National Institute of Standards & Technology

Report of Investigation

Reference Material 8554

IAEA-S-1

(Sulfur Isotopes in Silver Sulfide)

This Reference Material (RM) is the international measurement standard [1,2] that defines the Vienna Cañon-Diablo Troilite (VCDT) δ-scale ($\delta^{34}S_{VCDT}$) for relative isotope ratio measurements of sulfur (S), $R(^{34}S/^{32}S)$ [3]. The equivalent name for this RM, as used by the International Atomic Energy Agency (IAEA) and the U.S. Geological Survey (USGS) is IAEA-S-1. This material was formerly called NZ-1 (New Zealand) [4]. The International Union of Pure and Applied Chemistry (IUPAC) recommends all relative sulfur isotopic measurements be reported as $\delta^{34}S_{VCDT}$ [2,5]; relative sulfur isotopic values are given as $\delta^{34}S_{VCDT}$ in this document. A unit of RM 8554 (IAEA-S-1) consists of one bottle containing approximately 0.5 g of silver sulfide (Ag_2S).

Table 1. Reference Value for $\delta^{34}S_{VCDT}$, RM 8554 (IAEA-S-1)

NIST RM Number	IAEA Name	Reference Value[a,b] $\delta^{34}S_{VCDT}$
8554	IAEA-S-1	–0.30 ‰ (exact)

[a] The $\delta^{34}S_{VCDT}$ value is an exact value in units of per mil (‰) and is the anchor for the $\delta^{34}S_{VCDT}$ scale [2,4,5].
[b] The symbol ‰ is part per thousand and is equal to 0.001.

Metrological Traceability: VCDT is the accepted "stated reference" point for the sulfur isotope ratio measurement scale [2,5]. VCDT is realized primarily and explicitly through the silver sulfide RM 8554 (IAEA-S-1), where:

RM 8554 (IAEA-S-1) *Silver Sulfide*: $\delta^{34}S_{VCDT} \equiv -0.30$ ‰

Expiration of Value Assignment: RM 8554 (IAEA-S-1) is valid until **01 May 2030** provided the RM is handled and stored in accordance with instructions given in this Report of Investigation (see "Instructions for Handling and Storage"). This report is nullified if the RM is damaged, contaminated, or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Technical aspects involved in the issuance of this RM were coordinated through the NIST Chemical Sciences Division by J.L. Mann.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

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Steven J. Choquette, Director
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INSTRUCTIONS FOR HANDLING AND STORAGE

Handling and Storage: RM 8554 (IAEA-S-1) is stable at room temperature. To minimize the potential for contamination, it is recommended that this RM be stored in the container in which it is supplied.

Distribution: The distribution of RM 8554 (IAEA-S-1) is limited to one unit per three-year period.

PREPARATION AND ANALYSIS OF RM 8554

Preparation: RM 8554 (IAEA-S-1) was prepared and purified by B.W. Robinson, Lower Hutt, New Zealand from a sphalerite provided by S. Halas, Maria Curie-Skłodowskie University, Lublin, Poland [4].

Analytical Methods: When δ^{34}S values of the original Cañon-Diablo Troilite (CDT) were shown to be isotopically heterogeneous at a level of 0.4 ‰ [2,6], RM 8554 (IAEA-S-1) was selected as a replacement reference material. Mass spectrometric measurements of SF_6 preparations of RM 8554 (IAEA-S-1) showed that this material had a δ^{34}S value very near CDT that ranged from about –0.33 ‰ to –0.27 ‰ [4,7]. The VCDT scale was then established by assigning an exact δ^{34}S value of –0.30 ‰ to IAEA-S-1 [4,5].

Isotopic Homogeneity: Homogeneity assessment of 15 mg and 2.5 mg samples of RM 8554 (IAEA-S-1) [4] and many years of use by the isotope ratio community affirm that the material's homogeneity is suitable for present measurement applications.

REPORTING

Terminology: The terminology used here is based on the guidance given by IUPAC for isotope terminology, where stable isotope-number ratio refers to the number of atoms of one isotope relative to the number of atoms of a second isotope in the same system [2]. This is often abbreviated to stable isotope ratio. Isotope-delta value refers to the stable isotope-number ratio of a measured sample relative to the stable isotope-number ratio of a reference material (see example below). Isotope-amount ratio is numerically the same as isotope-number ratio but refers specifically to the amount (moles) of an isotope relative to the amount (moles) of another isotope in the same system [3].

Isotope-delta (δ) Values: The sulfur isotope-delta value of a measured sample ($\delta^{34}S_{sample}$) reported on the VCDT scale is defined as the difference in the measured isotope-number ratio of sulfur [$N(^{34}S)/N(^{32}S)$] in the sample relative to the stable isotope-number ratio of sulfur in VCDT [2,5]:

$$\delta^{34}S_{sample} = \frac{\left[\frac{N_{sample}(^{34}S)}{N_{sample}(^{32}S)}\right] - \left[\frac{N_{VCDT}(^{34}S)}{N_{VCDT}(^{32}S)}\right]}{\left[\frac{N_{VCDT}(^{34}S)}{N_{VCDT}(^{32}S)}\right]}$$

Normalization: The δ^{34}S value in a sample should be normalized to the VCDT δ-scale by calibrating the measurement with respect to the δ-value for RM 8554 (IAEA-S-1) and the δ-value from the appropriate ^{34}S-enriched or ^{34}S-depleted anchor RM. RM 8555 (IAEA-S-2) should be used as the anchor for the ^{34}S-enriched end while RM 8529 (IAEA-S-3) is appropriate for the ^{34}S-depleted end of the scale. A general formula for normalizing a measured sulfur isotope number ratio [$N(^{34}S)/N(^{32}S)$] using two laboratory standards (LS), LS1 (e.g., RM 8554 (IAEA-S-1)) and LS2 (e.g., RM 8555 (IAEA-S-2)) can be expressed as:

$$\delta^{34}S_{sample,cal} = \delta^{34}S_{LS1,cal} + \left(\delta^{34}S_{sample,WS} - \delta^{34}S_{LS1,WS}\right) \times f \qquad (1)$$

where the normalization factor f is:

$$f = \left(\delta^{34}S_{LS2,cal} - \delta^{34}S_{LS1,cal}\right) \Big/ \left(\delta^{34}S_{LS2,WS} - \delta^{34}S_{LS1,WS}\right) \qquad (2)$$

Note: In the above formulas, cal denotes calibrated measurements made versus the VCDT scale, and $\delta^{34}S_{LS1,cal}$ and $\delta^{34}S_{LS2,cal}$ are the conventionally fixed δ^{34}S values for RM 8554 (IAEA-S-1) and RM 8555 (IAEA-S-2). WS denotes measurements made versus a transfer gas (working standard), and $\delta^{34}S_{LS1,WS}$ and $\delta^{34}S_{LS2,WS}$ are the δ^{34}S values for calibrated laboratory working standards.

Reporting of Sulfur Stable Isotope-delta (δ) values: The following recommendations from IUPAC are provided for reporting $\delta^{34}S$ values [2,5,8]. It is recommended that:

- the use of meteoritic troilite and the reporting of $\delta^{34}S$ isotope-delta value data relative to Cañon-Diablo Troilite (CDT) be discontinued;
- all relative sulfur isotopic compositions be reported relative to VCDT;
- the VCDT scale be realized through the use of RM 8554 (IAEA-S-1), silver sulfide.

In addition, researchers are encouraged to report the isotopic composition of any internationally distributed sulfur isotopic reference materials [5,8] in their publications, as appropriate to the method, as though they have been interspersed among unknowns.

REFERENCES

[1] JCGM 200:2012; *International Vocabulary of Metrology — Basic and General Concepts and Associated Terms (VIM)*, 3rd ed.; Joint Committee for Guides in Metrology (JCGM) (2012); available at https://www.bipm.org/en/publications/guides (accessed Sep 2021).

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[3] Coplen, T.B.; *Guidelines and Recommended Terms for Expression of Stable-Isotope-Ratio and Gas-Ratio Measurement Results*; Rapid Commun. Mass Spectrom., Vol. 25, pp. 2538–2560 (2011).

[4] Robinson, B.W.; *Sulfur Isotope Standards;* In Reference and Intercomparison Materials for Stable Isotopes of Light Elements, in Proceedings of a Consultants Meeting Held in Vienna, 1–3 December 1993; IAEA-TECDOC-825: Vienna, Austria, pp. 39–45 (1995).

[5] Krouse, H.R.; Coplen, T.B.; *Reporting of Relative Sulfur Isotope-Ratio Data;* Pure Appl. Chem., Vol. 69(2) pp. 293–295 (1997).

[6] Beaudoin, G.; Taylor, B.E.; Rumble, D., III; Thiemens, M.; *Variations in the Sulfur Isotope Composition of Troilite from the Cañon-Diablo Iron Meteorite*; Geochimica et Cosmochimica Acta, Vol. 58, pp. 4253–4255 (1994).

[7] Stichler, W.; Gonfiantini, R.; Rozanski, K.; *Reference and Intercomparison Materials for Stable Isotopes of Light Elements;* In Proceedings of a Consultants Meeting Held in Vienna, 1–3 December 1993; IAEA-TECDOC-825: Vienna, Austria, pp. 7–11 (1995).

[8] Coplen, T.B.; Hopple, J.A.; Böhlke, J.K.; Peiser, H.S.; Rieder, S.E.; Krouse, H.R.; Rosman, K.J.R.; Ding, T.; Vocke, R.D. Jr.; Révész, K.M.; Lamberty, A.; Taylor, P.; De Bièvre, P; *Compilation of Minimum and Maximum Isotope Ratios of Selected Elements in Naturally Occurring Terrestrial Materials and Reagents*; U.S. Geological Survey Water-Resources Investigations Report 01-4222, (2002).

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Users of this RM should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.