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REVIEWS

A Short Review on Lu-Hf Isotope System in Zircon: Implications for Crustal Evolution

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Abstract | Zircon has been recognized as the unaltered part of the Earth's history which preserves nearly 4 billion year record of earth's evolution. Zircon preserves igneous and metamorphic processes during its formation and remains unaffected by sedimentary processes and crustal recycling. U-Pb and Lu-Hf in zircon work as geochronometer and geochemical tracer respectively. Zircon provide valuable information about the source composition of the rocks and the intrinsic details of an unseen crust-mantle processes. The world wide data of U-Pb and Lu-Hf isotope systems in zircon reveal crustal evolution through geological history. Moreover, the U-Pb age pattern of zircons show distinct peaks attributed to preservation of crustal rocks or mountain building during supercontinent assembly. The histogram of continental crust preservation shows that nearly one-third of continental crust was formed during the Archean, almost 20% was formed during Paleoproterozoic and 14% in last 400 Ma.

1 Introduction

The Lu-Hf isotope system in zircon has become an important tool for understanding crust-mantle differentiation processes (Patchett et al., 1981; Vervoort and Blichert-Toft, 1999; Vervoort and Patchett, 1996; Blichert-Toft and Albarede, 1997; Vervoort et al., 1999; Chauvel and Blichert-Toft, 2001). Zircon is a host of a series of elements like REE and isotopes such as, U-Th-Pb, Lu-Hf and Oxygen. U-Th-Pb isotopic system is used as a geochronometer while Lu-Hf isotopic system is used as a geochemical tracer. ^{176}Lu is an unstable radionuclide that produces stable ^{176}Hf through the spontaneous emission of β^- decay. The half life of the Lu-Hf system is approximately 35.7 billion years. ^{176}Lu comprises of 2.6% of the natural lutetium and the heaviest of the REEs. Lutetium (Lu) tends to stay mainly in heavy REE rich minerals such as, garnet, zircon and xenotime. Hafnium (Hf) is a high field strength element and geochemically identical to zirconium. This has enormous importance in the field of geoscience studies.

Hf is more incompatible than Lu during melting of mantle, thus Hf becomes concentrated in the continental crust relative to Lu, resulting in non-radiogenic and radiogenic ^{176}Hf/^{177}Hf isotopic ratios in the crust and depleted mantle reservoir (Fig. 1) respectively (Patchett et al., 1981). Due to low Lu/Hf ratios (typically <0.002), zircon preserves ^{176}Hf/^{177}Hf ratios very close to the initial ^{176}Hf/^{177}Hf ratios inherited from the magma during the formation. The intra-crystalline diffusion rate of Hf in zircon is very low (Cherniak et al., 1999), allowing the preservation of isotopic variations induced by interaction between various magmas (Griffin et al., 2002) or the presence of components from different ages during zircon crystallisation (Fig. 1). Therefore, Hf isotopes in zircon is an important tool for understanding the evolution of magma generation and differentiation processes, precisely silicic magma generation and evolution of continental crust.

In this review we explore the application of Lu-Hf isotope system, mainly in zircon as a geochemical tracer with a special emphasis on the implication of generation of the crust and the growth rate of continental crust.

2 Why We Use Zircon?

Zircon is a refractory, robust mineral and acquire growth zone during crustal melting events. Zircon crystallises from high silica melt and also

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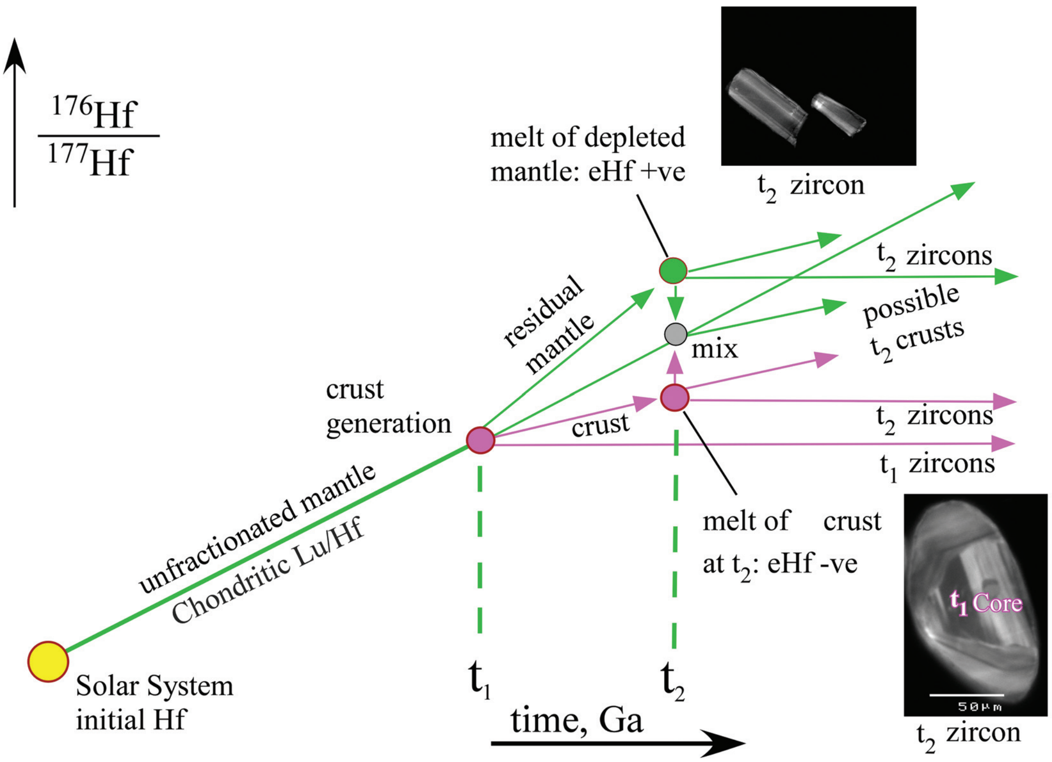

Figure 1: Schematic diagram of Hf isotopic evolution modified after Patchett et al. (1981) and Kinny and Mass (2003). Different episodes of partial melting at time t_1 and t_2 result in divergent Hf isotope evolution paths. Partial melting of mantle at time t_1 formed newly generated crust with low Lu/Hf and the residual mantle with high Lu/Hf. The zircon crystallising from the low Lu/Hf crustal melt will preserve its initial Hf ratio and diverge in composition with time during subsequent melting and crystallisation process. At time t_2 different component with different Hf isotopic ratios may contribute in the formation of new crust. Extraction of melt from purely depleted mantle source will have positive εHf value and subsequent mixing with undepleted or enriched reservoir will result in low positive, zero or negative εHf value depending on the balance of components. Inherited zircon cores at t_2 possibly have lower εHf than the newly crystallised host rock. The inset zircon images are from mafic and granitic rocks of Mt Daniel Complex, Fiordland, New-Zealand (S. Bhattacharya, unpublished thesis).

during high to medium grade of metamorphism, and is abundant in upper crustal rocks. Zircon preserves the isotopic signature through multiple episodes of sedimentary and magmatic recycling including sediment subduction (e.g. Gao et al., 2004). Zircon sustains prolonged weathering and erosion, for example, detrital zircons in clastic sediments preserve more temporal record of igneous and crustal growth episodes than the exposed basement (Wilde et al., 2001). Recent advancement in analytical techniques using plasma source mass spectrometry and laser ablation micro sampling revolutionised the field of Lu-Hf isotope analysis. The chemical and isotopic history preserved in the complex growth structure of zircon can now be successfully extracted with high precision and spatial resolution (Fig. 2). Since zircon has high Hf content (~1 wt %), Hf isotope ratios are almost not prone to any changes due to weathering, deformation and/or alteration, which generally disturb the bulk rock or other mineral isotope systems.

A large number of trace elements (~20–25) are increasingly reported in zircon by recent studies (Hoskin and Schaltegger, 2003). However, REE, P, U, Th are present in greatest abundance. Generally, the trace element composition of igneous zircon reflects the original magmatic composition and crystallisation environment from which they crystallised (Heaman et al., 1990; Maas et al., 1992; Belousova et al., 2002). Therefore, certain trace element data provide information about the protolith composition of detrital zircon and the origin of inherited zircon core, where, the original geological context is not preserved (Griffin et al., 2002). Zircons are present in both low-grade and high-grade metamorphic rocks. In low-grade metamorphic rocks it is usually inherited from the protolith and may depict signs of resorption or metamorphic overgrowth. In high-grade rocks,

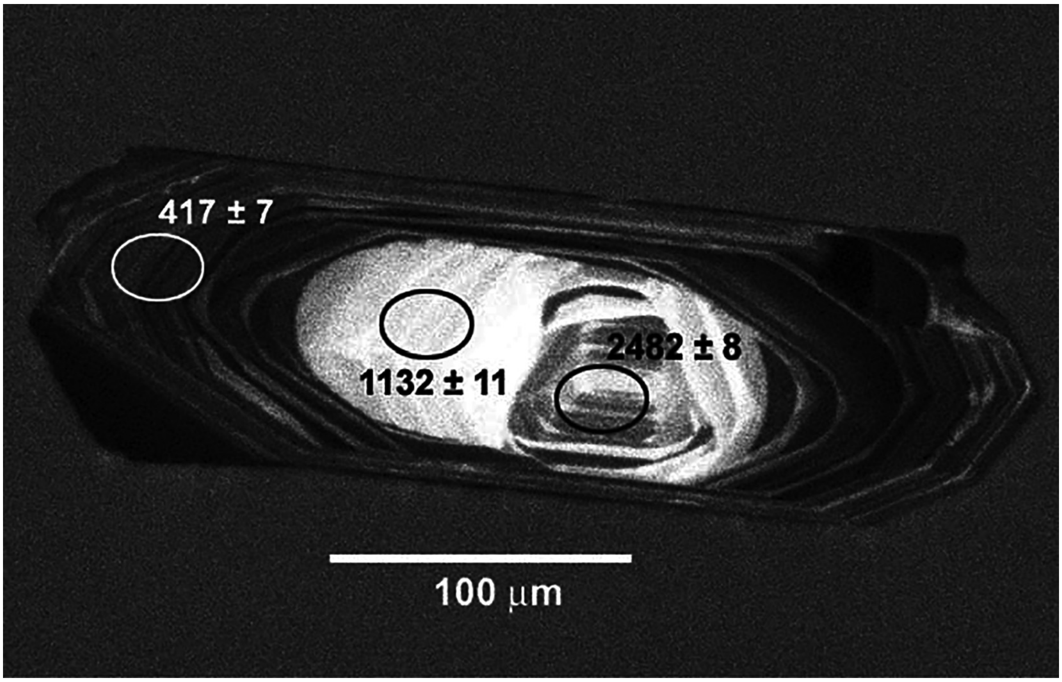

Figure 2: Zircon cathodoluminescence (CL) image is showing complicated multistage growth history from granitic rock (after Hawkesworth and Kemp, 2006). Inherited core formed at 2482 Ma followed by bright CL-core at 1132 Ma embedded by igneous zoning formed at 417 Ma.

zircon can form in various ways, such as; in solid state, by fluid precipitation, by recrystallisation of protolith zircon. Rubatto et al. (2003) shows that in case of high-grade metamorphism other minerals such as, garnet plays an important role in partitioning the HREE in zircon and garnet. Similarly, monazite affects the MREE and LREE distribution in zircon and monazite.

Hf isotopes coupled with oxygen isotopes in zircon provides an important tool to understand the mixing process precisely and can determine the contribution of different source components. The oxygen isotope ratios ($\delta^{18}O$) is generally changed by low temperature, surface processes with elevated $\delta^{18}O$ whereas, the $\delta^{18}O$ of mantle derived magma shows contrasting signature (5.7 ± 0.3‰). Several studies show that the original igneous $\delta^{18}O$ value remains unchanged in zircon even through high grade metamorphism and crustal fusion that occurs due to very slow oxygen diffusion rates through zircons (King et al., 1998; Peck et al., 2003). However, instrumental mass fractionation of $^{16}O/^{17}O$ with zircon HfO_2 content measured by ion microprobe needs great care while measuring oxygen isotopes in zircon.

3 Techniques

Several methods such as Thermal-Ionisation Mass Spectrometry (TIMS), secondary ion mass spectrometry (SIMS) and inductively coupled plasma-mass spectrometry (ICP-MC-MS) are used for measuring Hf isotopes in zircon. SIMS precision level is less than TIMS bulk zircon analyses; therefore, the method is not widely adopted. However, recent advancement techniques are mainly concentrated on in-situ zircon analyses using LA-ICP-MC-MS.

In LA-ICP-MC-MS technique, the laser is attached with the ICP-MC-MS. In this method, the material is ablated from a uniform zircon zoning by pulsed UV laser using spot size not less than 40–50 µm. Generally, helium is used as a carrier gas exciting the sample cell and combined with Ar and N_2 from the MC-MS and mixed in a Y-shaped tube before transporting into the ICPMS chamber (S. Bhattacharya, unpublished thesis). The laser repetition rate, cycles, spot size varies mainly depending on zircon. The major problem for the accurate measurement of Hf isotopes in zircon concerns the isobaric interference of ^{176}Lu and ^{176}Yb on ^{176}Hf. The isobaric interference correction of ^{176}Lu and ^{176}Yb on ^{176}Hf has been discussed by number of authors (e.g. Thirwall and Walder, 1995; Griffin et al., 2002; Woodhead et al., 2004; Hawksworth and Kemp, 2006). Different isotopes of Hf, Yb, Lu are set to be measured in faraday's cup. Easy sample preparation, quick analyses, depth profiling are the main advantages of laser ablation over other conventional methods.

4 Hf Isotopic Signature in Different Zircon Forming Environment

Magmatic Zircon: The pioneering work done by Patchett et al. (1981) indicated extreme variability of Lu-Hf values in zircon, obtained from mantle derived igneous rocks from Finland. 2.7 Ga old magmatic rocks from Archean block, southern Greenland yielded εHf values upto +14, whereas present day oceanic basalts have εHf values upto +23. Another suit of rocks from southern Finland show a less depleted εHf values close to zero (Patchett et al., 1981). This gives an excellent example of mantle heterogeneity. It was suggested that either two different mantle reservoirs coexisted together or the depleted magma is contaminated by older crustal material having an enriched Hf signature. The presence of such enriched reservoirs having highly negative εHf values of −12 and −10 in the lower crust was recognised from 1.8 Ga Natannen and Vainospää granites which intruded Archean rocks of Finland. These are interpreted as crustally derived melts. Oceanic crust return to the mantle by subduction process is another potential source of enriched Hf. Following the work of Patchett et al. (1981) several studies (e.g. Smith et al., 1987; Corfu and Stott, 1993) mainly in the contemporaneous suit of intrusions suggested that the zircon with low positive εHf values might indicate the crustal contamination and/or the presence of zircon xenocrysts. A wide variation in εHf from a single volcanic/plutonic suit may suggest an inherent heterogeneity in the magma source(s) (Smith et al., 1987).

Detrital Zircon: Being robust in nature, the zircon is not prone to weathering, transportation and sedimentation processes which results in accumulation of detrital zircon in clastic sedimentary sequences along the continental margin. Therefore, unaltered non-metamict zircons provide an important information about sedimentary provenance which is recorded in U-Pb and Hf isotopic composition. Therefore, both chronological and geochemical information can be used to delineate the likely sources (Fedo et al., 2003). Zircon being robust leads to fractionation of Hf from Lu as Hf is carried away by zircon during continental erosion and accumulates in the continental shelf (sands and turbidite deposits) deposits. On the other hand, deep marine sediments (such as, marine shale and clay) acquire a higher proportion of REE, i.e. high in Lu/Hf ratio. This goes up to 2.5 times the chondritic values for deep marine red clays and Mn nodules (Patchett et al., 1984). Stevenson and Patchett (1990) studied zircon from low grade quartz rich meta-sediments from the Canadian Shield, North Atlantic, Wyoming and Kaapvaal craton to understand the continental growth in the Archean, based on the concept that, if the large volume of continental crust existed in the early Archean, there should be considerable fractions of early Archean zircon which would be preserved in the younger sedimentary sequences. They concluded that before 3.0 Ga only small volume of continental crust had existed due the lack of older age signatures from zircon. Further, they suggested that major continent formation happened during Neoarchean and the erosion of large volume of continental crust resulted in extensive inheritance of Neoarchean zircon in the Paleoproterozoic sequences.

Bodet and Schaärer (2000) studied detrital zircon and baddeleyite grains from four major rivers draining present-day Indochina in order to understand the crustal formation of the sediment-covered Southeast Asian continent. The two different age groups, Proterozoic and ≤0.5 Ga were determined have different εHf range. Proterozoic age group >2.0 Ga have positive εHf values whereas 2.0–0.8 ages have variable εHf +8 to −8 mostly they derived from Phanerozoic cover sequence through a series of sedimentary cycles. On the other hand, zircons ≤0.5 Ga directly matched from the known orogenic events like Mesozoic Indosinian and Cenozoic Himalayan events and were considered to be derived from the plutons during those events.

Metamorphic Zircon: The presence of zircon overgrowth is problematic while studying the Hf isotopic composition of original magmatic or detrital zircons in ancient metamorphic rocks. Metamorphic zircons in high grade rocks have either similar (Hoskin and Black, 2000; Rubatto, 2002) or depleted (Hanchar and Rudnick, 1995) Hf and HREE abundance relative to igneous cores of the zircon. Therefore, in case of metamorphic zircon, Lu/Hf ratio is comparable or lower than typical igneous zircon and initial $^{176}Hf/^{177}Hf$ ratio should remain unchanged, thus, reliable in metamorphic zircon. In general, the ratio is highly variable depending on the source(s) of the Hf and the compositions of pre-existing and co-existing phases. In case of similar initial $^{176}Hf/^{177}Hf$ composition of zircon core and rim possibly indicate that they have formed in a closed system processes, either by solid state crystallisation of core or by dissolution of core (Fig. 3) during crustal melting event (Flowerdew et al., 2006; S. Bhattacharya, unplublished thesis). In case of slight difference in initial $^{176}Hf/^{177}Hf$ composition (not purely identical composition but having similar range) between the core and rim of zircon indicates the Hf isotopic heterogeneity in

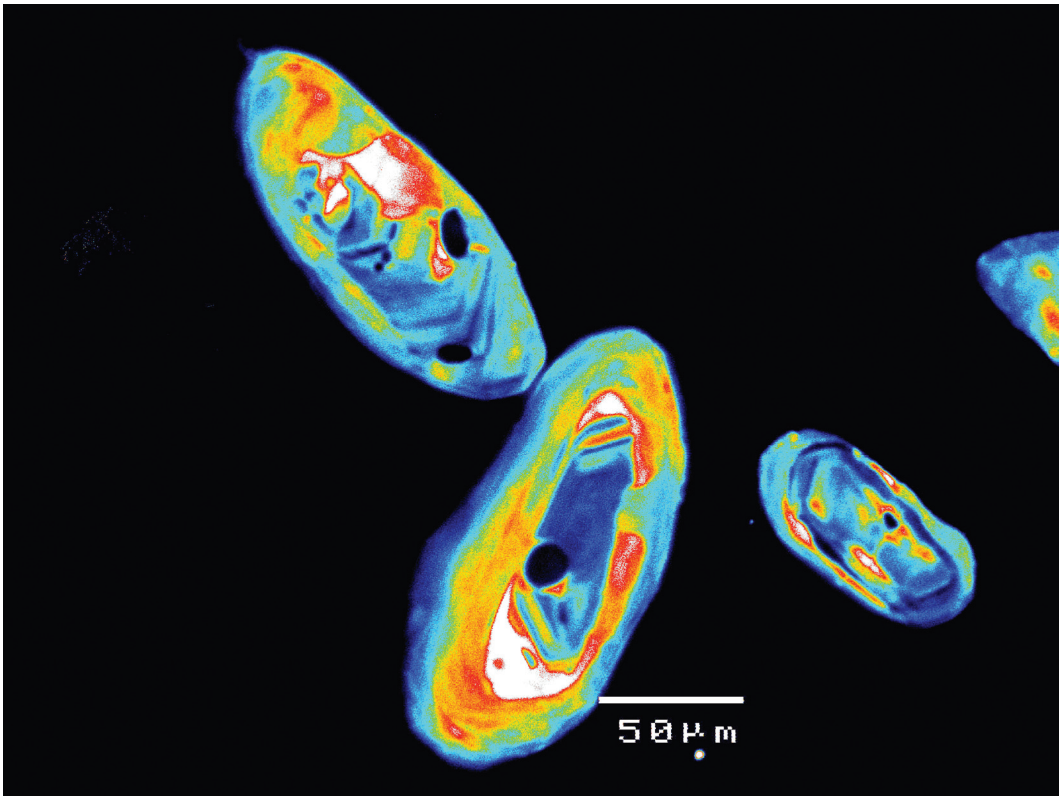

Figure 3: Zircon (at the centre) is showing igneous core and metamorphic rim from granitic rock of Mt Daniel Complex, Fiordland, New-Zealand (S. Bhattacharya, unpublished thesis).

the melt. This can be induced from the isotopic heterogeneity of the cores during their partial dissolution. If the Hf budget of the melt is mainly controlled by the dissolved cores and if mixing and homogenization does not occur, then Hf isotopic heterogeneity will be present in the rims, which is forming from this melt in a closed system process (Flowerdew et al., 2006). The presence of limited dissolution structures in zircon cores and the wide range of initial ^{176}Hf/^{177}Hf composition of the rims may suggest the formation of the rims in an open system process (Flowerdew et al., 2006). According to Gerdes and Zeh (2009), once initial ^{176}Hf/^{177}Hf ratio is incorporated into the zircon lattice during growth, it remains almost unaffected during later alteration processes which result in Pb-loss. Zircon overgrowth incorporates additional radiogenic ^{176}Hf formed by the decay of ^{176}Lu in the rock's matrix between successive zircon growth events. Therefore, zircon overgrowths generally have higher initial ^{176}Hf/^{177}Hf than previously grown domains.

5 Implication to Continental Crust Generation and Crustal Growth Rate

The continental crust constitutes 70% of the total volume of the Earth's crust. Keith O'Nions represented pioneering work to understand the age of the continents and the time scale of their evolution (O'Nions et al., 1983; O'Nions, 1984), which in turn helps to understand the formation of the continents and evolution of the Earth (Jacobsen and Wasserburg, 1979; O'Nions et al., 1979) by using Nd isotopes. However, the balance between the distributions of long lived radiogenic isotopic systems (particularly Sm-Nd) and the presence of actual volume of continental crust at any particular time remain ambiguous. The rate of differentiated upper continental crust formation relative to the new crustal material generated also remains unresolved. The challenge to understand the age and growth history of the continental crustal formation lies with the better understanding of the timing of major crust forming events. Basically there were two difficulties: i) the crust formation event was recorded upto 4.4–4.6 Ga (Wilde et al., 2001) whereas the record of early continent formation is fragmentary. This is especially problematic while dealing with the Archean cratons which covers only 7.5% of the earth surfaces. This cannot asses the real major pulses of crust forming event at that time from the surface rocks. ii) Assessing the balance between juvenile and recycled material at any point of time of crust formation has became highly ambiguous while interpreting with the whole rock data.

Granitic rocks are abundant in major crustal components throughout the earth's history. They incorporate multiple end member components including recycled crust (Gray 1984; Keay et al., 1987; Collins 1998). Therefore, a systematic mineralogical and chemical record of different components in granitic magmas and their sources is required to understand the crustal evolution process. With the development of in-situ analyses of U-Pb, Lu-Hf and oxygen isotopes in zircon revolutionised the models and concept on crustal evolution and petrogenesis of granite (Hawkesworth and Kemp, 2006) as being one of the major crustal components. Detrital zircons are good in recognising the hidden earth's history, providing the most representative samples in eroded source terranes. Data compilation by Belousova et al. (2010) shows U-Pb and Hf isotopic data of 13,800 zircons largely derived from detrital sources around the world to understand the crustal evolution process in geological history. Fig. 4 shows the broad range of ages from various continents worldwide. Other than Hadean population (Australia, Jack Hill quartzite) most continents are represented by wide range of ages and zircon with low εHf values are not restricted to any particular continent (Fig. 5). The negative εHf values are wide spread indicating the older crustal recycling which suggest a universal signature of producing continental crust. They suggested that about 60–70% of existing continental crust separated from the mantle before 2.5 Ga which is also mentioned by Condie and Aster, 2010 (Fig. 6). Therefore, at the end of Archean, crustal recycling was a more dominating process over the addition of net juvenile material to the continental crust formation. The presence of large volume of continental crust before the end of Archean and the thickness of felsic and mafic crust mainly rely on thermal models for the progressively cooling Earth (Hawkesworth et al., 2010 and references therein). Belousova et al. (2010) have quantitatively estimated the addition of net juvenile material over earth's history. The model suggested that the addition of juvenile material through time decreases stepwise and periodicity in the formation of new crust is less than it was supposed to be, in contrast to the peaks of magmatic ages. The estimated decrease of juvenile crustal material is as follows: 70% in the 4.0–2.2 Ga time interval, about 50% in the 1.8–0.6 Ga and possibly less than 50% after 0.6 Ga (Belousova et al., 2010). They have suggested that these changes may be linked to the supercontinents formation. On the other hand, the episodes of crust generation might be linked with the magmatism associated with the deep-seated mantle plumes (Hawkesworth et al., 2010 and references therein). The estimation of the

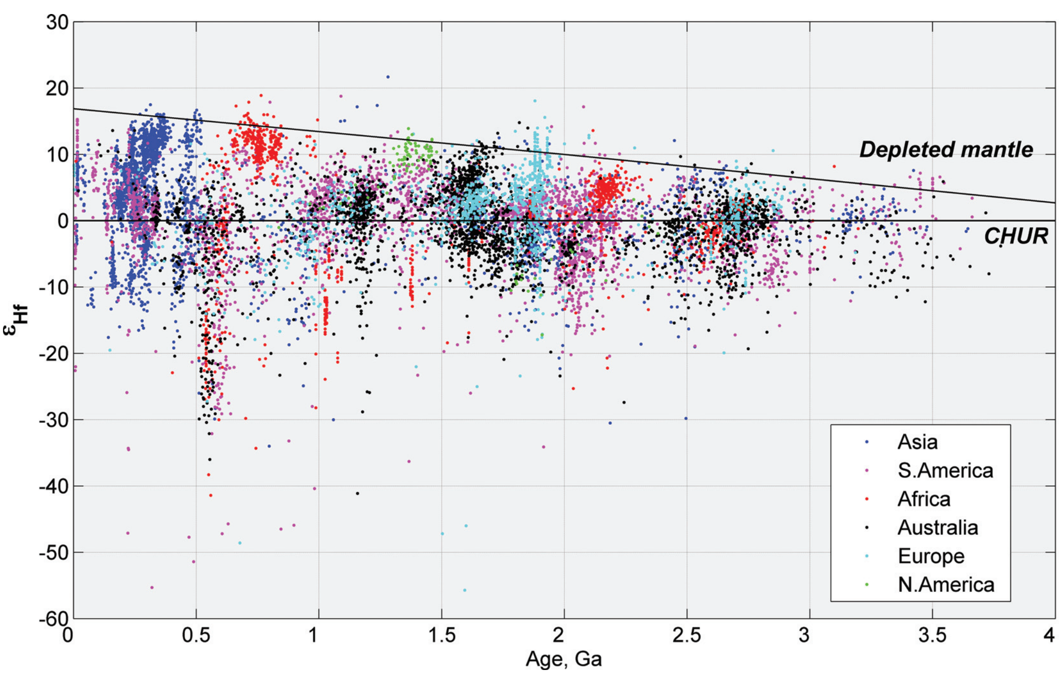

Figure 4: Worldwide data for age vs. εHf plot from zircons showing continental growth through geological history with accumulated data indicating supercontinent assembly. Data adopted and modified after Belousova et al., 2010).

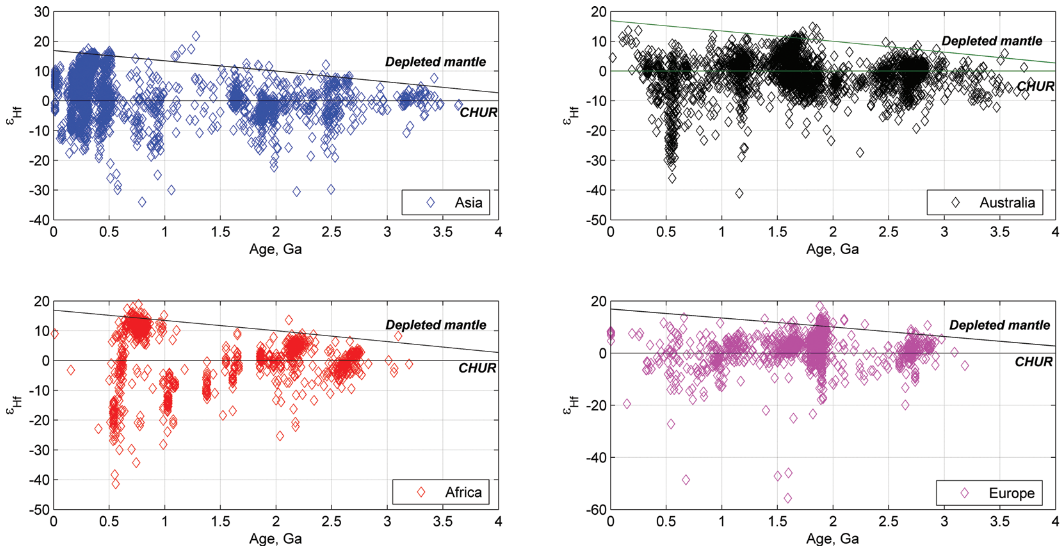

Figure 5: Plots of age vs. εHf from zircons for the continents- Asia, Africa, Australia, and Europe showing wide range of distribution of εHf values with ages. Data adopted and modified after Belousova et al. 2010.

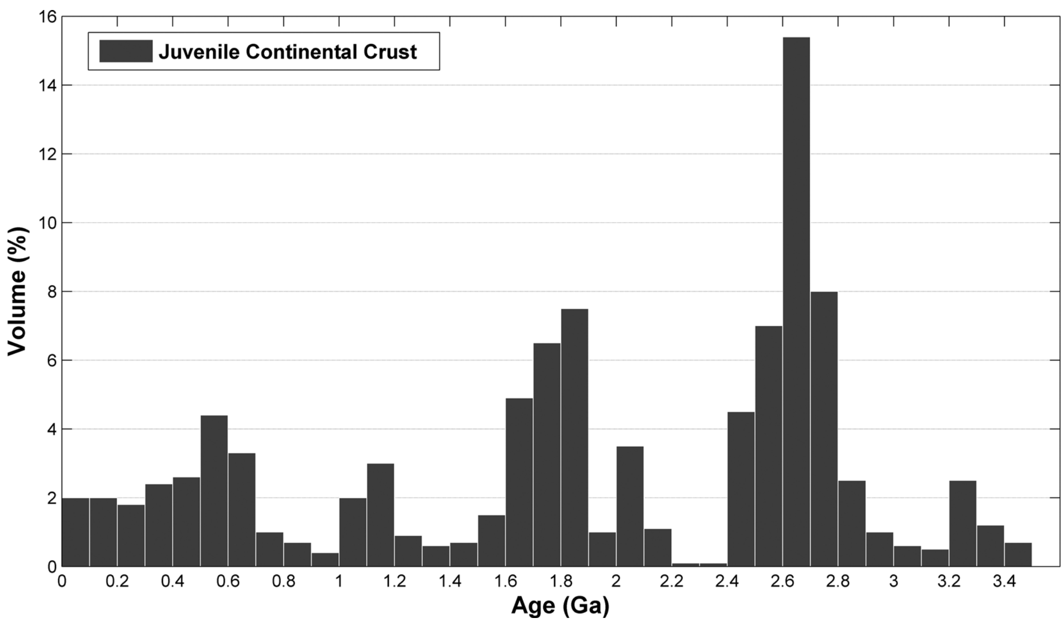

Figure 6: Distribution of U/Pb zircon ages from juvenile continental crust in 50-Ma bins based on a total volume of continental crust (modified after Condie, 1998; 2010).

rates of crust generation verses destruction along modern subduction zone is quite similar (Fig. 7) (Hawkesworth et al., 2010). That in turn implies that the present volume of continental crust was established 2–3 Ga ago.

6 Concluding Remarks

The Lu-Hf system in zircon is an important geochemical tracer and a key tool to understand the silicate magma generation and differentiation processes. A combined study of both U-Pb and Lu-Hf systematic is a robust tool to understand the petrogenetic processes and crustal growth history. Precise and accurate U-Pb age data (concordant results) is an important parameter to estimate Lu-Hf isotopic system in zircon in order to understand the petrogenetic record preserved in initial Hf ratios. Nowadays, in-situ analytical techniques, like CL and BSE imaging coupled with single grain ablation methods improved the

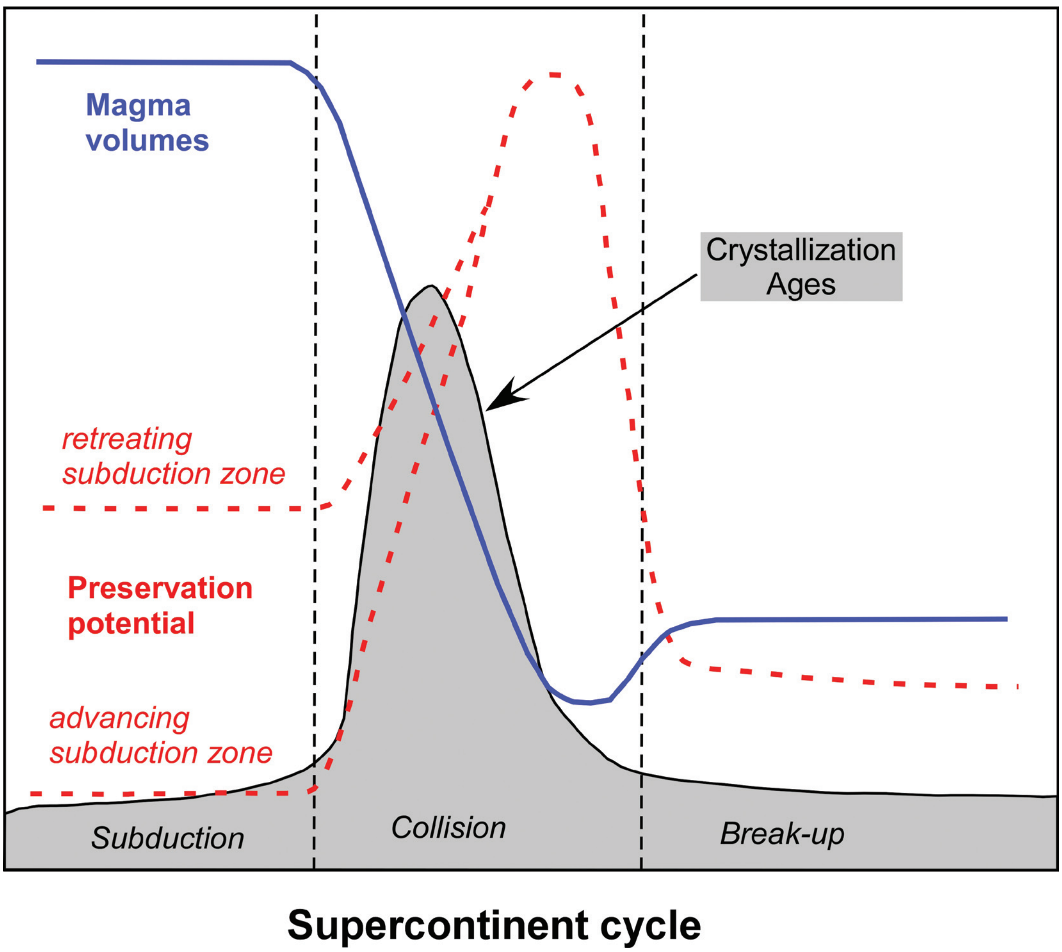

Figure 7: The continuous line shows the amount of magma generation the dashed line shows the preservation potential which vary with subduction, collision and breakup of a supercontinent. The likely preservation for crystallization ages of zircons is better for late-stage collisional phenomenon when supercontinents come together than for subduction or extension associated magmatism (after Hawkesworth et al., 2010).

quality of data for complexly zoned zircon having multiple ages. The basic advantage of using Hf isotopes in zircon is to understand crust-mantle differentiation process through time which provides a window to Earth's early differentiation history.

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