In situ U-Pb dating of 4 billion year old carbonates in 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 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⁻¹ U, and up to ca. 100 μg.g⁻¹ U in speleothems (e.g., Roberts et al., 2020). Carbonates 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 ²⁰⁷Pb/²⁰⁶Pb 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-thirds of dates younger than 50 Ma, and all but two 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} yr^{-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 ca. 4.1 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). Dating carbonate-rich fractions 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). As stated by Treiman (2021), “there is little evidence that anything had happened to ALH 84001 since 3.9 Ga” and the time of carbonate formation until it was launched from Mars ca. 14 Ma ago (Eugster et al., 1997), which is crucial with respect to the U-Pb system having remained closed since ALH 84001 carbonates formed.

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 N₂ was added to the He stream at a flow rate of 2 mL.min⁻¹ 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 $^{238}\text{U}^+/^{232}\text{Th}^+$ close to unity and minimising the $^{232}\text{Th}^{16}\text{O}^+/^{232}\text{Th}^+$ 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⁻¹ U, 2.32 μg.g⁻¹ Pb; Jochum et al., 2011) was used to correct for $^{207}\text{Pb}/^{206}\text{Pb}$ fractionation, while mass bias correction of the measured $^{238}\text{U}/^{206}\text{Pb}$ 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.

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 $^{206}\text{Pb}/^{238}\text{U}$ ratios (Paton et al., 2011). The reproducibility obtained on NIST614 for $^{207}\text{Pb}/^{206}\text{Pb}$ (±1.7%, $n = 9$, 95% confidence level) and $^{206}\text{Pb}/^{238}\text{U}$ (±1.6%, $n = 9$, 95% confidence level) ratios were propagated by quadrature addition into each analysis $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ individual uncertainties. Repeated analyses of the NIST612 glass yielded an average $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.871 ± 0.044 ($n = 8$, 2 standard deviation), which is within error of its known $^{207}\text{Pb}/^{206}\text{Pb}$ 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 a common $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.85 (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 $^{206}\text{Pb}/^{238}\text{U}$ ratios, which we also applied to all the samples analysed in the session. All calculated dates are associated with two uncertainties, the first one...
including the random uncertainties for each analysis (internal uncertainties on measured $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ 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 $^{235}\text{U}$ and $^{238}\text{U}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of 0.74 (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 consistent with a $^{238}\text{U}/^{206}\text{Pb}$ 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$^{-1}$ U and 0.1-0.5 μg.g$^{-1}$ Th (Table 1). When plotted in a Tera-Wasserburg $^{207}\text{Pb}/^{206}\text{Pb}$ vs. $^{238}\text{U}/^{206}\text{Pb}$ 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 $^{207}\text{Pb}/^{206}\text{Pb}$ date of 3967 ± 56/113 Ma ($n = 14$, MSWD = 1.9; Fig. 2B). Carbonate analyses plot on the concordia curve, indicating that they do not contain appreciable amount of common Pb. This is consistent with the measured $^{204}\text{Pb}$ intensities that are within error of 0 counts per second (Table 1).

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 $^{238}\text{U}$ and $^{235}\text{U}$ decay constants, the carbonate U-Pb concordia date is accompanied 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 and their $^{204}\text{Pb}$ intensities within error of 0 count per second. This is unusual, as in most examples in
terrestrial systems 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 Gyr-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 Myr-ago (Treiman, 2021), and indicates that this latter event did not reset the carbonate U-Pb chronometer. 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 Myr-ago (e.g., Jilly-Rehak et al., 2017, and references therein), which is within 10 Myr of the formation of the first solids in the Solar System. After this phase of early hydrothermal alteration, it is thought that not much happens to these samples 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.

Acknowledgments

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ICP-MS facility. Many thanks to Nick Roberts for providing us with the WC-1 calcite, Benjamin Brigaud and Thomas Blaise for the AUG-B6 calcite, and Victor Polyak for the Duff Brown Tank calcite.

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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 $2\sigma$ uncertainties.
Table 1: LA-ICP-MS results for ALH 84001 carbonates.

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<th>±</th>
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<th>U (µg/g)</th>
<th>(\text{Th}) (µg/g)</th>
<th>(\text{Th}/\text{U})</th>
<th>(\frac{^{238}\text{U}}{^{206}\text{Pb}}) ±</th>
<th>(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}) ±</th>
<th>conc. (%)(^{2})</th>
<th>(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}) ±</th>
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\(^{1}\)Background-corrected \(^{204}\text{Pb}\) intensity, calculated using the measured \(^{204}(\text{Pb+Hg})\) and \(^{202}\text{Hg}\), and a \(^{204}\text{Hg}/^{202}\text{Hg}\) of 0.22932.

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