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Evidence for microbial life in synsedimentary cavities from 2.75billion-year-old terrestrial environments

Rasmussen, B., Blake, T.S., Fletcher, I.R., and Kilburn, M.R.

SAMPLE LOCALITIES

The two main study areas are in the Nullagine Synclinorium (drill-hole BD2) and West Pilbara Basin (outcrop – CY) in the north Pilbara Craton (Blake, 2001) (Figure DR1). In each locality, samples were collected from the Hardey Formation of the Fortescue Group. In the East Pilbara region, the samples are mainly from the upper Hardey Formation, which has a SHRIMP U-Pb zircon age of 2752 ± 5 Ma, derived from a syn-depositional tuff bed (Blake et al., 2004).





ISOTOPE RATIO STANDARDS

The standards used were:

Sulfur – pyrrhotite "W1", with reference $\delta^{34}S_{CDT} = +0.3\%$ (Seccombe et al., 1977). Carbon – pyrobitumen "K-1", with reference $\delta^{13}C_{PDB} = -29.1\%$ (Fletcher et al., 2008).

PROCEDURES

Isotopic measurements were performed using the CAMECA NanoSIMS 50 ion microprobe in the Centre for Microscopy, Characterisation and Analysis (CMCA) at the University of Western Australia (UWA), Perth. This technique allows in situ C- and S-isotopic analysis at μ m scale with ~1‰ precision and reproducibility (Fletcher et al., 2008). Measurements were obtained using a Cs⁺ primary ion beam, with a net impact

energy of ~ 16 kV and a beam currents 0.5–2 pA, depending on the size of the final primary beam aperture.

Carbon analyses

A detailed description of the procedures for carbon isotope data acquisition and data reduction is given in Fletcher et al. (2008). The secondary ion mass analyzer was configured to record ¹²C⁻, ¹³C⁻, together with ¹⁶O⁻, and ²⁶[CN]⁻, all with electron-multiplier detectors operating in pulse-counting mode. The ¹⁶O⁻ provided a subsidiary (image) record of matrix/sample distribution, and ²⁶[CN]⁻ was used for real-time imaging, in conjunction with secondary electron imaging, for locating analysis sites. A 40 μ m mass analyzer entrance slit (ES-2) was used, beam divergence was limited using an aperture slit of 350 μ m (AS-1), and high-side energy filtering cut further 15% of secondary beam, resulting in a relative secondary beam transmission of ~45%. Under these conditions, ¹²C⁻ count rates were 2–3 x 10⁵ s⁻¹ and the mass resolving power (MRP; Cameca definition) was ~8000. In order to ensure separation of ¹³C⁻ from ¹²C¹H⁻, a 50 μ m exit slit was used to record ¹³C⁻. This gave a M/ δ M mass resolution of ~3850 at half peak height (~2725 at 1% peak height) with ¹³C⁻ well isolated from any ¹²C¹H⁻ tail. There are no potential isobars at masses 12 or 16, and those exit slits were left set at 75 μ m.

One C-isotope data acquisition session (referred to as C1) used 5x5 μ m analysis areas (as in Fletcher et al., 2008). In the second session (C2) this was reduced to 3x3 μ m to give more complete "coverage" (the proportion of analysis area occupied by sample) of sample grains <3 μ m wide. For session C1 the reproducibility of the data for the K-1 δ^{13} C standard was within the limits expected from internal data precision. For session C2 there was excess scatter amongst the standards data; this was propagated to the individual sample analyses. A 10% systematic uncertainty in the QSA correction model has been propagated to all data. Neither the uncertainties in the mean values for standards nor the uncertainties in the slopes of the standards regressions have been propagated to the sample data. The slope uncertainties are relatively minor and the uncertainty of the regression (1 SE, at the centroid) is given with the data plot for each session.

Sulfur analyses

The procedures for sulfur analyses are essentially the same as for carbon, with the secondary ion collectors repositioned to record ${}^{32}S^{-}$ and ${}^{34}S^{-}$. The standard (W1) was mounted a numerous chips in one disc in mount NM115. All analyses were made in a 3x3 µm areas centred in 4x4 µm rastered frames that were within larger pre-sputtered areas. The small analysis area was used because of the fine scale of some of the sample grains, and the "blanking" was employed to avoid crater-edge effects in the subsequent ion images that were recorded to determine coverage.

Since there are no known isobars at ${}^{32}S^{-}$ or ${}^{34}S^{-}$, both exit slits were set to 75 µm, giving wide, flat peak tops. For earlier analytical sessions (sessions 1–3) the entrance slit was ES-2 (40 µm) and the divergence slit was AS-2. Because of the high secondary ionisation efficiency for S under Cs⁻ bombardment, these relatively "open" conditions give high

secondary ion count rates, requiring substantial corrections (~55% in δ^{34} S) for guasisimultaneous secondary ion arrivals (QSA) — more than twice those required for C under similar instrument conditions and correspondingly more susceptible to any errors arising from inadequacies in the model for QSA corrections. Since the first-order corrections for S are questionable (Slodzian et al., 2004), and count rates for some samples were found to be appreciably different from those for the standards, this is clearly undesirable. For later analyses (sessions 4, 5), the entry and aperture slits were reduced to ES-3 ($30 \mu m$) and AS-4 (60 µm), cutting the secondary ion transmission to about a third of the previous conditions and reducing QSA corrections to <20%. Analytical session 4 was made specifically to compare data acquired under these conditions with data from the same sites obtained under the original conditions in session 3. Although we have not made a detailed assessment, we find that corrections based on the empirical QSA trend observed by Slodzian et al. (2004) are more appropriate than the theoretical corrections. The Slodzian trend gives better internal consistency for standards in several of the data sets (particularly the large set from Session 5, with MSWD reduced from 2.1 to 1.4), it gives visibly better reproducibility between sessions 3 and 4, and it improves internal consistency for some samples that gave widely varying counts rates. The absolute systematic uncertainty associated with the QSA corrections cannot be specified, but we have applied an uncertainty of 10% to the correction algorithm.

After each analysis, the analysis area was checked by viewing real-time ion images. When any discontinuities were observed, ion images were recorded of the $3x3 \mu m$ analysis area at 64x64 pixel resolution for subsequent determination of coverage. Coverage corrections and associated uncertainties were determined as outlined by Fletcher et al. (2008).

For three of the sessions, the reproducibility of the data for the sulfur standard - W1 was within the limits expected from internal data precision. For sessions 2 and 3 the excess (1σ) scatter was propagated to the individual sample analyses. A 10% systematic uncertainty in the QSA correction model has been propagated to all data. Neither the uncertainties in the mean values for standards nor the uncertainties in the slopes of the standards regressions have been propagated to the sample data. As for carbon, the uncertainty of the standards regression (1 SE, at the centroid) is given with the data plot for each session.

SULFUR ISOTOPE DATA

Data are presented on a session-by-session basis (Figures DR2-6), as well as in combination (Figure DR7), because of the variations noted above and differences in the sizes of the data sets. The fully-processed data (including those for W1) are normalised through the reference value for W1 and the least-squares regression for W1. Data from different polished thin-section discs probed in any single session are displayed with different symbols and all data can be cross-referenced with Table DR1 by session and sequence number.



Figure DR2. $\delta^{34}S_{CDT}$ data from analytical session 1. For W1 standard: n = 7; 1 SE = 0.26%; MSWD = 0.9.



Figure DR3. $\delta^{34}S_{CDT}$ data from analytical session 2. This is a short session, following tuning difficulties, resulting in a minimal number of standards analyses. There is significant scatter in the standards and a large uncertainty component from QSA due to relatively low count rates for the samples. It is possible that this mount had inadequate Au coating for this session. For W1 standard: n = 5; 1 SE = 0.8‰; MSWD = 3.3.



Figure DR4. $\delta^{34}S_{CDT}$ data from analytical session 3. For W1 standard: n = 9; 1 SE = 0.56‰; MSWD = 3.7. Analyses #11–#14 are from a different project (not listed in Table DR1) but are shown for comparison with Figure DR5.



Figure DR5. $\delta^{34}S_{CDT}$ data from analytical session 4. This session followed session 3, with reduced secondary ion transmission. It includes repeat analyses of session 3 sequence #s 7, 6, 11, 13 (note reversed order of the first two). For W1 standard: n = 5; 1 SE = 0.57‰; MSWD = 0.17. Analyses #7 and #8 are from a different project (not listed in Table DR1) but are shown for comparison with Figure DR4.



Figure DR6: $\delta^{34}S_{CDT}$ data from analytical session 5. This is the main data set comprising three days of analyses under sustained conditions, treated as a single session. For W1 standard: n = 23; 1 SE = 0.18‰; MSWD = 1.4.

Sample ^a	10 ⁶ cts ^b	p^{c}	±	$\delta^{34}S_{CDT}$	±	Sess ^d	Seq ^e
NG459							
NM108A-1	60.6	0.98	0.01	7.3	1.1	5	24
NM108A-2	64.8			5.8	1.1	5	23
NM108A-3	59.1	0.97	0.01	6.7	1.0	5	22
NM108A-4	47.4	0.86	0.03	2.9	1.3	5	21
NM108A-7	23.3	0.42	0.05	3.9	3.8	5	20
NG459							
NM108B-1	61.2			7.9	1.0	5	16
NM108B-2	67.9			6.1	1.3	5	15
NM108B-3	62.6			7.7	1.0	5	14
NM108B-4	58.0			-2.9	0.9	5	13
NM108B-4rep	64.7			0.4	1.1	5	17
NM108B-5	64.9			3.2	1.2	5	12
NG459							
NM108D-1	13.2			5.1	3.7	5	9
NM108D-2	48.5			1.4	1.2	5	8
NM108D-3	36.5			7.3	1.9	5	7
NM108D-5	59.5			6.2	0.9	5	5
NM108D-5 rep	64.1			7.3	1.1	5	6
NG452							
NM115A-1	56.8			-0.7	0.8	5	46
NM115A-3	62.7			-2.2	1.0	5	45
NM115A-4	62.1			0.2	1.0	5	44
NM115A-5	48.0			-2.0	1.0	5	59
NM115A-6	48.0			-1.4	1.0	5	60
NM115A-7	60.3			-2.4	0.9	5	47
NM115A-8	66.8			-4.0	1.2	5	43
NM115A-9	71.2			-8.5	2.4	2	6
NM115A-10	49.9	0.95	0.03	-5.5	1.4	5	42
NM115A-12	76.6			7.3	2.0	2	7
NM115A-13	60.2	0.97	0.02	-8.2	3.2	2	8
NM115A-14	53.8	0.99	0.01	-7.8	3.5	2	10
NM115A-15	56.1			-7.5	3.3	2	11
NM115A-16	18.0	0.98	0.02	-5.3	1.5	4	10
NG452							
NM115B-2	60.3	0.99	0.01	-4.3	3.0	2	12
NM115B-4	66.5			-1.3	1.7	3	7
NM115B-4rep	22.2			-0.3	1.4	4	3

TABLE DR1. COMPILED S-ISOTOPE DATA

NM115B-6	62.3			-3.6	2.2	3	6
NM115B-6rep	15.7			-5.1	1.8	4	4
NM115B-6	64.0			1.8	1.0	5	39
NM115B-7	12.5			3.0	7.4	3	8
NM115B-7	46.4			1.8	1.4	5	38
NM115B-8	22.5			2.3	2.9	5	37
NM115B-8rep	32.3			5.3	2.2	5	40
NG452							
NM115C-1	10.7			-2.9	4.0	5	36
NM115C-9	65.7	0.99	0.01	0.1	1.2	5	35
NG452							
NM115D-1	45.9	0.99	0.01	9.2	1.4	5	33
NM115D-1	49.6			-2.4	3.0	1	4
NM115D-2	27.1			4.4	2.4	5	54
NM115D-2	62.8	0.99	0.01	-1.0	1.7	1	5
NM115D-3	51.0			0.6	1.1	5	32
NM115D-3	64.8			0.3	1.6	1	6
NM115D-4	42.8	0.99	0.01	-4.6	1.6	5	31
NM115D-4	53.2	0.82	0.02	13.9	2.3	1	9
NM115D-4x	25.0			7.7	2.6	5	55
NM115D-4x	75.1			7.0	1.4	1	17
NM115D-5	51.9			6.8	1.0	5	30
NM115D-5a	68.7	0.99	0.01	0.5	1.6	1	10
NM115D-5b	64.9	0.90	0.02	2.9	2.0	1	11
NM115D-5c	75.3			-0.5	1.1	1	12
NM115D-5d	78.5			4.9	1.0	1	13
NM115D-5e	75.8			7.0	1.2	1	14
NM115D-5rep	39.3			8.5	0.9	5	57
NM115D-6	22.4			3.5	1.4	5	56
NM115D-21	59.2	0.72	0.03	19.0	3.1	2	3
NM115D-22	64.0	0.80	0.02	1.8	2.4	2	4
NM115D-23	79.3	0.98	0.01	5.0	1.9	2	5

^a NMxxxY-n: xxx = mount number; Y = disc of polished thin section in thatmount; n = analysis site number within Y. Analyses marked "r" are repeat analyses on a single site; "a"-"e" is a transect of closely-spaced analyses; "x" are sites adjacent to previous analyses (one of which was deleted). Other repeated analysis numbers are discrete sites analysed in a separate session. All sites are traceable using records on hardcopy optical images. ^b Total ³²S million counts recorded.

^c Coverage p, listed only where a correction has been made.

^d Analytical session.

^e Sequence number within session.



Figure DR7: All $\delta^{34}S_{CDT}$ data, identified by sample disc, in mount name-order (as in Table DR1).



Figure DR8. Histogram of all $\delta^{34}S_{CDT}$ data in Figure DR7.

CARBON ISOTOPE DATA

Data are presented on a session-by-session basis (Figures DR9 and DR10), as well as in combination (Figure DR11). The fully-processed data (including those for C-standard K-1) are normalised to the reference value for K-1 and the least-squares regression for K-1. Data from different polished thin-section discs probed in any single session are displayed with different symbols and the data can be cross-referenced with Table DR2 by session and sequence number. Data for K-1 are shown with 1 σ internal precision only.



Figure DR9. $\delta^{13}C_{PDB}$ data from analytical session C1. Analysis areas 5x5 μ m. For K-1 standard: n = 10; 1 SE = 0.3%; MSWD = 1.4.



Figure DR10. $\delta^{13}C_{PDB}$ data from analytical session C2. This session was at a different time than C1, with 3x3 μ m analysis areas. The data are consistent with Session C1 but have much poorer reproducibility. For K-1 standard: *n* = 12; 1 SE = 0.96‰; MSWD = 10.

Sample ^a	$10^6 \text{ cts}^{\text{b}}$	p^{c}	±	$\delta^{13}C_{PDB}$	±	Sess ^d	Seq ^e
NG450							
NM119A-1	126			-32.4	1.1	1	6
NM119A-1r	124			-29.4	1.0	1	7
NM119B-1	114	0.93	0.06	-49.9	1.4	1	8
NM119B-2	101	0.80	0.02	-45.2	1.1	1	9
NM119B-3	132			-55.4	3.1	2	6
NM119B-4	147			-51.7	2.9	2	7
NM119B-5	140			-54.2	3.0	2	8
NM119C-1	123	0.77	0.02	-50.9	1.3	1	12
NM119C-2	145	0.92	0.02	-50.5	1.0	1	13
NM119C-3	89	0.89	0.02	-25.4	3.6	2	14
NM119C-3r	87	0.89	0.02	-26.3	3.6	2	15
NM119C-4	152	0.99	0.01	-49.3	3.0	2	16
NM119D-1	144			-49.2	0.9	1	14
NM119D-3	35	0.58	0.10	-45.4	4.1	2	17
NM119D-3r	33	0.58	0.10	-43.3	4.1	2	18

TABLE DR2. COMPILED C-ISOTOPE DATA

^a NMxxxY-n: xxx = mount number; Y = disc of polished thin section in thatmount; n = analysis site number within Y. Analyses marked "r" are repeat analyses on a single site. Analysis sites are traceable using records on hardcopy optical images. ^b Total ¹²C million counts recorded.

^c Coverage p, listed only where a correction has been made. ^d Analytical session.

^e Sequence number within session.



Figure DR11. All $\delta^{13}C_{PDB}$ data, identified by sample disc, in mount name-order (as in Table DR2).

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