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*Geology* 2008;36;875-878
doi: 10.1130/G24861A.1

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# Episodic, mafic crust formation from 4.5 to 2.8 Ga: New evidence from detrital zircons, Slave craton, Canada

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## ABSTRACT

**The εHf and $\delta^{18}$O values in detrital zircons from the Slave craton, Canada, indicate three episodes of crust formation between ca. 4.5 and 2.8 Ga, namely at ca. 4.4–4.5 Ga, ca. 3.8 Ga, and ca. 3.4 Ga. Most of the juvenile crust appears to have been mafic in composition, and there is no clear evidence for initial granitic protocrust in the Hadean of the Slave craton. The range of initial εHf values in zircons increases from 3.9 to 2.8 Ga, indicating that both extraction of new material from mantle and reworking of the older crust are important for the secular evolution of the continental crust. A preliminary review of available Hf data in zircons suggests that the three episodes of crust generation may have been of global importance. The mafic crust formed in the Archean and the Hadean was then reworked for at least ~0.5–1.5 b.y., as indicated by data from the Slave craton, Gondwana, and the Limpopo Belt of Africa.**

## INTRODUCTION

The generation and recycling of continental crust back into the mantle largely determine the secular evolution of isotope ratios in the Earth's mantle. The secular evolution of the continental crust is more difficult to determine; it is unclear how representative individual, and in some cases isolated, segments of the continental crust may be, and average compositions inferred from continental sediments are difficult to interpret in terms of the possible ages of their source regions. Nonetheless, data on continental sediments remain the basis for many models for the generation and evolution of the crust (Allègre and Rousseau, 1984; Taylor and McLennan, 1995). The volume of stable continental crust appears to have increased with time, and significant volumes were stabilized between 3 and 2 Ga (Taylor and McLennan, 1995; Collerson and Kamber, 1999). In contrast, the ages of igneous rocks that represent new continental crust are characterized by marked peaks at 2.7, 1.9, and 1.2 Ga (McCulloch and Bennett, 1994; Condie, 1998), and 3.3 and 1.9 Ga peaks have also been observed for model ages from detrital and inherited zircon (Kemp et al., 2006). At issue is the extent to which such peaks are global, in the sense that they occurred at the same time in different landmasses. We present $^{176}$Hf/$^{177}$Hf and $\delta^{18}$O isotope ratios on dated detrital zircons ranging in age from 2.8 to 3.9 Ga from the Slave craton, Canada, to assess the extent to which they preserve evidence for distinct peaks of crust formation in the late Hadean and Early Archean.

The Central Slave Basement Complex records 10 episodes of predominately felsic magmatism from 4.05 Ga to 2.7 Ga (Bleeker, 2002), and it includes the Acasta gneiss complex, the oldest rocks currently known on Earth (Bowring and Williams, 1999). An inherited zircon age of 4.2 Ga (Iizuka et al., 2006) and subchondritic εHf of zircons from ca. 3.6 Ga Acasta gneisses (Amelin et al., 2000) indicate early formation of the continental crust in this area. We have analyzed 136 detrital zircons previously dated by Sircombe et al. (2001) from the ca. 2.8 Ga Mesoarchean protocratonic cover succession in the Slave craton. The range of ages of zircons analyzed for $^{176}$Hf/$^{177}$Hf and $\delta^{18}$O is 2812–3918 Ma, and the age distribution forms a number of peaks consistent with at least six magmatic episodes.

The advantage of using Hf isotopes in zircons is that both the U-Pb age and the Hf isotope ratios can be measured in situ. The Hf isotope ratios can be calculated for the time of the U-Pb ages, and the Hf model ages of crust extraction from depleted mantle can then be calculated. Oxygen isotopes are used to distinguish zircons that may have crystallized from magmas containing a contribution from continental sediments (i.e., with elevated $\delta^{18}$O; Valley et al., 2005), because such sediments yield hybrid model ages that are difficult to interpret. In contrast, zircons with lower, more mantle-like $\delta^{18}$O values are more likely to preserve Hf model ages that reflect actual crust-forming events.

To calculate the Hf model age from a zircon it is necessary to constrain, or to assume, the $^{176}$Lu/$^{177}$Hf ratio of the crustal material that was initially extracted from the mantle. This ratio may vary from ~0.03–0.02, typical for mafic magmas, to ~0.01, typical for granitic material, and magmas extracted from garnet-rich source rocks, such as Archean tonalite-trondhjemite-granodiorite, may have even lower $^{176}$Lu/$^{177}$Hf. Zircons from magmas of different ages derived from crust of the same mantle extraction age and composition will form a linear array on plots of Hf isotope ratios against crystallization age (see Fig. 1). The slopes of such arrays correspond to the $^{176}$Lu/$^{177}$Hf ratio of the crustal source of the magmas (e.g., Kemp et al., 2006), and that may in turn be used to constrain its composition. Analyzing zircons with a range of crystallization ages therefore gives the best constraints on both the $^{176}$Lu/$^{177}$Hf of the source and the model ages of crust extraction.

## METHODS AND RESULTS

Only grains with U-Pb ages within ±5% of concordia were analyzed for Hf and O isotopes, and cathodoluminescence and scanning electron microscope contrast imaging revealed that most grains were oscillatory zoned, consistent with magmatic origins. Oxygen isotopes were analyzed with a Cameca IMS 1270 ion microprobe at the Swedish Natural History Museum in Stockholm (Nordsims facility) following the method described by Nemchin et al. (2006). Subsequently, Hf isotopes were measured at the University of Bristol with a Finnigan Neptune multicollector inductively coupled plasma–mass spectrometer and a 193 nm ArF laser, using

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*Geology*, November 2008; v. 36; no. 11; p. 875–878; doi: 10.1130/G24861A.1; 4 figures; Data Repository item 2008224.

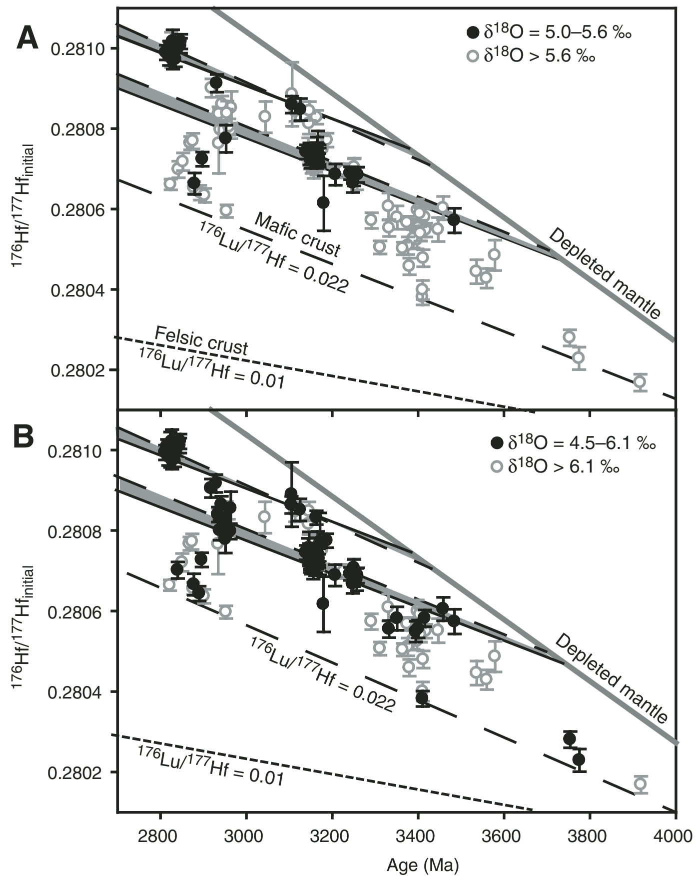

**Figure 1. Plot of initial $^{176}$Hf/$^{177}$Hf against zircon crystallization age. Initial $^{176}$Hf/$^{177}$Hf were calculated using λ176Lu of Söderlund et al. (2004). A: Zircons are divided into those with mantle-like δ$^{18}$O of 5.0‰–5.6‰ (Valley, 2003) and those with higher δ$^{18}$O. B: Zircons are divided into those with δ$^{18}$O of 4.6‰–6.0‰ (mantle-like value ± average 2σ error on individual zircon δ$^{18}$O analysis) and those with higher δ$^{18}$O. Solid black lines represent modeled evolution of crustal reservoir with $^{176}$Lu/$^{177}$Hf = 0.022 extracted from depleted mantle at different times; lines were led through analyses with the lowest $^{176}$Hf/$^{177}$Hf for a given cluster of zircon analyses with low δ$^{18}$O. Extraction ages for solid lines are 4.44 Ga, 3.75 Ga, and 3.38 Ga from bottom up. Long dashed lines represent regressions through zircons with low δ$^{18}$O; lower line has $R^2$ = 0.86, extraction age of 3.7 Ga, and $^{176}$Lu/$^{177}$Hf = 0.0225. Upper line has $R^2$ = 0.89, extraction age of 3.47 Ga, and $^{176}$Lu/$^{177}$Hf = 0.026. Areas between regressed lines and those based on low $^{176}$Hf/$^{177}$Hf values were shaded. Short-dashed line shows evolution of crustal reservoir with $^{176}$Lu/$^{177}$Hf = 0.01 and extraction age 4.44 Ga. Solid gray line represents evolution of depleted mantle calculated assuming present-day parameters of depleted mantle $^{176}$Hf/$^{177}$Hf = 0.28325 and $^{176}$Lu/$^{177}$Hf = 0.0384 (Chauvel and Blichert-Toft, 2001).**

methods and data reduction described in Hawkesworth and Kemp (2006). The oxygen data for unknowns and the 91500 standard and the Hf data for unknowns and Plesovice, Temora-2, and 91500 standards are presented in Table DR1 in the GSA Data Repository[1].

The initial $^{176}$Hf/$^{177}$Hf isotope ratios are plotted against crystallization age for the different zircons in Figure 1 (the complementary εHf versus age plot is Fig. DR1). Zircons with mantle-like δ$^{18}$O of 5.0‰–5.6‰ (Valley 2003) were assumed to yield nonhybrid $^{176}$Hf/$^{177}$Hf isotope ratios (Fig. 1A). Including zircons with a larger range of δ$^{18}$O (±2σ δ$^{18}$O from the mantle values) results in a larger spread of initial $^{176}$Hf/$^{177}$Hf ratios (Fig. 1B) around the data clusters defined in Figure 1A, suggesting that the spread is due to mixing with $^{18}$O-enriched material and that many of the zircons with higher δ$^{18}$O may exhibit hybrid $^{176}$Hf/$^{177}$Hf isotope ratios.

Most of the zircons with mantle-like δ$^{18}$O scatter around two arrays corresponding to $^{176}$Lu/$^{177}$Hf = 0.022–0.026 (Fig. 1). The aim is to estimate the $^{176}$Lu/$^{177}$Hf value of the crustal source rocks from arrays on plots of initial Hf isotope ratios against crystallization age. At present such arrays are not well enough defined to obtain precise estimates of $^{176}$Lu/$^{177}$Hf, but they can be used to contrast the evolution of mafic and granitic source rocks. Isotope evolution lines corresponding to slopes of $^{176}$Lu/$^{177}$Hf = 0.022–0.026 (mafic crust) and 0.01 (felsic crust) are both plotted in Figure 1, and most of the low δ$^{18}$O data are consistent with the $^{176}$Lu/$^{177}$Hf ≈ 0.022. The implications are (1) model ages for at least most of these samples should be calculated with mafic $^{176}$Lu/$^{177}$Hf = 0.022, (2) the crustal precursor formed at the time of the Hf model ages is mafic in composition, and (3) such a mafic crust is reworked and contributes to felsic magmatism for at least several hundred million years. We note that none of the zircons analyzed have crystallization ages within 100 m.y. from a depleted mantle evolution curve (see also Kemp et al., 2006). This may indicate that it typically takes ~100 m.y. after crust formation to generate magmas with sufficiently high silica to crystallize zircon and, therefore, supports a mafic composition for the crustal precursor.

Histograms of Hf model ages calculated using $^{176}$Lu/$^{177}$Hf of 0.022 highlight two peaks ca. 3.8 Ga and ca. 3.4 Ga for zircons with δ$^{18}$O of 5.0‰–5.6‰, whereas those with δ$^{18}$O outside this range exhibit a continuum of model ages (Fig. 2). A plot of zircon crystallization age against Hf model age demonstrates that the model ages of ca. 3.8 Ga are observed in zircons that range in crystallization age from 3.5 to 2.9 Ga (Fig. 2). Most of the zircons with Hf model ages between 4.5 and 3.8 Ga and crystallization ages back to 3.9 Ga have elevated δ$^{18}$O values. They are therefore interpreted to contain contributions from supracrustal source rocks, and the model ages could thus be hybrid ages. However, the highest model ages are consistently 4.4–4.5 Ga for zircons 2.8–3.9 b.y. old (Fig. 2), and those zircons plot on a single array with the slope corresponding to $^{176}$Lu/$^{177}$Hf ≈ 0.022 (Fig. 1). Such consistency is in agreement with the presence of mafic material that is inferred to be the oldest crust sampled by the zircons analyzed in this study that was derived from the mantle 4.4–4.5 Ga (Fig. 2). In other words, the few points that define that array may not be hybrids at all in the sense of having mixed $^{176}$Hf/$^{177}$Hf, but have mafic sources that interacted with water at low temperature. Zircons with model ages between 4.5 and 3.8 Ga are interpreted to reflect mixing of material from the 4.4–4.5 Ga and ca. 3.8 Ga terrains.

## DISCUSSION

The presence and composition of Jack Hills zircons have been regarded as indicative of preexisting granitic source rocks in Hadean (Blichert Toft and Albarède, 2008; Harrison et al., 2008). Such issues remain difficult to resolve, but the data from this study indicate that, at least in the Slave craton, the protocrust may have had relatively high $^{176}$Lu/$^{177}$Hf ratios (0.022–0.026) more indicative of mafic compositions (Fig. 3).

The predominance of a mafic crust on the early Earth is consistent with the scarcity of zircons with ages older than 3.8 Ga in the oldest sediments (3.71 ± 0.4 Ga, the Isua Greenstone Belt), and with some thermal modeling (Kamber et al., 2005). Kamber et al. (2005) suggested that the mafic crust was hydrated and continuously buried under new basaltic flows erupting on the surface. However, our data indicate a less dynamic environment in the Slave craton, as the rarity of low δ$^{18}$O zircons with model ages between 4.5 and 3.8 suggests that there was little juvenile material added to the crust in that period. A similar conclusion has been drawn from the Hf isotope results from the Jack Hills zircons in Australia

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[1] GSA Data Repository item 2008224, oxygen data for unknowns, 91500 standard, and the Hf data for unknowns, and standards and complementary figures (Figs. DR1 and DR2) to Figures 1 and 3, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

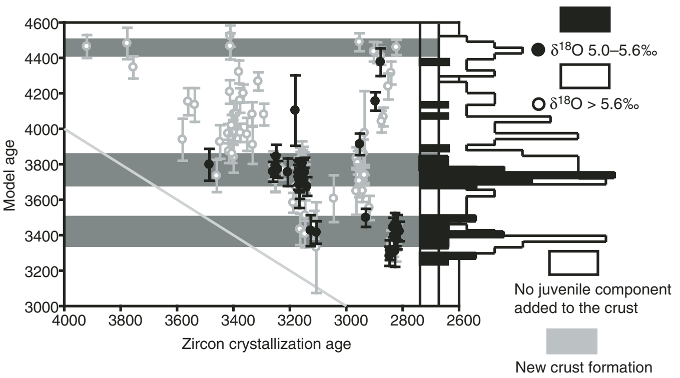

**Figure 2. Plot of zircon crystallization against model age. All zircons ages are ±5% concordant. Model ages of zircons represented by black ($\delta^{18}O$ = 5.0‰–5.6‰) and white dots ($\delta^{18}O$ > 5.6‰) were calculated with $^{176}Lu/^{177}Hf$ = 0.022 for the crustal reservoir as discussed in the text, and depleted mantle parameters of Chauvel and Blichert-Toft (2001). Gray bands mark periods during which new juvenile material was extracted from depleted mantle; white bands signify periods of relative quiescence and mostly crustal reworking. Histograms on right side of figure show distribution of model ages for zircons with $\delta^{18}O$ = 5.0‰–5.6‰ (black) and $\delta^{18}O$ > 5.6‰ (white). Gray solid line is the crystallization age = model age line.**

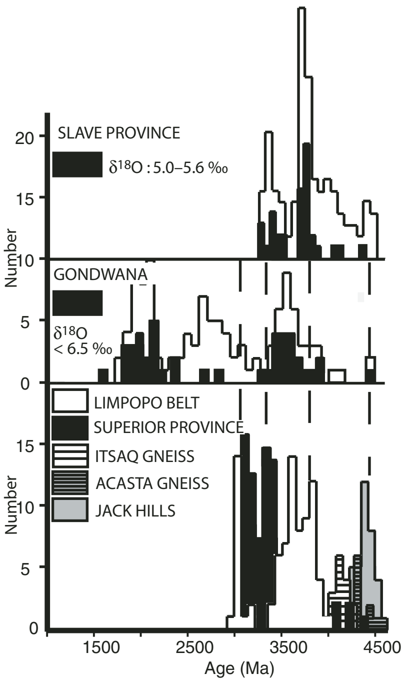

**Figure 4. Comparison of histograms of zircon Hf model ages. All data were recalculated using parameters referred to in Figure 1. Data sources as in Figure 3.**

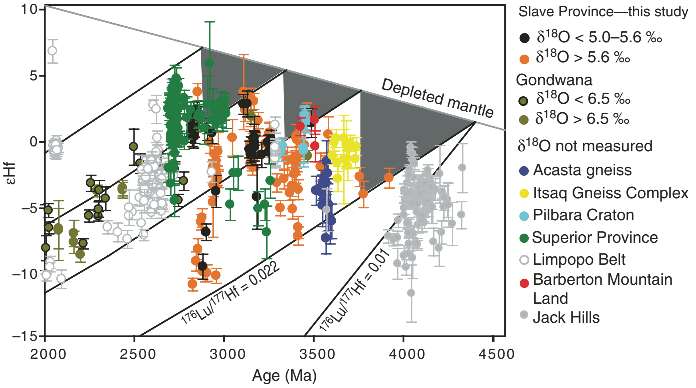

**Figure 3. Plot of εHf against zircon crystallization age. All data were recalculated using parameters referred to in Figure 1 and chondritic parameters of Blichert-Toft and Albarède (1997). Gray fields mark range of εHf in time that have not yet been measured in zircons, supporting hypothesis of episodic rather than continuous continental crust extraction (see text). Data used for comparison are from Amelin et al. (1999; Acasta, Itsaq gneisses, Pilbara Craton, Barberton Mountain Land), Davis et al. (2005; Superior Province), Kemp et al. (2006; Gondwana), Zeh et al. (2007; Limpopo Belt) and Harrison et al. (2008; Jack Hills). Data from Amelin et al. (1999), Kemp et al. (2006), and Zeh et al. (2007) are ±5% concordant. Vertical dashed lines mark continental crust extraction ages as modeled in Figure 1.**

that also do not record addition of a juvenile material in the Hadean after derivation ca. 4.4–4.5 Ga (Kramers, 2007; see also Harrison et al., 2008). We note that the mafic crust formed in the Slave craton in the early Hadean was reworked for more than 1.5 b.y., suggesting long-term preservation of the Hadean crust (Fig. 3).

In the Slave craton most of the low $\delta^{18}O$ zircons form two distinct peaks in the model age histogram (Fig. 2), suggesting that after the Hadean new, mafic crust was formed in two episodes ca. 3.8 Ga and ca. 3.4 Ga. Comparison of global zircon Hf model ages calculated using $^{177}Lu/^{176}Hf$ typical for mafic crust (Fig. 4) shows that (1) most areas are characterized by distinct peaks, but (2) no common peaks exist for all the areas for which Archean zircons are available, although some of them overlap. The ca. 3.4 Ga episode in the Slave craton is consistent with data from Gondwana (Kemp et al., 2006), and a similar peak is observed in the Superior craton (Davis et al., 2005). The next episode of crust extraction probably happened ca. 2.7–2.8 Ga and is consistent with extensive tholeiitic magmatism in the Slave craton ca. 2.7–2.8 Ga (Sircombe et al., 2001), and with the available data from the Superior craton and the Limpopo Belt of Africa (Davis et al., 2005; Zeh et al., 2007; Figs. 3 and 4).

Despite the coincidence of several peaks in the global Hf model ages record, many zircons have intermediate model ages. Such a picture is more consistent with the generation of new crust at different times in different places on the Earth, rather than with a few major global events. However, the range of εHf in zircons increases from 4.0 Ga to 2.7 Ga (Fig. 3), indicating that both the addition of juvenile material and remelting of older crust are important processes controlling the compositional evolution of the continental crust. The implication is that the range of εHf in zircons in any magmatic episode is controlled by mixing between different crustal reservoirs, and that this in turn yields hybrid model ages. So far only coupled analyses of Hf and O isotopes seem to discriminate between zircons derived from a single source and those of hybrid origin (Kemp et al., 2006). Since $\delta^{18}O$ is not known for many zircons from the global data set, we propose an alternative approach that might be used to distinguish mixed model ages from those of a new continental crust formation.

A prediction of a model in which the generation of the new continental crust occurred in four episodes, ca. 4.4–4.5 Ga, ca. 3.8 Ga, ca. 3.4 Ga, and ca. 2.7–2.8 Ga, is that no zircons would have εHf values that plot above the crust formation array (solid black lines in Fig. 3) before the new crust is extracted. In other words, we would expect "triangles" in the εHf versus zircon crystallization plot in which there are no data points. It is interesting that there are three such triangles in Figure 3 for which there are currently no data (see also Fig. DR2 for the complementary $^{176}Hf/^{177}Hf$ versus crystallization age plot), and they are consistent with the crust derivation events suggested by the zircons with mantle-like $\delta^{18}O$ from this study. The best defined is the period between ca. 3.4 and ca. 2.8 Ga, with data from both Slave and Superior cratons plotting along the array, until ca. 2.8 Ga, when the new mafic crust is extracted and can contribute as a mixing component producing a range of εHf compositions (Fig. 3). We note that the slope of this array again corresponds to $^{176}\mathrm{Lu}/^{177}\mathrm{Hf} \approx 0.022$, in support of our conclusion that juvenile crust is mafic in composition and has long residence times of at least 500 m.y. It is unclear whether the triangles with no data points will survive the analysis of more samples, but if they are real, the three triangles might be taken as further evidence that new crust was generated in pulses, and that the intermediate samples are mixtures of the sources available at the time of magmatism.

In summary, we argue that four episodes of mafic crust extraction can currently be recognized between 4.5 and 2.7 Ga. The period between each episode is ~0.3–0.6 b.y., and comparison of all the available data indicates that these episodes might be of global rather than regional importance (Fig. 3). Proterozoic zircons from the Gondwana supercontinent and the Limpopo Belt also yield Archean model ages (Kemp et al., 2006; Zeh et al., 2007; Fig. 3) suggesting long-term, global preservation of the crust formed in these episodes. The global evidence for preservation of ca. 3.8 Ga and ca. 3.4 Ga events is important in that it happened before the first 2.7 Ga global peak observed in zircon crystallization age distributions from igneous rocks (Condie, 1998).

## ACKNOWLEDGMENTS

We are grateful for helpful reviews by K. Condie and A. Gerdes and careful editing by D. Barth. Pietranik acknowledges Polish Science Foundation grant KOLUMB and SYNTHESYS grant SE-TAF 3238. We thank Kirstin Lindén for help with sample preparation in Stockholm. The Nordsim facility is operated jointly by Denmark, Finland, Norway, and Sweden; this is Nordsim publication 212. Storey acknowledges Natural Environment Research Council grant NE/D008891/1. Pietranik thanks the members of the Bristol Isotope Group for their scientific and moral support.

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Manuscript received 13 February 2008
Revised manuscript received 5 August 2008
Manuscript accepted 5 August 2008

Printed in USA