

Analytical Methods

SEM Scanning

Morphological and qualitative analyses of bulk rock and ore samples were performed using SEM-EDX. Wall rock and bulk ore samples were cut, polished, and mounted in epoxy resin. The epoxy surface was polished until a smooth mirror-like finish was obtained and then carbon coated before analysis. SEM studies for mineral analysis of representative wall-rock and bulk ore separate samples were conducted in two stages using a Hitachi 4300 SE/N Field Emission Scanning Electron Microscope at the Centre for Advanced Microscopy at the Australian National University.

Zircon U-Pb dating and trace element analyses

Zircons were separated from ~3 kg of crushed rock sample using standard density and magnetic separation techniques at the Langfang Geological Laboratory (Beijing). Approximately 100–200 zircon grains from each sample were mounted in an epoxy resin disc. Zircon grains from two representative samples (LIB CR01 and LIB KB01) were extracted and carefully handpicked under a binocular microscope, after which they were fixed into epoxy resin, thoroughly polished, and carbon-coated. The cathodoluminescent (CL) images of the zircons were obtained by using an Analytical Scanning Electron Microscope (JSM-IT300) fixed to a GATAN MINICL device. The imaging condition was 0.5–30 kV voltage of electric field and 72 μ A current of tungsten filament. Zircon U-Pb isotope and trace element concentration of zircons were simultaneously determined using a Geo Las Pro laser ablation system that consists of a COMPexPro 102 ArF excimer laser (wavelength of 193 nm and maximum energy of 200 mJ) and a MicroLas optical system and an Agilent 7900 ICP-MS at the Sample Solution Analytical Technology Co. Ltd., Wuhan, China. Helium was used as the carrier gas while argon was used as the make-up gas and mixed with the carrier gas via a T-connector before entering the ICP. A flow rate of 0.8–1 L/min for the carrier gas (He) was maintained during analysis. Laser ablation spots were carefully selected to avoid fluid and mineral inclusions in the zircon grains. Laser frequency was 5 Hz, ablation energy density was $\sim 8.0 \text{ J cm}^{-2}$, and

dwell time was 6 ms with an ablation spot size of 32 μm and depth of 20–40 μm . A background acquisition time of 18–20 s and data acquisition time of 50 s were adopted for each measurement. For the external reproducibility and calibration of mass discrimination and isotope fractionation, zircons 91500, GJ-1 and Plesovice (PLE) zircon were used. Element contents were also calibrated against the GJ-1 and PLE zircon standards. Data processing was performed using the excel-based ICP-MS-Data Cal software (Liu et al., 2008). A detailed description of analytical techniques and operating conditions can be found in Liu et al. (2010). The zircon U-Pb and trace elements results of the analyzed standards are given in Online Materials Table OM1 and Online Materials Table OM2. Overall, the analyses yielded mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 602.1 ± 1.5 Ma (MSWD = 1.5, n = 11) for the GJ-1 standard and 337.9 ± 0.9 Ma (MSWD = 2.8, n = 7) for the Plesovice standard (Online Materials Fig. 1), consistent with recommended values within error limits (Jackson et al., 2004; Sláma et al., 2008). Repeated trace element analysis for standard samples GJ-1 and PLE show better than <10% (2σ) precision values for most analyzed elements (Online Materials Table OM2).

Zircon Hf isotope analyses

In-situ zircon Lu-Hf isotope analysis was carried out at the Sample Solution Analytical Technology Co., Ltd., Wuhan, China using a Neptune Plus MC-ICP-MS equipped with a Geolas 193 nm ArF Laser Ablation System (LAS). Helium was used as the carrier gas within the ablation cell and was merged with argon (makeup gas) after the ablation cell with a carrier gas (He) flow rate of 0.5 L/min. Small amounts of nitrogen were added to the argon makeup gas flow for the improvement of sensitivity of Hf isotopes (Hu et al., 2012). Lu-Hf isotopic measurements were conducted on ablation spots adjacent to those for the U-Pb dating in a single spot ablation mode with a laser frequency of 8 Hz, laser spot beam of 44 μm and energy density of ~ 10.0 J cm^{-2} . The integration time for each Faraday cup during Zircon Hf analysis was 0.524s. Background and ablation signals were collected for 20 s and 50 s, respectively. The standard ratio of $^{176}\text{Hf}/^{175}\text{Lu}=0.02655$ was adopted to correct for atmospheric pressure interference of ^{175}Lu on ^{176}Hf while $^{176}\text{Hf}/^{175}\text{Lu}=0.5886$ was used for ^{176}Yb on ^{176}Hf based on the recommendation of Machado and Simonetti (2001). Analytical

signal selection and integration as well as mass bias calibration, were carried out using ICP-MS-Data Cal software (Liu et al., 2010). For the epsilon $\epsilon\text{Hf}(t)$ determination, chondrite ratios of $^{176}\text{Hf}/^{177}\text{Hf} = 0.282772$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0332$ (Belousova et al., 2006) were used. The single-stage Hf model ages (T_{DM1}) computations were conducted by using the depleted mantle ratios ($^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$) as described by Griffin et al. (2002). The calculations for the crustal Hf model ages (T_{DM2}) were performed by using $^{176}\text{Lu}/^{177}\text{Hf} = 0.015$ (Belousova et al., 2006) as the mean value for the continental crust. Calculation of $\epsilon\text{Hf}(t)$, TDM and fLu/Hf values used decay constant of 1.867×10^{-11} , $^{176}\text{Hf}/^{177}\text{Hf}$ CHUR = 0.282772, $^{176}\text{Hf}/^{177}\text{Hf}$ CHUR = 0.0332, $^{176}\text{Lu}/^{177}\text{Hf}$ DM = 0.0384, and $^{176}\text{Hf}/^{177}\text{Hf}$ DM = 0.283251 for the Chondritic Uniform Reservoir (CHUR) and Depleted Mantle (DM), respectively (Blichert-Toft and Albarède, 1997; Griffin et al., 2000; Söderlund et al., 2004).

Mineral Chemistry

Quantitative mineral compositional data were obtained using a JEOL JXA-8230 electron probe microanalyzer at Sample Solution Analytical Technology Co. Ltd., Wuhan. The instrument was operated in a wavelength-dispersive spectroscopy (WDS) mode at an accelerating voltage of 20 kV, beam diameter of 5 μm , and a 20 nA beam current. The natural and synthetic standard materials used for calibration against analyzed elements include Quartz (Si), Rutile (Ti), Johannsenite (Ca), Jadeite (Na), Olivine (Mg, Fe, Ni), Pyrope garnet (Al), Pyroxmagnite (Mn), Orthoclase feldspar (K), Fluroapatite (P, F), Iron Chromite (Cr), and Tugtupite (Cl). Peak counting times were 20 s for Ti, Mg, and Mn as well as 10 s for all remaining elements. Background counting times were: Si (5 s), Ti (10 s), Ca (5 s), Na (5 s), Mg (10 s), Al (5 s), Mn (10 s), Fe (5 s), K (5 s), P (5 s), Cr (5 s), Ni (5 s), F (5 s), and Ni (5 s). Raw data were corrected for the atomic number and absorption effects with a ZAF program. Minimum detection limits (for tourmaline) were (2σ , in ppm): Si (180), Ti (145), Ca (140), Na (95), Mg (80), Al (140), Mn (120), Fe (195), K (110), P (105), Cr (150), Ni (235), F (375), and Ni (45). The structural formulae of tourmaline ($\text{XY}_3\text{Z}_6[\text{T}_6\text{O}_{18}][\text{BO}_3]_3\text{V}_3\text{W}$) were calculated by normalizing to 15 cations in the tetrahedral and octahedral sites with element distribution to these different sites (T + Z + Y) according to nomenclature rules proposed

by Henry et al. (2011). All Fe was assumed to be Fe^{2+} . B_2O_3 contents were calculated by setting B=3 atoms per formula unit (apfu) and H_2O was estimated assuming $\text{OH} + \text{F} + \text{Cl} = 4$ apfu.

Tourmaline LA-ICP-MS trace element analyses

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) trace element spot analyses of tourmaline were performed with an Agilent 7900E Quadrupole ICP-MS instrument at the Sample Solution Analytical Technology Co. Ltd., Wuhan. Analyses were conducted using a Geolas Pro HD ablation system coupled with a 193 nm ArF excimer laser. The analysis employed a spot diameter and frequency of 32 μm and 5 Hz respectively, at a fluence of 5.5 J/cm^2 with a dwell time of 6 ms. Each analysis incorporated a background acquisition of approximately 15 s, followed by 50 s of data acquisition from the sample. Helium served as the carrier gas and mixed with the argon make-up gas (via a T-connector) prior to entering the ICP-MS. Element contents were calibrated against multiple-reference materials (USGS BCR-2G, BIR-1G, BHVO-2G, and NIST SRM610) without applying internal standardization (Liu et al., 2008). The trace element values of the standard samples are given in Online Materials Table OM3. The reproducibility, estimated from repeated analyses of the BCR-2G, BHVO-2G and BIR-1G standard samples are <10% (2σ) for Li, Sc, V, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb, Lu, Hf, and Th (Online Materials Table OM3). Data reduction and time-drift corrections were carried out using ICP-MS-Data Cal, an Excel-based software, by performing off-line selection, integrating background and analyzed signals and quantitative calibration for trace element analysis (Liu et al., 2008).

Tourmaline boron isotope analyses

In-situ tourmaline boron isotopic compositions were measured using a Neptune Plus laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP MS) coupled to a NewWave UP193 laser ablation system at Beijing GeoAnalysis Co. Ltd., China. Analyses were carried out with a beam diameter of 50 μm at a 10 Hz repetition rate with a laser energy density of 8 J/cm^2 . ^{10}B and ^{11}B static Faraday cups were used for simultaneous reception. High-purity He was used as the carrier gas to blow out

the aerosols produced by the ablation and sent to MC-ICP-MS for mass spectrometry testing with a gas (He) flow rate of 0.15 L/min. Detailed analytical procedures adopted are described in Hou et al. (2010) and Yang et al. (2015). Instrument calibration and boron isotope fractionation were corrected using the standard-sample bracketing method. The data were reduced offline using an in-house Excel© spreadsheet to correct for gas and instrumental background, instrumental mass bias, and drift. To ensure instrument stability and analytical quality, the internal tourmaline standard (IMR RB1) was analyzed repeatedly and yielded weighted mean $\delta^{11}\text{B}$ values of $-13.85 \pm 0.35\text{‰}$ (2σ , $n = 10$), consistent with reported values of $-12.96\text{‰} \pm 0.97\text{‰}$ (2σ , $n = 57$) by LA-MC-ICPMS and -12.22 ± 1.1 (2σ , $N = 8$) by P-TIMS testing (Hou et al., 2010).

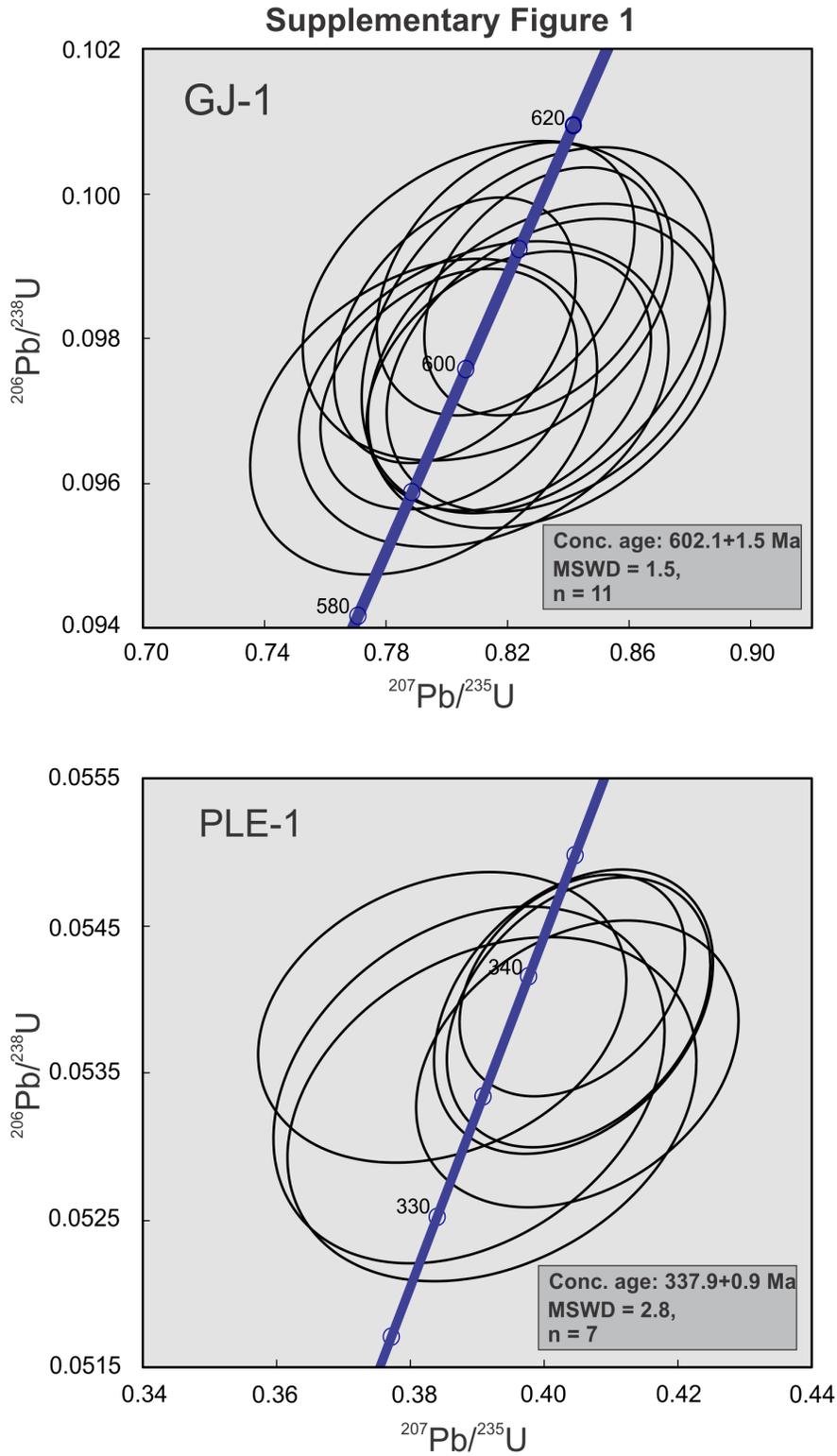


Figure OM1. Zircon U-Pb concordia for standard zircon samples GJ-1 and the Plesovice (PLE).

REFERENCES

- Belousova, E., Griffin, W., O'REILLY, S.Y., 2006. Zircon crystal morphology, trace element signatures and Hf isotope composition as a tool for petrogenetic modelling: examples from Eastern Australian granitoids. *Journal of Petrology* 47, 329-353.
- Blichert-Toft, J., Albarède, F., 1997. The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system. *Earth and Planetary Science Letters* 148, 243-258.
- Griffin, W., Pearson, N., Belousova, E., Jackson, S.v., Van Achterbergh, E., O'Reilly, S.Y., Shee, S., 2000. The Hf isotope composition of cratonic mantle: LAM-MC-ICPMS analysis of zircon megacrysts in kimberlites. *Geochimica et cosmochimica acta* 64, 133-147.
- Griffin, W., Wang, X., Jackson, S., Pearson, N., O'Reilly, S.Y., Xu, X., Zhou, X., 2002. Zircon chemistry and magma mixing, SE China: in-situ analysis of Hf isotopes, Tonglu and Pingtan igneous complexes. *Lithos* 61, 237-269.
- Henry, D.J., Novák, M., Hawthorne, F.C., Ertl, A., Dutrow, B.L., Uher, P., Pezzotta, F., 2011. Nomenclature of the tourmaline-supergrout minerals. *American Mineralogist* 96, 895-913.
- Hou, K., Li, Y., Xiao, Y., Liu, F., Tian, Y., 2010. In situ boron isotope measurements of natural geological materials by LA-MC-ICP-MS. *Chinese Science Bulletin* 55, 3305-3311.
- Hu, Z., Liu, Y., Gao, S., Liu, W., Zhang, W., Tong, X., Lin, L., Zong, K., Li, M., Chen, H., 2012. Improved in situ Hf isotope ratio analysis of zircon using newly designed X skimmer cone and jet sample cone in combination with the addition of nitrogen by laser ablation multiple collector ICP-MS. *Journal of Analytical Atomic Spectrometry* 27, 1391-1399.
- Jackson, S.E., Pearson, N.J., Griffin, W.L., Belousova, E.A., 2004. The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U-Pb zircon geochronology. *Chemical geology* 211, 47-69.
- Liu, Y., Hu, Z., Gao, S., Günther, D., Xu, J., Gao, C., Chen, H., 2008. In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard. *Chemical Geology* 257, 34-43.
- Liu, Y., Hu, Z., Zong, K., Gao, C., Gao, S., Xu, J., Chen, H., 2010. Reappraisal and refinement of zircon U-Pb isotope and trace element analyses by LA-ICP-MS. *Chinese Science Bulletin* 55, 1535-1546.
- Machado, N., Simonetti, A., 2001. U-Pb dating and Hf isotopic composition of zircon by laser-ablation-MC-ICP-MS. *Laser ablation-ICPMS in the Earth sciences: Principles and applications* 29, 121-146.

- Sláma, J., Košler, J., Condon, D.J., Crowley, J.L., Gerdes, A., Hanchar, J.M., Horstwood, M.S., Morris, G.A., Nasdala, L., Norberg, N., 2008. Plešovice zircon—a new natural reference material for U–Pb and Hf isotopic microanalysis. *Chemical Geology* 249, 1-35.
- Söderlund, U., Patchett, P.J., Vervoort, J.D., Isachsen, C.E., 2004. The ^{176}Lu decay constant determined by Lu–Hf and U–Pb isotope systematics of Precambrian mafic intrusions. *Earth and Planetary Science Letters* 219, 311-324.
- Yang, S.-Y., Jiang, S.-Y., Zhao, K.-D., Dai, B.-Z., Yang, T., 2015. Tourmaline as a recorder of magmatic–hydrothermal evolution: an in situ major and trace element analysis of tourmaline from the Qitianling batholith, South China. *Contributions to Mineralogy and Petrology* 170, 1-21.