NJUCal-1: A New Calcite Oxygen Isotope Reference Material for Microbeam Analysis

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Calcite is a common mineral in various types of rocks and mineral deposits, and its oxygen isotopic compositions are widely used to reconstruct palaeotemperature and to trace rock genesis and ore-forming processes. However, the availability of high-quality matrix-matched calcite reference materials for oxygen isotope microanalysis is limited. A new natural calcite specimen (NJUCal-1) was analysed in this study to investigate its potential as a reference material for microbeam oxygen isotope measurement. Detailed textural and major elemental examinations reveal no internal zoning of ground grains. During six measurement sessions, a total of 463 spot analyses of oxygen isotope ratios were applied on ~ 200 randomly selected grains using secondary ion mass spectrometry, Nanjing. Taking all six sessions together, the spot-to-spot repeatability is 0.28‰ (2s), and the repeatability is better than 0.31‰ (2s) for individual sessions, indicating that the NJUCal-1 calcite is quite homogeneous in its oxygen isotopic compositions and can be used as a new reference material for microbeam oxygen isotope measurement. The mean $\delta^{18}O_{VPDB}$ value determined by gas source isotope ratio mass spectrometry is -22.58 ± 0.16‰ (2s, n = 22), which is proposed as the recommended value for this potential reference material.

Keywords: calcite, reference material, NJUCal-1, oxygen isotope, secondary ion mass spectrometry, SIMS.

The oxygen isotopic compositions of calcite have been frequently used to determine palaeotemperatures, to constrain thermal histories during metamorphism and to trace ore-forming processes (Wenzel *et al.* 2000, Schwinn *et al.* 2006, Ferry *et al.* 2010). Previous studies have revealed that complex zoning is common in calcite (Lee *et al.* 2008, Branson *et al.* 2015, Casella *et al.* 2018) and that different zonations could have distinct oxygen isotopic compositions ($\delta^{18}O$). High spatial resolution secondary ion mass spectrometry (SIMS) can produce an analysis crater of approximate 10 μm for routine analysis and has been widely used to investigate intra-grain isotope variations (Crowe *et al.* 2001, Ferry *et al.* 2014, Li *et al.* 2018, Giuliani *et al.* 2019). SIMS analysis requires matrix-matched reference materials to correct instrument mass fractionation (IMF; Eiler *et al.* 1997). In this contribution, we characterised a calcite sample

(NJUCal-1), which revealed an uncertainty $\delta^{18}O$ value is 0.28‰ (2s) determined by SIMS. Our results show that the NJUCal-1 is sufficiently chemically homogenous to be used as a reference material for microbeam oxygen isotope analysis. A total of 30 g (in batches of about 5–10 mg) of 0.1–1 mm-sized calcite grains are available upon request to the corresponding authors to LA-MC-ICP-MS or SIMS laboratories worldwide.

Sample description and preparation

The samples used in this study were collected from the supergiant Huayangchuan carbonatite-hosted uranium-polymetallic deposit in the Qinling Orogen, Central China (Zheng *et al.* 2020b). Multiple stages of mineralisation have been observed in the Huayangchuan deposit, and

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NJUCal-1 (originally named ZK8401-10) was collected from the main mineralisation stage in which calcite is most abundant. The age of the carbonatite at Huayangchuan, constrained by LA-ICP-MS titanite U-Pb dating, is 209 ± 2.9 Ma (Zheng *et al.* 2020a). The collected sample consists mostly of calcite with only minor barite (Figure 1). The ca. 110 g rock specimen was crushed and sieved, after which the calcite grains were handpicked under a binocular microscope. The process, combined with backscattered electron imaging (BSE; Figure S1), confined the purity of the handpicked calcite grains better than 98%. The total mass of the handpicked pure calcite grains is around 45 g. For this work, about 200 calcite grains each about 0.5 mm in diameter were randomly selected and cast into an epoxy mount (G986). The grains were mounted at the centre part (15 mm in diameter) of the mount. A few large NJUCal-1 grains (~ 1 mm) and grains of another sample (ZK4804-198) from the same deposit were also mounted at the centre of the same epoxy mount (Figure 2a). In session 6, a large grain of the recently characterised calcite RM (Oka calcite) for oxygen isotope measurement (Tang *et al.* 2020) was also mounted at the centre of mount G986. Repeated SIMS oxygen isotope measurements were undertaken on the large grains in each session to monitor the instrument stability. The mount was platinum-coated (~ 30 nm thick) before SIMS analysis.

Analytical techniques

SIMS

The analysis was conducted using a CAMECA IMS 1300-HR[3] instrument that was recently installed at the State Key Laboratory for Mineral Deposits Research, Nanjing University, China. A primary $^{133}Cs^+$ ion beam (1.8–3.4 nA current and 20 keV total impact energy) was

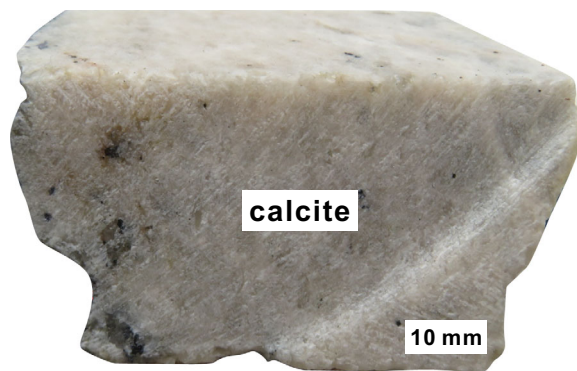**Figure 1. Photograph of NJUCal-1 calcite hand specimen. The total mass of this sample is around 110 g.**

focused on the sample surface. A 10 μm × 10 μm raster was used in this study, and a normal-incidence electron gun was used for charge compensation. An NMR field sensor was applied to stabilise the magnetic field. The signals of ^{16}O and ^{18}O were collected simultaneously using two Faraday cups at positions L'2 and H'2, respectively. The L'2 and H'2 positions were configured with a resistor circuit of 10^{10} Ω and 10^{11} Ω, respectively. The mass resolving power (MRP, $M/\Delta M$), measured at 50% peak height, was set at ~ 2500 to minimise isobaric interferences. The total analytical time was about 4.5 min per pit: 100 s pre-sputtering (to remove the Pt coating); ~ 60 s automatic centring of the secondary ions in the field aperture, and a total of 80 s integration of secondary ions (twenty cycles × 4 s). The counting rate of ^{16}O was approximately 2.2×10^9–3.2×10^9 cps. To evaluate the reliability of the analytical protocols in this study, well-characterised zircon reference materials (91500, Penglai and Qinghu) were also analysed. The data reduction processes are as follows.

Instrumental bias correction factors for $\delta^{18}O$ were determined by $\delta^{18}O_{raw}$ measurements of the RM as follows:

$$\alpha_{(SIMS)} = \left(^{18}O/^{16}O\right)_{standard\ raw} \Big/ \left(^{18}O/^{16}O\right)_{standard\ recommended} \quad (1)$$

$$\left(^{18}O/^{16}O\right)_{sample} = \left(^{18}O/^{16}O\right)_{measured} \Big/ \alpha_{(SIMS)} \quad (2)$$

Corrected $^{18}O/^{16}O$ ratios were normalised to the Vienna Peedee belemnite (VPDB) or the Vienna standard mean ocean water (VSMOW) according to Equation (3) and taken as true δ-value ($\delta^{18}O$).

$$\delta^{18}O_{sample} = \left[\left(^{18}O/^{16}O\right)_{sample} \Big/ \left(^{18}O/^{16}O\right)_{VPDB/SMOW} - 1 \right]$$
$$(3)$$

The analysis of this study was conducted in six sessions. The influence of *X-Y* effect on oxygen isotopes was also investigated (Figure 2).

Gas source isotope ratio mass spectrometry (GS-IRMS)

GS-IRMS was conducted at the Beijing Research Institute of Uranium Geology and the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The NJUCal-1 calcite was handpicked under a binocular microscope to ensure high purity (> 98%) and then baked at a temperature of 105 °C
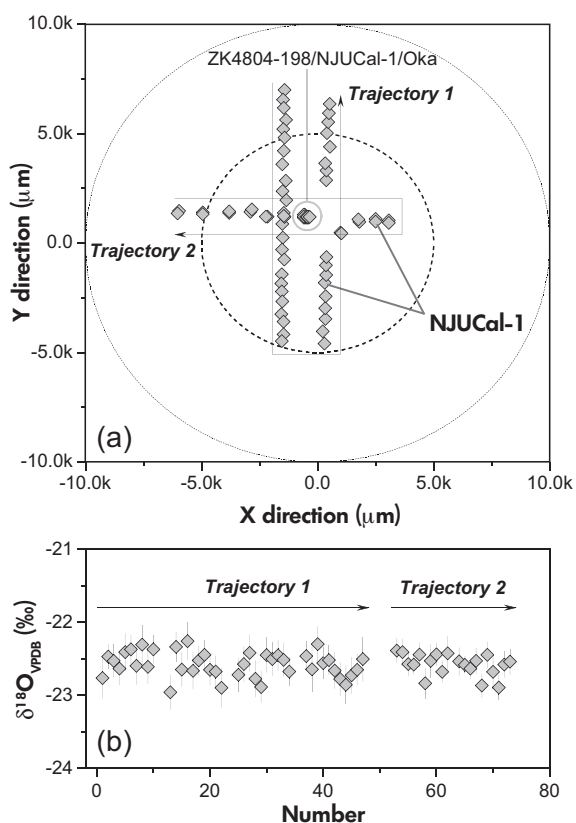
Figure 2. Designed analytical trajectories to investigate potential influence of (a) the *X-Y* effect and (b) observed $\delta^{18}O_{VPDB}$ values.

before analysis. NJUCal-1 powder was collected on a weighing paper and transferred to a standard 12 ml headspace sample vial. After this, the samples were flushed with helium flow for 8 min using a Gasbench II device (Thermo Fisher Scientific, Bremen, Germany). Phosphoric acid was manually dosed to the flushed samples to generate CO_2. The samples were reacted with acid at 72 °C for more than 4 h. The resulting CO_2 was measured for oxygen isotopic composition using a Gasbench II device attached to a MAT 253 gas source isotope ratio mass spectrometer (Thermo Fisher Scientific). The instrumental drift and mass bias were corrected using calibrator-sample bracketing technique, with repeated measurements of reference materials (i.e., IAEA-603, CO-18, LSVEC, NBS-18, GBW04405 and GBW04416) before and after every five NJUCal-1 analyses. Analytical uncertainties for individual analysis were better than 0.2‰ (2*s*).

The oxygen isotopic ratios of the reference materials given by the instrument were normalised to the VPDB according to Equation (3), and taken as raw δ-value ($\delta^{18}O_{raw}$). The raw and true $\delta^{18}O$ values of all the RMs in a

given session were taken together to generate a linear correlation (Table S3), which was then applied to NJUCal-1 to calibrate its $\delta^{18}O$ values.

Electron probe microanalysis (EPMA)

The major element compositions of NJUCal-1 were determined using a JEOL JXA-8530F Plus EPMA at the CAS Key Laboratory of Crust-Mantle Materials and Environments, University of Science and Technology of China (USTC), China. Analytical conditions for the analysis were set at a 15 kV accelerating voltage, a 5 nA beam current and a 20 μm beam size. The reference materials used for data correction were calcite for CaO, bustamite for MnO, celestite for SrO, haematite for FeO, dolomite for MgO, albite for Na_2O and apatite for P_2O_5. The detection limit for all elements is approximately 0.02–0.04 g/100 g. Analytical settings for elemental mapping are a 15 kV accelerating voltage, 50 nA beam current, 2 μm step size and a 30 ms dwell time for each point. An accelerating voltage of 15 kV was adopted for BSE imaging.

Results

EPMA

EPMA data are summarised in Table S1, and the results show that NJUCal-1 is composed of 51.38 ± 0.71 g/100 g CaO, 1.49 ± 0.0.22 g/100 g MnO, 0.74 ± 0.22 g/100 g SrO, 0.62 ± 0.12 g/100 g FeO, 0.43 ± 0.10 g/100 g MgO and possibly traces of Na_2O and P_2O_5. Major elemental mapping shows no internal zoning (Figure 3), indicating that NJUCal-1 is homogeneous at micrometre-scale for its major element concentrations.

SIMS

The oxygen isotope results for the zircon reference materials are present in Figure 4. Detailed results can be found in Table S2. The corrected $\delta^{18}O_{VSMOW}$ value for Qinghu (+5.33 ± 0.34‰, *n* = 35, 2*s*) is consistent with its recommended value (+5.39 ± 0.22‰, 2*s*, Li *et al.* 2013), indicating that the analytical protocol in this study is reliable. The SIMS results for NJUCal-1 calcite from all six sessions are presented in Figure 5. Two standard deviations for individual sessions range from 0.23 to 0.31‰ (Figure 5a), and analytical uncertainty, assessed by repeated analysis of single grain, ranged from 0.13 to 0.35‰ (Figure 6). No significant *X-Y* effect (Kita *et al.* 2009) was identified within 7.5 mm from the centre of the mount since no systematic change in $\delta^{18}O_{VPDB}$ was observed (Figure 2b).
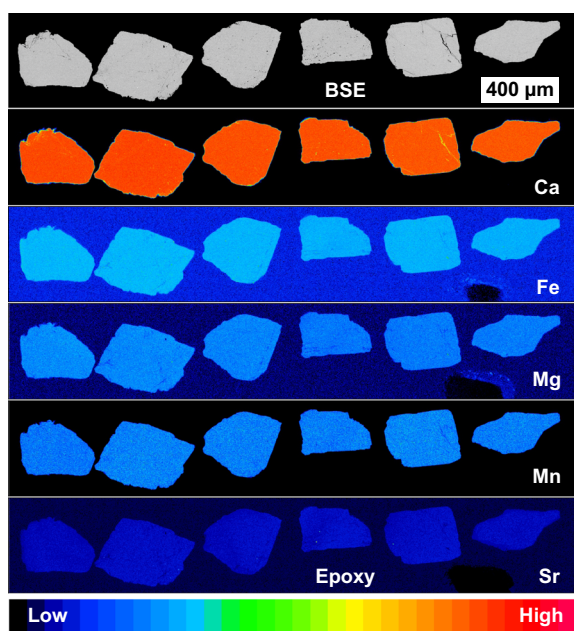
Figure 3. BSE imaging and major elemental mapping of NJUCal-1 calcite.

GS-IRMS

Randomly selected fragments of the NJUCal-1 calcite were analysed twenty-two times by GS-IRMS, yielding a mean $\delta^{18}O_{VPDB}$ = -22.58 ± 0.16‰ (2s, n = 22). Detailed measurement results are given in Table 1 and Figure 7. Original results are given in Table S3.

Discussion

The homogeneity index (H) is used to assess the homogeneity of the oxygen isotopic composition of

NJUCal-1 calcite. The H-index denotes the ratio of measurement precision to the expected total combined uncertainty, which includes both instrumental uncertainty and sample heterogeneity (Batanova et al. 2019). An H-index of 1 implies that the sample is homogeneous within the measurement uncertainty of individual measurement, whereas an H-index > 3 indicates significant isotopic heterogeneity. Repeated analysis on one calcite grain (NJUCal-1, ZK4804-198 or Oka) was used to constrain 'measurement uncertainty'. For NJUCal-1, the obtained H-index mostly cluster around 1 (Figure 6), indicating good isotopic homogeneity. This is supported by the normal distribution of the corrected $\delta^{18}O$ values (Figure 5b). There is one session that plots near the y = 3x line. In this session, only three spots on one calcite grain were analysed, which may be too few to assess analytical uncertainty of this session.

Except for the H-index, the mean square weighted deviation (MSWD) of the repeated measurement results was also applied to estimate sample homogeneity, where a MSWD close to 1 indicates that the variance of repeat measurements can be explained by within-spot uncertainty, which suggests homogeneity of a given sample within analytical uncertainty. All the data of this study were processed using the Isoplot software (version 4.15; Ludwig 2003), and the results are presented in Table 2. The calculated MSWD values of NJUCal-1 in all sessions have a small variation and typically range from 1.4 to 3.0. Because most of the sessions have an H-index around 1 (except for the session with H-index around 3), instrument performance could not have added significant additional uncertainties, which implies that there is genuine heterogeneity in the $\delta^{18}O$ values of NJUCal-1. This is supported by the fact that some spots in Figure 5 can be resolved from majority of the data even when measurement repeatability precision (2SE) is considered. In spite of this, the oxygen isotopic
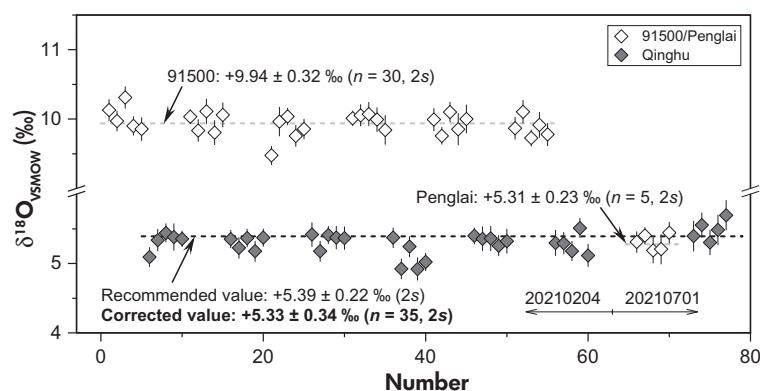

Figure 4. Corrected oxygen isotope results for zircon reference materials.
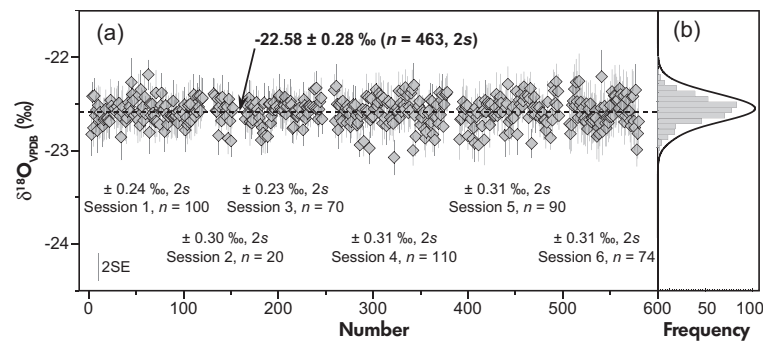
Figure 5. Corrected $\delta^{18}O_{VPDB}$ value (a) and distribution pattern (b) of NJUCal-1 calcite.
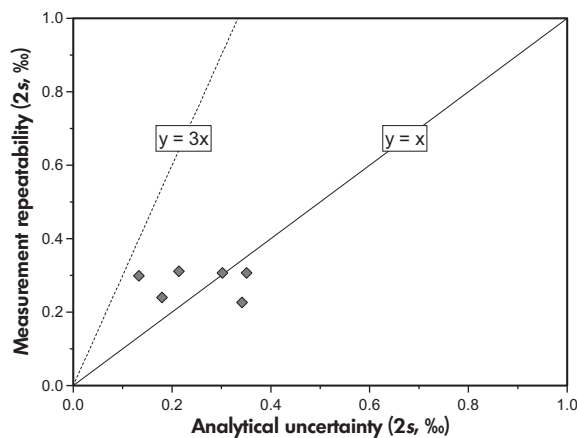

Figure 6. Assessment of homogeneity of sample NJUCal-1 calcite. Values of homogeneity index of 1 (solid line) and 3 (dashed line) are shown.

inhomogeneity of NJUCal-1 (0.28‰, 2s) is equal to (0.31‰, 2s; Kita *et al.* 2009) or better than previous reported calcite RMs (0.44 to 0.76‰, 2s; Kozdon *et al.* 2009, 0.54‰, 2s; Tang *et al.* 2020). In light of this, we conclude that NJUCal-1 is sufficiently homogeneous enough to serve as a potential reference material for microbeam oxygen isotope analysis.

In session 6, the oxygen isotopic composition of NJUCal-1 was corrected by routinely analysed Oka calcite, and the results average at -21.66 ± 0.31‰ (2s, n = 74). This result is about 1‰ higher than that determined using GS-IRMS (Figure 7). This inconsistency could not have resulted from poor instrumental performance because the results for the zircon reference materials analysed in this session are consistent with their recommended values (Table S2). The 2s value for NJUCal-1 is better than 0.31‰ for an individual session and could not fully account for the observed inconsistency either. Additional uncertainty must have resulted from the heterogeneity of the oxygen isotopic

Table 1.
GS-IRMS oxygen isotope results for NJUCal-1 calcite

Lab	Session	$\delta^{18}O_{VPDB}$ (‰)	$\delta^{18}O_{VSMOW}$ (‰)	2s (‰)
Beijing	1	-22.61	7.55	0.20
Beijing	1	-22.60	7.56	0.20
Beijing	1	-22.49	7.68	0.20
Beijing	1	-22.51	7.66	0.20
Beijing	1	-22.50	7.66	0.20
Beijing	2	-22.56	7.60	0.20
Beijing	2	-22.61	7.55	0.20
Beijing	2	-22.50	7.67	0.20
Beijing	2	-22.62	7.54	0.20
Beijing	2	-22.61	7.55	0.20
Guiyang	2	-22.56	7.60	0.09
Guiyang	2	-22.44	7.73	0.11
Guiyang	2	-22.54	7.63	0.15
Guiyang	2	-22.49	7.67	0.11
Guiyang	2	-22.49	7.67	0.11
Guiyang	2	-22.57	7.60	0.12
Guiyang	2	-22.58	7.58	0.11
Guiyang	2	-22.74	7.42	0.05
Guiyang	2	-22.70	7.46	0.11
Guiyang	2	-22.59	7.57	0.10
Guiyang	2	-22.65	7.51	0.14
Guiyang	2	-22.73	7.43	0.12

See Figure 7 for plot.

composition of Oka calcite, which is supported by its relatively large 2s value (2s = 0.54‰). Hence, it is very likely that we have measured a piece of Oka calcite whose oxygen isotopic composition deviates significantly from its recommended value.

Ramsey and Wiedenbeck (2018) calculated a theoretical prediction on the required number of measurements to achieve a target uncertainty. Here, we present a simple empirical approach to estimate the number for a specific RM to achieve a target accuracy. The approach presented here

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Table 2.
Summary table with the key data from all measurement sessions in this study

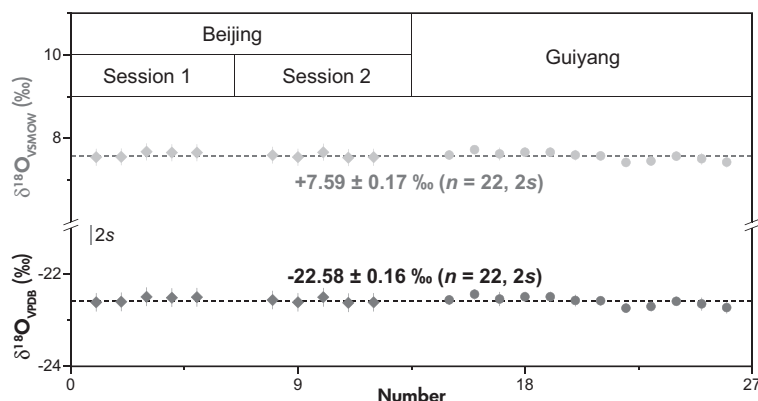| Session	2s ‰	Median spot 2SE ‰	MSWD	Excess error (2s) ‰	Number of spots	Number of rejected spots
1	0.24	0.22	1.4	0.14	99	0
2	0.30	0.17	2.9	0.23	20	0
3	0.23	0.19	1.5	0.14	70	0
4	0.31	0.19	3.0	0.25	110	0
5	0.31	0.20	2.8	0.24	90	0
6	0.31	0.25	1.6	0.19	74	0
All	0.28	0.20	2.1	0.21	463	0

Excess error was calculated using Isoplot.

Figure 7. The $\delta^{18}O_{VPDB}$ and $\delta^{18}O_{VSMOW}$ values of NJUCal-1 calcite determined by GS-IRMS.

acknowledges that there is ubiquitous heterogeneity in any proposed RM, which is true in nearly all cases, and it assumes that the IMF could be precisely determined when enough measurements are made on the RM (Ramsey and Wiedenbeck 2018). Under this assumption, the number of required spot measurements is inversely correlated with the uncertainty of IMF. Consequently, in a binary plot of 'number of total measurements' and 'mean $\delta^{18}O_{VPDB}$', the latter should become gradually invariable when more measurements are obtained (Figure 8). For NJUCal-1, the required numbers of measurements to achieve a deviation of 'observed $\delta^{18}O_{VPDB}$' from the 'true $\delta^{18}O_{VPDB}$' lower than 0.1 and 0.05‰ are 5 and 40, respectively, and the corresponding numbers of grains are 2.5–5 and 20–40 since one or two spots were made on one grain. The observation in this study indicates that a minimum of about five grains is needed to be analysed to achieve a deviation of 'observed $\delta^{18}O_{VPDB}$' from the 'true $\delta^{18}O_{VPDB}$' lower than 0.1‰, generally consistent with the theoretical prediction made in Ramsey and Wiedenbeck (2018). Note that the required number of grains to achieve a target uncertainty

varies along with the homogeneity of selected RM and analytical protocol, which should be estimated with respect to a specific RM and measurement session. We also note that when the number of total measurements reaches 75, the mean $\delta^{18}O_{VPDB}$ of NJUCal-1 does not change much even when more measurements are made. This means that the number of grains we used for homogeneity test (i.e., 200), which is much larger than 75, is large enough to make the selected grains representative of the whole sample. Future characterisation of reference materials and quality control of SIMS/LA-MC-ICP-MS data could benefit from the discussion above.

Conclusions

The measurement reproducibility of NJUCal-1 by CAMECA IMS 1300-HR[3] is better than 0.31‰ ($^{18}O/^{16}O$, 2s). This, together with H-index and MSWD results, indicates comparable homogeneity to the well-characterised calcite materials UWC-1 and UWC-3. The observed $\delta^{18}O$ variability in NJUCal-1 is less than 0.28‰ (2s) at the scale of
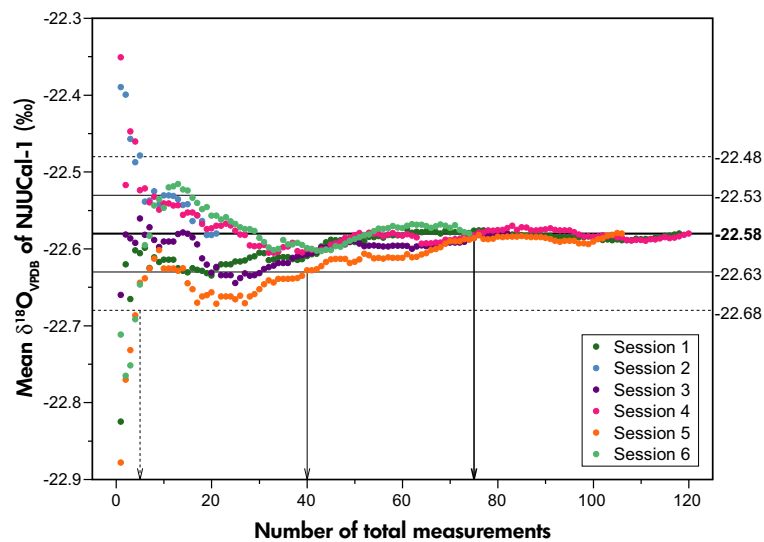
Figure 8. Variation trend of mean $\delta^{18}O_{VPDB}$ with the number of total measurements. The mean $\delta^{18}O_{VPDB}$ is increasingly stable with increasing number of total measurements, and it can be regarded as invariable after the number of total measurements reaches 75.

the whole sample, and thus, it can serve as a potential reference material for microbeam measurement of oxygen isotopes. We propose a recommended $\delta^{18}O_{VPDB}$ value (determined by GS-IRMS) of -22.58 ± 0.16‰ (2s, $n = 22$) for the NJUCal-1 calcite.

Acknowledgements

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability statement

The data that supports the findings of this study are available in the supplementary material of this article.

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Supporting information

The following supporting information may be found in the online version of this article:

Figure S1. Backscattered electron-imaging result for NJUCal-1 calcite.

Table S1. EPMA measurement results for major elements (g/100 g) in NJUCal-1 calcite.

Table S2. Original $^{18}O/^{16}O$ ratios of NJUCal-1 calcite and zircon reference materials (91500, Penglai and Qinghu).

Table S3. Original $^{18}O/^{16}O$ ratios of calcite reference materials for GS-IRMS analysis.

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