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Hf isotopic evidence for Paleoarchean (> 3.5 Ga) crustal components in the Korean Peninsula

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ABSTRACT: We report *in-situ* Hf isotopic data on five inherited zircon components, dated at > 3.0 Ga from previous Sensitive High Resolution Ion Microprobe (SHRIMP) U-Pb analyses. These data are useful for constraining the timing and nature of very pristine crustal materials in South Korea. $^{176}Hf/^{177}Hf$ isotope ratios, measured using a laser ablation Multi-collector Induced Coupled Plasma Mass Spectrometer (MC-ICP MS), range from 0.28044 to 0.28075, corresponding to the present-day $\varepsilon_{Hf}(0)$ of −70 to −81. They yield two-stage Hf model ages of ca. 4.1 to 3.5 Ga at the time of zircon crystallization from a magma, depending on tenable crustal evolution models. Our results provide the first Hf isotopic evidence for existence of Paleoarchean (>3.5 Ga) crustal components in the Korean Peninsula.

Key words: Hf isotope, zircon, Archean, continental crust, Korean Peninsula

1. INTRODUCTION

The Korean Peninsula represents a tectonic collage consisting of three Precambrian blocks: from north to south, Nangrim (NM), Gyeonggi (GM) and Yeongnam (YM) massifs (Fig. 1). Traditionally, much of crustal materials that constitute these massifs have been considered to be Archean in age (Lee, 1987). This consideration is in general endorsed by Nd isotopic data indicative of prevalent crustal growth event during the Neoarchean (ca. 2.5–2.9 Ga) (Lan et al., 1995; Cheong et al., 2000; Lee et al., 2003). A few Nd isotopic model ages ranging up to ca. 3.8 Ga even hint a possible existence of Paleoarchean rocks (e.g., Lan et al., 1995), which is further substantiated by recent finding of inherited zircon component dated at ca. 3.64 Ga in a Mesozoic sandstone from the GM (Jeon et al., 2007). The primitive nature of the Archean crustal materials, however, has been almost completely erased by subsequent tectono-magmatic and metamorphic events largely during the Paleoproterozoic (Lee et al., 2003; Sagong et al., 2003). It is thus difficult to constrain the timing and nature of pristine crustal materials of the Korean Peninsula.

Because of its high U/Pb ratio and its resistance to later magmatic, metamorphic and alteration processes, zircon is widely used to date the magmatic emplacement of parent rocks. The zircon dating is therefore very useful for identifying ancient crustal remnants but does not provide conclusive information on whether the crust is juvenile or reworked. This additional information can be provided by Hf isotope composition of zircon, however, because low Lu/Hf ratio and high Hf concentration allow zircon to be used as a proxy for initial Hf isotope composition of their host magma. Hence, a combined U-Pb and Hf isotopic data on zircons are useful for not only identifying ancient crustal remnants but also characterizing the nature (e.g. juvenile or reworked) of zircon-bearing host magmas. In this study we report Hf isotopic data on five spots of inherited zircon components of >3.0 Ga, based on previous SHRIMP U-Pb analyses, in order to constrain the timing and nature of very pristine crustal materials in southern parts of the Korean Peninsula.

2. SAMPLE DESCRIPTION AND SHRIMP U-Pb ZIRCON AGES

Five spots of zircon grains, dated at >3.0 Ga from previous SHRIMP U-Pb analyses, were selected for *in-situ* Hf isotope analysis (Fig. 2). These zircons are from: (1) biotite gneiss in northeastern GM (sample GGR8R #29) (Cho and Kim, 2003); (2) granitic gneiss in southwestern YM (sample SC50 #11) (this study); and (3) Mesozoic sandstone (from the Nampo Group) in western flank of the GM (samples DC02 #54, DC02 #55 and HS19-4 #74) (Jeon et al., 2007) (Fig. 1). Further information on the petrography and SHRIMP analyses of zircon grains are available elsewhere (Cho and Kim, 2003; Jeon et al., 2007). The GGR8R and SC50 are crystalline gneisses produced by Paleoproterozoic (ca. 1.9–

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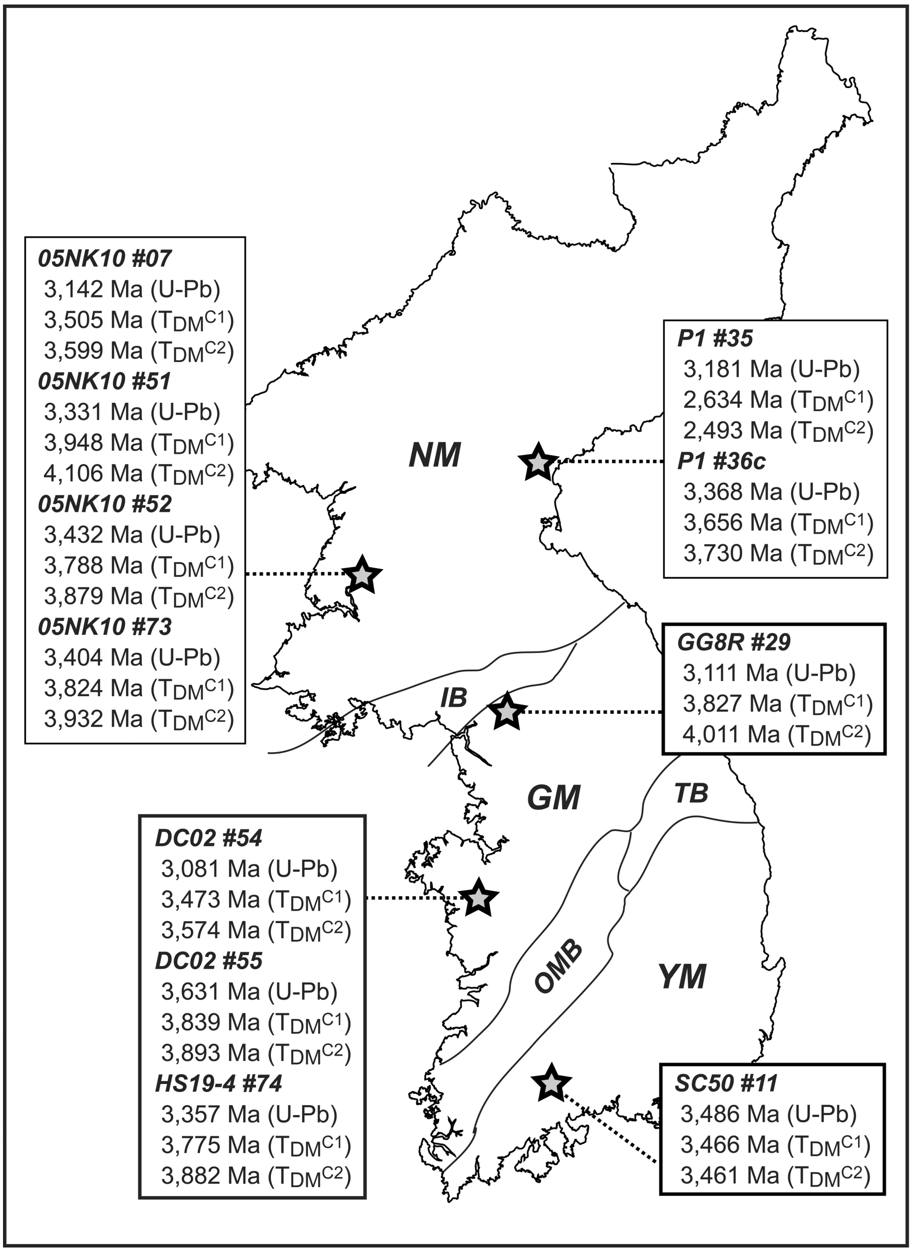

Fig. 1. A map showing the localities of rock samples containing >3.0 Ga zircon components (from Cho and Kim, 2003; Jeon et al., 2007; Wu et al., 2007; this study). The U-Pb, $T_{DM}C1$ and $T_{DM}C2$ ages in the box correspond to the SHRIMP $^{207}Pb/^{206}Pb$ age and two-stage Hf model ages, using average felsic crust (C1) (Lu/Hf = 0.009; Amelin et al., 1999) and average continental crust (C2) (Lu/Hf = 0.015; Griffin et al., 2002), respectively, for the zircon's host reservoir. Abbreviations: NM, Nangrim massif; IB, Imjingang belt; GM, Gyeonggi massif; OB, Ogcheon belt; and YM, Yeongnam massif.

1.8 Ga) high-grade metamorphism and crustal anatexis of sedimentary protoliths. These gneisses contain a variety of detrital zircon components inherited from ca. 3.5–2.1 Ga igneous and metamorphic events (Cho and Kim, 2003; Cho, *unpublished*). The two spots of samples GGR8R #29 and SC50 #11 were obtained from the inherited core domains yielding common Pb-corrected $^{207}Pb/^{206}Pb$ ages of 3,111 Ma and 3,486 Ma, respectively (Cho and Kim, 2003; Cho, *unpublished*) (Table 1). Their high Th/U ratios (0.84 and 1.08) together with oscillatory zoning patterns are indicative of magmatic origin. All the spots of samples DC02 #54, DC02 #55 and HS19-4 #74 were obtained from the inherited core domains of detrital zircons giving the $^{207}Pb/^{206}Pb$ ages of 3,638 Ma to 2,966 Ma (Jeon et al., 2007) (Table 1). All the inherited cores show complex internal structures consisting of both blurred- and sharply-zoned domains (Fig. 2), the former of which may represent either post-magmatic alteration (metamictization or recrystallization and/or homogenization) or later metamorphic overgrowth. Despite of the textural evidence for partial disturbance of primary zoning, however, both domains yield nearly identical U-Pb ages and Th/U ratios in samples DC02 #54 and DC02 #55 (Table 1; Fig. 2), suggesting that they belong to single age domain. For texturally ambiguous zircons a significant chemical characteristics are Th/U ratios for discriminating magmatic zircons from metamorphic ones. The Th/U ratios are generally higher than 0.1–0.2 for the former, but are much lower than 0.1 for the latter (Rubatto and

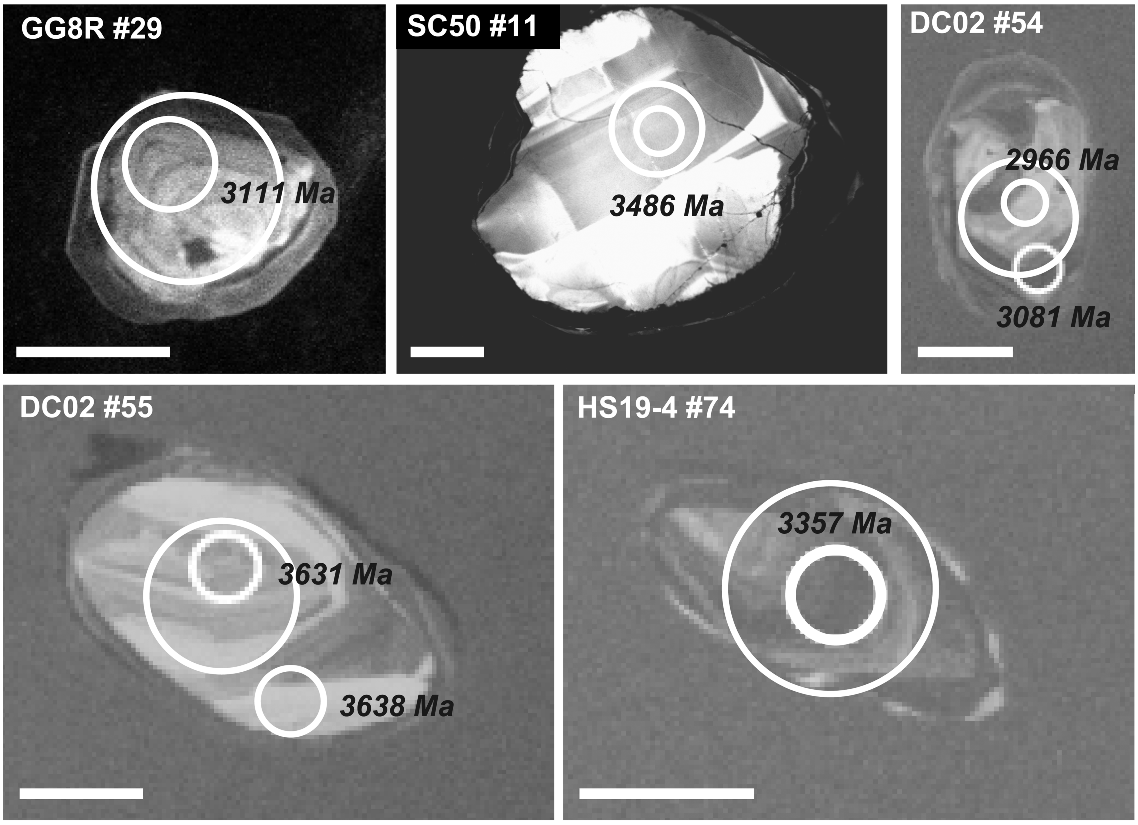

Fig. 2. Cathodoluminescence images of the >3.0 Ga zircon grains from the Gyeonggi and Yeongnam massifs. Each spot of the SHRIMP analysis (ca. 30 μm in diameter) is shown together with the common Pb-corrected $^{207}Pb/^{206}Pb$ age. These SHRIMP spots are encompassed by bigger circles (ca. 60 μm in diameter) denoting the Hf analytic spots. Scale bar represents 50 μm in length.

Table 1. Lu-Hf isotope data for >3.0 Ga zircons from the Korean Peninsula

Grain Spot	Age (Ma)[a]	Th/U	discor (%)	$^{176}Yb/^{177}Hf$	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$ (± 2σ)	$^{176}Hf/^{177}Hf_i^b$	$\varepsilon_{Hf}(0)$	$\varepsilon_{Hf}(t)$	T_{DM} (Ma)	$f_{Lu/Hf}$	T_{DM}^{C1} (Ma)[c]	T_{DM}^{C2} (Ma)	T_{DM}^{C3} (Ma)
Gyeonggi and Yeongnam massifs (This study)														
GG8R#29	3,111±25	0.84	7	0.014590	0.00044	0.280564±28	0.280538	-78.1	-8.9	3,666	-0.99	3,827	4,011	4,396
SC50#11	3,486±14	1.08	2	0.025216	0.00090	0.280742±20	0.280682	-71.8	5.0	3,470	-0.97	3,466	3,461	3,450
DC02#54	3,081±6	0.33	2	0.028149	0.00081	0.280798±21	0.280751	-69.8	-2.1	3,388	-0.98	3,473	3,574	3,784
	2,966±20	0.33	-3											
DC02#55	3,631±10	0.33	0	0.022428	0.00062	0.280481±19	0.280437	-81.0	-0.3	3,793	-0.98	3,839	3,893	4,005
	3,638±40	0.28	-2											
HS19-4#74	3,357±8	0.57	25	0.027464	0.00076	0.280573±12	0.280524	-77.8	-3.7	3,683	-0.98	3,775	3,882	4,106
Nangrim massif (Wu et al., 2007)														
05NK10#07	3,142±14	-	22.1	0.034832	0.00105	0.280784±33	0.280721	-70.3	-1.7	3,428	-0.97	3,505	3,599	3,794
05NK10#51	3,331±5	-	5.3	0.040345	0.00115	0.280501±22	0.280427	-80.3	-7.7	3,818	-0.97	3,948	4,106	4,437
05NK10#52	3,432±5	-	0.8	0.031778	0.00089	0.280562±26	0.280503	-78.2	-2.6	3,711	-0.97	3,788	3,879	4,070
05NK10#73	3,404±6	-	4.5	0.050982	0.00153	0.280587±26	0.280487	-77.3	-3.9	3,739	-0.95	3,824	3,932	4,158
P1#35	3,181±7	-	3.3	0.009481	0.00029	0.281238±25	0.281220	-54.2	17.0	2,759	-0.99	2,634	2,493	2,199
P1#36c	3,368±4	-	1.5	0.007733	0.00022	0.280606±55	0.280592	-76.6	-1.0	3,590	-0.99	3,656	3,730	3,885

[a]Age denotes the domain $^{207}Pb/^{206}Pb$ age previously dated by SHRIMP (Cho and Kim, 2003; Jeon et al., 2007) and LA-ICPMS (Wu et al., 2007).
[b]Initial Hf isotope ratios were calculated at U-Pb ages derived from either SHRIMP and LA-ICPMS.
[c]Two-stage model ages were calculated using $^{176}Lu/^{177}Hf$ of 0.009 for average felsic crust (C1, Amelin et al., 1999), of 0.015 for average continental crust (C2, Griffin et al., 2002), and of 0.022 for average mafic crust (C3, Vervoort and Patchett, 1996), respectively.
Used parameters: $\lambda=1.865\times10^{-11}$ yr^{-1}; $^{176}Lu/^{177}Hf=0.0332$ and $^{176}Hf/^{177}Hf=0.282772$ for chondritic reservoir (Blichert-Toft and Albarede, 1997); $^{176}Lu/^{177}Hf=0.0384$ and $^{176}Hf/^{177}Hf=0.28325$ for depleted mantle (Nowell et al., 1998; Griffin et al., 2000).

Gebauer, 2000; Rubatto, 2002). Because of their high Th/U ratios (0.28 to 0.57) (Table 1), therefore, all the inherited core domains of the detrital zircons are considered as magmatic origin. The $^{207}Pb/^{206}Pb$ age of 3,357 Ma for HS19-4 #74 shows a significant discordance (25%) that could be attributed to a recent Pb loss.

3. ANALYTICAL METHODS AND RESULTS

3.1. Analytical Methods

The *in situ* Hf analytical procedures of zircon have been described in detail elsewhere (Xu et al., 2002; Wu et al., 2006) and only a brief outline is given here. All the measurements were carried out using a Golas-193 laser ablation microprobe, attached to a Neptune multi-collector ICP MS, at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing. The laser system (MicroLas, Göttingen, Germany) is equipped with a 193 nm UV ArF excimer laser and a homogenizing, imaging optical system. In this study, 63 μm spot size was applied during the ablation with laser repetition rate of 10 Hz. All the laser spots were positioned to encompass the analytical spots derived from previous SHRIMP dating, which cause no practical effect on measured Hf isotopic ratios because of large areal difference between laser ablation and ion probing. During the analysis, isobaric interference corrections of ^{176}Lu on ^{176}Hf were not taken into account owing to the extremely low $^{176}Lu/^{177}Hf$ in zircon (normally <0.002), although $^{175}Lu/^{176}Lu$= 0.02655 is used for elemental fractionation correction. The isobaric interference of ^{176}Yb on ^{176}Hf was, however, corrected using the mean fractionation index proposed by Iizuka and Hirata (2005). The applied value of $^{176}Yb/^{172}Yb$ is 0.5886 (Chu et al., 2002; Vervoort et al., 2004). During the analysis, $^{176}Hf/^{177}Hf$ ratio of 0.282300±6 (2σ, n=37) and of 0.282956±12 (2σ, n=15) was obtained for standard zircons 91500 and FM0411, respectively. These values are identical with those obtained by the solution method (Woodhead et al., 2004; Wu et al., 2006). All the Lu-Hf isotope results are reported with the 2σ error (Table 1).

In this study we used the decay constant for ^{176}Lu of 1.865×10^{-11} yr^{-1} (Scherer et al., 2001) and the chondritic ratios of $^{175}Hf/^{177}Hf$ (=0.282772) and $^{176}Lu/^{177}Hf$ (=0.0332) (Blichert-Toft and Albarede, 1997). The results are denoted as the conventional $\varepsilon_{Hf}(t)$ values representing the 0.1‰ difference between the sample and the chondritic uniform reservoir (CHUR) at the time of magma crystallization. Single-stage model ages (T_{DM}) were calculated using the measured $^{176}Lu/^{177}Hf$ ratios, referred to a model depleted mantle (DM) with a present-day $^{176}Hf/^{177}Hf$ ratio of 0.28325 (Nowell et al., 1998) and $^{176}Lu/^{177}Hf$ ratio of 0.0384 (Griffin et al., 2000). Two-stage model ages ($T_{DM}{}^{C}$) were calculated for the source rock of magma by assuming mean $^{176}Lu/^{177}Hf$ values of 0.015 for the average continental crust (Griffin et al., 2002), 0.009 for average felsic crust (Amelin et al., 1999), and 0.022 for the mafic crust (Vervoort and Patchett, 1996).

3.2. Results

Lu-Hf isotope data for five spots of >3.0 Ga zircon components of the GM and YM (this study) as well as the NM (from Wu et al., 2007) are given in Table 1. Because the spot diameter of the laser ablation analysis is about two times bigger than that of the SHRIMP analysis, Hf isotopic data may partly incorporate younger age domains especially for zircons with small domain of inheritance. Such an incorporation may cause an increase in measured $^{176}Hf/^{177}Hf$ ratios, resulting in the underestimation of the Hf model age. However, this effect of mixed analysis is likely to be insignificant for our Hf isotope measurements, because the majority of each analytic spot apparently belongs to single age domain (Fig. 2). Relatively large ablation area may also vaporize some minerals or fluid/melt inclusions embedded within targeted area of zircon. Because Hf concentrations of zircon (and baddeleyite) vary normally in the order of 10^4 ppm relative to most terrestrial rocks and minerals, which have usually less than 50 ppm of Hf (Faure, 1986), however, these inclusions have practically no effect on the measured Hf isotopic ratios of zircon.

The $^{176}Lu/^{177}Hf$ ratios of zircons from the GM and YM range from 0.000437 to 0.000895, which are similar to those from the NM (Wu et al., 2007). The $^{176}Hf/^{177}Hf$ ratios range from 0.280437 to 0.280751, corresponding to the present-day $\varepsilon_{Hf}(0)$ values of –69.8 to –81.0. These values are also similar to those of the NM, except for one zircon component (P1 #35) (Table 1). Initial $^{176}Hf/^{177}Hf$ ratio of the zircon grain, P1 #35, from the NM is exceptionally high ($\varepsilon_{Hf}(t)$=17), which is possibly attributed to an influx of metamorphic fluid with high $^{176}Hf/^{177}Hf$ (Zheng et al., 2005), and is excluded for further discussion. The initial $\varepsilon_{Hf}(t)$ values, except for one zircon component (SC50 #11), range from –0.3 to –8.9 at the time of zircon crystallization from a magma, and are comparable to –1.0 to –7.7 from the NM. All of these negative values indicate variable participation of reworked crustal materials at the time of magmatic zircon crystallization. A zircon component, SC50 #11, has the initial $\varepsilon_{Hf}(t)$ value of +5, which plots along the putative evolution line of the depleted mantle through time. Because Th/U ratios of zircons crystallized from mafic rocks are usually greater than 1.0 (Amelin, 1998), high Th/U ratio (=1.08), combined with DM-like initial $\varepsilon_{Hf}(t)$ value of this zircon component suggests a crystallization from juvenile mafic source rock.

4. DISUSSION

4.1. Limitations in the Hf Model Age

Some fixed and at least best-estimated parameters are assumed in order to extract reliable age information from the model age calculation approach. It is beyond the scope of this study to address all the questions related to Lu-Hf isotopic system. However, large uncertainty in the ^{176}Lu decay constant severely limits the usefulness of Lu-Hf isotope system as a reliable geochronometer (see Amelin and Davis, 2005). Two different groups of values for the ^{176}Lu decay constant have been determined by recent high-precision experiments. The λ^{176}Lu values of $1.86–1.87\times10^{-11}$ yr^{-1} were determined by age comparisons using terrestrial minerals of Proterozoic and Neoarchean ages (Scherer et al., 2001; Söderlund et al., 2004), whereas a value of $\sim1.94\times10^{-11}$ yr^{-1} was determined from age comparison studies of meteorites (Patchett and Tatsumoto, 1980; Blichert-Toft et al., 2002; Bizzaro et al., 2003). The reason for the apparent discrepancy in meteorite versus terrestrial mineral λ^{176}Lu values is currently unknown (Amelin and Davis, 2005). In this study, we chose the λ^{176}Lu value of 1.865×10^{-11} yr^{-1} (Scherer et al., 2001), because it is calibrated via terrestrial materials rather than meteorites. For our Lu-Hf isotopic dataset, using λ^{176}Lu of 1.94×10^{-11} yr^{-1} will yield apparently 120 to 160 Ma younger Hf model ages than terrestrial λ^{176}Lu. In addition to the ^{176}Lu decay constant issue, the existing parameters of CHUR and DM commonly used for the model age expression may not be representative for the bulk silicate Earth (e.g. Patchett et al., 2004). This discrepancy results in the implicit uncertainty in the DM parameters, which are further propagated to the uncertainty in Hf model age calculation for terrestrial materials. Finally, unlike Hf model ages from whole-rock samples, a single zircon with known age can be used to calculate two-stage Hf model ages. With the initial Hf isotope composition at the time of zircon crystallization, average Lu/Hf of the source reservoir of a zircon's host rock needs to be assumed in order to estimate the timing of separation from the depleted mantle for the reservoir. The estimated Hf model age for a zircon therefore strongly depends on source parameters. Using high Lu/Hf typical of average mafic crust as a potential host reservoir provides a maximum Hf model age, whereas calculations assuming a felsic rock type yield minimum Hf model ages (Nebel et al., 2007). Hence the Hf model age can only be treated as absolute age information with large a priori uncertainty.

4.2. Paleo- to Mesoarchean Crustal Evolution of the Korean Peninsula

Previous studies, mainly based on U-Pb zircon geochronology, identified a few of Paleo- to Mesoarchean zircon components, indicative of the existence of >3.0 Ga crustal materials in the Korean Peninsula (e.g. Cho and Kim., 2003; Zhao et al., 2006; Jeon et al., 2007; Wu et al., 2007). At the time of zircon crystallization, except for SC50 #11, all the zircon components have the initial $\varepsilon_{Hf}(t)$ values of –0.3 to –8.9, indicative of their derivation from variably reworked (and evolved) rather than juvenile crustal materials. Using average Archean felsic crust (^{176}Lu/^{177}Hf=0.009; Amelin et al., 1999) and average continental crust (^{176}Lu/^{177}Hf=0.015; Griffin et al., 2002) as zircon's host reservoirs, two-stage Hf model ages are estimated to be in the range of 3.95 Ga to 3.45 Ga and 4.11 Ga to 3.46 Ga, respectively (Table 1; Fig. 3). These Hf model ages suggest that all the zircon components are derived from source reservoirs evolved from the Hadean to Paleoarchean (ca. 4.1 to 3.5 Ga) juvenile crusts from the depleted mantle. Comparison between U-Pb and two-stage Hf model ages for all the Archean zircon components except for SC50 #11 suggests a crustal residence time of about 260 Ma to 900 Ma for juvenile crustal materials, prior to the formation of parental magma producing the zircon crystal.

In a time (Ga) versus $\varepsilon_{Hf}(t)$ diagram (Fig. 3), it is apparent, though not convincing because of limited number of data, that two crustal evolution trends are notable, assuming that all the zircons were evolved from the source reservoir defined by average Archean felsic crust with ^{176}Lu/^{177}Hf ratio of 0.009 (Amelin et al., 1999). The first, defined by five out of eleven zircon components, corresponds to the crustal evolution trend emerging from ca. 3.8 Ga juvenile crust derived from the depleted mantle. The second, defined by three zircon components including one juvenile zircon component (SC50 #11), is delineated by the crustal evolution trend emerging from ca. 3.5 Ga juvenile crust. This observation suggests that at least two distinct (ca. 3.8 Ga and 3.5 Ga)

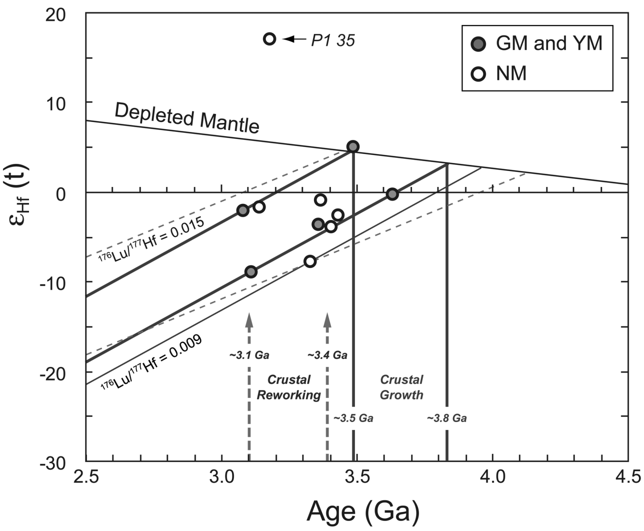

Fig. 3. Hf isotope evolution diagram for >3.0 Ga zircon components from the GM and YM (this study) and NM (after Wu et al., 2007), using either average felsic crust (solid line; ^{176}Lu/^{177}Hf = 0.009; Amelin et al., 1999) or average continental crust (dashed line; ^{176}Lu/^{177}Hf = 0.015; Griffin et al., 2002). The DM evolution line is calculated using the values of present-day ^{176}Hf/^{177}Hf ratio of 0.28325 (Nowell et al., 1998) and ^{176}Lu/^{177}Hf ratio of 0.0384 (Griffin et al., 2000).

events can be attributed to the pristine crustal growth of the Korean Peninsula during the Paleoarchean. A significant difference (ca. 200 Ma to 700 Ma) between the distribution of U-Pb ages and Hf model ages for the majority of zircon components implies that these pristine crustal materials are variably reworked during the subsequent crustal differentiation processes. One of such reworking processes is inferred to occur at ca. 3.4 Ga, immediately after the juvenile crustal growth event at ca. 3.5 Ga (Fig. 3). During this reworking event, host magmas of ca. 3.4 Ga zircon components could be produced by re-melting of ca. 3.8 Ga juvenile crustal materials, together with partial mixing of ca. 3.5 Ga ones. Another crustal reworking event is apparent at ca. 3.1 Ga, when much of ca. 3.5 Ga and lesser amount of ca. 3.8 Ga juvenile crustal materials are evolved to produce magmas crystallizing ca. 3.1 Ga zircon components (Fig. 3).

In summary, combined U-Pb and Hf isotopic data on zircons are useful for not only identifying ancient crustal remnants but also characterizing the nature of zircon-bearing host magmas, that is, juvenile or reworked. Our combined U-Pb and Hf isotopic results suggest the possible existence of Paleoarchean (>3.5 Ga) crustal materials in the Korean Peninsula. In addition, based on our Hf isotope data, the very early stage of crustal evolution history of the peninsula can be attributed to the Paleoarchean (ca. 3.8 Ga and 3.5 Ga) juvenile crustal growth and Mesoarchean (ca. 3.4 Ga and ca. 3.1 Ga) crustal reworking events, although further work is necessary for confirming our preliminary result in the future.

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