Available online at www.sciencedirect.com

ScienceDirect

Chemical Geology 247 (2008) 100–118

CHEMICAL GEOLOGY INCLUDING ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Simultaneous determinations of U–Pb age, Hf isotopes and trace element compositions of zircon by excimer laser-ablation quadrupole and multiple-collector ICP-MS

Hong-Lin Yuan [a,b,*], Shan Gao [a,b], Meng-Ning Dai [a], Chun-Lei Zong [a], Detlef Günther [c], Gisela Helene Fontaine [c], Xiao-Ming Liu [a], ChunRong Diwu [a]

[a] *State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an, 710069, China*
[b] *State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Sciences, China University of Geosciences, 430074, China*
[c] *Laboratory of Inorganic Chemistry, ETH Zurich, 8093 Zurich, Switzerland*

Received 11 April 2007; received in revised form 8 October 2007; accepted 9 October 2007

Editor: R.L. Rudnick

Abstract

We describe an *in situ* method for simultaneous measurement of U–Pb–Hf isotopes and trace element compositions of zircons using a quadrupole and multiple-collector inductively-coupled-plasma mass spectrometer (Q-ICP-MS and MC-ICP-MS, respectively) connected to a single excimer laser-ablation system. A laser-generated zircon aerosol was split behind the ablation cell into two transport tubes via a Y-shaped connector and simultaneously introduced into the two mass spectrometers. Hafnium isotopes were measured on the MC-ICP-MS instrument, while U–Pb ages and trace element compositions were determined using the Q-ICP-MS. The precision and accuracy of this method was evaluated using six well-known and widely used zircon standards (91500, Temora-2, GJ-1, Mud Tank, BR266 and Monastery). Analyses were carried out using spot sizes of 32, 44 and 60 μm. For the 44 and 60 μm spot, the resulting U–Pb ages, Hf isotopic and rare earth element (REE) compositions of these six zircons agree with recommended/reported values within 2σ error. The difference in relative standard deviations (RSD) of ^{206}Pb/^{238}U ages between split-flow measurements and those obtained separately on the Q-ICP-MS is within ~20% for 91500, Temora-2 and GJ-1, and ~60% for Mud Tank (due to its lower U and Pb concentrations). Our method provides a precise approach for determining the U–Pb age and the Hf isotopic and trace element compositions of zircon within a single ablation event. This is in particular important for analysis of zircons that are small or contain complicated zoning patterns. Finally, the REE composition of zircon BR266 is more homogeneous than other zircons and could be a suitable standard by which to benchmark new standards for microprobe analyses of zircons.

Keywords: Zircon; Hf isotopes; U–Pb dating; Trace elements; Laser ablation; ICP-MS

1. Introduction

Zircon ($ZrSiO_4$) is one of the most widely used accessory minerals in determining the age, origin, and

---

* Corresponding author. State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an, 710069, China. Tel.: +86 29 88305924; fax: +86 29 88303447.
E-mail address: hlyuan@263.net (H.-L. Yuan).

0009-2541/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2007.10.003

thermal history of rocks and deciphering the evolution of the crust and mantle of the Earth in terms of U–Th–Pb–Hf–O isotopic systematics and trace element compositions. The utility of zircon is mainly due to its high closure temperature, resistance to late disturbance, and high concentrations of the parent element uranium, daughter element hafnium, and rare earth elements (REE), especially heavy rare earth elements (HREE), coupled with an extremely low Lu/Hf ratio and negligible incorporation of the daughter element lead and parent element lutetium during crystallization. In addition, two geochronometers (^{235}U–^{207}Pb and ^{238}U–^{206}Pb) can be used to test the concordance of the determined age (Patchett et al., 1981; Kinny and Maas, 2003; Harrison et al., 2005; Hawkesworth and Kemp, 2006a).

The zircon thermometer also provides important information on the formation and evolution of the continental crust (Watson and Harrison, 2005; Watson et al., 2006). Prior to 1995, Hf isotopic compositions were generally measured by thermal-ionization mass spectrometry (TIMS), but multiple-collector inductively-coupled-plasma mass spectrometry (MC-ICP-MS) (Walder et al., 1993; Halliday et al., 1998; Albarède et al., 2004) has become a powerful alternative method in recent years. The ICP-based technique provides a high-temperature plasma source that ionizes elements with high first-ionization potentials, such as hafnium. The number of studies undertaken using the Lu–Hf isotopic system has increased dramatically with the advent of the MC-ICP-MS technique, although the mass bias of this approach is about 10 times greater than that typically measured by TIMS.

It is therefore necessary to characterize the mass bias in greater detail, especially for those cases in which isobaric interference corrections are applied (Chu et al., 2002; Vance and Thirlwall, 2002). It has been suggested that mass bias in MC-ICP-MS can be corrected using elements with comparable masses to the element of interest (e.g., Zn for Cu, Tl for Pb) (Longerich et al., 1987; Maréchal et al., 1999; Kamenov et al., 2004; Wu et al., 2006a).

The exceptional ionization efficiency of the plasma source, easy sample handling, and absence of polyatomic interference makes MC-ICP-MS the preferred technique for Lu–Hf isotope analyses of zircon (Andersen et al., 2002; Griffin et al., 2002; Woodhead et al., 2004). Indeed, the importance of the Lu–Hf isotopic system in zircon, as measured by MC-ICP-MS, is widely accepted (Blichert-Toft and Albarède, 1997; Blichert-Toft et al., 1999; Zheng et al., 2005; Wu et al., 2006b).

Zircon grains commonly exhibit a complicated growth zonation, particularly in metamorphic rocks. In such cases, *in situ* microanalysis, cathodoluminescence (CL) images, and backscattered electron (BSE) images are required for accurate interpretations of the geological significance of multiple zircon ages (Hoskin and Schaltegger, 2003). Therefore, the simultaneous *in situ* analysis of U–Pb isotopes, Hf isotopes, and trace elements is important in determining zircon geochronology and interpreting geological ages. Although large-geometry SIMS instruments (e.g., the sensitive high-resolution ion microprobe, or SHRIMP) are powerful in this regard, this approach is hampered by the following shortcomings: limited access to instrumentation, sensitivity to the so-called matrix effects, and failure to analyze Hf isotopes. Recent improvements in instrumentation and methodology show that laser-ablation-inductively-coupled-plasma mass spectrometry (including quadrupole and multiple collector, abbreviated as LA-Q-ICP-MS and LA-MC-ICP-MS) has become a powerful tool, providing age dates and trace element concentrations comparable to those of SIMS in terms of both accuracy and precision (Horn et al., 2000; Ballard et al., 2001; Li et al., 2000, 2001; Belousova et al., 2002; Košler et al., 2002; Jackson et al., 2004; Yuan et al., 2004; Paul et al., 2005; Simonetti et al., 2005). More importantly, LA-MC-ICP-MS is currently the only method that can be used to determine *in situ* Hf isotopic compositions (Griffin et al., 2000; Woodhead et al., 2004; Woodhead and Hergt, 2005; Hawkesworth and Kemp, 2006a,b; Wu et al., 2006a).

Previous *in situ* determinations of zircon U–Pb ages and trace element and Hf isotopic compositions using LA-Q-ICP-MS and LA-MC-ICP-MS have been carried out either on different domains of single zircons [e.g., ablation spots for Hf isotopic analyses have been placed close to the spots used for age dating and trace element analysis (Griffin et al., 2000)], on a similar location with different cycles [e.g., one cycle for standard hafnium analysis and a second cycle for measurements of lead isotopes (Woodhead et al., 2004)], or on similar spot locations but with different spot sizes [e.g., a small crater for U–Pb dating and a larger crater on similar locations for Lu–Hf isotope analyses (Wu et al., 2006b)]. In any case, the data are not generated from a single sampling site during a single laser-ablation analysis.

Because zircon is commonly zoned in terms of age and composition, analyses obtained using the above methods represent best estimates, and may or may not be exactly correlative. Woodhead et al. (2004) simultaneously determined ^{207}Pb/^{206}Pb ages and Hf isotope data for zircon from a single ablation using an excimer laser-ablation MC-ICP-MS (Nu Plasma) configuration. The authors suggested that the relatively small amount of sample consumed by the SIMS technique means that