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# *In situ* sulfur isotopes ($\delta^{34}S$ and $\delta^{33}S$) analyses in sulfides and elemental sulfur using high sensitivity cones combined with the addition of nitrogen by laser ablation MC-ICP-MS

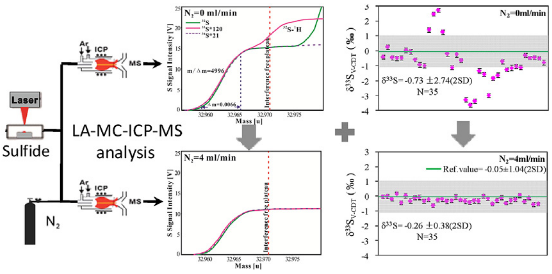
Jiali Fu [a], Zhaochu Hu [a, b, *], Wen Zhang [a], Lu Yang [a, c], Yongsheng Liu [a], Ming Li [a], Keqing Zong [a], Shan Gao [a], Shenghong Hu [a]

[a] *State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, PR China*
[b] *The Beijing SHRIMP Center, Institute of Geology, Chinese Academy of Geological Sciences, Beijing 102206, PR China*
[c] *National Research Council Canada, 1200 Montreal Rd., Ottawa, Ontario K1A 0R6, Canada*

## HIGHLIGHTS

- A new approach to obtain *in situ* S isotope data in sulfides and elemental sulfur.
- The use of Jet sample cone and X Skimmer cone improves S sensitivity by a factor of 3.6.
- Addition of $N_2$ efficiently reduces polyatomic interferences and stabilizes the mass bias.
- Effective reduction of matrix effect by using the line scan ablation under the optimized fluence.
- $\delta^{33}S_{V\text{-}CDT}$ and $\delta^{34}S_{V\text{-}CDT}$ values in 12 reference materials are reported.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The sulfur isotope is an important geochemical tracer in diverse fields of geosciences. In this study, the effects of three different cone combinations with the addition of $N_2$ on the performance of *in situ* S isotope analyses were investigated in detail. The signal intensities of S isotopes were improved by a factor of 2.3 and 3.6 using the X skimmer cone combined with the standard sample cone or the Jet sample cone, respectively, compared with the standard arrangement (H skimmer cone combined with the standard sample cone). This signal enhancement is important for the improvement of the precision and accuracy of *in situ* S isotope analysis at high spatial resolution. Different cone combinations have a significant effect on the mass bias and mass bias stability for S isotopes. Poor precisions of S isotope ratios were obtained using the Jet and X cones combination at their corresponding optimum makeup gas flow when using Ar plasma only. The addition of 4–8 ml $min^{-1}$ nitrogen to the central gas flow in laser ablation MC-ICP-MS was found to significantly enlarge the mass bias stability zone at their corresponding optimum makeup gas flow in these three different cone combinations. The polyatomic interferences of OO, SH, OOH were also significantly reduced, and the interference free plateaus of sulfur isotopes became broader and flatter in the nitrogen mode ($N_2 = 4$ ml $min^{-1}$). However, the signal intensity of S was not increased by the addition of nitrogen in this study. The laser fluence and ablation mode had significant effects on sulfur isotope fractionation during the analysis of sulfides and elemental sulfur by laser

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* Corresponding author. State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, PR China.
*E-mail address:* zchu@vip.sina.com (Z. Hu).

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ablation MC-ICP-MS. The matrix effect among different sulfides and elemental sulfur was observed, but could be significantly reduced by line scan ablation in preference to single spot ablation under the optimized fluence. It is recommended that the $d_{90}$ values of the particles in pressed powder pellets for accurate and precise S isotope analysis should be less than 10 μm. Under the selected optimized analytical conditions, excellent agreements between the determined values and the reference values were achieved for the IAEA-S series standard reference materials and a set of six well-characterized, isotopic homogeneous sulfide standards (PPP-1, $MoS_2$, MASS-1, P-GBW07267, P-GBW07268, P-GBW07270), validating the capability of the developed method for providing high-quality *in situ* S isotope data in sulfides and elemental sulfur.

## 1. Introduction

Sulfur, the 10th most abundant element in the universe and the 14th most abundant element in the Earth's crust, is a highly volatile element, consisting of four stable isotopes, $^{32}S$, $^{33}S$, $^{34}S$, and $^{36}S$, with relative isotopic abundances of approximately 94.99, 0.75, 4.25 and 0.01%, respectively [1–3]. Generally, the sulfur isotopic composition is expressed in delta (δ) notation (per mill, ‰) as follows:

$$\delta^{x}S[\text{‰}] = \left[({}^{x}S/{}^{32}S)_{\text{sample}} \Big/ ({}^{x}S/{}^{32}S)_{\text{standard}} - 1\right] \times 1000 \tag{1}$$

where x is 33, 34 or 36, and the accepted standard is Vienna Canyon Diablo Troilite (VCDT) with $\delta^{34}S = 0.0$‰ by definition [4].

**Table 1**
Typical operating parameters for NEPTUNE MC-ICPMS and ArF 193 nm laser.

| | |
|---|---|
| **Mass spectrometer setup** | |
| MC-ICP-MS | NEPTUNE *Plus* |
| RF power | 1200 W |
| Pt-guard electrode | On, grounded |
| Plama Ar gas flow rate | 16.0 l $min^{-1}$ |
| Auxiliary Ar gas flow rate | 1.00 l $min^{-1}$ |
| Ar makeup gas flow rate | 0.2–1.4 l $min^{-1}$ |
| Interface cones | a. Standard sample cone + H skimmer cone (Ni)<br>b. Standard sample cone + X skimmer cone (Ni)<br>c. Jet sample cone + X skimmer cone (Ni) |
| **Data acquisition parameters** | |
| Acquisition type | Static |
| Detection system | Nine Faraday cups |
| Cup configuration | $^{32}S$ (L3), $^{33}S$ (C), $^{34}S$ (H3) |
| Resolution mode | Medium resolution (~4000) |
| Signal integration time | 0.262 s |
| Signal analysis protocol | 1 Block, 200 cycles |
| **GeoLas 2005 laser ablation system** | |
| Wavelength | 193 nm, excimer laser |
| Pulse length | 15 ns |
| Carrier gas | Helium (0.5 l $min^{-1}$) |
| Scan mode | Single spot and line scan mode |
| Spot diameter | 24–60 μm |
| Ablation duration | 34 s |
| Pulse rate | 3–6 Hz |
| Laser fluence | 1.6–4.8 J $cm^{-2}$ |

Variations of the $\delta^{34}S$ on earth are large (up to 180‰), where a difference of 1–2‰ is significant in geology; consequently, the light stable element S and its isotopic composition have been well proven to be a very important geochemical tracer in diverse fields of geosciences, such as the igneous, sedimentary, hydrothermal, and biological processes on the earth [2,5,6]. Accurate and precise methodologies are desired for the measurement of sulfur isotope ratios in various sample matrices. Traditionally, the measurement of sulfur isotope composition is conducted using gas-source mass spectrometry (GS-MS) in which, sulfur is introduced as gaseous $SO_2$ or $SF_6$ [7–11]. For $SF_6$ analysis, this is the preferred technique for the high-precision determination of sulfur isotope ratios (<0.1‰) [10] compared with $SO_2$ analysis (0.1–0.25‰) [12,13]. In the last decade, several other bulk analytical techniques have been used for sulfur isotope ratio determinations, such as multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) (precision of approximately 0.2‰, 2s) [14–19], and multi-collector thermal ionization mass spectrometry (MC-TIMS) (precision <0.1‰, 2s) [20].

Although bulk analysis methods for sulfur isotopes (*e.g.*, GS-MS, MC-TIMS and MC-ICP-MS) can produce high precision [21], potentially useful and important geochemical information, such as features of mineral growth, recrystallization and metasomatism preserved at the sub-grain scale, is lost. Moreover, bulk analysis methods require the sample preparation step for mineral separation, which is complex and time-consuming. Therefore, *in situ* microanalysis of sulfur isotopes is preferred for many applications.

**Table 2**
A list of twelve samples studied.

| Sample name | Material | Description | Reference |
|---|---|---|---|
| IAEA-S-1 | Synthetic $Ag_2S$ | Powder, distributed by the International Atomic Energy Agency, Vienna, Austria | [61] |
| IAEA-S-2 | Synthetic $Ag_2S$ | Powder, distributed by the International Atomic Energy Agency, Vienna, Austria | [61] |
| IAEA-S-3 | Synthetic $Ag_2S$ | Powder, distributed by the International Atomic Energy Agency, Vienna, Austria | [61] |
| IAEA-S-4 | S(elemental) | Powder, distributed by the International Atomic Energy Agency, Vienna, Austria | [13] |
| GBW04414 | Synthetic $Ag_2S$ | Powder, distributed by the Institute of Reference Materials and Measurements, China | [61] |
| GBW04415 | Synthetic $Ag_2S$ | Powder, distributed by the Institute of Reference Materials and Measurements, China | [61] |
| GBW07267 | Pyrite | Powder, produced by the Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, China | [52] |
| GBW07268 | Chalcopyrite | Powder, produced by the Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, China | [52] |
| GBW07270 | Sphalerite | Powder, produced by the Institute of Rock and Mineral Analysis, Ministry of Geology and Mineral Resources, China | [52] |
| PPP-1 | Pyrite | Single crystal, from the Sukhoi Log deposit, Russia | [51] |
| MASS-1 | Synthetic sulfide | Pressed powder pellet, produced by precipitating amorphous metal sulphides from solution with an Fe–Cu–Zn–S matrix | [62] |
| $MoS_2$ | Molybdenite | Single crystal, from a Mo deposit of the Luanchuan ore field in the East Qingling Mo mineralization belt, Central China | This study |