**中科院地质与地球物理研究所**

****

**MC-ICP-MS**

**实验室分析方法描述**

**2021.12.03 北京**

**为了方便大家写论文时正确描述实验室的分析方法及仪器参数，中科院地质与地球物理研究所MC-ICP-MS实验室特提供以下分析方法描述范例，以供参考 （2021.12）。**

**如果采用的四级杆(Q)-ICP-MS，请参考Q-ICP-MS部分的方法描述; 如果采用的是扇形双聚焦(SF)-ICP-MS，请参考SF-ICP-MS部分的方法描述; 如果采用的是多接收(MC)-ICP-MS, 请参考MC-ICP-MS部分的方法描述.**

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# 1 四级杆(Q)-ICP-MS

## 1.1 *In situ* trace element analysis by LA-Q-ICP-MS

**方法描述**

Trace element contents of **clinopyroxene /amphibole…** were determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Agilent 7500a Q-ICP-MS instrument (Agilent Technologies, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The approach is similar to those outlined in **Wu et al. (2018)** with isotopes measured using a peak-hopping mode with a laser beam diameter of ca. **XX** m and **XX** Hz repetition rate. The laser energy density is **~4.0** J/cm2. Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. ARM-1 reference glass **(Wu et al., 2019, 2021)**was used as calibration material, and NIST SRM 610and BCR-2G were analyzed for data quality control. **Silicon (29Si)** was used as an internal standard. The resulting data were reduced based on the GLITTER program **(Griffin et al., 2008)**. For most trace elements (>0.10 g/g), the accuracy is better than ±10 % with analytical precision (1 RSD) of ±10%.

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## 1.2 Zircon U-Pb dating and trace element analyses by LA-Q-ICP-MS

**方法描述**

The U-Pb isotope compositions of zircon were measured *in situ* using an Agilent 7500a Quadrupole-ICP-MS coupled with a GeoLasHD 193 nm ArF excimer laser ablation system or **an Analyte G2 193 nm ArF excimer laser ablation system** at Institute of Geology and Geophysics, Chinese Academy of Sciences. Detailed analytical procedure followed those outlined in **Xie et al. (2008)**. For most data reported here the density of energy at the ablation spots was **~4.0** J cm-2 at **80** mJ output of energy and laser beam diameters were ca. **XX**m at a repetition rate of **XX** Hz. The dwell time for each isotope was set at 6 ms for 29Si, 49Ti, 93Nb, 181Ta, 91Zr and REE, 15, 15, 30, 15 ms for 204Pb, 206Pb, 207Pb and 208Pb and 10 ms for 232Th and 238U. Each spot analysis comprised 20 s of gas background followed by 50 s of sample ablation. ARM-1 **(Wu et al., 2019, 2021)** were applied to calibrate the trace element concentration for all spot analyses. 91500 zircon (TIMS 207Pb/206Pb age = 1065.4 ± 0.3 Ma, 1s, n = 11; **Wiedenbeck et al. 1995**) or GJ-1 zircon (TIMS 206Pb/238U age = 599.8 ± 4.5 Ma; **Jackson et al., 2004**) was treated as an external reference zircon to calibrate mass bias and instrument drift, which measured twice every ten analyses. Another reference zircon SA01 (TIMS 206Pb/238U age = 535.08 ± 0.32 Ma; **Huang et al., 2020**) was analyzed as an unknown to monitor the quality of age data. The 207Pb/206Pb, 206Pb/238U, 207Pb/235U and 208Pb/232Th ratios were calculated using the GLITTER program, whereas the 235U signal was calculated from 238U on the basis of the ratio 238U/235U = 137.818 **(Hiess et al. 2012)**. The age calculations and plotting of Concordia diagrams were made using ISOPLOT (v3.23) **(Ludwig 2003)**.

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## 1.3 *In situ* bastnäsite trace element and U-Th-Pb age analysis

**方法描述**

An Agilent 7500a Q-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** was used to determine trace element compositions and U-Pb ages. A matrix-matched in house reference material consisting of a crystal of K-9 bastnäsite was used to correct for U-Th-Pb fractionation and instrumental mass discrimination. Two K-9 and LZ1384 or MAD809 analyses were measured after every five unknown bastnäsite spots. All measured 207Pb/206Pb, 207Pb/235U, 206Pb/238U and 208Pb/232Th isotopic ratios of the K-9 reference material during sample analyses were regressed and corrected following the method of **Yang et al. (2014, 2019).** Standard deviations of the calibrated isotope ratios include those from sample, external standard, and deviations from the external reference materials. The 207Pb correction method was applied for common Pb correction assuming a Pb composition equivalent to **Stacey and Kramers (1975),** intercept ages or 206Pb/238U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). Similarly, considering the lower U content of most bastnäsites, we also conducted 208Pb/232Th age calculation after common 207Pb correction **(Yang et al., 2019).**

Quantitative results for trace elements were obtained via the external calibration of relative elemental sensitivities using ARM-1 standard (**Wu et al., 2019, 2021**) and normalization of each analysis to 140Ce as the internal standard using the Glitter software. The Ce2O3 content in bastnäsite samples was determined by electron microprobe analysis.

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## 1.4 *In situ* titanite trace element and U-Pb age analysis

**方法描述**

An Agilent 7500a Q-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** was used to determine trace element compositions and U-Pb ages. A matrix matched titanite reference material (BLR-1) was used as external standard to correct 207Pb/206Pb, 206Pb/238U, 207Pb/235U (235U = 238U/137.818) and 208Pb/232Th ratios. Two BLR-1 and Ontraio analyses were measured after every eight unknown samples. All measured 207Pb/206Pb, 207Pb/235U and 206Pb/238U isotopic ratios of the BLR-1 reference material during sample analyses were regressed and corrected following the method of **Ma et al. (2019).** Trace element concentrations were calibrated using 43Ca as the internal standard (CaO contents were measured previously by EPMA) and using ARM-1 (**Wu et al., 2019, 2021**) as the external standard material. Isotopic and elemental fractionation plus instrumental mass bias were calibrated using Glitter 4.0 software **(Griffin et al. 2008).** For multiple groups of standards, we select the option for the interpolation of linear fit to ratios to perform drift corrections. Signal sections of each analysis were selected independently to get the very similar interval for standards and unknowns. The relative standard deviation of reference values for BLR-1 titanite was set at 2%. The U-Pb ages and weighted mean ages were calculated using the ISOPLOT 3.0 software package **(Sun et al., 2012, Ma et al. 2019).**

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## 1.5 *In situ* monazite trace element and U-Pb age analysis

**方法描述**

An Agilent 7500a Q-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** was used to determine trace element compositions and U-Pb ages. A matrix matched monazite reference material (Namaqualand) was used as external standard to correct 207Pb/206Pb, 206Pb/238U, 207Pb/235U, and 208Pb/232Th ratios. Monazite reference materials (E0013 or Jefferson) were used as quanlity control materials. Two Namaqualand and one E0013 (or Jefferson) analyses were measured after every eight unknown samples. All measured 207Pb/206Pb, 206Pb/238U, 207Pb/235U and 208Pb/232Th isotopic ratios of the Namaqualand reference material during sample analyses were regressed and corrected following the method of **Liu et al. (2012).** Trace element concentrations were calibrated using 140Ce as the internal standard (Ce2O3 contents were measured previously by EPMA) and using ARM-1 (**Wu et al., 2019, 2021**) as the external standard material. Isotopic and elemental fractionation plus instrumental mass bias were calibrated using Glitter 4.0 software **(Griffin et al. 2008).** For multiple groups of standards, we select the option for the interpolation of linear fit to ratios to perform drift corrections. Signal sections of each analysis were selected independently to get the very similar interval for standards and unknowns . The U-Pb and Th-Pb ages and weighted mean ages were calculated using the ISOPLOT 3.0 software package **(Ludwig et al., 2003).**

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## 1.6 *In situ* xenotime trace element and U-Pb age analysis

**方法描述**

An Agilent 7500a Q-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** was used to determine trace element compositions and U-Pb ages. A matrix matched xenotime reference material (MG-1) was used as external standard to correct 207Pb/206Pb, 207Pb/235U, and 206Pb/238U ratios. Xenotime reference material BS-1 was used as quanlity control material. Two MG-1 and BS-1 analyses were measured after every eight unknown samples. All measured 207Pb/206Pb, 207Pb/235U, and 206Pb/238U isotopic ratios of the MG-1 reference material during sample analyses were regressed and corrected following the method of **Liu et al. (2011).** Trace element concentrations were calibrated using 89Y as the internal standard (Y2O3 contents were measured previously by EPMA) and using ARM-1 (**Wu et al., 2019, 2021**) as the external standard material. Isotopic and elemental fractionation plus instrumental mass bias were calibrated using Glitter 4.0 software **(Griffin et al. 2008).** For multiple groups of standards, we select the option for the interpolation of linear fit to ratios to perform drift corrections. Signal sections of each analysis were selected independently to get the very similar interval for standards and unknowns. The U-Pb ages and weighted mean ages were calculated using the ISOPLOT 3.0 software package **(Ludwig et al., 2003).**

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## 1.7 *In situ* columbite-tantalite trace element and U-Pb age analysis

**方法描述**

An Agilent 7500a Q-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** was used to determine trace element compositions and U-Pb ages. A matrix matched columbite-tantalite reference material (Coltan139) was used as external standard to correct 207Pb/206Pb, 207Pb/235U, and 206Pb/238U ratios. Columbite-tantalite reference material Coltan17 was used as quanlity control material. Two Coltan139 and Coltan17 analyses were measured after every eight unknown samples. All measured 207Pb/206Pb, 207Pb/235U and 206Pb/238U isotopic ratios of the Coltan139 reference material during sample analyses were regressed and corrected following the method of **Che et al. (2015).** The lower intercepted age of coltan 17 yielded 502±2.8 Ma (n=11, MSWD=1.5), which are consistent with the age of 502 Ma dated by an independent LA-ICP-MS approach (**Gäbler et al. 2011**). Trace element concentrations were calibrated using 93Nb as the internal standard (Nb2O5 contents were measured previously by EPMA) and using ARM-1 (**Wu et al., 2019, 2021**) as the external standard material. Isotopic and elemental fractionation plus instrumental mass bias were calibrated using Glitter 4.0 software **(Griffin et al. 2008).** For multiple groups of standards, we select the option for the interpolation of linear fit to ratios to perform drift corrections. Signal sections of each analysis were selected independently to get the very similar interval for standards and unknowns. The U-Pb ages and weighted mean ages were calculated using the ISOPLOT 3.0 software package **(Ludwig et al., 2003).**

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# 2 扇形磁场双聚焦(SF)-ICP-MS

## 2.1 *In situ* analysis of ultra-low trace elements by LA-SF-ICP-MS

**方法描述**

Trace element abundances of **olivine/orthopyroxene/carbonate minerals…** were determined by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The approach is similar to that outlined in **Wu et al. (2018)** with isotopes measured using a peak-hopping mode with a laser diameter of ca. **XX** m and **XX** Hz repetition rate. The laser energy density is **~4.0** J/cm2. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability. Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. ARM-3 reference glass was used for external calibration **(Wu et al., 2019, 2021)** and BIR-1G glass were used for quality control monitoring. **Silicon (29Si) or Calcium (43Ca)** was used as an internal standard. The resulting data were reduced based on the GLITTER program **(Griffin et al., 2008)**. For most trace elements (>0.005 g/g), the accuracy is better than ±10 % with analytical precision (1 RSD) of ±10%.

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## 2.2 Concurrent determinations of Fo value and trace element of olivine by LA-SF-ICP-MS

**方法描述**

Simultaneous quantification of Forsterite content and minor-trace elements in olivine was performed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. Laser diameter of ca. **44** m and **5** Hz repetition rate and energy density of ~4.0 J/cm2 were used. The measured isotopes are 7Li, 23Na, 25Mg, 27Al, 29Si, 31P, 43Ca, 45Sc, 49Ti, 51V, 53Cr, 55Mn, 57Fe, 59Co, 60Ni, 63Cu, 67Zn, 69Ga and 89Y. The details of measurements procedures and calibration technique can be found in **Wu et al., (2020).** The resulting data were reduced based on the Iolite program with a home-made DRS approach **(Wu et al. 2018).** The precision and accuracy of Fo values are better than 0.3. The detection limits for most trace elements are better than 0.05 g/g.

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## 2.3 High spatial resolution zircon U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (5-16 m) zircon U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Wu et al., (2020).** Laser diameter of 5-16 m and **5** Hz repetition rate and energy density of ~3.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability. Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. Standard zircon 91500 is used as the primary calibration material. Newly developed standard zircon SA01 **(Huang et al., 2020)**is analyzed as a quality control material. The accuracy and precision of weighted mean 206Pb/238U ages are better than 1.0% for 16 m, 1.0% for 10 m, 1.5% for 5 m spots.

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## 2.4 *In situ* wolframite U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (30-44 m) wolframite U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Yang et al., (2020).** Laser diameter of 30-44 m and **5** Hz repetition rate and energy density of ~3.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability (**Wu et al., 2020**). Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. Newly developed in house wolframite YGX-2113 is used as the primary calibration material. Newly developed standard wolframite Sewa or SHM **(Yang et al., 2020)**is analyzed as a quality control material. The accuracy and precision of weighted mean 206Pb/238U ages are better than ~1.0% for 44 m. The 207Pb correction method was applied for common Pb correction assuming a Pb composition equivalent to **Stacey and Kramers (1975),** intercept age or 206Pb/238U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). The concentrations of U-Th-Pb were reduced using Iolite software with “Trace\_Element” DRS and the Semi quantitative standardisation method. NIST SRM 612 is used as external calibrator and ARM-3 (**Wu et al., 2019, 2021**) is used for the quality control. The yielded results match with the published data with a discrapacy of 20 %.

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## 2.5 *In situ* garnet U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (30-44 m) garnet (schorlomite and grossular-andradite) U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Yang et al., (2018)**. Laser diameter of 30-44 m and **5** Hz repetition rate and energy density of ~3.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability (**Wu et al., 2020**). Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. Newly developed in house schorlomite **WS20, PL34, Willsboro (主标名称)** is used as the primary calibration material. Newly developed standard schorlomite **IR18, 15MC Mali（副标名称）(Yang et al., 2018; Seman et al., 2017)**is analyzed as a quality control material. The accuracy and precision of weighted mean 206Pb/238U ages are better than ~1.0% for 44 m. The 207Pb correction method was applied for common Pb correction assuming a Pb composition equivalent to **Stacey and Kramers (1975),** intercept age or 206Pb/238U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). The concentrations of U-Th-Pb were reduced using Iolite software with “Trace\_Element” DRS and the Semi quantitative standardisation method. NIST SRM 612 is used as external calibrator and ARM-3 (**Wu et al., 2019, 2021**) is used for the quality control. The yielded results match with the published data with a discrapacy of 20 %.

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## 2.6 *In situ* vesuvianite U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (60 m) andradite U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Wei et al., (2021).** Laser diameter of 60 m and **5** Hz repetition rate and energy density of ~5.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability (**Wu et al., 2020**). Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. The **(主标名称)** were used as primary reference materials, respectively. Newly developed in house andradite**（副标名称）**is used as the quality control material. The accuracy and precision of weighted mean 206Pb/238U ages are better than ~2.0% for 60 m. The 207Pb correction method was applied for common Pb correction assuming a Pb composition equivalent to **Stacey and Kramers (1975),** intercept ages or 206Pb/238U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). The concentrations of U-Th-Pb were reduced using Iolite software with “Trace\_Element” DRS and the Semi quantitative standardisation method. NIST SRM 612 is used as external calibrator and ARM-3(**Wu et al., 2019, 2021**) is used for the quality control. The yielded results match with the published datawith a discrapacy of 20 %.

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## 2.7 *In situ* cassiterite U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (30-44 m) cassiterite U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Yang et al., (2022).** Laser diameter of 30-44 m and **5** Hz repetition rate and energy density of ~3.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability (**Wu et al., 2020**). Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. Newly developed in house cassiterite **(主标名称)** is used as the primary calibration material. Newly developed standard cassiterite **(主标名称)** **(Yang et al., 2022)**is analyzed as a quality control material. The accuracy and precision of weighted mean 206Pb/238U ages are better than ~1.0% for 44 m. The 207Pb correction method was applied for common Pb correction assuming a Pb composition equivalent to **Stacey and Kramers (1975),** intercept age or 206Pb/238U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). The concentrations of U-Th-Pb were reduced using Iolite software with “Trace\_Element” DRS and the Semi quantitative standardisation method. NIST SRM 612 is used as external calibrator and ARM-3 (**Wu et al., 2019, 2021**) is used for the quality control. The yielded results match with the published data with a discrapacy of 20 %.

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## 2.8 *In situ* allanite U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (30-44 m) allanite U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Yang et al., (2022).** Laser diameter of 30-44 m and **5** Hz repetition rate and energy density of ~3.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability (**Wu et al., 2020**). Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. Newly developed in house allanite **(主标名称)** is used as the primary calibration material. Newly developed standard allanite **(副标名称)** **(Yang et al., 2022)**is analyzed as a quality control material. The accuracy and precision of weighted mean 206Pb/238U ages are better than ~1.0% for 44 m. The 207Pb correction method was applied for common Pb correction assuming a Pb composition equivalent to **Stacey and Kramers (1975),** intercept age or 206Pb/238U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). The concentrations of U-Th-Pb were reduced using Iolite software with “Trace\_Element” DRS and the Semi quantitative standardisation method. NIST SRM 612 is used as external calibrator and ARM-3 (**Wu et al., 2019, 2021**) is used for the quality control. The yielded results match with the published data with a discrapacy of 20 %.

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## 2.9 *In situ* calcite U-Pb dating by LA-SF-ICP-MS

**方法描述**

High spatial resolution (30-44 m) calcite U-Pb dating was performed using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) employing an Element XR HR-ICP-MS instrument (Thermo Fisher Scientific, USA) coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** at the State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The details of measurements procedures and calibration technique can be found in **Wu et al., (2022).** Laser diameter of 30-44 m and **5** Hz repetition rate and energy density of ~3.0 J/cm2 were used. The Element XR is equipped with the so-called “jet-interface”, comprising of a jet sample cone, an X-version skimmer cone and a high capacity vacuum pump (OnTool Booster 150, Asslar, Germany). This leads to a signal enhancement in laser sampling mode by a factor of 3-5, resulting in an improved detection capability (**Wu et al., 2020**). Helium was employed as the ablation gas to improve the transporting efficiency of ablated aerosols. **WC-1 (主标名称)** **(Roberts et al., 2017)** is used as the primary calibration material. **Duff Brown Tank (副标名称)** **(Hill et al., 2016)**is analyzed as a quality control material. Intercept ages calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the 207Pb/206Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept). The concentrations of U-Th-Pb were reduced using Iolite software with “Trace\_Element” DRS and the Semi quantitative standardisation method. NIST SRM 612 is used as external calibrator and ARM-3 (**Wu et al., 2019, 2021**) is used for the quality control. The yielded results match with the published data with a discrapacy of 20 %.

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# 3 多接收(MC)-ICP-MS

## 3.1 *In situ* Hf isotope ratio analysis of zircon by LA-MC-ICP-MS

**方法描述**

Zircon Hf isotopes were measured using a Neptune (Plus) MC-ICP-MS (Thermo Fisher Scientific, USA) equipped with a GeoLasPro 193 nm ArF excimer laser ablation system (Geolas HD, Lambda Physik, Göttingen, Germany) **or an Analyte G2 193 nm ArF excimer laser ablation system** which is hosted at the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing, China. Detailed analytical procedure was described in **Wu et al., 2006, Xie et al., 2008 and Huang et al 2022.** In this study, ca. **44** m of spot size, **4** Hz of laser repetition rate, and **4.0** J cm-2 of fluence were applied. A single analysis consisted of a block of 200 cycles with 0.131 s integration time per cycle. Measured Hf isotope ratios were corrected for mass fractionation using an exponential law with 179Hf/177Hf = 0.7325. The correction of isobaric interference of 176Yb on 176Hf is the key point in obtaining precise and accurate 176Hf/177Hf values for in-situ zircon Hf isotopic measurements. 176Yb/172Yb ratio of 0.5887 **(Vercoort et al., 2004)** and the βYb value obtained from the sample spot analysis itself were applied for the Yb correction. The reference zircon SA01 was measured as an unknown to check the quality of Hf isotopic data of samples and the obtained value of 176Hf/177Hf is \_\_\_ ± \_\_, identical with the value of 0.282293 ± 7 (2SD) by a solution method **(Huang et al., 2020)** within analytical uncertainty.

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## 3.2 *In situ* Sr-Nd isotope analysis by LA-MC-ICP-MS

**方法描述**

*In situ* Sr-Nd isotopic measurement by LA-MC-ICP-MS following the method of **Yang et al., (2009, 2014, 2019)**, hence only a brief description is given below. All analyses were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing.

***In situ* Sr isotopic analysis**

A Neptune (Plus) MC-ICP-MS coupled to a 193nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) or **an Analyte G2 193 nm ArF excimer laser ablation system** was used to determine Sr isotopic compositions. A spot size of 40 - 90 µm was employed with a 6-8 Hz repetition rate and an energy density of ~6 J/cm2, depending on the Sr concentration of the samples. The Sr isotopic data were acquired by static multi-collection in low-resolution mode using nine Faraday collectors. Prior to laser analysis, the Neptune (Plus) MC-ICP-MS was tuned using a standard solution to obtain maximum sensitivity. A typical data acquisition cycle consisted of a 30 s measurement of the Kr gas blank with the laser switched off, followed by 60 s of measurement with the laser ablating. Two (AP1 or MAD) in house reference materials were measured after every ten unknown sample for external calibration **(Yang et al., 2014 and Xu et al 2022)**. Data reduction was conducted offline and the potential isobaric interferences were accounted for in the following order: Kr, Yb2+, Er2+ and Rb. Finally, the 87Sr/86Sr ratios were calculated and normalized from the interference-corrected 86Sr/88Sr ratio using an exponential law. The whole data reduction procedure was performed using an in house Excel VBA (Visual Basic for Applications) macro program.

***In situ* Nd isotopic analysis**

A Neptune (Plus) MC-ICP-MS coupled to a 193 nm ArF excimer laser ablation system was used to determine Nd isotopic analysis. Prior to laser analyses, the Neptune (Plus) MC-ICP-MS was tuned and optimized for maximum sensitivity using a JNdi-1 standard solution. A laser spot size of 16 - 32 μm was employed with a 6-8 Hz repetition rate, depending on the Nd concentration of the samples. Each spot analysis consisted of approximately 60 s data acquisition with the laser fire on. Two measurements of the AP-1 or AP-2 *in house* reference material were measured after every ten unknown. The MAD in house secondary reference material were analyzed in each analytical session and treated as an unknown sample during the data-reduction procedure **(Yang et al., 2014)**.

In order to obtain accurate 147Sm/144Nd and 143Nd/144Nd data by LA-MC-ICP-MS, care must be taken to adequately correct for the contribution of the isobaric interference of 144Sm on the 144Nd signal. The Sm interference correction is complicated by the fact that the 146Nd/144Nd ratio, which is conventionally used to normalize the other Nd isotope ratios, is also affected by Sm interference. As a result, the mass bias correction of 144Sm interference on 144Nd cannot be applied directly from the measured 146Nd/144Nd ratio. In this work, we have adopted the recently revised Sm isotopic abundances (147Sm/149Sm = 1.08680 and 144Sm/149Sm = 0.22332) **(Yang et al., 2014)**. Firstly, we used the measured 147Sm/149Sm ratio to calculate the Sm fractionation factor and the measured 147Sm intensity by employing the natural 147Sm/144Sm ratio of 4.866559 to estimate the Sm interference on mass 144. Then the interference-corrected 146Nd/144Nd ratio can be used to calculate the Nd fractionation factor. Finally, the 143Nd/144Nd and 145Nd/144Nd ratios were normalized using the exponential law. The 147Sm/144Nd ratio of unknown samples can also be calculated using the exponential law after correcting for isobaric interference of 144Sm on 144Nd as described above. The 147Sm/144Nd ratio was then externally further calibrated against the 147Sm/144Nd ratio of a K-9 reference material during the analytical sessions **(Yang et al., 2014)**. The raw data were exported offline and the whole data reduction procedure was performed using an in house Excel VBA (Visual Basic for Applications) macro program.

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## 3.3 Sr-Nd-Hf-Pb isotope analysis by solution MC-ICP-MS

**方法描述**

Analytical protocol of Sr-Nd-Hf-Pb isotopic compositions by Neptune Plus MC-ICP-MS after DGA and Sr resin chemical purification for one sample digestion. Chemical purifications were undertaken by ion-exchange resin. The analytical protocol is described in detail and can be found elsewhere (**Yang et al., 2010, 2011, 2012; Li et al., 2016; Chu et al., 2019)**, and only a brief description is given here.

About 100-150 mg fine sample powder were dissolved in 2.5 ml concentrated HF, 0.2 ml HNO3 and HClO4 on a hot plate (or using steel-jacketed Teflon bombs placed in an oven at 190 °C) for one week. Following complete dissolution, each sample was dried down at high temperature (fuming HClO4) on a hot plate; then the mixture was treated with 14 M HNO3, evaporated to dryness overnight, and taken up in 3 M HNO3 + 3% m/v H3BO3. The capsule was resealed and placed on a hot plate at 100 °C overnight in preparation for chemical purification.

The first stage was the separation of Sr-Pb, Nd and Hf from the matrix using Eichrom DGA resin (50–100 μm, 2 ml). The major element fraction were eluted and collected using 3 M HNO3 + 3% m/v H3BO3, meanwhile Sr and Pb fractions were collected for further purification. Then the column was rinsed with 12 M HNO3 to remove effectively any remaining Ca before collection of the Hf fraction, followed by separation of Hf using 3.5 M HNO3+0.2 M HF mixture. Finally, the Nd fraction was eluted with 2 M HCl. The second stage involved the Sr and Pb fraction was further purified by Sr-specific resin (100–150 μm, 0.2 ml) prior to mass spectrometric measurement **(Yang et al., 2012; Li et al., 2016)**.

Sr, Nd, Hf and Pb isotopic ratios were measured using a Thermo Scientific Neptune Plus MC-ICP-MS. Whole procedural blanks were less than 100 pg Sr, 50 pg for Nd, 50 pg for Hf and Pb 150pg for Pb. The 87Sr/86Sr, 143Nd/144Nd and 176Hf/177Hf ratios were normalized to 86Sr/88Sr=0.1194, 146Nd/144Nd=0.7219 and 179Hf/177Hf=0.7325, respectively, using the exponential law. During the period of data acquisition, standard analyses yielded results of 87Sr/86Sr=0.710249±12 (2SD, n=15) for NBS987, 143Nd/144Nd=0.512115±12 (2SD, n=15) for JNdi-1, and 176Hf/177Hf=0.282185±10 (2SD, n=15) for Alfa Hf 14374. Similarly, the average of the measured Pb standard SRM 981 (200 ng g-1 Pb doped with 50 ng g-1 Tl of SRM 997), corrected on-line for mass fractionation using 205Tl/203Tl = 2.3871, was 208Pb/204Pb = 36.7018 ± 0.0019 (2SD, n=7), 207Pb/204Pb= 15.4826 ± 0.0005 (2SD, n=7) and 206Pb/204Pb = 16.9298 ± 0.0006 (2SD, n=7), respectively, which is consistent with our previous data or other colleagues reported data by MC-ICP-MS or TIMS **(Xie et al., 2005, Chen et al., 2014; Li et al., 2016)**.

In addition, USGS reference materials BCR-1 and BHVO-2 were also processed for Sr–Nd–Hf isotopes, and gave ratios of 0.704977±12 and 0.703474±11 for 87Sr/86Sr, 0.512655±05 and 0.513000±15 for 143Nd/144Nd and 0.282866±06 and 0.283109±05 for 176Hf/177Hf, respectively, which is identical, within error, to the recommended values **(Weis et al., 2005, 2006, 2007)**. In the meantime, GSR-3 together with CGSG glasses was conducted for Pb isotopic analysis, and gave value of 37.8269 ± 0.0122 (2s, n=4) for 208Pb/204Pb, 15.4783 ± 0.0013 (2s, n=4) for 207Pb/204Pb and 17.7519 ± 0.0159 (2s, n=4) for 206Pb/204Pb, respectively, which is also consistent, with analytical uncertainties with previously reported data by Nu MC-ICP-MS (**Fourny et al., 2016).**

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