

## Supplementary Material

### A1. Sample preparation and EA-IRMS analyses

Sample preparation followed standard protocols (Stüeken *et al.*, 2020). The outer surfaces were cut off with a water-cooled rock saw, and the interior was hammered into sub-cm chips. The chips were cleaned sequentially in methanol, 1M HCl and DI-water (18.2 MΩ) and then pulverized in an agate ball mill. The powders were decarbonated with two treatments of 2M HCl at 60°C and then washed three times with DI-water.

The dried residues were weighed into tin capsules and analysed by flash combustion in an EA IsoLink, coupled via a ConFlo IV to a MAT253 isotope ratio mass spectrometer. Sulphur isotopes were calibrated with IAEA-S2 and IAEA-S3, while carbon and nitrogen isotopes were calibrated with USGS-40 and USGS-41. Blanks were monitored with empty tin capsules and subtracted. We also processed an aliquot of baked silica sand (1100 °C overnight) with the same method (milling, decarbonation, drying) and found a contamination of 14.4 µg/g TOC with an isotopic composition of -28.5 ‰, which was subtracted from all analyses. For nitrogen and sulphur, the procedural contamination measured with the silica sand was negligible (TN ~ 0.2 µg/g, TS undetectable), but this result was verified with additional tests (see Section A3). Data are expressed in delta notation ( $\delta = [R_{\text{sample}}/R_{\text{standard}} - 1] \cdot 1000$ ), where  $R = {}^{13}\text{C}/{}^{12}\text{C}$ ,  ${}^{15}\text{N}/{}^{14}\text{N}$ , or  ${}^{34}\text{S}/{}^{32}\text{S}$ . The standard is VPDB for  $\delta^{13}\text{C}$ , atmospheric air for  $\delta^{15}\text{N}$  and VCDT for  $\delta^{34}\text{S}$ . Replicate analyses of a subset of samples gave standard deviations of 0.2‰, 0.2‰ and 0.3‰, respectively, for peak areas greater than 10 Vs. Below this threshold, the precision deteriorated to about 1‰ for carbon and nitrogen isotopes (not relevant here for  $\delta^{34}\text{S}$ ). For samples with signal intensities less than 5 Vs (~ 10 µg/g TN) isotopic measurements are unreliable and will not be reported. Following general convention, ratios of organic carbon to nitrogen (C/N) will be expressed in units of mol/mol, whereas all other ratios, including organic carbon to total sulphur, are given in g/g.

### A2. Offline sealed-tube combustion

For low nitrogen abundance samples (<5 Vs measured using EA-IRMS), nitrogen isotopes, we analysed using an established sealed tube combustion method designed for the analysis of silicate bound nitrogen (Boocock *et al.*, 2020). This consists of an offline vacuum line and an offline tube cracker operating under continuous flow attached to a Thermofisher MAT253 isotope

ratio mass spectrometer at the STAiG labs, University of St Andrews. Sample powders were oxidized in an evacuated quartz glass tube in the presence of CuO at 1000°C for c.4 h, followed by c.2 h at 600°C (Boocock *et al.*, 2020). This technique ensures complete liberation of lattice-bound ammonium from silicate rocks. Results were calibrated with USGS-61 and USGS-62 and are expressed in delta notation ( $\delta^{15}\text{N}$ ) relative to atmospheric air. BHVO-2 was used for quality control and gave a value of  $+1.9 \pm 0.6$  ‰, in reasonably good agreement with previous measurements (Feng *et al.*, 2018; Boocock *et al.*, 2020). The results from the EA and sealed-tube combustion method are in good agreement, as shown in Figure A1.

### A3. Quantification of procedural blanks

As the total nitrogen concentration in many of our samples is very small, we performed additional tests with pure mineral phases purchased from online mineral shops to verify that the sample preparation protocol did not add significant amounts of contaminants. The minerals tested included three phyllosilicates (kaolinite, muscovite, biotite) and three tectosilicates (orthoclase, plagioclase, quartz) (Fig. A2). The hand specimens were first rinsed with DI-water (18.2 M $\Omega$ ) to remove surficial dust and then dried in an oven. Once dry, each specimen was split into multiple chunks by tapping it with a hammer on the lab bench, covered with fresh aluminium foil. Smaller pieces were transferred into a pestle and mortar and hand-crushed into a fine powder. The pestle and mortar were made of agate and cleaned in between samples with DI-water and methanol. The hand-crushed powder was analysed with the EA-IRMS following the procedure described above.

Larger aliquots of each mineral were pulverized with the same procedure as pure samples: The larger pieces were first taken to the rock saw and cut into thin slivers (~ 5 mm thickness). These slivers were made purposely thin to maximize contact with the saw blade and increase our sensitivity to potential contaminants. The cut slivers were then hammered into sub-cm-sized chips, using a steel pestle and steel plate, and the chips were cleaned with methanol, 1M HCl, and DI-water. This cleaning protocol is identical to what was used for all our Archean samples. After the chips had dried, they were pulverized in the agate ball mill. One aliquot of the powder was directly analysed by EA-IRMS while a second aliquot was processed with the decarbonation protocol that was also applied to all Archean samples. Around 0.5g of powder were weighed into pre-combusted Pyrex centrifuge tubes and mixed with 10ml of 2M HCl. The tubes were loosely capped and stored

in an oven at 70°C overnight. The next day, the tubes were centrifuged and the acid was decanted. The residue was washed three times with DI-water and then set to dry for three days in an oven. The dry, decarbonated powder was stored in pre-combusted scintillation vials. Each aliquot of powder was analysed between 2-4 times.

Our results (Fig. A3, Table A4) show that the maximum amount of statistically resolvable contamination obtained from the rock saw and milling procedure is  $2.2 \pm 0.3 \mu\text{g/g}$  (2 SD). However, with the subsequent decarbonation step this value decreases to  $1.0 \pm 0.3 \mu\text{g/g}$ . These values are for the plagioclase sample for which the measured nitrogen concentration increased from  $0.9 \pm 0.2 \mu\text{g/g}$  to  $3.0 \pm 0.2 \mu\text{g/g}$  (2 SD). The only mineral that showed a larger average increase was kaolinite which changed from  $49.4 \pm 27.2 \mu\text{g/g}$  to  $55.2 \pm 10.2 \mu\text{g/g}$ , but this concentration also decreased to  $44.8 \pm 4.7 \mu\text{g/g}$ , and in any case the heterogeneity in this mineral is too large to identify differences with confidence. The most precise measurements were obtained for plagioclase, orthoclase, biotite and quartz, and in all cases the net increase in total nitrogen concentration across the entire protocol was  $1 \mu\text{g/g}$  or less. For some minerals, including biotite, the concentration decreased significantly during the sawing and milling protocol, which we attribute to the intermediate washing step of the rock chips. This step likely removes loosely some bound contaminants that were retained in the hand-crushed aliquot. Overall, the amount of nitrogen contamination during sample preparation is therefore negligible.

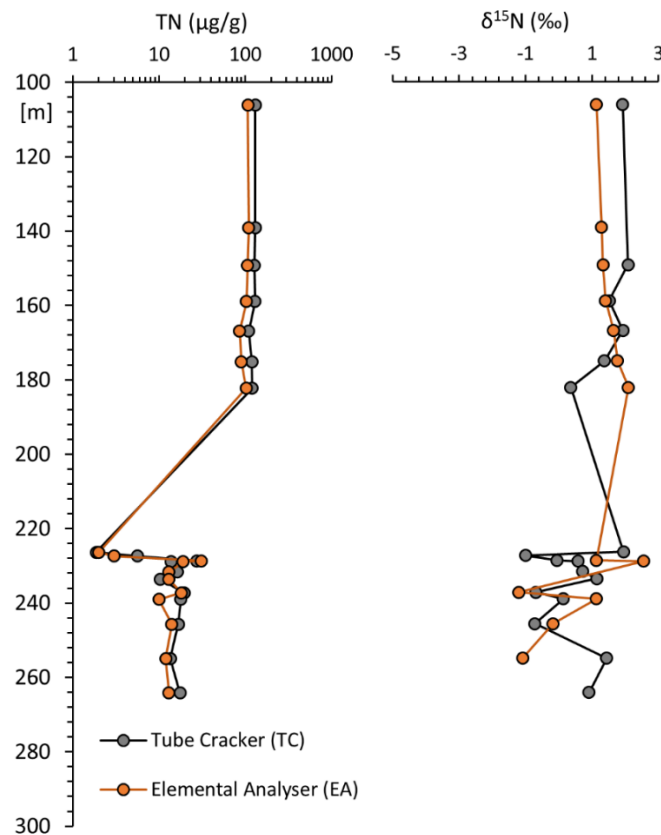
The decarbonation step removed significant amounts of nitrogen from the biotite, likely because the acid treatment mobilized some of the iron from the mineral and thereby destabilized it. We observed a yellow discoloration of the acid during the decarbonation. The amount of nitrogen remaining was too small to obtain isotopic data, but in the case of muscovite, where we were able to measure nitrogen isotopes, the decarbonated aliquot ( $\delta^{15}\text{N} = +2.8 \pm 0.8 \text{‰}$ , 2 SD) overlapped within error with the non-decarbonated aliquot ( $+3.4 \pm 0.2 \text{‰}$ ) (both processed with the rock saw and ball mill). This is also the case for kaolinite ( $2.6 \pm 2.8 \text{‰}$  versus  $5.8 \pm 2.4 \text{‰}$ , 2 SD), although the heterogeneity of this sample makes it more difficult to interpret. We therefore conclude that the acid step does not significantly perturb the nitrogen isotope signal, even if it were to remove some of the indigenous nitrogen from the sample.

For carbon, the maximum increase from the rock saw and ball mill was also found to be  $6.9 \pm 3.5 \mu\text{g/g}$ , which is of similar magnitude as the  $14.4 \mu\text{g/g}$  that we had previously measured with the baked silica sand. Total carbon decreased when the minerals were treated with acid, but

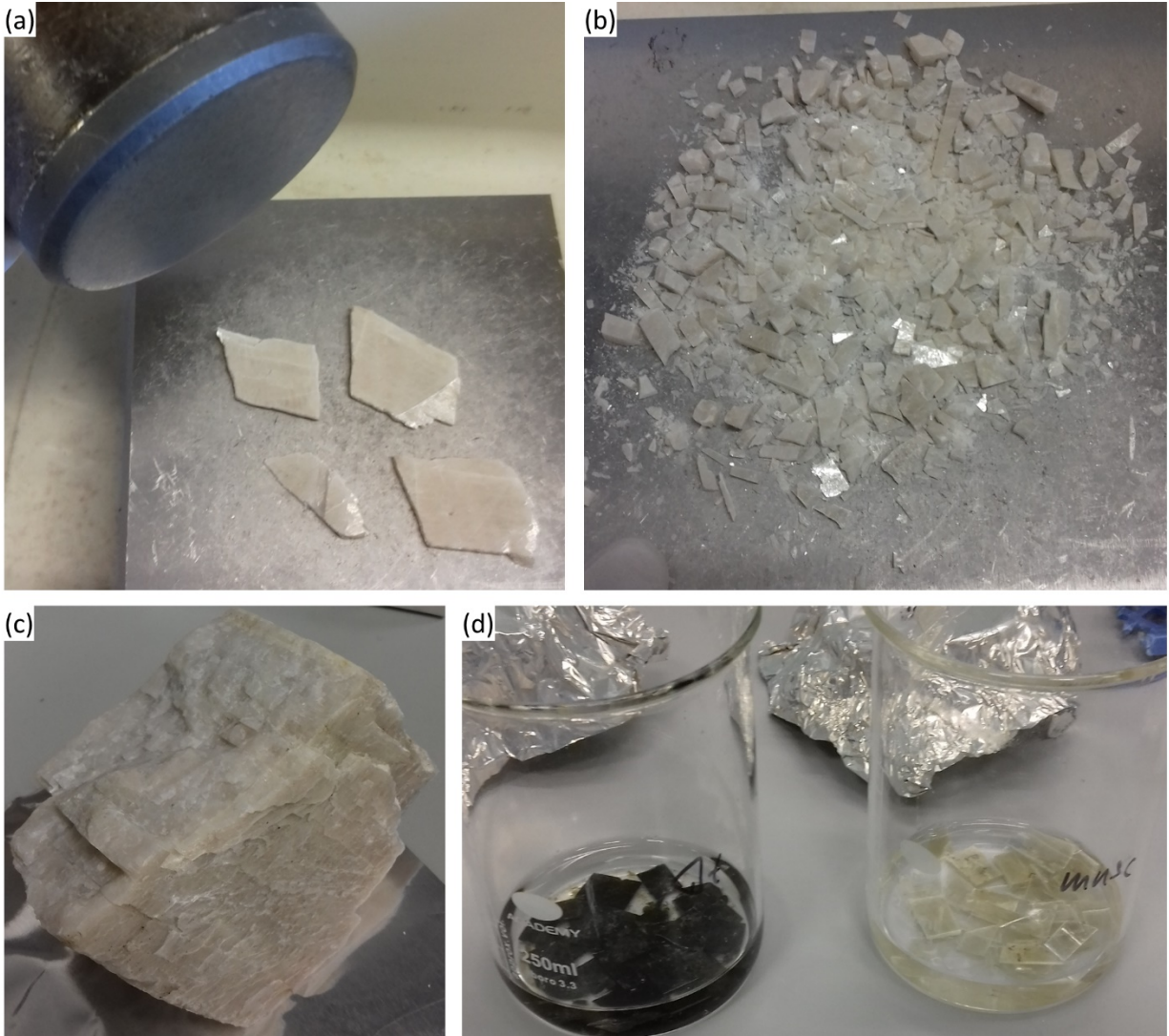
we note that this decrease could also be related to removal of minor interstitial carbonates. We therefore use the value of 14.4  $\mu\text{g/g}$  with an isotopic value of -28.5 ‰ as our best estimate of maximum organic carbon contamination.

#### A4. Major element abundances

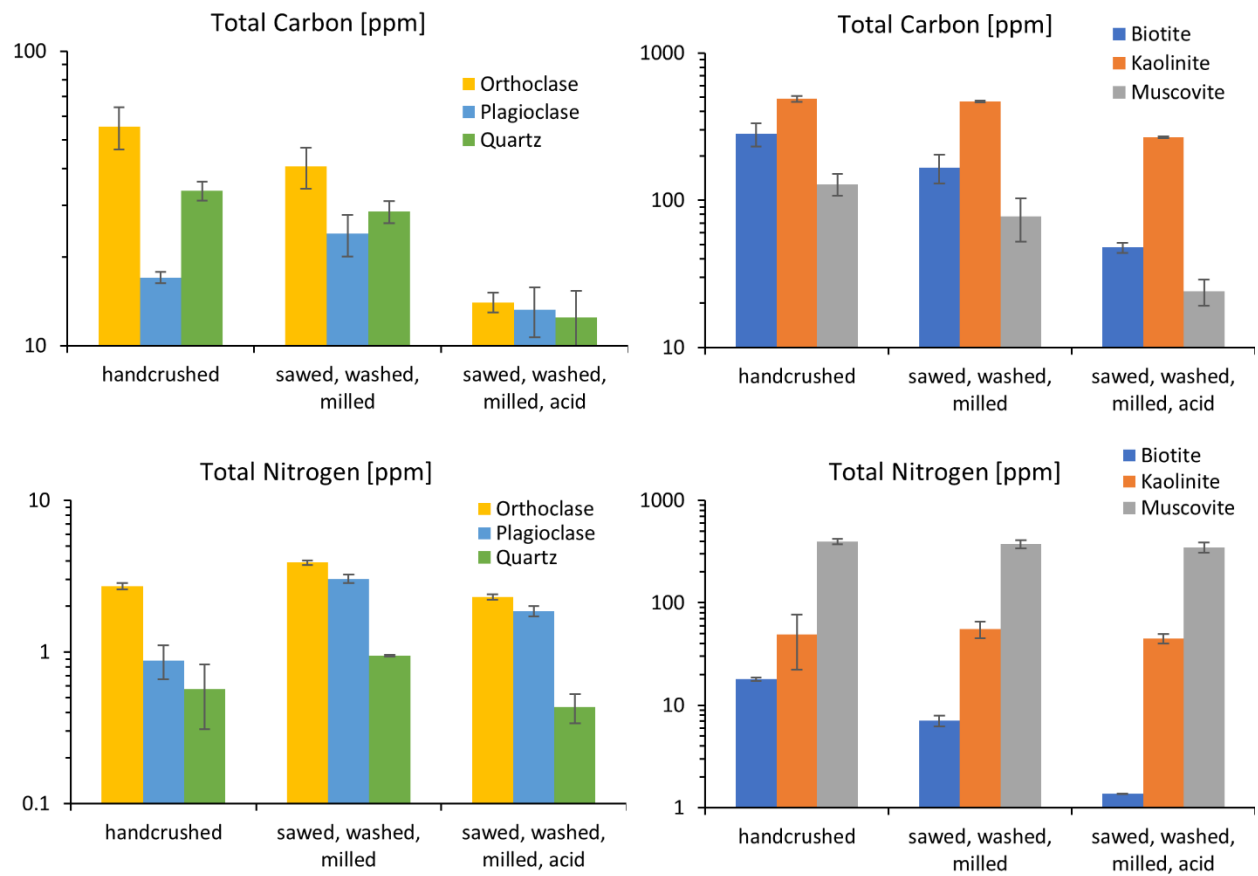
Outcrop samples were submitted to ALS Global for major element abundance analyses by method ME-MS61. This method includes a four-acid digestion of rock powders, followed by ICP-MS and ICP-OES analyses. Reproducibility of major elements was better than 4%.



**Figure A1:** Method comparison for nitrogen abundance and isotopic measurements, showing good agreement between the tube cracker (offline combustion system) and the elemental analyser.



**Figure A2: Images of mineral phases during sample preparation.** (a) sliced orthoclase just after the rock saw, lying on the steel plate, ready to be hammered into little chips. (b) orthoclase chips on the steel plate. (c) initial orthoclase mineral that was purchased from an online shop. (d) Chips of biotite (left) and muscovite (right) undergoing washing in between the rock saw and the ball mill. Note: due to their flaky and soft morphology, these two minerals along with kaolinite were not hammered with the steel pestle.



**Figure A3: Results from contamination tests.** Error bars are  $\pm 2$  SD.

**Table A1: EA-IRMS data.** Shales, marker chert and sericite samples are from drill core VSD007, all others are from outcrop. Depths in the core samples are relative to the length of the core. TOC and TN are in units of  $\mu\text{g/g}$ , TS is in wt. %. All isotopic data are expressed in units of permil. C/N ratios are in units of mol/mol; C/S ratios are in g/g. <sup>1</sup>For the recharge quartz-chlorite(-plagioclase) samples, the depth is equal to the stratigraphic distance from the drill core. <sup>2</sup>For all samples from the discharge zone as well as for the granophyre samples the depth is equal to the stratigraphic distance from the paleo-seafloor.

Depth [m]	TOC	$\delta^{13}\text{C}$	TN	$\delta^{15}\text{N}$	C/N	TS	$\delta^{34}\text{S}$	C/S
<b>Shale:</b>								
106.15	4423.2	-31.55	107.0	1.13	48.2	0.01	2.37	54.26
107.76	2471.1	-31.79	58.3	1.11	49.4	0.11	2.92	2.27
108.5	4805.1	-31.98	103.5	1.55	54.1	0.01	0.97	38.82
126.55	4425.9	-31.96	119.2	0.96	43.3	0.01	2.25	45.94
136.95	2674.1	-31.94	105.4	2.03	29.6	0.04	1.03	7.35
139.1	3470.6	-32.56	110.5	1.29	36.6	0.03	1.83	10.18
149.285	9421.6	-30.58	105.5	1.33	104.1	0.03	1.99	34.78
153.6	5464.8	-30.73	31.6	-0.18	201.9	0.06	1.03	9.88
158.92	5067.1	-31.04	102.6	1.41	57.6	0.04	1.93	14.15
166.92	3718.3	-32.70	86.1	1.65	50.4	0.13	1.13	2.85
172.83	7713.4	-30.54	92.8	1.46	96.9	0.03	1.98	26.65
175.115	3573.0	-31.21	89.6	1.77	46.5	0.08	3.54	4.69
182.215	4866.8	-30.54	102.2	2.09	55.6	0.02	2.06	23.10
190.58	6446.5	-32.64	53.9	2.38	139.4	0.40	0.48	1.61
<b>Marker chert:</b>								
197.975	128	-31.67	15.1	1.32	9.8		1.56	0.00
222.57	1789	-33.29	54.2	2.85	38.5	0.07	2.30	2.43
224.35	334	-31.32	7.3		53.5	0.90	0.04	0.04
226.35	604	-35.07	1.5		457.0	0.05	4.88	1.21
226.93	116	-29.89	1.0		132.4	0.17	0.18	0.08
227.35	305	-32.62	3.3		109.1	0.11	0.83	0.30
<b>Sericite alteration zone<sup>1</sup>:</b>								
228.65	25	-25.42	30.9	1.13	0.9	0.07	4.44	0.05
228.91	31	-26.93	19.2	2.55	1.9	0.25	3.28	0.02
230.66	23	-25.71	20.8	-2.26	1.3	0.02	4.18	0.19
231.65	16	-25.12	13.1		1.4	0.02	2.43	0.12
233.58	20	-22.25	13.1		1.7	0.02	3.34	0.17
237.25	51	-23.14	17.7	-1.20	3.4	0.29	3.97	0.02
239.01	50	-37.52	9.7	1.13	6.0	0.10	2.03	0.06
245.68	21	-38.72	14.4	-0.17	1.7	0.00		1.85
248.92	10	-30.34	5.1	0.00	2.3	0.01	1.13	0.34
254.94	8	-22.62	11.5	-1.09	0.9	0.00		3.27
258.78	5	-22.20	9.1	0.88	0.6	0.11	1.92	0.02
264.16	15	-24.71	13.4		1.3	0.13	1.92	0.02

269.02	16	-27.15	8.4	0.71	2.3	0.03	0.29	0.09
272.52	8	-19.95	10.8	-0.09	0.9	1.03	3.09	0.00
273.23	8	-21.76	10.8	0.03	0.8	0.02	1.90	0.12
276	16	-22.16	20.7	-1.78	0.9	0.07	-0.18	0.05
278.5	13	-26.31	19.4	-0.09	0.8	0.06	1.67	0.05
<b>Recharge quartz-chlorite(+/-plagioclase) alteration zone<sup>1</sup>:</b>								
480	18	-31.03	10.9		2.0	0.01	0.64	0.48
650			8.2			0.00	2.49	0.51
1600	23	-3.14	3.6	-3.67	7.5	0.30	0.94	0.01
1750	5	-47.54	4.2		1.3			
1800	14	-38.93	4.5		3.7			
1850			4.3					
2000	10	-21.52	2.2	-2.83	5.1	0.01	2.98	0.44
2100			4.3	-3.53		0.01	3.15	0.05
<b>Granophyre<sup>2</sup>:</b>								
5450	8.0	-12.34	4.8	-4.31	1.9			
5400	2.7	-21.26	5.1		0.6			
5220	6.5	-14.53	4.7		1.6	0.01	3.26	0.21
<b>Discharge quartz-chlorite(+/-plagioclase) alteration zone<sup>2</sup>:</b>								
4000	10.3	0.12	3.6		3.3			
3540	2.8	-44.15	4.6		0.7			
<b>Discharge kaolinite<sup>2</sup>:</b>								
2950	23.14	-26.27	14.3		1.9	0.17	1.69	0.02

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**Table A2: Offline sealed-tube combustion data.** Isotopic data are in permil; TN is in units of  $\mu\text{g/g}$ . \*Data marked with a star were used in the final data compilation shown in Figures 2 and 3 in the main text. For all other samples, the EA-IRMS data were used (Table A1). Depths are as in Table A1.

Depth [m]	$\delta^{15}\text{N}$	TN
<b>Core samples:</b>		
106.15	1.92	130
139.1	2.08	131
149.29	1.52	128
158.92	1.93	129
166.92	1.38	110
175.12	0.36	119
182.22	1.95	120
226.35*	-0.99	2
227.35*	-0.06	6
228.65	0.57	27
228.91	0.71	14
231.65*	1.14	16
233.58*	-0.69	10
237.25	0.13	19
239.01	-0.72	18
245.68	1.44	17
254.94	0.91	14
264.16*	1.25	17
<b>Outcrop samples:</b>		
2000*	-2.83	3
2100*	-3.53	2
5450*	-4.31	3
1600*	-3.67	4

**Table A3: Major element abundances.** All elements are in units of wt. %. Data from the drill core were supplied by the Geological Survey of Western Australia; data from outcrop samples were obtained in this study (see Section A3). For explanation of depths, refer to Table A1.

Depth [m]	Al [%]	Na [%]	K [%]	Mg [%]	Ca [%]	Fe [%]
<b>Marker chert:</b>						
222.57	3.4	0.02	1.02	1	0.01	2.96
224.35	2.07	0.01	0.63	0.55	0.01	2.31
226.35	0.71	0.01	0.29	0.08	0.01	0.75
226.93	0.755	0.01	0.31	0.08	0.01	0.85
227.35	0.8	0.01	0.33	0.08	0.01	0.95
<b>Sericite alteration zone:</b>						
228.65	5.42	0.05	2.49	0.27	0.06	0.78
228.91	4.89	0.05	2.21	1.49	3.11	2.08
230.66	6.56	0.07	3.02	0.76	1.15	1.09
231.65	4.94	0.05	2.19	0.73	0.83	1.1
233.58	4.52	0.05	1.95	0.63	0.67	1.01
237.25	5.49	0.06	2.53	0.76	1.06	0.95
239.01	5.45	0.07	2.35	0.78	0.49	0.86
245.68	4.9	0.07	2.1	0.91	0.93	0.85
248.92	5.61	0.07	2.28	1.54	1.14	1.39
254.94	5.41	0.04	2.12	1.11	0.47	1.12
258.78	5.78	0.06	2.47	0.93	1.07	0.91
264.16	6.38	0.07	2.78	0.98	1.14	1.43
269.02	6.81	0.08	3.02	1.07	0.62	1.06
272.52	5.57	0.05	2.39	0.99	1.46	1.38
273.23	7.4	0.09	3.35	1.02	1.12	1
276.00	4.78	0.04	2.04	1.15	1.73	1.15
278.50	7.31	0.06	3.2	1.15	1.12	1.19
<b>Recharge quartz-chlorite(+/-plagioclase) alteration zone:</b>						
480	5.71	0.04	1.73	2.34	2.19	4.63
650	5.8	0.03	3.03	0.94	0.83	1.01
1600	6.26	1.17	1.7	1.91	2.58	9.66
1750	6.16	0.02	0.16	5.14	0.28	13.6
1800	6.86	1.93	0.21	4.54	0.31	4.35
1850	6.13	2.92	0.08	2.04	2.15	7.58
2000	5.92	0.98	3.63	0.67	0.73	1.69
2100	6.1	3	3.45	0.04	0.71	0.37
<b>Granophyre:</b>						
5450	5.71	2.29	2.36	0.12	1.32	0.55
5400	5.77	2.26	1.94	0.14	1	0.53
5220	5.69	2.29	2	0.17	1.86	0.86

**Discharge quartz-chlorite(+/-plagioclase) alteration zone:**

4000	5.78	0.02	0.06	3.56	0.07	10.2
3540	6.31	2.65	0.24	2.64	1.76	8.36

**Discharge kaolinite:**

2950	4.54	0.04	2.13	0.17	0.02	0.27
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**Table A4: Contamination tests of pure mineral phases.** SWM = sawed, washed, and milled. Acid = treated with 2M HCl as in the decarbonation procedure. Blank cells = isotopic values could not be determined.

	TC [μg/g]	1σ [μg/g]	δ <sup>13</sup> C [‰]	1σ [‰]	TN [μg/g]	1σ [μg/g]	δ <sup>15</sup> N [‰]	1σ [‰]
Biotite_handcrushed	282.63	11.15	-30.92		17.92	0.36	-2.97	0.50
Biotite_SWM	166.94	3.19	-31.86	0.51	7.08	0.41	-2.77	0.84
Biotite_SWM_acid	47.73	1.51	-32.88	0.13	1.37	0.00		
Kaolinite_handcrushed	489.78	25.16	-28.44	0.94	49.38	13.58	4.37	1.41
Kaolinite_SWM	468.75	18.31	-28.41	0.62	55.18	5.09	2.56	1.43
Kaolinite_SWM_acid	267.11	1.90	-27.63	0.17	44.77	2.35	5.84	1.18
Muscovite_handcrushed	128.80	11.04	-24.78	1.49	395.54	12.13	4.87	0.00
Muscovite_SWM	77.96	12.77	-40.89	1.15	372.86	17.24	3.37	0.08
Muscovite_SWM_acid	24.11	2.44	-34.88	1.16	347.67	20.29	2.80	0.40
Orthoclase_handcrushed	55.37	4.51	-22.00	0.39	2.72	0.07		
Orthoclase_SWM	40.61	3.24	-17.87	0.58	3.90	0.07		
Orthoclase_SWM_acid	14.01	0.54	-30.81	0.26	2.31	0.05		
Plagioclase_handcrushed	17.04	1.26	-25.45	0.27	0.88	0.11		
Plagioclase_SWM	23.96	1.20	-24.56	0.60	3.03	0.10		
Plagioclase_SWM_acid	13.22	1.45	-31.27	0.67	1.86	0.07		
Quartz_handcrushed	33.60	0.37	-28.09	0.15	0.57	0.13		
Quartz_SWM	28.48	1.94	-30.88	0.24	0.94	0.01		
Quartz_SWM_acid	12.46	1.27	-29.04	0.36	0.43	0.05		

## References

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