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ACCURATE CALIBRATION OF THE V-CDT SCALE: PROPOSED $\delta^{34}S$ VALUES FOR CALIBRATION MATERIALS AND METHODS OF CORRECTION FOR SO2-BASED ANALYSES

B. E. Taylor (Chair), T. Ding, S. Halas, O. Breas, and B. W. Robinson

This report summarizes the recommendations of a working group focused on sulfur isotope and includes: (1) $\delta^{34}S$ values of Ag_2S recommended for reference materials IAEA-S-2 and IAEA-S-3, based on analyses using SF_6 for mass spectrometry, as confirmed by absolute ratio measurements; (2) $\delta^{34}S$ values consistent with the V-CDT for several other reference and/or intercomparison materials IAEA-SO-5, IAEA-SO-6, NBS-127, NBS-123, and IAEA-S-4; (3) recommended procedures to correct both new and old isotopic compositions based on SO_2 mass spectrometry to the SF_6-based V-CDT scale; and (4) brief discussion of tasks to be carried out by the working group in the near future to increase the span of $\delta^{34}S$ currently and provide additional isotopic analyses using two different SF_6-based methods. The isotopic compositions and methods for correction of SO_2-based data suggested herein, places the calibration of the V-CDT scale on a firm basis.

SF_6-Based Analyses of Ag_2S: IAEA-S-2 and IAEA-S-3

Isotopic analysis of IAEA-S-2 and IAEA-S-3 were carried out by fluorination to produce SF_6 for mass spectrometry by two different techniques: (1) fluorination with BrF_5 of ca.4 mg in a conventional fluorination line (IMD-Beijing; Ding), and (2) laser-assisted fluorination of 0.7-1.5 mg with pure F_2 in a laser preparation line for micro-analysis (MILES; G.S.C.-Ottawa; Taylor). The results are quite comparable. A slight scale contraction noted in the measurements of the G.S.C., most probably due to the small sample size involved, was removed by normalization (a very small correction) to results from the IMD-Beijing. These data are shown in the table below.

Table 1. Isotopic Date on IAEA Ag2S

Reference Material	$\delta^{34}S$	S.D.	$\delta^{34}S_{V\text{-}CDT}$	S.D.	
IAEA-S-1			-0.300		*DEFINITION*
IAEA-S-2			22.67	0.15	IMD-Beijing
	22.28	0.81	22.66*	0.81	GSC-Ottawa

IAEA-S-3			-32.55	0.12	IMD-Beijing
	-32.11	0.38	-32.24*	0.38	GSC-Ottawa

* values normalized to those from IMD-Beijing to account for minor scale contraction

Slightly larger standard deviations for data acquired with MILES (GSC-Ottawa) are due to the high reactivity of Ag_2S with F_2 during micro-analysis. Nevertheless, the agreement of these results is excellent considering the different techniques and very different sample sizes involved, and provide a strong basis for accurate calibration of the V-CDT scale.

As a point of interest, although the isotopic composition of IAEA-S-1 has been defined as –0.3 ‰ on the V-CDT scale, the accuracy of the SF_6 method provides the possibility to experimentally check this definition. Measurements at the GSC-Ottawa, indicate $\delta^{34}S_{V\text{-}CDT}$ values for two different specimens of troilite from the Cañon Diablo meteorite of 0.13 ± 0.11 (GSC #0303-15) and 0.14 ± 0.08 (Harvard Univ. 440h). These results are wholly compatible with measured uncertainty of 0.16 ‰ on the value of –0.3 ‰ for IAEA-S-1 measured at IMD-Beijing. These data suggest a slight departure of the V-CDT scale from the previously used CDT scale (by 0.1 ‰) which is, nevertheless, within the apparent variation of $\delta^{34}S$ values found for various samples of CDT (e.g., Beaudoin and Taylor, 1994).

Confirmation by Measurement of Absolute Isotope Ratios

Close correspondence was found between relative isotope ratio measurements of IAEA-S-2 and IAEA-S-3 using the SF_6 method at the IMD-Beijing (Ding, 1999) and the G.S.C.-Ottawa (Taylor, 2000) and absolute ratio measurements carried out by Dr. Ding at the IRMM-Geel (Ding, 1999?). This correspondence further indicates the accuracy of the SF_6-based measurement, lends particular strength to the $\delta^{34}S$ values recommended for IAEA-S-2 and IAEA-S-3 by the sulfur isotope working group. The recommended $\delta^{34}S$ values (below) are, in fact, mean values of the isotope ratio measurements and the absolute ratio measurements.

Recommended Values of $\delta^{34}S$ for IAEA-S-2 and IAEA-S-3

The following data are averaged to provide recommended values of both $\delta^{34}S$ and associated uncertainties (calculated as the root mean square of deviations divided by the square root of the number of samples).

Table 2. Recommended Values for IAEA S-Isotope Calibration Materials

Reference Material	$\delta^{34}S$	S.D.	V-CDT Recommended $\delta^{34}S$	S.D.	
IAEA-S-1	-0.300		**-0.3**		*DEFINITION*

IAEA-S-2	22.67	0.15			IMD-Beijing
	22.66	0.81			GSC-Ottawa
	22.64	0.11			IRMM-Geel
			22.66	**0.13**	
IAEA-S-3	-32.55	0.12			IMD-Beijing
	-32.24	0.38			GSC-Ottawa
	-32.06	0.11			IRMM-Geel
			-32.30	**0.12**	

We emphasize here that the uncertainty (S.D., one standard deviation) recommended is the uncertainty of knowing the $\delta^{34}S$ value of the calibration material, based on two SF_6 methods plus absolute ratio determination. It should not be confused with the uncertainty associated with determining this value by individual laboratories.

NBS-127, IAEA-SO-5 and, IAEA-SO-6, and NBS-123 and IAEA-S-4

Excellent agreement is found between SF_6-based isotopic measurements and SO_2-based measurements (SO^+ mass spectrometry, with proper corrections for oxygen isotope composition and a good estimate of the cross mixing correction) of IAEA-SO-5 and IAEA-SO-6. Additional data on other inter-comparison materials were discussed.

Table 3. Isotopic Date on Sulfates

Reference Material	$\delta^{34}S$	S.D.	$\delta^{34}S_{V\text{-}CDT}$	S.D.	
IAEA-SO-5			0.49	0.11	IMD-Beijing
			0.48	0.06	Lublin
	0.98	0.20	1.16	0.20	GSC-Ottawa*
IAEA-SO-6			-34.05	0.08	IMD-Beijing
			-34.30	0.08	Lublin
	-33.34	0.10	-33.48	0.10	GSC-Ottawa*
NBS-127	21.41	0.20	21.78	0.20	GSC-Ottawa
NBS-123	17.84	0.05	18.17	0.05	GSC-Ottawa
IAEA-S-4	15.80	0.10	16.11	0.10	GSC-Ottawa

Provisional $\delta^{34}S_{V\text{-}CDT}$ values and uncertainties for barium sulfates are (IAEA-SO-5) 0.49 ± 0.09 ‰, and (IAEA-SO-6) -34.18 ± 0.07 ‰. These data are based on IMD-determined (Ding) values by the SF_6 method and on Lublin-determined (Halas) SO_2-

based values for direct analysis of sulfate, with properly applied oxygen isotope and cross-mixing corrections. The data submitted by the G.S.C.-Ottawa (Taylor) although adequately precise, appear to have suffered from isotopic fractionation during the preparation of Ag_2S using the Kiba method; sulfates cannot be directly fluorinated. The sulfate-to-Ag_2S conversions accomplished in Beijing using the well-known Thode solution were evidently not isotopically affected. Additional measurements, as described later, will be made in order to provide a basis for firm IAEA-recommended $\delta^{34}S_{V\text{-}CDT}$ values for these intercomparison materials.

The $\delta^{34}S_{V\text{-}CDT}$ value of 21.78 for NBS-127 supplied by the G.S.C.-Ottawa (Taylor) may have also suffered from isotopic fractionation during reduction to Ag_2S. This will be re-checked via analysis of a separately prepared Ag_2S (see later discussion) and direct analysis (Lublin) of the sulfate. The single value for IAEA-S-4, also based on fluorination of Ag_2S, provides a provisional value on the SF_6-based V-CDT scale. However, it is unknown whether there has been any isotopic fractionation of IAEA-S-4 during the Kiba extraction.

Comparison of SF_6-Based and SO_2-Based Scales and Recommended Methods of Calibration and Correction

Calibration to the V-CDT scale and elimination of scale expansion/contraction can be accomplished by careful measurement in each laboratory of SF_6 produced from IAEA-S-2 and IAEA-S-3; measurement of IAEA-S-1 should then give a $\delta^{34}S_{V\text{-}CDT}$ value of –3.0 ‰ (within the external analytical uncertainty of the laboratory). However, very few laboratories analyze sulfides by fluorination; oxidation to SO_2 is typical. In the figure below, we compare isotopic data derived from measurements made with SF_6 and SO_2.
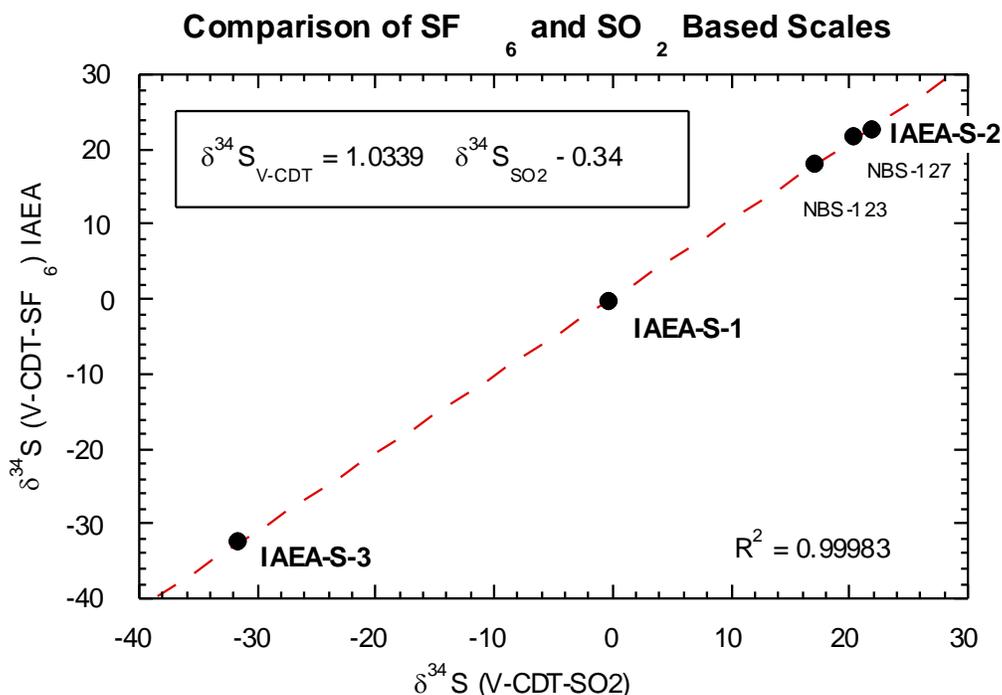
Comparison of SF$_6$ and SO$_2$ Based Scales

Figure 1. Comparison of $\delta^{34}S$ values for IAEA-S-1 to –3, NBS-123 and NBS-127 based on SF$_6$ and SO$_2$ methods. The values of $\delta^{34}S$ V-CDT (SF$_6$) plotted are those recommended above; $\delta^{34}S$ (SO$_2$) values are the currently IAEA recommended values.

The slope of the SF$_6$/SO$_2$ correlation (1.0339) is virtually identical to that of Reese (1.0348; 1978) and Beaudoin and Taylor (1.035; 1994) who determined average slopes of 1.035. This slope may vary slightly from instrument to instrument. Taylor (2000) reported a slope of 1.026, but this is based on SF$_6$ measurements affected by a very small scale contraction. In any case, it is evident that a correction to SO$_2$-based data is required. The very high degree of correlation ($R^2 = 0.99983$) provides a strong basis for the following recommended correction procedure SO$_2$-based data.

Laboratories using oxidative preparation techniques to yield SO$_2$ for mass spectrometry should carefully calibrate their working standard(s) using IAEA-S-2 and IAEA-S-3, and thereby determine a correction algorithm of the form

$$\delta^{34}S_{V-CDT} = mx + y$$

where x is $\delta^{34}S$ value determined on SO$_2$. It should be very close to 1.035, but may vary with specific mass spectrometer and laboratory. The close agreement between SF$_6$-based values of $\delta^{34}S$ for IAEA-SO-5 and IAEA-SO-6 and the $\delta^{34}S$ values on SO$_2$ based measurements where a correction of 1.04 was employed (Halas, 2000; see Table 3) indicates that the correction of ca. 3.5 % is essentially due to "cross-mixing" effects in the ion source (e.g., Meijer, et al., 1999). Relative to other gases, the effect for SO$_2$ appears to be relatively large. We should endeavor to quantify this effect by direct measurement.

Consequences of Adoption of the SF$_6$-Based V-CDT Scale

Previously published sulfur isotope data primarily relied on analyses with SO$_2$ It is now evident that these data were subject to an error of some 3-4 % in addition to variable isotopic scale contraction. Adoption of the above-recommend SF$_6$-based V-CDT scale results in several significant consequences: (1) the reported range of δ^{34}S for natural abundance will be expanded somewhat; (2) isotopic fraction factors (α) will require recalculation, yielding a increase by a factor of approximately 1.035; and (3) certain familiar reference points in earth science (e.g., isotopic composition of sea water; sulfate-age curve) will require recalculation/modification. These consequences will be investigated immediately.

Additional Isotopic Measurements

Barium sulfates IAEA-SO-5, IAEA-SO-6 and NBS 127 will be analyzed further in Lublin (Halas) and, after reduction to Ag$_2$S, analyzed again by SF$_6$ techniques in Beijing (Ding) and Ottawa (Taylor). These data will permit final determination of recommended δ^{34}S$_{V\text{-}CDT}$ values for IAEA supplied sulphates. Similarly, determination of δ^{34}S for NBS-123 at IMD-Beijing will provide additional data for evaluation of this sphalerite on the V-CDT scale (currently: 18.17$\pm$ 0.05 ‰, G.S.C-Ottawa).

Additional Reference Materials

It is advisable to have reference materials that lie as near as possible to the extremes of the range of natural abundance in order to provide for normalization of measurements over most of the natural range of isotopic abundance, i.e. to avoid scale contraction/expansion.

Sulfur Isotope Reference Materials. Dr. Tiping Ding has offered to provide a sufficient quantity of a natural (Cambrian-age) sulfate from China that has a value of δ^{34}S of ca. 60-90 ‰, among the highest naturally occurring values of δ^{34}S known; it should also have, incidentally, a relatively high value of δ^{18}O. Ding will undertake to purify this natural sulfate via solution and re-precipitation, and to homogenize the final product. A portion of the sulfate will be available for reduction to Ag$_2$S, which Dr. Brian Robinson has agreed to do if the IAEA can provide a contract to cover the preparation costs. The preparation of Ag$_2$S from the Chinese sulfate sample would be carried out in the same manner as used for IAEA-S-1, -2, and –3. The sulfur isotope composition of this additional sample of Ag$_2$S could then be accurately determined by the SF$_6$ method. The sulfur isotope working group strongly urges that this be undertaken. This reference point would permit even greater accuracy in the control of isotopic scale contraction than currently available via IAEA-S-2 and IAEA-S-3.

Oxygen Isotope Composition of Sulfate.

Agreement on the oxygen isotope isotope composition of barium sulphate intercomparison materials is not sufficiently good to recommend adoption of $\delta^{18}O$ at this time. For example, the current mean value of $\delta^{18}O$ is 9.10 ± 0.5 ‰ for NBS-127, from five submitting labs; variations exceed 1.0 ‰ for IAEA-SO-5 and IAEA-SO-6. Clearly, more data are needed. In addition, a barium sulphate intercomparison material is needed with as low as value of $\delta^{18}O$ as possible (e.g., -30 ‰).

References

Beaudoin, G., Taylor, B. E., Rumble III, D., and Thiemens, M., 1994, Variations in the sulfur isotope composition of troilite from the Cañon Diablo iron meteoritie: Geochim. Cosmochim. Acta, v. 58, p. 4253-4255.

Ding, T., Bai, R., Li, Y., Wan, D., Zou, X., and Zhang, Q., 1999, Determination of the absolute 32S/34S ratio of IAEA-S-1 reference material and V-CDT sulfur isotope standard : Science in China: v. 42, p. 45-51.

Ding, T., et al, 2000, Calibrated sulfur isotope abundance ratios of IAEA-S-1, IAEA-S-2, and IAEA-S-3 reference materials, two Chinese standards and V-CDT and a reassment of the atomic weight of sulfur: Geochim. Cosmochim. Acta (submitted).

Halas, S. and Szaran, J., 2000, Calibration of IAEA sulfate standards vs VCDT with special emphasis on reduction of systematic errors: Report to the 8th Advisory Group Meeting on Future Trends in Stable Isotope Reference Materials and Laboratory Quality Assurance; September 18-22, 2000, IAEA Headquarters, Vienna, Austria.

Meijer, H .A. J., Neubert, R. E. M., and Visser, G. H., 1999, Cross contamination in dual inlet isotope ratio mass spectrometers: International Journal of Mass Spectrometry, v. 198, 45-61.

Rees, C. E., 1978, Sulphur isotope measurements using SO_2 and SF_6: Geochim. Cosmochim. Acta, v. 42, p. 383-389.

Taylor, B. E., 2000, Calibration of the sulfur isotope scale by laser-induced fluorination of sulfides to SF_6 using pure F_2: Report to the 8th Advisory Group Meeting on Future Trends in Stable Isotope Reference Materials and Laboratory Quality Assurance; September 18-22, 2000, IAEA Headquarters, Vienna, Austria.