Evidence for extremely rapid magma ocean crystallization and crust formation on Mars

Laura C. Bouvier1,8, Maria M. Costa1,8, James N. Connelly1, Ninna K. Jensen1, Daniel Wielandt2, Michael Storey2, Alexander A. Nemchin3, Martin J. Whitehouse4, Joshua F. Snape4, Jeremy J. Bellucci5, Frédéric Moynier5, Arnaud Agranier6, Bleuenn Gueguen6, Maria Schönbächler7 & Martin Bizzarro1*

The formation of a primordial crust is a critical step in the evolution of terrestrial planets but the timing of this process is poorly understood. The mineral zircon is a powerful tool for constraining crust formation because it can be accurately dated with the uranium-to-lead (U–Pb) isotopic decay system and is resistant to subsequent alteration. Moreover, given the high concentration of hafnium in zircon, the lutetium-to-hafnium (176Lu–176Hf) isotopic decay system can be used to determine the nature and formation timescale of its source reservoir1–3. Ancient igneous zircons with crystallization ages of around 4,430 million years (Myr) have been reported in Martian meteorites that are believed to represent regolith breccias from the southern highlands of Mars4–6. These zircons are present in evolved lithologies interpreted to reflect re-melted primary Martian crust4, thereby potentially providing insight into early crustal evolution on Mars. Here, we report concomitant high-precision U–Pb ages and Hf-isotope compositions of ancient zircons from the NWA 7034 Martian regolith breccia. Seven zircons with mostly concordant U–Pb ages define 207Pb/206Pb dates ranging from 4,476.3 ± 0.9 Myr ago to 4,429.7 ± 1.0 Myr ago, including the oldest directly dated material from Mars. All zircons record unradiogenic initial Hf-isotope compositions inherited from an enriched, anesitic-like crust extracted from a primitive mantle no later than 4,547 Myr ago. Thus, a primordial crust existed on Mars by this time and survived for around 100 Myr before it was reworked, possibly by impacts4,5, to produce magmas from which the zircons crystallized. Given that formation of a stable primordial crust is the end product of planetary differentiation, our data require that the accretion, core formation and magma ocean crystallization on Mars were completed less than 20 Myr after the formation of the Solar System. These timescales support models that suggest extremely rapid magma ocean crystallization leading to a gravitationally unstable stratified mantle, which subsequently overturns, resulting in decompression melting of rising cumulates and production of a primordial basaltic to anesitic crust4–5.

The emergence of a stable primordial crust is a fundamental step in the early history of rocky, potentially habitable planets. Primordial crust formation is the end product of a long sequence of events, including planetary accretion, establishment of a global magma ocean, core formation and, finally, silicate differentiation. Existing constraints6–12 for the timing of each of these events allow for primordial crust formation in terrestrial planets over timescales of approximately 5 to 100 Myr, a range that precludes a full understanding of early planet formation. In the Solar System, Mars offers the opportunity to better constrain the timing of planet-formation processes, given its relatively simple geologic history as a stranded planetary embryo13 as well as the wealth of information from Martian meteorites and spacecraft exploration14. From the meteorite record, the accretion of Mars is inferred to have been mostly completed within about 5 Myr of the formation of the Solar System14, whereas the crystallization of the magma ocean leading to the extraction of a primordial crust may have occurred over timescales of approximately 30 to 100 Myr after accretion10,15,16. However, these timescales for silicate differentiation are based on the modelled abundances of the short-lived 182Hf and 146Sm nuclides during planetary differentiation inferred from young Martian meteorites and, hence, are highly model dependent.

A more robust approach to dating early planetary differentiation on Mars requires the identification of material that formed in the earliest evolutionary stages of the planet. On Earth, such a record is preserved in the Jack Hills of Western Australia, which contains ancient zircons17 as old as around 4,370 Myr. Although zircon is not common in Martian meteorites, two recent studies have reported the presence of approximately 4,430–Myr-old zircons in the Martian regolith breccia NWA 7533/7034, which is thought to have originated from the southern highlands of Mars4.5. The breccia contains clasts that are interpreted to be of igneous, sedimentary and impact origin, preserved in a fine-grained matrix. Zircons have been identified in the igneous and sedimentary clasts as well as within the matrix. Collectively, these grains are likely to provide the earliest tangible record of crust formation processes on Mars. However, the typical (small) sizes of these zircons prevent us from obtaining the concomitant U–Pb ages and Hf isotope compositions of sufficient precision using in situ techniques.

We conducted a systematic search for zircons in a bulk crushed rock aliquot of the NWA 7034 meteorite. Although this approach does not provide a petrological context for individual zircons, it is the only means of ensuring the recovery of grains sufficiently large (>30 μm) to permit high-precision U–Pb chronology and Hf isotope measurements using solution-based methods. Irrespective of their petrological context, these zircons faithfully record information about the nature of their source reservoir. This rationale is recognized in studies using the Jack Hills detrital zircons to probe the early terrestrial crustal record17. A total of seven grains were extracted and analysed for U–Pb dating and Lu–Hf systematics. Their sizes ranged from around 50 μm to 110 μm and they were found to represent different morphologic types, including rounded pieces, irregular anhedral pieces, and euhedral pieces with well-defined faces and a flat prismatic shape (Extended Data Fig. 1). Common to all of them was the general absence of fractures and inclusions, as well as any evidence of radiation damage. The zircons returned 207Pb/206Pb ages ranging from 4,476.3 ± 0.9 Myr to 4,429.7 ± 1.0 Myr (Table 1). Importantly, five of the seven grains are concordant within their stated uncertainties, grain S22b is 1.2% discordant and grain S22a is 3.0% discordant (Table 1). The larger degree of discordance for grain S24b is consistent with its higher U content of 46 parts per million (p.p.m.) relative to the other zircons we investigated. On the basis of textural information and geological context, the zircons from

1Centre for Star and Planet Formation and Natural History Museum of Denmark, University of Copenhagen, Copenhagen, Denmark. 2Department of Applied Geology, Curtin University, Perth, Western Australia, Australia. 3Swedish Museum of Natural History, Stockholm, Sweden. 4Laboratoire Géosciences Océan (UMR CNRS 6538), Université de Bretagne Occidentale et Institut Universitaire Européen de la Mer, Plouzané, France. 5Institute of Geochemistry and Petrology, ETH, Zurich, Switzerland. 6These authors contributed equally: Laura C. Bouvier, Maria M. Costa.

*Corresponding author. E-mail: bizzarro@snm.ku.dk

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Table 1 | U–Pb age data and $^{176}$Lu–$^{176}$Hf systematics of NWA 7034 zircons and the Hf isotope composition of the 91500 terrestrial zircon standard

| Sample   | $^{207}$Pb/$^{206}$Pb age (Myr) | $^{207}$Pb/$^{235}$U age (Myr) | $^{206}$Pb/$^{238}$U age (Myr) | $^{176}$Lu/$^{177}$Hf | $^{176}$Hf/$^{177}$Hf | $^{178}$Hf/$^{177}$Hf | $^{180}$Hf/$^{177}$Hf | $\epsilon$Hf |
|----------|-------------------------------|--------------------------------|-------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|------------|
| S22b5    | 4,448.7 ± 1.8                 | 4,445.1 ± 6.3                  | 4,437.3 ± 22.1                 | 0.000805               | 0.279891 ± 10         | 1.46718 ± 2          | 1.88666 ± 6          | −1.92 ± 0.37 |
| S22b4    | 4,447.0 ± 1.4                 | 4,457.8 ± 5.7                  | 4,421.9 ± 19.8                 | 0.000799               | 0.279907 ± 09         | 1.46719 ± 2          | 1.88665 ± 5          | −0.71 ± 0.32 |
| S23b9    | 4,447.0 ± 1.5                 | 4,441.0 ± 4.8                  | 4,427.7 ± 16.5                 | 0.000911               | 0.279908 ± 16         | 1.46721 ± 2          | 1.88669 ± 6          | −1.70 ± 0.58 |
| S24b2    | 4,429.7 ± 1.0                 | 4,355.2 ± 4.3                  | 4,195.9 ± 12.8                 | 0.001057               | 0.279922 ± 06         | 1.46719 ± 2          | 1.88667 ± 3          | −2.06 ± 0.26 |
| S24b4    | 4,474.0 ± 0.8                 | 4,470.1 ± 2.9                  | 4,461.4 ± 9.9                  | 0.001055               | 0.279906 ± 06         | 1.46719 ± 2          | 1.88667 ± 3          | −1.57 ± 0.26 |
| S24b7    | 4,473.9 ± 0.9                 | 4,476.5 ± 2.8                  | 4,483.3 ± 9.5                  | 0.000742               | 0.279887 ± 05         | 1.46720 ± 1          | 1.88667 ± 3          | −1.27 ± 0.19 |
| S29b10   | 4,476.3 ± 0.9                 | 4,474.5 ± 3.6                  | 4,470.6 ± 12.5                 | 0.001191               | 0.279926 ± 07         | 1.46721 ± 2          | 1.88669 ± 4          | −1.21 ± 0.30 |
| **Average** |                              |                                |                               |                       | 1.46720 ± 2          | 1.88669 ± 3          |                       |            |
| 91500-1  | 0.282308 ± 06                 | 0.46721 ± 1                    | 0.88670 ± 3                    |                        |                       |                       |                       |            |
| 91500-2  | 0.282314 ± 11                 | 0.46718 ± 2                    | 0.88674 ± 4                    |                        |                       |                       |                       |            |
| 91500-3  | 0.282311 ± 06                 | 0.46718 ± 2                    | 0.88670 ± 4                    |                        |                       |                       |                       |            |
| 91500-4  | 0.282311 ± 05                 | 0.46718 ± 1                    | 0.88668 ± 2                    |                        |                       |                       |                       |            |
| 91500-5  | 0.282309 ± 05                 | 0.46719 ± 1                    | 0.88669 ± 2                    |                        |                       |                       |                       |            |
| 91500-6  | 0.282309 ± 06                 | 0.46716 ± 1                    | 0.88664 ± 2                    |                        |                       |                       |                       |            |
| 91500-7  | 0.282317 ± 05                 | 0.46718 ± 1                    | 0.88667 ± 3                    |                        |                       |                       |                       |            |
| **Average** | 0.282311 ± 06                 | 0.46718 ± 2                    | 0.88669 ± 6                    |                        |                       |                       |                       |            |

Age uncertainties are 2σ. Hf isotope ratios are reported normalized to the composition of the JMC-475 Hf standard. Uncertainties on the Hf isotope ratios reflect the 2-standard-error internal precision in the last decimal places. The external reproducibility of the $^{176}$Hf/$^{177}$Hf ratio is estimated to be 22 p.p.m., based on the analyses of the seven 91500 zircon aliquots. U–Pb data are reported in full in Supplementary Table 1.
crust produced by decompression melting of rising cumulates, following overturn of the gravitationally unstable stratified mantle. We note that recent estimates that suggest a low crustal bulk density for Mars (2,582 ± 209 kg m⁻³, ref. 25) could, in principle, also be consistent with a more evolved average crustal composition. Using an andesite-like \(^{176}\text{Lu}/^{177}\text{Hf}\) ratio of about 0.011 estimated from terrestrial rocks\(^{23,26}\) defines a minimum formation age of 4,547 Myr for the source reservoir. An andesite-like composition for the nature of this source reservoir is further reinforced by the observation that the initial Hf isotope compositions of the approximately 4,450-Myr-old and 4,430-Myr-old zircons are also consistent with extraction from the same source (Fig. 2b). Indeed, taking the data at face value for each of the age groups returns a slope corresponding to an andesite-like \(^{176}\text{Lu}/^{177}\text{Hf}\) ratio of about 0.011. The fact that more evolved compositions for a primordial crust are not predicted by any model provides confidence that the formation age of this reservoir cannot be younger than 4,547 Myr. Therefore, this minimum age for the source of the NWA 7034 zircons represents the oldest differentiated silicate reservoir yet identified on Mars. Ancient Martian zircons with ages comparable to that reported here have been identified in igneous, evolved lithologies that are interpreted to reflect re-melted primary Martian crust\(^7\). The enriched composition for the NWA 7034 zircon source reservoir inferred from the andesite-like \(^{176}\text{Lu}/^{177}\text{Hf}\) ratio is consistent with this interpretation. Thus, our data require that a primordial crust existed on Mars by 4,547 Myr ago and that it survived for about 100 Myr before it was reworked to produce magmas, possibly by impacts\(^{8,9}\), from which the NWA 7034 zircons crystallized. We infer that this primordial crust represents a global reservoir given its longevity and the extended period of reworking indicated by the zircon data.

The new timescales reported here for stabilization of the primordial Martian crust have far-reaching implications for understanding the accretion and differentiation history of Mars. Given that the formation of a stable primordial crust is the end product of the initial planetary differentiation, our data require that accretion, core formation and magma ocean crystallization on Mars was completed within 20 Myr of the formation of the Solar System. Such short timescales for primary accretion are predicted by planet formation models invoking pebble accretion where growth is fuelled by the gas-drag-assisted accretion of millimetre-sized objects, which leads to the efficient formation of Mars-sized embryos within the approximately 5-Myr lifetime of the protoplanetary disk\(^{27,28}\). Moreover, these timescales are also consistent with estimates based on the short-lived \(^{182}\text{Hf}/^{182}\text{W}\) decay system for the timing of core formation, which is inferred to have occurred within 10 Myr of the formation of the Solar System\(^{29}\). By contrast, some recent studies have suggested that magma ocean crystallization was protracted on Mars, perhaps lasting up to 100 Myr after differentiation of the planet, on the basis of model ages deduced from the abundances of short-lived radionuclides in young Martian meteorites\(^{10,15,16}\). Such a protracted magma ocean crystallization is inconsistent with the data presented here and with thermal models suggesting that the solidification history of Mars must have been completed within about 10 Myr of accretion\(^7\). As such, the timing of silicate differentiation inferred from short-lived radionuclides in young Martian meteorites may not reflect primary differentiation of the planet but rather a younger, mantle-scale, fractionation event. Finally, our data and interpretation are fully consistent with models suggesting rapid magma ocean crystallization leading to a gravitationally unstable stratified mantle, which subsequently overturns, resulting in decompression melting of rising cumulates and extraction of a primordial basaltic-to-andesitic crust\(^6,7\). The extensive resurfacing of Mars by volcanism over the planet’s history suggests that if any primordial crust is preserved, it will be deeply buried and may only be exposed in deep craters.

**Online content**

Any Methods, including any statements of data availability and Nature Research reporting summaries, along with any additional references and Source Data files, are available in the online version of the paper at https://doi.org/10.1038/s41586-018-0222-z.

One possibility is an andesite-like source, because rocks with such evolved compositions have been identified on Mars based on in situ observations\(^{24}\). Moreover, some magma ocean crystallization models\(^6,7\) predict basaltic-to-andesitic compositions for the primary Martian
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Author contributions M.B. designed and led the research project. M.M.C., J.N.C. and M.B. identified and separated the zircons and performed analytical work related to the U–Pb isotope systematics of the zircons. L.C.B., J.N.C. and M.B. performed analytical work related to the 176Lu–176Hf systematics of the zircons. N.K.J., D.W., M.S., M.J.W., J.F.S., J.J.B., A.A.N., F.M., A.A. and B.G. assisted in sample preparation and zircon identification. All authors participated in the interpretation of the data. The manuscript was written by L.C.B., M.M.C., J.N.C. and M.B.

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Correspondence and requests for materials should be addressed to M.B.

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METHODS
A total of seven zircon grains were extracted from a crushed bulk rock aliquot of NWA 7034 and analysed for U–Pb and Lu–Hf systematics. Given the limited number of zircons recovered from the crushing process and their small sizes, only one of the larger grains (S25b10) was chemically abraded. This pre-treatment consisted of thermally annealing the less metamict domains of the crystal over three days at 900 °C, followed by dissolution of the un-annealed portions using concentrated HF for 12 h at 180 °C in Teflon capsules. Before complete dissolution, all zircon grains were cleaned in Pyrex beakers in an ultrasonic bath with alternating steps of warm 3.5 M HNO₃, H₂O₂ and acetone. As we assumed that each grain might represent a different age, the grains were processed as single grains. The individual crystals were dissolved in separate PTFE Teflon capsules in a HF:HNO₃ (3:1) mixture, together with the mixed 260Pb:209Pb:231U:238U EARTHTIME U–Pb tracer, for four days at 210 °C. The dissolved samples were evaporated to dryness and redissolved in 3.1 M HCl overnight. Uranium and lead were separated from the matrix elements by anion chromatography using 50-µl Teflon columns⁴ and dried down together with 8 µl of 0.1 M H₂PO₄. They were loaded with silica gel⁵ on previously outgassed zone-refined Re filaments. The Pb and U isotopic ratios of the sample + tracer mixture were measured using the Triton Thermo-Fisher thermal ionization mass spectrometer at the Centre for Star and Planet Formation, University of Copenhagen, where each isotope was sequentially counted in a single axial ion counting system with Pb as Pb⁺, and U as UO₂⁶⁺. The data were reduced offline and instrumental mass fractionation was accounted for by a linear mass-dependent fractionation law based on the 208Pb/206Pb tracer of the fraction. After 1 pg of laboratory Pb blank was removed from the analyses, the remainder of common Pb was assumed, and the interference correction procedure used to correct for any instrumental mass-dependent fractionation of U was accounted for using the 235U/233U tracer of the fraction, which included a correction for the isobaric interference of 214Pb on the 235U tracer peak mass. 267.34±0.025 U tracer ratio of mass 137.38 (ref. 38) and the 238U and 235U decay constants of ref. 39 were used for calculation of U/Pb ratios and ages. All ratios and age uncertainties are quoted at the 95% confidence level. The Hf isotope composition and Lu/Hf ratios of individual zircons were determined from the same sample digestion as that used for U–Pb age determination. Following collection of the high-field-strength element and rare-earth element (REE) washes from the U–Pb purification, approximately 5% of the solution was aliquoted for Lu/Hf ratio determination. The Hf was purified from the remaining solution by a two-step procedure using TEVA-spec and TODGA resins (Eichrom Industries) based on protocols outlined in refs 19 and 20. Zr was quantitatively separated from Hf, Ti and REE using 100-150 µm TEVA-spec resin in a 120-µl column. The fractions containing high-field-strength elements and REE were loaded in 0.6 ml of 10.5 M HCl and a Hf + Ti + REE cut was successively collected with 3.6 ml of 10.5 M HCl and 4.2 ml of 9.5 M HCl. Zr was recovered with 3.0 ml of 6 M HCl. Hf was purified from Ti and REE using 50-100 µm TODGA resin in 200-µl columns. The fraction containing Hf was collected on the H₂ Faraday detector connected to an amplifier with 10¹¹-Ω feedback resistor. Sample analyses were interspaced by analyses of the calibrated Lu–Hf standard solution as follows: Lu–Hf standard (1), Lu–Hf standard (2), sample-1, Lu–Hf standard (3), Lu–Hf standard (4). Samples and standard were matched to within about 5%. Total procedural blanks were <5 fg for Lu and negligible for all samples considering the amount of Hf available for analysis. The 177Hf beam was collected on the axial secondary electron multiplier, whereas the 177Hf beam was not collected on the H2 Faraday detector connected to an amplifier with a 10¹¹-Ω feedback resistor. Sample analyses were interspaced by analyses of the calibrated Lu–Hf standard solution as follows: Lu–Hf standard (1), Lu–Hf standard (2), sample-1, Lu–Hf standard (3), Lu–Hf standard (4). Samples and standard were matched to within about 5%. Total procedural blanks were <5 fg for Lu and negligible for all samples considering the amount of Hf available for analysis. The Lu–Hf standard solution was prepared gravimetrically to match the typical Lu/Hf ratio of Hf and is accurate to 2%. The external reproducibility of our approach was estimated by repeated analysis of the 91500 zircon standard. Analysis of ten individual aliquots of a single dissolution of the 91500 zircon standard yielded a 206Pb/204Pb ratio of 0.10030±0.000016 (2 standard deviations), which corresponds to an external reproducibility of 0.5% for the Lu/Hf ratio. Potential fractionation of Lu during Lu–Hf purification was evaluated by measuring the Lu/Hf ratios of aliquots of the 91500 zircon standard before and after U–Pb purification. Our tests demonstrate that potential fractionation of the Lu/Hf during U–Pb purification is less than 0.4%. Combining this with the uncertainty of the Lu–Hf standard solution, the external reproducibility of 0.5% and the potential fractionation of 0.4%, we infer an accuracy of 2.1% for our Lu/Hf ratio measurements. This represents the total uncertainty on the Lu/Hf ratio reported here and has been propagated in the final uncertainties quoted for the initial Hf isotope composition of the NWA 7034 zircons.

Data availability. Here and has been propagated in the final uncertainties quoted for the initial Hf isotope composition of the NWA 7034 zircons. The data in this study are available within the paper and the Methods. All other data are available from the corresponding author upon reasonable request.

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Extended Data Fig. 1 | Photomicrographs of the NWA 7034 zircons analysed in this study taken under natural light. Given the small size and limited number of zircons recovered from the crushing process, we considered it to be preferable not to conduct additional imaging (using cathodoluminescence) because this necessitates extra manipulation of the individual grains, thereby increasing the risk of losing zircons. The fact that the zircons have mostly concordant U–Pb ages confirms their simple igneous history and, therefore, additional imaging to investigate potential zoning is not required here.