

Supporting Information for

Microbial metallome on early Earth: Insights from combined Cd, Ba, and Ni isotopes in stromatolites

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Materials and methods

Two visibly well-preserved hand specimens of stromatolites from the Pongola Supergroup were collected in the White Mflozi inlier. They were cut, polished, and petrographically analyzed using a secondary electron microscope (SEM). Stromatolitic laminae are partly silicified and alternating with carbonate layers. Stromatolite chips within the carbonate matrix indicate very early silicification in a high-energy aqueous environment.

Quantitative trace element maps of 1.5cm x 1.5cm were analyzed using in situ LA Q-ICP-MS analyses at ChemLab, Shanghai, using external 3D-trace element calibration to a set of reference materials (NIST glasses 610, 612 and carbonate nano-powders Jct-NP, Jcp-NP) and processing in lolite[®] software.

Ten micro-cores (ø 4mm) were drilled and homogenized to powder in an agate mortar for trace metal and C-O-Cd-Ni isotope analyses. C-O isotopes were analyzed on orthophosphoric acid leachates using an isotope ratio mass spectrometer (Thermo MAT 253 IR-MS) at the State Key Laboratory of Mineral Resources Research (SKLMR) at Nanjing University.

For trace metal and Cd isotope analyses, ~0.5 g sample powder was either reacted with ultrapure 1M pH 5-buffered acetic acid for carbonate leachates or a mix of double distilled concentrated HNO₃ (6mL) and H.F. (4mL) in screw-top 30 mL Savillex[®] beakers (72 hrs at 120 °C) for bulk digestion. Solutions were then dried down, aliquots diluted in 2% HNO₃, and trace elements analyzed at Freie Universität Berlin (FUB) using a sector-field inductively coupled mass-spectrometer (Thermo Element XR ICP-MS) and linear calibration to matrix matching carbonate

standards. For Cd isotope analyses, aliquots containing ~100 ng Cd were mixed with an inhouse 106-108 Cd double spike, followed by Cd purification (1) and isotope composition analysis using a thermal ionization mass spectrometer (Thermo TIMS) and offline double spike inversion and isotope dilution computation at FUB.

For Ba isotopes, ~100 mg of the same sample powder was weighed into acid-washed centrifuge tubes, washed with M.Q. and sodium acetate (buffered to pH ~8), and then leached in 1M HAc overnight at room temperature (2). After centrifugation, supernatants were dried down, and aliquots containing ~50 ng Ba were mixed with an in-house Ba double spike at SKLMR, followed by Ba purification and isotope composition analysis using a multi-collector inductively coupled mass spectrometry (Thermo Neptune Plus MC ICP-MS) and offline double spike inversion and isotope dilution computation.

For Ni isotopes, ~10 mg of sample powder was leached with 1M HAc, followed by a two-step Ni purification and isotope composition analysis using a Thermo Neptune Plus MC ICP-MS at the China University of Geoscience, Beijing, with the standard sample bracketing method.

Authigenic carbonate δE_{auth} has been calculated by subtracting the influx of detrital silicate components using the samples' EI/Al ratio and comparing this with either BSE or time equivalent diamictites concentrations and isotopic compositions (SI).

REE anomaly and authigenic fraction calculations:

Post Archean Australian Shale (subscript N) normalized Europium anomalies were calculated from BaO isobaric interference corrected Eu concentrations (3) following the equations given in Lawrence et al., 2006 (4):

$$\text{Eq. 1: } E_{UN}/E_{UN}^* = Eu / (Sm_N^2 * Tb)^{1/3}$$

Post Archean Australian Shale (subscript N) normalized Europium anomalies were calculated following the equations given in Lawrence et al., 2006 (4), avoiding overinterpretation from neighboring La anomalies:

$$\text{Eq. 2: } C_{EN}/C_{EN}^* = C_{EN}/Pr_N(Pr_N/Nd_N)$$

In order to calculate detrital input corrected authigenic carbonate (acetic acid leachable phase) elemental compositions and isotope compositions the following calculations were performed following (5):

$$\text{Eq. 3: } \delta R_{auth} = (\delta R_{sample} * (fEI * [EI]_{det} + (1-fEI) * [EI]_{auth}) - (\delta R_{BSE} * [EI]_{det} * fEI)) / ([EI]_{auth} * (1-fEI))$$

With:

$$\text{Eq. 4: } [EI]_{auth} = [EI] - ([EI]_{det} * ([Al]/Al \text{ in detrital reservoir}))$$

$$\text{Eq. 5: } [EI]_{det} = [EI] - [EI]_{auth}$$

$$\text{Eq. 6: } fEI = [EI]_{det} / [EI]_{auth} * 100$$

As detrital reservoir for calculation of authigenic components average Cd and Al concentrations of the Kaapvaal craton were taken from the [GEOROC](#) database (Cd = 67 µg/g (n = 109), Al = 53743 µg/g (n = 5108)). Additionally, different detrital reservoirs were implemented here as to match potential authigenic enrichment from detrital silicate background sedimentation. While BSE and UCC values overlap in the case of Ni and Cd isotope systematics, Ba isotope compositions in BSE are systematically heavier than UCC. For a mafic volcanism dominated Archean lithosphere the heavier BSE value thus represents a better constraint for the detrital component into the Pongola stromatolite formation environments. In Fig.3 Mesoarchean diamictite values are also plotted as currently best fit for a time-equivalent continental detrital composite.

Detrital component reservoirs:

	UCC δ	UCC conc.	BSE δ	BSE conc.	MDA δ	MDA conc.
Ba	0	638 µg/g	0.06	1.3 µg/g	-0.053	374 µg/g
Ni	0.2	47 µg/g	0.23	>2000 µg/g	0.063	158.5 µg/g
Cd	0.15	147 µg/g	-0.03	38 µg/g	n.a.	n.a.
Al		40,750 µg/g		9,315 µg/g		26,832
References	(6–10)		(8, 10, 11)		(12–14)	

Fully-quantitative element mapping using Iolite®

Quantitative trace element maps of 1.5cm x 1.5cm were analyzed using in situ LA Q-ICP-MS analyses at ChemLab, Shanghai, using external 3D-trace element calibration to a set of reference materials (NIST glasses 610, 612 and carbonate nano-powders Jct-NP, Jcp-NP) and processing in Iolite® software (15–17).

The Iolite® spatial integration mode allowed for the assessment of local element enrichments that we have defined as carbonate infill, mat surface, silicified mat and stromatolitic carbonate clast (Fig. S1):

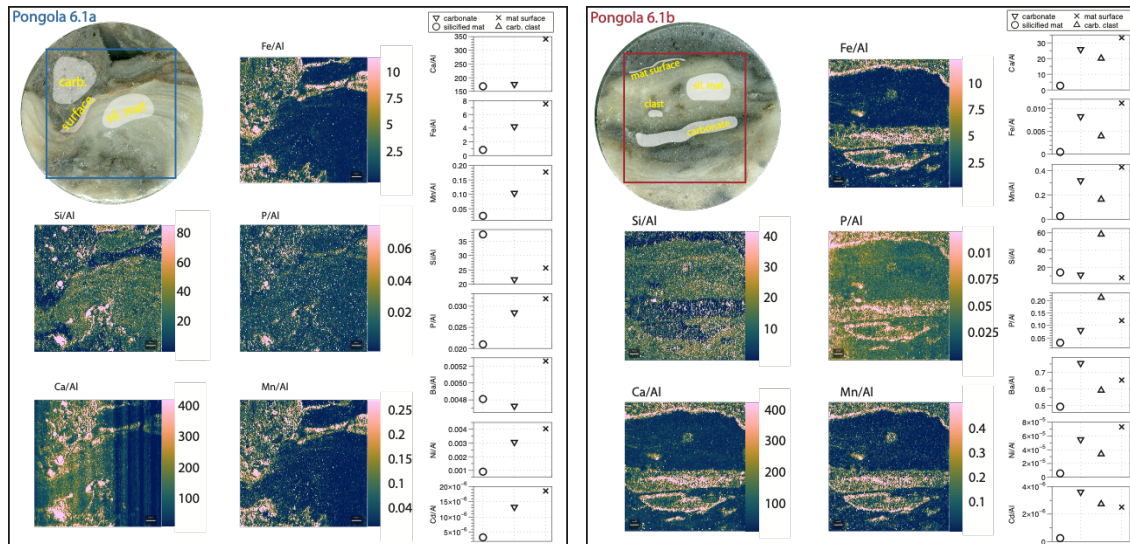


Fig. S1: Fully quantitative element maps including spatial enrichments of Cd, Ni, Ba, P, Si, Mn, Fe, and Ca normalized to Al

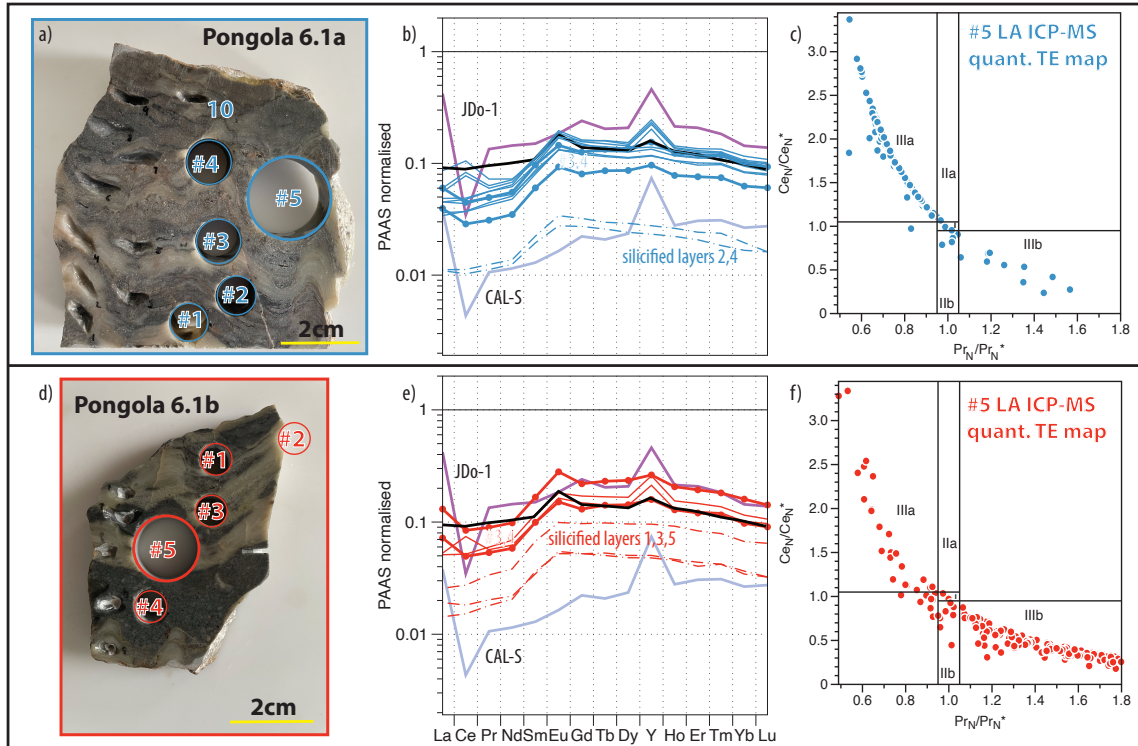


Fig. S2: a,d) hand specimen photographs with drill holes and drill path locations; b,e) PAAS normalized REY patterns of acetic leachates in drill cores #3 and #4 (dotted lines) and diamond coated drill paths 1 to 10 of hand specimen 6.1a and 1 to 5 of hand specimen 6.1b, respectively. Dashed lines represent silicified layers. Black line for comparison from authigenic carbonate leachates (18); c,f) classic Bau-plot(19) of Pr/Pr^* vs Ce/Ce^* anomalies showing true negative Ce anomalies (IIIb) in LA-ICP-MS analyses of Pongola stromatolites.

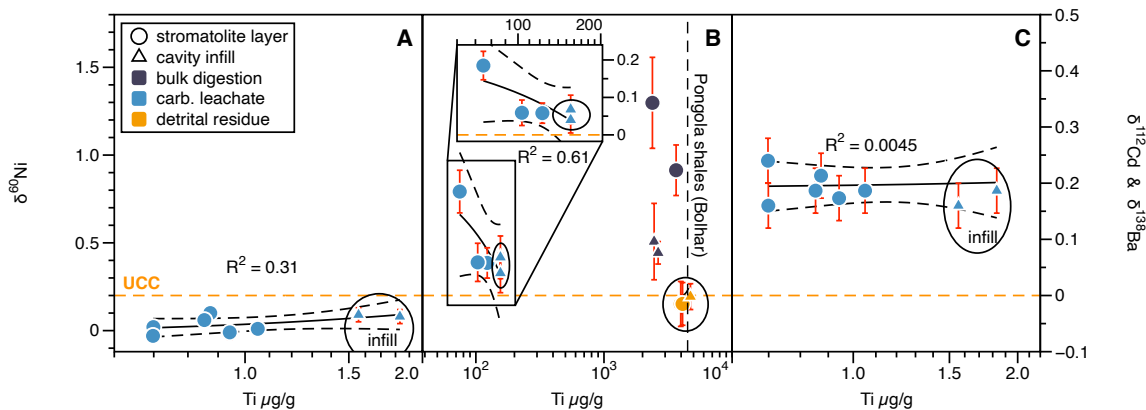


Fig. S3: Influence of detrital silicate contamination in authigenic carbonate leachates of the Pongola stromatolites. While HAC leachates of partly silicified stromatolitic carbonates show low concentrations of almost immobile Ti, detrital infill between stromatolitic domes, as well as bulk digestion and silicate residue digestion of the domes show elevated Ti concentrations that approach average Ti concentrations of Pongola shales ((18)).

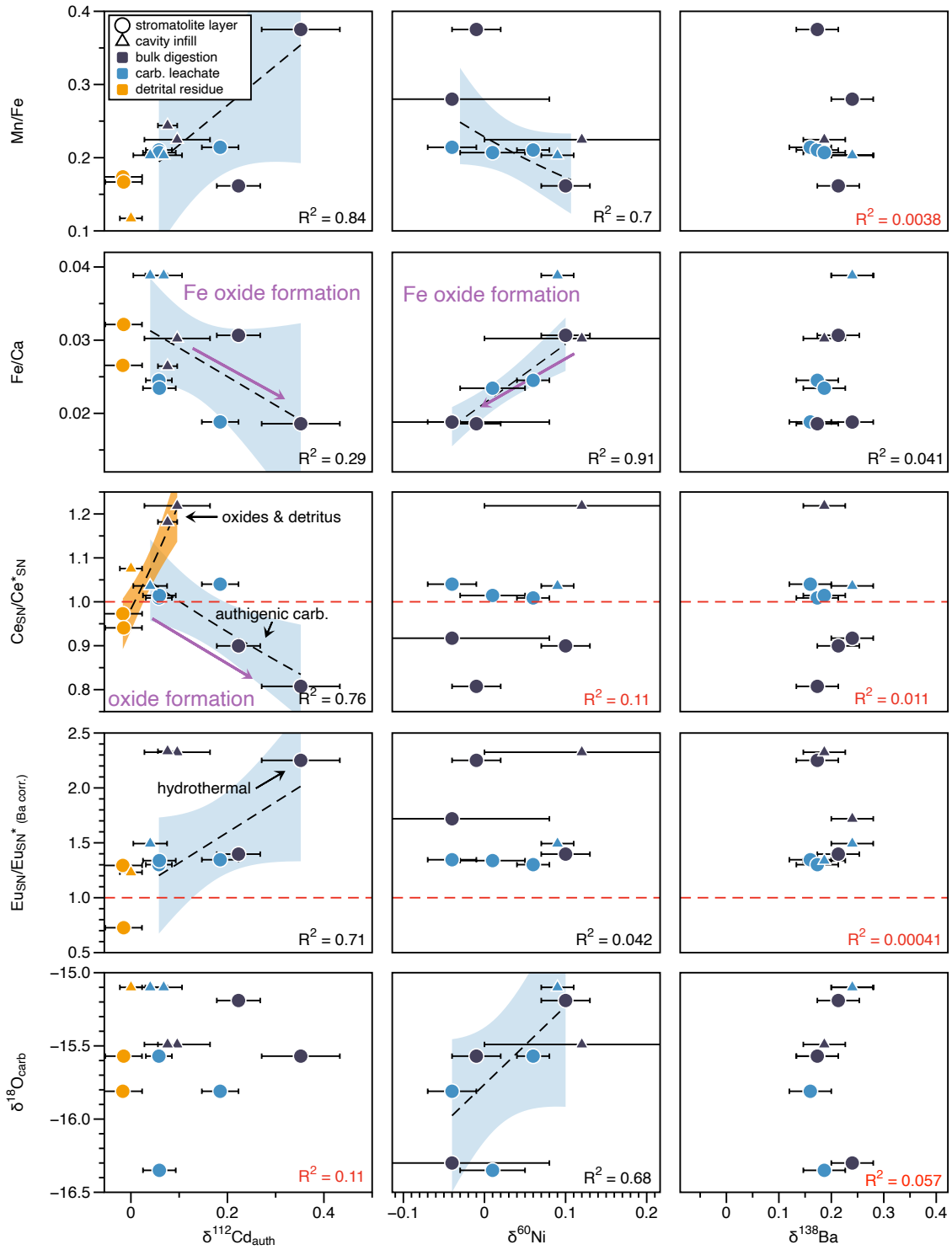


Fig. S4: Assessment of influence of meteoric or hydrothermal fluid-flow and oxide formation on Cd, Ni and Ba isotopic compositions. All R^2 are calculated on 95% confidence intervals with linear correlation.

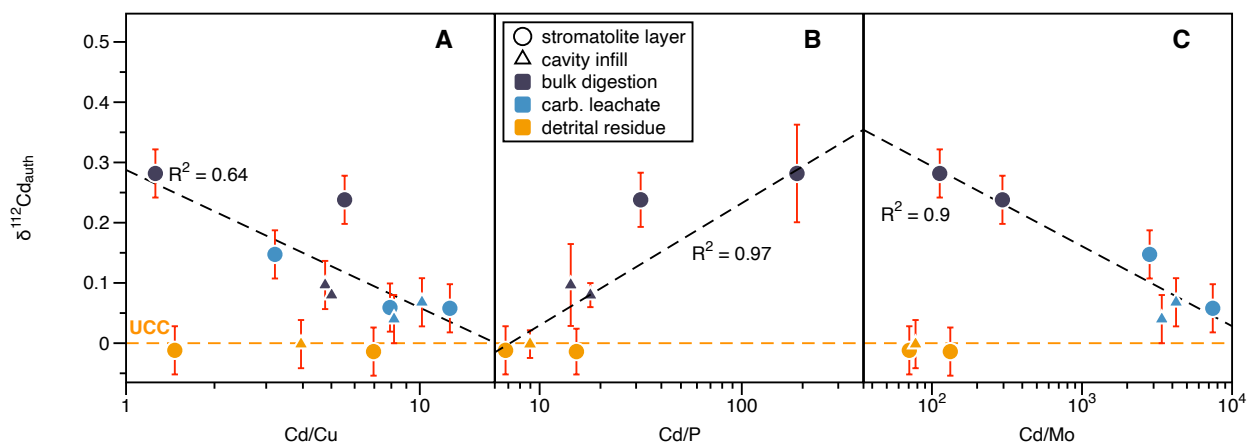


Fig. S5: Cd isotopic composition correlations with Cd over Cu, P and Mo concentrations. All R^2 are calculated on log linear correlations and 95% confidence intervals.

Table S1: Major element concentrations in leachates, bulk and detrital fractions of Pongola stromatolites and carbonate reference materials

name		Mg (wt %)	Al (wt %)	P (µg/g)	S (µg/g)	Ca (wt %)	Mn (wt %)	Fe (wt %)
6.1a-3-leach	leach	2.86	0.403	not calibrated	65.0	16.3	0.0658	0.307
6.1a-4-leach	leach	4.93	0.700	not calibrated	194	22.5	0.116	0.552
6.1b-3-leach	leach	4.59	0.788	not calibrated	79.6	20.9	0.102	0.491
6.1b-4-leach	leach	21.2	0.666	not calibrated	107	27.2	0.215	1.06
6.1a-3	detritus	-	0.870	169	160	-	0.0906	0.521
6.1a-4	detritus	-	0.516	156	125	-	0.100	0.598
6.1b-3	detritus	-	0.908	272	142	-	0.0873	0.554
6.1b-4	detritus	-	1.05	144	97.8	-	0.0236	0.201
6.1a-1	bulk	3.82	0.325	169	224	20.2	0.100	0.619
6.1a-2	bulk	3.34	0.925	7.68	114	19.6	0.137	0.365
6.1b-1	bulk	3.86	0.121	186	54.2	16.2	0.110	0.490
6.1b-1#	bulk	4.00	0.183	173	42.5	19.1	0.123	0.506
6.1b-2	bulk	6.42	0.696	555	220	38.5	0.2029	0.725

Table S2: Trace element concentrations and REY ratios in leachates, bulk and detrital fractions of Pongola stromatolites and carbonate reference materials

name	Al	Si	Zr	Mn	Na	Ba	Li	Sc	Y	Th	Pa	U	Co	Ni	Sr	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Ti	V	Cr	Ga	Zn	Yt ₀	Co ₀	Yt ₀ ¹	Eu ₀ /Yt ₀	Pr ₀ /Yt ₀	Sr ₀ /Yt ₀	Sm ₀ /Yt ₀	Eu ₀ /Yt ₀	Sr ₀ /Yt ₀	Sum ₀
6.13-1-leach	112	171	6.68	0.311	24.0	3.16	1.965	1.51	2.29	0.274	1.8	0.335	0.001	0.375	0.057	0.465	2.60	0.077	0.216	0.008	0.177	0.026	0.177	0.026	0.177	0.026	1.29	74.8	3.61	37.9	321	192	38.7	1.04	0.976	1.35	0.486	7.06			
6.14-leach	212	218	21.2	0.385	120	5.74	0.405	2.30	3.56	0.437	1.8	0.336	0.001	0.388	0.074	0.639	4.18	0.131	0.406	0.045	0.289	0.040	0.289	0.040	0.289	0.040	2.35	123	6.56	29.8	330	1373	36.2	1.01	0.980	1.30	0.483	1.0			
6.15-leach	313	75.6	6.69	0.681	121	3.17	0.411	2.75	3.94	0.471	1.8	0.351	0.001	0.688	0.09	0.668	4.29	0.137	0.413	0.044	0.275	0.039	0.275	0.039	0.275	0.039	2.21	203	5.86	23.6	330	363	38.7	1.01	0.980	1.34	0.548	2.11			
6.16-leach	317	174	11.8	0.655	259	4.69	1.16	4.99	6.72	0.790	3.8	0.925	0.001	1.026	0.12	0.719	1.10	0.204	0.551	0.089	0.452	0.084	0.452	0.084	0.452	0.084	4.18	256	5.94	25.4	441	282	38.7	1.04	0.980	1.48	0.537	3.08			
6.13-1-detritus	172	713	40.1	7.73	92.6	307	35.4	1.37	1.31	0.180	0.448	0.086	0.075	0.036	0.060	0.096	0.036	0.060	0.036	0.060	0.036	0.060	0.036	0.060	0.036	0.030	39.719	50.6	73.9	791	461	63.3	0.973	1.01	1.29	1.47	2.38				
6.13-4-detritus	2.85	80.7	35.1	73.4	85.7	251	17.9	0.789	0.720	0.027	0.286	0.029	0.022	0.041	0.020	0.031	0.046	0.020	0.031	0.020	0.031	0.020	0.031	0.020	0.040	0.040	0.040	41.063	57.5	77.5	341	496	21.7	0.941	1.02	0.772	1.50	2.00			
6.13-3-detritus	4.33	383	55.2	10.6	98.7	498	17.5	3.60	3.20	0.075	0.084	0.001	0.033	0.142	0.021	0.066	0.024	0.021	0.066	0.024	0.066	0.024	0.066	0.024	0.040	56.897	64.7	102	438	448	21.3	1.06	0.947	1.24	1.38	8.50					
6.13-4-detritus	0.840	94.0	63.9	6.04	37.0	87.7	16.7	13.0	13.5	1.17	0.485	0.149	0.370	0.056	0.435	3.05	0.095	0.321	0.050	0.333	0.055	0.321	0.055	0.321	0.055	2.87	47.304	44.7	96.1	331	588	26.1	1.08	0.933	1.23	1.01	33.6				
6.13-1-bulk	4.90	80.2	29.2	6.71	93.8	198	38.1	0.362	0.252	0.028	0.08	0.022	0.026	0.004	0.022	0.036	0.004	0.022	0.036	0.004	0.022	0.036	0.004	0.022	0.036	0.040	36.561	54.3	72.2	964	598	26.7	0.900	1.05	1.40	0.844	0.88				
6.13-2-bulk	1.80	120	6.87	0.411	96.8	49.7	12.9	0.196	0.110	0.025	0.066	0.001	0.013	0.033	0.007	0.027	0.004	0.004	0.011	0.002	0.008	0.001	0.002	0.008	0.001	0.040	23.862	36.0	31.9	1153	255	29.4	0.807	1.11	1.25	0.598	0.69				
6.13-1-bulk	2.80	126	5.25	0.046	78.0	19.3	0.411	0.386	0.138	0.011	0.039	0.006	0.008	0.009	0.006	0.012	0.094	0.003	0.008	0.002	0.007	0.001	0.002	0.007	0.001	0.090	24.829	39.1	49.2	556	391	37.5	1.22	0.884	0.999	0.537	0.48				
6.13-1H-bulk	3.03	141	14.2	0.007	92.8	42.2	0.411	0.180	0.143	0.013	0.048	0.007	0.021	0.021	0.007	0.015	0.007	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.016	26.473	40.4	52.7	615	386	36.6	0.771	1.13	1.33	0.515	0.42				
6.13-2-bulk	5.21	505	11.8	0.068	199	134	27.8	0.619	0.444	0.045	0.157	0.023	0.008	0.034	0.004	0.034	0.008	0.034	0.004	0.034	0.008	0.034	0.004	0.034	0.008	0.030	93.977	68.4	76.5	1033	386	30.0	0.937	1.04	1.17	0.811	1.41				
PG 6.13-1L	1.46	949	22.1	1.78	194	0.116	0.024	1.73	3.47	0.421	1.79	0.463	0.031	0.358	0.081	0.528	3.19	0.04	0.075	0.037	0.233	0.034	0.075	0.037	0.233	0.034	4.91	5.35	10.3	28.8	39.5	78.4	30.6	0.965	1.01	1.36	0.591	9.91			
PG 6.13-2L	0.119	1.384	20.9	1.17	25.4	0.013	0.022	0.419	0.818	0.099	0.428	0.08	0.064	0.127	0.020	0.113	0.628	0.022	0.059	0.007	0.047	0.007	0.047	0.007	0.047	0.007	3.15	2.59	3.95	27.8	506	703	28.5	1.02	0.984	1.06	0.673	2.30			
PG 6.13-3L	1.12	111	32.9	2.51	245	0.299	0.200	3.28	8.37	0.639	2.46	0.572	0.966	0.699	0.304	0.931	3.62	0.116	0.318	0.042	0.266	0.037	0.266	0.037	0.266	0.037	10.5	11.4	14.4	46.1	63.3	79.7	31.2	1.46	0.835	1.49	0.767	17.7			
PG 6.13-4L	0.102	1.337	16.3	0.878	29.7	0.016	0.001	0.427	0.894	0.110	0.466	0.110	0.466	0.110	0.466	0.110	0.466	0.110	0.466	0.110	0.466	0.110	0.466	0.110	0.466	0.110	2.71	2.26	2.97	25.9	37.7	64.7	28.7	0.993	0.999	1.23	0.639	2.54			
PG 6.13-5L	3.42	887	24.2	1.66	206	0.115	0.024	1.86	3.89	0.495	2.10	0.541	0.87	0.679	0.309	0.640	3.78	0.138	0.399	0.044	0.282	0.041	0.282	0.041	0.282	0.041	4.79	6.83	9.91	32.4	70.8	141	29.5	0.958	1.01	1.48	0.592	11.3			
PG 6.13-6L	1.71	228	14.5	0.964	250	0.122	0.018	1.71	3.79	0.495	2.18	0.615	0.90	0.728	0.314	0.728	6.62	0.142	0.386	0.051	0.337	0.047	0.337	0.047	0.337	0.047	4.42	5.43	5.93	28.6	75.9	105	46.6	0.976	1.00	1.36	0.483	11.5			
PG 6.13-7L	0.644	1.714	13.6	0.895	168	0.049	0.000	1.39	2.25	0.374	1.6	0.445	0.466	0.562	0.289	0.521	3.14	0.105	0.388	0.058	0.237	0.035	0.237	0.035	0.237	0.035	3.75	3.49	3.82	25.8	29.5	35.1	29.9	0.988	0.988	1.43	0.534	8.9			
PG 6.13-8L	0.678	291	19.5	1.35	280	0.129	0.022	2.12	6.17	0.529	2.30	0.811	0.207	0.728	0.126	0.670	6.03	0.134	0.360	0.047	0.292	0.043	0.292	0.043	0.292	0.043	4.59	7.38	9.58	28.0	61.3	73.4	40.0	1.47	0.824	1.50	0.579	14.5			
PG 6.13-9L	1.24	1.781	15.8	1.29	284	0.071	0.009	1.90	6.62	0.538	2.4	0.826	0.215	0.796	0.123	0.662	6.29	0.137	0.371	0.048	0.300	0.044	0.300	0.044	0.300	0.044	4.39	5.00	5.20	27.0	42.1	395	46.9	1.48	0.829	1.52	0.594	15.2			
PG 6.13-10L	9.00	933	19.8	1.27	165	0.058	0.027	1.90	7.97	0.293	1.73	0.462	0.466	0.594	0.099	0.593	5.46	0.118	0.327	0.044	0.275	0.040	0.275	0.040	0.275	0.040	4.27	4.82	8.79	27.8	24.0	283	46.3	0.980	1.01	1.28	0.456	9.11			
PG 6.13-11L	0.479	70.773	19.830	1.215	51	0.173	0.040	0.73	1.449	0.179	0.74	0.192	0.083	0.244	0.089	0.125	1.29	0.045	0.115	0.016	0.097	0.014	0.097	0.014	0.097	0.014	3.057	3.2	4.17	30.95	8.10	16.1	28.8	0.970	1.01	1.28	0.589	4.5			
PG 6.13-12L	2.51	483.9	18	1.02	778	0.10	0.025	2.0	5.9	0.50	2.1	0.56	0.179	0.69	0.120	0.66	5.75	0.129	0.353	0.046	0.285	0.042	0.285	0.042	0.285	0.042	4.4	4	5.5	28.8	28.85	93.8	44.5	1.44	0.880	1.422	0.56	13.6			
PG 6.13-13L	1.04	2.737.4	29.8	1.71	107.4	0.050	0.023	0.982	2.18	0.298	1.296	0.375	0.113	0.451	0.076	0.450	2.59	0.091	0.288	0.030	0.189	0.028	0.189	0.028	0.189	0.028	5.93	4.57	6.201	44.9	14.67	25.68	28.4	0.92	1.028	1.30	0.50	6.80			
PG 6.13-14L	4.05	259.88	12.81	0.962	293	0.054	0.024	1.95	4.12	0.528	2.34	0.652	0.888	0.795	0.330	0.778	6.98	0.133	0.417	0.052	0.325	0.046	0.325	0.046	0.325	0.046	4.90	4.85	5.584	30.3	25.461	114.990	46.6	0.997	0.99	1.34	0.52	12.5			
PG 6.13-15L	4.98	628.721	17.842	0.847	47.498	0.014	0.016	0.546	1.211	0.159	0.696	0.202	0.020	0.143	0.041	0.136	1.362	0.046	0.125	0.016	0.103	0.014	0.103	0.014	0.103	0.014	3.037	2.694	3.556	26.225	17.739	30.464	29.609	0.963	1.008	1.166	0.493	3.68			
PG 6.13-16L	0.174	10.89	6.48	0.39	146.782	0.38	0.07	16.06	2.76	1.18	4.90	0.83	0.0	1.12	0.06	0.97	12.42	0.21	0.59	0.07	0.41	0.06	0.41	0.06	0.41	0.06	0.33	27.889	7.74	12.79	0.957	87.74	98.49	0.28	1.50	1.10	0.93	29.53			
PG 6.13-17L	0.174	10.89	6.48	0.39	146.782	0.38	0.07	16.06	2.76	1.18	4.90	0.83	0.0	1.12	0.06	0.97	12.42	0.21	0.59	0.07	0.41	0.06	0.41	0.06	0.41	0.06	0.33	27.889	7.74	12.79	0.957	87.74	98.49	0.28	1.50	1.10	0.93	29.53			
PG 6.13-18L	0.172	0.753	300	0.014	342	0.111	0.304	0.272	0.221	0.020	0.120	0.006	0.466	0.031	0.005	0.029	0.365	0.006	0.000	0.003	0.019	0.003	0.003	0.019	0.003	0.078	6.83	4.61	2.05	0.741	8.68	98.8	0.841	1.08	0.999	0.533	0.91				
PG 6.13-19L	0.172	0.753	300	0.014	342	0.111	0.304	0.272	0.221	0.020	0.120	0.006	0.466	0.031	0.005	0.029	0.365	0.0																							

Table S3: Isotopic compositions in leachates, bulk and detrital fractions of Pongola stromatolites and carbonate reference materials

name	$\delta^{13}\text{C(VPDB)}$	SE	$\delta^{18}\text{O(VPDB)}$	SE	CdID $\mu\text{g/g}$	$\delta^{112}\text{Cd}$	2SD	$\delta^{112}\text{Cd}_{\text{auth}}$	Cd _{auth} $\mu\text{g/g}$	Cd _{det} $\mu\text{g/g}$	BaID $\mu\text{g/g}$	$\delta^{138}\text{Ba}$	2SD	Ni $\mu\text{g/g}$	$\delta^{60}\text{Ni}$	2SD
PG 6.1a-1 leach	1.96	0.08	-15.19	0.09							7.95	0.21	0.04	88	0.10	0.03
PG 6.1a-2 leach	2.15	0.05	-15.57	0.04							3.21	0.17	0.04	120	-0.01	0.03
PG 6.1a-3 leach	2.07	0.05	-15.81	0.07	1.18	0.19	0.038	0.19	1.18	0.00001	2.79	0.16	0.04	17.1	-0.04	0.03
PG 6.1a-4 leach	1.93	0.07	-15.57	0.05	3.44	0.058	0.027	0.06	3.44	0.00002	3.55	0.19	0.04	27.8	0.06	0.02
PG 6.1b-1 leach	1.98	0.06	-15.49	0.06							3.41	0.19	0.04	126	0.12	0.12
PG 6.1b-2 leach	2.01	0.11	-16.3	0.07							7.17	0.24	0.04	505	-0.04	0.12
PG 6.1b-3 leach	1.97	0.07	-16.35	0.08	2.89	0.059	0.034	0.06	2.89	0.00001	5.02	0.19	0.04	75.6	0.01	0.04
PG 6.1b-4 leach	1.99	0.04	-15.1	0.09	4.11	0.040	0.035	0.04	4.11	0.00002	3.61	0.16	0.04	174	0.09	0.02
PG 6.1b-4# leach					5.11	0.068	0.038	0.07	5.11	0.00002						
6.1a-3 detritus					1.30	-0.015	0.04	-0.02	1.30	0.0011						
6.1a-4 detritus					2.72	-0.015	0.038	-0.02	2.72	0.0009						
6.1b-4 detritus					0.90	-0.002	0.023	0.00	0.900	0.0031						
6.1a-1 bulk					4.21	0.22	0.045	0.22	4.21	0.00061						
6.1a-2 bulk					1.74	0.34	0.081	0.34	1.74	0.00018						
6.1b-1 bulk					2.83	0.096	0.068	0.10	2.83	0.00007						
6.1b-1# bulk					3.44	0.076	0.02	0.08	3.44	0.00015						
JD0-1.1 leach	4.91	0.05	-4.52	0.07	0.55	0.30	0.066	0.3	0.550		2.8	0.333	0.04			
JD0-1.2 leach					0.55	0.39	0.094	0.39	0.551							
JLs-1.1 leach	2.03	0.04	-4.5	0.07	0.15	-0.21	0.012	-0.21	0.146		48.7	0.027	0.04			
JLs-1.2 leach					0.15	-0.20	0.07	-0.2	0.150							
CAL-5.3 leach	2.87	0.04	-4.27	0.06	0.30	0.17	0.024	0.13	0.299							
CAL-5.4 leach					0.30	0.13	0.04	0.13	0.302							

SI references

Paton, C., Hellstrom, J., Paul, B., Woodhead, J. and Hergt, J. (2011) Lolite: Freeware for the visualisation and processing of mass spectrometric data. *Journal of Analytical Atomic Spectrometry*. doi:10.1039/c1ja10172b.

Woodhead, J., Hellstrom, J., Hergt, J., Greig, A. & Maas, R (2007) Isotopic and elemental imaging of geological materials by laser ablation Inductively Coupled Plasma mass spectrometry. *Journal of Geostandards and Geoanalytical Research*, 31, p. 331-343.

1. S. V. Hohl, S. J. G. Galer, A. Gamper, H. Becker, Cadmium isotope variations in Neoproterozoic carbonates - A tracer of biologic production? *Geochem Perspectives Lett*, 32–44 (2016).
2. Y.-B. Lin, *et al.*, Accurate Determination of Barium Isotopic Compositions in Sequentially Leached Phases from Carbonates by Double Spike-Thermal Ionization Mass Spectrometry (DS-TIMS). *Anal Chem* 92, 2417–2424 (2019).
3. P. Dulski, Interferences of oxide, hydroxide and chloride analyte species in the determination of rare earth elements in geological samples by inductively coupled plasma-mass spectrometry. 350, 194–203 (1994).
4. M. G. Lawrence, B. S. Kamber, The behaviour of the rare earth elements during estuarine mixing—revisited. 100, 147–161 (2006).
5. S. Viehmann, *et al.*, Metal cycling in Mesoproterozoic microbial habitats: Insights from trace elements and stable Cd isotopes in stromatolites. *Gondwana Res* 67, 101–114 (2019).
6. R. L. Rudnick, S. G. T. crust, 2003, Composition of the continental crust.
7. A.-D. Schmitt, S. J. G. Galer, W. Abouchami, Mass-dependent cadmium isotopic variations in nature with emphasis on the marine environment. *Earth and Planetary Science Letters* 277, 262–272 (2009).
8. H. Pickard, *et al.*, The cadmium and zinc isotope compositions of the silicate Earth – implications for terrestrial volatile accretion. *Geochim Cosmochim Acta* (2022) <https://doi.org/10.1016/j.gca.2022.09.041>.

9. V. Cameron, D. Vance, C. Archer, C. H. House, A biomarker based on the stable isotopes of nickel. *Proceedings of the National Academy of Sciences* 106, 10944–10948 (2009).
10. B. Gueguen, O. Rouxel, E. Ponzevera, A. Bekker, Y. Fouquet, Nickel Isotope Variations in Terrestrial Silicate Rocks and Geological Reference Materials Measured by MC-ICP-MS. *Geostand Geoanal Res* 37, 297–317 (2013).
11. W.-Y. Li, *et al.*, Barium isotopic composition of the mantle: Constraints from carbonatites. *Geochim Cosmochim Acta* 278, 235–243 (2020).
12. X.-Y. Nan, *et al.*, Barium isotopic composition of the upper continental crust. 233, 33–49 (2018).
13. R. M. Gaschnig, *et al.*, Onset of oxidative weathering of continents recorded in the geochemistry of ancient glacial diamictites. *Earth Planet Sc Lett* 408, 87–99 (2014).
14. S.-J. Wang, R. L. Rudnick, R. M. Gaschnig, H. Wang, L. E. Wasylenki, Methanogenesis sustained by sulfide weathering during the Great Oxidation Event. *Nat Geosci* 12, 296–300 (2019).
15. K. P. Jochum, *et al.*, Nano-Powdered Calcium Carbonate Reference Materials: Significant Progress for Microanalysis? 124, 1–15 (2019).
16. C. Paton, J. Hellstrom, B. Paul, J. Woodhead, J. Hergt, Iolite: Freeware for the visualisation and processing of mass spectrometric data. 26, 2508–11 (2011).
17. J. Woodhead, J. Petrus, Exploring the advantages and limitations of in situ U–Pb carbonate geochronology using speleothems. *Geochronol* 1, 69–84 (2019).
18. R. Bolhar, A. Hofmann, M. Siahi, Y. Feng, C. Delvigne, A trace element and Pb isotopic investigation into the provenance and deposition of stromatolitic carbonates, ironstones and associated shales of the ~ 3.0 Ga Pongola Supergroup, Kaapvaal Craton. *Geochimica et Cosmochimica Acta* 158, 57–78 (2015).
19. M. Bau, P. Dulski, Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa (1996) [https://doi.org/10.1016/0301-9268\(95\)00087-9](https://doi.org/10.1016/0301-9268(95)00087-9).