In situ U-Pb dating of 4 billion year old carbonates in the martian meteorite Allan Hills 84001

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Abstract. *In situ* carbonate U-Pb dating studies have proliferated dramatically in recent years. Almost all these studies have targeted relatively young terrestrial calcite up to Carboniferous in age. To assess the robustness of the carbonate U-Pb chronometer in deep-time, we carried out *in situ* U-Pb analyses in magnesite-ankerite-calcite carbonates in the martian meteorite Allan Hills (ALH) 84001. Carbonates in ALH 84001 formed at *ca*. 3.94 Ga, and there is little evidence that much happened to this rock since then, making it an ideal sample to test the robustness of the U-Pb system in old carbonates. We obtained a concordant date of 3941 ± 49/110 Ma (n = 14, MSWD = 2.0), which is identical to the step-leaching Rb/Sr date determined previously. These results thus confirm that old carbonates are amenable to U-Pb dating in samples that have had a relatively simple history post-carbonate formation.

1 Introduction

Analytical developments in laser ablation – inductively coupled plasma mass spectrometry (LA-ICP-MS) over the last decade have driven important progress in *in situ* dating of carbonates, and in particular of calcite and occasionally dolomite, using the radioactive decay of uranium (U) into lead (Pb) (see the recent review by Roberts *et al.*, 2020, for example). Indeed, biogenic, diagenetic, and vein carbonates can typically incorporate up to *ca*. 10-20 µg/g U, and up to *ca*. 100 µg/g U in speleothems (e.g., Roberts *et al.*, 2020). Carbonates typically also incorporate initial Pb, meaning that multiple analyses on carbonate samples often yield linear arrays in a Tera-Wasserburg inverse concordia diagram, providing information on both the $^{207}Pb/^{206}Pb$ composition of the initial Pb and the age of formation of the carbonates. Recent applications of carbonate U-Pb dating using LA-ICP-MS include constraining the timing of sedimentation, lithification, and diagenesis (e.g., Drost *et al.*, 2018; Godeau *et al.*, 2018; Mueller *et al.*, 2020; Brigaud *et al.*, 2021), faulting (e.g., Ring and Gerdes, 2016; Roberts and Walker, 2016; Goodfellow *et al.*, 2017; Nuriel *et al.*, 2017; 2019; Hansman *et al.*, 2018; Beaudoin *et al.*, 2018; Holdsworth *et al.*, 2019; Smeraglia *et al.*, 2019), aragonite to calcite conversion in ammonites (Li *et al.*, 2014), alteration of oceanic crust (Coogan *et al.*, 2016), veining, hydrothermalism, and mineralisation (Burisch *et al.*, 2017; 2018; Parrish *et al.*, 2018; Walter *et al.*, 2018; Bertok *et al*., 2019; Drake *et al.*, 2019; 2020; MacDonald *et al*., 2019), palaeoclimate reconstructions (Nicholson *et al.*, 2020), and hominin dispersion (Scardia *et al.*, 2019), for example.

All these *in situ* studies have targeted relatively young samples (younger than *ca*. 465 Ma), with two-third of dates younger than 50 Ma, and all but three younger than 300 Ma (Supplementary Table S1). This is consistent with the accepted idea that carbonates are not very resistant to resetting of their U-Pb isotope systematics when thermal- and/or fluid-related alteration events take place after their formation (e.g., Roberts *et al.*, 2020). However, a few studies have focused on dating older carbonate samples, using wet chemistry to isolate Pb isotopes, and obtained Pb/Pb isochron dates ranging between *ca*. 1.60 and 2.84 Ga (Moorbath *et al.*, 1987; Bau *et al.*, 1999; Ray *et al.*, 2003; Sarangi *et al.*, 2004; Farey *et al.*, 2013). These Pb/Pb dates have been interpreted as dating the deposition of these carbonates, suggesting that in some settings the Pb isotope systematics of carbonates can remain undisturbed for billions of years. To further assess the robustness of the carbonate U-Pb chronometer in deep time, we decided to attempt *in situ* LA-ICP-MS U-Pb dating of carbonates in the martian meteorite Allan Hills 84001 (ALH 84001). The formation of these carbonates has been dated at 3.94 ± 0.02 Ga (2σ) using Rb-Sr analyses on acid leachates via thermal ionisation mass spectrometry (Borg *et al.*, 1999; Beard *et al.*, 2013; date recalculated using a ^{87}Rb decay constant of 1.3972×10^{-11} a^{-1}; Villa *et al.*, 2015).

The meteorite ALH 84001 is an orthopyroxenite, a cumulate rock mostly comprising orthopyroxene, olivine, and chromite (e.g., Mittlefehldt, 1994), which formed 4.09 ± 0.03 Ga ago as suggested by Lu-Hf and Pb/Pb dating (Bouvier *et al.*, 2009; Lapen *et al*., 2010). Carbonate-rich areas are irregularly scattered throughout ALH 84001, appearing as spherical or hemispherical globules, discs along fractures, and irregular fillings in orthopyroxene (see review by Treiman (2021), and references therein). The patches of carbonates show strong compositional zoning ranging from calcite-rich to magnesite-siderite solid solution compositions (e.g., Corrigan and Harvey, 2004; Holland *et al*., 2005). These carbonates likely formed at low temperature (*ca*. 10-20 °C; Halevy *et al.*, 2011; del Real *et al.*, 2016) during fluid-rock interactions that were broadly contemporaneous with the main shock event recorded in ALH 84001 (e.g., Treiman, 2021). In order to test the robustness of the U-Pb system in *ca*. 4 Ga-old carbonates, it is essential to understand the geological history of those carbonates to assess whether there have been affected by any hydrous or other alteration event since their formation.

Dating carbonate-rich fractions in ALH 84001 using the Rb-Sr system yielded a precise formation age of 3.94 ± 0.02 Ga (2σ; Borg et al., 1999; Beard et al., 2013), which is consistent with a less precise Pb/Pb isochron corresponding to a date of 4.045 ± 0.090 Ga (2σ; Borg *et al.*, 1999). The formation of these carbonates occurred at low temperature (<20 °C) and likely involved mixing of two different water sources, one rich in Ca, the other rich in Fe (e.g., Halevy *et al.*, 2011, del Real *et al.*, 2016; Bridges *et al.*, 2019, Treiman, 2021). These carbonate-forming fluids equilibrated with the atmosphere at the time, unlike igneous minerals in the matrix (Shaheen *et al.*, 2015). A contemporaneous impact event raised the temperature of surrounding plagioclase to *ca*. 1400°C, melting it to produce glass, and faulting carbonate globules (Mittlefehldt, 1994). Following this, Treiman (2021) states *"there is little evidence that anything had happened to ALH84001 since 3.9Ga"*, until another impact event at *ca*. 14 Ma, which caused the progenitor material that formed ALH84001 to be ejected from Mars (Eugster *et al*., 1997). After *ca*. 14 Ma in space, ALH 84001 parent meteoroid fell to Antarctica *ca*. 13,000 years ago (Eugster *et al.*, 1997) and remained buried deep in the ice for millennia, only emerging at the surface of the Allan Hills ice field probably no more than 500 years ago (Krähenbühl *et al.*, 1998). Finally, there is extensive olivine and glass of plagioclase composition in ALH 84001 with no evidence of any alteration to clays or phyllosilicates. Modelling of Ar diffusion within the constituent minerals implies that the progenitor material for ALH 84001 was not subjected to temperatures >30 °C for any 'long duration' (Cassata *et al.*, 2010, Shuster and Weiss, 2005). All these lines of evidence indicate that the minerals in ALH 84001 were not exposed to hydrous fluids or temperatures >25-30 °C during the last 3.9 Ga (e.g., Treiman, 2021).

2 Studied sample

The studied polished section (Fig. 1) was derived from a chip of the ALH84001,287 allocation from the NASA Ancient Mars Meteorite Program. The section contains patches of carbonates, associated with chromite, in between larger orthopyroxene grains (Fig. 1). The carbonates display the range of compositions typical for ALH 84001 carbonates, from Mg-rich magnesite to Ca-rich calcite, with intermediate Fe-rich ankerite areas (Fig. 1). The Mg- and Fe-rich carbonates seem to be part of broken rosettes, while Ca-rich carbonates appear associated with maskelynite (Fig. 1).

3 Laser Ablation – Inductively Coupled Plasma Mass Spectrometer analyses

U-Pb analyses were carried out at the University of Manchester using a Teledyne Photon Machines Analyte Excite+ 193 nm ArF excimer laser ablation system equipped with a HelEx II active 2-volume ablation cell, coupled to an Agilent 8900 triple quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS) using a signal-smoothing device (see Supplementary Table S2 for a summary of the analytical setup and data processing procedure).

The material ablated from target carbonates was carried to the ICP-MS by high purity He, which was mixed with Ar before injection into the plasma source. High purity N_2 was added to the He stream at a flow rate of 2 mL/min to enhance sensitivity. Tuning of the ICP-MS and mass calibration were performed at the start of the analytical session by optimising the ion signals during ablation of the NIST SRM 612 reference glass, while maintaining $^{238}U^+/^{232}Th^+$ close to unity and minimising the $^{232}Th^{16}O^+/^{232}Th^+$ ratio (*ca*. 0.3%). Glass and carbonates were ablated using a 25 µm laser beam size, a fluence of 4 J/cm^2, and a repetition rate of 5 Hz. Each analyses lasted 50 s and was preceded by 30 s counting time of the gas blank (background). The masses analysed and corresponding dwell times are reported in Supplementary Table S2.

The reference glass NIST614 (0.823 µg/g U, 2.32 µg/g Pb; Jochum *et al.*, 2011) was used to correct for $^{207}Pb/^{206}Pb$ fractionation, while mass bias correction of the measured $^{238}U/^{206}Pb$ ratios was carried out using repeated analyses of the reference calcite WC-1, which has a thermal ionisation mass spectrometry (TIMS) age of 254.4 ± 6.4 Ma (Roberts *et al.*, 2017). To ensure accuracy, the Duff Brown Tank (DBT) calcite (64.0 ± 0.7 Ma; Hill *et al.*, 2016) and AUG-B6 calcite (43.0 ± 1.0 Ma; Pagel *et al.*, 2018) were also analysed and used as secondary reference materials. Since there is no U/Pb magnesite-ankerite carbonate reference material, we have to rely on using a calcite reference material to correct for U/Pb fractionation in ALH 84001 carbonates.

Data processing was carried out using Iolite v4.5, using the NIST614 glass as primary reference material to remove instrument baseline contributions, mass bias of Pb isotopes, and downhole fractionation and instrumental drift of $^{206}Pb/^{238}U$ ratios (Paton *et al.*, 2011). The reproducibility obtained on NIST614 for $^{207}Pb/^{206}Pb$ (±1.7%, n = 9, 95% confidence level) and $^{206}Pb/^{238}U$ (±1.6%, n = 9, 95% confidence level) ratios were propagated by quadrature addition into each analysis $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ individual uncertainties. Repeated analyses of the NIST612 glass yielded an average $^{207}Pb/^{206}Pb$ ratio of 0.871 ± 0.044 (n = 8, 2 standard deviation), which is within error of its known $^{207}Pb/^{206}Pb$ ratio of 0.90745 ± 0.00004 (Baker *et al.*, 2004).

The data obtained for the reference calcite WC-1 were then plotted in a Tera-Wasserburg diagram using IsoplotR (Vermeesch, 2018), and yielded a lower intercept uncorrected date of 255.2 ± 5.9 Ma (95% confidence level, MSWD = 1.1, n = 10) for a discordia anchored at the common $^{207}Pb/^{206}Pb$ ratio of 0.85 ± 0.04 determined by Roberts *et al.* (2017). To obtain the known intercept age of 254.4 ± 6.4 Ma for the WC-1 calcite, we applied a linear correction factor of 1.0031 to the measured $^{206}Pb/^{238}U$ ratios, which we also applied to all the samples analysed in the session, as is commonly done for carbonate U-Pb dating by LA-ICP-MS (e.g., Roberts *et al.*, 2017; Drost *et al.*, 2018; Kylander-Clark, 2020). All calculated dates are associated with two uncertainties, the first one including the random uncertainties for each analysis (internal uncertainties on measured $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ ratios and reproducibility on repeated NIST614 analyses), while systematic uncertainties (2.5% uncertainty on the WC-1 age, and 0.14% and 0.11% on the ^{235}U and ^{238}U decay constants, respectively; Jaffey *et al.*, 1971) are propagated by quadratic addition in the second one.

The data obtained on the DBT calcite yielded a lower intercept date of 64.9 ± 2.2/2.8 Ma (95% confidence level, MSWD = 2.9, n = 12) for a discordia anchored at a common $^{207}Pb/^{206}Pb$ ratio of 0.74 ± 0.02 calculated based on isotope dilution and multi-collector ICP-MS analyses (Hill *et al.*, 2016) (Supplementary Fig. S1). Because of its lower U abundance and younger age, the data obtained on the AUG-B6 calcite are less precise, yielding a concordia date of 40.8 ± 2.0/2.2 Ma (95% confidence level, MSWD concordance + equivalence = 2.2, n = 8) (Supplementary Fig. S1), which is identical to a $^{238}U/^{206}Pb$ weighted average date of 41.6 ± 2.1/2.3 Ma (95% confidence level, MSWD = 0.4, n = 8). All results are available in Supplementary Table S3.

4 Results

The carbonates analysed in ALH 84001 contain *ca*. 0.1-0.4 µg/g U and 0.1-0.5 µg/g Th (Table 1). When plotted in a Tera-Wasserburg $^{207}Pb/^{206}Pb$ vs. $^{238}U/^{206}Pb$ diagram, ALH 84001 carbonates yield a concordant date of 3941 ± 49/110 Ma (n = 14, MSWD = 2.0; Fig. 2A), which is identical to a weighted mean $^{207}Pb/^{206}Pb$ date of 3967 ± 56/113 Ma (n = 14, MSWD = 1.9;

Fig. 2B). In detail, the Mg-rich and Ca-rich carbonate analyses yield concordia dates of 3890 ± 72 Ma (2σ, MSWD = 1.5, *n* = 8) and 3995 ± 69 Ma (2σ, MSWD = 2.4, *n* = 6), respectively; U-Pb dates for these two carbonate compositions are, therefore, indistinguishable when uncertainties are considered. Carbonate analyses plot on the concordia curve, indicating that they do not contain appreciable amount of common Pb. This is consistent with the measured ^{204}Pb intensities that are within error of 0 counts per second, although it is fair to point out that this observation is qualitative, considering the large uncertainties associated with the ^{202}Hg, ^{204}(Hg+Pb), and calculated ^{204}Pb count rates (Table 1 and Supplementary Table S3). It is noteworthy that ^{202}Hg intensities in ALH 84001 carbonates are about an order of magnitude higher than in the terrestrial carbonate standards (Supplementary Table S3). This could indicate that martian carbonates contain higher Hg abundances than terrestrial carbonates. Alternatively, we think that this extra Hg likely originates from contamination of the ALH 84001 section by Au coating applied in the past for secondary ion mass spectrometry studies.

5 Discussion and implications

5.1 Comparison with previous ALH 84001 carbonate dating studies

In situ U-Pb dating of carbonates in ALH 84001 using LA-ICP-MS yields a concordia date of 3941 ± 49/110 Ma, which is identical to the carbonate step-leaching Rb-Sr isochron date of 3.94 ± 0.02 Ga (Borg *et al.*, 1999; Beard *et al.*, 2013) and the less precise Pb/Pb isochron date of 4.045 ± 0.090 Ga (Borg *et al.*, 1999). Before propagating the ±2.5% uncertainty associated with the age of the primary U-Pb reference carbonate WC-1, and the uncertainties associated with the ^{238}U and ^{235}U decay constants, the carbonate U-Pb concordia date is associated with a fairly precise 2σ uncertainty of ±1.2%, which increases to ±2.8% when all uncertainties are propagated. This suggests that *in situ* U-Pb dating of carbonates has the potential to yield precise dates, but also highlights the need to reduce uncertainties on reference materials. Our LA-ICP-MS results also indicate that using a calcite primary reference material for correcting U/Pb fractionation in Mg- and Fe-rich carbonate matrices, such as magnesite and ankerite, produce accurate dates (within the obtained uncertainties). A final point worth highlighting is the fact that carbonates in ALH 84001 do not contain appreciable amount of common Pb, as indicated by their concordant U-Pb date of *ca*. 3.94 Ga. This is unusual, as in most examples in terrestrial system carbonates, do contain common Pb incorporated during their crystallisation (e.g., Roberts *et al.*, 2020). This observation suggests that the fluids from which ALH 84001 carbonates formed contained very little Pb.

5.2 Robustness of the carbonate U-Pb chronometer and further applications

Our *in situ* LA-ICP-MS analyses confirm that carbonates in ALH 84001 formed *ca*. 3.94 Ga-ago, and that the U-Pb chronometer in these carbonates has remained closed to any disturbance event since they formed. This is consistent with the suggestion that not much happened to ALH 84001 between 3.9 Ga and its launch from Mars 14 Ma-ago (Treiman, 2021), and indicates that this latter event did not reset the carbonate U-Pb chronometer. From the evidence summarised in section 1, Treiman (2021) concluded that minerals in ALH 84001, including the carbonates, have neither experienced temperatures in excess of *ca*. 25°C nor exposure to any hydrous fluids since 3.9 Ga, leading to the conclusion that the climate of Mars has remained globally cold and dry since then. Any aqueous events occurring on Mars due to a globally warmer and wetter climate therefore took place before 3.9 Ga. Heating and aqueous alteration events due to meteoroid impacts could have occurred at any time but these would have been strictly localised. Our U-Pb data back-up the view that the carbonates in ALH 84001 have not experienced any alteration since they formed, supporting the conclusion that the progenitor material of ALH 84001 was not exposed to hydrous fluids or high temperature events for the last 3.9 Ga, suggesting a globally cold and dry Mars since then.

On the other hand, carbonates in terrestrial Archean samples are probably not the best suited for U-Pb dating as most Archean formations would have been heated up to at least low greenschist metamorphic conditions and/or been affected by hydrothermal alteration, because the Earth is geologically active and harbours a complex hydrological cycle. On the other hand, results of this study open up opportunities for dating old carbonates in samples that have had a relatively simple history post-carbonate formation. For example, volatile-rich carbonaceous chondrites (e.g., CI and CM chondrites) typically contain carbonates formed during fluid-rock interactions on their parent-asteroids *ca*. 4563-4561 Ma-ago (e.g., Lee *et al.*, 2014; Jilly-Rehak *et al.*, 2017, and references therein), which is within 10 Myr of the formation of the first solids in the Solar System. Bulk CI and CM chondrites contain ~10 ng/g U (e.g., Braukmüller et al., 2018; Turner et al., 2021), a significant proportion of which being potentially hosted in labile phases such as carbonates (e.g., Burkhardt *et al.*, 2019; Turner et al., 2021). As they make up ~1-2 vol.% of CM chondrites (e.g., Lee *et al.*, 2014), these carbonates could host a few 100's ng/g U, which is similar to the U abundance in the ALH 84001 carbonates analysed here. After this phase of early hydrothermal alteration during which carbonates formed, it is thought that not much happens to volatile-rich carbonaceous chondrites on their parent asteroids until they end up on the Earth as meteorite fragments. Carbonates in carbonaceous chondrites could thus be prime targets to further constrain the timing of hydrothermal alteration on volatile-rich asteroids using the U-Pb dating chronometer.

Data availability

Raw LA-ICP-MS data and metadata are provided in Supplementary Material.

Author contribution

ICL acquired and prepared the sample. RT designed the experiment, performed the analysis, and interpreted the results. RT prepared the manuscript with contributions from ICL.

Competing interests

The authors declare that they have no conflict of interest.

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Figures and captions

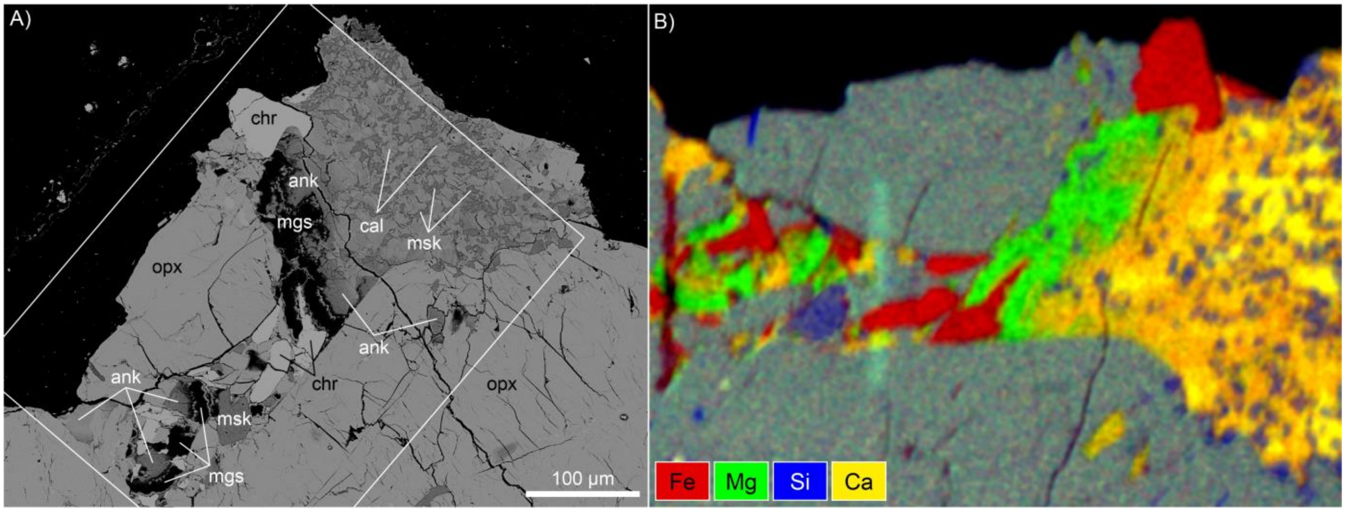

Figure 1: Backscattered electron image (A) and composite X-ray map (B) of the target carbonate patches in ALH 84001. Mineral abbreviations are ank = ankerite, cal = calcite, chr = chromite, mgs = magnesite, msk = maskelynite, opx = orthopyroxene.

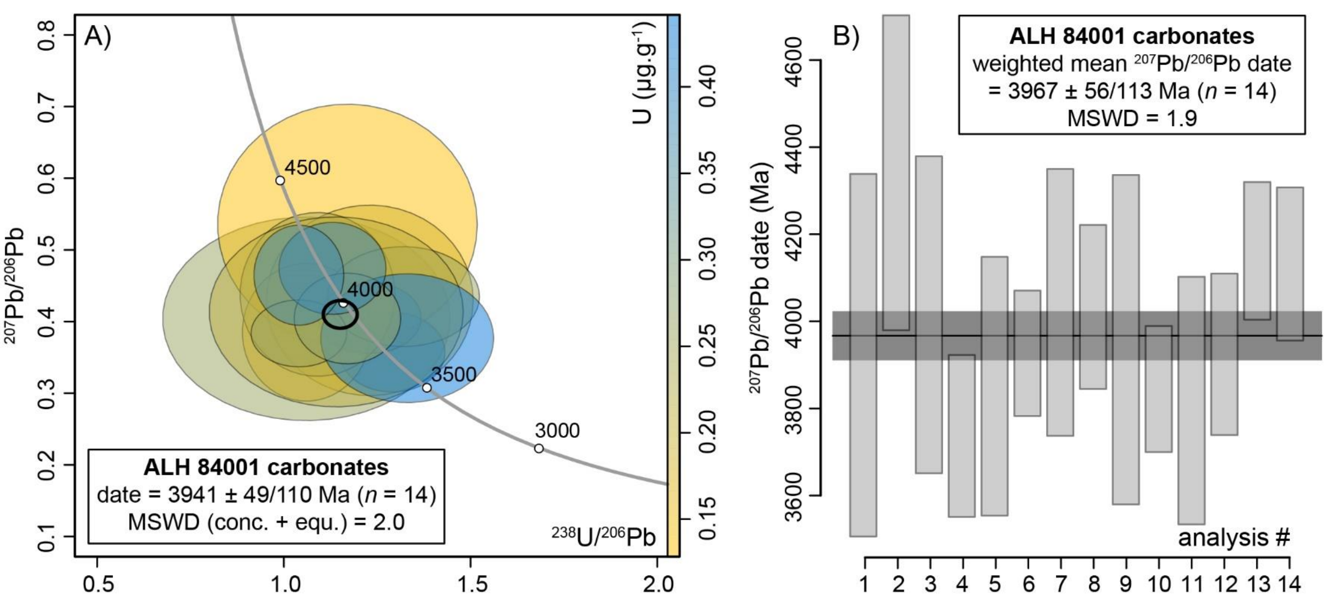

Figure 2: Tera-Wasserburg $^{207}Pb/^{206}Pb$ vs. $^{238}U/^{206}Pb$ diagram (A) and $^{207}Pb/^{206}Pb$ dates (B) obtained on ALH 84001 carbonates. Ellipses (A) and error bars (B) correspond to 2σ standard errors. The bold black ellipse in (A) corresponds to the calculated concordia date and associated uncertainty.

Table 1: LA-ICP-MS results for ALH 84001 carbonates.

							Ratios ± 2σ (%)					Dates ± 2σ (Ma)			
Analysis #	**^{204}Pb (cps)[1]**	**±**	**Pb (μg/g)**	**U (μg/g)**	**Th (μg/g)**	**Th/U**	**^{238}U/^{206}Pb**	**±**	**^{207}Pb/^{206}Pb**	**±**	**conc. (%)[2]**	**^{207}Pb/^{206}Pb**	**±**	**^{206}Pb/^{238}U**	**±**
MgRich_1	100	110	0.11	0.26	0.20	0.76	1.06	29.2	0.4037	28.3	109	3923	370	4270	853
MgRich_3	-123	82	0.12	0.14	0.08	0.57	1.17	23.9	0.5356	25.2	92	4342	327	3976	671
MgRich_4	10	50	0.13	0.19	0.12	0.64	1.23	18.1	0.4295	24.9	96	4016	329	3835	504
MgRich_5	-4	42	0.20	0.41	0.50	1.21	1.29	8.8	0.3570	12.5	99	3737	178	3698	244
MgRich_6	27	49	0.10	0.18	0.13	0.74	1.06	13.0	0.3850	20.1	111	3852	275	4274	395
MgRich2_1	1	36	0.25	0.39	0.48	1.25	1.23	9.0	0.4049	9.8	98	3927	140	3840	254
MgRich2_2	-18	70	0.12	0.24	0.22	0.92	1.09	15.3	0.4378	21.0	104	4044	282	4197	456
MgRich2_4	-34	41	0.11	0.26	0.27	1.02	1.32	12.4	0.4347	12.9	90	4034	180	3642	335
CaRich_1	50	93	0.06	0.22	0.09	0.41	1.14	24.0	0.4134	25.8	103	3958	340	4070	686
CaRich_2	-2	33	0.10	0.26	0.18	0.68	1.04	9.9	0.3834	9.8	113	3845	140	4346	306
CaRich_3	20	100	0.19	0.43	0.42	0.98	1.33	14.0	0.3767	19.2	95	3819	264	3618	376
CaRich_4	-5	40	0.16	0.27	0.27	0.98	1.17	9.8	0.4042	12.6	101	3925	177	3983	285
CaRich_5	-7	52	0.06	0.38	0.09	0.24	1.13	10.2	0.4742	10.9	98	4163	152	4082	300
CaRich_6	19	45	0.03	0.37	0.08	0.21	1.04	9.3	0.4646	12.1	105	4132	169	4347	288

[1]Background-corrected ^{204}Pb intensity, calculated using the measured ^{204}(Pb+Hg) and ^{202}Hg, and a ^{204}Hg/^{202}Hg of 0.22932.

[2]Concordance (100 × ^{206}Pb/^{238}U date / ^{207}Pb/^{206}Pb date).