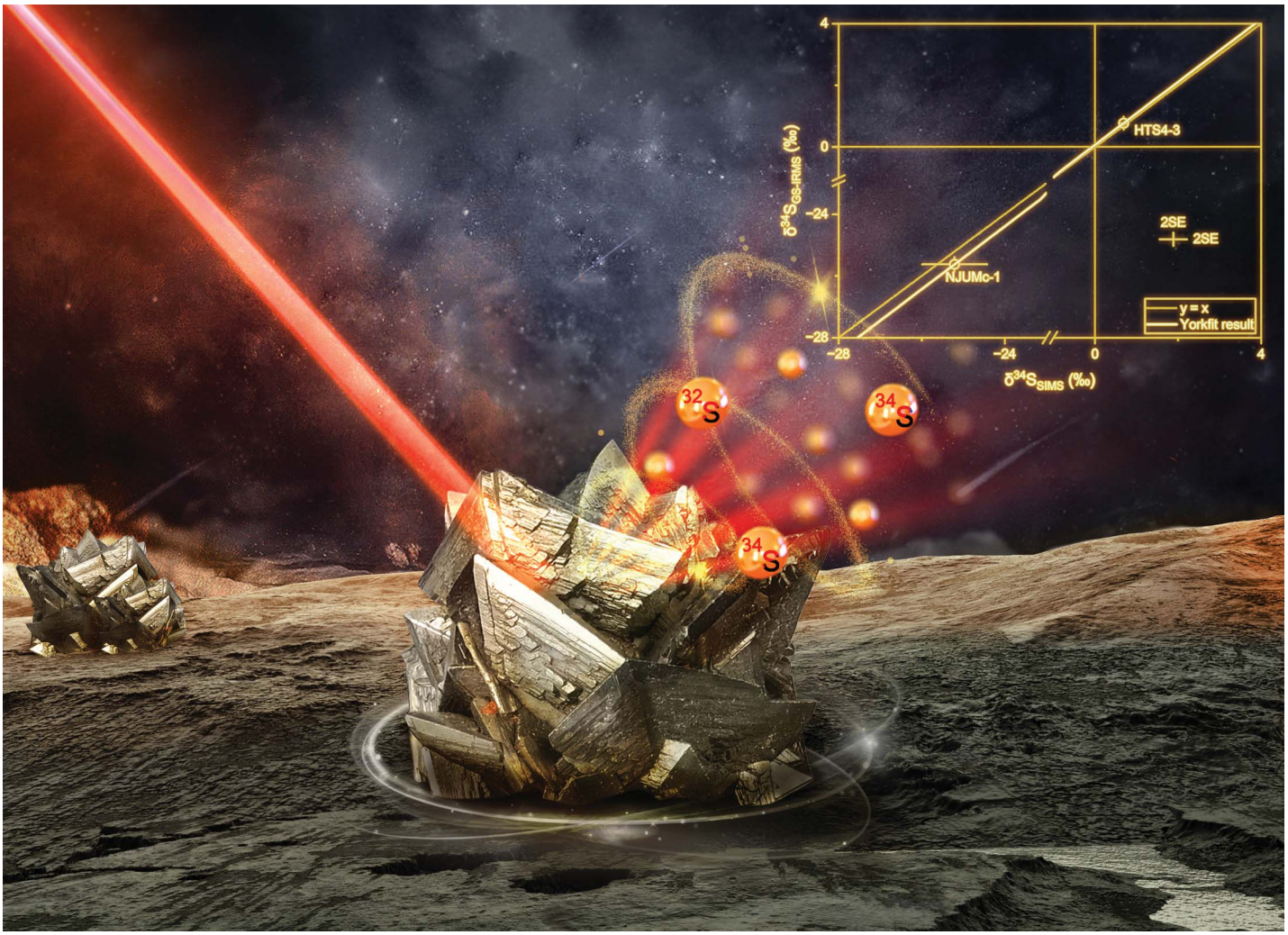

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The feasibility of using a pyrite standard to calibrate the sulfur isotope ratio of marcasite during SIMS analysis

Pyrite standard is commonly used to calibrate the sulfur isotope ratios of marcasite during SIMS analysis. But the feasibility of this calibration regime has not been investigated. We investigated this topic by analyzing a natural marcasite (NJUMc-1) with Cameca IMS 1300-HR^3. The average $\delta^{34}S$ value of NJUMc-1 calibrated by a pyrite standard agrees well with the result determined using gas source isotope ratio mass spectrometry, indicating that it is feasible to calibrate the sulfur isotopic ratios of marcasite with a pyrite standard.

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The feasibility of using a pyrite standard to calibrate the sulfur isotope ratio of marcasite during SIMS analysis†

Rucao Li,[ab] Xiao-Lei Wang,*[b] Yue Guan,[b] Jing Gu[c] and Lan-Lan Tian[b]

Marcasite (FeS_2, orthorhombic) is a dimorph of pyrite (FeS_2, isometric), which has been reported in many kinds of ore deposits and sedimentary rocks. The sulfur isotopic composition of marcasite could be used to track ore-forming fluid source(s) and ocean acidification events in deep time. However, matrix-matched standards for marcasite are scarce, and in practice a pyrite standard is commonly used to calibrate the sulfur isotope ratios of marcasite. But the feasibility of this calibration regime needs to be carefully evaluated. In this contribution, we investigated this topic by analyzing a natural marcasite (NJUMc-1) with a newly installed Cameca IMS 1300-HR^3. The sulfur isotopic composition of NJUMc-1 varies significantly (from ~−35‰ to ~−17‰). A total of 135 spots were applied on NJUMc-1 marcasite (4 outliers were rejected), and when the analyzing spot number reaches 70, the average $\delta^{34}S$ of marcasite becomes invariant, indicating that the number of grains we analyzed is large enough to represent the whole sample. The results of NJUMc-1 are calibrated using the pyrite standard UWPy-1. In this calibration regime, the average $\delta^{34}S$ value of NJUMc-1 is −25.21‰ ± 0.78‰ (2 SE), which agrees well with the result determined using gas source isotope ratio mass spectrometry (−25.63‰ ± 0.24‰, 2 SE, n = 2). This consistency indicates that it is feasible to calibrate the sulfur isotopic ratios of marcasite with a pyrite standard and a new marcasite standard is not a prerequisite for sulfur isotope determination of marcasite using SIMS. Besides, this study shows that instrumental mass fractionation (IMF) could be precisely determined for samples with obvious heterogeneity (*e.g.*, HTS4-3 and NJUMc-1), and by inference, the isotopic composition of unknowns could be precisely determined with an inferior "secondary" standard with obvious heterogeneity, as long as enough grains were analyzed.

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1. Introduction

Marcasite (FeS_2, orthorhombic) is a dimorph of pyrite (FeS_2, isometric) and generally forms at temperature < 160 °C.[1,2] It has been frequently reported in many kinds of hydrothermal ore deposits[3–7] and sporadically in sedimentary rocks.[8–10] It is a metastable phase relative to pyrite[11] and cannot be preserved when ambient temperatures exceed 160 °C for a long period (*e.g.*, >1 Myr).[1,11] The detailed formation process for marcasite remains a topic of ongoing investigation, but both experimental work[1] and *ab initio* calculations[12] suggest that it forms exclusively under acidic conditions (pH < 5.5), which potentially explains why marcasite is far less common than pyrite. Despite this, marcasite in sedimentary rocks has become the focus of some research because it is indicative of acidic conditions in deep time.[10,13,14]

Sulfur has four stable isotopes (^{32}S, ^{33}S, ^{34}S, and ^{36}S), which have natural abundances of approximately 95.04%, 0.75%, 4.20%, and 0.01%, respectively.[15] Since the difference in their atomic masses is relatively large, sulfur isotopes could be easily fractionated in geological processes. Sulfur isotopic composition is generally expressed as $\delta^{34}S$ ($\delta^{34}S = 1000 \times [(^{34}S/^{32}S_{sample})/(^{34}S/^{32}S_{standard}) - 1]$), and the reported $\delta^{34}S$ values are significantly variable (from −60 to over +140‰).[16–20] Because of the different sulfur isotopic compositions of different reservoirs,[18] the sulfur isotope system is frequently used as a key tracer in many geochemical processes.[18,21–26]

Recently, the sulfur isotopic composition of marcasite has been used to trace ore-forming fluid sources and ore-forming processes.[3,4] Besides, considering the unique acidic conditions needed for marcasite formation, researchers have used marcasite and its sulfur isotopic composition to track ocean acidification events in Earth's history.[10,13,14] In many cases, marcasite occurs as intergrowth with pyrite.[3,4] Since marcasite and pyrite have similar physical properties, it is hard to separate marcasite

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† Electronic supplementary information (ESI) available: Supplementary material 1. Original sulfur isotope ratios of HTS4-3, UWPy-1 and NJUMc-1. See DOI: https://doi.org/10.1039/d3ja00009e

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from the marcasite-pyrite intergrowth. Consequently, *in situ* analytical methods, notably secondary ion mass spectrometry (SIMS), are frequently used to determine the sulfur isotopic composition of marcasite. However, matrix-matched standards for marcasite are scarce, and in practice a pyrite standard is recently used to calibrate the sulfur isotopic composition of marcasite during SIMS analysis.[3] But the accuracy of this calibration regime has not been fully evaluated. In this contribution, we investigate this topic by analyzing a natural marcasite (NJUMc-1) using the Cameca IMS 1300-HR^3 at Nanjing University. The results show a small (0.42‰) deviation from the value calibrated using a pyrite standard and prove the reliability of this calibration regime for SIMS analysis. This study also shows how to determine the isotopic compositions of unknown samples with an inferior "secondary" standard that has obvious heterogeneity.

2. Sample description and analytical technique

2.1. Sample description and preparation

The marcasite sample (NJUMc-1), which is bought from the internet, was collected from the San Juan de Reyes mine in Guanajuato, Mexico. The sample is crushed to an ~80 mesh and handpicked under a binocular microscope. About 200 grains of NJUMc-1 marcasite were randomly selected and mounted in the middle of a mount S060 (Fig. 1). The epoxy mount was carefully polished several times with gradually finer diamond paste. The mount was washed in ethanol and de-ionised water, and subsequently placed in an oven and heated at 50 °C for 3 h. The mount was gold-coated (~30 nm thick) before SIMS analysis.

One pyrite sample (HTS4-3) is also analyzed for comparison. The HTS4-3 sample is collected from the Hongtoushan copper–zinc deposit, which is assigned to volcanogenic massive sulfide (VMS) deposits.[27,28] The host rocks were metamorphosed to upper amphibolite facies.[27,28] Sample HTS4-3 was collected from the alteration zone of the deposit. This sample is also crushed to an ~80 mesh and handpicked under a binocular microscope. About 150 randomly selected HTS4-3 pyrite grains were mounted in a mount LRC2201 (Fig. 1) and this mount is treated in a similar manner to that for S060.

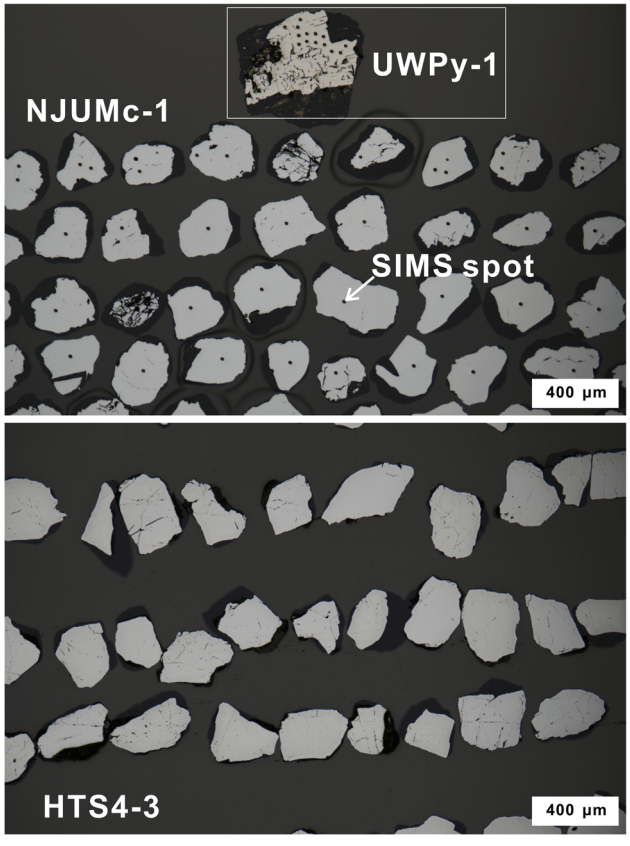

Fig. 1 Photomicrographs of the samples used in this study (UWPy-1, NJUMc-1 and HTS4-3). A total of two analytical sessions were applied on NJUMc-1, and the first session is failed, and only the result of the second session is used in this study. This explains why there are two analysis spots in some NJUMc-1 grains.

2.2. Laser Raman micro-spectrometry

All the marcasite grains in the mount S060 were first checked under a microscope (reflected light) since marcasite shows strong pleochroism (plane-polarized light) and anisotropy (crossed-polarized light). To further confirm that the analyzed grains are marcasite, we applied laser Raman micro-spectrometry analysis. One UWPy-1 grain in the mount S060 is also analyzed for comparison. An Ar^+ ion laser was operated at a 532 nm excitation wavelength with an exposure time of 30 s and a laser power of 10 mW in the interval between 250 and 500 cm^{-1}. A microscope was used to focus the excitation beam, whose spatial resolution was around ~2 μm.

2.3. SIMS analysis

The isotopic analysis was conducted using a newly installed Cameca IMS 1300-HR^3 instrument, hosted at the State Key Laboratory for Mineral Deposits Research, Nanjing University, China. The Cameca IMS 1300-HR^3 has a similar structure and ion path compared with the Cameca IMS 1280.[29] There are two main changes for the Cameca IMS 1300-HR^3: (1) the new radio frequency (RF) plasma oxygen source, which could potentially improve spatial resolution and reproducibility; (2) the 10^{12} Ω resister Faraday cup, which could potentially measure signals with a low counting rate. A primary $^{133}Cs^+$ ion beam (~2 nA current and 20 keV total impact energy) was focused on the sample surface. A 10 × 10 μm^2 raster was used in this study and a normal-incidence electron gun was used for charge compensation. An NMR field sensor was applied to stabilize the magnetic field. ^{32}S and ^{34}S were collected simultaneously using two Faraday cups at positions L′2 and H′2, respectively. The L′2 is configured with a 10^{10} Ω resistor circuit, and the H′2 with 10^{11} Ω. The mass resolving power (MRP, $M/\Delta M$), measured at 50% peak height, was set at ~2200 to minimize possible isobaric interference. The total analytical time was about 4.5 minutes per pit: 100 s pre-sputtering (to remove the Au coating); ~60 s automatic centering of the secondary ions in the field aperture; a total of 80 s integration of secondary ions (20 cycles × 4 s). The

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pyrite standard used in this study is UWPy-1.[30] The data reduction process is the same as that in reported literature.[31]

Detailed SIMS results could be found in the ESI 1.†

2.4. Gas source ratio mass spectrometry (GS-IRMS)

The sulfur isotopic compositions of HTS4-3 and NJUMc-1 were determined by GS-IRMS at the Institute of Geochemistry, Chinese Academy of Sciences. The grains were mixed with copper oxide and crushed to a 200 mesh. The sulfides were reacted with copper oxide at 980 °C under a vacuum pressure of 2×10^{-2} Pa, and the product SO_2 was measured with a MAT-251 mass spectrometer. The measurement precision, expressed as two standard deviation (2 SD), is better than ± 0.20‰.

3. Results and discussion

3.1. The feasibility of using a pyrite standard to calibrate marcasite during SIMS analysis

The main Raman shifts for the analyzed grain of NJUMc-1 on the mount S060 are at ~324 cm^{-1} and 386 cm^{-1} (Fig. 2), confirming the affinity of marcasite. For comparison, the Raman shifts for UWPy-1 pyrite are at 340 cm^{-1} and 376 cm^{-1} (Fig. 2).

Since no marcasite standard is available so far, a natural marcasite sample (NJUMc-1) with significant variation in its $\delta^{34}S$ values (Fig. 3 and 4) is used for this study. To determine whether marcasite could be calibrated using a pyrite standard, we need to determine whether marcasite and pyrite have the same IMF. If yes, the result of the marcasite calibrated using the pyrite standard during SIMS analysis should agree with its recommended value. This problem is easy to solve if we have a marcasite standard, but it may also be able to be solved with a natural sample with finite variation in its $\delta^{34}S$ values. The average $\delta^{34}S$ of a natural marcasite sample could be determined using GS-IRMS, and the problem left is to analyze enough grains that are representative of the whole sample during SIMS analysis. As for SIMS analysis, we suggest that when the average isotope ratio becomes invariant, the number of analyses is large enough to represent the whole sample. To test this hypothesis, we analyzed a natural pyrite (HTS4-3) sample first. The results

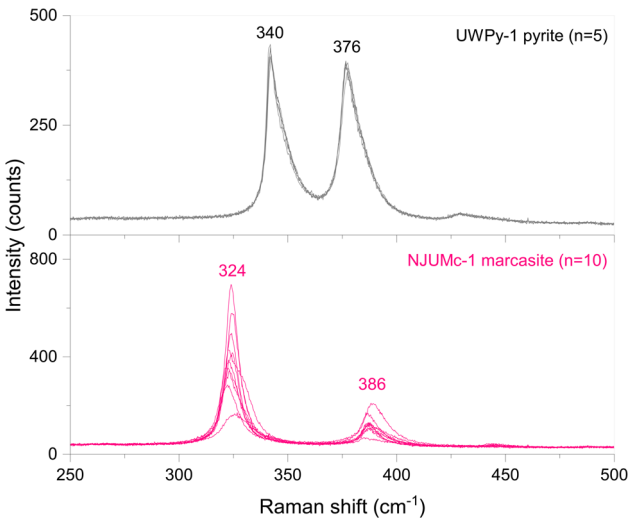

Fig. 2 Raman spectra for UWPy-1 pyrite and NJUMc-1 marcasite.

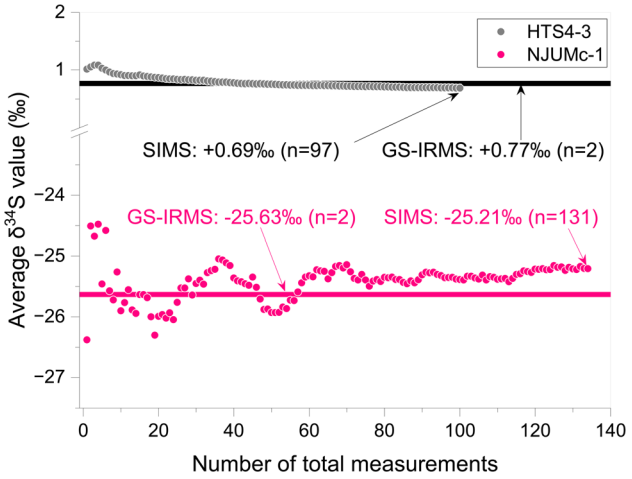

Fig. 3 Average $\delta^{34}S$ values of HTS4-3 pyrite and NJUMc-1 marcasite determined using SIMS. GS-IRMS results for both samples are also shown for comparison. The $\delta^{34}S$ value of NJUMc-1 calibrated using UWPy-1 is −25.21‰, which agrees well with the result determined using GS-IRMS (−25.63‰, $n = 2$), indicating that it is feasible to calibrate marcasite results using a pyrite standard during SIMS analysis.

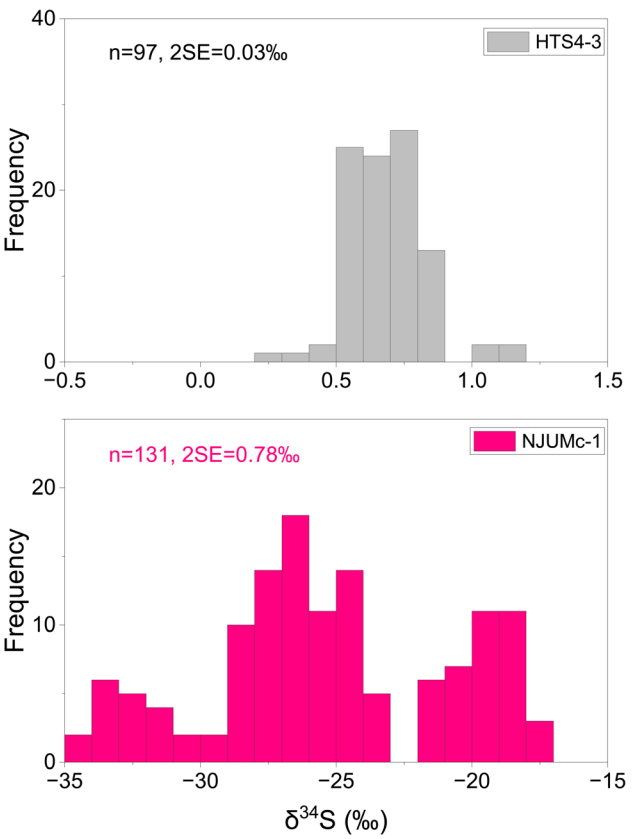

Fig. 4 Frequency histogram of the $\delta^{34}S$ values of HTS4-3 pyrite and NJUMc-1 marcasite. The 2 SE values (0.03‰ for HTS4-3 and 0.78‰ for NJUMc-1) are also shown.

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Table 1 GS-IRMS results for HTS4-3 pyrite and NJUMc-1 marcasite

Sample ID	δ^{34}S (‰)	2 SD (‰)
HTS4-3@1	+0.66	0.20
HTS4-3@2	+0.88	0.20
NJUMc-1@1	−25.51	0.20
NJUMc-1@2	−25.75	0.20

show that after the number of analyses reaches 10, the δ^{34}S of HTS4-3 gradually becomes invariant (Fig. 3), meaning that about 10 random grains of HTS4-3 may be able to represent the whole sample. Finally, a total of 100 grains of HTS4-3 were analyzed (3 spot analyses outside of the 2SD error range were rejected), and the corrected δ^{34}S value is +0.69‰ ± 0.03‰ (2 SE), which agrees well with the result determined using GS-IRMS (average at +0.77‰ ± 0.21‰, 2 SE, $n = 2$, Table 1). The results of HTS4-3 indicate that the approach mentioned above is feasible, which is then applied to the natural marcasite sample NJUMc-1. The results show that the average δ^{34}S of NJUMc-1 gradually becomes invariant when the number of analyses reaches ~70 (Fig. 3). Finally, a total of 135 grains were analyzed (4 spot analyses outside of the 2SD error range were rejected), and the average δ^{34}S calibrated using the pyrite standard UWPy-1 is −25.21‰ ± 0.78‰ (2 SE), which agrees well with the result determined using GS-IRMS (average at −25.63‰ ± 0.24‰, 2 SE, $n = 2$, Table 1). This means that the IMF for pyrite and marcasite during SIMS analysis is generally the same, and it is feasible to calibrate marcasite results using the pyrite standard. It is worth noting that the number of analyses to represent the whole sample for HTS4-3 ($n = 10$) and NJUMc-1 ($n = 70$) is significantly different, and this is mainly because they have different ranges in their δ^{34}S values (Fig. 4). We also did Yorkfit for the SIMS and GS-IRMS data (Fig. 5, ESI 1†), and the result shows that the regression line has a slope very close to 1 and an intercept very close to 0, which further indicates that the sulfur isotopic ratio

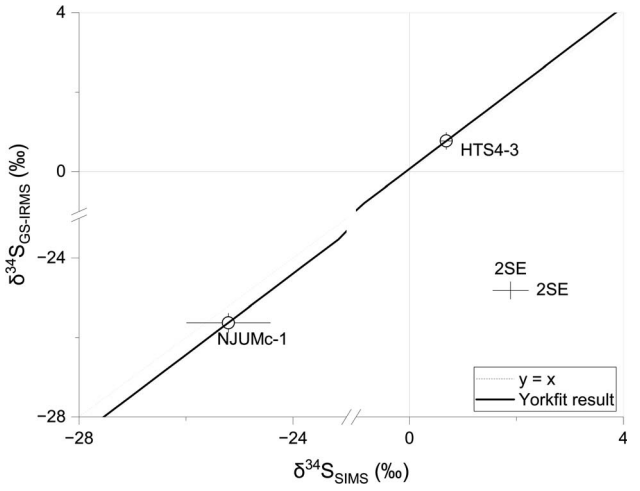

Fig. 5 Yorkfit result of SIMS and GS-IRMS data in this study. The slope and intercept were 1.01926 and 0.068118, and very close to 1 and 0, respectively. The standard errors for the slope and intercept were 0.0041 and 0.00291, respectively.

of marcasite can be calibrated with the pyrite standard during SIMS analysis.

3.2. Implications for isotope determination with a less homogeneous "standard" during SIMS analysis

The IMF during SIMS isotope ratio determination is matrix-dependent, which requires matrix-matched reference materials (RMs) to correct IMF.[32] But matrix-matched RMs are scarce, and researchers were frequently frustrated when a good idea was retarded by the absence of appropriate RMs. Then, a question arises spontaneously: would it be possible to precisely determine objective isotope ratios without a RM? Or more practically, how can researchers accurately determine objective isotope ratios using an inferior "standard" with obvious heterogeneity?

The essence of using a matrix-matched standard for data calibration is to constrain the IMF during SIMS analysis. The IMF, by definition, is the difference between the true value and the raw value given by the machine before IMF correction. The true value of the isotope ratio of a sample (RM or heterogeneous sample) could be determined using GS-IRMS. Then the only problem left is to get the average raw value of an isotope ratio that are representative of the sample (RM or heterogeneous sample). Theoretically, one can get an average value of any isotope ratio of any sample as long as enough analysis spots were applied. The only difference for a RM and heterogeneous sample is that only a few grains of the RM are representative of the whole RM, but to represent the heterogeneous sample many more grains of this sample should be analysed. In practice, one need not analyse all grains of a sample to constrain the IMF because natural samples—especially for moderately homogeneous standards—only exhibit finite variation. At this time, the question becomes how to judge whether the number of analysed grains is large enough to represent the whole sample. The results in this study offer a good criterion, *i.e.*, when the average isotopic ratios become invariant, the number of analysed grains is large enough to make them representative of the whole sample (Fig. 3). For HTS4-3 and NJUMc-1, the deviation between the results of SIMS and GS-IRMS is 0.08‰ and 0.42‰ (Fig. 3), respectively, which is comparable with or slightly larger than the uncertainty of GS-IRMS. This indicates that if we use HTS4-3 or NJUMc-1 as the "standard" to calibrate unknown samples, we can yield accurate results as long as enough grains are analysed (*e.g.*, $n > 10$ for HTS4-3 and $n > 70$ for NJUMc-1). It is obvious that more grains are needed to be analysed if the sample has large variation (Fig. 3 and 4). This approach is more time-consuming than the circumstance where a RM is available, but it is worth to do so if the isotopic composition of unknown samples could be precisely determined when no RM is available. The approach discussed here could be applied to other isotope systems and mineral phases.

4. Conclusions

Since marcasite standards are scarce, a pyrite standard is commonly used to calibrate the sulfur isotopic composition of

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marcasite during SIMS analysis. However, the reliability of this calibration regime has not been investigated. In this contribution, we investigate this problem by measuring a natural marcasite sample (NJUMc-1) using SIMS and calibrating its sulfur isotopic composition with a pyrite standard (UWPy-1). The calibrated average $\delta^{34}S$ value of NJUMc-1 ($-25.21‰ \pm 0.78‰$, 2 SE, $n = 131$) agrees well with the result determined using GS-IRMS ($-25.63‰ \pm 0.24‰$, 2 SE, $n = 2$). This study proves the reliability of calibrating the sulfur isotopes of marcasite using a pyrite standard during SIMS analysis. The results in this study indicate that the IMF of an inferior "secondary" standard could be precisely determined when enough grains are analyzed, *i.e.*, when average isotopic ratios become invariant.

Author contributions

Rucao Li conceived the presented idea. Xiao-Lei Wang supervised the project. Rucao Li took the lead in writing the manuscript. Rucao Li, Yue Guan and Lan-Lan Tian conducted the SIMS analysis, and Jing Gu conducted the GS-IRMS analysis. All authors reviewed and edited the paper.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 J. B. Murowchick and H. L. Barnes, *Geochim. Cosmochim. Acta*, 1986, **50**, 2615–2629.
2 M. A. A. Schoonen and H. L. Barnes, *Geochim. Cosmochim. Acta*, 1991, **55**, 1505–1514.
3 T. Nozaki, T. Nagase, T. Ushikubo, K. Shimizu, J.-i. Ishibashi and D/V Chikyu Expedition 909 Scientists, *Geology*, 2021, **49**, 222–227.
4 Y.-F. Wu, J.-W. Li, K. Evans, A. E. Koenig, Z.-K. Li, H. O'Brien, Y. Lahaye, K. Rempel, S.-Y. Hu, Z.-P. Zhang and J.-P. Yu, *Econ. Geol.*, 2018, **113**, 1093–1132.
5 J. A. Steadman and R. R. Large, *Econ. Geol.*, 2016, **111**, 1731–1752.
6 F. W. Beales, *Econ. Geol.*, 1975, **70**, 943–948.
7 R. L. Reynolds and M. B. Goldhaber, *Econ. Geol.*, 1983, **78**, 105–120.
8 J. Schieber, *Deep Sea Res., Part II*, 2007, **54**, 1312–1326.
9 J. Schieber, *J. Sediment. Res.*, 2011, **81**, 447–458.
10 R. N. Bryant, C. Jones, M. R. Raven, J. D. Owens and D. A. Fike, *Chem. Geol.*, 2020, **553**, 119808.
11 F. Gronvold and E. F. Westrum, *Inorg. Chem.*, 1962, **1**, 36–48.
12 D. A. Kitchaev and G. Ceder, *Nat. Commun.*, 2016, **7**, 13799.
13 R. N. Bryant, R. Ogliore, M. Gomes, J. D. Pasteris, D. A. Fike, *Sedimentary Marcasite: a Proxy for Ocean Acidification?*, December 01, 2020, **https://ui.adsabs.harvard.edu/abs/2020AGUFMPP021..02B/abstract**.
14 E. Lounejeva, J. A. Steadman, T. Rodemann, R. R. Large, L. Danyushevsky, D. Mantle, K. Grice and T. J. Algeo, in *Large Igneous Provinces*, ed. R. E. Ernst, A. J. Dickson and A. Bekker, 2020, pp. 377–399, DOI: **10.1002/9781119507444.ch16**.
15 T. B. Coplen, J. K. Böhlke, P. De Bievre, T. Ding, N. Holden, J. Hopple, H. Krouse, A. Lamberty, H. Peiser and K. Revesz, *Pure Appl. Chem.*, 2002, **74**, 1987–2017.
16 Z. Lin, X. Sun, J. Peckmann, Y. Lu, L. Xu, H. Strauss, H. Zhou, J. Gong, H. Lu and B. M. A. Teichert, *Chem. Geol.*, 2016, **440**, 26–41.
17 R. Li, H. Chen, R. R. Large, L. Zhao, Y. Liu, J. Jiao, X.-P. Xia and Q. Yang, *Chem. Geol.*, 2020, **552**, 119781.
18 R. R. Seal, *Sulfide Mineralogy and Geochemistry*, 2006, vol. 61, pp. 633–677.
19 H. Drake, N. M. W. Roberts, M. Reinhardt, M. Whitehouse, M. Ivarsson, A. Karlsson, E. Kooijman and M. Kielman-Schmitt, *Commun. Earth Environ.*, 2021, **2**, 102.
20 Y. Chen, Z. Xie, S. Dong, Q. Lei and J. Gao, *J. Anal. At. Spectrom.*, 2022, **37**, 2529–2536.
21 S. Aoyama, M. Nishizawa, K. Takai and Y. Ueno, *Earth Planet. Sci. Lett.*, 2014, **398**, 113–126.
22 M. Chen, I. H. Campbell, Y. Xue, W. Tian, T. R. Ireland, P. Holden, R. A. Cas, P. C. Hayman and R. Das, *Econ. Geol.*, 2015, **110**, 1411–1423.
23 J. Labidi, P. Cartigny, C. Hamelin, M. Moreira and L. Dosso, *Geochim. Cosmochim. Acta*, 2014, **133**, 47–67.
24 X. Lang, W. Tang, H. Ma and B. Shen, *Earth Planet. Sci. Lett.*, 2020, **533**, 116056.
25 R. Li, H. Chen, N. Wu, X. Wang and X. Xia, *Chem. Geol.*, 2021, **575**, 120230.
26 N. Wu, J. Farquhar and D. A. Fike, *Geochim. Cosmochim. Acta*, 2015, **164**, 352–364.
27 L. Gu, Y. Zheng, X. Tang, K. Zaw, F. Della-Pasque, C. Wu, Z. Tian, J. Lu, P. Ni, X. Li, F. Yang and X. Wang, *Ore Geol. Rev.*, 2007, **30**, 1–29.
28 Y. Zhang, F. Sun, B. Li, L. Huo and F. Ma, *Ore Geol. Rev.*, 2014, **57**, 78–86.
29 N. T. Kita, T. Ushikubo, B. Fu and J. W. Valley, *Chem. Geol.*, 2009, **264**, 43–57.
30 T. Ushikubo, K. H. Williford, J. Farquhar, D. T. Johnston, M. J. Van Kranendonk and J. W. Valley, *Chem. Geol.*, 2014, **383**, 86–99.
31 R. Li, X.-P. Xia, H. Chen, N. Wu, T. Zhao, C. Lai, Q. Yang and Y. Zhang, *Geostand. Geoanal. Res.*, 2020, **44**, 485–500.
32 J. M. Eiler, C. Graham and J. W. Valley, *Chem. Geol.*, 1997, **138**, 221–244.

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