

Analytical Methods of Whole-Rock Geochemistry, Zircon U–Pb Dating, Sr–Nd Isotopic and *in Situ* Hf Isotopes

1. Whole-Rock Major and Trace Elements

Whole-rock major elements were analyzed with a PANalytical Axiosadvance (Axios PW4400) X-ray fluorescence (XRF) spectrometer at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The analytical precision was better than 2% for all of the oxides.

Whole-rock trace elements, including rare earth elements (REEs), were measured at Nanjing FocuMS Technology Co. Ltd. About 40 mg rock powder was mixed with 0.5 mL HNO₃ and 1.0 mL HF in high-pressure PTFE bombs. These bombs were steel-jacketed and placed in the oven at 195 °C for 48 h for mafic samples. Rock digestion diluent was nebulized into Agilent Technologies 7700x quadrupole ICP–MS (Hachioji, Tokyo, Japan) to determine the trace elements. Deviations were better than ±10% for the elements that exceeded 10 ppm and better than ±5% for the elements that exceeded 50 ppm. More detailed descriptions of these analytical methods are presented in [1]. The wide range of LOIs in anorthosites and gabbros (Table S2) and field and petrographic observations (Figures 3 and 4) show that Dongco and Lanong ophiolites experienced varying degrees of alteration. Therefore, the major element contents of the samples are recalculated to 100% in the geochemical diagrams based on an anhydrous hypothesis.

2. SIMS Zircon U–Pb Dating

Zircons from the Dongco anorthosite (XDC08) were dated by Secondary ion mass spectrometry (SIMS), a CAMECA IMS1280-HR system, at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (SKLaBIG GIG CAS). The analytical procedure is similar to that described by Li et al. (2009) [2]. The O₂[−] primary ion beam with an intensity of ~10 nA was accelerated at −13 kV. The ellipsoidal spot is about 20 μm × 30 μm in size. The aperture illumination mode (Kohler illumination) was used with a 200 μm primary beam mass filter (PBMF) aperture to produce even sputtering over the entire analyzed area. Oxygen flooding was used to increase the O₂ pressure to 5 × 10^{−6} Torr in the sample chamber, enhancing Pb⁺ sensitivity to a value of ~25 cps/nA/ppm for zircon. This great enhancement of Pb⁺ sensitivity is crucial to improve precision of ²⁰⁷Pb/²⁰⁶Pb zircon measurement. Positive secondary ions were extracted with a 10 kV potential. In the secondary ion beam optics, a 60 eV energy window was used, together with a mass resolution of ~5400. Rectangular lenses were activated in the secondary ion optics to increase the transmission at high mass resolution. A single electron multiplier was used in ion-counting mode to measure secondary ion beam intensities by the peak jumping sequence: 196 (⁹⁰Zr²¹⁶O, matrix reference), 200 (⁹²Zr²¹⁶O), 200.5 (background), 203.81 (⁹⁴Zr²¹⁶O, for mass calibration), 203.97 (Pb), 206 (Pb), 207 (Pb), 208 (Pb), 209 (¹⁷⁷Hf¹⁶O₂), 238 (U), 248 (²³²Th¹⁶O), 270 (²³⁸U¹⁶O₂), and 270.1 (reference mass). The integration times for these mass are 1.04, 0.56, 4.16, 0.56, 6.24, 4.16, 6.24, 2.08, 1.04, 2.08, 2.08, 2.08, and 0.24 s. Each measurement consisted of seven cycles, and the total analytical time per measurement was ~12 min. Calibration of Pb/U ratios is relative to the standard zircon Plesovice (337.13 Ma) [3], which was analyzed once every four unknowns, based on an observed linear relationship between ln (²⁰⁶Pb/²³⁸U) and ln (²³⁸U¹⁶O₂/²³⁸U) [4]. A long-term uncertainty of 1.5% (1 RSD) for ²⁰⁶Pb/²³⁸U measurements of the standard zircons was propagated to the unknowns [5], despite that the measured ²⁰⁶Pb/²³⁸U error in a specific session is generally around 1% (1 RSD) or less. U and Th concentrations of unknowns were also calibrated relative to the standard zircon Plesovice, with Th

and U concentrations of 78 and 755 ppm, respectively [3]. Measured compositions were corrected for common Pb using non-radiogenic ^{204}Pb . Common Pb is very low and is largely derived from laboratory contamination introduced during sample preparation [6]. An average of present-day crustal composition [7] is used for the common Pb. A secondary standard zircon Qinghu [8] was analyzed as unknown to monitor the reliability of the whole session. Twenty-five analytical spots conducted during the course of this study yield a concordia age of 169.0 ± 3.7 Ma (mean square of weighted deviation, MSWD = 0.28, $n = 25$). Uncertainties on single analyses are reported at the 1σ level; mean ages for pooled U–Pb analyses are quoted with a 95% confidence interval. Data reduction was carried out using the Isoplot/Ex 3 software [9].

3. LA–ICP–MS Zircon U–Pb Dating and *in Situ* Hf Isotopic Analysis

U–Pb geochronology of Lanong ophiolitic anorthosite (16XLN03) and gabbro (16XLN07) zircons conducted by LA–ICP–MS Nanjing FocuMS Technology Co. Ltd. Teledyne Cetac Technologies Analyte Excite laser–ablation system (Bozeman, Montana, USA) and Agilent Technologies 7700x quadrupole ICP–MS (Hachioji, Tokyo, Japan) were combined for the experiments. The 193 nm ArF excimer laser, homogenized by a set of beam delivery systems, was focused on zircon surface with fluence of 6.0 J/cm^2 . Ablation protocol employed a spot diameter of 35 μm at 8 Hz repetition rate for 40 s (equating to 320 pulses). Helium was applied as carrier gas to efficiently transport aerosol to ICP–MS.

Zircon 91500 was used as the primary reference material and zircon GJ-1 was used for quality control and validation. Lead abundance of zircon was externally calibrated against NIST SRM 610 with Si as internal standard, while Zr as internal standard for other trace elements [10,11]. Data reduction was performed offline by the ICPMSDataCal software [11,12].

In addition, zircon Hf isotopic ratios were measured by a LA–MC–ICP–MS at Nanjing FocuMS Technology Co. Ltd. Teledyne Cetac Technologies Analyte Excite laser–ablation system (Bozeman, Montana, USA) and Nu Instruments Nu Plasma I MC–ICP–MS (Wrexham, Wales, UK) were used. A 193 nm ArF excimer laser, homogenized by a set of beam delivery systems, was focused on zircon surface with a fluence of 6.0 J/cm^2 . Ablation protocol employed a spot diameter of 50 μm at 8 Hz repetition rate for 40 s (equating to 320 pulses). Helium was applied as carrier gas to efficiently transport aerosol to MC–ICP–MS. We employed several reference zircons, including 91500, GJ-1, Plešovice, Mud Tank, and Penglai, as primary and secondary reference materials throughout the analysis.

4. Whole-Rock Sr–Nd Isotopic Analysis

High-precision Sr–Nd isotopic measurements were carried out at Nanjing FocuMS Technology Co. Ltd. Geological rock powder was decomposed by high-pressure PTFE bombs. Strontium, Nd were all purified from the same digestion solution by two steps column chemistry. The first exchange column combined with BioRad AG50W \times 8 and Sr Spec resin was used to separate Sr. Neodymium was separated from the other REE on the second column with Ln Spec-coated Teflon powder.

The Sr-, Nd-bearing elution was dried down and re-dissolved in 1.0 mL 2 wt. % HNO_3 . Small aliquots of each were analyzed using Agilent Technologies 7700x quadrupole ICP–MS (Hachioji, Tokyo, Japan) to determine the exact contents of Sr and Nd. Diluted solution (50 ppb Sr, 50 ppb Nd doping with 10 ppb Tl) were introduced into Nu Instruments Nu Plasma II MC–ICP–MS (Wrexham, Wales, UK) by Teledyne Cetac Technologies Aridus II desolvating nebulizer system (Omaha, NE, USA).

Raw data of isotopic ratios were corrected for mass fractionation by normalizing to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ for Sr, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ for Nd with exponential law. International isotopic standards (NIST SRM 987 for Sr, JNdi-1 for Nd) were periodically analyzed to correct instrumental drift.

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