw data. For example, for isotope measurements performed with mass spectrometric techniques, biases resulting from non-linearities in the measurement system result in scale contraction/expansion that can cause deviations of several per mil. As noted by Gonfiantini[48] and Coplen et al.,[49] two-point calibrations of the δD, $\delta^{18}O$, and $\delta^{13}C$ scales substantially improve the agreement among laboratories; reducing the variability by half in the case of $\delta^{13}C$. The zero of the sulfur delta scale occurs at the middle of the range observed for natural samples. By bounding the scale with two 'bias-free' S isotope reference materials at each extreme that cover the range of S isotope compositions observed in environmental samples, an appropriate scaling factor can be obtained for correction, thus improving consistency as well as the potential accuracy of the measurements.

The determination of bias-free correction factors is extremely important for mass-independent analyses. The recent discovery of anomalous S isotope compositions that significantly deviate from mass-dependent trends in rocks older than 2.0 Ga, in volcanic horizons in ice cores, and in modern sulfate aerosols has increased the need for accurate or bias-free sulfur reference materials.[50–55] The determination of mass-independent isotope fractionation (MIF) requires both $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ to be measured in the sample in order to calculate $\Delta^{33}S$ and $\Delta^{36}S$ ($\Delta^{33}S = \delta^{33}S - k\,\delta^{34}S$, $\Delta^{36}S = \delta^{36}S - k\,\delta^{34}S$). Effects as small as $|\Delta^{33}S| = 0.05‰$ are now considered resolvable. Because these values are calculated and not direct measurements, $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ determinations require, at a minimum, isotopically homogeneous reference materials with accurate and precise assigned values for calibration and correction. In the case of $\Delta^{33}S$ and $\Delta^{36}S$ anomalies, small errors in scale calibration can have serious consequences. For example, if the assigned $\delta^{34}S$ value for one of the IAEA end-member reference materials used to anchor the VCDT scale deviates from its true value by 0.5‰, a deviation of up to 0.25‰ can occur in

$\Delta^{33}S$, thereby producing an apparent mass-independent effect. This issue becomes even more critical in light of the more recent discovery that material transfer within biological and biogeochemical systems can produce small magnitude mass-independent effects (<0.2‰) for both $\Delta^{33}S$ and $\Delta^{36}S$.[56–59]

CONSENSUS VALUES OF THE 8TH IAEA ADVISORY WORKING GROUP

The ranges of the individual $\delta^{34}S_{VCDT}$ values used in the determinations of the consensus values for IAEA-S-2 and IAEA-S-3 are 0.03‰ and 0.50‰, respectively (Table 2 and Figs. 1(a) and 1(b)). While the aforementioned ranges in values suggest good agreement for IAEA-S-2 data the IAEA-S-3 results are not in agreement. Note that the range in IAEA-S-3 values is larger than the 0.4‰ range in isotopic composition observed for CDT by Beaudoin et al.[2] which was attributed to isotopic inhomogeneity and led to the creation of IAEA-S-1 and the VCDT scale. Because each of these laboratories used the same value for VCDT for normalization, the results for IAEA-S-3 should show variances similar to those observed for IAEA-S-2. Assessing whether the IMD or IRMM methods differ was evaluated by comparing the averages of the techniques assuming (1) the variability in method A (IMD) and method B (IRMM) is unknown but equal, and (2) variability in method A (IMD) and method B (IRMM) is known from previous experience and the standard deviations $\hat{\sigma}_A$ and $\hat{\sigma}_B$ are known.[60] For the first case, it was found that the mean value determined by IMD differs from that determined by IRMM at not only the 95% level of significance but also at the 99% level. The second case yielded the same results. A t-test, assuming equal variances, similarly shows that the means differed at the 95% and 99% levels. It is clear that these values differ and therefore one or both must be in error. Note that the GSC data cannot be used to resolve this issue as they are not independent because the values were normalized to those obtained by IMD to account for scale contraction. Detailed examination of the data also suggests there may be some arithmetical errors in the calculation of the mean for IAEA-S-3 and the associated variances (T.-P. Ding, personal communication, 2008). Thus, while the suggested value for IAEA-S-2 appears to be robust and consistent, the same cannot be said for the value for IAEA-S-3.

SULFUR ISOTOPE MEASUREMENT METHODS USED FOR PREVIOUS CONSENSUS VALUE DETERMINATIONS

Because of the real and variable biases of most S isotopic methods only values measured using SF_6 chemistries were used in the determinations of the consensus values for IAEA-S-2 and IAEA-S-3. The SF_6 techniques used by IMD and GSC are relative-difference techniques while the technique used by IRMM is an absolute isotope ratio measurement. IMD and IRMM used a conventional BrF_5 method for SF_6 preparation and GSC used a laser-assisted F_2 method.[4–6,8,9] SF_6 techniques are preferred over SO_2 methods for extracting and introducing sulfur into the G-IRMS system for reasons

mentioned earlier and are consequently less biased and have higher precision ($<0.1‰$).

When the 8th IAEA Advisory Working Group met (2000) the SF_6 techniques were the best methods available for S isotope analysis and were the most suitable for value assignment. However, the variations observed for IAEA-S-3 suggests either isotopic heterogeneity or that potential difficulties exist in the application of correction for biases. The Avogadro technique takes advantage of the benefits of the SF_6 method and yields highly precise data, yet the procedure is quite complex and involves a number of important assumptions compared with the relative-difference G-IRMS techniques for S isotope ratio measurements. To obtain an absolute isotope amount ratio, the observed ion-current ratio is converted into an isotopic amount ratio using the 'Avogadro procedure' which requires mass fractionation at the inlet system and different ionization probabilities of the different isotopic species to be accounted for, in addition to residual systematic effects stated to be of unknown origin.[9] The correction factors are derived from the synthetically prepared mixtures and account for mass fractionation at the inlet system based on the kinetic gas theory, effusion, and adsorption/desorption effects while the ionization probabilities are assumed to be equal to unity with a 10^{-6} relative uncertainty. The correction factor for the residual effects is a simple True/Experimental correction derived from comparing the observed ion-current ratio with the prepared isotope amount ratio values of the prepared mixtures. The relative-difference technique eliminates the need for many of these types of assumptions because the sample is being compared with the standard.

REVISED δ^{34}S REFERENCE VALUES FOR IAEA-S-2 AND IAEA-S-3

The relative-difference MC-TIMS technique provides an independent method needed to evaluate the observed deviations in IAEA-S-3. The data measured using this technique (Table 4 and Fig. 2) suggest that the values reported by IMD (Table 2 and Fig. 2) for both IAEA-S-2 and IAEA-S-3 are consistent with the MC-TIMS measurements. Although the 8th IAEA Advisory Working Group included the values reported by both the GSC and the IRMM in their determination of the recommended $\delta^{34}S_{VCDT}$ values for IAEA-S-2 and IAEA-S-3 (Table 2 and Figs. 1(a) and 1(b)), these values are excluded here for the reasons mentioned earlier. The revised $\delta^{34}S_{VCDT}$ reference values for IAEA-S-2 and IAEA-S-3 and their associated expanded uncertainties (95% C.I.) are summarized in Table 5 and Fig. 3. The revised values are $22.62 \pm 0.16‰$ and $-32.49 \pm 0.16‰$ for IAEA-S-2 and IAEA-S-3, respectively. The corresponding $1\hat{\sigma}$ precisions are 0.088 and 0.087‰, respectively. Note that expanded uncertainties are being reported in addition to the precision specific measures – standard deviations ($\hat{\sigma}$). All values were normalized to VCDT with an assigned value of $-0.3‰$. The reported $1\hat{\sigma}$ precisions for the previously recommended values in 2000 for IAEA-S-2 (0.13‰) and IAEA-S-3 (0.12‰) are larger.

The $\delta^{34}S_{VCDT}$ value determined for IAEA-S-2 is nearly identical to the previous estimate (Fig. 3(a)) and provides confirmation of the value (IAEA-S-2 = $22.66 \pm 0.13‰$ ($1\hat{\sigma}$))

Table 4. δ^{34}S data results for IAEA-S-2 and IAEA-S-3 from NIST

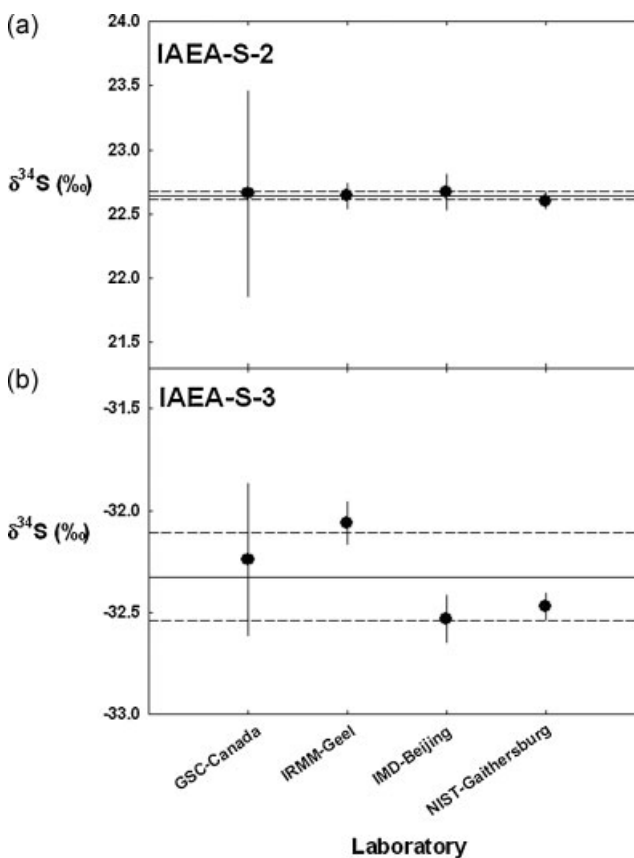| Standard	IAEA-S-2 ($\delta^{34}S \times 10^3$ (‰))		IAEA-S-3 ($\delta^{34}S \times 10^3$ (‰))
Individual measurement results	22.61	22.56	−32.37
	22.54	22.42	−32.45
	22.57	22.53	−32.56
	22.53	22.62	−32.55
	22.66	22.65	−32.51
	22.67	22.61	−32.47
	22.55	22.60	−32.47
	22.63	22.73	−32.38
	22.65	22.66	
	22.67		
Mean	22.60		−32.47
$1\hat{\sigma}$	0.071		0.070
SE	0.016		0.025
N	19		8
Combined uncertainty (u_c)	0.072		0.077
Expanded uncertainty (U) k = 2	0.144		0.153
Relative expanded uncertainty (%)	0.639		0.472

Figure 2. δ^{34}S results reported by NIST for IAEA-S-2 (a) and IAEA-S-3 (b) compared to the results from the labs included in the previous consensus value assignments. The value for IMD here has been changed from −32.55 to −32.53 due to the error in the calculation of the mean. The solid line is the mean of all the data and the dashed lines and error bars are $1\hat{\sigma}$ uncertainties.

Table 5. δ^{34}S values used to determine the revised recommended value along with the reported consensus value for comparison

	Laboratory	Mean (δ^{34}S $\times 10^3$ (‰))	1$\hat{\sigma}$	n	u_c	U^c	Relative expanded uncertainty (%)
IAEA-S-2	IMD	22.67	0.15	4			
	NIST	22.60	0.071	19			
	Revised reference value	22.62[a]	0.088	23	0.082	0.163	0.721
	Reported consensus value	22.66	0.13[b]				
IAEA-S-3	IMD	−32.53	0.12	4			
	NIST	−32.47	0.070	8			
	Revised reference value	−32.49[a]	0.087	12	0.078	0.155	0.477
	Reported consensus value	−32.30	0.12[b]				

[a] The revised recommended value only includes those measurements from IMD and NIST. See text for details.
[b] The uncertainty excludes that from GSC. Only a 1$\hat{\sigma}$ is reported as that is all that was originally reported.
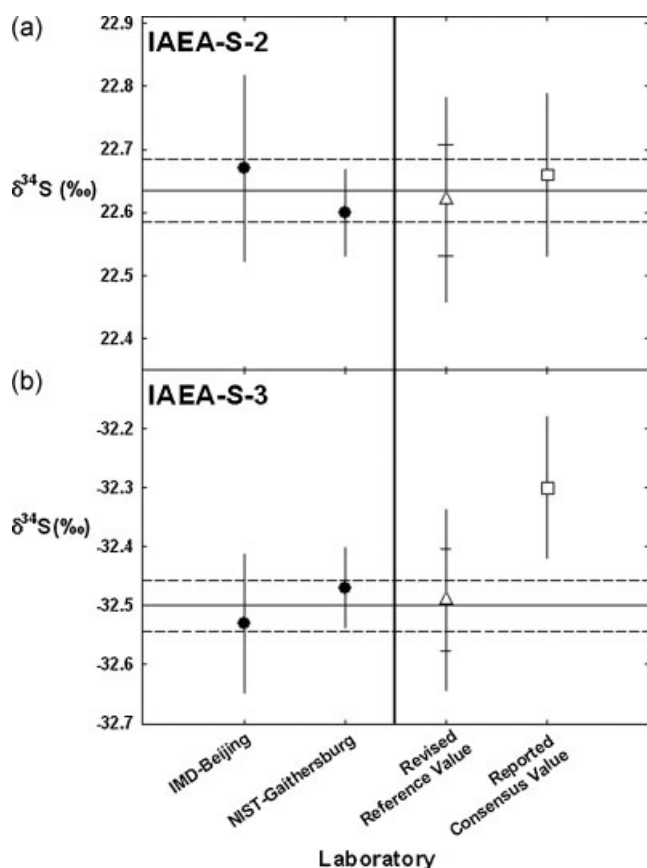[c] k = 2.

Figure 3. The individual laboratory results of IMD and NIST included in the recommended revised value compared with the previous consensus estimate of the 'true value' of the 8th Working Group for IAEA-S-2 (a) and IAEA-S-3 (b). The solid line is the mean of the individual laboratory data. The error bars for the individual laboratory results to the left of the vertical solid black line are 1$\hat{\sigma}$. The inner error bars for the recommended revised value are 1$\hat{\sigma}$ as are those for the reported consensus value. The outer error bar (without a cap) for the recommended revised value is the expanded uncertainty (capital U) with k = 2. The revised recommended value only includes the NIST and IMD values. The reported consensus value excludes the uncertainty from GSC. Please refer to text for explanation.

previously suggested for use by the 8th IAEA Advisory Working Group (Table 2 and Figs. 1(a), 3(a)).[4,5] The new estimate for IAEA-S-3 (−32.49 ± 0.087‰ (1$\hat{\sigma}$)) is more negative but also falls within the 1$\hat{\sigma}$ of the previously determined consensus value (−32.30 ± 0.12‰ (1$\hat{\sigma}$)) (Table 2 and Figs. 1(b), 3(b)); however, not only does the previous consensus value include determinations from both GSC and IRMM, both of which are possibly biased, but the values were determined by mean of means analysis rather than using the individual data taken together. As a result, the previously reported consensus value for IAEA-S-3 is unlikely to be representative of the best value. Thus the revised reference value recommended for use here is a better approximation of the true value and certainly a more consistent value for the positive and negative sides of the sulfur δ-scale. In both cases, the revised value assignments are confirmed by the double-spike MC-TIMS technique, and ultimately provide more rigorous bounds for the sulfur scale. Therefore, it is recommended that δ^{34}S values be measured and expressed relative to VCDT on a scale normalized using the revised reference values of +22.61‰ for IAEA-S-2 and −32.49‰ for IAEA-S-3. The use of the revised values will allow for improved consistency in data reported by laboratories using other techniques, including those which use SO_2 methods of analysis.

CONCLUSIONS

Studies have shown that the comparability of interlaboratory isotope measurements is considerably improved when reference materials spanning a wide range of δ values are used and measurements are normalized according to simple linear rules.[48,49,61,62] For appropriate normalization, consistent and bias-free values for the reference materials are required. The foregoing is especially true as new techniques (e.g. CF-IRMS, ICPMS and SIMS) are brought into use, for which the correction procedures may be both non-traditional and more complex. The revised δ^{34}S values and uncertainties recommended here for IAEA-S-2 and IAEA-S-3 have been reassessed and include the new values determined using an independent mass spectrometric technique. These more rigorous reference values provide additional bounds on the δ^{34}S scale and create a basis from which independent laboratories can measure and report not only δ^{34}S values, but also Δ^{33}S and Δ^{36}S that are intercomparable and should agree within reported measurement uncertainties.

REFERENCES

1. Krouse HR, Coplen TB. *Pure Appl. Chem.* 1997; **69**: 293.
2. Beaudoin G, Taylor BE, Rumble D, Thiemens M. *Geochim. Cosmochim. Acta* 1994; **58**: 4253.
3. Robinson BW. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, IAEA-TECDOC-825, IAEA: Vienna, 1995; 39.
4. Taylor BE, Ding T, Halas S, Breas O, Robinson BW. Accurate calibration of the V-CDT Scale: proposed δ34S values for calibration and reference materials and methods of correction for SO2-based analyses. In *Report of Sulfur Isotope Working Group 8th Advisory Group Meeting on Future Trends in Stable Isotope Reference Materials and Laboratory Quality Assurance*, September 18–22, 2000, IAEA Headquarters, Vienna, Austria.
5. Taylor BE, Ding T, Halas S, Breas O, Robinson BW. Accurate calibration of the V-CDT sulfur isotope scale: proposed δ34S values for calibration and reference materials and methods of correction for SO2-based analysis; Eos. Trans. AGU, 82(20), Spring Meet. Suppl. Abstract V21A-04, 2001.
6. Ding T, Valkiers S, Kipphardt H, De Bievre P, Taylor PDP, Gonfintini R, Krouse R. *Geochim. Cosmochim. Acta* 2001; **65**: 2433.
7. Analytical Quality Control Services Reference Materials Catalogue 2004–2005, IAEA: Vienna, Austria, January 2004; 64.
8. Ding T, Bai R, Li Y, Wan D, Zou X, Zhang Q. *Science in China, Series D: Earth Sciences* 1999; **42**: 45.
9. Ding T, Valkiers S, Kipphardt H, Quetel C, De Bievre P, Taylor PDP, Gonfintini R. *Int. J. Mass Spectrom.* 2000; **197**: 131.
10. Mann JL, Kelly WR. *Rapid Commun. Mass Spectrom.* 2005; **19**: 3429.
11. Thode HG, Monster J, Dunford HB. *Geochim. Cosmochim. Acta* 1961; **25**: 150.
12. Fritz P, Drimmie RJ, Nowicki VK. *Anal. Chem.* 1974; **46**: 164.
13. Leskovsek H, Marsel J, Kosta L. *Isotopenpraxis* 1974; **10**: 375.
14. Robinson BW, Kusakabe M. *Anal. Chem.* 1975; **47**: 1179.
15. Rees CE. *Geochim. Cosmochim. Acta* 1978; **42**: 383.
16. Rees CE. *Geochim. Cosmochim. Acta* 1978; **42**: 377.
17. Hoering TC, Prewitt CT. *Annual Report of the Director, Geophysical Laboratory, Carnegie Institution* 1987–88; 122.
18. Gao X, Thiemens MH. *Geochim. Cosmochim. Acta* 1991; **55**: 2671.
19. Giesemann A, Jager H-J, Norman AL, Krouse HR, Brand WA. *Anal Chem.* 1994; **66**: 2816.
20. Grassineau NV, Mattey DP, Lowery D. *Anal. Chem.* 2001; **73**: 220.
21. Studley SA, Ripley EM, Elswick ER, Dorais MJ, Fong J, Finkelstein D, Pratt LM. *Chem. Geol.* 2002; **192**: 141.
22. Baublys KA, Golding SD, Young E, Kamber BS. *Rapid Commun. Mass Spectrom.* 2004; **18**: 2765.
23. Kaufman AJ, Johnston DT, Farquhar J, Masterson AL, Lyons TW, Bates S, Anbar AD, Arnold GL, Garvin J, Buick R. *Science* 2007; **317**: 1900.
24. Ono S, Wing B, Rumble D, Farquhar J. *Chem. Geol.* 2006; **225**: 30.
25. Hu GX, Rumble D, Wang PL. *Geochim. Cosmochim. Acta* 2006; **67**: 3101.
26. Mason P, Kaspers K, Bergen M. *J. Anal. At. Spectrom.* 1999; **14**: 1067.
27. Prohaska T, Latkoczy C, Stingeder G. *J. Anal. At. Spectrom.* 1999; **14**: 1501.
28. Krupp EM, Pecheyran C, Meffan-Main S, Donard OFX. *Anal. Bioanal. Chem.* 2004; **378**: 250.
29. You C-F, Li M-D. *J. Anal. At. Spectrom.* 2005; **20**: 1392.
30. Clough R, Evans P, Catterick T, Evans EH. *Anal. Chem.* 2006; **78**: 6126.
31. Santamaria-Fernandex R, Hearn R. *Rapid Commun. Mass Spectrom.* 2008; **22**: 408.
32. Craddock PR, Rouxel OJ, Ball LA, Bach W. *Chem. Geol.* 2008; **253**: 102.
33. Mason PRD, Kosler J, de Hoog JCM, Sylvester PJ, Meffan-Main S. *J. Anal. At. Spectrom.* 2006; **21**: 177.
34. Bendall C, Lahaye Y, Fiebig J, Weyer S, Brey GP. *Appl. Geochem.* 2006; **21**: 782.
35. Riciputi LR. *Rapid Commun. Mass Spectrom.* 1996; **10**: 282.
36. Paterson BA, Riciputi LR, McSween HY. *Geochim. Cosmochim. Acta* 1997; **61**: 601.
37. Riciputi LR, Paterson BA, Ripperdan RL. *Int. J. Mass Spectrom.* 1998; **178**: 81.
38. Christensen LE, Brunner B, Truong KN, Mielke RE, Webster CR, Coleman M. *Anal. Chem.* 2007; **79**: 9261.
39. Macfarlane AW, Shimizu N. *Geochim. Cosmochim. Acta* 1991; **55**: 525.
40. Hervig RL. *Rapid Commun. Mass Spectrom.* 2002; **16**: 1774.
41. Russell WA, Papanastassiou DA, Tombrello TA. *Geochim. Cosmochim. Acta* 1978; **42**: 1075.
42. Johnson TM, Herbel MJ, Bullen TD, Zawislanski PT. *Geochim. Cosmochim. Acta* 1999; **63**: 2775.
43. Esat MJ. *Nucl. Instrum. Methods B* 1984; **233**: 545.
44. MacNamara J, Thode HG. *Phys. Rev.* 1950; **78**: 307.
45. Gonfiantini R. *Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations*, Sept. 19–21, 1983, Report to the Director General; IAEA: Vienna, 1984.
46. Stichler W. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, IAEA-TECDOC-825, IAEA: Vienna, 1995; 67–674.
47. Verkouteren RM, Klinedinst DB. *Value Assignment and Uncertainty Estimation of Selected Light Stable Isotope Reference Materials: RMs 8543–8545, RMs 8562–8564, RM 8566*, NIST Special Publication 260–149, National Institute of Standards and Technology: Gaithersburg, MD, 2004.
48. Gonfiantini R. *Nature* 1978; **271**: 534.
49. Coplen TB, Brand WA, Gehre M, Groning M, Meijer HA, Toman B, Verkouteren RM. *Anal. Chem.* 2006; **78**: 2439.
50. Farquhar J, Bao H, Thiemens MH. *Science* 2000; **289**: 756.
51. Baroni M, Thiemens MH, Delmas RJ, Savarino J. *Science* 2007; **315**: 84.
52. Romero A, Thiemens MH. *J. Geophys. Res.* 2003; **108**: 4524.
53. Savarino J, Romero A, Cole-Dai J, Bekki S, Thiemens MH. *Geophys. Res. Lett.* 2003; **30**: 2131.
54. Ding T, Wan D, Bai R, Yu T, Li J. *Mass independent sulfur isotope fractionation discovered in aerosol of Beijing*, Goldschmidt Conf. Abstracts, 2006.
55. Ohmoto H, Yamaguchi KE, Ono S. *Science* 2001; **292**: U5.
56. Farquhar J, Bao H, Thiemans MH, Hu G, Rumble D III. *Science* 2001; **292**: U6.
57. Farquhar J, Johnston DT, Wing BA, Habicht KS, Canfield DE, Airieau S, Thiemens MH. *Geobiology* 2003; **1**: 27.
58. Johnston DT, Farquhar J, Wing BA, Kaufman AJ, Canfield DE, Habicht KS. *Am. J. Sci.* 2005; **305**: 645.
59. Johnston DT, Wing BA, Farquhar J, Kaufman AJ, Strauss H, Lyons TW, Kah LC, Canfield DE. *Science* 2005; **310**: 1477.
60. Natrella MG. *Experimental Statistics*, National Bureau of Standards Handbook 91, National Bureau of Standards: Washington, DC, 1963.
61. Bohkle JK, Coplen TB. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*, IAEA-TEC-DOC-825, IAEA: Vienna, 1995; 51–566.
62. Brand WA, Coplen TB. *Fresenius J. Anal. Chem.* 2001; **370**: 358.