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In Situ U-Pb Dating and Trace Element Analysis of LA-ICP-MS Standard Zircon

Yuan Gao, Lihao Song

School of Earth Science and Engineering, Shandong University of Science and Technology, Qingdao, Shandong, 266590, China.

Abstract

Zircon is one of the most common accessory minerals in nature. Due to its good physical and chemical stability, high sealing temperature, rich in U, Th and other radioactive elements, and low content of common Pb, which has preserved its original features throughout the long geological history, has therefore become an effective tool for tracing the evolutionary history of the Earth. Accurate geological sample composition information is the most basic and important premise to reveal the formation of geological bodies and the evolution of geological events. The development of geological analysis and testing technology has greatly promoted the development of geochemistry and the whole earth science. Secondary Ion Mass Spectrometer (SIMS), for example, Sensitive High Resolution Ion Microprobe (SHRIMP) produced by Australia, Cameca IMS Ion Probe produced by Cameca, France, and Laser-Etched Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS), are currently used for in-situ micrometer determination. Since the invention of laser and inductively coupled plasma combined technology in the 1980s, laser denudation inductively coupled plasma mass spectrometer (LA-ICP-MS) has rapidly developed into a powerful tool for the direct determination of elemental composition and isotope ratios of solid samples. Compared with the secondary ion probe (SIMS), the main advantages of this technique include simple sample preparation process, short analysis time, high sensitivity, and less sample consumption, etc., and it has become an important tool for zircon U-Pb dating and trace element analysis.

Keywords

Zircon; LA-ICP-MS; Standard Zircon.

1. Introduction

This paper, by using the shandong university of science and technology key laboratory of depositional mineralization and sedimentary minerals configuration of Agilent 7900 and Geolas HD 193 nm excimer laser ablation system, the determination of trace elements and U - Pb isotopes in a point to get at the same time, using the method of 91500, Gj-1, plesovice and Qinghu four zircon sample, a field geological samples determination, obtain its U - Pb and trace elements of information age, by comparing the previous experimental results, the validation precision of experimental apparatus.

2. Experimental overview

ICP-MS is the full name of inductively coupled plasma mass spectrometry. The instrument model used in this experiment is Agilent 7900. It combines the high temperature (8000K) ionization characteristics of ICP with the advantages of sensitive and fast scanning of quadrupole mass spectrometer to form an element analysis, isotope analysis and morphology analysis technology. The

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technique provides very low detection limit, very wide dynamic linear range, very wide dynamic linear range, simple spectral line, less interference, high analysis precision, fast analysis speed and can provide isotopic information. Compared with the old Agilent 7700 instrument, its high salt tolerance, dynamic range extension ability and signal-to-noise ratio are significantly improved.

Laser ablation system for the Coherent laser company Geolas HD ArF excimer laser, laser as the ArF uv excimer laser, wavelength of 193 nm, by laser, optical system, mechanical system and observation system and the corresponding computer control system and package, etc, can undertake mineral and trace element microanalysis zircon U - in situ Pb isotope determine years, single pulse energy 200 mj, more than 20 hz pulse frequency, the optical system and light and focus its energy density can be up to 50 j/cm^2,The denudation pit diameters can be set as 4, 8, 16, 24, 32, 44, 60, 90, 120μm.

The combined principle of laser (LA) and inductively coupled plasma mass spectrometry (ICP-MS) is as follows (Figure 1) :After laser to generate laser beam via a series of optical path system focused on the sample surface, in the light path system at the same time with microscopic observation window (such as CCD camera) or microscope to observe the surface condition, sample within denudation pool pool (or samples), laser aerosol particles in the sample surface erosion, again by the carrier gas (helium or argon) in the transmission of aerosol particles to ICP plasma volatile, atomization and ionization of ion after screening quality analyzer under test by detector counting.

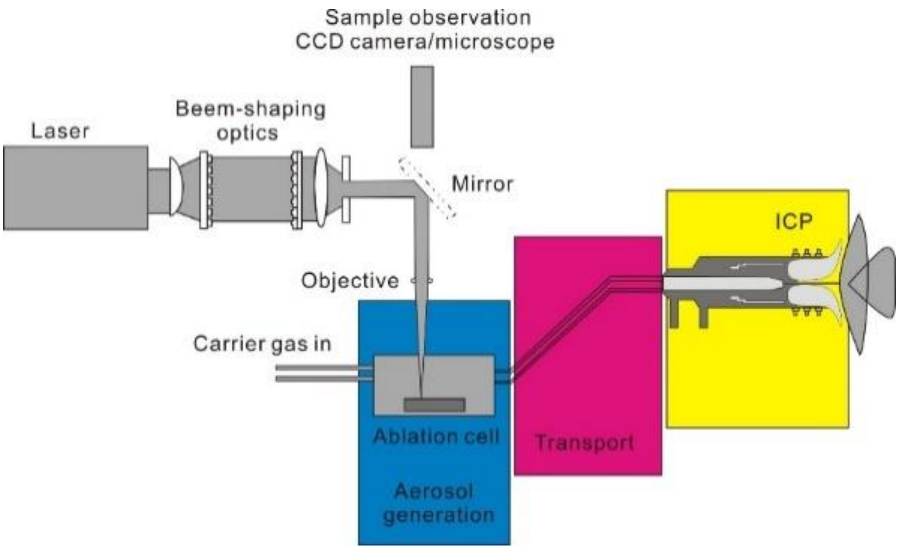

Fig. 1 Schematic diagram of LA-ICP-MS analysis

2.1 Sample preparation

NIST 610 cut into small pieces, and then standard zircon, Plesovice, Gj 91500-1 and Qinghu particles together with double-sided adhesive on the glass slide, put PVC ring, after will be fully mixed epoxy resin and curing agent injection PVC ring, after waiting for resin cured fully to spin out the samples from the glass slide, and carries on the polishing, until samples reveal a smooth plane. Before sample determination, HNO3 with a volume fraction of 3% was used to clean the sample surface to remove contamination on the sample surface. The methods for preparing zircon standard samples are basically the same as those reported in relevant literature (Song Biao et al., 2002; Wang Lan et al., 2012; Peng Lu et al., 2017; Luan Yan et al., 2019)

2.2 Experimental methods

Due to the limitations of isotope analysis in the LA-ICPMS U-Pb dating experiments of zircons at the present stage. For example, low abundance sensitivity and non-flat peak (Liu et al., 2010) have a great impact on the accuracy of zircon dating. Therefore, the sensitivity and stability of the experimental instrument can be improved by adding auxiliary gases to suppress the effects of multi-

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atom interference and matrix effect (Hu et al., 2008). The auxiliary gas N_2 was added in this experiment to enhance the signal strength and improve the accuracy of the experiment. Figure 2 shows the signal interfaces of four standard zircons, 91500, Plesovice, GJ-1 and Jinghu.

In this experiment, solution atomization was firstly adopted. By changing different parameters, debugging solutions representing a full range of quality, namely 7Li, 89Y and 238U debugging solutions containing 1 ng/g, were used for debugging, so as to maximize the signal and minimize the coefficient of variation. Then the laser system is connected, and the beam spot diameter is 32μm.The laser denudation frequency is 6Hz.The sampling method is single point denudation. He was used as the carrier gas of denudation material, and the flow rate was 650 mL /min. The energy density is 10J/cm2.Due to the use of high purity Ar and He gas (99.99%), the background of 204Pb and 202Hg is mostly less than 100 counts.

The ICP-MS data were collected by a single mass peak, and the residence time of single point was set as 6ms (Si and Ca), 15ms (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) and 10ms (Ti, Nb, Ta, Zr, REE, 232Th and 238U), respectively. The NIST610 glass standard sample was denuded by line scanning and then adjusted to obtain the optimal acquisition parameters of LA-ICP-MS. For the determination of zircon standard samples GJ-1, Plesovice and QingHu, 91500 was adopted as the external standard; for the determination of zircon standard sample 91500, GJ-1 was used as the external standard; for the contents of trace elements of all zircons, NIST610 was used as the external standard and Si was used as the internal standard. In other words, NIST610+ standard + standard +5 samples + standard + standard + standard +NIST610 was used in the test. The gas background acquisition time of each analysis point was 15s, the signal acquisition time was 60S, and the washing time was 15s.Offline processing for the data analysis, including the selection of sample and the blank signal, the sensitivity drift correction, element content and U-Th-Pb isotope ratio and age calculation) by professor from China university of geosciences (wuhan) yong-sheng Liu written ICPMSDataCal software for data processing (Liu et al., 2008), the ratio of isotope fractionation correction see literature (ke-jun hou, etc., 2009) weighted average age and the harmonic map drawn using Isoplot 3.0 (Ludwig, 2003).

3. Experimental results and analysis

The zircons 91500, GJ-1, Plesovice and Qinghu have been systematically determined under the condition of a laser spot diameter of 32μm and a frequency of 5Hz.Because the 204Pb count of these standard zircons was close to the background value during the measurement, the normal lead was not corrected. The U-Pb harmonic diagram and ^{206}Pb/^{238}U age value of the determined results are shown in Figure 3.

3.1 91500 zircon

Zircon 91500 is the most widely used solid standard of U-Pb, Lu-Hf and O isotopes in the world. It is a 238g original single grain of zircon preserved in the Harvard Museum of Mineralogy, located in Renfrew, Ontario, Canada. Wiedenbeck et al., (1995) determined the ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages by TIMS were 1062±0.8Ma and 1065±0.6Ma, respectively. Lopez et al., (2001) obtained a ^{207}Pb/^{206}Pb age of 1066.6±1.4Ma; Liu Xiaoming et al. 2007 used LA-ICP-MS to obtain the ^{206}Pb/^{238}U age of 1064.4±4.8Ma under the small spot beam diameter of 20μm.In 2012, Wang Lan et al. used NewWave213nm laser and ThermoFisherXSeries2 quadpole plasma mass spectrometry to test the speck beam diameter of 30μm and obtained a weighted average age of 1059±11Ma for the ^{206}Pb/^{238}U zircons. In 2017, Peng Lu et al. used LA-ICP-MS to test the diameter of the spot beam was 24μm, and the weighted average age of ^{206}Pb/^{238}U was 1062.3±9.3Ma. In 2019, Lun Yan et al. used Agilent 7700X quadrupole plasma mass spectrometry and the supporting Analyte Excite 193nm gas excimer laser denudation system to measure its ^{206}Pb/^{238}U weighted average age of 1063.8±6.6Ma. Therefore, it is generally believed that the formation age of 91500 standard zircon is about 1065Ma.

This paper uses GJ-1 as the external standard to test the 91500 standard zircon. The weighted average age of ^{206}Pb/^{238}U is 1065.4±4.8Ma at 21 test points, and the test points are all located on the concordant line (Fig. 2a), which is consistent with the results reported above within the error range.

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3.2 GJ-1 zircon

The $^{206}Pb/^{238}U$ age of the LA-ICP-MS zircon GJ-1 is 610.0 ±1.7Ma, which is the standard for U-Pb determination in the Laboratory of Continental Geochemistry and Metallogeny (GEMOC), Macquarie University, Australia. Liu Xiaoming et al. 2007 used LA-ICP-MS to obtain the $^{206}Pb/^{238}U$ age of 603.2±2.4Ma under the small speckle beam diameter of 20μm.The $^{206}Pb/^{238}U$ age was determined by LA-ICP-MS in 2012 to be 604.4±4.7Ma under the 30μm diameter beam spot. Luan Yan et al. measured its $^{206}Pb/^{238}U$ age as 605±3Ma.

In this paper, a total of 20 points of the GJ1 standard zircon were measured using 91500 as the external standard. The data showed a good degree of concordant, and the $^{206}Pb/^{238}U$ age was 607.4±3.1Ma (Fig. 2b), which was consistent with the previous reported data within the error range.

3.3 Plesovice zircon

Plesovice zircons originated from potassium-rich granulites in the southern part of the Bohemian Hills in the Czech Republic. Plesovice zircons appear as pale pink-brown equiaxed or long columnar euhedral crystals with sizes ranging from 1 to 6mm. The cathode luminescence images show distinct zonations. Slama et al., 2008, using the TIMS method, showed that the U-Pb age was basically similar, and the $^{206}Pb/^{238}U$ age was 337±0.37Ma.The data measured by LA-ICP-MS by Hou Kejun et al. 2009 showed that the $^{206}Pb/^{238}U$ age was (337.3±0.9) Ma with good consonance degree, and the U-Pb data measured by Wang Lan et al. 2012 were basically located on the harmonic line, and the weighted average age of $^{206}Pb/^{238}U$ was (338.7±2.4) Ma. Peng Lu et al. 2017 and Luan Yan et al. 2019 measured its $^{206}Pb/^{238}U$ weighted average ages as 337.9±2.8Ma and 338.8±1.4Ma respectively, and the measured data showed that its ages were in congener Taking 91500 as the external standard, the U-Pb ages of 26 Plesovice zircons at test points obtained in this paper are all located on the concordant line, with a weighted mean of $^{206}Pb/^{238}U$ age of 337.3±1.6Ma (Fig. 2C), which is consistent with the previous reported results within the error range.

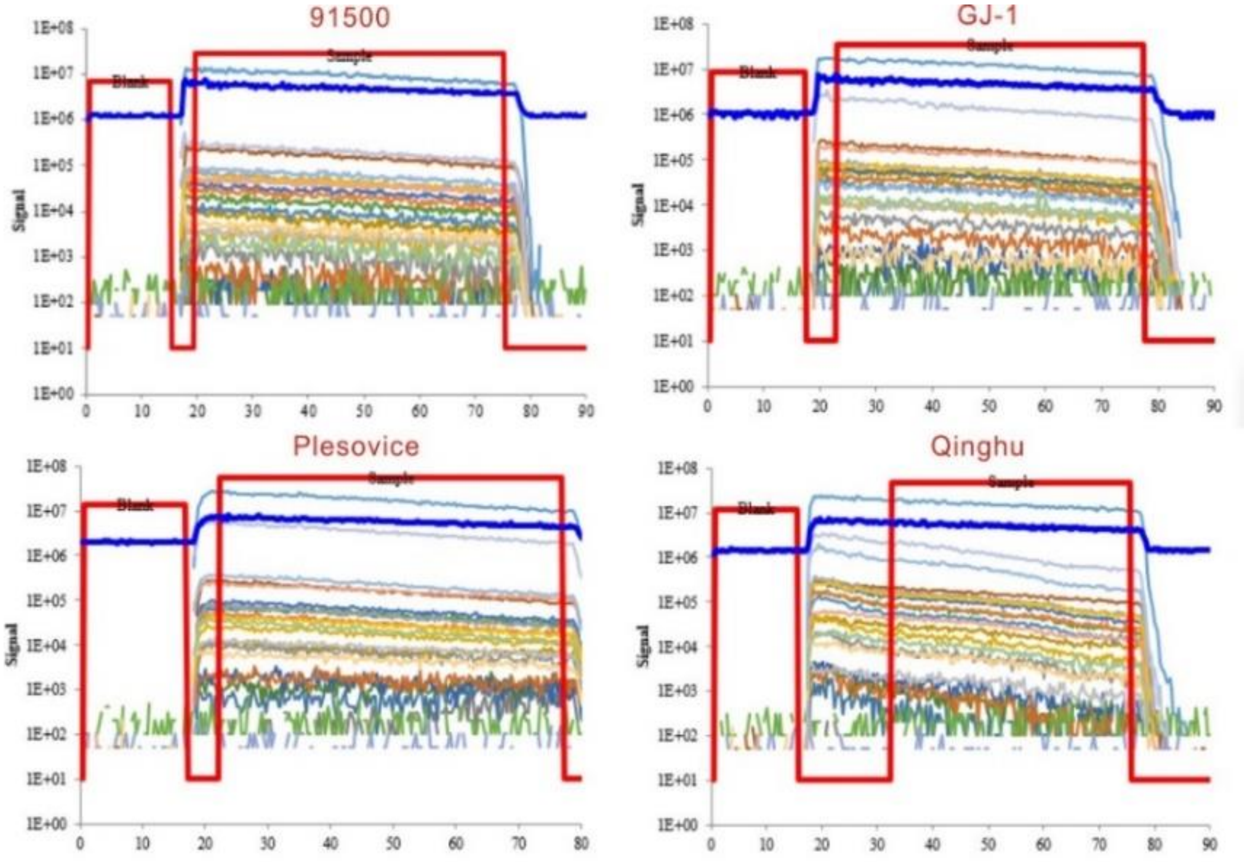

Fig. 2 Zircon signal selection interface of 91500, GJ-1, Plesovice and Qinghu

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3.4 Qinghu zircon

This zircon is an internal standard of the Ion Probe Laboratory of the Institute of Geology and Geophysics, Chinese Academy of Sciences. It was produced in the Qinghu alkaline complex at the border of Guangdong and Guangxi. In 2009, Li Xianhua et al tested the microzone U-Pb ages of 592 Qinghu zircons from 7 groups, and the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ages were 159.7±3.8Ma and 159.4±5.9Ma, respectively (Li et al., 2009).Hou Kejun et al. obtained a $^{206}Pb/^{238}U$ age of 159.7±0.5Ma by LA-MC-ICPMS in 2009.Wang Lan et al. 2012, Peng Lu et al. 2017, and Luan Yan et al. 2019 obtained the weighted average ages of $^{206}Pb/^{238}U$ by LA-ICP-MS, which were 158.9±1.7Ma, 160.0±2.0Ma and 159.9±0.7Ma, respectively. The U-Pb ages of 24 Qinghua standard zircons are all located on the concordant line. The weighted average age of $^{206}Pb/^{238}U$ is 159.5±1.1Ma, which is consistent with the results reported by previous authors.

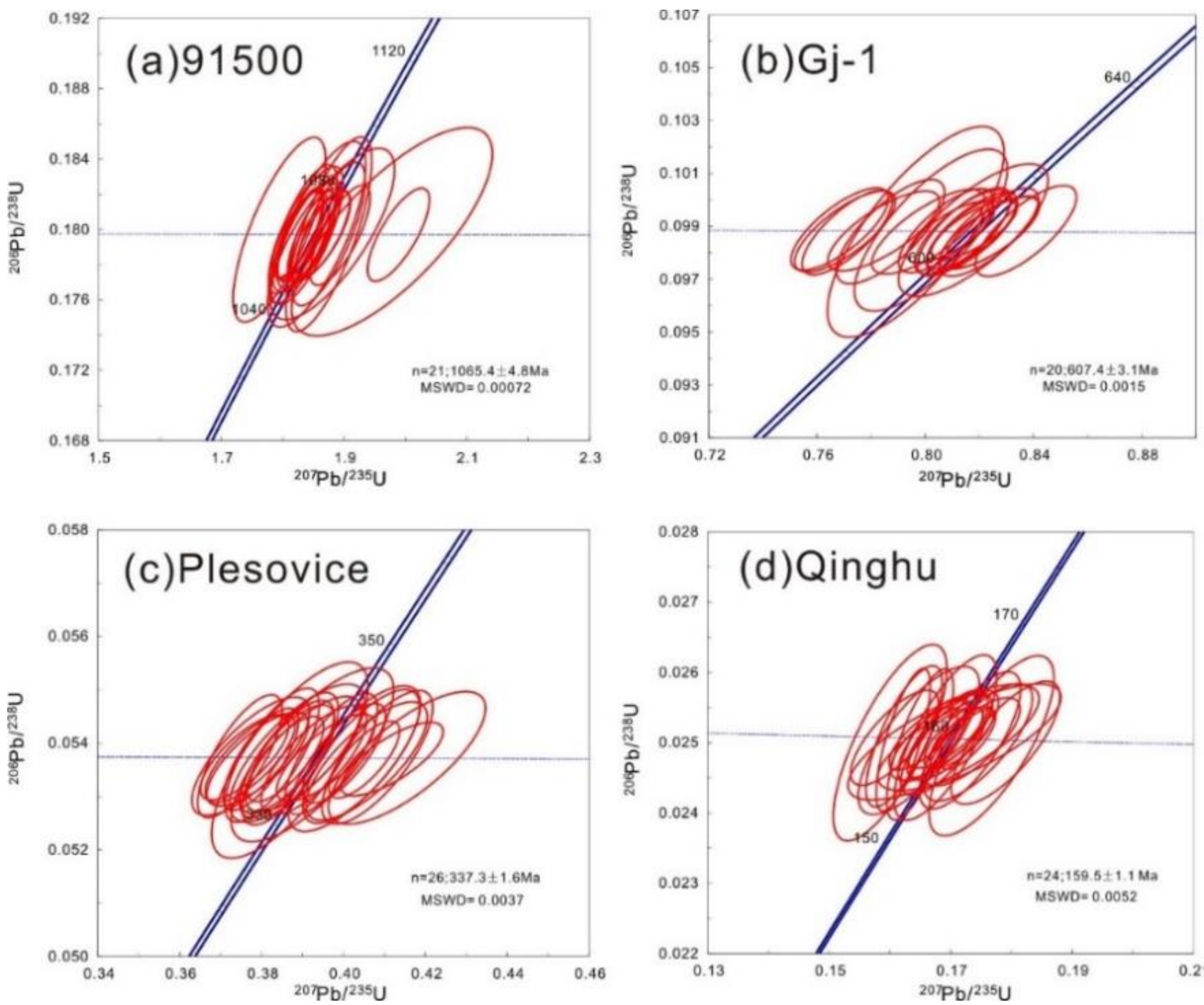

Fig. 3 Concordant zircon ages of 91500, GJ-1, Plesovice and Qinghu

4. Trace element analysis results of standard zircon

Due to the uneven distribution of trace elements in natural zircons, the range of trace elements in all standard zircons is wide. The results show that the average Ce value of some elements in 91500 zircon is 2.149×10-6 (2.89×10^{-6}-2.19×10^{-6}).The average Nd value was 0.171×10^{-6} (0.28×10^{-6}-0.18×10^{-6}); average value was 0.337×10^{-6} (0.628×10^{-6}-0.39×10^{-6});The mean value of Dy was 8.959×10^{-6} (17.4×10^{-6}-9.59×10^{-6});The mean TM value was 4.757×10^{-6} (10.5×10^{-6}-5.59×10^{-6});The mean value of YB was 53.339×10^{-6} (109×10^{-6}-73×10^{-6}).The average zircon Er of GJ-1 is 26.97×10-6 (32.3×10^{-6}-

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27.1×10^{-6}).TM mean value 5.58×10-6 (6.84×10^{-6}-5.65×10^{-6});The mean value of YB was 57.43×10^{-6} (77.9×10^{-6}-66.3×10^{-6});The mean value of Pb was 39.17×10^{-6} (36×10^{-6}-23.1×10^{-6});TH mean value 5.5610^{-6} (11.8×10^{-6}-7.5×10^{-6});U Average 359.5610^{-6} (333×10^{-6}-202×10^{-6}).The mean value of Plesovice zircon Pb was 49.50 (41.6×10^{-6}-27.5×10^{-6});The average value of U is 767.87×10^{-6} (650×10^{-6}-430×10^{-6}), slightly higher than the recommended value, and the average content of other elements is within the range. The mean Yb value of the Qinghu zircon is 155.59×10^{-6} (562×10^{-6}-163×10^{-6}); The average value of Lu is 29.63×10^{-6} (85.3×10^{-6}-31.2×10^{-6}), and the average content of other elements are all within the range. The recommended values in brackets are Yuan et al., 2008, Wang Lan et al., 2012.As can be seen from the standard curve distribution of chondrites (data from Taylor et al., 1985) of the four standard zircons (Fig. 4), the four zircons all have different distribution patterns: 91500 has a weak negative Eu anomaly, relatively uniform REE content, and no negative Eu anomaly (Fig. 4a);The contents of rare earth elements in GJ-1 zircon are relatively uniform, and there is no negative Eu anomaly (Fig. 4b).Both the Pple? Ovice and Qinghu zircons have obvious negative Eu anomalies and significant changes in trace element contents (Fig. 4c, d). The chondrite standard curves of the four standard zircons mentioned above are consistent with previous studies (Liu Xiaoming et al., 2007; Wang Lan et al., 2012; Luan Yan et al. 2019).

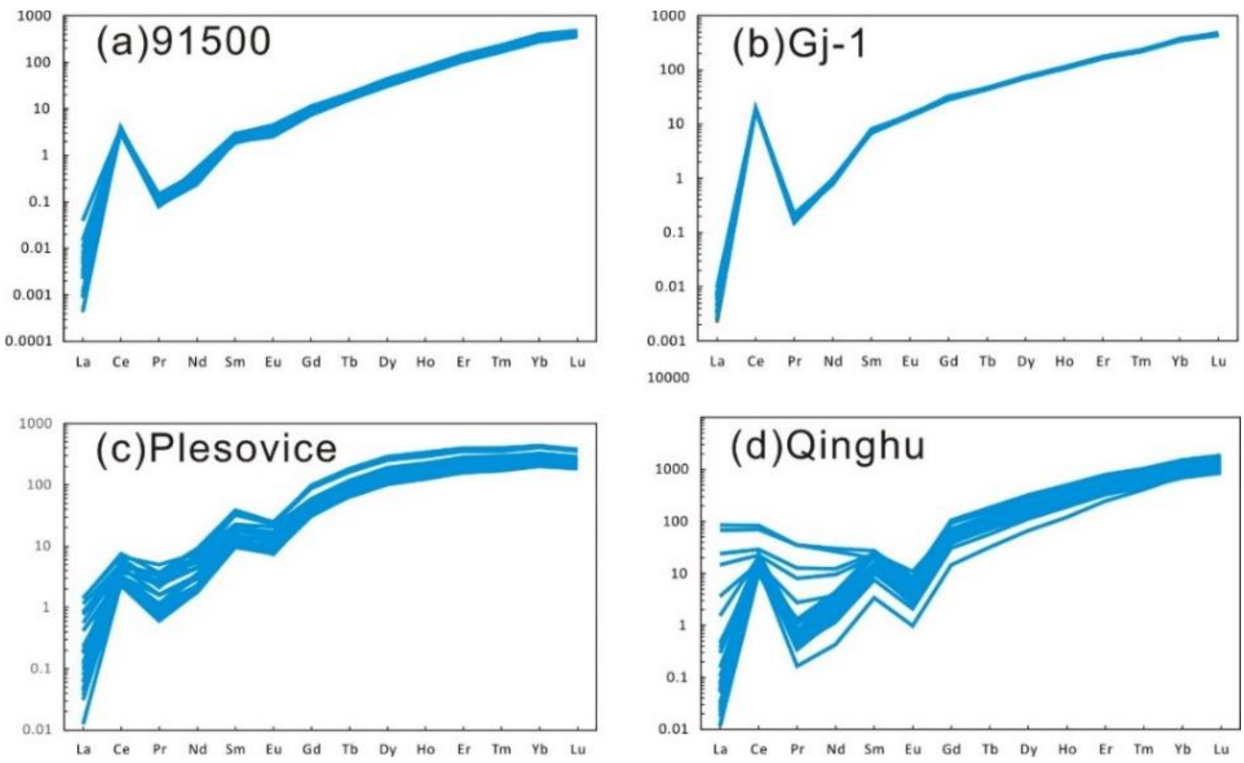

Fig. 4 Distribution pattern of normalized rare earth elements in 91500, GJ-1, Plesovice and Qingh standard zircon chondrites

5. Conclusion

In this experiment, Agilent 7900 and Geolas HD ARF excimer lasers were used to conduct zircon and trace element tests on four standard zircon samples, and the age of 91500 zircon standard samples was 1065.4±4.8Ma.The age of the GJ-1 zircon is 607.4±3.1Ma.The age of Plesovice zircon is 337.3±1.6Ma.The age of the Qinghu zircon standard sample is 159.5±1.1Ma, and the age data obtained from the above tests are consistent with the previous research results within the error range. Due to uneven distribution of trace elements in the natural zircon, zircon trace element changes caused by each standard range is larger, the experiments, the part of the trace elements data does not fall within the recommended range, but also with the recommended values were similar, and four zircon

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standard sample distribution patterns of ree chondrite standardized and predecessors' studying results are consistent.

Therefore, both age and trace elements of the standard sample in this experiment are very accurate, which indicates that the instrument used in this experiment and the method established in this experiment are accurate and reliable for zircon U-Pb dating and in situ determination of trace elements.

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