Supplementary File: Duration and nature of the end-Cryogenian (Marinoan) glaciation

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U-Pb geochronology

U-Pb dates were obtained by the chemical abrasion isotope dilution thermal ionisation mass spectrometry (CA-ID-TIMS) method on selected single zircon grains (Tables 1 and 2), extracted from an aliquot of Sample DW-1 and NAV-00-2B. Sample DW-1 is located at 15.14693E 20.20940S; Sample NAV-00-2B was reported in Hoffmann et al. (2004).

Zircon grains were isolated from the rock sample using standard magnetic and density separation techniques, annealed in a muffle furnace at 900°C for 60 hours in quartz beakers. Zircon crystals, selected for analyses based on external morphology, were transferred to 3 ml Teflon PFA beakers, washed in dilute HNO_3 and water, and loaded into 300 µl Teflon PFA microcapsules. Fifteen microcapsules were placed in a large-capacity Parr vessel, and the crystals partially dissolved in 120 µl of 29 M HF for 12 hours at 180°C. The contents of each microcapsule were returned to 3 ml Teflon PFA beakers, the HF removed and the residual grains immersed in 3.5 M HNO3, ultrasonically cleaned for an hour, and fluxed on a hotplate at 80°C for an hour. The HNO_3 was removed and the grains were rinsed twice in ultrapure H_2O before being reloaded into the same 300 µl Teflon PFA microcapsules (rinsed and fluxed in 6 M HCl during crystal sonication and washing) and spiked with the EARTHTIME mixed ^{233}U-^{235}U-^{205}Pb-^{202}Pb tracer solution (ET2535). These chemically abraded grains were dissolved in Parr vessels in 120 µl of 29 M HF with a trace of 3.5 M HNO_3 at 220°C for 60 hours, dried to fluorides, and then re-dissolved in 6 M HCl at 180°C overnight. U and Pb were separated from the zircon matrix using an HCl-based anion exchange chromatographic procedure[1] eluted together and dried with 2 µl of 0.05N H_3PO_4.

Pb and U were loaded on a single outgassed Re filament in 5 µl of a silica-gel/phosphoric acid mixture[2], and U and Pb isotopic measurements made on a Thermo Triton multi-collector thermal ionisation mass spectrometer equipped with an ion-counting SEM detector. Pb isotopes were measured by peak-jumping all isotopes on the SEM detector for 100 to 150 cycles. Pb mass fractionation was externally corrected using a mass bias factor of 0.14 ± 0.03%/a.m.u. determined via measurements of ^{202}Pb/^{205}Pb (ET2535)-spiked samples analysed during the same experimental period. Transitory isobaric interferences due to high-molecular weight organics, particularly on ^{204}Pb and ^{207}Pb, disappeared within approximately 30 cycles, and ionisation efficiency averaged 10^4 cps/pg of each Pb isotope. Linearity (to ≥1.4 x 10^6 cps) and the associated deadtime correction of the SEM detector were monitored by repeated analyses of NBS982, and have been constant since installation in 2006. Uranium was analysed as UO_2+ ions in static Faraday mode on 10^{12} ohm resistors for 150 to 200 cycles, and corrected for isobaric interference of $^{233}U^{18}O^{16}O$ on $^{235}U^{16}O^{16}O$ with an $^{18}O/^{16}O$ of 0.00206. Ionisation efficiency averaged 20 mV/ng of each U isotope. U mass fractionation was corrected using the known $^{233}U/^{235}U$ ratio of the ET2535 tracer solution.

Data reduction was done using the open-source ET Redux system[3,4] using the algorithms of McLean et al.[4], ET2535 tracer solution[5,6] and U decay constants recommended by Jaffey et al.[7]. A value of 138.818 ± 0.045 was used for the $^{238}U/^{235}U_{zircon}$ based upon the work of[8] whereas a value of 137.88 was used in the prior study[20] study. $^{206}Pb/^{238}U$ ratios and dates were corrected for initial ^{230}Th disequilibrium using a Th/U[magma] = 3 ±1 resulting in an increase in the $^{206}Pb/^{238}U$ dates of ~0.09 Myr (no Th correction was made for date presented in Hoffmann et al.[9]. All common Pb in analyses was attributed to laboratory blank and subtracted based on the measured laboratory Pb isotopic composition and associated uncertainty. U blanks were estimated at 0.1 pg, based upon replicate total procedural blanks.

In this manuscript the date uncertainties reporting is as A/B/C and reflect the following sources: (A) analytical, (B) analytical + tracer solution and (C) analytical + tracer solution + decay constants. The A uncertainty is the internal error based on analytical uncertainties only, including counting statistics, subtraction of tracer solution, and blank and initial common Pb subtraction. It is given at the 2σ confidence interval. This error should be considered when comparing our date with $^{206}Pb/^{238}U$ dates from other laboratories that used the same EARTHTIME tracer solution or a tracer solution that was cross-calibrated using related gravimetric reference materials. The B uncertainty includes uncertainty in the tracer calibration and should be used when comparing our dates with those derived from laboratories that did not use the same EARTHTIME tracer solution or a tracer solution that was cross-calibrated using relatable gravimetric reference material[9,10]. The C uncertainty includes A and B in addition to uncertainty in the ^{238}U decay constant[7]. This uncertainty level should be used when comparing our dates with those derived from other decay schemes (e.g. $^{40}Ar/^{39}Ar$, ^{187}Re-^{187}Os).

Ten zircon U-Pb dates were obtained and are presented in Supplementary Table 1 (and Figure 6A of the main paper). All dates are concordant and yield a weighted mean ^{207}Pb/^{206}Pb date of 639.1 ± 1.7/1.8/5.0 Ma (MSWD = 0.38, n = 10). The U-Pb data for this same sample dataset is not so simple and does not form a coherent population and yield an MSWD that indicates excess scatter. One fraction (z16) is distinctly younger than the main cluster (see Fig. 6A main paper) and is considered to reflect residual Pb-loss. The remaining nine data points yield a weighted mean ^{206}Pb/^{238}U date of 639.59±0.42 Ma (internal uncertainties only 95% conf., MSWD = 6.4), but with an MSWD value that still indicates excess scatter. Evaluation of this dataset shows a strong clustering around 639.5 Ma and yield a weighted mean ^{206}Pb/^{238}U date of 639.29 ± 0.26/0.31/0.75 Ma (95% conf. MSWD = 2.6). We consider this to be the best approximation of the zircon population within sample DW-1 that best represents the timing of eruption, and hence the age for the stratigraphic level at which DW-1 was sampled within the Ghaub Formation.

Fifteen zircon U-Pb dates are presented in Table 1 and are presented graphically in Figure 6A of the main paper. A coherent set of ^{207}Pb/^{206}Pb dates yield a weighted mean ^{207}Pb/^{206}Pb date of 634.8 ± 1.5/1.7/4.9 Ma (MSWD = 0.96, n = 15). The U-Pb data for this same sample dataset is also not so simple and does not form a coherent population. One fraction (z12) is normally discordant with a younger U-Pb age indicating Pb-loss and is disregarded from further discussion. The remaining fractions have ^{238}U/^{206}Pb dates that do not overlap and there is no correlation with ^{207}Pb/^{238}U dates such that the data form a short linear array that plots across the concordia band (defined by the ^{235}U and ^{238}U decay constants uncertainties[7]), with two values reversely discordant. Based upon analyses of chemically abraded zircon data we would expect closed system zircon to plot towards the lower limits of the concordia uncertainty band[11,12]. However, in this data set, analyses plot from this region towards and across the upper uncertainty bound (see Fig. 6A in the main paper). Based upon long-term reproducibility of U-Pb data from the NIGL ID-TIMS laboratory, and coherent U-Pb data obtained for a high proportion of samples analysed, we suggest this variation is real and not an artefact of mass spectrometry and that this reflects real U/Pb variation in the analysed sample (which has been annealed and leached). One option is that the older U-Pb dates reflecting analyses of pre-eruptive zircon, and the apparent lack of corresponding variation in the ^{207}Pb/^{206}Pb dates is due to being obscured by their larger uncertainties. An alternative is that the analyses with older ^{238}U/^{206}Pb dates are from a single concordant age population and that these older dates reflect un-supported radiogenic Pb. Whilst this is unlikely to occur at a bulk level (i.e., single crystal) it is possible that in zircons with fine scale U zonation redistribution of radiogenic Pb occurs at the sub-micron level[13,14], which is then enhanced by the thermal annealing and chemical leaching process[15]. This possibility requires further investigation.

Either of these scenarios for explaining the scatter in the NAV-00-2B U-Pb require an interpretive framework where the younger dates are considered to most closely reflect the age of the erupted zircons and inferentially the age of the ash layer. This in turn requires the subjective selection of a date from which to derive an interpreted age for the sample. In Figure 1 we show a number of viable interpretations for this sample, selecting different sub-populations from the cluster of youngest dates. Our preferred interpreted date is Interpretation B, a weighted mean $^{206}Pb/^{238}U$ date based upon the youngest five dates: 635.21 ± 0.59/0.61/0.92 Ma (95% conf. MSWD = 3.4). We consider this to be the best approximation of the zircon population within sample NAV-00-2B that best represents the timing of eruption, and hence the age for the stratigraphic level at which NAV-00-2B was sampled within the Ghaub Formation. Each of the other alternative interpreted ages (Fig. 1) overlap with each other and thus the choice of interpreted date has no significant impact. We consider that alternative interpretations based upon the older age (ca. 636.5 Ma) are much more difficult to justify as they require the cluster of concordant overlapping dates at ca. 635.5 Ma to be too young due to Pb-loss, which we consider highly unlikely.

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Supplementary File Table 1. U-Pb analyses of Sample DW-1.

Table 1. U-Pb geochronology data for Sample DW-1

Mean = 639.29±0.26 [0.041%] 95% conf.
Wtd by data-pt errs only, 0 of 9 rej.
MSWD = 2.6, probability = 0.008

DW-1	Dates (Ma)								Composition			
Fraction	206Pb/ 238U a	±2σ abs	207Pb/ 235U a	±2σ abs	207Pb/ 206Pb a	±2σ abs	Corr. coef.	% disc b	Th/ U c	Pb* (pg) d	Pbc (pg) e	Pb*/ Pbc f
Zircon												
z4	639.8913333	0.593356873	[illegible]	[illegible]	[illegible]3143716	5.254532308	0.46132761	-0.090246937	0.327013873	11.0945386	0.319776778	34.69463498
z11	639.9597341	0.61116763	[illegible]	[illegible]	[illegible]0903181	4.419005959	0.444784829	0.176353311	0.333060166	38.57476318	1.064909851	36.22350112
z16	~~637.4957221~~	~~0.40515678~~	[illegible]	[illegible]	[illegible]6570565	3.932135184	0.35297439	0.493451899	0.32174235	19.93618539	0.43823687	45.49180309
z17	639.0061232	0.303639676	[illegible]	[illegible]	[illegible]0301121	5.005617457	0.249856013	-0.152972577	0.323888831	30.22943263	0.902513177	33.49472718
z21	638.8758748	0.477552232	638.4905503	1.058814803	637.1271885	4.310621783	0.454308748	-0.274464237	0.30921582	13.59503911	0.288702932	47.09006243
z22	639.6185865	0.385317862	639.3808723	1.567990007	638.5409702	6.992279451	0.18125451	-0.168762282	0.323381833	12.20140233	0.5066661	24.08174208
z24	639.3983143	0.357451224	639.2112335	0.995533127	638.5500308	4.275124401	0.324633254	-0.132845268	0.303400454	12.45031276	0.298627603	41.69176809
z25	639.0243525	0.437395676	639.3931888	1.951032642	640.6967066	8.618269804	0.231042999	0.26102117	0.317045465	13.53249896	0.744581906	18.17462772
z26	639.1746318	0.395637107	639.8462088	1.663527279	642.2181997	7.280926619	0.270989422	0.473914918	0.322849444	9.54954437	0.394464528	24.20887988
z27	639.3743696	0.518935497	639.9054507	3.063162745	641.7809117	13.69295819	0.163923419	0.374978758	0.322526696	18.45161327	1.643269872	11.22859585

	Isotopic Ratios								
	206Pb/ 204Pb g	206Pb/ 238U h	±2σ %	207Pb/ 235U h	±2σ %	207Pb/ 206Pb h	±2σ %	208Pb/ 232Th h	±2σ %
z4	2191.901766	0.104356865	0.097406106	0.877744978	0.273430886	0.0610295	0.242138987	-	-
z11	2283.914697	0.104368583	0.100319739	0.878568751	0.229445772	0.061079918	0.202943566	-	-
z16	2872.317701	0.103946541	0.066748714	0.874839743	0.195417113	0.061067613	0.179965816	-	-
z17	2118.54203	0.104205227	0.049911498	0.875946448	0.240065945	0.060993075	0.23040829	-	-
z21	2982.862756	0.104182917	0.078514014	0.875391464	0.223398226	0.060967484	0.197704085	-	-
z22	1528.448508	0.104310141	0.063279853	0.877036592	0.330497673	0.061007561	0.323425933	-	-
z24	2647.031	0.104272408	0.058722617	0.876723024	0.209876385	0.061007818	0.19607984	-	-
z25	1159.850691	0.10420835	0.07189601	0.87705936	0.411228915	0.061068739	0.399461002	-	-
z26	1536.499467	0.104234091	0.065017487	0.877897009	0.350451737	0.061111967	0.337115973	-	-
z27	722.4353758	0.104268306	0.08525453	0.878006577	0.645267067	0.061099539	0.636046517	-	-

a Isotopic dates calculated using the decay constants λ238 = 1.55125E-10 and λ235 = 9.8485E-10 (Jaffey et al. 1971).
b % discordance = 100 - (100 * (206Pb/238U date) / (207Pb/206Pb date))
c Th contents calculated from radiogenic 208Pb and the 230Th-corrected 206Pb/238U date of the sample, assuming concordance between the U-Pb and Th-Pb systems.
d Total mass of radiogenic Pb.
e Total mass of common Pb.
f Ratio of radiogenic Pb (including 208Pb) to common Pb.
g Measured ratio corrected for fractionation and spike contribution only.
h Measured ratios corrected for fractionation, tracer and blank.

Supplementary File Table 2. U-Pb analyses of Sample NAV-00-2B.

Table 2. U-Pb geochronology data table for Sample NAV-00-2B

Mean = 635.48±0.53 [0.083%] 95% conf.
Wtd by data-pt errs only, 0 of 7 rej.
MSWD = 5.1, probability = 0.000

MSWD = 1.9, probability = 0.13

NAV-00-2B	Dates (Ma)								Composition			
Fraction	206Pb/ 238U a	±2σ abs	207Pb/ 235U a	±2σ abs	207Pb/ 206Pb a	±2σ abs	Corr. coef.	% disc b	Th/ U c	Pb* (pg) d	Pbc (pg) e	Pb*/ Pbc f
Zircon												
~~z1~~	~~630.325841~~	~~1.427257764~~	~~632.3425419~~	~~1.500599293~~	~~639.5593176~~	~~4.16779408~~	~~0.795684556~~	~~1.443724817~~	~~0.98958822~~	~~25.95531637~~	~~0.244748012~~	~~106.0491409~~
z2	**634.8152933**	**0.361089668**	[illegible]	[illegible]	[illegible]229458	3.268830557	0.442587284	0.111349646	0.781902518	32.11375832	0.488536297	65.73464149
z3	**635.0074513**	**0.616782193**	[illegible]	[illegible]	[illegible]642267	11.02132127	0.224344287	-0.481550138	0.836137413	29.01789356	1.796549443	16.152015
z4	**635.1102299**	**1.041523352**	[illegible]	[illegible]	[illegible]918621	5.189286138	0.552189166	-0.081685227	0.914774793	9.246059087	0.185963632	49.71971655
z5	**635.4811482**	**0.480901223**	[illegible]	[illegible]	[illegible]428952	6.55450615	0.261349317	0.44830873	0.921515449	24.2462356	0.818413401	29.62590246
z6	**635.9269141**	**0.537359089**	[illegible]	[illegible]	[illegible].7631766	4.551318296	0.3880762	-0.34141104	0.689124473	17.39778845	0.399523434	43.54635294
z7	636.0251646	0.491656154	636.4320058	1.569225339	637.8769387	6.814527199	0.304270314	0.290302723	0.793830482	20.44741294	0.770848267	26.52585963
z8	636.0837863	0.465091109	636.9009847	1.969787668	639.8016166	8.951018375	0.094388782	0.58109111	0.688131315	21.51517978	1.116393504	19.27203956
z9	636.4896941	0.346890026	636.6197383	1.05222859	637.0814001	4.612233493	0.268022026	0.092877607	0.89792076	25.57007839	0.56140369	45.54668745
z10	636.5327889	0.450326407	636.9122513	2.014466507	638.2588544	8.926365678	0.231526821	0.270433457	1.003725792	29.83487454	1.432269794	20.83048505
z11	636.5415143	0.530421956	636.3381731	1.125291111	635.6160755	5.042806223	0.225758259	-0.145597133	0.99329867	14.90304587	0.203369322	73.28069793
z12	636.6413477	0.907141109	635.5496194	1.665459327	631.6691892	6.851032134	0.431192877	-0.787145967	0.688643899	8.542737957	0.259901246	32.86916894
z13	637.0590132	0.742630458	636.914865	1.878832927	636.4034476	7.940933599	0.375616243	-0.103011012	0.889628354	27.29746509	0.783902052	34.8225458
z14	637.2110942	0.904405834	635.060404	1.952228537	627.413444	6.212033955	0.893290154	-1.56159392	0.927082525	11.04128128	0.315825711	34.96004566
z15	638.9526717	0.97786515	637.5635782	1.842922873	632.6433353	7.314631558	0.495113811	-0.997297539	1.018274826	9.36347568	0.244435542	38.30652286

	Isotopic Ratios								Fraction
	206Pb/ 204Pb g	206Pb/ 238U h	±2σ %	207Pb/ 235U h	±2σ %	207Pb/ 206Pb h	±2σ %	208Pb/ 232Th h	±2σ %
~~z1~~	~~5657.914072~~	~~0.102719384~~	~~0.237682284~~	~~0.864070528~~	~~0.318821774~~	~~0.06103645~~	~~0.191054195~~	—	—
z2	3688.313952	0.103487614	0.059727721	0.868901235	0.168555117	0.060922052	0.148389858	-	-
z3	908.4355099	0.103520508	0.101992359	0.867741875	0.524910654	0.060821432	0.510749441	-	-
z4	2708.596134	0.103538102	0.1722019	0.868949178	0.288743899	0.060895704	0.238887211	-	-
z5	1618.630386	0.1036016	0.079466399	0.870998998	0.315635823	0.061001944	0.302957196	-	-
z6	2504.826885	0.103677916	0.088736539	0.869787694	0.229380104	0.060872268	0.20891154	-	-
z7	1494.863496	0.103694737	0.081177473	0.871593226	0.331858556	0.060988733	0.315085512	-	-
z8	1118.756286	0.103704774	0.076784578	0.872457866	0.416348587	0.061043327	0.414921316	-	-
z9	2492.366572	0.103774273	0.057235328	0.871939294	0.222477296	0.060966187	0.211893889	-	-
z10	1122.441766	0.103781652	0.07429709	0.872478643	0.425786815	0.060999561	0.413664883	-	-
z11	3912.570586	0.103783146	0.08751051	0.871420278	0.238000926	0.060924688	0.232058769	-	-
z12	1895.423855	0.10380024	0.149640369	0.869967484	0.352561718	0.060813101	0.316460832	-	-
z13	1913.492038	0.103871757	0.122426573	0.872483463	0.397117512	0.060946982	0.367586862	-	-
z14	1904.844159	0.1038978	0.149062248	0.869066744	0.413497059	0.060693092	0.286414064	-	-
z15	2042.545659	0.104196072	0.160751715	0.873680147	0.389242486	0.060840616	0.338147365	-	-

a Isotopic dates calculated using the decay constants λ238 = 1.55125E-10 and λ235 = 9.8485E-10 (Jaffey et al. 1971).
b % discordance = 100 - (100 * (206Pb/238U date) / (207Pb/206Pb date))
c Th contents calculated from radiogenic 208Pb and the 230Th-corrected 206Pb/238U date of the sample, assuming concordance between the U-Pb and Th-Pb systems.
d Total mass of radiogenic Pb.
e Total mass of common Pb.
f Ratio of radiogenic Pb (including 208Pb) to common Pb.
g Measured ratio corrected for fractionation and spike contribution only.
h Measured ratios corrected for fractionation, tracer and blank.

Supplementary File Figure 1. U-Pb concordia diagram for zircon analyses of Sample NAV-00-2B.