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Geochemical applications of *in situ* isotopic analyses by laser ablation

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Abstract
Isotopic compositions of geological material are a kind of 'DNA' that has been widely used in geochemistry to identify various sources of rocks and processes that have shaped our Earth. Traditionally, radiogenic Sr, Nd and Hf isotopic ratios were determined on whole-rock samples through dissolution, chemical separation using time-consuming liquid chromatographic exchange and measurement by thermal ionization mass spectrometry (TIMS). This kind of bulk analysis cannot provide spatial information with high resolution, although it is commonly thought that most geological materials are heterogeneous in both occurrence and composition. The advent of inductively coupled plasma mass spectrometry (ICP-MS), however, makes it possible to measure isotopic ratios on the scale of sub-grains if laser ablation sampling is used. China, like other countries in the world, has installed numerous quadruple and multi-collector (MC) ICP-MS instruments with laser ablation systems, which are currently being used for *in situ* zircon U-Pb dating, and Sr-Nd and Hf isotopic measurements. After reviewing technical developments, this paper briefly describes the geochemical applications of *in situ* laser ablation techniques for *in situ* isotopic analysis of minerals, deciphering the petrogenesis of magmatic rocks, and identifying sediment provenances.

Keywords: Geochemical applications; Isotopic analysis; *In situ* analysis; Laser ablation

1. Introduction

Traditionally, isotopic data were obtained by chemical separation using ion-exchange columns after complete sample digestion, followed by purification of Sr, Nd and Hf fractions, and then measurement by Thermal Ionization Mass Spectrometry (TIMS). However, this solution method is a bulk analysis and the obtained isotope data are therefore an average of the sample. Since natural geological materials are generally heterogeneous, isotopic analyses should be conducted using high resolution micro-analytical techniques, such as *in situ* analyses by Secondary Ionization Mass Spectrometry (SIMS) and Laser Ablation (LA) Inductively Coupled Plasma Mass Spectrometry (ICP-MS), or Multi-collector (MC) ICP-MS. During the past few decades, *in situ* LA-(MC) -ICP-MS techniques have developed rapidly, and have been widely applied in geochemistry, including measurements of trace elements, radiogenic Pb, Sr, Nd, Hf and Os isotopes, and non-traditional Li, B and Mg isotopes (Sylvester, 2001, 2008).

Chinese Earth sciences have greatly benefited from the above technical developments since the first installation of ICP-MS in early 1990s. Subsequently, laser ablation attached analytical systems have been established in numerous universities and institutes, with *in situ* laser ablation data first reported for Pb isotopes by Liu et al. (1998) and Yan et al. (1998), for Sr isotopes

by Wei et al. (2002), for Nd isotopes by Yang et al. (2008) and for Hf isotopes by Li et al. (2003).

2. In situ laser ablation techniques

LA-ICP-MS analytical systems consist of three essential parts, LA (laser ablation), ICP (Inductively coupled plasma) and MS (mass spectrometry, quadruple (Q) or multi-collector (MC)). Whatever isotopes are being analysed, instrumental mass bias or discrimination, elemental fractionation and potential matrix effects must be overcome.

2.1 *In situ* zircon U-Pb age determination

The first *in situ* zircon U-Pb age data conducted by laser ablation were published in early 1990s (Feng et al., 1993; Fryer et a., 1993). Due to the low efficiency of older generation laser systems, only $^{207}Pb/^{206}Pb$ ages from Precambrian zircons were obtained by these pioneer works. To overcome elemental fractionation, Li et al. (2000) proposed a raster scanning mode to get reliable age data for the Phanerozoic zircons. Subsequently, Li et al. (2001) developed a method to simultaneously obtain U-Pb age and trace element compositions, which was used by Yuan et al. (2003, 2004) and many others (Liu et al., 2007; Xie et al., 2008). Since then, laser ablation has become a common method for zircon U-Pb age measurements in China although, two SIMS instrument facilities, SHRIMP II and CAMECA 1280, have also been established (Liu et al., 2006; Li et al., 2009). Laser ablation has now become a routine technique to date zircon and other accessory minerals, such as baddeleyite, monazite, titanite, rutile, allanite, perovskite, xenotime, eudialyte, zirconolite, calzirtite, uraninite, and davidite (KoÅ¡ler et al., 2001; Jackson et al., 2004; Chang et al., 2006; Simonetti et al., 2006; Cocherie and Robert, 2008; Frei and Gerdes, 2009). In China, for example, perovskite, titanite and eudialyte have been dated by U-Pb using *in situ* laser ablation techniques (Yang et al., 2009; Wu et al., 2010a; Li et al., 2010). The U-Pb ages obtained by laser ablation in China were mostly with quadruple ICP-MS. There is no report that ion counters in MC-ICP-MS instruments have been used, which would permit more accurate detection of common lead.

2.2 *In situ* Sr isotopic analysis

The first reported *in situ* Sr isotopic analysis was by Christensen et al. (1995) on gastropods and plagioclase crystals. With 150-300 μm spot sizes and raster mode, they obtained $^{87}Sr/^{86}Sr$ ratios identical within errors to those obtained by TIMS analyses. Since then, in situ Sr isotopic data have been reported for apatite, carbonate, allanite, titanite, clinopyroxene, perovskite, eudialyte, basalt groundmass and melt inclusions (c.f. Vroon et al., 2008). Lately, Sr isotopic analysis of fluid inclusions has been reported from China (Yuan et al., 2009). The main obstacle in Sr isotopic analysis is interference of ^{87}Rb on ^{87}Sr, which requires that the analysed material must have extremely low Rb/Sr ratios of <0.02 (Vroon et al., 2008; Yang et al., 2009; Wu et al., 2010b). Although some minerals such as clinopyroxene, eudialyte and zirconolite have high Sr concentrations, their high HREE contents result in significant interferences of doubly charged ions on Sr isotopes if Yb/Sr is in excess of 0.1 (Vroon et al., 2008; Wu et al., 2010b). Nevertheless, *in situ* Sr isotopic data have great potential to decipher the petrogenesis of magmatic rocks, melt-rock interactions, and seawater isotopic variations (Davidson et al., 2007), although high precision Sr isotopic data comparable to Nd isotopic data are difficult to obtain (Figure 1a).

2.3 *In situ* Nd isotopic analysis

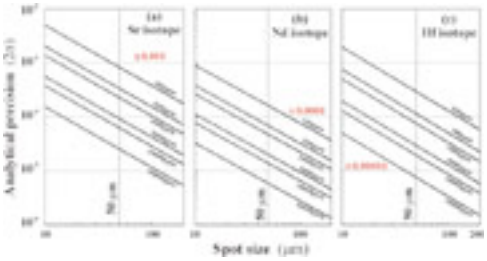

Figure 1
click image to enlarge

Nd isotopic compositions are important tracers for petrogenesis and crust-mantle evolution of the Earth. However, there is a paucity of studies of mineral *in situ* Nd isotopic analyses except for apatite, titanite, ferromanganese nodules, perovskite, monazite, allanite, eudialyte, zirconolite, and calzirtite (Foster and Vance, 2006; McFarlane and McCulloch, 2007; Yang et al., 2009; Wu et al., 2010b, 2010c). Theoretically, any material with high Nd concentrations can be analyzed *in situ* for Nd isotopes. For example, a precision of 100 ppm can be obtained for 60-80μm spot sizes (Figure 1b) on NIST610, which has a Nd concentration of 440 ppm (Yang et al., 2008). The main difficulty is isobaric interferences of Ce and Sm on Nd, which can be reasonably corrected (Yang et al., 2009).

Although high precision *in situ* Nd isotopic compositions are easier to obtain than those of Sr, appropriate external standards for *in situ* Nd isotopic analysis are lacking because almost all natural materials show some variations in Sm/Nd ratios. Synthetic standards have been recently developed (McFarlane and McCulloch, 2007), but natural mineral standards are required to overcome potential matrix effects.

2.4 In situ Hf isotopic analysis

Hf is another important isotopic tracer used to study geological processes. However, Hf isotopes cannot be determined easily by traditional TIMS techniques, and MC-ICP-MS techniques are best suited for Hf isotopic analysis. In terms of *in situ* analysis by laser ablation, the minerals commonly used are zircon and baddeleyite since both of them have high Hf concentrations and low Lu/Hf ratios (Thirlwall and Walder 1995; Griffin et al., 2000; Kinny and Mass, 2003; Wu et al., 2007). More recently, Hf isotopic compositions have been reported for eudialyte, zirconolite and calzirtite (Wu et al., 2010b). The main interference is ^{176}Yb on ^{176}Hf. This correction was traditionally done assuming Yb has the same fractionation as Hf during the analysis (Li et al., 2003; Xu et al., 2004), but later experiments indicated that this is not the case (Woodhead et al., 2004; Iizuka and Hirata, 2005; Wu et al., 2006). Therefore, the most commonly used protocol is measuring the mass bias of Yb directly during analyses. Evidently, it is impossible to get reliable Hf isotopic data if the Yb/Hf ratio is as high as 0.02 (Wu et al., 2006). In our experience, the minerals that can be analyzed *in situ* for Hf isotopes include zircon, baddeleyite, rutile, eudialyte, zirconolite and calzirtite. With a spot size of 60 μm or less, Hf concentrations in excess of 1000 ppm are required to get reasonable Hf isotopic ratios (Figure 1c).

In situ analytical techniques developed in China include the simultaneous determination of zircon U-Pb ages, Hf isotopic compositions and trace element contents (Yuan et al., 2008; Xie et al., 2008). The ablated aerosol is carried by helium and split into two transport tubes using a three-way pipe and introduced simultaneously into the Q-ICPMS and MC-

ICPMS. The proportion of ablated material carried into the two instruments was controlled by three mass flow controllers. There is no significant mass fractionation when different proportions of ablated material were carried into the Q-ICPMS and MC-ICPMS (Xie et al., 2008). This simultaneous technique can also be applied to other accessory minerals for U-Pb ages, Sr or Nd isotopic compositions and trace element analyses (Yang et al., 2009; Wu et al., 2010a, 2010b), such as used in metamorphic zirconology (Xia et al., 2009; Chen et al., 2010). Table 1 presents a summary of object minerals that can be analyzed by the simultaneous *in situ* technique.

Table 1 Simultaneous determination of isotopic compositions using Q-ICP-MS and MC-ICP-MS

Q-ICP-MS	**MC-ICP-MS**	**Mineral**
U-Pb age and/or trace elements	Sr isotopes	Apatite, calcite, allanite, epidote, titanite, perovskite, eudialyte
	Nd isotopes	Apatite, calcite, titanite, perovskite, mozanite, allanite, epidote, eudialyte, zirconolite, calzirtite
	Hf isotopes	Zircon, baddeleyite, eudialyte, zirconolite, calzirtite

Another achievement is the combined analyses of Hf isotope by MC-ICP-MS and O isotope by CAMECA 1280 for zircons (Li et al., 2009b, 2010), a technique that has been used by other researchers to decipher the petrogenesis of granite and continental crustal growth (Hawkesworth and Kemp, 2006; Kemp et al., 2006, 2007). Similarly, numerous studies in China have used a combination of *in situ* U-Pb dating, Hf isotopic compositions and O isotope analysis (Zhang et al., 2006, 2008; Zheng et al., 2006, 2007; Zhao et al., 2008).

3. Geochemical applications

3.1 Isotopic investigation of eudialyte

Eudialytes are a group of complex Na-Ca zirconosilicate minerals that generally occur in peralkaline agpaitic syenites. Given that eudialytes are easily altered and commonly contain inclusions of earlier-crystallized minerals, *in situ* laser ablation is the most suitable method to determine their U-Pb ages, and Sr, Nd and Hf isotopic compositions. Electron microprobe and LA-ICP-MS analysis of eudialytes from nepheline syenites in numerous localities indicate that this mineral typically has high contents of U, Pb, Nb, Ta, Zr, Hf and REEs. Analysis of an in-house standard eudialyte by both solution and laser ablation methods demonstrates that precise and accurate U-Pb ages can be obtained after correction for the common Pb content. The high Sr, Nd and Hf contents in most eudialyte, coupled with the generally low Rb/Sr and Lu/Hf ratios, also permit the precise determination of *in situ* Sr, Nd and Hf isotopic ratios by LA-MC-ICP-MS methods. In our experience, eudialyte is the only mineral investigated to date for which it is possible to determine simultaneously U-Pb ages and Sr, Nd and Hf isotopic compositions (Wu et al., 2010b).

3.2 Hf isotopic constraint on magma mixing

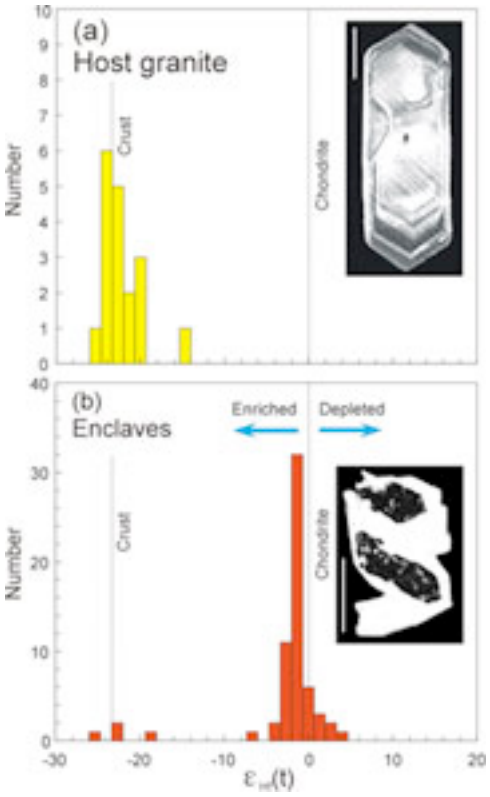

Figure 2
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Magma mixing has been widely recognized from field observations, whole rock geochemistry and Nd and Sr isotopic data in both plutonic and volcanic environments. The basis of such interpretations is the recognition of the primitive sources of mafic and felsic magmas. However, identifying the specific sources that contributed to the origin of granitoids has long been a problem, since both magma mixing and wall-rock assimilation can significantly modify the rock chemistry. This can result in homogeneous Nd and Sr isotopic compositions in what were initially discrete components within a single pluton or batholith. Considering that zircon, a ubiquitous accessory mineral in both granites and enclosed microgranular enclaves, is extremely resistant to later geological processes and can survive post-crystallization thermal disturbances, Yang et al. (2007) conducted a comprehensive *in situ* zircon U-Pb and Hf isotopic study of mafic microgranular enclaves and host granitoids from the Early Cretaceous Gudaoling batholith in NE China. The zircon U-Pb age of the enclaves (120 ± 1 Ma) is identical to that of the host monzogranite (120 ± 1 Ma), establishing that the mafic and felsic magmas were coeval. The enclaves have $_{\varepsilon Hf}(t)$ values of +4.5 to -6.2, which is distinct from $_{\varepsilon Hf}(t)$ of -15.1 to -25.4 obtained for the host monzogranite (Figure 2). This indicates that both depleted mantle and ancient crustal sources contributed to their origin. The depleted mantle component was not previously revealed by whole-rock geochemical and Sr-Nd isotopic studies, demonstrating that the zircon Hf isotopic data can be a powerful geochemical tracer with the potential to provide unique petrogenetic information. Some ancient crustal contamination is indicated by inherited zircons with considerably older U-Pb ages and low $_{\varepsilon Hf}(t)$ values. Hafnium isotopic variations in the Early Cretaceous zircons rule out simple crystal-liquid fractionation or restite unmixing as the major genetic link between enclaves and host rocks. Instead, mixing of mantle-derived mafic and ancient crustal-derived felsic magmas can reasonably explain these data (Yang et al., 2007).

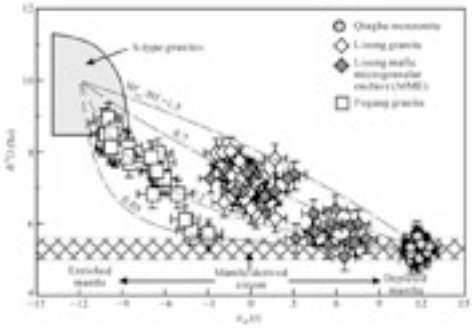

Figure 3
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An interesting discovery during previous studies is that zircons from granites always show Hf isotopic variations, which are definitively beyond the analytical precision, and should shed light on the composition of magma from which the zircon crystallized. A typical example comes from Hf-O isotopic analyses of granites in southeastern China by Li et al. (2009b), who demonstrated that granitic rocks (Figure 3), whether granite (Lisong granite), dioritic enclave (Lisong diorite) or individual pluton (Fogang granite), show a systematic Hf-O variation, such as previously shown by Kemp et al. (2007) for the granites in the Lachlan Fold Belt of southeastern Australia. Evidently, the studied Lisong dioritic enclave crystallized from depleted mantle-derived magma which is constrained by data from the Qinghu monzonite, whereas the Lisong and Fogang granites were formed by magma mixing to varying degrees between mantle- and crustal-derived melts. Therefore, *in situ* analysis of zircon Hf-O isotopes is a powerful tool to identify mixing during magma evolution.

3.3 Juvenile Hf isotopic compositions of the Ladakh-Gangdese batholith in Tibet

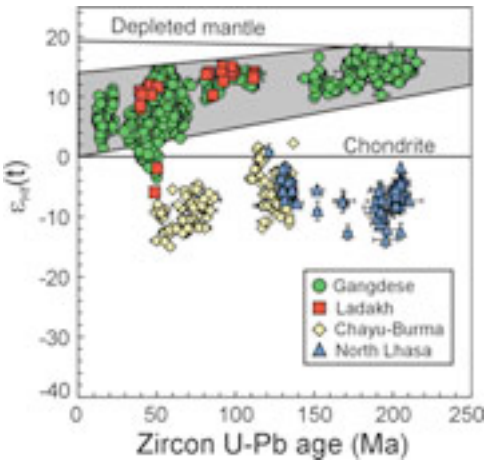

Figure 4
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In Tibet, during oceanic closure, terrane amalgamation and collision and subsequent post-orogenic processes between India and Asia, resulted in the production of various kinds of granites. The best studied granites in the region are the Transhimalayan batholith, exposed along the southern margin of the Lhasa terrane and extending from the Kohistan-Ladakh batholith in the west through the Gangdese batholith in the middle to the Chayu-western Yunnan (Dianxi)-Burma batholith in the east, with a length of >3000km. Although this gigantic batholith has attracted much academic attention over the past decades, its geochronological framework, petrogenesis and relationship with Tethysan ocean closure and India-Asia collision remain unclear. Our U-Pb age data suggest four discrete stages of magmatic activities, specifically ~205-152, ~109-80, ~65-41 and ~33-13 Ma, with the stage of 65-41 Ma being the most prominent. The Hf isotopic data indicate that the Gangdese batholith has positive $_{\varepsilon Hf}(t)$ values (Figure 4, Chiu et al., 2009; Ji et al., 2009), which are comparable to those of the Kohistan-Ladakh batholiths in the west (Ravikant et al., 2009), but markedly different from those of the Chayu-Burma batholiths in the east (Liang et al., 2008). This newly established zircon U-Pb age and Hf isotope database for the Gangdese batholith can be used as a tracer for the source-to-sink relation of the sediments eroded from the southern Tibetan Plateau (Liang et al., 2008; Cina et al., 2009; Hoang et al., 2009; Wu et al., 2010c).

3.4 *In situ* Sr-Nd isotopic compositions of Mengyin kimberlitic perovskites

Kimberlite is a kind of igneous rock from which the initial isotopic compositions of magmas are hard to be obtained because it is commonly contaminated by both crustal and mantle materials and also shows extensive

alteration and weathering following emplacement. Fortunately, perovskite ($CaTiO_3$) can be used to circumvent this problem since it occurs mainly in the kimberlite groundmass and crystallizes early in the magmatic history, along with ilmenite, rutile and magnesian chromite. Therefore, perovskite has the potential to record the primary geochemical and isotopic signature of the magma prior to any contamination. Furthermore, perovskite is normally resistant to weathering and tends to remain fresh when other constituents have been intensely altered.

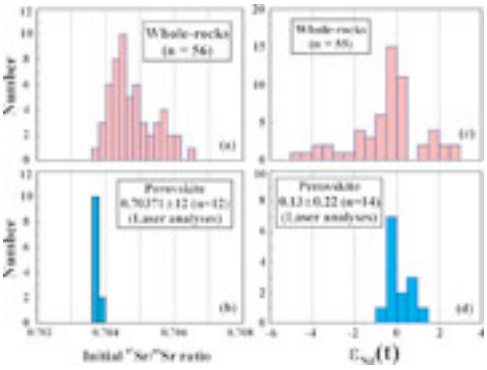

Figure 5
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Numerous kimberlitic samples from Mengyin in eastern China were selected for U-Pb dating and Sr-Nd-Hf isotopic analysis of perovskite. *In situ* U-Pb analyses of fresh perovskite yield an age of 470 ± 4 Ma, which is considered the emplacement age of the Mengyin kimberlite. However, altered perovskite shows Pb loss and yields Paleozoic-Mesozoic ages, indicating that perovskite is not as resistant to isotopic modification as suggested previously. *In situ* Sr-Nd isotopic analyses by laser ablation of perovskite grains collected from the main Mengyin kimberlite record uniform Sr and Nd isotopic compositions with an average initial 87Sr/86Sr ratio of 0.70371 ± 12 and $_{\varepsilon Nd}(t)$ value of 0.13 ± 0.22, which are identical, within uncertainties, to the values obtained by solution analyses of the perovskite. However, they are significantly different from the whole rock data (Figure 5), indicating that initial Sr-Nd isotopic ratios calculated from whole rock measurements on kimberlites are likely to record mixed isotopic signatures due to crustal contamination and subsequent alteration. This conclusion is also supported by the Hf isotopic data for perovskite. Therefore, our studies (Yang et al., 2009; Wu et al., 2010a), combined with those by others (Paton et al., 2007a, 2007b; Woodhead et al., 2009), indicate that meaningful isotopic ratios for kimberlite can only be obtained from single minerals such as perovskite.

4. Concluding remarks

Most natural materials show compositional zoning, hence isotopic variations within individual mineral grains are vital to deciphering precise and detailed geodynamic processes. For this reason, *in situ* laser ablation analysis has become an important frontier in geochronology and isotopic geochemistry. LA-(MC)-ICP-MS techniques have distinct advantages over traditional bulk analysis. Firstly, *in situ* laser ablation can decipher subtle isotopic variations at high spatial resolution on a sub-grain scale. For example, we can obtain reliable isotopic data from thin section with clear petrogenetic implications. Secondly, LA-(MC)-ICP-MS works under atmospheric pressure, which makes it convenient to change the sampling mode during analyses. Thirdly, laser ablation does not need time-consuming sample preparation, with isotopic analyses within minutes. However, laser ablation is destructive to the sample, although the consumed volume is much smaller than by the traditional TIMS method, but larger than SIMS, which has an ablation depth of only 2-3 μm. Therefore, for precious samples, such as minerals from

meteorites, our suggestion is that the laser ablation should be conducted after SIMS analyses.

Other factors that should be considered during laser ablation analyses are the potential matrix effects, necessitating the use of various standards. In addition, *in situ* laser ablation is a relative analysis, with TIMS being the only analysis that produces absolute isotopic data.

Acknowledgments

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Appendix - Figure 1

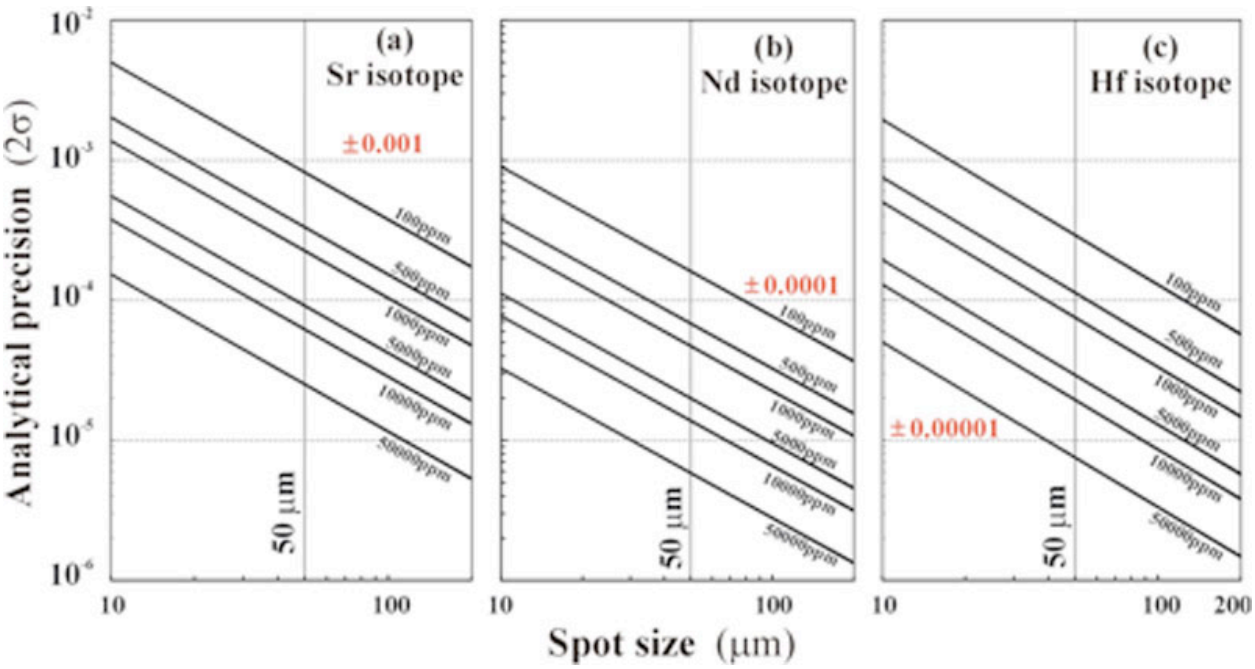

Figure 1. Relationship between element concentrations and precision of isotopic measurement for LA-ICP-MS (Neptune MC-ICP-MS in Beijing, 193nm GeoLas+ laser). The repetition rate is fixed at 8-10 Hz (after Wu et al., 2010b).

Appendix - Figure 2

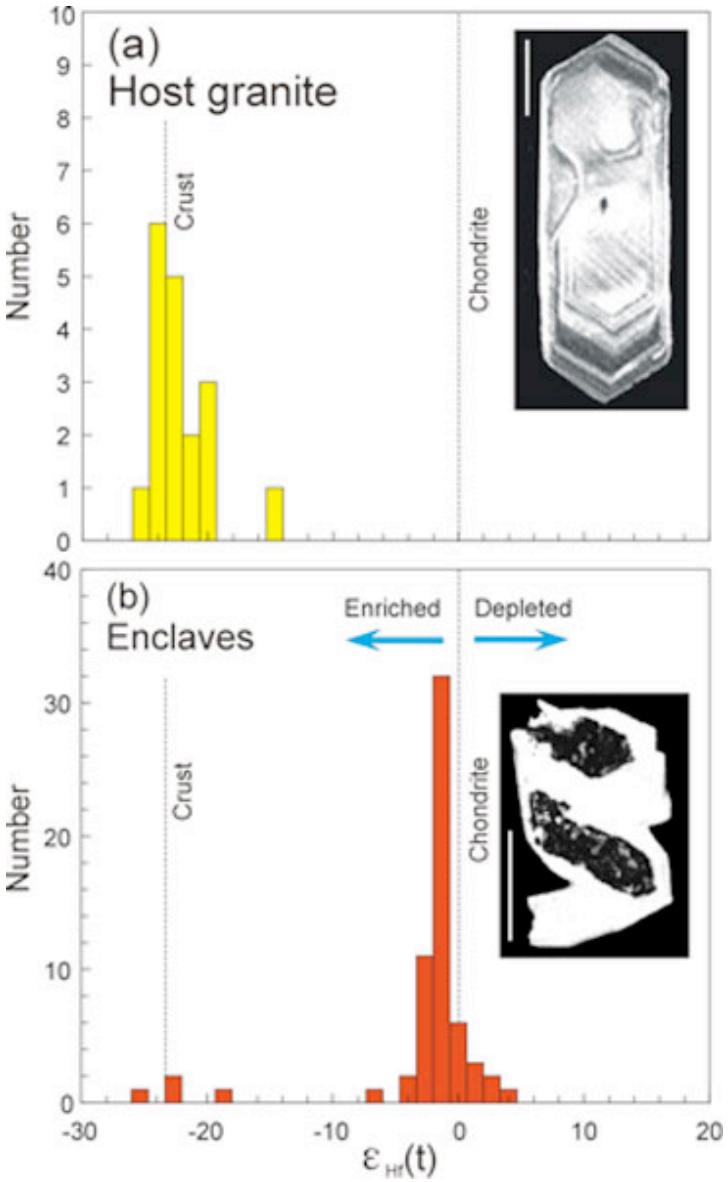

Figure 2. Histograms of $_{\varepsilon Hf}(t)$ values of zircons from (a) host granite and (b) mafic enclaves from the Gudaoling batholith in NE China. The $_{\varepsilon Hf}(t)$ values of all zircons were calculated at 120 Ma, the crystallization age of mafic enclaves and host granite. Scale bar is 50 μm (after Yang et al., 2007).

Appendix - Figure 3

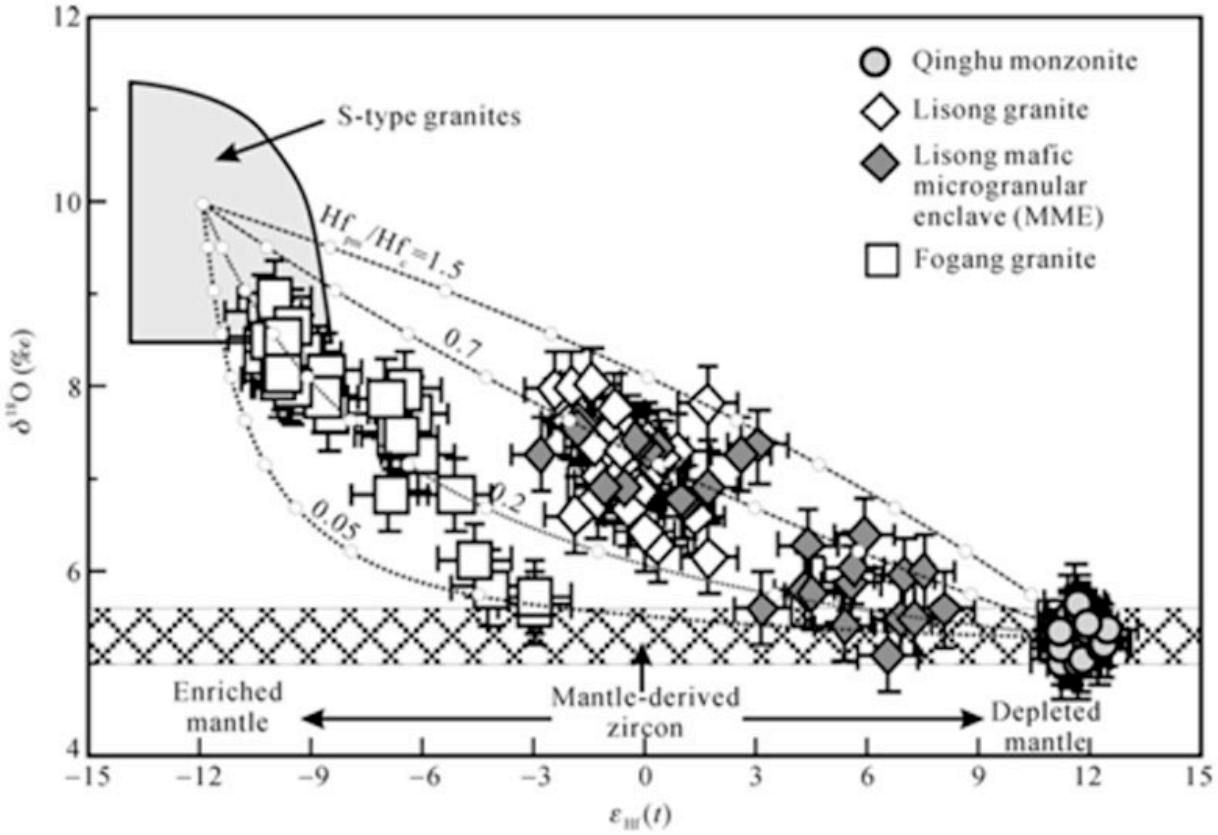

Figure 3. Hf-O isotopic variations of zircons from Qinghu, Lisong and Fogang plutons (after Li et al., 2009b). The dotted lines denote two-component mixing trends between mantle- and crustal-derived magmas.

Appendix - Figure 4

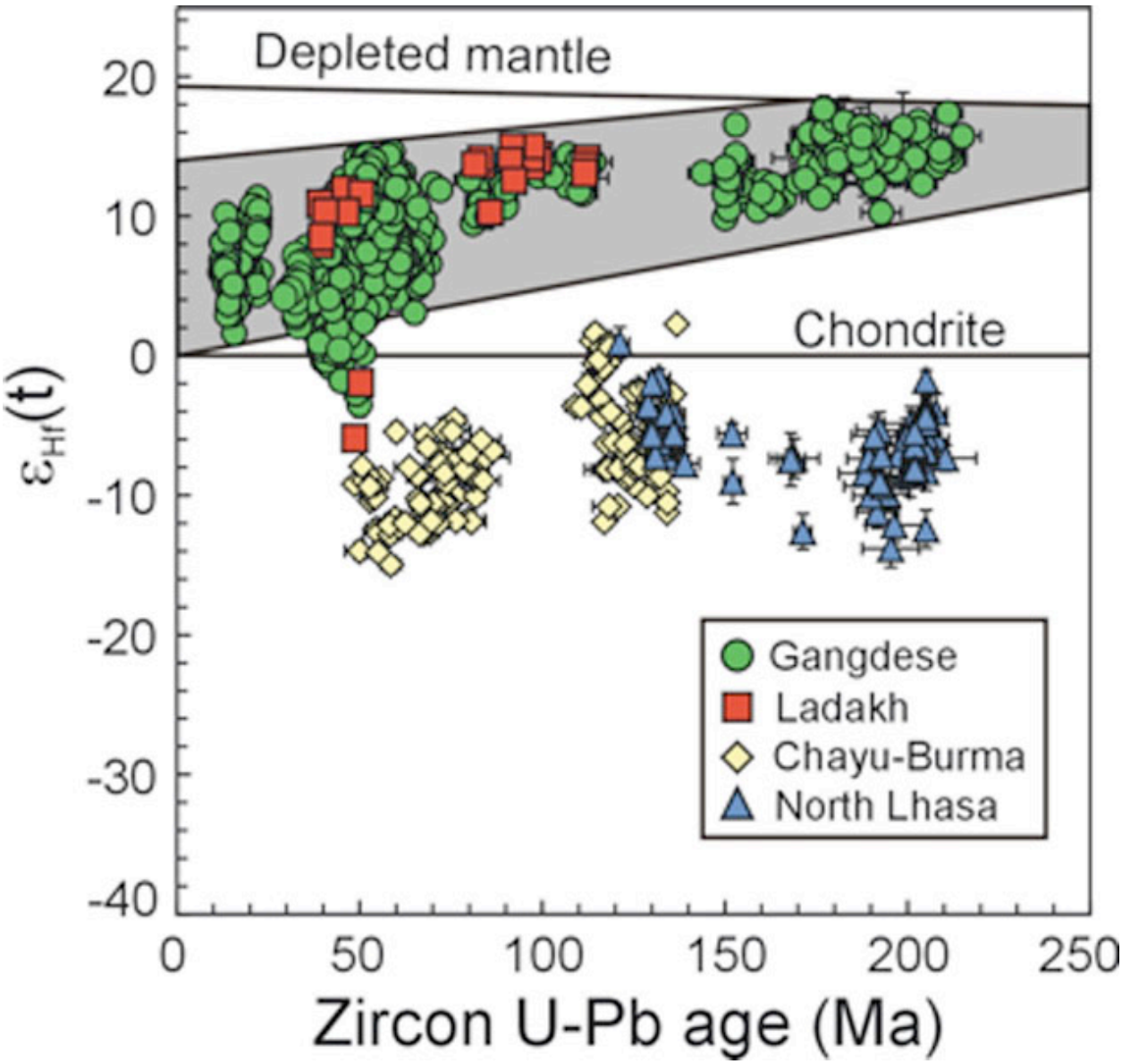

Figure 4. Comparisons of zircon Hf isotopic compositions from different batholiths in the Transhimalayan belt and the northern Lhasa terrane. Zircons from the Gangdese and Ladakh batholiths have positive $_{\varepsilon Hf}(t)$ values; whereas those from the Chayu-Burma batholith and the North Lhasa terrane have negative $_{\varepsilon Hf}(t)$ values, suggesting their derivation from the juvenile and ancient crusts, respectively (after Ji et al., 2009).

Appendix - Figure 5

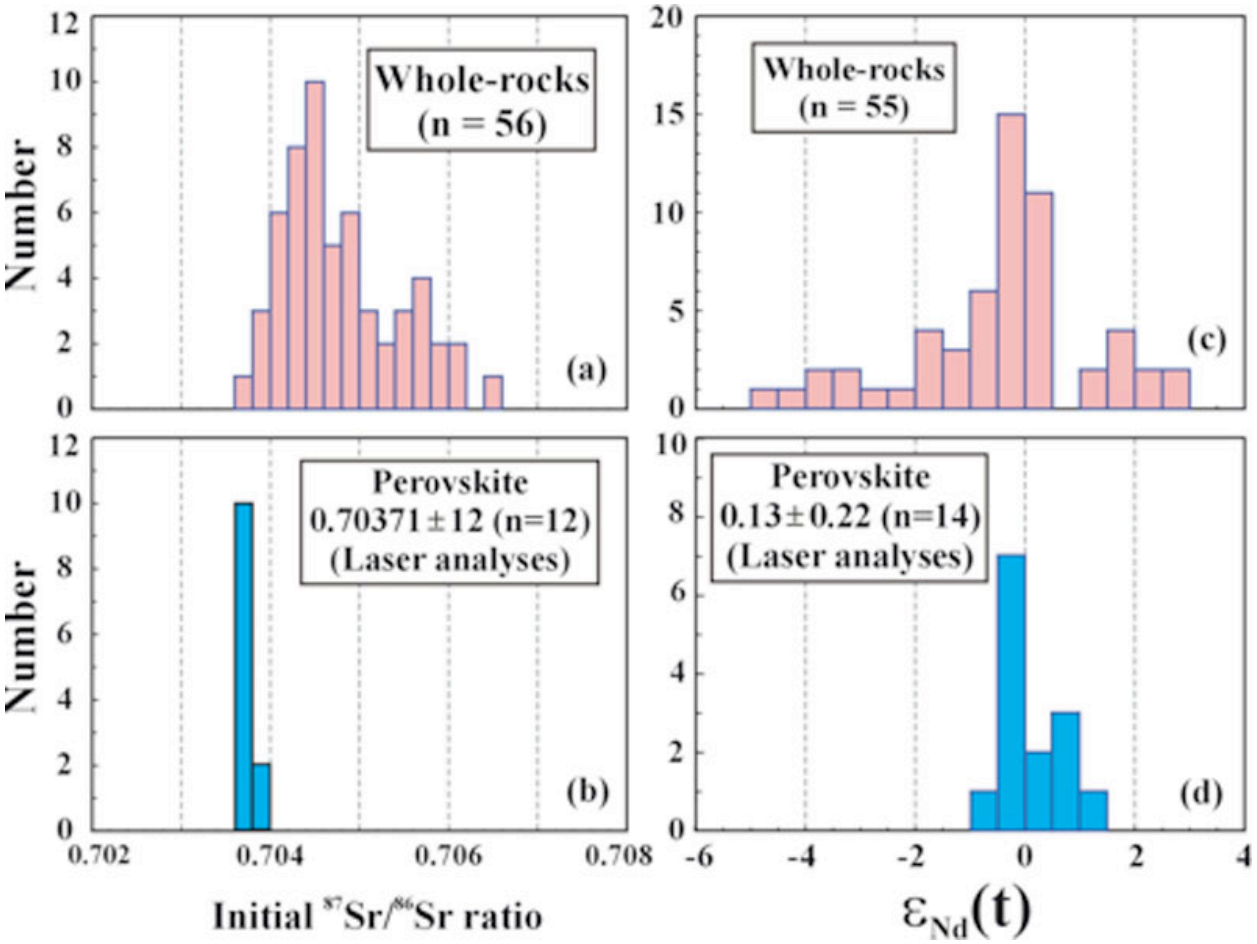

Figure 5. Histograms comparing the initial Sr-Nd isotopic compositions of perovskite with whole-rock values for the Mengyin kimberlites (after Yang et al., 2009). (a) Whole-rock Sr isotopes; (b) Perovskite Sr isotopes (laser analyses); (c) Whole-rock Nd isotopes, and (d) Perovskite Nd isotopes (laser analyses)

About the Author

Fu-Yuan Wu is a professor and the deputy director of the Institute of Geology and Geophysics, Chinese Academy of Sciences. He obtained his PhD in 1990 from Changchun College of Geology (now the College of Earth Sciences in Jilin University). He worked on granite petrology in Changchun until 2003, when he moved to the Institute of Geology and Geophysics in Beijing. His research is focused on granite petrogenesis, mantle geochemistry, geochronology, and isotopic geochemistry. He is a member of editorial board for *Chemical Geology*.