

4 Analytical methods

4.1 Zircon U-Pb geochronology

Zircon samples and cathodoluminescence (CL) images were made at Beijing Zhongke Kuangyan Testing Technology Co., Ltd. All samples were crushed and their zircon grains separated using conventional magnetic separation and heavy liquid techniques. Zircon grains were handpicked and embedded in an epoxy resin, polished to expose their interiors for optical microscopy and CL imaging. Samples were then polished to EBSD standards using colloidal silica and carbon coatings. CL images of individual grains were collected using a Tescan MIRA 3 field emission scanning electron microscope.

Zircon U-Pb analyses were made at Beijing Quick-Thermo Science & Technology Co., Ltd., utilizing an ESI New Wave NWR ^{193}U (TwoVol2) laser ablation system connected to an Agilent 8900 ICP-QQQ instrument. Zircon grains, individually mounted and polished in an epoxy, underwent laser ablation in a continuous stream of helium (He) mixed with nitrogen (N_2) and argon (Ar) downstream before entering the torch region of the ICP-QQQ instrument. Following the warm-up and connection of the ICP-QQQ instrument with the laser ablation system, the ICP-MS underwent initial optimization to achieve stable plasma conditions through fine-tuning of the laser and ICP-QQQ settings. Continuous monitoring of the $^{232}\text{Th}^{16}\text{O}^+ / ^{232}\text{Th}^+$ ratios (always $\leq 0.2\%$) and $^{238}\text{U}^+ / ^{232}\text{Th}^+$ ratios (always between 0.95 and 1.05) was conducted during the ablation of NIST SRM 612 in line-scan mode. 91500-zircon was used as the primary reference material for U-Pb age determinations, and the Plešovice zircon served as the

secondary reference (Wiedenbeck et al., 1995). Background subtractions and corrections were conducted using the Iolite data reduction package integrated into the Wavemetrics Igor Pro data analysis software (Paton et al., 2010) to account for laser-induced downhole elemental fractionation. ISOPLOT 4.15 software (Ludwig, 2003) was utilized to generate Concordia diagrams.

4.2 Hf isotopes

In situ analyses of Hf isotopes of zircons were carried out using a Geolas HD excimer ArF laser ablation system coupled with a Neptune Plus (Thermo Fisher, Germany) Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) instrument at the Guangxi Key Laboratory of Hidden Metallic Ore Deposits Exploration, Guilin University of Technology. Data acquisition of zircons was performed in single spot ablation mode with a spot size of 44 μm . Ablated samples from the laser ablation cell were transported to the ICP-MS torch using helium as the carrier gas. The transportation process involved passing through a mixing chamber that was combined with argon. The laser ablation energy density used in this study was approximately 7.0 J cm^{-2} . During each measurement, a background signal was acquired for a duration of 18 seconds, followed by an acquisition of the ablation signal for 50 seconds. Ratios of $^{176}\text{Lu}/^{175}\text{Lu} = 0.02656$ (Blichert-Toft et al., 1997) and $^{176}\text{Yb}/^{173}\text{Yb} = 0.79639$ (Fisher et al., 2014) were determined to correct for the isobaric interferences of ^{176}Lu and ^{176}Yb on ^{176}Hf . The Hf and Yb isotope ratios were then normalized to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ and $^{173}\text{Yb}/^{171}\text{Yb} = 1.132685$ (Fisher et al., 2014) using an exponential correction for mass bias. Zircon GJ1 was utilized as the reference standard

during routine analyses. Offline selection, integration of analyzed signals, and mass bias calibrations were performed using ICPMSDataCal software (Liu et al., 2010). The $\varepsilon_{\text{Hf}}(t)$ values were determined assuming chondritic values of $^{176}\text{Lu}/^{177}\text{Hf} = 0.282785$ and $^{176}\text{Hf}/^{177}\text{Hf} = 0.0336$ (Bouvier et al., 2008). The T_{DM1} ages were calculated by referencing the depleted mantle, assuming a present-day $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$ (Griffin et al., 2000). Additionally, the two-stage continental crust model ages (T_{DM2}) were obtained by plotting the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of zircons back to the depleted mantle evolutionary curve using the average continental crust's $^{176}\text{Lu}/^{177}\text{Hf}$ value of 0.015 (Griffin et al., 2000). The $\varepsilon_{\text{Hf}}(t)$ values and crustal model ages (T_{DM2}) were calculated based on the zircon $^{206}\text{Pb}/^{238}\text{U}$ ages.

4.3 Whole rock geochemistry

The bulk-rock samples were subjected to geochemical analysis at ALS Chemex Co. Ltd in Guangzhou. Prior to analysis, the samples underwent a preparation process, including crushing to a size finer than 200-mesh and removal of weathered surfaces. Homogeneous glass beads were then produced by mixing the crushed samples with $\text{Li}_2\text{B}_4\text{O}_7$ and LiBO_2 and heating them at temperatures ranging from 1050 to 1100 °C. Major elements were determined using XRF-1500 Sequential X-ray Fluorescence Spectrometry on fused glass beads. The analytical precision, assessed through certified standards and duplicate analyses, ranged from $\pm 1\%$ to $\pm 2\%$. The analysis of trace elements and Rare Earth Elements (REE) was performed using an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS). For each sample, approximately 50 mg of powder were combined with a lithium metaborate flux, thoroughly mixed, and fused at

a temperature of 1000 °C within a furnace. Subsequently, the resulting molten mixture was cooled and dissolved in a 4% solution of nitric acid (HNO₃) with a volume of 100 ml. The ICP-MS data, obtained at the parts per million (ppm) level, exhibits an analytical precision of less than 5%.

4.4 Sr-Nd isotopes

Whole rock Sr-Nd isotopic measurements were carried out at Nanjing FocuMS Technology Co. Ltd. The Sr and Nd isotopic samples were initially dissolved using a mixture of acids (HF+HClO₄). Subsequently, they were subjected to a reaction under high-temperature conditions for at least half a day in a sealed Teflon digestion vessel. The Sr obtained through the Isotope Concentration (IC) process underwent secondary purification, while the purification of Nd utilized the HDEHP back-extraction technique. The testing instrument employed was the Triton thermal ionization mass spectrometer. Throughout the entire sample testing process, the measured background levels for the BCR-2Nd standard and NBS-987Sr standard were as follows: $^{143}\text{Nd}/^{144}\text{Nd} = 0.512202 \pm 30$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.710425$. The isotopic ratios of $^{88}\text{Sr}/^{86}\text{Sr} = 8.37521$ and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ were used as internal standard indices for mass fractionation correction. Isoplot, a standard software program, was utilized for isochron fitting calculations.

References:

- Blichert-Toft, J., Chauvel, C. and Albarede, F., 1997. Separation of Hf and Lu for high-precision isotope analysis of rock samples by magnetic sector-multiple collector ICP-MS: Contributions to mineralogy and petrology, v.127 no.3 p.248-260, <https://doi.org/10.1007/s004100050278>.
- Bouvier, A., Vervoort, J.D. and Patchett, P.J., 2008. The Lu - Hf and Sm - Nd isotopic composition of

CHUR: Constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets: *Earth and Planetary Science Letters*, v.273 no.1-2 p.48-57, <https://doi.org/10.1016/j.epsl.2008.06.010>.

Fisher, C.M., Vervoort, J.D. and Hanchar, J.M., 2014. Guidelines for reporting zircon Hf isotopic data by LA-MC-ICPMS and potential pitfalls in the interpretation of these data: *Chemical geology*, v.363 p.125-133, <https://doi.org/10.1016/j.chemgeo.2013.10.019>.

Griffin, W.L. et al., 2000. The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites: *Geochimica et cosmochimica acta*, v.64 no.1 p.133-147

Liu, Y.S. et al., 2010. Continental and oceanic crust recycling-induced melt – peridotite interactions in the Trans-North China Orogen: U – Pb dating, Hf isotopes and trace elements in zircons from mantle xenoliths: *Journal of petrology*, v.51 no.1-2 p.537-571, <https://doi.org/10.1093/petrology/egp082>.

Ludwig, K.R., 2003. User' s manual for Isoplot/EX, version 3.00: A geochronological toolkit for Microsoft Excel, v.4 p.71

Paton, C. et al., 2010. Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction: *Geochemistry, Geophysics, Geosystems*, v.11 no.3 p.n/a-n/a, <https://doi.org/10.1029/2009GC002618>.

Wiedenbeck, M. et al., 1995. Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analyses: *Geostandards Newsletter*, v.19 no.1 p.1-23, <https://doi.org/10.1111/j.1751-908X.1995.tb00147.x>.