# Low-temperature aqueous alteration of Martian zircon during the late Amazonian period

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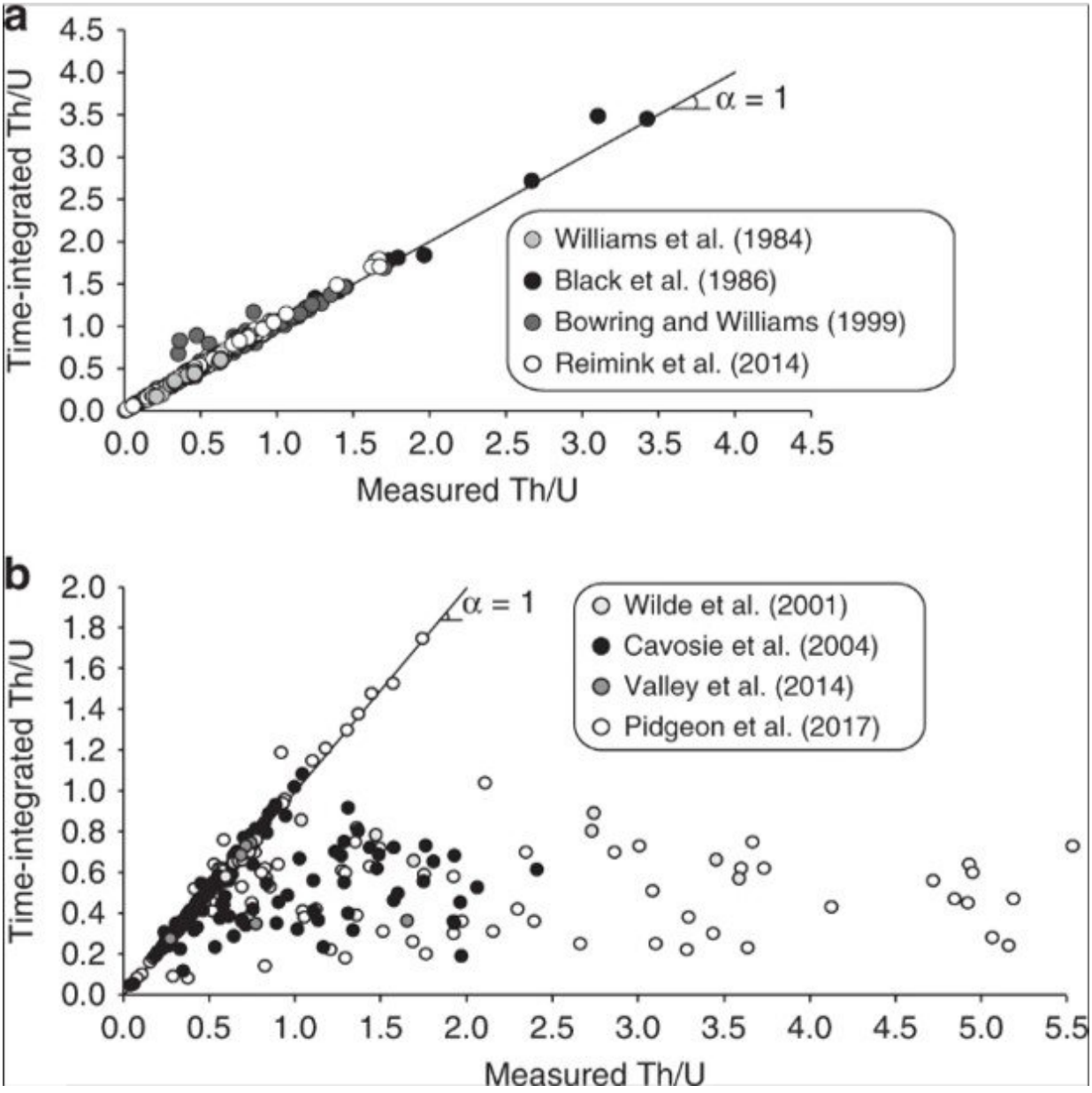


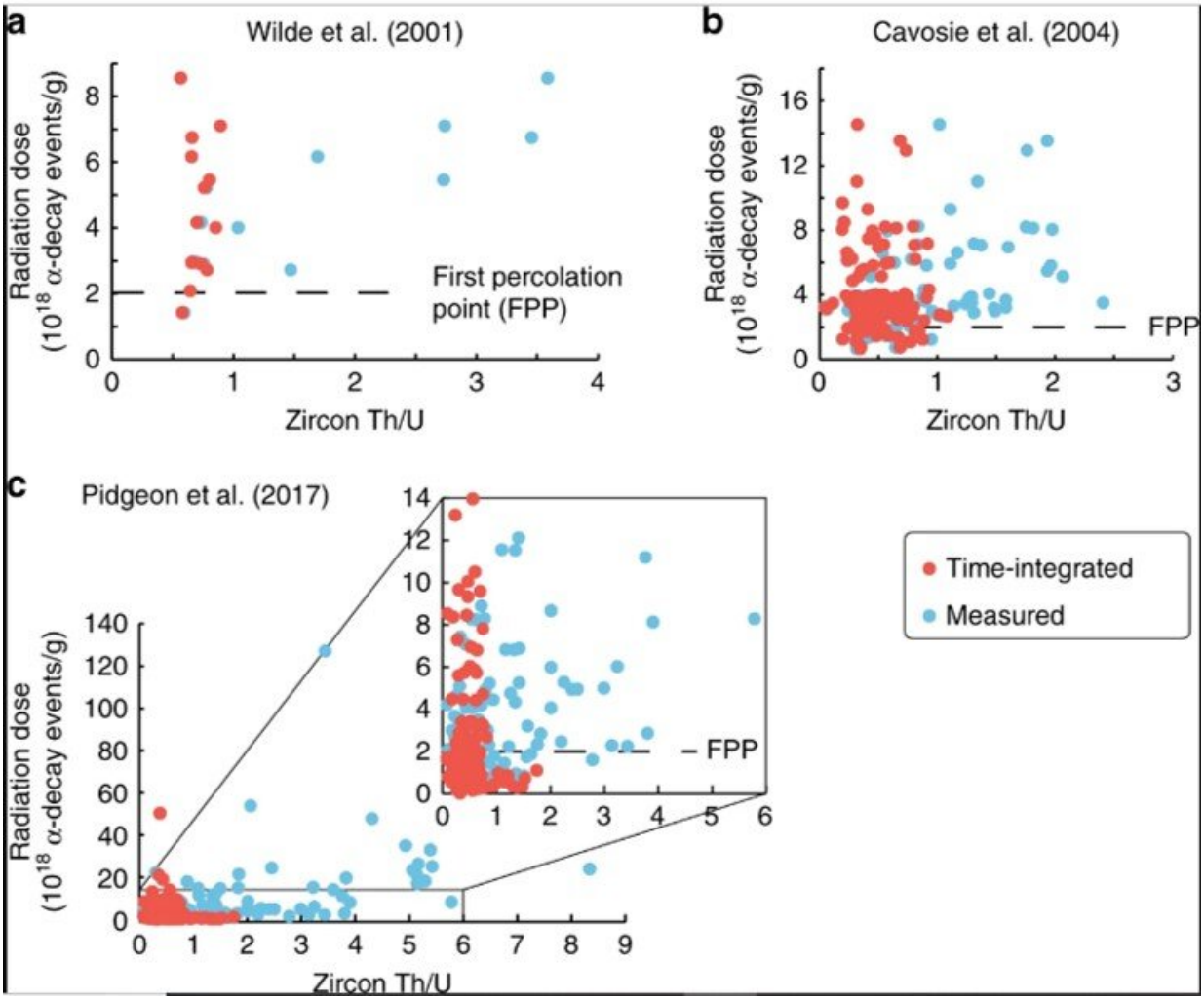
Comparison of measured and time-integrated Th/U in zircon. The panel a is for oldest known terrestrial igneous zircons, whereas panel b is for oldest known terrestrial detrital zircons from Western Australia. Time-integrated means calculated from measured 208Pb/206Pb ratio and 207Pb/206Pb age. Corresponding data can be found in Credit: Nature Communications, doi: 10.1038/s41467-019-10382-y

Many accounts at present support the presence of liquid water on Mars, where hydrated minerals testify to past processes of aqueous weathering in Martian meteorites such as NWA 7533/7034. Planetary scientists aim to estimate the timing of weathering on the Martian crust to help understand its evolution, the availability of liquid water and habitability on Mars. In a recent study, Martin Guitreau and Jessica Flahaut at the University of Manchester, U.K., and the National Center for Scientific Research in France, presented a new method based on U-Th-Pb (Uranium-Thorium-Lead) isotope dating systems. Using the technique, Guitreau and Flahaut investigated if Zircon crystals underwent low-temperature aqueous alteration, similar to observations with Hadean-aged detrital crystals from Western Australia.

The data for NWA 7533 Zircons showed evidence for aqueous alteration, and modeling the evolving U-Th-Pb isotope system indicated the latest alteration to have occurred in the late Amazonian period (227-56 Ma). The finding largely expands the time duration in which liquid water was available near the Martian surface—suggesting that Mars may still be habitable, based on the evidence. Results of the study are now published on *Nature Communications*.

Zircon is a robust time capsule extensively used in U-Pb geochronology

and in the study of magmatic/metamorphic processes on Earth. Planetary scientists have testified this process using terrestrial detrital Zircon predating to 4378 million years. Nevertheless, the alpha-particle emission and α-recoil cascades due to U and Th decay can damage the crystal lattice, causing radiation to accumulate in zirconium at different rates based on the concentrations (ratio) of U and Th. This stage is defined as the "first percolation point" after which chemical elements can be more readily mobilized than in pristine crystals. The progressive amorphization can induce crystal lattice expansion and crack formation in Zircon to enhance the crystal's sensitivity to thermal events as observed with ancient Zircons from Jack Hills, Western Australia.



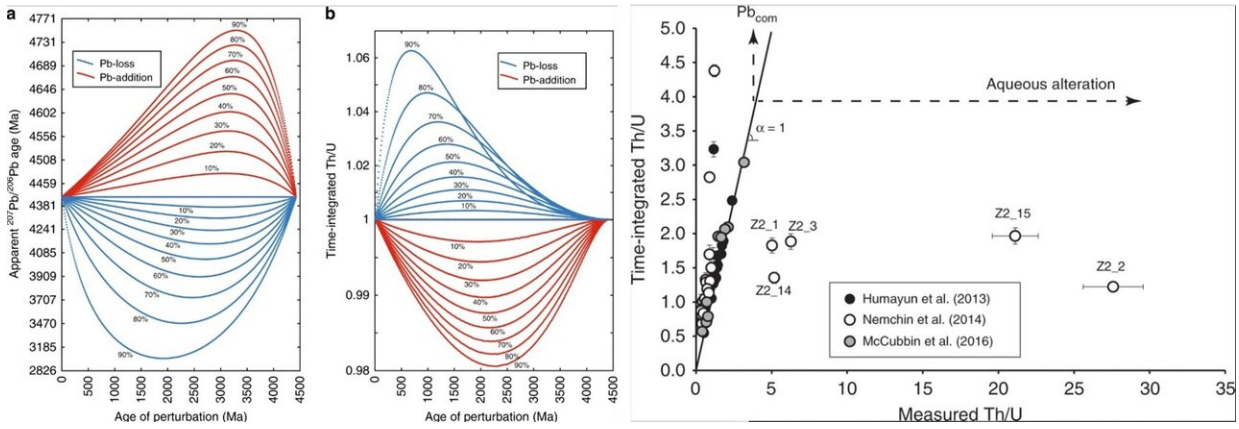
Calculated radiation doses as a function of Th/U in zircon. The panels a, b and c correspond to data from previous studies. Note the general upward-opening fan shape distribution of data above the first percolation point (stage at which amorphous domains become connected). Corresponding data can be found in
Credit: Nature Communications, doi: 10.1038/s41467-019-10382-y

In the present work, Guitreau and Flahaut explored if decoupling between the measured and time-integrated Th/U in Zircon could proxy for low-temperature aqueous alterations and then outlined the principles of their new method. When the scientists applied the method to extraterrestrial zircons on the moon for comparison with Martian zircons, they obtained evidence for low-temperature aqueous weathering on Mars.

When they modeled the evolution of the U-Th-Pb isotope systems of zircon to determine the development of decoupling between the measured and time-integrated Th/U, they discovered the alteration occurred at 1500-1700 Ma; as a much younger event. The event corresponded to the late Amazonian period, which is generally considered cold and dry on Mars. As a result, the present work demonstrated the availability of water near the Martian surface in the recent past, suggesting its presence in the present day.

To investigate the sensitivity of Zircon, the scientists considered chemical modifications as well as isotopic resetting during preservation of the lattice. To assess these conditions, they used macroscopic visual criteria and microscopic methods including transmission electron microscopy, Raman spectroscopy, X-ray diffraction, nuclear magnetic resonance and atom probe tomography. A simpler, indirect approach is to also calculate the radiation dose that a zircon sample underwent (alpha

decay events per gram of sample) using chronological information provided by U-Pb isotype systems and U and Th concentrations. For example, when scientists calculated the radiation doses of Jack Hills zircon datasets, they showed decoupling between the measured and time-integrated Th/U ratios in zircon domains. In this instance, radiation doses appeared to accumulate beyond the first percolation point, however the process required verification prior to its use on aqueous alterations beyond Earth.

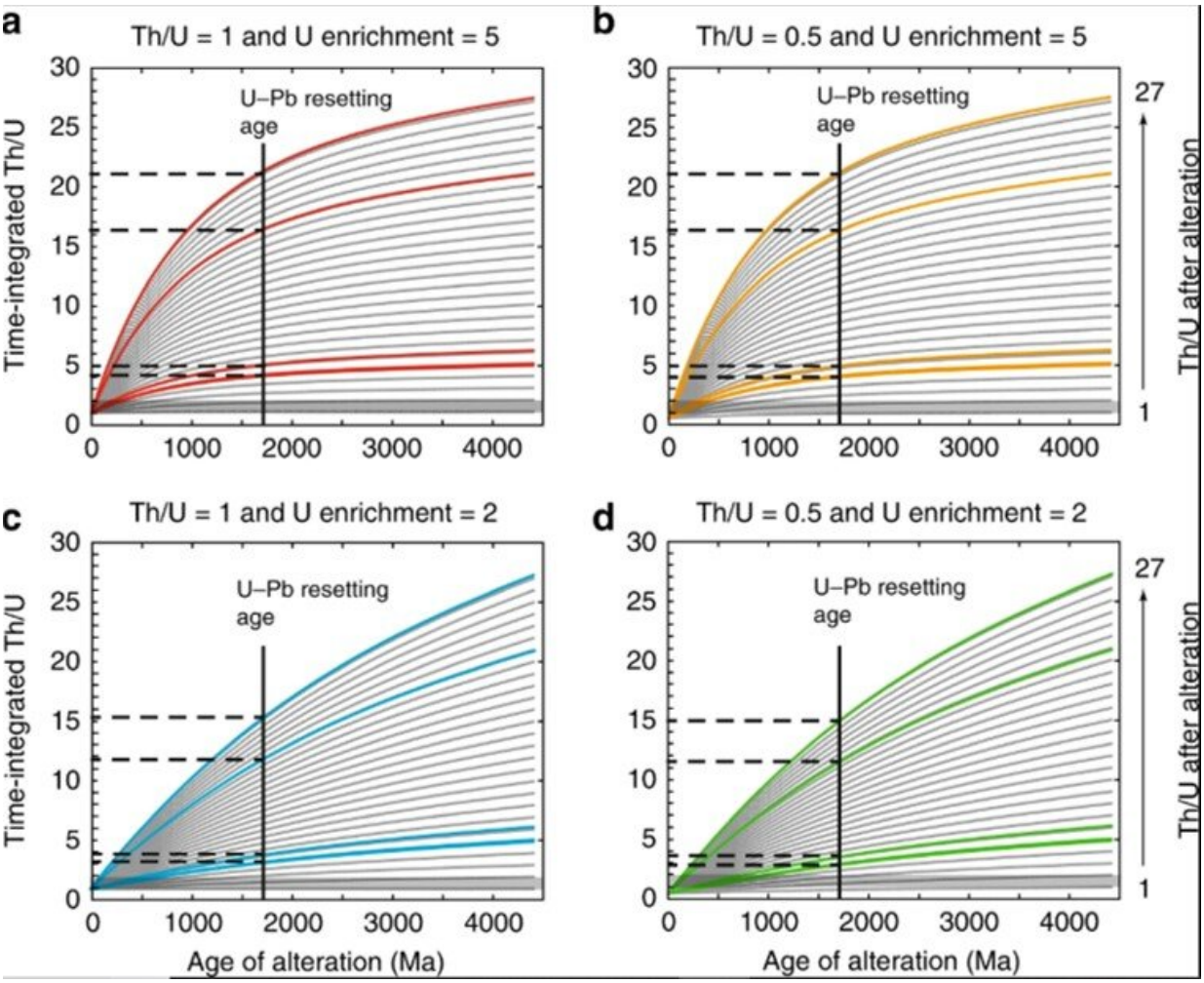



LEFT: Influence of Pb mobility on present-day 207Pb/206Pb ages and time-integrated Th/U. The panel (a) shows the effect of Pb-loss and Pb-addition on determined 207Pb/206Pb ages for a 4430 Ma zircon with original Th/U of 1, whereas the panel (b) presents the effect of Pb-loss and Pb-addition on time-integrated Th/U for the same zircon. Percentages next to the dotted-curves correspond to the degree of Pb-loss or Pb-addition. The age of perturbation refers to the age at which the Pb is lost or added. Note that Pb-addition corresponds to local increase in radiogenic Pb concentration and not addition of common Pb. This figure illustrates the great sensitivity of 207Pb/206Pb ages to Pb mobility whereas it has a limited effect on time-integrated Th/U. RIGHT: Time-integrated Th/U as a function of that measured for Martian zircons. Data are from previous studies. Note the large decoupling between measured and time-integrated Th/U for domains within zircon Z2 from NWA 7533. Measured Th/U are also well outside the common magmatic range, much as what can be seen in

Jack Hills zircons. Error bars represent two standard errors on analytical measurements. Corresponding data can be found in Credit: Nature Communications, doi: 10.1038/s41467-019-10382-y

Via extensive experiments, Guitreau and Flahaut showed that decoupling between the measured and time-integrated Th/U exhibited by terrestrial zircons as a proxy for zircon alterations by aqueous solutions at low temperatures. Upon comparison, the scientists showed that lunar (moon) zircons exhibited anomalously high Th/U in compliance with the common range for terrestrial larva/magma based igneous (fiery) zircon. This was expected since there is no evidence for liquid water on the moon.

Similarly, Martian zircon crystals obtained from the meteorite NWA 7533 and the matrix of NWA 7034 showed consistent measurements and time-integrated Th/U ratios. Based on existing data and the present calculations, Guitreau and Flahaut interpreted the horizontal distribution as evidence for low temperature alterations of Martian zircon grains by aqueous solutions—much like the crystals from Western Australia. The present findings using decoupling between the measured and time-integrated Th/U ratios reinforced the idea of the availability of liquid water in the Martian subsurface. The phenomenon induced advanced weathering of radiation-damaged zircon crystals.

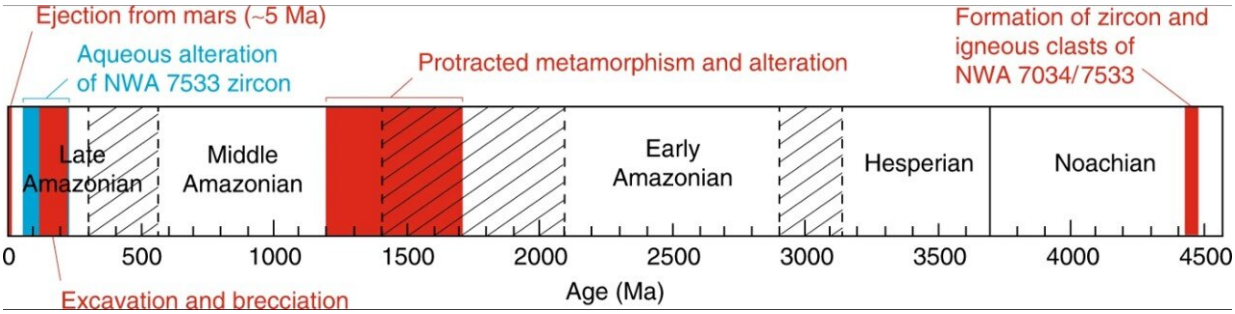



Results for the two-stage model simulating Martian zircon evolution. Models were run for U enrichment factors of 5 for panels (a) and (b), whereas a factor of 2 was used for the results presented in panels (c) and (d). The pre-alteration Th/U was set to 1 for models shown in panels a and c, and it was set to 0.5 in panels (b) and (d). Th/U ratios increased by alteration were set to 1–27 and 0.5–27, depending on the pre-alteration Th/U. Colored curves correspond to measured Th/U in zircon Z2 domains. The U–Pb resetting age corresponds to the lower intercept of the general Discordia line displayed in a previous study and is represented by a solid vertical line. The horizontal dashed lines, which are the intercepts between the colored curves and the solid vertical line, indicate the time-integrated Th/U deduced from our model. The gray-shaded zones between Th/U values of 1 and 2 correspond to the time-integrated Th/U exhibited by zircon Z2 domains. These results show that time-integrated Th/U derived from

the current model are higher than those exhibited by zircon Z2 domains, and, hence, alteration at 1700 Ma (or 1500 Ma) cannot account for the observed decoupling between measured and time-integrated Th/U in the study. Credit: Nature Communications, doi: 10.1038/s41467-019-10382-y

To understand the timing of Marian aqueous weathering, Guitreau and Flahaut developed a two-stage model of the U-Th-Pb isotope evolution in the present work. They tested if an aberration event (deviation) at 1500 or 1700 Ma could have accounted for the observed decoupling between the measured and time-controlled Th/U and the zircon alteration in NWA 7533. In the first stage of the model, Guitreau and Flahaut investigated zircon formation at 4430 Ma, followed by the second stage as an alteration event on increasing U and Th concentrations to alter zircon in the NWA 7533 meteorite. Using the two-stage model, they showed that uranium could be enriched by 2-5 times the original concentration to match both Jack Hills and Martian Zircon data. The results indicated that the observed levels of Th/U could have occurred at 1700 Ma or 1500 Ma.

The scientists further implemented the model with an additional stage to form a three-stage model, using the same Th/U ratios and Uranium enrichment factors as in the two-stage model. The results showed that while the determined alteration ages remained very young, the specific alterations recorded by the scientists occurred during the late Amazonian period.




Timeframe for Martian crust evolution. Displayed are details of knowledge about the history of NWA 7034/7533 and paired stones. The igneous crystallization of NWA7034/7533 zircons and clasts are derived from previous studies. Metamorphism and alteration ages are from additional studies. Brecciation age range is also from previous investigations, and so is the age of ejection. Corresponding data can be found in Credit: Nature Communications, doi: 10.1038/s41467-019-10382-y

In this way, Guitreau and Flahaut presented their new data with robust evidence from existing investigations to indicate that the low-temperature alteration event recorded in NWA zircons occurred in the late Amazonian period on Mars. They assume that the availability of water for weathering in the late-Amazonian was likely controlled by impact-induced hydrothermal activity.

The observations in the present study were consistent with post-brecciation (rock fragmentation) zircon alteration, and the youngest volcanic activity on Mars could also have played a role due to alterations with the current cryosphere. The recorded alterations of Zircons in the NWA 7533 meteorite represented the youngest episode of persistent aqueous alteration thus far reported on Mars. The results support the concept that Mars may yet be habitable relative to the evidenced availability of liquid water in its recent past.

**More information:** Martin Guitreau et al. Record of low-temperature aqueous alteration of Martian zircon during the late Amazonian, *Nature Communications* (2019). DOI: 10.1038/s41467-019-10382-y

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