



**CANADIAN
CENTRE *for*
ISOTOPIC
MICROANALYSIS**

CCIM-SIMS

MICROBEAM REFERENCE MATERIAL CHEMISTRY: ARAGONITE S0436, DATA RELEASE 06-2024

CCIM RESEARCH REPORT 24-02

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SAMPLE INFORMATION

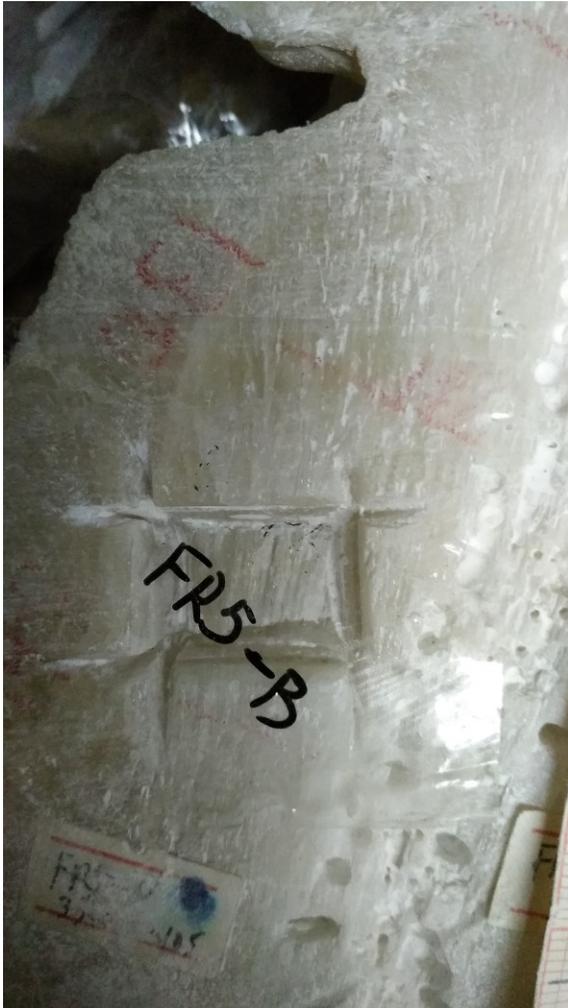
Date of validity	2024-06-12
CCIM root sample number	S0436
CCIM sub-sample number(s)	
Alias (CCIM or external) sample names	
Isotope systems calibrated with this RM*	18O-16O, 13C-12C
Trace elements calibrated with this RM*	
Material type	mineral
Mineral name	aragonite
Other material type	
Material composition (basic)	CaCO ₃
Material original growth context if known	mono-mineral occurrence
Originating rock type	speleothem, stalagmite
Co-occurring minerals (if relevant as RM)	
Co-occurring CCIM RM sample numbers	
Colour	grey, white
Translucence	clear, cloudy
Source of material	T.-Y. Li, Southwest University, China
Originating geographic location	Furong Cave, Chongqing, China
Originating geological information	speleothems within Cambrian limestone and dolomite (Li et al., 2011)
Form of material in use as RM	many individual sub-samples/pieces, < 1mm
Form of material in reserve	<input checked="" type="checkbox"/> sub-samples, mm to cm size <input checked="" type="checkbox"/> original bulk/rock sample
Sub-sample available to qualified researchers	case-by-case basis

*see section "Reference Values Summary" for current numbers.

ADDITIONAL SAMPLING INFORMATION

The RM is a 1.2 g saw-cut piece excised from stalagmite FR5 (Li et al. (2011), Li et al. (2021)) measuring 17 x 13 x 8 mm, from the 410–420 mm (~30 ka BP) horizon (Li et al., 2021). Figure 1 (Li, pers. comm, 2017) shows the cut-out location as ‘FR5-B’.

Figure 1: Photo of portion of stalagmite showing location of sub-sample FR5-B. Total image width 45 mm.



PLAIN LIGHT IMAGES

MACRO-SAMPLE

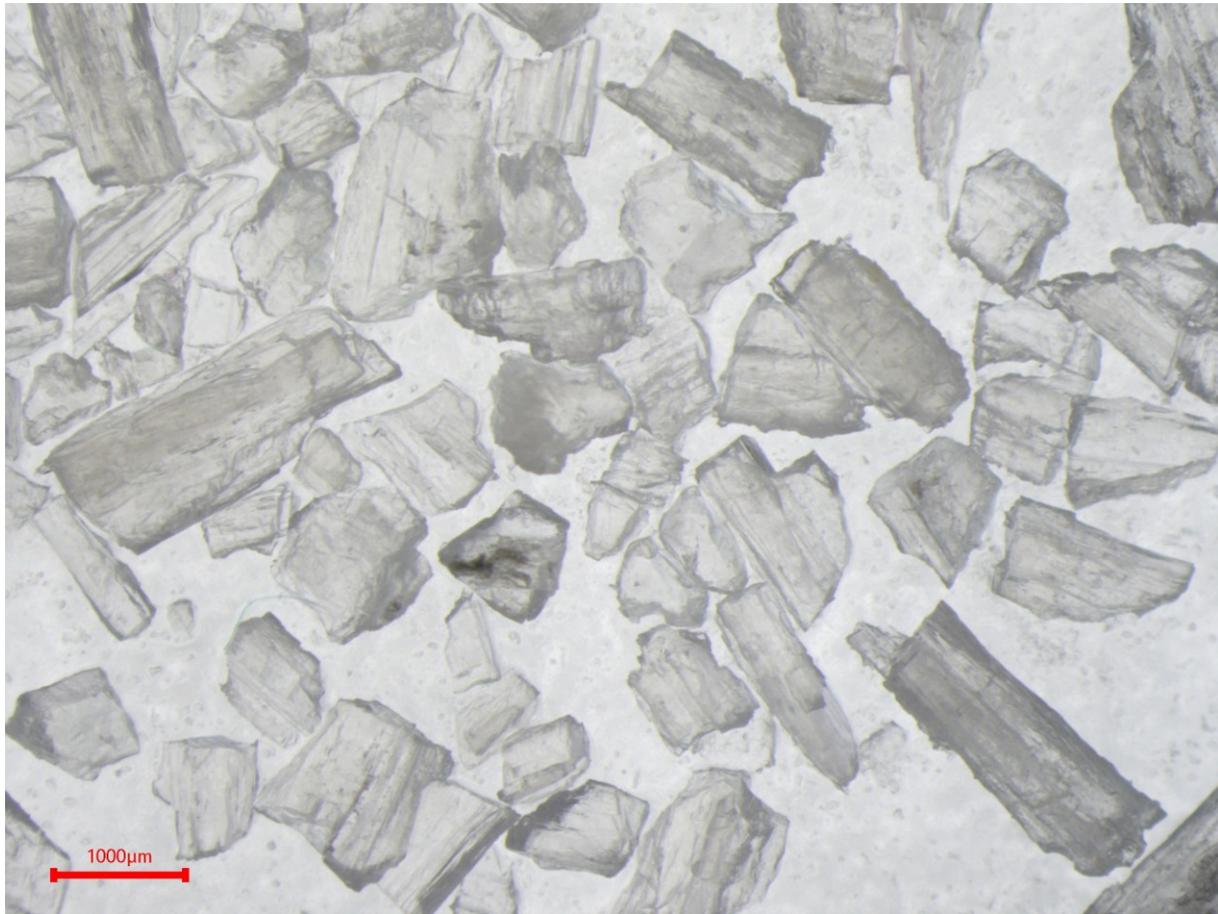
The sample comprises coarse crystals of aragonite appearing as prismatic and acicular crystals perpendicular to the stalagmite growth layering. As documented elsewhere Li et al. (2011), FR5 shows minor calcite infiltration and no transformation of aragonite to calcite.

Figure 2: Incident light image of whole sample S0436 before fragmentation.



STEREO-MICROSCOPE

Figure 3: Fragmented sample of S0436 in a form suited to SIMS analysis, transmitted light.



SCANNING ELECTRON MICROSCOPY

BACKSCATTERED ELECTRONS (BSE)

Figure 4: BSE image of the whole sample S0436 prior to fragmentation in epoxy mount M0286, exposing one face that was ground and polished. Dark areas are voids filled with epoxy. The rare bright streaks are imaging (charging) artifacts due to cracks.



The following sequence of four overlapping BSE images span a central section of S0436 from top to bottom in M0286. Numbers show locations of SIMS spot analyses for oxygen isotopes within session IP17054B. There are subtle, patchy variations in backscattered electron response. The spot numbers circled are analysis locations with small positive SIMS $\delta^{18}\text{O}$ anomalies (see SIMS section).

Figure 5: BSE image 1 of 4 from O-isotope transect of S0436.

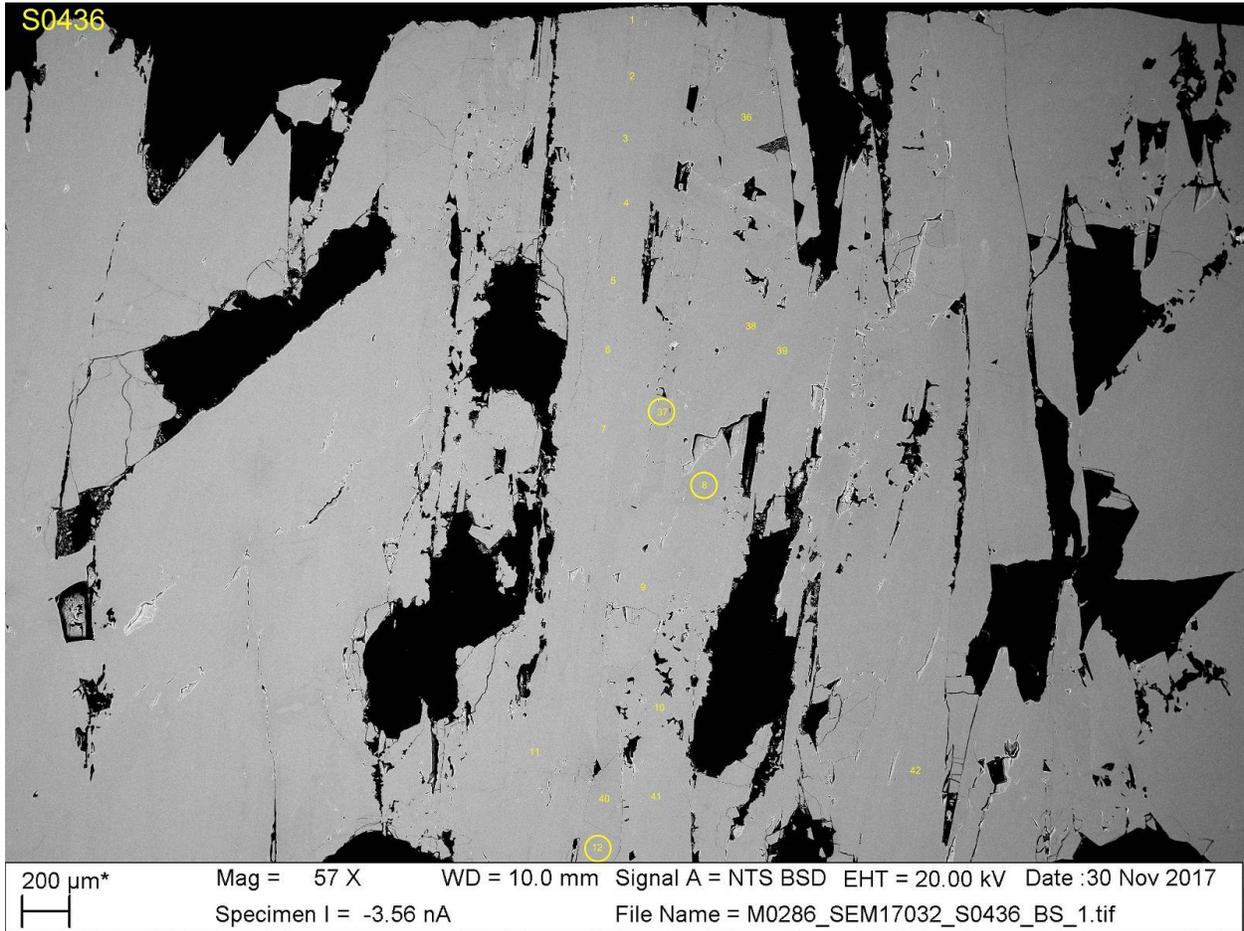


Figure 6: BSE image 2 of 4 from O-isotope transect of S0436.

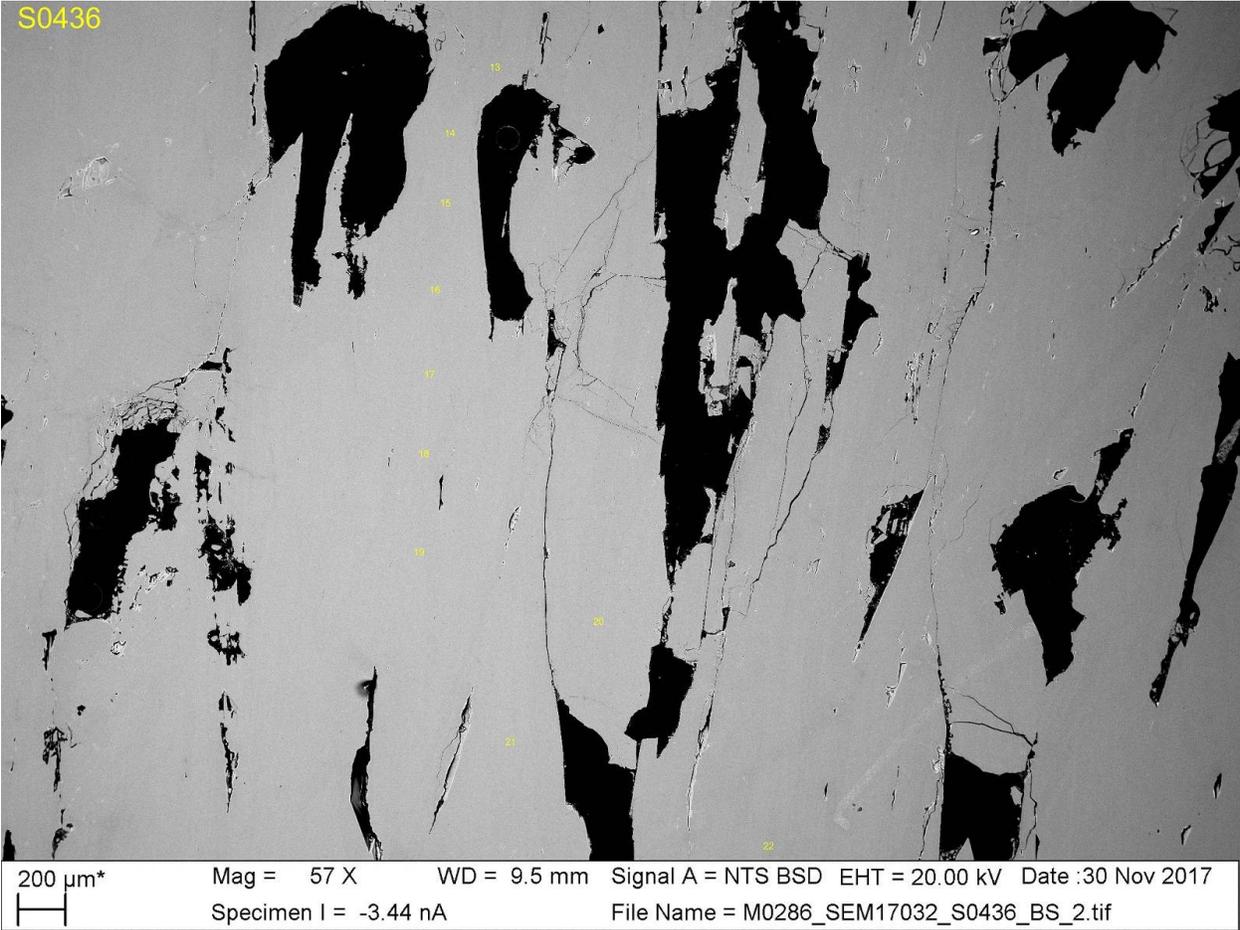


Figure 7: BSE image 3 of 4 from O-isotope transect of S0436.

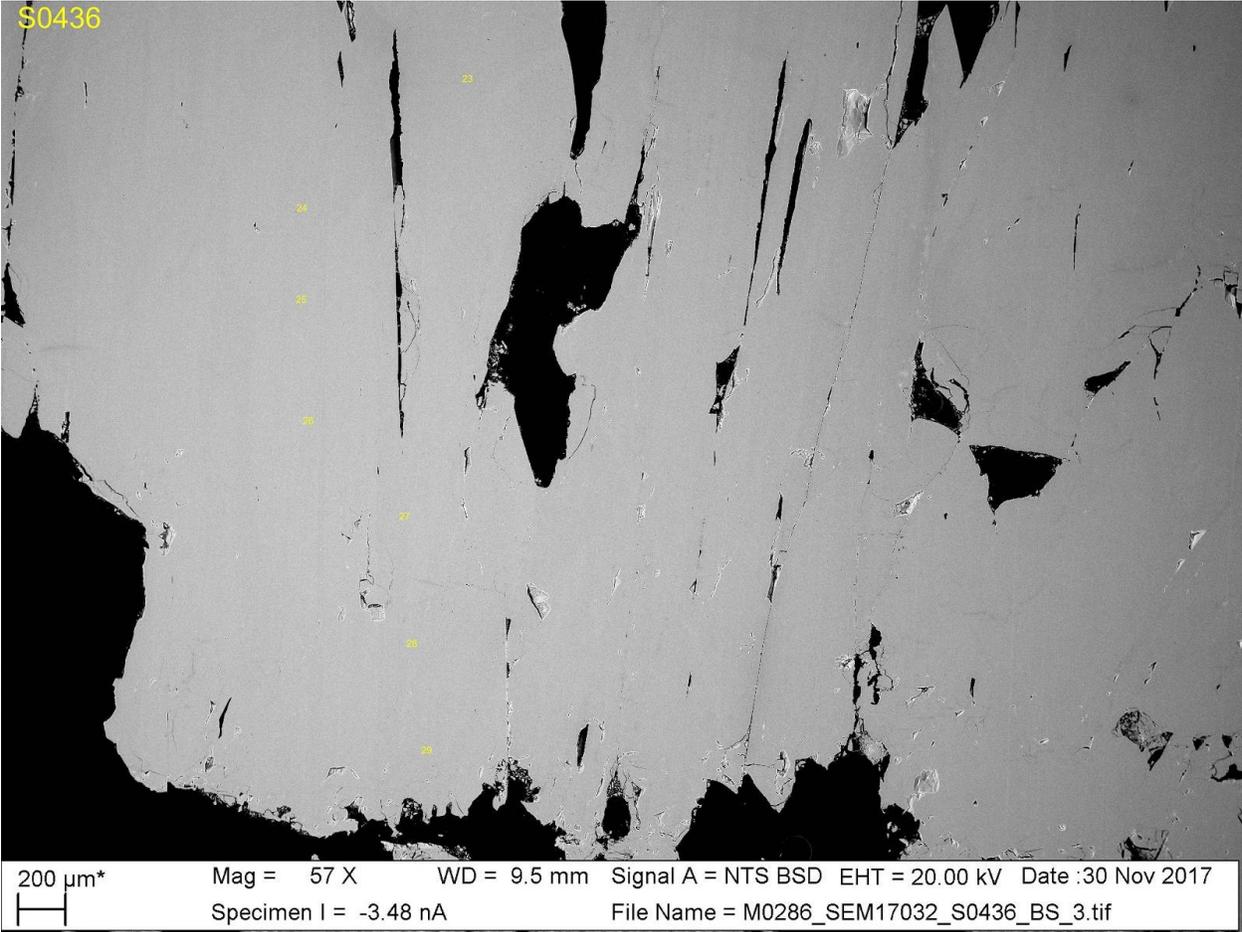


Figure 8: BSE image 4 of 4 from O-isotope transect of S0436.

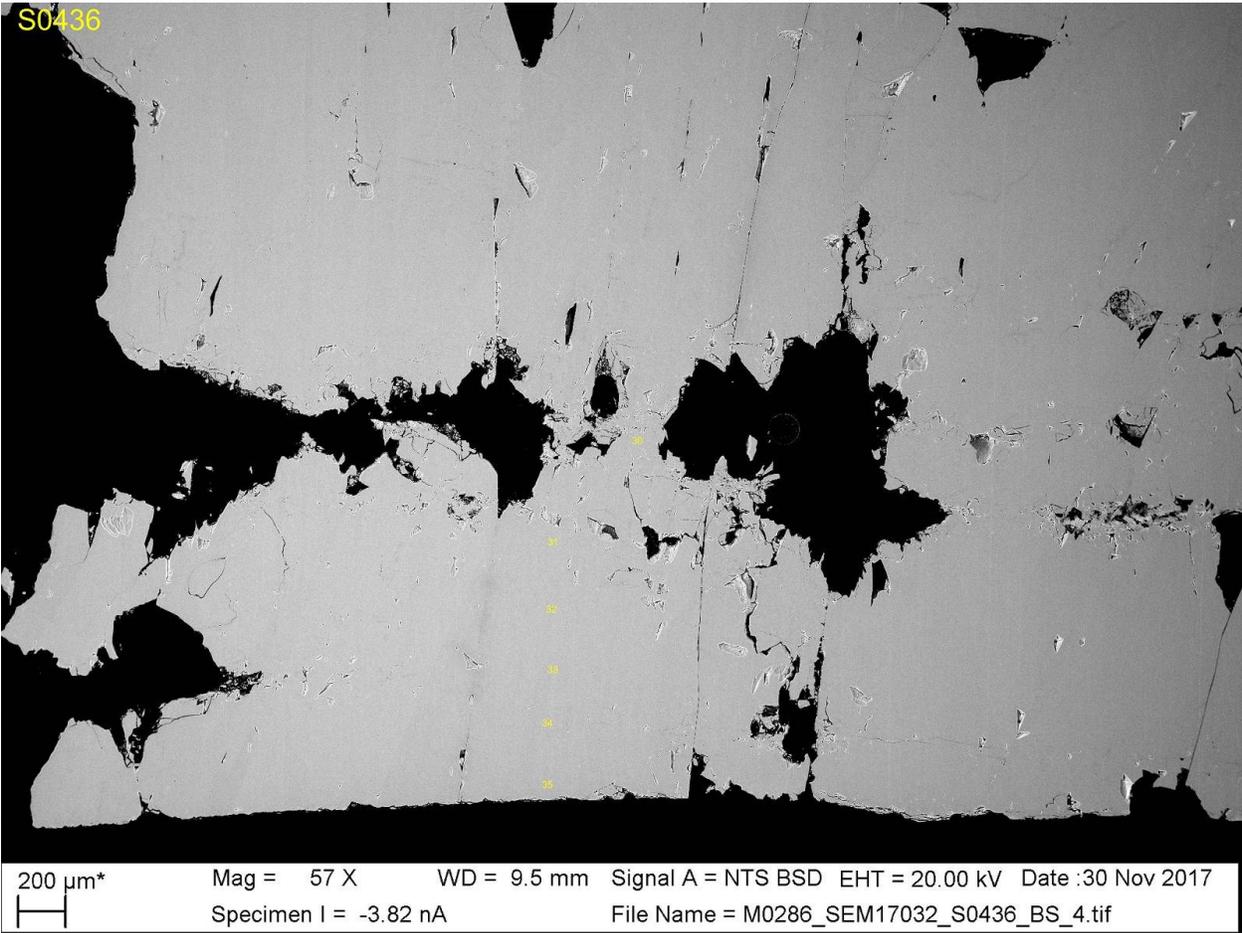


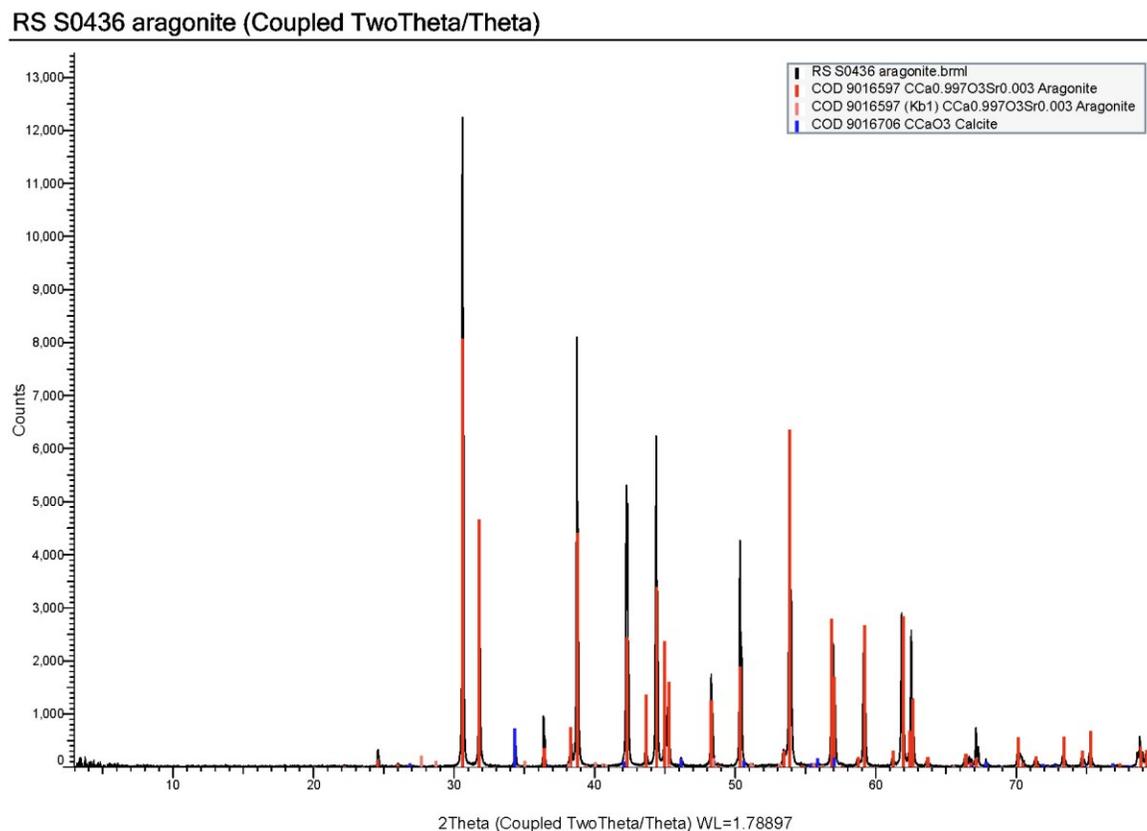
Figure 9: BSE image of fragments (bottom two rows) of S0436 in an epoxy grain mount, with S0161 calcite fragments partially visible at top. Subtle streaky zoning is visible from a minority of fragments of S0436.



CRYSTAL/STRUCTURAL CHARACTERIZATION

The phase composition of S0436 was verified by powder X-Ray Diffraction (XRD) performed on 20 mg of S0436 crystal fragments crushed in ethanol for about 2 minutes, which were then prepared as smear mounts on glass plates. The XRD analysis was carried out with a Bruker D8 Advance equipped with a Cobalt tube at an acceleration voltage of 35 keV and a 40 mA current. Samples were scanned over a 2Θ axis from 3° to 80° at a step size of 0.02° and a scan speed of 1s. The carbonate species were quantified via spectral regressing and deconvolution of the sample spectrum and fitting to Rietveld crystal structure models. The XRD spectrum of S0436 in Figure 10 demonstrates its composition to be at least 97 % aragonite, with calcite as the minor additional phase in the bulk sample. Confocal micro-Raman spectroscopy confirms the aragonite structure and absence of transformation of aragonite to calcite (Australian National University, L. Otter, pers. comm, 2024).

Figure 10: Powder X-ray diffraction spectrum of S0436 aragonite.

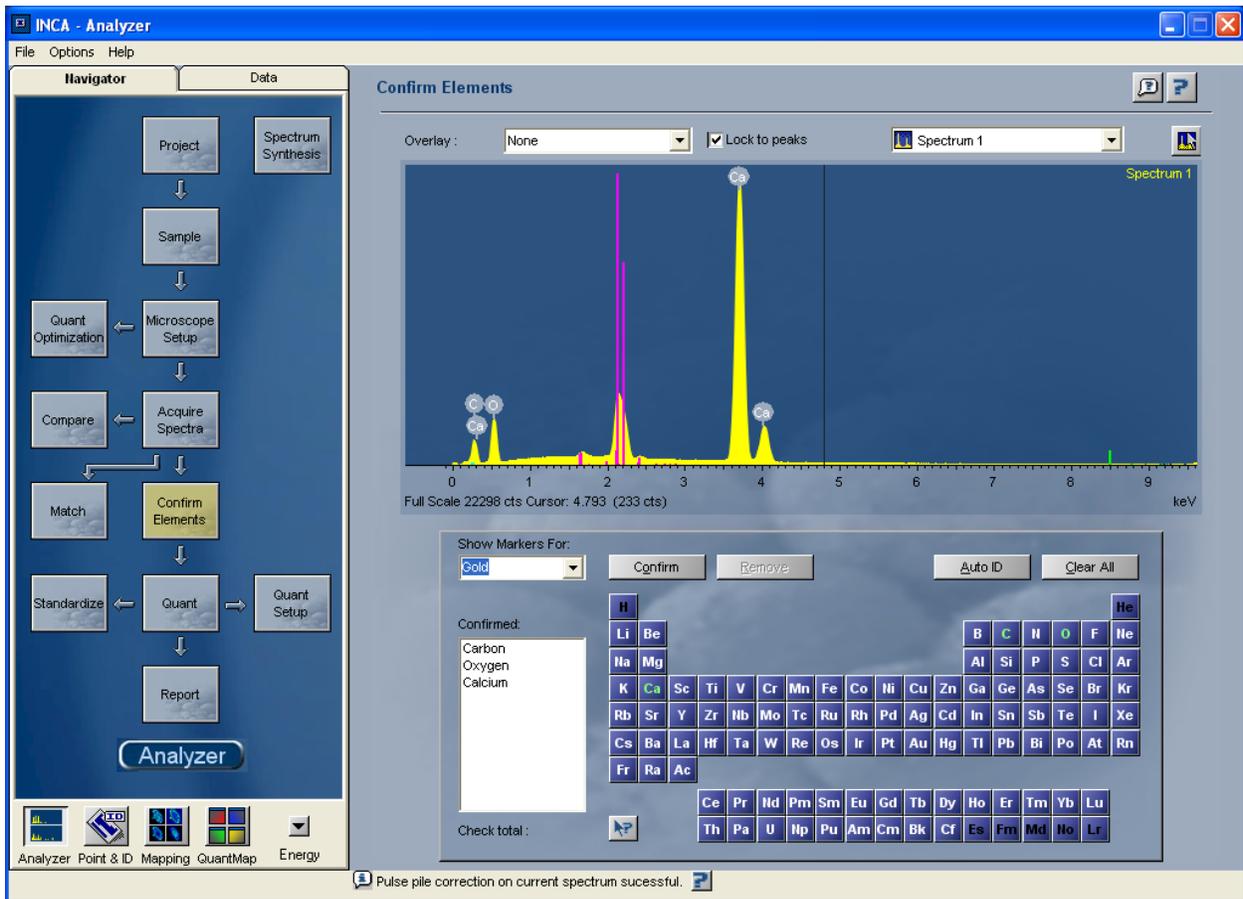


MAJOR AND TRACE ELEMENTS

ENERGY DISPERSIVE (EDS) X-RAY SPECTRA

A typical EDS spectrum at 20 kV electron energy (Fig. 11) indicates a chemically pure aragonite, with no significant minor elements in solid solution. Unlabeled peaks are from the conductive Au coating. Electron probe micro analysis-WDS measurements confirm the absence of detectable Na, Mg, and Sr (L. Otter, pers. comm., 2024).

Figure 11: EDS spectrum of S0436 aragonite.



ISOTOPES

GAS-SOURCE ISOTOPE RATIO MASS SPECTROMETRY

Tables 1 and 2 summarize available GS-IRMS data for RM S0436, with current working reference values shown. Acid fractionation factors for aragonite from Kim et al. (2007).

Table 1: C-isotope analyses of S0436 by GS-IRMS.

13C-12C								
Data set	Date	median $\delta^{13}\text{C}_{(\text{VPDB})}$ ‰	N	std dev ‰	sample mass mg	Laboratory	Source	Comments
1	2018-05-03	0.09	8	0.07	0.6	Veizer Lab, University of Ottawa	this study	replicate aliquots of powdered sub-sample, thus not indicative of RM homogeneity; Gas Bench II and Delta XP MS (Thermo Finnigan), 24°C acid reaction, aragonite acid fractionation factor of Kim et al. (2007)
Current CCIM reference value	2024-06-05	0.09						

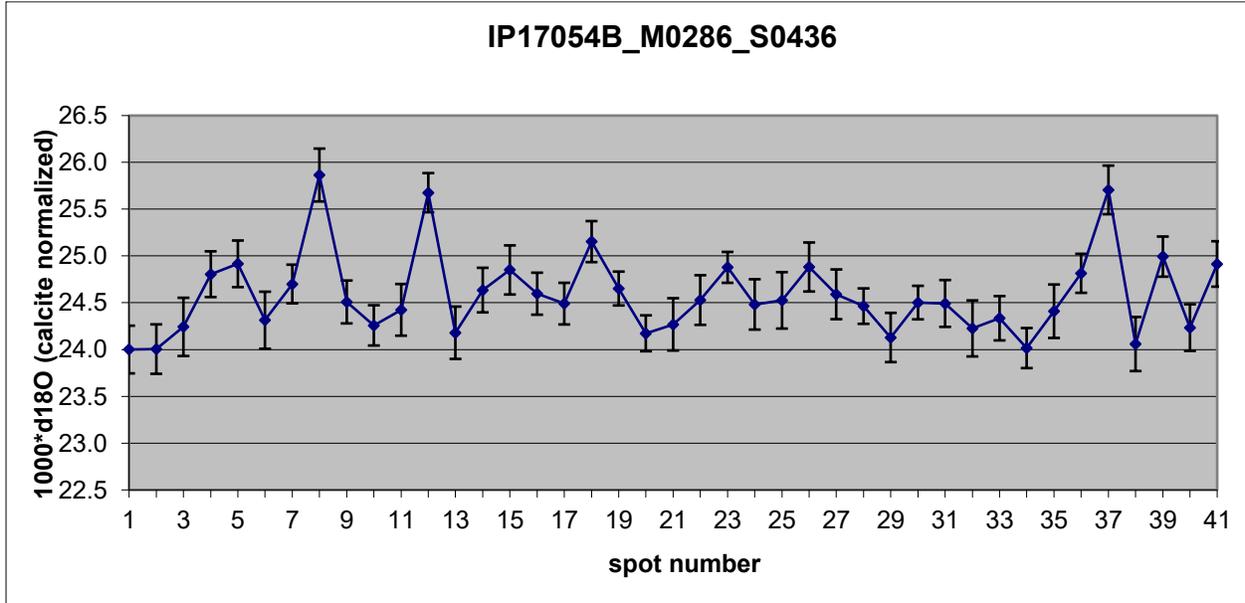
Table 2: O-isotope analyses of S0436 by GS-IRMS.

18O-16O									
Data set	Date	median $\delta^{18}\text{O}_{(\text{VSMOW})}$ ‰	median $\delta^{18}\text{O}_{(\text{VPDB})}$ ‰	N	std dev ‰	sample mass mg	Laboratory	Source	Comments
1	2018-05-03	23.82	-6.88	8	0.03	0.6	Veizer Lab, University of Ottawa	this study	replicate aliquots of powdered sub-sample, thus not indicative of RM homogeneity; Gas Bench II and Delta XP MS (Thermo Finnigan), 24°C acid reaction, aragonite acid fractionation factor of Kim et al. (2007)
Current CCIM reference value	2024-06-05	23.82	-6.88						

SECONDARY ION MASS SPECTROMETRY

Prior to fragmenting the whole sample S0436, $\delta^{18}\text{O}$ measurements were acquired from a top-to-bottom cross-section from mount M0286 within session IP17054B (Fig. 12, see also data set 1 in Table 3, and Figs. 5 to 8). Data were calibrated relative to RM S0161 calcite.

Figure 12: SIMS O-isotope transect across S0436 in M0286. Errors are $\pm 2\sigma$.



Compared to the spot-to-spot variance of S0161 ($s = 0.10 \text{ ‰}$), all 41 spots across S0436 are more scattered, yielding a spot-to-spot $s = 0.44 \text{ ‰}$ (range 1.9 ‰), indicating $\delta^{18}\text{O}$ heterogeneity beyond measurement uncertainties (excess variance compared with primary RM, $s = 0.34 \text{ ‰}$). There is no overall systematic variability related to position across the sampled area, but there appears to be some zoning indicated in more localized areas, such as the $\sim 1 \text{ ‰}$ gradation from spots 1 through 5, and 20 to 23 (Fig.12). Three $\delta^{18}\text{O}$ measurements (Fig. 12) yielded clearly anomalous values of $\sim +1 \text{ ‰}$ relative to the sample mean. These particular analyses were from crystal areas that had faintly darker BSE response compared to immediately adjacent regions and they had well-defined and straight crystal boundaries (Fig. 5). It is unknown whether these anomalies reflect true isotopic heterogeneity, or are an analytical bias from an unknown matrix effect, but the latter seems unlikely given that their secondary ion signal strengths were not different. Excluding three of these analyses reduces the sample $\delta^{18}\text{O}$ standard deviation to 0.30 ‰, and range = 1.2 ‰ (Table 3).

The session IP17055 comprises random analyses of $\delta^{18}\text{O}$ on fragments of the whole sample mounted in M0287 (Data set 2 in table following), which is representative of typical use of the RM S0436. Calibration as before was relative to RM S0161 calcite with identical analytical performance. The results for S0436 are similar to IP17054B in showing a spot-spot $s = 0.36 \text{ ‰}$ (range 1.5 ‰), and excess scatter relative to the primary RM (0.26 ‰).

Data set 3 compiles results from session IP19056 examining $\delta^{13}\text{C}$ in S0436 from M0287. Consistent with the $\delta^{18}\text{O}$ findings, there is slight excess scatter ($s = 0.27 \text{ ‰}$) compared to the homogeneous reference material S0161 calcite.

Together, these results indicate a small, but measureable amount of O- and C-isotopic variability at micron- to mm-scale within S0436. The BSE images of the fragments do not provide any information on the systematics of this heterogeneity. Consequently, it is advised to analyze several fragments (typically 5 or more) in determining an unbiased mean O- and C-isotopic composition that can be normalized to the reference value determined on the bulk sample. Note that for both isotope systems, for these data there is a bias of +0.7 to +0.9 ‰ in the apparent aragonite composition when normalized using calcite as the primary RM. The specific bias value is likely affected by SIMS analytical conditions as well as other variables that are the subject of further research, but is an important correction to the final aragonite data.

Table 3: SIMS C- and O-isotope analyses of RM S0436.

		units	1	2	3
	Data set		1	2	3
	Instrument		CCIM IMS1280	CCIM IMS1280	CCIM IMS1280
	Session		IP17054B	IP17055	IP19056
	CCIM Mount #		M0286	M0287	M0287
	Primary beam		Cs+	Cs+	Cs+
	Secondary ions		180-, 160-	180-, 160-	13C-, 12C-
	Primary impact energy	keV	20	20	20
	probe diameter	x 10 ⁻⁶ m	15	15	15
	Mass resolution	m/Δm (10%)	2250, 1950	2250, 1950	2950, 1950
	Multi-detectors		H'2, L'2	H'2, L'2	EM, L'2
S0161, calcite	# grains/fragments		1	3	2
	# spots		23	39	14
	Assumed reference value d18O(VSMOW)	1000*δ	25.31	25.31	
	Assumed reference value d13C(VPDB)	1000*δ			0.11
	session standard deviation	‰	0.10	0.10	0.24
	typical spot uncertainty, 2σ	‰	0.26	0.25	0.62
S0436 aragonite	# grains/fragments		whole sample in situ	13	11
	# spots		41	31	25
	session median d18O(VSMOW)	1000*δ	24.48	24.76	
	session median d13C(VPDB)	1000*δ			1.00
	session standard deviation, all data	‰	0.44	0.36	0.51
	range	‰	1.9	1.5	1.8
	# rejects (anomalous compositions)		3		
	session standard deviation after rejects	‰	0.30		
	range after rejects	‰	1.2		
	typical spot uncertainty, 2σ	‰	0.25	0.22	0.60
	excess scatter compared with primary RM	‰	0.34	0.26	0.27
	reference value (IRMS), VSMOW	1000*δ	23.82	23.82	
	reference value (IRMS), VPDB	1000*δ			0.09
	aragonite-calcite bias	‰	0.66	0.94	0.91

REFERENCE VALUES SUMMARY

Table 4: Aragonite RM S0436 current reference values. The uncertainties listed are conservative estimates of the bulk sample due to the single source of GS-IRMS data currently available, and do not reflect the larger micro-variation documented.

Isotope-chemical system	Current reference value	Unit	± estimate (same units as value)	Normalization
18O-16O	+23.82	1000• $\delta^{18}\text{O}$	0.3	VSMOW
18O-16O	-6.88	1000• $\delta^{18}\text{O}$	0.3	VPDB
13C-12C	+0.09	1000• $\delta^{13}\text{C}$	0.3	VPDB

DEFINITIONS AND TERMINOLOGY

For stable isotope terminology and normalizing values, the following sources were used:

Coplen et al. (2002)

Coplen (2011)

Brand et al. (2014)

Kim et al. (2015)

7. ACKNOWLEDGMENTS

L. Otter is thanked for reporting on the results of micro-Raman spectroscopy, WDS analyses, and for review of the report.

8. REFERENCES

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