

Effects of Thermal Annealing and Chemical Abrasion on In-situ U-Pb Dating of Complex Ancient Zircons by Laser Ablation ICP-MS

Xiong Yang,^a Shi-Xin Gao,^a Da Wang,^{a,*} Xiao-Fei Qiu,^b Xi-Run Tong,^b Dong-Yang Ju,^c and Zhao-Feng Zhang,^{a,*}

^a Research Center for Planetary Science, College of Earth and Planetary Sciences, Chengdu University of Technology, Chengdu 610059, P. R. China

^b Wuhan Center of China Geological Survey, Wuhan 430205, P. R. China

^c State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, P. R. China

Received: August 20, 2024; *Revised:* October 16, 2024; *Accepted:* October 16, 2024; *Available online:* October 16, 2024.

DOI: 10.46770/AS.2024.179

ABSTRACT: Zircon U-Pb geochronology has been widely used for determining the age of geologic processes. However, for very ancient zircon samples (*e.g.*, ~3.8 Ga), the quality of U-Pb dating results may be affected by the relatively high-grade of loss caused by the crystal damage through radioactive decay of U and Th. Here, we present a comparative study to explore the effect of thermal annealing (TA) and chemical abrasion (CA) on zircon U-Pb geochronology using zircon samples from some of the oldest igneous rocks on Earth (the Acasta Gneiss and the Muzidian Gneiss complexes), with the goal of getting better constrained zircon U-Pb ages of ancient rocks. Prior to the laser ablation dating experiments, all zircon samples and reference standards were thermally annealed (850 °C ~ 1050 °C/48 h), and a subset of thermally annealed zircon samples was then selected for chemical abrasion treatment (partial dissolution using hydrofluoric acid at 170 °C for 12 h), in order to remove radiation damaged domains. The results show that the U-Pb ages of CA zircon grains appear to be more concordant with smaller MSWDs than those of the TA and untreated zircon grains, indicating that the partial dissolution treatment of thermally annealed zircon grains effectively removed domains with Pb loss, leaving the rest of the zircon crystal lattice relatively unaffected. Therefore, for complex and ancient (> 3.8 Ga) zircon samples, chemical abrasion prior to laser ablation is shown to be useful for reducing Pb loss and data scatter. Thermal annealing appears to improve the matrix match between the unknown and reference zircon grains, which is especially useful for the dating of high U, young zircon samples. Additionally, our results show no systematic difference in the trace elements and Hf isotopic compositions between treated and untreated zircon samples, which demonstrates that the treatments do not have negative effect on the trace elements and Lu-Hf isotopic compositions in zircons.

INTRODUCTION

Zircon (ZrSiO_4 ; tetragonal space group $I4_1/amd$) is an important accessory mineral, commonly present in igneous,^{1,2} metamorphic,³⁻⁵ and sedimentary rocks^{6,7} in the form of crystalline phases, xenocrystic, and recrystallized grains, and is also found in extraterrestrial materials such as lunar rocks and meteorites.⁸

Zircon is popular for U-Pb geochronology taking advantage of its incorporation of U and Th at the eight-coordinated Zr^{4+} site in its lattice, with minimum initial common Pb during primary growth.⁹ Thus, the vast majority of Pb in zircon is radiogenic, through the alpha decay of ^{238}U , ^{235}U , and ^{232}Th .¹⁰ In addition, zircon has a very low Gibbs energy¹¹ and therefore a very stable crystal structure, which facilitates its preservation in a variety of geologic

environments. In addition, the closure temperature (750 ± 100 °C)¹²⁻¹⁹ of Pb in zircon is relatively high compared to other datable accessory minerals (*i.e.*, apatite, monazite,²⁰ titanite), which makes it extremely useful for dating high-temperature geologic processes.

However, zircon can be metamict due to the radiation damage of crystal lattice by fission tracks and the decay of U and Th.^{21,22} At the metamict state, the internal atomic binding force of the zircon crystal is greatly reduced, causing the loss of radiogenic Pb through diffusion and fluid reactions under low-temperature conditions,²³ challenging its reliability as a U-Pb geochronometer. Efforts have been made to improve the concordance of U-Pb dating by eliminating radioactivity-induced damage domains of zircon. These include air abrasion, acid related treatments,²⁴⁻²⁶ chemical abrasion (CA) and thermal annealing (TA), particularly for the case of ID-TIMS dating which typically involve the dissolution of entire zircon grains, chemical separation and purification of U and Pb aliquots using chromatography, and then measurements of the isotopic compositions.²⁷⁻³¹ A practical approach to eliminate or minimize the effect of Pb loss was to mechanically remove the outer domains of the zircon by air abrasion.²⁶ The outer part of zircon grains usually contains a higher concentration of U and Th, and is often exposed to fluids, accumulating radioactivity-induced damage.³² Another popular method is thermal annealing, which makes the displaced atoms in the lattice return to the original position after gaining energy at high temperature (800 °C- 1100 °C)²⁸ so that the lattice damaged by radiation gradually heals and returns to the crystalline state.^{24,28-30,33} The last method is chemical abrasion which chemically removes the radiation-damaged domains of zircon based on their relatively high solubility in hydrofluoric acid compared to well-crystallized parts of zircon.^{25,34-36} While these physical and chemical treatments of zircon crystals have been shown to be effective in eliminating Pb loss due to radiation damage, and typically followed by the high-precision solution-based analysis (*e.g.*, Isotope Dilution U-Pb analysis using TIMS) to determine the U-Pb age, they are also potentially helpful for the rapid in-situ laser ablation U-Pb dating of ancient zircon samples subject to a high grade of Pb loss.

Previous studies have demonstrated that in-situ zircon U-Pb dating could benefit from thermal annealing with no known negative outcome.^{24,30} Yet, how chemical abrasion treatment would affect the in-situ zircon U-Pb ages of ancient, complex zircon grains is less clear. Importantly, previous experiments were mostly done on zircon reference materials which are usually gem quality pegmatitic crystals^{10,37}, while complex, ancient zircon grains may be different. Only a few studies have tested the effect of thermal annealing and chemical abrasion on ancient zircons. For example, Wiemer *et al.*²⁴ presented a microstructural and U-Pb systematics study comparing pristine, thermally annealed and chemically abraded ~ 3.5 Ga zircon from a quartz-dioritic gneiss in

the Pilbara craton. Their study has found that Raman spectroscopy on the pristine zircon reveals a positive correlation between the grade of structural damage and U content. Characterization of treated zircon grains using hyper-spectral cathodoluminescence (CL) and Raman spectroscopy suggest structural recovery of point defects, but not yet full repair of high-damage amorphous areas. In addition, Wiemer *et al.*²⁴ found that the most reliable (*i.e.*, accurate and precise) U-Pb ages were achieved through CA treatment, while the effects of pre-analytical treatment are case-specific and controlled by the initial state of the zircon or zircon domain, leading to the general conclusion that standardization of pre-analytical treatment is not recommended. However, whether pre-analytical treatment is useful for laser ablation zircon U-Pb dating is likely depending on the situation of the samples. The tested ancient sample in Wiemer *et al.*²⁴ was from the east Pilbara craton which has shown to have a relatively simple thermal history.³⁸ Given the lack of a comparative study focusing on the most ancient zircon samples with complex geologic/thermal history, the effect of the treatments on older zircon grains subject to substantial Pb loss is yet unclear. For example, in theory, modern Pb loss only affects the Pb/U age with insignificant change of the ²⁰⁷Pb/²⁰⁶Pb age, however, the study of Wiemer *et al.*²⁴ showed a more complicated systematics with the potential improvement of the ²⁰⁷Pb/²⁰⁶Pb age after the treatments (the weighted average ²⁰⁷Pb/²⁰⁶Pb ages of untreated and CA-treated zircon grains of the same sample are 3273 ± 310 Ma and 3389 ± 86 Ma, respectively), suggesting the need of further investigation of older zircon samples with higher grade of Pb loss. Therefore, in this study, we choose complex ancient zircon samples undergone complex post-crystallization thermal events,³⁹ including some of the oldest igneous rocks on Earth (the ~ 4.0 Ga Acasta Gneiss complex^{40,41} and the ~ 3.8 Ga Muzidian Gneiss complex⁴²), in order to further explore the effects of these treatments with respect to the U-Pb ages, trace elements and Lu-Hf isotope compositions.

EXPERIMENTAL

Sample preparation

Samples and materials. Samples used for zircon thermal annealing and chemical abrasion experiments include four zircon reference material Plešovice,⁴³ 91500,⁴⁴ FC-1,⁴⁵ GJ-1⁴⁶ and seven Eoarchean samples. These Eoarchean samples are >3.8 Ga igneous rocks from two of the most ancient terranes on Earth, the Acasta Gneiss Complex (AGC) in Canada (JR13-108, JR13-207, AB13-04) and the Muzidian Gneiss Complex (MGC) in central China (20MZD09, 20MZD11, 22YX05 and 22YX09) (Table 1). The AGC is comprised of polymetamorphic gneisses and foliated granitoids which are exposed along the western margin of the Slave Province in the Northwest Territories, Canada.⁴¹ The rocks of the AGC range in age from 4.03 Ga to ca. 2.94 Ga and were

Table 1. The description and experiment conditions of all zircon samples

Experiment group	U (10×10^6)	Th (10×10^6)	Age (Ma)	Reference	TA conditions	CA conditions
Plešovice	911.2	94.6	337.1 ± 0.4	Sláma <i>et al.</i> ⁴³	850 °C/48 h	/
91500	84.8	30.1	1064.5 ± 0.6	Wiedenbeck <i>et al.</i> ⁴⁴	850 °C/48 h	/
FC-1	933.9	683.7	1099.0 ± 0.6	Paces and Miller, ⁴⁵	850 °C/48 h	/
GJ-1	264.2	8.7	599.7 ± 2.7	Jackson <i>et al.</i> ⁴⁶	850 °C/48 h	/
20MZD09	464.0	176.3	3772 ± 27	Wang <i>et al.</i> ⁴²	850 °C/48 h	/
22YX05-1	806.0	250.8	3843 ± 46	this study	850 °C/48 h	/
22YX05-2	766.1	378.0			850 °C/48 h	PDA*(170 °C/12 h)
22YX09-1	693.7	281.8	3822 ± 28		850 °C/48 h	/
22YX09-2	805.3	346.1			950 °C/48 h	/
22YX09-3	477.0	209.4			1050 °C/48 h	/
22YX09-4	1068.1	547.8			850 °C/48 h	PDA*(170 °C/12 h)
AB13-04-1	700.8	314.0	3923 ± 190	Bauer <i>et al.</i> ⁴¹	850 °C/48 h	/
AB13-04-2	761.2	277.8			1050 °C/48 h	/
AB13-04-3	666.0	480.0			850 °C/48 h	PDA*(170 °C/12 h)
JR13-207-1	716.0	377.7	4003 ± 23	Reimink <i>et al.</i> ⁴⁰	850 °C/48 h	/
JR13-207-2	370.9	238.4			850 °C/48 h	PDA*(170 °C/12 h)
JR13-108	558.1	392.0	3997 ± 6		850 °C/48 h	/
20MZD11	1045.4	161.1	3806 ± 28	Wang <i>et al.</i> ⁴²	850 °C/48 h	/

* PDA indicates partial dissolution analysis.

modified during post-formation metamorphic events. The oldest units in the AGC are 4.03 and ~4.02 Ga followed by later periods of magmatic activity at 3.96–3.94 Ga, 3.74–3.72 Ga, 3.66–3.58 Ga, ~3.4 Ga and ~2.9 Ga.^{40,47–52} Zircon grains were extracted from tonalite gneiss samples JR13-108, JR13-207 and AB13-04 with ages of 3997 ± 6 Ma (²⁰⁷Pb/²⁰⁶Pb age),⁴⁰ 4003 ± 23 Ma (²⁰⁷Pb/²⁰⁶Pb age)⁴⁰ and 3923 ± 190 Ma (upper intercept age),⁴¹ respectively. The MGC is an Eoarchean gneiss complex in the northern edge of the Yangtze Craton where Archean basement rocks are sparsely exposed.⁴² The Eoarchean rocks (3.9 Ga–3.5 Ga) in the MGC were first reported by Qiu *et al.*⁵³ and then Wang *et al.*⁴² Zircon grains were separated from tonalite samples 20MZD09 and 20MZD11 with ages of 3772 ± 27 Ma and 3806 ± 28 Ma.⁴² Two new tonalite samples 22YX05 and 22YX09 collected at a nearby outcrop are also investigated in this study. The details (age, size, morphology, color and CL image characteristics, *etc.*) of these zircon samples are given in the Supporting Information. All zircon samples were divided into two groups (1) thermal annealing only and (2) thermal annealing followed by partial dissolution treatment. The references of the zircon samples and the conditions of the experiments are also given in Table 1.

Thermal annealing. Thermal annealing was carried out at the Institute of Geochemistry, Chinese Academy of Sciences. The annealing equipment of zircon was a box-type resistance furnace (SRJX-4-13, Taiste), the temperature control range was 300 ~ 1300 °C at room temperature, and the temperature fluctuation was ±5 °C. Approximately 200 intact grains for each experimental group (Fourteen groups were thermally annealed and four thermally annealed groups followed by partial dissolution treatment) in a total of seven Eoarchean zircon samples were carefully selected for thermal annealing experiment under binocular stereotypic microscope. Thermal annealing was performed in 3 mL corundum crucibles with lids at 850 °C, 950 °C,

and 1050 °C for 48 h. For each zircon standard (Plešovice, 91500, GJ-1 and FC-1), 10 grains or fragments of similar sizes (~200 μm) were randomly selected for thermal annealing experiment (850 °C/48 h) along with unknown samples (Table 1). Following heating, the samples were left in the furnace to cool for a few hours. The annealed zircon grains were then cleaned in 4 N HNO₃ followed by rinse and sonicate with Milli-Q water to remove any surface contamination.^{54,55}

Chemical abrasion. Chemical abrasion was completed in the clean lab of the Research Center for Planetary Science, Chengdu University of Technology (CDUT). After thermal annealing, a subset of four zircon samples (JR13-207, AB13-04, 22YX05 and 22YX09) were selected for further partial dissolution experiment. For each of these four zircon samples, approximately half of the thermally annealed (850 °C/48 h) zircon grains (~100 grains) were processed (Table 1). Zircon samples were loaded into 3 mL Teflon microcapsules (Savillex) for leaching in concentrated hydrofluoric acid inside a Parr-type dissolution vessel at 170 °C for 12 hours for partial dissolution. After the partial dissolution step, the zircon samples were cooled to room temperature, residual hydrofluoric acid was carefully pipetted out of each vial, and zircon grains were rinsed in 3 N HCl and Milli-Q water for three times.^{28,30,54,55}

Zircon mounting and imaging. After thermal annealing and chemical abrasion, all zircon grains were then mounted in epoxy resin and cured. After the zircon mounts were polished to the approximate half-depth of most grains, the zircon samples were imaged for cathodoluminescence (CL) using a field emission scanning electron microscope (Quanta 250 FEI) at the Chengdu University of Technology.

Analytical methodology

Raman spectroscopy. Raman spectroscopy of zircon was performed at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Raman spectra were acquired using the Labram HR Evolution Raman spectrometer. Measurements were made using a 532 nm diode laser and the laser power to the zircon surface was 20 mW. All measurements were made using an 1800 gmm⁻¹ grating, a 100 μm slit, a 400 ~ 100 μm confocal pinhole, and a 20× long working distance objective lens. This setup has a spectral resolution better than 0.6 cm⁻¹ and a spatial resolution of <1 to ~5 μm. All laser Raman analyses were performed before LA-ICPMS U-Pb dating to avoid the effects of the ablation pit.²⁴

Zircon Laser ablation U-Pb dating and trace element measurement. Zircon U-Pb dating measurements were performed in two laboratories. The first session of the zircon U-Pb dating (20MZD09, 20MZD11, 22YX05, 22YX09, AB13-04, JR13-207 and JR13-108) was conducted at the Laboratory of Isotope Geochemistry, Wuhan Center of China Geological Survey (CGS-Wuhan). U-Pb dating session 1 and trace elements measurement of annealed zircon samples were performed using a 193 nm ArF excimer laser ablation system (RESolution, Applied Spectra) coupled with ICAP-Q inductively coupled plasma mass spectrometry (Thermo Scientific). The diameter of the laser spot was 29 μm, and the total time of single spot analysis was 65 s, including 10 s for background acquisition (gas blank), 30 s of data acquisition from the sample, and 25 s wash-out time. The energy density and frequency used are 4 J/cm² and 4 Hz, respectively (Table S1). The second session of zircon U-Pb dating (Plešovice) was completed at the Research Center for Planetary Science, Chengdu University of Technology. The U-Pb dating session 2 was carried out using a 193 nm ArF excimer laser ablation system (Teledyne Analyte Excite) coupled with ICAP-RQ inductively coupled plasma mass spectrometry (Thermo Scientific). The diameter of the laser spot was 25 μm, and the energy density and frequency of the laser were 3 J/cm² and 7 Hz, respectively. For individual analysis, the background acquisition is 15 s containing 8 s laser warm-up, 30 s of data acquisition, and 25 s for washout (Table S1). In both U-Pb dating sessions, the primary reference material is TA 91500 (1064.5 ± 0.6 Ma),⁴⁴ and the quality control standards are TA GJ-1 (reference ²⁰⁶Pb/²⁰⁸U age=599.7 ± 2.7 Ma)⁴⁶ and TA FC-1 (reference ²⁰⁷Pb/²⁰⁶Pb age=1099.0 ± 0.6 Ma).⁴⁵ The analytical sessions in both laboratories give identical results on the quality control standards (CGS-Wuhan session, GJ-1: ²⁰⁶Pb/²⁰⁸U age=600.2 ± 2.7 Ma (MSWD=0.7, N=10), FC-1: ²⁰⁷Pb/²⁰⁶Pb age=1098.0 ± 5.1 Ma (MSWD=0.6, N=27); CDUT session, GJ-1: ²⁰⁶Pb/²⁰⁸U age=601.2 ± 2.2 Ma (MSWD=1.3, N=35); FC-1: ²⁰⁷Pb/²⁰⁶Pb age=1100.2 ± 4.0 Ma, (MSWD=1.0, N=28)) (Table S2, Fig. S1). For the trace elements measurement, NIST 610 glass was the primary reference material and ²⁹Si was the internal standard.⁵⁶ Zircon standards 91500 and GJ-1⁵⁷ were used as quality control standards for trace element measurement and the results were all within 10% error of the reference value (Table S3). All data were

reduced offline using Iolite v4 software.⁵⁶ All U-Pb age calculations and plotting of concordia diagrams were performed using the Isoplot Excel add-in.⁵⁸ The results of the LA-ICP-MS measurement for zircon samples and standards are presented in Table S2, S3 and S4. The uncertainty of a single analysis is reported as 2SE of in-run error propagating the uncertainty of decay constant and the external reproducibility of primary standard by a smoothed line-fitting scheme in Iolite.

Laser ablation Hf isotopes. Zircon in-situ Lu-Hf isotope compositions were determined using a 193 nm ArF excimer laser ablation system (RESolution, Applied Spectra) coupled with a Neptune Plus multi-collector ICPMS (Thermo Scientific) at the Laboratory of Isotope Geochemistry, Wuhan Center of China Geological Survey. Analysis parameters include a spot size of 43 μm, an energy density of 6 J/cm², and a frequency of 6 Hz. For single spot analysis, signals of ¹⁸⁰Hf, ¹⁷⁹Hf, ¹⁷⁸Hf, ¹⁷⁷Hf, ¹⁷⁶(Hf+Yb+Lu), ¹⁷⁵Lu, ¹⁷³Yb, and ¹⁷¹Yb were collected for 60 s during laser ablation in static mode, following 30 s of gas background acquisition (Table S1). The ¹⁷⁶Yb interference is corrected relative to ¹⁷⁶Yb/¹⁷³Yb of 0.79381.⁵⁹ The mass bias of Yb and Hf were corrected using exponential law, normalized to ¹⁷³Yb/¹⁷¹Yb=1.132685⁵⁹ and ¹⁷⁹Hf/¹⁷⁷Hf=0.7325.⁶⁰ Interference from ¹⁷⁶Lu (on ¹⁷⁶Hf) is corrected relative to ¹⁷⁶Lu/¹⁷⁵Lu=0.02655⁶¹ and using the mass bias factor of Hf.⁶² Data were reduced offline using Iolite v4 software with a customized Hf data reduction scheme after Fisher *et al.*⁶³ and Wang *et al.*⁶⁴ Untreated and TA 91500 were used as the primary standard (¹⁷⁶Hf/¹⁷⁷Hf=0.282305 ± 6)⁶⁵ for untreated and TA samples, respectively. The high Yb/Hf zircon standard R33 (reference: ¹⁷⁶Hf/¹⁷⁷Hf=0.282764 ± 14,⁶³ this study: ¹⁷⁶Hf/¹⁷⁷Hf=0.282771 ± 13) was analyzed frequently to monitor the effectiveness of interference correction. Other quality control standards are the untreated GJ-1 (reference: ¹⁷⁶Hf/¹⁷⁷Hf=0.282000 ± 5,⁶⁶ this study: ¹⁷⁶Hf/¹⁷⁷Hf=0.282009 ± 23) and untreated FC-1 (reference: ¹⁷⁶Hf/¹⁷⁷Hf=0.282184 ± 16,⁶⁷ this study: ¹⁷⁶Hf/¹⁷⁷Hf=0.282181 ± 23) zircons, the measured ¹⁷⁶Hf/¹⁷⁷Hf are in good agreement with reference values (Table S5, Fig. S2).

RESULTS AND DISCUSSION

Effects of the thermal annealing

Zircon morphology. The zircon grains selected for this experiment have mostly light yellow to gray color, glassy to greasy luster, and transparent to translucent transparency (Fig. S3), which are typical of metamict zircon.⁶⁸⁻⁷² After thermal annealing, the colors of the Muzidian zircon samples were lightened to colorless, the transparency was changed to transparent, and the luster was changed to glassy (Fig. S3). In comparison, the Acasta zircon grains showed an increase in zircon transparency after annealing,

Fig. 1 Examples of Raman spectra ($100 \sim 1200 \text{ cm}^{-1}$) obtained in this study. (a) and (b): Representative Raman spectra comparing untreated with annealed zircon grains. (c): The ν_3 (SiO_4) peaks at $\sim 1008 \text{ cm}^{-1}$ are shown in detail. FWHM= the full-width at half maximum.

but less lightening of their colors that were mostly yellow to light yellow (Fig. S3i-n), which is in general agreement with the previous phenomenon of thermally annealing zircon with moderate metamict.⁵⁵ At present, there are two main views on the cause of zircon color: one is that the decay of radioactive elements such as U, Th, and Pb causes damage to the crystal structure of untreated zircon, resulting in lattice defects and the formation of cavity color centers, thus showing various colors and reduced transparency. The other view is that the color is directly related to the elements with electrovalence change such as Fe, Ti, and U in zircon.⁶⁸⁻⁷² Therefore, the improvement in zircon's appearance after heat treatment indicates that the thermal annealing was able to greatly reduce the radiation-induced crystalline defects caused by radiation, and thus increased transparency and changed color (Fig. S3).⁶⁸ The color change may be related to the change in valence of elements such as Fe, Ti, and U in zircon during annealing in the open air (i.e., a relatively oxidizing environment).⁷²⁻⁷⁴ The observed changes in zircon color, luster, and transparency indicate that thermal annealing can recover radiation damage in zircon and restore the crystallinity of zircon to a certain extent. In addition, the CL image characteristics (brightness and oscillatory zoning) of untreated and thermally annealed zircon are essentially the same, indicating that the trace element content (U, Y, Dy, and Tb) of the zircon surface has not changed (Fig. S4).

Microstructural state. The Raman spectroscopy of zircon was used to evaluate the metamict degree of zircon quantitatively and the effect of the thermal annealing temperature. The systematic shift of zircon Raman bands and the full-width at half maximum (FWHM) of the ν_3 (SiO_4) anti-symmetrical stretching mode of the B1g Raman band at $\sim 1008 \text{ cm}^{-1}$ are sensitive to the degree of

decay-related lattice distortion (i.e., commonly called "metamict").⁷⁵⁻⁷⁸ As the degree of decay damage increases, Raman band intensity reduces along with the increase of the FWHM and frequency shift towards lower wavenumbers.^{79,80} Nasdala *et al.*^{76,77} systematically classified the metamict degree of zircon based on the FWHM values corresponding to the vibrational peak at 1008 cm^{-1} . Weak, moderate and strong damages correspond to the cutoffs of FWHM values at 5 cm^{-1} , 10 cm^{-1} , and 20 cm^{-1} , respectively. Multiple Raman analyses were performed on several zircon grains from each sample (untreated and thermal annealing) to assess intra-crystalline variations of radioactivity-induced damage. Measured ν_3 (SiO_4) positions and HWHM are reported in Table S5. Fig. 1 shows that the Acasta and Muzidian zircon samples have average ν_3 (SiO_4) positions of 1003.32 cm^{-1} and wider HWHM values of 9.06 cm^{-1} , the typical features observed for metamict zircons.^{76,77} CA-TIMS or TA-LA-ICPMS uses high temperature treatment (in the range of $800 \text{ }^\circ\text{C}$ - $1100 \text{ }^\circ\text{C}$ for 48 h)²⁸ to recover zircon lattice radiation damage from natural alpha, alpha recoil, and spontaneous fission processes. Our experiment results show that heating at the temperatures $>850 \text{ }^\circ\text{C}$ (and up to $1050 \text{ }^\circ\text{C}$ for two zircon samples) for 48 hours, the position and HWHM values of the annealed zircon returned to $\sim 1008 \text{ cm}^{-1}$ and below 5 cm^{-1} , respectively, identical to the values of the gem quality zircon reference standard, suggesting a sufficient annealing condition (Table S6, Fig. 1). Based on the previous systematic classification of the degree of recrystallization of zircon,^{76,77} the untreated Muzidian zircon grains are slightly metamict and has recovered its crystal structure after thermal annealing, while the untreated Acasta zircon samples are moderately metamict and still slightly metamict annealing at $850 \text{ }^\circ\text{C}/48 \text{ h}$. This suggests that the Acasta zircon samples have a higher grade of metamictization,

Fig. 2 Comparative results between untreated and thermally annealed Plešovice. The red solid line shows the average value of untreated Plešovice, the blue shows the average value of thermal annealing, and the shading shows the error (2σ).

which requires a highly temperature (up to 1050 °C) to recover the crystal structure (Fig. 1b). This is because that the metamictization of zircon has three stages. The first stage is the accumulation of point defects, causing the slight expansion and disorder of zircon; the second stage is the distortion of crystal lattice and the gradual transformation to amorphous while the lattice structure is still dominated by crystalline; in the third stage, the zircon lattice is completely amorphous.⁸¹

Thermal annealing is the opposite of the metamict process, but the high-temperature thermal annealing of metamict zircon is thought to be a dynamic process controlled mainly by temperature and time, involving multiple annealing stages and the decomposition of $ZrSiO_4$. First of all, for the thermal annealing time, annealing durations within the ID-TIMS U-Pb community typically range between 48 h and 60 h.²⁸ Annealing studies of radiation damage in zircon demonstrate that annealing only weakly depends on heating duration after the first few hours of heating.³⁷ Thus, the time difference between 48 h and 60 h is not expected to significantly change zircon crystallinity or affect chemical abrasion outcomes.⁵⁵ Secondly, based on the thermal annealing temperature, the annealing process of slight to moderate metamict zircon was divided into two stages. When the temperature was lower than 1000 K, the point defects in the crystal were gradually eliminated and the crystals underwent a restoration of the short-range ordering; while the temperature was higher than 1000 K, the crystals started to recrystallize as a restoration of the long-range ordering.⁸² Therefore, the annealing temperature of 850 °C only reaches the first stage of crystal structure recovery and

removes the point defects in the Muzidian zircon samples (Fig. 1a). A higher temperature up to 1050 °C would reach the second stage of crystal structure recovery, making the damaged crystal lattice of Acasta zircon to gradually heal (Fig. 1b). Based on our results, we suggest that the required annealing conditions for the maximum recovery (up to 80%⁸²) of a damaged zircon grain may vary depending on the metamict degree, and therefore the measurements of the Raman band and FWHM values would be useful. However, for highly metamict zircon, thermal annealing is not the inverse of radiation damage accumulation, but a likely decomposition of $ZrSiO_4$ to form ZrO_2 and SiO_2 .^{80,83}

Trace elements. The commonly used reference zircon material, Plešovice zircon, has been thoroughly characterized to test any possible compositional variation caused by annealing.⁴³ Consequently, we explore the potential effect of annealing on zircon trace-element composition. Trace element abundances were measured for untreated and annealed zircon samples of Plešovice, 20MZD09, and 20ZMD11. The trace element results are given in Table S3. Fig. 2 shows comparative results of trace element abundances between untreated and thermally annealed fragments of Plešovice. The comparative results indicate that there is no significant change in the mean values of the commonly used elemental ratios in zircon such as Th/U, Yb/Dy, Sm/Yb, and Yb/Gd, after the annealing. In addition, on the chondrite-normalized REE plots (Fig. 3),⁸⁴ the untreated and thermally annealed zircon samples (zircon standard and natural igneous zircon) are shown to be consistent. Moreover, the CL images (Fig. S4) of thermally annealed zircon grains show magmatic oscillatory

Fig. 3 Chondrite-normalized REE patterns for untreated and thermally annealed zircon samples. The gray area is the trace element range of untreated zircon. The REE of Chondrite is quoted from McDonough and Sun (1995).⁸⁴ The annealing condition for all samples in the figure is 850 °C/48 h. Zircon trace element data were measured at the Laboratory of Isotope Geochemistry, Wuhan Center of China Geological Survey (CGS-Wuhan).

zoning identical to the original, untreated grains. In conclusion, annealing of zircon samples at 850 °C for 48 h does not lead to any fractionation of trace elements at a spatial resolution of ~30 μm.³⁰

Matrix effects. Elemental and downhole fractionation are two of the most important factors in the determination of highly accurate and precise zircon U-Pb ages by laser ablation. The matrix effects refer to the difference in radiation damage between the unknown and the reference zircon. During LA-ICPMS, a mismatch of matrix potentially introduces differences in the laser ablation depth and laser down-hole fractionation.^{30,36,85,86} Allen and Campbell³⁶ suggested that the different degree of radiation damage between the reference and unknown materials correspond to a disparity in physical properties. For highly damaged zircon grains, Pb in the region immediately adjacent to the ablation hole is more likely to escape than U during laser ablation, which leads to a potentially high ²⁰⁶Pb/²³⁸U apparent age. In theory the matrix effects only affect the ²⁰⁶Pb/²³⁸U ratios and not the ²⁰⁷Pb/²⁰⁶Pb ratios. For young zircons using ²⁰⁶Pb/²³⁸U ages, it is important to eliminate the matrix effect.

Fig. 4 Ablation pit profiles of zircon samples. (a), (c), (e), (g) and (i): 3D view of zircons. (b), (d), (f), (h) and (j): Cross-sectional view of zircons.

The natural variation in the U and Th concentration of zircon, and hence the amount of accumulated radiation damage,²¹ has a direct influence on zircon ablation rates.^{36,86} Generally, the more radiation damage accumulates, the faster the ablation rate is. Plešovice has relatively high and variable U concentrations, and thus accumulates more radiation damage in the crystal (Fig. 1a).⁸⁷ Previous Raman spectra studies show that Plešovice has variable FWHM, with values ranging from 5 cm⁻¹ to 16 cm⁻¹, consistent with the characteristics of slightly to moderately damaged zircon.¹⁴ In our measured depth profile of the laser ablation craters, the thermally annealed grains show a more consistent crater shape than that of untreated grains (Fig. 4). This could be interpreted by the structural recovery of zircon due to thermal annealing. With regard to the ablation depths, the untreated zircon samples are approximately 25% deeper than the thermally annealed counterparts, which is consistent to Crowley *et al.*⁸⁸ and Donaghy *et al.*⁸⁹ Thermally annealed and chemically abraded zircon grains

Fig. 5 The weighted average ²⁰⁶Pb/²³⁸U age of untreated and thermally annealed Plešovice zircon. The red solid line shows the ²⁰⁶Pb/²³⁸U age mean of the untreated Plešovice, and the blue shows the mean of the thermal annealing. The error of the mean age is 2σ. Zircon U-Pb dating (Plešovice) was completed at the Research Center for Planetary Science, Chengdu University of Technology (CDUT).

Fig. 6 U-Pb Concordia diagrams. The upper intercept age of untreated 20MZD09 (f) is 3772 ± 25 Ma.⁴² The upper intercept age of untreated 20MZD11 (p) is 3806 ± 28 Ma.⁴² The points in the pink ellipse in Fig. (k) indicate the minimum crystallization age of untreated JR13-108 (3997 ± 6 Ma).⁴⁰ The points in the pink ellipse in Fig. (m) indicate the minimum crystallization age of untreated JR13-207 (4003 ± 23 Ma).⁴⁰ The crystallization age of untreated AB13-04 is 3923 ± 190 Ma (Fig. r).⁴¹ (a-e): Concordia plot of U-Pb analyses of 22YX09. (f-g): Concordia plot of U-Pb analyses of 20MZD09. (h-j): Concordia plot of U-Pb analyses of 22YX05. (k-l): Concordia plot of U-Pb analyses of JR13-108. (m-o): Concordia plot of U-Pb analyses of JR13-207. (p-q): Concordia plot of U-Pb analyses of 20MZD11. (r-u): Concordia plot of U-Pb analyses of AB13-04. All ellipses are plotted with 2σ . Zircon U-Pb dating was completed at the Laboratory of Isotope Geochemistry, Wuhan Center of China Geological Survey (CGS-Wuhan).

show similar ablation depth ($\sim 8 \mu\text{m}$), suggesting that the chemical abrasion does not affect the zircon crystallinity.

The results of Allen and Campbell³⁶ showed that the $^{206}\text{Pb}/^{238}\text{U}$ age of untreated Plešovice was 339.7 ± 1.8 Ma (MSWD=3.7, N=29), while the $^{206}\text{Pb}/^{238}\text{U}$ age of Plešovice was reduced to 337.9 ± 1.2 Ma (MSWD=2.6, N=31) after thermal annealing treatment. The reduction of the $^{206}\text{Pb}/^{238}\text{U}$ age of Plešovice is also observed in our experiment (Fig. 5). In this experiment, laser Raman

spectroscopy and U-Pb dating were performed on the untreated ($D_a=1.05 \times 10^{18} \text{ a/g}$) and annealed Plešovice ($D_a=6.10 \times 10^{17} \text{ a/g}$), and the results showed that our untreated Plešovice grains give Raman position and FWHM values of 1005.93 cm^{-1} and 5.52 cm^{-1} , showing slight damage compared with annealed values of 1007.03 cm^{-1} and 4.78 cm^{-1} (Table S6, Fig. 1a). Using annealed 91500 as the reference material, fifty-one analyses of the untreated Plešovice define a $^{206}\text{Pb}/^{238}\text{U}$ weighed average age of 341.4 ± 1.0 Ma (MSWD=2.1, N=51), while the annealed Plešovice analyses

Table 2. Comparison of the weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of untreated, thermally annealed, and chemically abraded samples

Sample	Untreated	TA (850 °C/48 h)	TA (850 °C/48 h)+CA (HF/170 °C/12 h)
22YX05	3628 ± 56 Ma (N=37, MSWD=11.5)	3689 ± 69 Ma (N=26, MSWD=7.3)	3739 ± 19 Ma (N=84, MSWD=3.9)
22YX09	3628 ± 50 Ma (N=52, MSWD=10.1)	3695 ± 31 Ma (N=77, MSWD=9.6)	3760 ± 13 Ma (N=70, MSWD=3.4)
JR13-207	3619 ± 200 Ma (N=12)	3727 ± 88 Ma (N=33, MSWD=18)	3955 ± 15 Ma (N=33, MSWD=3.7)
AB13-04	3871 ± 157 Ma (N=4, MSWD=18)	3667 ± 130 Ma (N=14, MSWD=3.1)	3942 ± 22 Ma (N=40, MSWD=3.6)
20MZD09	3587 ± 60 Ma (N=32, MSWD=10.5)	3612 ± 130 Ma (N=19, MSWD=1.5)	/
20MZD11	3527 ± 50 Ma (N=49, MSWD=7.0)	3548 ± 130 Ma (N=22, MSWD=4.0)	/

gave a weighted average age of 337.1 ± 0.8 Ma (MSWD=2.2, N=73) (Fig. 5). Although both ages of Plešovice agree with the ID-TIMS reference age, within errors, the annealed analyses give a slightly more accurate age, which is consistent with Allen and Campbell's³⁶ finding that thermal annealing of both reference and unknown zircons at 850 °C for 48 hours in air can eliminate the alpha-dose-induced differences in measured $^{206}\text{Pb}/^{238}\text{U}$. In addition, thermally annealed quality control standards GJ-1 and FC-1 (normalized against annealed 91500) yielded $^{206}\text{Pb}/^{238}\text{U}$ ages of 601.2 ± 2.2 Ma (MSWD=1.3, N=35) (c.f., untreated: 601.7 ± 1.4 , MSWD=0.8, N=16)⁹⁰ and 1100.2 ± 4.0 Ma (MSWD=1.0, N=28) (c.f., untreated: 1122 ± 6 Ma, MSWD=2.7, N=28),³⁶ respectively, suggesting the improvement of matrix match between different zircon crystals after annealing. Therefore, the Raman, U-Pb age and ablation rate results collectively indicate that (1) the thermal annealing process itself does not cause U/Pb fractionation, and thus cause no significant matrix effect; (2) the age of damaged zircon samples may be improved by thermal annealing, especially of high U natural zircons that are moderately metamict.²⁴

Thermal annealing vs. chemical abrasion

U-Pb ages. The U-Pb results of Eoarchean zircon samples are typically discordant due to high degree of Pb loss (Fig. 6). Here we present the comparative age results of samples treated by thermal annealing and chemical abrasion amid the improvement of zircon U-Pb dating of ancient rocks. The comparison of the experimental results shows that the U-Pb ages of untreated, thermally annealed, and chemically abrasion zircon grains from the same sample are consistent with each other, within error, indicating that these treatments do not affect the accuracy of the upper intercept U-Pb age results (Fig. 6). For example, the upper intercept age of the samples 22YX05 and are 3837 ± 29 Ma (N=37) and 3840 ± 21 Ma (N=52) (untreated), 3846 ± 18 Ma (N=26) and 3852 ± 10 Ma (N=78) after thermal annealing, and 3875 ± 12 Ma (N=110) and 3863 ± 16 Ma (N=70) after chemical abrasion treatment. However, the lower intercept ages are less consistent with relatively large errors, and do not match any of known local geologic events.⁵³ These could be the result of Pb loss (ancient and modern) with natural annealing of the zircon grains, which yielded geologically meaningless lower intercept ages. Structural recovery during natural thermal annealing results in rejection of Pb, progressing from low-to higher damage portions.⁹¹ If higher

damage sites become isolated and inaccessible for leaching, Pb will be trapped. Recent studies using high-resolution scanning transmission electron microscopy⁹² and atom probe tomography,^{93,94} have demonstrated the existence of randomly distributed nm-scale Pb clusters, particularly in ancient zircon, accumulated and trapped during metamorphism that led to Pb loss. The discordia of thermally annealed zircon analyses may represent an example of mixing of different U-Pb components.²⁴ The inclusion of the high-U cluster data lowered the slope of the discordia line and shifted the lower intercept towards younger (or negative) ages.

In general, the improvements on the MSWD values of the upper intercept ages and the $^{207}\text{Pb}/^{206}\text{Pb}$ ages indicate that the chemical abrasion appears to be an effective pre-analytical treatment. For example, the MSWDs of the upper intercept age of samples 22YX05 and 22YX09 were reduced from 11.5 and 10.1 to 7.3 and 9.6 by thermal annealing alone, and further reduced to 3.9 and 3.4 by chemical abrasion, respectively. The MSWD values of the upper intercept ages moved much closer to MSWD=1 after the CA treatments (Table 2, Fig. 6), compared to the untreated results. The treatment also results in clear improvement on the $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Table 2, Fig. 7), which could indicate that the release of the concentrated Pb (e.g., metallic Pb nanospheres⁹¹ or nm-scale Pb clusters²⁴) generated during high-grade metamorphism. For example, sample 22YX05 has a weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3628 ± 56 Ma (N=37) prior to the treatment, while the weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of TA and CA treated zircon grains of the same sample are 3689 ± 69 Ma (N=26) and 3739 ± 19 Ma (N=84), respectively (Table 2, Fig. 7).

Here we use the median of percentage concordance ($(^{206}\text{Pb}/^{238}\text{U} \text{ age}/^{207}\text{Pb}/^{206}\text{Pb} \text{ age}) \times 100$) of U-Pb ages to measure the effectiveness of the thermal annealing versus chemical abrasion (Fig. 8), in order to reflect the degree of change in $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages after the treatments. The median values of percentage concordance after thermal annealing are broadly consistent with the untreated zircon samples. In contrast, the median of percentage concordance after chemical abrasion increases by various degrees compared to that of the untreated and thermal annealed zircon (e.g., for 22YX05 and 22YX09, untreated 80-84%, TA 85-89%, CA 90-91%, Fig. 8). The insignificant effect of thermal annealing alone suggests that the natural annealing likely occurred after the crystallization of zircon, which already

Fig. 7 Comparison of the weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of untreated, thermally annealed, and chemically abraded zircon samples. (a-c): The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 22YX05. (d-f): The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 22YX09. (g-i): The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of JR13-207. (j-l): The weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ ages of AB13-04.

repaired the structural damage of zircon to some extent, because radiation damage of zircon can be self-recovering when the ambient temperature of zircon is higher than the self-annealing temperature of zircon.³⁶ Self-annealing also explains our observation that a great proportion of the ~3.8 Ga Muzidian zircon grains have a relatively clear and transparent appearance. In addition, the theoretical D_α value of zircon also indicates that natural annealing occurred after the formation of zircon.⁹⁴ Murakami *et al.*⁹⁵ suggest that a value greater than $8 \times 10^{18} \alpha/\text{g}$ indicates an amorphous state of zircon. All of the ancient zircon

samples have D_α values greater than $8 \times 10^{18} \alpha/\text{g}$ (22YX05: $2.89 \times 10^{19} \alpha/\text{g}$, 22YX09: $2.05 \times 10^{19} \alpha/\text{g}$, Table S4), indicating that the zircon grains were highly metamict. Given the relatively low degree of apparent metamictization shown by the zircon laser Raman results (Table S6), post-crystallization natural annealing likely reset the D_α values. Therefore, the thermal annealing treatment would be less effective on the ancient zircon grains already undergone self-annealing with a transparent appearance.

Chemical abrasion following thermal annealing appears to be

Fig. 8 Comparison of the concordance of untreated, thermally annealed, and chemically abraded zircon samples. The solid red line shows the age concordance for untreated zircon, the solid blue line shows the age concordance for thermally annealed zircon, the solid yellow line shows age concordance for chemically abraded zircon and the dashed line indicates the median age concordance. (a): The age concordance of 22YX09. (b): The age concordance of 22YX05. (c): The age concordance of JR13-207. (d): The age concordance of AB13-04.

effective (Figs. 6-8). This is most likely because the partial dissolution method using hydrofluoric acid can remove the exposed, damaged domains that are easier to be dissolved, and thus effectively reduced the Pb loss observed in the U-Pb data.^{28,88} Additionally, chemical abrasion appears to have a more significant effect on the Acasta zircon grains than the Muzidian zircon grains, which is particularly true for sample JR13-207 whose age concordance has increased by nearly 20% from the TA treatment alone (from ~80 to ~100%, Fig. 8). This is possibly due to the different degrees of radiation damage between the Muzidian and Acasta zircon grains. Even after thermal annealing, not all zircons respond the same way to a particular set of partial dissolution steps.^{55,96} The progression of dissolution steps can be explained with a combination of physical accessibility plus solubility-inducing lattice distortions caused by high U + Th + correlated trace-element concentrations.⁹⁷ According to the McKenna *et al.*,^{55,96} the dissolution mechanism of low and high radiation-damaged zircons is different. For high radiation-damage zircon samples, besides the highly damaged rims, acid easily accesses crystal cores to dissolve inclusions and interior zones during a

short leaching duration (4 h), leaving behind an inclusion-free residue with a higher degree of crystallinity. The most common acid paths into crystal cores in the Acasta zircon grains of this study are possibly fractures that are spatially associated with radiation damage zones and inclusions (Fig. S4). In comparison, the mechanics of zircon dissolution is possibly different for the less-damaged Muzidian samples. Micro-CT measurements to show that dissolution in highly crystalline material is crystallographically controlled and strongly anisotropic.⁵⁵ Although fractures spatially associated with large mineral inclusions still play an important role for the acid to attack the grain interiors, grains were predominantly dissolved from rim to core along the crystal's c axis (Fig. 14a, 15b, 16c in McKenna *et al.*, 2023⁹⁶). Consequently, the Muzidian zircon crystals with high aspect ratios (*e.g.*, 3:1, Fig. S4) were possibly dissolved more slowly than the more equant grains such as the Acasta zircon. In addition, this can be explained by the core-rim structure of zircon grains. The Acasta zircon grains are smaller and the interior structure of the zircon grains is relatively simple (Fig. S4). In contrast, the Muzidian zircon grains are larger in size and have a

Fig. 9 $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic compositions of untreated (red) and thermally annealed (blue) Plešovice. The mean $^{176}\text{Hf}/^{177}\text{Hf}$ of the untreated Plešovice (red) is 0.282484 ± 0.000020 (2σ) and the mean $^{176}\text{Hf}/^{177}\text{Hf}$ of the thermally annealed (blue) Plešovice is 0.282482 ± 0.000012 (2σ). Zircon Hf isotopic data were measured at the Laboratory of Isotope Geochemistry, Wuhan Center of China Geological Survey (CGS-Wuhan).

Fig. 10 Hf isotopic compositions of untreated, thermally annealed and chemically abraded Archean zircon samples. (a) and (b) represent the mean $^{176}\text{Hf}/^{177}\text{Hf}$ of FC-1 and GJ-1, respectively. (c) and (d) represent the initial ϵHf value of 22YX05 and AB13-04, respectively.

more complex, clear core-rim structure, where the older core is of the most interest. Therefore, it is more difficult for the hydrofluoric acid to attack the radiation damaged domains in the core, given the better crystallinity and higher aspect ratios of the Muzidian zircon grains.

Collectively, applying the treatment of combined thermal annealing and chemical abrasion prior to the laser ablation U-Pb analysis is shown to be a useful approach^{29,30,96,98} that helps improve the age results of very ancient, complex zircon samples, such as the ~4.0-3.8 Ga zircon in this study. But for ancient zircon samples with significant radiation damage, there is the possibility

that the entire grain may dissolve during chemical abrasion,^{89,99} so careful evaluation of the radiation damage of zircon grains is very important prior to the chemical abrasion treatment. On the other hand, for highly metamict zircon that complete dissolution may occur during chemical abrasion, the treatment may be used as a supplement to the regular U-Pb dating. Compared with untreated zircon grains, the U-Pb age data of treated zircon grains show better age concordance, less scattered discordia regression with better MSWDs and smaller uncertainties, and significantly improvement on the apparent $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Figs. 6-8). A potential pitfall of the pre-analytical treatment may be reducing the spread of the discordant data points that may increase the

uncertainty of the regression for the upper intercept age. This is possible, but not a significant concern shown by our data. Given the substantial Pb loss of the > 3.8 Ga zircon grains, our results show that reducing the spread to some extent actually improved the regression of the discordia line and yielded a more reliable upper intercept age with less scattered data (Fig. 6a-j). The scatters in the untreated zircon grains are possibly related to the highly damaged zircon domains that were indeed effectively removed with chemical abrasion treatment. For example, for the samples JR13-207 and AB13-04, the treatment significantly reduced the Pb loss, so that the U-Pb analyses of the treated zircon grains yielded a number of concordant data points. In such situation, depending on the distribution of the U-Pb data, we recommend using the most concordant data points as the anchor for the upper intercept age, or taking the weighted mean age of the most concordant points as the crystallization age of the sample (Fig. 6e, 6j, and 6o).

Hf isotopic compositions. The Hf isotopic compositions of untreated and, annealed zircon standards were determined. The Hf isotopic results are given in Table S5. Forty-nine analyses were performed on seven annealed Plešovice fragments (~200 μm), yielding a mean of 0.282482 ± 0.000012 (2SD, N=49) (Fig. 9, Table S5), which is identical with the mean value of untreated Plešovice analyses (0.282484 ± 0.000020 , 2SD, N=118, Fig. 9, Table S5), both agree with the reference value of 0.282482 ± 0.000014 .⁴³ The measurement of untreated quality control standards FC-1 and GJ-1 yielded $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282181 ± 23 (2SD, N=27) and 0.282009 ± 23 (2SD, N=20), respectively. In comparison, annealed FC-1 and GJ-1 yielded consistent $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282183 ± 16 (2SD, N=27) and 0.282008 ± 13 (2SD, N=20), respectively. Our new data show that the thermal annealing pretreatment have no negative effect on the Hf isotopic compositions with no observed elemental mobility.

The potential role of chemical abrasion treatment in zircon Hf isotopic systematics was tested using two Eoarchean samples (22YX05 and AB13-04). The Hf isotope measurements yielded identical initial ϵ_{Hf} values for the untreated, thermal annealing and chemical abrasion groups (Fig. 10, Muzidian sample 22YX05: -2.5 ± 1.1 untreated, -2.4 ± 1.4 TA, -2.5 ± 1.9 CA; Acasta sample AB13-04: -4.2 ± 1.9 untreated, -4.1 ± 1.5 TA, and -4.2 ± 1.4 CA). Therefore, the new data demonstrate that chemical abrasion have no effect on the Lu-Hf systematics despite the partial dissolution of zircon domains. This is consistent with the conclusions drawn in Amelin *et al.*¹⁰⁰ and Bauer *et al.*⁹⁹ that chemical abrasion does not alter the Hf isotopes of zircons. Furthermore, these results suggest that the pre-treatments do not cause mobility of REEs, especially Yb and Lu, which are the most important factors for accurate determination of Hf isotopic compositions of zircon.^{29,62,101,102}

CONCLUSION

Our experiments show that the pre-treatment of chemical abrasion is effective to reduce the influence of Pb loss in the complex ancient zircon prior to LA-ICP-MS U-Pb dating. For the complex ancient (>3.8 Ga) zircon samples in this study, the chemically abraded U-Pb zircon data show a general improvement in U/Pb age concordance and weighted average $^{207}\text{Pb}/^{206}\text{Pb}$ age compared with untreated and thermally annealed zircon grains. Radiation damaged domains were removed using hydrofluoric acid at a temperature of 170 °C, with the rest of the zircon crystal lattice relatively unaffected. Our experiments indicate that the thermal annealing can recover the radioactivity-induced damage of zircon to a certain extent, and improve the matrix match of different zircon grains. Our analytical results also show that the pre-analytical treatments do not cause elemental fractionation or have a negative effect on the measurement of Hf isotopic compositions. We suggest that the pre-analytical treatments of thermal annealing and chemical abrasion are useful for getting better constrained U-Pb ages of ancient zircon samples with substantial Pb loss, such as the samples from Acasta and Muzidian Gneiss Complexes.

ASSOCIATED CONTENT

The supporting information (Tables S1-S6 and Figs. S1-S4) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION



Da Wang received his PhD degree in Geology from Washington State University in 2018. He is a research professor at the Research Center for Planetary Science, College of Earth and Planetary Sciences, Chengdu University of Technology. His research focuses on the evolution of early Earth and early solar system using radiogenic isotopes.



Zhaofeng Zhang received his PhD degree in Isotope geochemistry from University of Science and Technology of China in 2001. He is a research professor at the Research Center for Planetary Science, College of Earth and Planetary Sciences, Chengdu University of Technology. His research focuses on the analytical techniques, major reservoirs and fractionation mechanisms of non-traditional isotopes and their

applications in Earth and planetary sciences.

Corresponding Author

* Da Wang

Email address: da.wang@cdut.edu.cn

*Z. F. Zhang

Email address: zzf@cdut.edu.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

J. Reimink and A. Bauer are thanked for providing Acasta samples (JR13-207, JR13-108, and AB13-04). Thanks to Jianguo Li for his assistance in Raman spectroscopy at the Institute of Geochemistry, Chinese Academy of Sciences. Xin Li, Yajun An, and Fang Liu are also acknowledged for their help with analytical facilities at the Research Center for Planetary Science, Chengdu University of Technology. We are appreciative of the editorial handling by Professor Wei Guo, as well as comments by five anonymous reviewers that greatly improved the manuscript. This is a contribution from the CDUT-CGS (Wuhan) Joint Analytical Laboratory for Planetary Materials. This study was supported by the National Natural Science Foundation of China (42330102).

REFERENCES

1. W. Q. Ji, F. Y. Wu, S. L. Chung, J. X. Li, and C. Z. Liu, *Chem. Geol.*, 2009, **262**, 229-245. <https://doi.org/10.1016/j.chemgeo.2009.01.020>
2. X. H. Li, W. X. Li, Z. X. Li, C. H. Lo, J. Wang, M. F. Ye, and Y. H. Yang, *Precambrian Res.*, 2009, **174**, 117-128. <https://doi.org/10.1016/j.precamres.2009.07.004>
3. M. Zhai, *Geosci. Front.*, 2014, **5**, 457-469. <https://doi.org/10.1016/j.gsf.2014.01.003>
4. M. J. Kohn, S. L. Corrie, and C. Markley, *Am. Mineral.*, 2015, **100**, 897-908. <https://doi.org/10.2138/am-2015-5064>
5. D. Rubatto and J. Hermann, *Chem. Geol.*, 2007, **241**, 38-61. <https://doi.org/10.1016/j.chemgeo.2007.01.027>
6. T. Andersen, *Chem. Geol.*, 2005, **216**, 249-270. <https://doi.org/10.1016/j.chemgeo.2004.11.013>
7. G. Gehrels, P. Kapp, P. DeCelles, A. Pullen, R. Blakey, A. Weislogel, L. Ding, J. Guynn, A. Martin, and N. McQuarrie, *Tectonics*, 2011, **30**, TC5016. <https://doi.org/10.1029/2011TC002868>
8. D. E. Moser, K. R. Chamberlain, K. T. Tait, A. K. Schmitt, J. R. Darling, I. R. Barker, and B. C. Hyde, *Nature*, 2013, **499**, 454-457. <https://doi.org/10.1038/nature12341>
9. T. E. Krogh, *Earth Planet. Sci. Lett.*, 1993, **119**, 1-18. [https://doi.org/10.1016/0012-821X\(93\)90002-Q](https://doi.org/10.1016/0012-821X(93)90002-Q)
10. M. Ende, C. Chutimun, P. W. Reiners, D. A. Zamyatin, S. E. M. Gain, R. Wirth, and L. Nasdala, *Lithos*, 2021, **406**, 106523. <https://doi.org/10.1016/j.lithos.2021.106523>
11. A. J. G. Ellison, and A. Navrotsky, *J. Am. Ceram. Soc.*, 1992, **75**, 1430-1433. <https://doi.org/10.1111/j.1151-2916.1992.tb04205.x>
12. D. J. Cherniak, and E. B. Watson, *Rev. Mineral. Geochem.*, 2003, **53**, 113-143. <https://doi.org/10.2113/0530113>
13. L. Nasdala, W. Wenzel, G. Vavra, G. Irmer, T. Wenzel, and B. Kober, *Contrib. Mineral. Petrol.*, 2001, **141**, 125-144. <https://doi.org/10.1007/s004100000235>
14. L. Nasdala, P. W. Reiners, J. I. Garver, A. K. Kennedy, R. A. Stern, E. Balan, and R. Wirth, *Am. Mineral.*, 2004, **89**, 219-231. <https://doi.org/10.2138/am-2004-0126>
15. J. I. Garver and P. J. J. Kamp, *Tectonophysics*, 2002, **349**, 203-219. [https://doi.org/10.1016/S0040-1951\(02\)00054-9](https://doi.org/10.1016/S0040-1951(02)00054-9)
16. M. K. Rahn, M. T. Brandon, G. E. Batt, and J. I. Garver, *Am. Mineral.*, 2004, **89**, 473-484. <https://doi.org/10.2138/am-2004-0401>
17. P. W. Reiners, I. H. Campbell, S. Nicolescu, C. M. Allen, J. K. Hourigan, J. I. Garver, J. Mattinson, and D. S. Cowan, *Am. J. Sci.*, 2005, **305**, 259-311. <https://doi.org/10.2475/ajs.305.4.259>
18. J. K. W. Lee, I. S. Williams, and D. J. Ellis, *Nature*, 1997, **390**, 159-162. <https://doi.org/10.1038/36554>
19. D. J. Cherniak and E. B. Watson, *Chem. Geol.*, 2001, **172**, 5-24. [https://doi.org/10.1016/S0009-2541\(00\)00233-3](https://doi.org/10.1016/S0009-2541(00)00233-3)
20. K. Suzuki, M. Adachi, and I. Kajizuka, *Earth Planet. Sci. Lett.*, 1994, **128**, 391-405. [https://doi.org/10.1016/0012-821X\(94\)90158-9](https://doi.org/10.1016/0012-821X(94)90158-9)
21. L. Nasdala, J. M. Hanchar, A. Kronz, and M. J. Whitehouse, *Chem. Geol.*, 2005, **220**, 83-103. <https://doi.org/10.1016/j.chemgeo.2005.03.012>
22. M. V. McGloin, A. G. Tomkins, G. P. Webb, K. Spiers, C. M. MacRae, D. Paterson, and C. G. Ryan, *Geology*, 2016, **44**, 15-18. <https://doi.org/10.1130/G37238.1>
23. L. T. Silver, and S. Deutsch, *J. Geo.*, 1963, **71**, 721-758. <https://doi.org/10.1086/626951>
24. D. Wiemer, C. M. Allen, D. T. Murphy, and I. Kinaev, *Chem. Geol.*, 2017, **466**, 285-302. <https://doi.org/10.1016/j.chemgeo.2017.06.019>
25. G. R. Tilton, *Eos, Transactions American Geophysical Union*, 1956, **37**, 224-230. <https://doi.org/10.1029/tr037i002p00224>
26. T. E. Krogh, *Geochim. Cosmochim. Acta*, 1982, **46**, 637-649. [https://doi.org/10.1016/0016-7037\(82\)90165-x](https://doi.org/10.1016/0016-7037(82)90165-x)
27. R. Mundil, K. R. Ludwig, I. Metcalfe, and P. R. Renne, *Science*, 2004, **305**, 1760-1763. <https://doi.org/10.1126/science.1101012>
28. J. M. Mattinson, *Chem. Geol.*, 2005, **220**, 47-66. <https://doi.org/10.1016/j.chemgeo.2005.03.011>
29. R. Kryza, Q. G. Crowley, A. Larionov, C. Pin, T. Obercdziedzic, and K. Mochacka, *Gondwana Res.*, 2012, **21**, 757-767. <https://doi.org/10.1016/j.gr.2011.07.007>
30. L. A. Solari, C. Ortega-Obregón, and J. P. Bernal, *Chem. Geol.*, 2015, **414**, 109-123. <https://doi.org/10.1016/j.chemgeo.2015.09.008>
31. K. E. Watts, M. A. Coble, J. A. Vazquez, C. D. Henry, J. P. Colgan, and D. A. John, *Chem. Geol.*, 2016, **439**, 139-151. <https://doi.org/10.1016/j.chemgeo.2016.06.013>
32. M. H. Huyskens, S. Zink, and Y. Amelin, *Chem. Geol.*, 2016, **438**, 23-35. <https://doi.org/10.1016/j.chemgeo.2016.05.013>
33. C. M. Allen and I. H. Campbell, *Chem. Geol.*, 2012, **332**,

- 157-165. <https://doi.org/10.1016/j.chemgeo.2012.09.038>
34. F. Chen, W. Siebel, and M. Satir, *Chem. Geol.*, 2002, **191**, 155-164. [https://doi.org/10.1016/s0009-2541\(02\)00154-7](https://doi.org/10.1016/s0009-2541(02)00154-7)
 35. J. M. Mattinson, *Contrib. Mineral. Petrol.*, 1994, **116**, 117-129. <https://doi.org/10.1007/bf00310694>
 36. W. C. McClelland, and J. M. Mattinson, *Geochim. Cosmochim. Acta*, 1996, **60**, 3955-3965. [https://doi.org/10.1016/0016-7037\(96\)00214-1](https://doi.org/10.1016/0016-7037(96)00214-1)
 37. U. Ginster, P. W. Reiners, L. Nasdala, and C. Chanmuang, *Geochim. Cosmochim. Acta.*, 2019, **249**, 225-246. <https://doi.org/10.1016/j.gca.2019.01.033>
 38. R. Salerno, J. Vervoort, C. Fisher, A. Kemp, and N. Roberts, *Earth Planet. Sci. Lett.*, 2021, **572**, 117139. <https://doi.org/10.1016/j.epsl.2021.117139>
 39. C. M. Fisher, A. M. Bauer, and J. D. Vervoort, *Earth Planet. Sci. Lett.*, 2020, **530**, 115900. <https://doi.org/10.1016/j.epsl.2019.115900>
 40. J. R. Reimink, T. Chacko, R. A. Stern, and L. M. Heaman, *Precambrian Res.*, 2016, **281**, 453-472. <https://doi.org/10.1016/j.precamres.2016.06.007>
 41. A. M. Bauer, C. M. Fisher, J. D. Vervoort, and S. A. Bowring, *Earth Planet. Sci. Lett.*, 2017, **458**, 37-48. <https://doi.org/10.1016/j.epsl.2016.10.036>
 42. D. Wang, X. F. Qiu, and R. W. Carlson, *Earth Planet. Sci. Lett.*, 2023, **605**, 118037. <https://doi.org/10.1016/j.epsl.2023.118037>
 43. J. Sláma, J. Košler, D. J. Condon, J. L. Crowley, A. Gerdes, J. M. Hanchar, and M. J. Whitehouse, *Chem. Geol.*, 2008, **249**, 1-35. <https://doi.org/10.1016/j.chemgeo.2007.11.005>
 44. M. A. P. C. Wiedenbeck, P. Alle, F. Y. Corfu, W. L. Griffin, M. Meier, F. V. Oberli, and W. Spiegel, *Geostand. Newsl.*, 1995, **19**, 1-23. <https://doi.org/10.1111/j.1751-908X.1995.tb00147.x>
 45. J. B. Paces and J. D. Miller, *J. Geophys Res: Sol Ea.*, 1993, **98**, 13997-14013. <https://doi.org/10.1029/93JB01159>
 46. S. E. Jackson, N. J. Pearson, W. L. Griffin, and E. A. Belousova, *Chem. Geol.*, 2004, **211**, 47-69. <https://doi.org/10.1016/j.chemgeo.2004.06.017>
 47. S. A. Bowring, J. E. King, T. B. Housh, C. E. Isachsen and F.A. Podosek, *Nature*, 1989, **340**, 222-225. <https://doi.org/10.1038/340222a0>
 48. S. A. Bowring, I. S. Williams, and W. Compston, *Geology*, 1989, **17**, 971-975. [https://doi.org/10.1130/0091-7613\(1989\)017<0971:GGFTSP>2.3.CO;2](https://doi.org/10.1130/0091-7613(1989)017<0971:GGFTSP>2.3.CO;2)
 49. S. A. Bowring and I. S. Williams, *Contrib. Mineral. Petrol.*, 1999, **134**, 3-16. <https://doi.org/10.1007/s004100050465>
 50. T. Iizuka, T. Komiya, Y. Ueno, I. Katayama, Y. Uehara, S. Maruyama, T. Hirata, S. P. Johnson, and D. J. Dunkley, *Precambrian Res.*, 2007, **153**, 179-208. <https://doi.org/10.1016/j.precamres.2006.11.017>
 51. S. J. Mojzsis, N. L. Cates, G. Caro, D. Trail, O. Abramov, M. Guitreau, J. Blichert-Toft, M. D. Hopkins, and W. Bleeker, *Geochim. Cosmochim. Acta*, 2014, **133**, 68-96. <https://doi.org/10.1016/j.gca.2014.02.019>
 52. J. R. Reimink, T. Chacko, R. A. Stern, and L. M. Heaman, *Nat. Geosci.*, 2014, **7**, 529-533. <https://doi.org/10.1038/ngeo2170>
 53. X. F. Qiu, X. R. Tong, T. Jiang, and N. U. Khattak, *Gondwana Res.*, 2021, **89**, 119-130. <https://doi.org/10.1016/j.gr.2020.08.014>
 54. P. Widmann, J. Davies, and U. Schaltegger, *Chem. Geol.*, 2019, **511**, 1-10. <https://doi.org/10.1016/j.chemgeo.2019.02.026>
 55. A. J. McKenna, I. Koran, B. Schoene, and R. A. Ketcham, *Geochronology*, 2023, **5**, 127-151. <https://doi.org/10.5194/gchron-5-127-2023>
 56. C. Paton, J. Hellstrom, B. Paul, J. Woodhead, and J. Hergt, *J. Anal. At. Spectrom.*, 2011, **26**, 2508-2518. <https://doi.org/10.1039/c1ja10172b>
 57. S. Piazzolo, E. Belousova, A. La Fontaine, C. Corcoran, and J. M. Cairney, *Chem. Geol.*, 2017, **456**, 10-18.
 58. K. R. Ludwig, BGC Special Publ. 1a, Berkeley., 2003, **4**, 1-70. <https://searchworks.stanford.edu/view/6739593>
 59. I. Segal, L. Halicz, and I. T. Platzner, *J. Anal. At. Spectrom.*, 2003, **18**, 1217-1223. <https://doi.org/10.1039/B307016F>
 60. P. Patchett and M. Tatsumoto, *Nature*, 1980, **288**, 571-574. <https://doi.org/10.1038/288571a0>
 61. J. D. Vervoort, P. J. Patchett, U. Söderlund, and M. Baker, *Geochem. Geophys. Geosy.*, 2004, **5**, 11. <https://doi.org/10.1029/2004GC000721>
 62. C. M. Fisher, J. M. Hanchar, S. D. Samson, B. Dhuime, J. Blichert-Toft, J. D. Vervoort, and R. Lam, *Chem. Geol.*, 2011, **286**, 32-47. <https://doi.org/10.1016/j.chemgeo.2011.04.013>
 63. C. M. Fisher, J. D. Vervoort, and J. M. Hanchar, *Chem. Geol.*, 2014, **363**, 125-133. <https://doi.org/10.1016/j.chemgeo.2013.10.019>
 64. D. Wang, J. D. Vervoort, C. M. Fisher, R. S. Lewis, and A. Buddington, *Precambrian Res.*, 2022, **379**, 106780. <https://doi.org/10.1016/j.precamres.2022.106780>
 65. J. Blichert-Toft, *Chem. Geol.*, 2008, **253**, 252-257. <https://doi.org/10.1016/j.chemgeo.2008.05.014>
 66. M. L. A. Morel, O. Nebel, Y. J. Nebel-Jacobsen, J. S. Miller, and P. Z. Vroon, *Chem. Geol.*, 2008, **255**, 231-235. <https://doi.org/10.1016/j.chemgeo.2008.06.040>
 67. J. D. Woodhead and J. M. Hergt, *Geostand. Geoanal. Res.*, 2005, **29**, 183-195. <https://doi.org/10.1111/j.1751-908X.2005.tb00891.x>
 68. L. Nasdala, C. L. Lengauer, J. M. Hanchar, A. Kronz, R. Wirth, P. Blanc, and A. M. Seydoux-Guillaume, *Chem. Geol.*, 2002, **191**, 121-140. [https://doi.org/10.1016/s0009-2541\(02\)00152-3](https://doi.org/10.1016/s0009-2541(02)00152-3)
 69. T. Chen, H. Ai, M. Yang, S. Zheng, and Y. Liu, *Gems Gemol.*, 2011, **47**, 36-41. <https://doi.org/10.5741/GEMS.47.1.36>
 70. T. Laithummanoon and W. Wongkokua, *Journal of King Mongkut's University of Technology North Bangkok*, 2013, **23**, 261-269. https://www.researchgate.net/publication/290396335_Effect_of_heat_treatment_on_color_of_natural_zircon
 71. U. Kempe, M. Trinkler, A. Pöppel, and C. Himcinschi, *Can. Mineral.*, 2016, **54**, 635-660. <https://doi.org/10.3749/canmin.1500093>
 72. D. J. Mackey, W. A. Runciman, and E. R. Vance, *Phys. Rev. B*, 1975, **11**, 211. <https://doi.org/10.1103/PhysRevB.11.211>
 73. K. Nassau, London: Butterworths., 1984. <https://www.osti.gov/etdweb/biblio/6323616>
 74. M. S. Rupasinghe and A. Senaratne, *J. Gemm.*, 1986, **20**, 168-170. <https://doi.org/10.15506/jog.1986.20.3.168>
 75. T. Geisler, R. T. Pidgeon, W. Van Bronswijk, and R. Pleyzier, *Eur. J. Mineral.*, 2001, **13**, 1163-1176. <https://doi.org/10.1127/0935-1221/2001/0013-1163>
 76. L. Nasdala, R. T. Pidgeon, D. Wolf, and G. Irmer, *Miner. Petrol.*, 1998, **62**, 1. <https://doi.org/10.1007/BF01173760>
 77. L. Nasdala, G. Irmer, and D. Wolf, *Eur. J. Mineral.*, 1995, **7**, 471-478. <https://doi.org/10.1127/ejm/7/3/0471>
 78. L. Nasdala, R. T. Pidgeon, D. Wolf, and G. Irmer, Chanmuang,

- Geochim. Cosmochim. Acta*, 1996, **60**, 1091-1097.
[https://doi.org/10.1016/0016-7037\(95\)00454-8](https://doi.org/10.1016/0016-7037(95)00454-8)
79. C. S. Palenik, L. Nasdala, and R. C. Ewing, *Am. Mineral.*, 2003, **88**, 770-781. <https://doi.org/10.2138/am-2003-5-606>
80. M. Zhang, E. K. Salje, I. Farnan, A. Graeme-Barber, P. Daniel, R. C. Ewing, and H. Leroux, *J. Phys-Condens. Mat.*, 2000, **12**, 1915. <https://doi.org/10.1088/0953-8984/12/8/333>
81. E. K. H. Salje, J. Chrosch, and R. C. Ewing, *Am. Mineral.*, 1999, **84**, 1107-1116. <https://doi.org/10.2138/am-1999-7-813>
82. T. Geisler, M. Ulonska, H. Schleicher, R. T. Pidgeon, and W. van Bronswijk, *Contrib. Mineral. Petr.*, 2001, **141**, 53-65. <https://doi.org/10.1007/s004100000202>
83. R. T. Pidgeon, P. G. Chapman, M. Danišik, and A. A. Nemchin, *Am. Mineral.*, 2017, **102**, 1066-1072. <https://doi.org/10.2138/am-2017-5901>
84. W. F. McDonough, and S. S. Sun, *Chem. Geol.*, 1995, **120**, 223-253. [https://doi.org/10.1016/0009-2541\(94\)00140-4](https://doi.org/10.1016/0009-2541(94)00140-4)
85. A. Von Quadt, D. Gallhofer, M. Guillon, I. Peytcheva, M. Waelle, and S. Sakata, *J. Anal. At. Spectrom.*, 2014, **29**, 1618-1629. <https://doi.org/10.1039/c4ja00102h>
86. E. Marillo-Sialer, J. Woodhead, J. Hergt, A. Greig, M. Guillon, A. Gleadow, and C. Paton, *J. Anal. At. Spectrom.*, 2014, **29**, 981-989. <https://doi.org/10.1039/C4JA00008K>
87. E. Marillo-Sialer, J. Woodhead, J. M. Hanchar, S. M. Reddy, A. Greig, J. Hergt, and B. Kohn, *Chem. Geol.*, 2016, **438**, 11-24. <https://doi.org/10.1016/j.chemgeo.2016.05.014>
88. Q. G. Crowley, K. Heron, N. Riggs, B. Kamber, D. Chew, B. McConnell, and K. Benn, *Minerals*, 2014, **4**, 503-518. <https://doi.org/10.3390/min4020503>
89. E. E. Donaghy, M. P. Eddy, F. Moreno, and M. Ibañez-Mejia, *Geochronology*, 2024, **6**, 89-106. <https://doi.org/10.5194/gchron-6-89-2024>
90. J. T. Sliwinski, M. Guillon, C. Liebske, I. Dunkl, A. von Quadt, and O. Bachmann, *Chem. Geol.*, 2017, **472**, 8-21. <https://doi.org/10.1016/j.chemgeo.2017.09.014>
91. M. A. Kusiak, D. J. Dunkley, R. Wirth, M. J. Whitehouse, S. A. Wilde, and K. Marquardt, *Proc. Natl. Acad. Sci. USA*, 2015, **112**, 4958-4963. <https://doi.org/10.1073/pnas.1415264112>
92. J. W. Valley, A. J. Cavosie, T. Ushikubo, D. A. Reinhard, D. F. Lawrence, D. J. Larson, P. H. Clifton, T. F. Kelly, S. A. Wilde, D. E. Moser, and M. J. Spicuzza, *Nat. Geosci.*, 2014, **7**, 219-223. <https://doi.org/10.1038/ngeo2075>
93. E. M. Peterman, S. M. Reddy, D. W. Saxey, D. R. Snoeyenbos, W. D. A. Rickard, D. Fougereuse, and A. R. C. Kylander-Clark, *Sci. Adv.*, 2016., **2**, e1601318. <https://doi.org/10.1126/sciadv.1601318>
94. H. D. Holland and D. Gottfried, *Acta Crystallogr.*, 1955, **8**, 291-300. <https://doi.org/10.1107/s0365110x55000947>
95. T. Murakami, B. C. Chakoumakos, R. C. Ewing, G. R. Lumpkin, and W. J. Weber, *Am. Mineral.*, 1991, **76**, 1510-1532. http://www.minsocam.org/ammin/AM76/AM76_1510.pdf
96. A. J. McKanna, B. Schoene, and D. Szymanowski, *Geochronology*, 2023, **6**, 1-20. <https://doi.org/10.5194/gchron-6-1-2024>
97. V. Köppel and J. Sommerauer, *Contrib. Mineral. Petr.*, 1974, **43**, 71-82. <https://doi.org/10.1007/bf00384653>
98. B. L. Howard, G. R. Sharman, J. L. Crowley, and E. R. Wersan, *Terra Nova*, 2024, Early View. <https://doi.org/10.1111/ter.12742>
99. A. M. Bauer, J. D. Vervoort, and C. M. Fisher, *Geochim. Cosmochim. Acta.*, 2020, **283**, 85-102. <https://doi.org/10.1016/j.gca.2020.05.023>
100. Y. Amelin, S. L. Kamo, and D. C. Lee, *Can. J. Earth Sci.*, 2011, **48**, 141-160. <https://doi.org/10.1139/e10-091>
101. C. Ortega-Obregón, L. Solari, A. Gómez-Tuena, M. Elías-Herrera, F. Ortega-Gutiérrez, and C. Macías-Romo, *Int. J. Earth Sci.*, 2014, **103**, 1287-1300. <https://doi.org/10.1007/s00531-013-0933-1>
102. F. Y. Wu, Y. H. Yang, L. W. Xie, J. H. Yang, and P. Xu, *Chem. Geol.*, 2006, **234**, 105-126. <https://doi.org/10.1016/j.chemgeo.2006.05.003>