



# Hf isotopes in zircon from the western Superior province, Canada: Implications for Archean crustal development and evolution of the depleted mantle reservoir

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## Abstract

U–Pb and Hf isotopic measurements on zircons from the western Superior province confirm that the area contains at least three distinct terrane types. Juvenile terranes that formed mostly within the time span 2.75–2.68 Ga occupy much of the western Wabigoon subprovince as well as granite-greenstone belts to the south. Juvenile 3.0 Ga terranes that were reworked over the time span 2.7–3.0 Ga occupy the south-central part of the Wabigoon subprovince and the North Caribou block in the Sachigo subprovince. Rocks with mantle extraction ages as old as 3.5 Ga and zircon U–Pb ages extending to 3.3 Ga characterize a third type of terrane represented by the Winnipeg River subprovince. This terrane was strongly reworked during the late Archean.

Arc-related magmatism was ongoing at 2.71–2.75 Ga in the different terranes, which probably accreted over the time span 2.71–2.68 Ga. Enriched Hf and high O isotopic signatures in late sanukitoid-suite plutons appear to be correlated, which suggests that assimilation of Mesoarchean crust was an important factor in their magmatic evolution.

Enriched Hf isotopic signatures in detrital and igneous zircon from parts of the north-central Wabigoon subprovince support previous suggestions that the Winnipeg River terrane extends eastward beyond the Winnipeg River subprovince. The Winnipeg River subprovince was probably being uplifted and eroded into the Quetico sedimentary basin shortly after 2700 Ma, as shown by detrital zircons with enriched Hf isotopic signatures and Meso- to Paleoproterozoic ages. The pattern of ages and isotopic signatures from the North Caribou block and the south-central Wabigoon subprovince are similar, suggesting that these terranes are correlative. If so, the south-central Wabigoon terrane may have been tectonically transported from the north.

Hf isotopic compositions of zircon from juvenile Archean sources are remarkably consistent and define an average  $\varepsilon_{\text{Hf}}$  value of  $+3.5 \pm 0.2$  for samples with an average age of 2724 Ma and a best estimate of  $+2.7 \pm 0.4$  at 3000 Ma. Thus, the Neoproterozoic depleted mantle reservoir beneath the Superior province appears to have been isotopically well mixed.  $\varepsilon_{\text{Hf}}$  values were calculated using a value of  $1.865 \times 10^{-5} \text{ Ma}^{-1}$  [Scherer, E., Munker, C., Mezger, K., 2001. Calibration of the Lutetium–Hafnium clock. *Science* 293, 683–687] for the  $^{176}\text{Lu}$  decay constant, which is thus far the best reproduced estimate and the one most consistent with depleted mantle evolution results based on Nd isotopes and Nb/Th ratios. A linear Hf mantle growth curve defined by these

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values and recent MORB intersects the chondritic Hf growth curve during the early Archean (3.4–4.0 Ga). This could indicate that the earliest formation of significant amounts of enriched crust coincides with ages of the oldest preserved rocks, but such a conclusion is contradicted by evidence from  $^{142}\text{Nd}$  and  $^{143}\text{Nd}$  in early Archean rocks for significant mantle depletion during the Hadean eon (>4.0 Ga). Both lines of evidence might be reconciled if Hadean enriched crust were largely remixed with its depleted mantle source near the beginning of the Archean, leaving only fragmentary evidence of its existence in the oldest rocks. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

U–Pb dating of zircon in the Superior province has revealed a near continuous record of magmatism within the time range 2650–3000 Ma but the vast majority of rocks formed within the last 100 m.y. of this period. Precise dating of these rocks has contributed important information toward understanding Neoproterozoic tectonic processes, in particular showing that the Superior province consists of terranes with distinct histories and degrees of crustal reworking. Age data on zircons from igneous and sedimentary rocks (Davis, 1998) together with field and geophysical observations (White et al., 2003) in the context of the western Superior Lithoprobe transect, support earlier proposals that the Superior province was assembled from successive collisions with such terranes (Langford and Morin, 1976; Card, 1990).

Nd isotopic work by Henry et al. (1998, 2000) and Tomlinson et al. (2003) has greatly helped in recognizing and delineating the extent of different terranes in the Superior province. Variations in the  $^{176}\text{Hf}$  isotope from decay of  $^{176}\text{Lu}$  can distinguish juvenile mantle from older crustal sources in a way similar to Nd isotopes (Patchett, 1983). It has been shown that Hf isotopic variations are closely coupled to Nd isotopes in the crust and mantle (Blichert-Toft and Albarède, 1997; Vervoort and Blichert-Toft, 1999) but measurements of Hf isotopes in zircon have some advantage over Nd isotope measurements on whole rocks. Zircon contains Hf as a major (1–2%) and highly immobile component, so there is less possibility of disturbance and minimal age correction is required to arrive at the primary Hf isotopic ratio. U–Pb dating also provides a precise age of crystallization on the same sample used for Hf measurement. The development of multi-collector mass spectrometers with inductively couple plasma sources (MC-ICPMS) has greatly facilitated rapid and precise

analysis of Hf isotopes in small zircon samples including analysis of single detrital grains that can potentially reveal the magmatic pre-history of sedimentary source terrains.

Hf isotopes contained within collections of dated zircon provide a rich potential source of data. The Jack Satterly Geochronology Laboratory has archived zircon from thousands of previously dated rocks. Using MC-ICPMS, Hf isotopes were measured on dated zircon from 62 igneous rock units plus 25 detrital zircon grains from Archean metasedimentary rocks in the western Superior province. Most samples come from northwest Ontario. The mass spectrometer analyses were done over a four-day period and expand the previously available Hf database in the region by a factor of four. The objective of this study was to acquire data over as wide an area as possible to test whether Hf isotopic compositions can be used to identify distinct tectonic terranes. Samples were selected from seven different areas of the western Superior province that may represent terranes with distinctly different histories. They are from a variety of lithologies, including volcanic rocks, syn-volcanic plutons, gneisses, late plutons, and detrital zircons. The zircons cover an age range of greater than 600 m.y. The data present a broad picture of terrane histories in the western Superior province and in some cases allow sources of detrital zircon to be isotopically distinguished. Pending acceptance of a well established value for the  $^{176}\text{Lu}$  decay constant, the data also help constrain evolution of late Archean depleted mantle beneath the region, which has a bearing on global development of the early continental crust.

## 2. Background

The Superior province has been divided into sub-provinces based on contrasts in principal lithologies

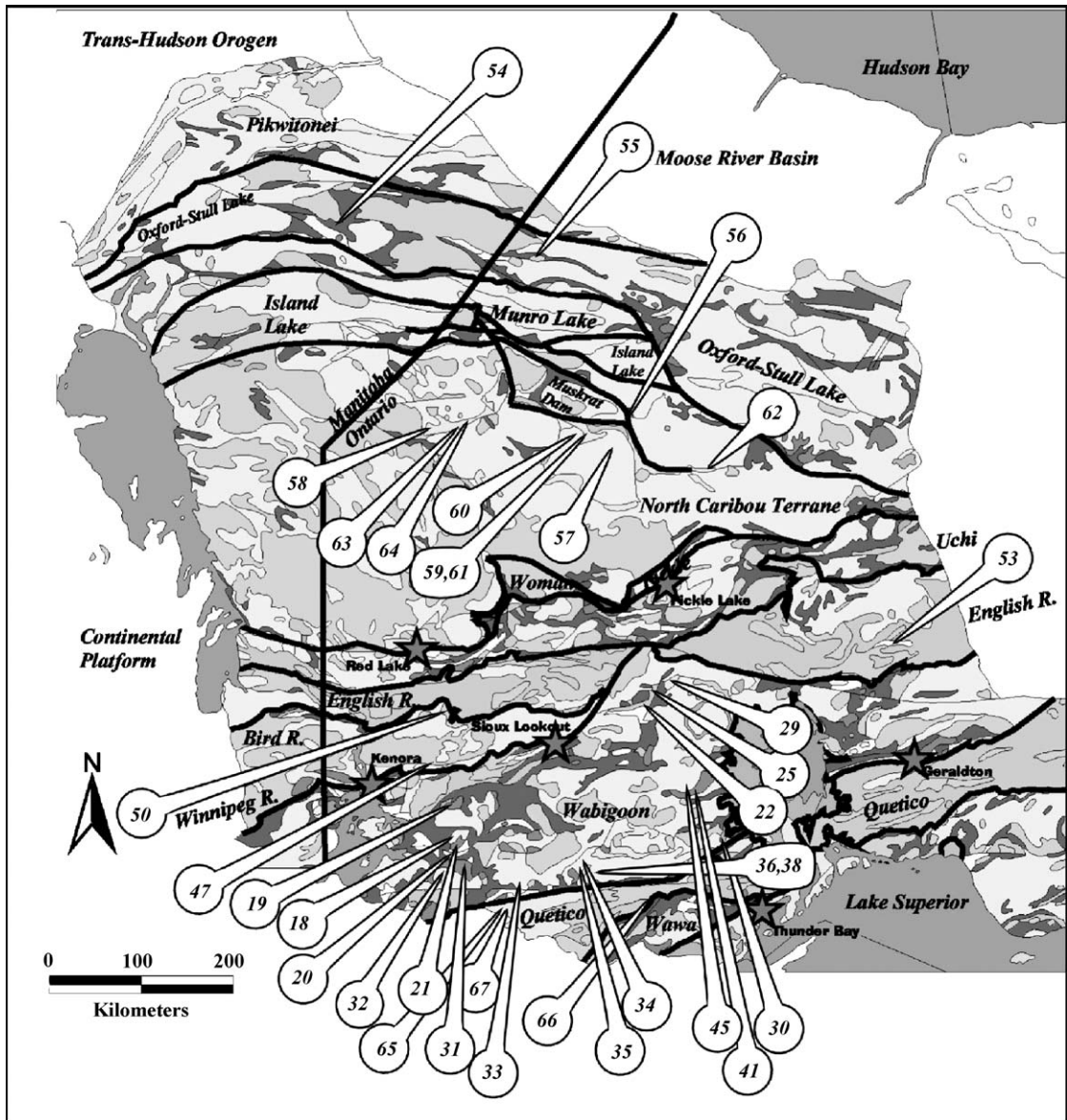


Fig. 1. Geological map of the western Superior province showing sample locations. Subprovince divisions are after Card and Ciesielski (1986).

and metamorphic grade (Fig. 1 based on Card and Ciesielski, 1986). The northern part of the study area contains the granite-greenstone Sachigo and Uchi subprovinces, the metasedimentary English River subprovince, and the metaplutonic Winnipeg River subprovince. The latter two areas are generally metamorphosed to mid-amphibolite or granulite facies.

Further south is the granite-greenstone Wabigoon subprovince, followed by the metasedimentary Quetico subprovince and finally the granite-greenstone Shebandowan belt. The Shebandowan belt is the western extension of the Wawa subprovince, which is probably correlative with the Abitibi subprovince further east.

Smith et al. (1987) followed by Stevensen and Patchett (1990) and Corfu and Noble (1992) presented the earliest studies of Hf isotopic ratios in the Superior province. These confirmed the juvenile character of igneous rocks in the southern Abitibi and Wawa subprovinces, already suspected from U–Pb dating. However, Hf isotopes in bulk detrital zircon fractions from a number of Archean sandstones indicated that rocks as old as about 3.0 Ga were probably present in the provenance (Stevensen and Patchett, 1990). Later Hf measurements by Corfu and Stott (1993a, 1996) in the Uchi subprovince showed a distribution of  $\epsilon_{\text{Hf}}$  values that range between depleted mantle and 3.0 Ga crustal growth curves. Based on U–Pb geochronology and field investigations, the Uchi subprovince was previously suggested to have developed over a 300 m.y. period in an Andean-type tectonic setting along the margin of a 3.0 Ga old terrane to the north, the North Caribou terrane (Stott and Corfu, 1991; Thurston et al., 1991). The early Hf isotopic data support this model and provide evidence that the North Caribou terrane contains no components significantly older than 3.0 Ga.

Other studies based on U–Pb age and Nd isotopic measurements have shown that the western Superior province contains a number of terranes with different histories. The restricted time span for igneous activity in the greenstone-dominated western part of the Wabigoon subprovince and the absence of older zircon inheritance led Davis et al. (1988) to suggest that this was a juvenile oceanic arc that began to form at 2.77 Ga and accreted at 2.70–2.71 Ga. A similar history has been found for the Shebandowan greenstone belt (Corfu and Stott, 1998, 1993b), which is co-extensive with the Wawa and Abitibi subprovinces to the east. In contrast, the Sachigo and Winnipeg River subprovinces contain abundant Mesoarchean rocks. The Winnipeg River subprovince contains some of the oldest rocks yet dated in the region, with gneisses as old as 3310 Ma (Melnyk et al., submitted) and Nd model ages extending back to 3.4 Ga (Henry et al., 2000; Dickin et al., 1990). The boundaries of these different terranes are not always coincident with subprovince boundaries. The reworked 3.0 Ga North Caribou terrane comprises parts of the Sachigo subprovince and probably extends into the northern margin of the Uchi subprovince. The south-central part of the Wabigoon subprovince is also suggested to have formed from reworking of a juvenile 3.0 Ga terrain (Davis and Jackson, 1988; Tomlinson

et al., 2003) while Nd isotopes from the north-central part show evidence for older Mesoarchean sources that may be correlative with rocks in the Winnipeg River subprovince (Tomlinson et al., 2003).

Mesoarchean terranes in the Superior province characteristically contain locally developed units of quartz-rich arenite. Dated detrital zircons from these units are all older than 2.8 Ga, pre-dating the most intense period of arc-related magmatism, which began at about 2750 Ma. Their detrital zircons generally reflect the ages of nearby Mesoarchean igneous rocks. These units are suggested to be indicative of an early period of continental stability and development of platform sequences (Thurston and Chivers, 1990).

Some of the most important evidence for tectonic processes comes from U–Pb ages of detrital zircons in sandstones and conglomerates from the greenstone belts and from metaturbidites that make up the supracrustal component of the Quetico and English River subprovinces and the Pontiac subprovince in the southeastern Superior province. Their detrital zircons constrain sediment deposition to the period 2.71–2.68 Ga (Davis, 1998, 2002; Davis et al., 1990). Depositional ages appear to become younger from north to south across the southern Superior province. They generally correspond to the early part of regional deformation in any given area and locally post-date calc-alkaline and tholeiitic volcanism by several million years (Davis, 1998, 2002). Based partly on this evidence, it has been proposed that the Superior province was built by accretion of arcs and continental fragments from the south over this time period (Percival and Williams, 1989). This process was coeval with emplacement of syn and late tectonic ‘sanukitoid suite’ plutons derived from melting of previously metasomatized mantle (Shirey and Hanson, 1984; Stern et al., 1990).

### 3. Analytical methods

Many of the samples were dated in previous studies by U–Pb analysis of zircon at the Royal Ontario Museum. In some cases washes from the U–Pb columns, which contain Zr and Hf, had been saved from the original studies. In others, new grains were picked from the abraded zircon fractions and analyzed for both U–Pb and Hf isotopes. Zr–Hf column wash solutions were dried down and converted to weak HNO<sub>3</sub>–HF

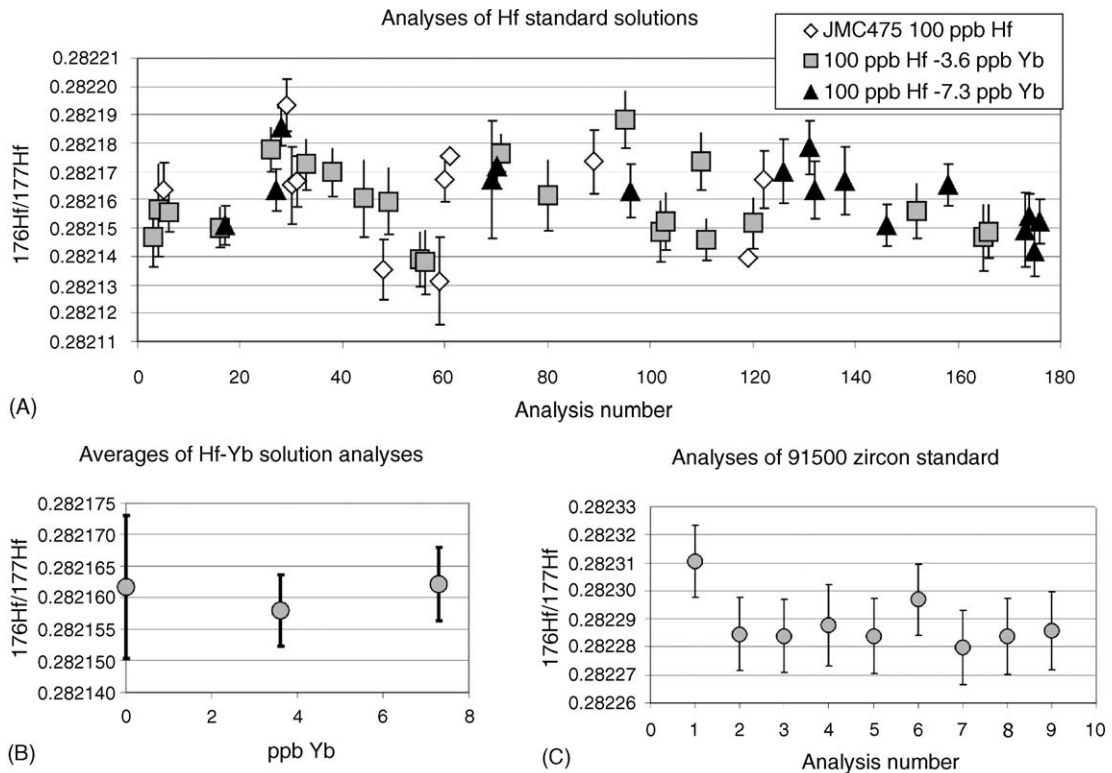


Fig. 2. (A) Measured values of Hf standards on the Plasma 54 instrument over the four-day period during which samples were measured. (B) Average values of  $^{176}\text{Hf}/^{177}\text{Hf}$  for standard solutions containing different Yb/Hf values. (C)  $\epsilon_{\text{Hf}}$  values measured for zircon standard 91500.

solutions, which were then aspirated directly into the plasma. Solutions were unspiked, and Lu/Hf ratios were determined directly by measuring the  $^{175}\text{Lu}$  and  $^{177}\text{Hf}$  isotopes using the Plasma 54 at the NERC lab in Keyworth, U.K. (Nowell and Parrish, 2001). Corrections were made to Hf isotopes for Lu and Yb isobars by monitoring the  $^{173}\text{Yb}$  and  $^{175}\text{Lu}$  peaks. The major correction to the  $^{176}\text{Hf}$  peak was for  $^{176}\text{Yb}$ . Sensitivity to the  $^{176}\text{Yb}$  correction was monitored by analyzing 100 ppb Hf solutions of JMC475. Different solutions containing 0 ppb Yb, 3.6 ppb Yb and 7.2 ppb Yb were used to test for bias to Hf isotopic measurements from the Yb correction (Fig. 2A). Averages of these separate standards are presented in Fig. 2B and show no systematic bias. Interference from REE-oxides was minimized by the use of a desolvating nebulizer. This is confirmed by the fact that  $^{180}\text{Hf}/^{177}\text{Hf}$  and  $^{178}\text{Hf}/^{177}\text{Hf}$  show no correlation with Lu/Hf.  $R^2$  values are less than 0.02 for  $^{176}\text{Lu}/^{177}\text{Hf}$  plotted against all other Hf isotopic ratios (all ratios reported in Table 2).

All errors are given at two standard deviations. Errors in  $\epsilon_{\text{Hf}}$  are a combination of internal and external errors. Although internal standard errors for  $^{176}\text{Hf}/^{177}\text{Hf}$  are generally less than  $\pm 0.2\epsilon$  unit for all but the smallest samples, values of the JMC475 standard showed fluctuations outside of measurement errors during some periods (Fig. 2A). The series of measurements was divided into twelve periods over four days in which sample measurements could be bracketed by standards measured under relatively uniform instrumental operating conditions. The average of standard measurements during each of these periods was used to normalize sample results relative to an assumed  $^{176}\text{Hf}/^{177}\text{Hf}$  value of 0.282160 for JMC475. These averages and the normalization factors are shown in Table 1 and are referenced to the Hf data in Table 2. The average of all 49 determinations of JMC475 is  $0.282160 \pm 0.000028$  (2 sigma).

Previous Hf isotopic studies have shown that Zr–Hf washes from the U–Pb columns preserve the true Lu/Hf

Table 1  
Normalization factors for analyses based on values measured for the JMC 475 standard

Norm. ref.	Run interval	JMC 475 measured	Errors 1 sig	Normalisation factors
1	3–17	0.282154	0.000006	1.000022
2	16–27	0.282161	0.000013	0.999998
3	31–44	0.282167	0.000005	0.999974
4	44–49	0.282152	0.000014	1.000029
5	49–55	0.282149	0.000014	1.000038
6	55–59	0.282136	0.000004	1.000085
7	60–89	0.282170	0.000005	0.999963
8	89–111	0.282164	0.000016	0.999987
9	119–120	0.282146	0.000009	1.000051
10	122–138	0.282169	0.000006	0.999968
11	138–146	0.282159	0.000011	1.000004
12	146–176	0.282152	0.000007	1.000029

Normalization Reference number is crossreferenced to Table 2. Run interval is the range of run numbers over which the normalization is applied (see Fig. 1A).

ratios of the samples (Amelin et al., 1999). However, inter-element fractionation in the plasma can amount to a deviation from the true value estimated at 3–15% by Nowell and Parrish (2001). Measurements of solutions from the 91500 zircon standard gave an average  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of  $0.000220 \pm 0.000052$ . A consistent value of  $0.000295 \pm 0.000030$  was measured for this standard by Amelin et al. (2000) and by Wiedenbeck et al. (1995). The Lu/Hf ratios are adjusted upward by a factor of  $1.34 \pm 0.40$  to allow for this bias and its error is propagated into the errors in  $\varepsilon_{\text{Hf}}$ . Normalized  $^{176}\text{Hf}/^{177}\text{Hf}$  values measured on solutions of the 91500 zircon standard are presented in Fig. 2C. Most of these analyses agree within error except for one outlier. The average  $^{176}\text{Hf}/^{177}\text{Hf}$  value of the nine measurements is  $0.282298 \pm 20$ , which becomes  $0.282289 \pm 20$  after normalization to the nearest JMC475 standard measurements. The values measured by Wiedenbeck et al. (1995), Amelin et al. (2000) and Goolaerts et al. (2004) are  $0.282302 \pm 8$ ,  $0.282317 \pm 28$ , and  $0.282301 \pm 8$ , respectively, after normalization to the average value of JMC475 found here. Our unnormalized value shows a better agreement, which suggests that short period instability may still bias the measurements to some extent.

## 4. Results

### 4.1. Calculation of $\varepsilon_{\text{Hf}}$ and model ages

The resistance of Archean zircon to isotopic exchange of Hf was evaluated by Corfu and Noble

(1992), who found that zircon fractions from uniform aged populations with variable but moderate discordance (<10%) have indistinguishable Hf isotopic ratios. This is to be expected since Hf is a relatively immobile element with a high concentration in zircon. In the present study, most of the Hf isotopic analysis were done on near-concordant zircon and are therefore likely to represent primary values.

Results of Hf isotopic measurements are given in Table 2. Except in the case of detrital and inherited zircons, most analyses were done on rocks with well-characterized ages based on multiple U–Pb zircon analyses. Previously unpublished U–Pb results are given in Table 3. Rock samples are given sequential reference numbers in Table 2. Those in boldface are from previously unpublished projects and are located on the map in Fig. 1. References to previously published data sets are given in Table 2. Samples are grouped in the same order in Tables 2 and 3.

Calculated values of  $\varepsilon_{\text{Hf}}$  are plotted on Figs. 3–5 against age. For Archean samples,  $\varepsilon_{\text{Hf}}$  depends strongly on the value chosen for the  $^{176}\text{Lu}$  decay constant because of its effect on the chondritic reference curve. In this work, we have adopted the value of  $1.865 \pm 0.015 \times 10^{-5} \text{ m.y.}^{-1}$  proposed by Scherer et al. (2001), based on U–Pb and Lu–Hf dating of mineral phases in terrestrial rocks. Results published by Corfu and Noble (1992) and Corfu and Stott (1993b, 1996) are lowered by 1  $\varepsilon_{\text{Hf}}$  unit after adjustment for accepted values of  $^{176}\text{Hf}/^{177}\text{Hf}$  ( $0.282772 \pm 29$ ) and  $^{176}\text{Lu}/^{177}\text{Hf}$  ( $0.0332 \pm 2$ ) in chondrites (Blichert-Toft and Albarède, 1997), as well as the decay constant and

Table 2  
Lu–Hf isotopic data on zircons from the western Superior province

Map Ref. <sup>a</sup>	Analysis	Sample	Rock	Geological Unit	Age (Ma)	Age Ref. <sup>a</sup>	<sup>176</sup> Lu/ <sup>177</sup> Hf	<sup>176</sup> Hf/ <sup>177</sup> Hf <i>i</i> (initial)	EHft	2 sig abs	TDM (Mafic)	TDM (Felsic)
Superior model												
Shebandowan subprovince												
1	dwd3186	C92-25	Rhyolite	Shebandowan belt	2722	1	0.001090	0.281159	4.1	1.5	2675	2694
Western Wabigoon subprovince												
<i>Southwest Kakagi Lake–Savant Lake volcanic belt</i>												
2	dwd3179	DD81-12	Qtz. Monzonite	Ottertail pluton	2685	u, 2	0.000486	0.281133	2.3	0.5	2785	2745
3	dwd3176	K76-30	Qtz. Monzonite	Taylor Lake stock	2693	u, 3	0.000385	0.281126	2.3	1.2	2796	2755
3	dwd3210	K76-30	Qtz. monzonite	Taylor Lake stock	2693	u, 3	0.000522	0.281129	2.4	1.0	2786	2749
4	dwd3178	DD81-29	Qtz. monzonite	Heronry pluton	2701	u, 4	0.000416	0.281139	2.9	0.5	2752	2732
5	dwd321	DD84-16	Qtz. diorite	Canoe Lake stock	2709	5	0.000365	0.281157	3.7	0.6	2694	2700
6	dwd320	DD84-19	Gnd.	High Lake stock, late	2709	5	0.000569	0.281117	2.3	0.7	2802	2765
7	dwd3212	DD81-16	Granodiorite	Aulneau bath., late	2710	u, 4	0.000568	0.281144	3.3	1.0	2728	2721
8	dwd3219	DD78-49	Rhyolite tuff	Stephen Lake Fm.	2711	u, 6	0.000629	0.281160	3.9	0.7	2683	2694
9	dwd3213	DD81-17	Tonalite	Aulneau bath., early	2717	u, 4	0.000529	0.281145	3.5	1.0	2715	2716
10	dwd285	DD84-15	Trondhjemite	Atikwa Lake pluton	2718	7	0.000519	0.281142	3.4	0.6	2724	2721
11	dwd3214	DD90-33	Rhyolite	Sunset Channel Fm.	2719	u, 8	0.000493	0.281156	3.9	0.6	2686	2699
12	dwd295	DD81-19	Felsic volcanic	Zigzag Island Fm.	2720	8	0.001284	0.281093	1.7	1.1	2851	2799
13	dwd521	DD86-7	QFP fragmental	Calm Lake, WGB	2722	2	0.001195	0.281137	3.4	1.0	2731	2727
14	dwd3211	DD81-30	Tonalite gneiss	Sabaskong batholith	2722	u, 6	0.000564	0.281127	3.0	0.6	2758	2744
14	dwd3177	DD81-30	Tonalite gneiss	Sabaskong batholith	2722	u, 6	0.000315	0.281138	3.4	0.5	2731	2727
15	dwd3184	DD85-9	Dacite volcanic	Shoal Lake	2727	u, 5	0.001890	0.281104	2.3	1.5	2814	2779
16	dwd518	DD86-4	Felsic volcanic	Mine Center	2728	2	0.001238	0.281122	3.0	1.1	2765	2750
17	dwd3215	DD78-24	Rhyolite	Dash Lake	2728	u, 6	0.000642	0.281141	3.6	0.7	2715	2720
18	dwd284	DD83-3	Trondhjemite	Lawrence Lake pluton	2730	7	0.000599	0.281138	3.6	0.7	2720	2724
19	dwd282	DD83-10	Qtz. Diorite	Mulcahy Lake	2732	7	0.000428	0.281145	3.9	0.6	2699	2712
20	dwd281	DD84-1	Gnd.	Straw Lake	2732	7	0.001062	0.281123	3.1	1.0	2759	2748
21	dwd3191	DD81-32	Qtz. diorite	Bluffpoint diorite	2732	u, 7	0.000493	0.281135	3.5	1.1	2726	2728
21	dwd3191A	DD81-32	Qtz. diorite	Bluffpoint diorite	2732	u, 7	0.000515	0.281136	3.6	0.6	2722	2726
<i>Northeast Kakagi Lake–Savant Lake volcanic belt</i>												
22	dwd3188	DD90-60	Qtz. Porphyry	Handy Lake	2701	u, 3	0.000588	0.281062	0.2	0.7	2956	2854
23	dwd313	DD83-11	Diorite clast	Kashawegama Lake	2704	9	0.000744	0.281065	0.4	0.8	2943	2848
24	dwd3217	DD78-18	Tonalite	Beidelman Bay pluton	2732	u, 11	0.001874	0.281065	1.0	1.5	2911	2840
25	dwd3189	DD90-62	Qtz. Porphyry	Hough Lake	2732	u, 3	0.001740	0.281067	1.1	1.7	2908	2838
26	dwd3194	JH82-4	Rhyolite	S. Sturgeon Lake volc	2735	u, 10	0.001219	0.281085	1.8	1.5	2855	2807
27	dwd3216	DD78-32	Dacite volcanic	Handy Lake Gp., base	2745	u, 11	0.000414	0.281140	4.0	0.6	2698	2717
28	dwd3181	DD84-2	Felsic volcanic	Fourbay Lake	2775	u, 9	0.000555	0.281079	2.5	0.6	2826	2806
28	dwd3181A	DD84-2	Felsic volcanic	Fourbay Lake	2775	u, 9	0.000516	0.281096	3.1	0.6	2779	2778
29	dwd3208	OGS88-1	Quartz arenite	Jutten Group	3256	u, 12	0.000948	0.280603	−3.2	1.3	3534	3423
Central Wabigoon subprovince												
<i>Marmion Terrane</i>												
30	dwd439	DD85-2	Gabbro peg.	Lac des Iles	2693	u	0.000449	0.281139	2.7	0.6	2760	2733
31	dwd483	S78-20	Qtz. Monzonite	Jackfish Lake pluton	2698	u	0.000265	0.281120	2.2	0.5	2806	2763
33	dwd490	DD81-7	Gnd. Gneiss	Hillyer Creek dome	2750	u	0.000345	0.281026	0.0	0.6	2997	2898
34	dwd454	DD85-18	Foliated tonalite	Hardtack Lake	2932	u	0.000457	0.280945	1.4	0.6	3002	2974
35	dwd3182	DD88-15	Rhyolite	Finlayson Lake belt	2934	u	0.000543	0.280946	1.5	0.6	2998	2972
36	dwd491	DD84-6	Altered tonalite	Marmion Batholith	2957	u	0.000384	0.280925	1.2	0.6	3027	2999
37	dwd367	DD84-10	Tonalite gneiss	Marmion Batholith	2978	13	0.000427	0.280926	1.8	0.6	2998	2990
38	dwd384	DD85-17	Qtz. Diorite	Marmion Batholith	3000	u	0.000426	0.280940	2.8	0.6	2936	2961
39	dwd368	DD84-9	Felsic volcanic	Lumbly Lake belt	3000	13	0.000758	0.280927	2.3	0.9	2972	2983
40	dwd299	DD84-8	Felsic volcanic	Lumbly Lake belt	3000	13	0.000673	0.280940	2.8	0.7	2936	2962

<i>North-central area</i>												
41	dwd3180	DD96-10	Qtz. monzonite	Roaring River complex	2697	u	0.000213	0.281111	1.8	0.4	2831	2777
42	dwd3190	98KYT-37	Rhyolite	N. Obonga Lake	2707	u, 14	0.000456	0.281106	1.9	1.1	2832	2782
43	dwd459	DD85-28	Felsic volcanic	Obonga Lake belt	2726	14	0.000829	0.281114	2.6	1.0	2789	2764
44	dwd453	DD85-29	Felsic volcanic	Obonga Lake belt	2732	14	0.000706	0.281167	4.6	0.8	2642	2678
45	dwd3024	DD96-11	Foliated gnd.	Roaring River complex	2739	u	0.000807	0.281074	1.5	1.0	2879	2823
46	dwd475	DD83-20	Tonalite	Caribou Lake	3075	9	0.000696	0.280739	-2.6	1.3	3382	3260
<i>Winnipeg River subprovince</i>												
47	dwd3193	DD96-14	Tonalite gneiss	Winnipeg River belt	2721	u, 15	0.000445	0.280913	-4.7	1.2	3329	3087
48	dwd474	DD81-18	Tonalite gneiss	Tannis Lake	3050	9	0.000388	0.280756	-2.6	1.2	3367	3240
49	dwd3207	C83-32HS	Gnd. gneiss	Cedar Lake pluton	3188	u, 16	0.000901	0.280588	-5.3	1.3	3650	3466
49	dwd3206	C83-32HS	Gnd. gneiss	Cedar Lake pluton	3225	u, 16	0.000832	0.280573	-5.0	1.2	3647	3479
<i>Bird River subprovince</i>												
50	dwd3185	DD85-20	Felsic porphyry	Separation Lake belt	2723	u	0.000877	0.281012	-1.1	0.8	3063	2927
<i>English River subprovince</i>												
51	dwd3192	C87-39	Tonalite	English River belt	2688	u, 17	0.000291	0.281003	-2.2	1.1	3129	2953
52	dwd3218	C88-29	Tonalite	Bluffy L. diorite	2698	u, 17	0.000344	0.281130	2.5	0.6	2778	2746
53	dwd3187	97GRS700	Rhyolite	Melchett Lake belt	2726	18	0.000822	0.281147	3.8	0.7	2700	2711
<i>Sachigo subprovince</i>												
<i>Igneous rocks</i>												
54	dwd304	DD82-1	Felsic volcanic	Oxford Lake group	2709	u	0.000550	0.281122	2.5	0.7	2787	2756
55	dwd3068	88GRS501	Dacite tuff	Ellard Lake	2732	19	0.000485	0.281031	-0.2	1.1	3002	2895
56	dwd458	DD85-26	Tonalite gneiss	DeBliques Lake	2860	12	0.000438	0.281007	1.9	1.0	2920	2896
57	dwd457	DD85-21	Trondhjemite	N. Caribou Lake Bath.	2870	12	0.000551	0.280987	1.5	0.9	2960	2924
58	dwd3183	DD87-20	Rhyolite	Sandy Lake belt	2945	19	0.000543	0.280962	2.3	0.6	2940	2942
59	dwd449	DD85-23	Felsic volcanic	Eyapamikama Lake	2980	12	0.000492	0.280920	1.6	0.7	3011	2999
60	dwd456	DD85-27	Tonalite	Weagamow Bath.	2990	12	0.000517	0.280911	1.5	0.9	3024	3011
61	dwd455	DD85-22	Trond. Clast	Eyapamikama Lake	3009	12	0.000856	0.280908	1.9	1.1	3012	3011
<i>Quartz arenite detrital zircons</i>												
62	dwd3071	88GRS114	Qtzite clasts	Heaton Lake	2853	19	0.000511	0.281005	1.7	0.9	2934	2902
63	dwd3090	88GRS408	Pebbly arkose	Sandy Lake	2905	19	0.000719	0.280997	2.6	2.2	2896	2899
64	dwd3091	88GRS398	Qtzite boulder	Sandy Lake	2917	19	0.001432	0.281076	5.7	3.2	2671	2769
62	dwd3072	88GRS114	Qtzite clasts	Heaton Lake	2980	19	0.000298	0.280953	2.8	0.8	2924	2946
62	dwd3070	88GRS114	Qtzite clasts	Heaton Lake	2981	19	0.000658	0.280933	2.1	0.9	2978	2979
<i>Quetico subprovince detrital zircons</i>												
65	dwd3205	Q98-10	Sandstone	Quetico, Rainy Lake	2700	u	0.000553	0.281085	1.0	1.2	2896	2818
65	dwd3204	Q98-10	Sandstone	Quetico, Rainy Lake	2700	u	0.000618	0.280963	-3.4	0.9	3220	3013
65	dwd3201	Q98-10	Sandstone	Quetico, Rainy Lake	2702	u	0.000496	0.281053	-0.1	0.6	2978	2868

Table 2 (Continued)

Map Ref. <sup>a</sup>	Analysis	Sample	Rock	Geological Unit	Age (Ma)	Age Ref. <sup>a</sup>	<sup>176</sup> Lu/ <sup>177</sup> Hf	<sup>176</sup> Hf/ <sup>177</sup> Hf i (initial)	EHft	2 sig abs	TDM (Mafic)	TDM (Felsic)
Superior model												
66	dwd3195	DD88-18	Sandstone	Quetico belt, south	2706	u	0.000318	0.281133	2.8	1.1	2761	2739
65	dwd3173	Q98-10	Sandstone	Quetico, Rainy Lake	2708	u	0.000706	0.281055	0.1	1.3	2966	2863
67	dwd3167	Q98-4	Sandstone	Quetico, Rainy Lake	2716	u	0.000809	0.280995	-1.9	1.3	3117	2957
65	dwd3171	Q98-10	Sandstone	Quetico, Rainy Lake	2719	u	0.000483	0.280983	-2.2	1.2	3146	2976
66	dwd3197	DD88-18	Sandstone	Quetico belt, south	2725	u	0.000784	0.281071	1.1	0.9	2905	2833
66	dwd3198	DD88-18	Sandstone	Quetico belt, south	2740	u	0.000290	0.281094	2.2	0.6	2826	2791
66	dwd3199	DD88-18	Sandstone	Quetico belt, south	2742	u	0.000289	0.281053	0.8	0.7	2932	2856
65	dwd3202	Q98-10	Sandstone	Quetico, Rainy Lake	2776	u	0.000424	0.281003	-0.2	0.6	3026	2926
66	dwd3196	DD88-18	Sandstone	Quetico belt, south	2790	u	0.001552	0.281044	1.6	1.6	2902	2857
65	dwd3203	Q98-10	Sandstone	Quetico, Rainy Lake	2812	u	0.000398	0.281047	2.2	0.6	2869	2846
67	dwd3168	Q98-4	Sandstone	Quetico, Rainy Lake	2888	u	0.000264	0.280957	0.8	1.2	3021	2968
65	dwd3175	Q98-10	Sandstone	Quetico, Rainy Lake	2935	u	0.000487	0.280973	2.5	1.3	2922	2927
65	dwd3174	Q98-10	Sandstone	Quetico, Rainy Lake	3031	u	0.000387	0.280701	-5.0	1.2	3532	3333
67	dwd3169	Q98-4	Sandstone	Quetico, Rainy Lake	3235	u	0.001138	0.280507	-7.1	2.0	3808	3580
Analysis	Sample	<sup>179</sup> Hf/ <sup>177</sup> Hf (measured)	2 sig abs	<sup>180</sup> Hf/ <sup>177</sup> Hf (Mass Corr. <sup>b</sup> )	2 sig abs	<sup>178</sup> Hf/ <sup>177</sup> Hf (Mass Corr. <sup>b</sup> )	2 sig abs	<sup>176</sup> Hf/ <sup>177</sup> Hf (Mass Corr. <sup>b</sup> )	2 sig abs	Norm. Ref. <sup>c</sup>		
Shebandowan subprovince												
dwd3186	C92-25	0.75065	0.00013	1.88664	0.00048	1.46733	0.00012	0.281211	0.000033	6		
Western Wabigoon subprovince												
<i>Southwest Kakagi Lake–Savant Lake volcanic belt</i>												
dwd3179	DD81-12	0.74926	0.00002	1.88735	0.00004	1.46765	0.00002	0.281177	0.000004	7		
dwd3176	K76-30	0.74940	0.00003	1.88685	0.00009	1.46744	0.00003	0.281156	0.000010	8		
dwd3210	K76-30	0.75229	0.00002	1.88669	0.00005	1.46740	0.00002	0.281166	0.000007	2		
dwd3178	DD81-29	0.74925	0.00001	1.88742	0.00004	1.46769	0.00001	0.281178	0.000004	7		
dwd321	DD84-16	0.75107	0.00002	1.88699	0.00005	1.46742	0.00002	0.281174	0.000004	12		
dwd320	DD84-19	0.75120	0.00002	1.88695	0.00003	1.46754	0.00001	0.281148	0.000005	12		
dwd3212	DD81-16	0.75204	0.00003	1.88660	0.00007	1.46738	0.00003	0.281184	0.000008	2		
dwd3219	DD78-49	0.75136	0.00003	1.88668	0.00006	1.46740	0.00002	0.281198	0.000008	1		
dwd3213	DD81-17	0.75209	0.00003	1.88667	0.00005	1.46738	0.00002	0.281183	0.000006	2		
dwd285	DD84-15	0.75134	0.00002	1.88671	0.00006	1.46748	0.00002	0.281170	0.000006	12		
dwd3214	DD90-33	0.75221	0.00002	1.88666	0.00004	1.46738	0.00001	0.281184	0.000005	1		
dwd295	DD81-19	0.75163	0.00003	1.88676	0.00010	1.46750	0.00004	0.281175	0.000011	12		
dwd521	DD86-7	0.75129	0.00005	1.88662	0.00007	1.46741	0.00003	0.281215	0.000008	1		
dwd3211	DD81-30	0.75223	0.00002	1.88668	0.00004	1.46739	0.00001	0.281174	0.000007	3		
dwd3177	DD81-30	0.74932	0.00001	1.88736	0.00004	1.46765	0.00001	0.281170	0.000007	7		
dwd3184	DD85-9	0.74908	0.00004	1.88771	0.00016	1.46779	0.00006	0.281247	0.000014	7		
dwd518	DD86-4	0.75083	0.00002	1.88742	0.00005	1.46765	0.00002	0.281218	0.000010	10		
dwd3215	DD78-24	0.75198	0.00002	1.88669	0.00004	1.46739	0.00001	0.281180	0.000005	1		
dwd284	DD83-3	0.75125	0.00002	1.88699	0.00005	1.46761	0.00003	0.281172	0.000008	12		
dwd282	DD83-10	0.75158	0.00002	1.88666	0.00005	1.46747	0.00002	0.281167	0.000007	12		
dwd281	DD84-1	0.75155	0.00002	1.88688	0.00005	1.46759	0.00002	0.281189	0.000008	12		
dwd3191	DD81-32	0.75068	0.00005	1.88649	0.00005	1.46731	0.00002	0.281159	0.000007	5		
dwd3191A	DD81-32	0.74878	0.00002	1.88744	0.00005	1.46770	0.00002	0.281183	0.000006	7		
<i>Northeast Kakagi Lake–Savant Lake volcanic belt</i>												
dwd3188	DD90-60	0.74929	0.00003	1.88657	0.00008	1.46736	0.00004	0.281079	0.000013	6		
dwd313	DD83-11	0.75106	0.00005	1.88801	0.00025	1.46800	0.00011	0.281109	0.000007	12		
dwd3217	DD78-18	0.75189	0.00002	1.88667	0.00003	1.46741	0.00001	0.281191	0.000004	1		
dwd3189	DD90-62	0.75116	0.00007	1.88644	0.00013	1.46731	0.00004	0.281178	0.000014	5		
dwd3194	JH82-4	0.75096	0.00006	1.88659	0.00010	1.46734	0.00004	0.281163	0.000020	4		
dwd3216	DD78-32	0.75171	0.00002	1.88667	0.00007	1.46742	0.00002	0.281163	0.000008	1		
dwd3181	DD84-2	0.74933	0.00001	1.88707	0.00004	1.46755	0.00001	0.281129	0.000007	7		
dwd3181A	DD84-2	0.75131	0.00002	1.88692	0.00005	1.46756	0.00002	0.281125	0.000004	12		
dwd3208	OGS88-1	0.75224	0.00003	1.88662	0.00006	1.46740	0.00003	0.280683	0.000012	2		

Central Wabigoon subprovince										
<i>Marmion Terrane</i>										
dwd439	DD85-2	0.75054	0.00004	1.88703	0.00004	1.46746	0.00001	0.281162	0.000006	12
dwd483	S78-20	0.75042	0.00002	1.88730	0.00005	1.46762	0.00002	0.281147	0.000008	10
dwd490	DD81-7	0.75069	0.00002	1.88742	0.00005	1.46767	0.00002	0.281059	0.000010	10
dwd454	DD85-18	0.75030	0.00003	1.88695	0.00005	1.46745	0.00002	0.280971	0.000004	12
dwd3182	DD88-15	0.74886	0.00002	1.88705	0.00006	1.46755	0.00002	0.280997	0.000008	7
dwd491	DD84-6	0.75015	0.00002	1.88735	0.00005	1.46761	0.00002	0.280963	0.000007	10
dwd367	DD84-10	0.75103	0.00003	1.88691	0.00007	1.46742	0.00003	0.280951	0.000007	12
dwd384	DD85-17	0.75073	0.00003	1.88746	0.00011	1.46765	0.00005	0.280965	0.000004	12
dwd368	DD84-9	0.750771	0.00003	1.887828	0.00007	1.467788	0.00003	0.280977	0.000010	12
dwd299	DD84-8	0.75133	0.00002	1.88698	0.00004	1.46756	0.00002	0.280984	0.000005	12
<i>North-central area</i>										
dwd3180	DD96-10	0.74919	0.00001	1.88731	0.00003	1.46764	0.00002	0.281136	0.000004	7
dwd3190	98KYT-37	0.75079	0.00004	1.88649	0.00008	1.46730	0.00003	0.281127	0.000008	5
dwd459	DD85-28	0.75054	0.00003	1.88737	0.00005	1.46764	0.00002	0.281171	0.000008	11
dwd453	DD85-29	0.74967	0.00005	1.88787	0.00011	1.46781	0.00005	0.281208	0.000007	12
dwd3024	DD96-11	0.75015	0.00004	1.88734	0.00008	1.46765	0.00003	0.281117	0.000014	9
dwd475	DD83-20	0.74916	0.00002	1.88736	0.00005	1.46766	0.00002	0.280798	0.000009	8
Winnipeg River subprovince										
dwd3193	DD96-14	0.75023	0.00010	1.88656	0.00018	1.46728	0.00004	0.280933	0.000014	5
dwd474	DD81-18	0.74906	0.00001	1.88716	0.00003	1.46758	0.00001	0.280790	0.000007	8
dwd3207	C83-32HS	0.75223	0.00003	1.88665	0.00008	1.46738	0.00003	0.280663	0.000010	2
dwd3206	C83-32HS	0.75233	0.00002	1.88668	0.00005	1.46739	0.00002	0.280643	0.000007	2
Bird River subprovince										
dwd3185	DD85-20	0.74782	0.00003	1.88795	0.00008	1.46793	0.00003	0.281084	0.000008	7
English River subprovince										
dwd3192	C87-39	0.74988	0.00005	1.88653	0.00011	1.46733	0.00003	0.281012	0.000008	5
dwd3218	C88-29	0.75170	0.00003	1.88667	0.00020	1.46738	0.00002	0.281148	0.000008	1
dwd3187	97GRS700	0.74869	0.00003	1.88664	0.00007	1.46737	0.00002	0.281181	0.000008	6
Sachigo subprovince										
<i>Igneous rocks</i>										
dwd304	DD82-1	0.75138	0.00003	1.88692	0.00008	1.46753	0.00003	0.281152	0.000010	12
dwd3068	88GRS501	0.74934	0.00004	1.88757	0.00012	1.46774	0.00005	0.281051	0.000022	9
dwd458	DD85-26	0.75080	0.00002	1.88732	0.00007	1.46762	0.00003	0.281038	0.000013	11
dwd457	DD85-21	0.75058	0.00002	1.88720	0.00003	1.46757	0.00001	0.281027	0.000006	11
dwd3183	DD87-20	0.74890	0.00002	1.88721	0.00007	1.46758	0.00003	0.281014	0.000007	7
dwd449	DD85-23	0.74981	0.00003	1.88719	0.00008	1.46754	0.00003	0.280950	0.000010	12
dwd456	DD85-27	0.75044	0.00002	1.88721	0.00004	1.46757	0.00002	0.280950	0.000006	11
dwd455	DD85-22	0.75084	0.00001	1.88717	0.00003	1.46756	0.00001	0.280973	0.000005	11
<i>Quartz arenite detrital zircons</i>										
dwd3071	88GRS114	0.75011	0.00002	1.88763	0.00007	1.46778	0.00003	0.281028	0.000013	9
dwd3090	88GRS408	0.74780	0.00007	1.88797	0.00025	1.46785	0.00008	0.281054	0.000049	8
dwd3091	88GRS398	0.74866	0.00008	1.88784	0.00033	1.46777	0.00009	0.281187	0.000079	8
dwd3072	88GRS114	0.74870	0.00003	1.88725	0.00008	1.46760	0.00005	0.280962	0.000015	9
dwd3070	88GRS114	0.74966	0.00002	1.88721	0.00008	1.46758	0.00003	0.280969	0.000010	9
Quetico subprovince detrital zircons										
dwd3205	Q98-10	0.75241	0.00003	1.88673	0.00009	1.46743	0.00003	0.281124	0.000017	2
dwd3204	Q98-10	0.74978	0.00003	1.88661	0.00008	1.46737	0.00004	0.281013	0.000020	3

Table 2 (Continued)

Analysis	Sample	$^{176}\text{Hf}/^{177}\text{Hf}$ (measured)	2 sig abs	$^{180}\text{Hf}/^{177}\text{Hf}$ (Mass Corr <sup>b</sup> )	2 sig abs	$^{178}\text{Hf}/^{177}\text{Hf}$ (Mass Corr <sup>b</sup> )	2 sig abs	$^{176}\text{Hf}/^{177}\text{Hf}$ (Mass Corr <sup>b</sup> )	2 sig abs	Norm. Ref. <sup>c</sup>
dwd3201	Q98-10	0.75040	0.00007	1.88650	0.00008	1.46734	0.00002	0.281095	0.000007	3
dwd3195	DD88-18	0.75111	0.00004	1.88654	0.00006	1.46735	0.00002	0.281147	0.000011	4
dwd3173	Q98-10	0.74886	0.00003	1.88728	0.00008	1.46765	0.00003	0.281108	0.000013	8
dwd3167	Q98-4	0.74868	0.00002	1.88731	0.00006	1.46764	0.00002	0.281055	0.000008	8
dwd3171	Q98-10	0.74874	0.00003	1.88720	0.00005	1.46759	0.00002	0.281020	0.000008	8
dwd3197	DD88-18	0.75109	0.00005	1.88642	0.00009	1.46734	0.00003	0.281133	0.000016	3
dwd3198	DD88-18	0.75099	0.00005	1.88658	0.00008	1.46736	0.00003	0.281122	0.000013	3
dwd3199	DD88-18	0.75079	0.00004	1.88667	0.00010	1.46734	0.00004	0.281081	0.000016	3
dwd3202	Q98-10	0.75001	0.00003	1.88653	0.00007	1.46731	0.00002	0.281041	0.000011	3
dwd3196	DD88-18	0.75092	0.00005	1.88660	0.00009	1.46733	0.00004	0.281147	0.000015	4
dwd3203	Q98-10	0.74983	0.00003	1.88648	0.00008	1.46729	0.00003	0.281083	0.000011	3
dwd3168	Q98-4	0.74874	0.00003	1.88723	0.00007	1.46758	0.00002	0.280980	0.000012	8
dwd3175	Q98-10	0.74939	0.00003	1.88749	0.00009	1.46775	0.00004	0.281014	0.000015	8
dwd3174	Q98-10	0.74930	0.00003	1.88731	0.00007	1.46759	0.00002	0.280735	0.000012	8
dwd3169	Q98-4	0.74856	0.00004	1.88731	0.00011	1.46754	0.00005	0.280606	0.000037	8

<sup>a</sup> Map Ref.: Sample numbers in bold are located on Fig. 1. Others are located in their referenced publications. Age Ref.: u—unpublished analysis, U—Pb data are given in Table 3. More extensive U—Pb data are presented in numbered references: 1. Corfu and Stott, 1998; 2. Davis et al., 1989; 3. Davis, 1995; 4. Davis and Edwards, 1986; 5. Davis and Smith, 1991; 6. Davis and Edwards, 1982; 7. Davis and Edwards, 1985; 8. Ayer and Davis, 1997; 9. Davis et al., 1988; 10. Davis et al., 1985; 11. Davis and Trowell, 1982; 12. Davis and Moore, 1991; 13. Davis and Jackson, 1988; 14. Tomlinson et al., 2002; 15. Cruden et al., 1997; 16. Corfu, 1988; 17. Corfu et al., 1995; 18. Davis, 1999; 19. Davis and Stott, 2002.

<sup>b</sup> Mass Corr.: Corrected for exponential mass fractionation assuming true  $^{179}\text{Hf}/^{177}\text{Hf}=0.7325$ .

<sup>c</sup> Norm. Ref.: Normalization values based on JMC475 are given in Table 1.

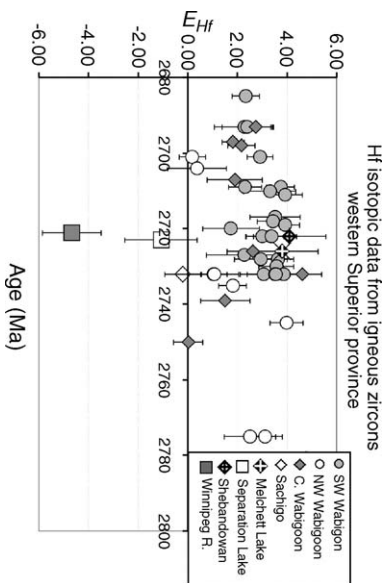


Fig. 3. Age vs.  $\epsilon_{\text{Hf}}$  for late Archean zircons from the western Superior transect area.

normalization value for JMC475 chosen in the present work. Differences in  $\epsilon_{\text{Hf}}$  values for zircons of the same age are only weakly dependent on the assumed decay constant so the choice of decay constant is of relatively small importance when the data are used for terrane characterization. However, accurate knowledge of the absolute values for  $\epsilon_{\text{Hf}}$  is important for quantifying the amount of crustal contamination and for determining the degree of mantle depletion in the early Earth. Discussion of the choice of decay constant and consequences of using alternative proposed values is presented in Section 5.3 below.

The Lu—Hf ratio in zircon is highly fractionated relative to the magma from which it crystallized. Therefore, model ages must be determined by using an inferred

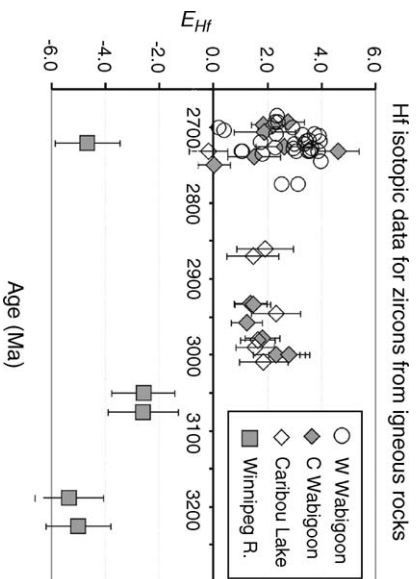


Fig. 4. Age vs.  $\epsilon_{\text{Hf}}$  for middle and late Archean zircons from the western and central Wabigoon, Winnipeg River and Sachigo sub-provinces.

Table 3

## U–Pb isotopic data on zircon analyzed for Hf isotopes from the western Superior province

Analysis no.	Sample	Wt. (mg)	U (ppm)	Th/U	PbCom (pg)	<sup>207</sup> Pb/ <sup>204</sup> Pb	<sup>206</sup> Pb/ <sup>238</sup> U	2 sig	<sup>207</sup> Pb/ <sup>235</sup> U	2 sig	<sup>207</sup> Pb/ <sup>206</sup> Pb	2 sig	Disc. (%)	Correl. coeff.
1. Shebandowan subprovince														
dwd3186	C92-25	0.017	63	0.50	0.7	10405	0.5274	0.0016	13.645	0.045	2721.7	1.7	−0.4	0.9517
Western Wabigoon subprovince														
2. Southwest Kakagi Lake–Savatt Lake volcanic belt														
dwd3179	DD81-12	0.048	72	0.89	3.6	5789	0.5124	0.0014	12.970	0.038	2685.3	1.7	0.8	0.9328
dwd3176	K76-30	0.007	224	0.81	0.7	13722	0.5166	0.0013	13.135	0.035	2692.8	1.8	0.4	0.9122
dwd3210	K76-30	0.030	262	0.82	24.5	1712	0.4942	0.0025	12.553	0.065	2691.4	2.1	4.6	0.9705
dwd3178	DD81-29	0.019	135	0.69	2.3	6926	0.5107	0.0025	13.051	0.066	2701.4	1.4	1.9	0.9858
dwd3212	DD81-16	0.005	213	0.50	3.4	1955	0.5146	0.0012	13.116	0.032	2696.9	2.2	0.9	0.8394
dwd3219	DD78-49	0.015	75	0.77	1.7	4232	0.5232	0.0012	13.446	0.034	2710.5	2.0	−0.1	0.8795
dwd3213	DD81-17	0.011	79	0.38	4.0	1363	0.5217	0.0013	13.449	0.038	2715.7	1.8	0.4	0.9228
dwd3214	DD90-33	0.030	57	0.56	1.5	7226	0.5205	0.0018	13.427	0.048	2716.7	1.7	0.7	0.9578
dwd3211	DD81-30	0.026	169	0.21	40.2	476	0.4022	0.0021	10.335	0.055	2710.3	2.5	23.0	0.9603
dwd3177	DD81-30	0.016	63	0.23	9.8	655	0.5198	0.0026	13.455	0.071	2722.3	2.3	1.1	0.9655
dwd3184	DD85-9	0.011	197	0.50	2.5	5520	0.5187	0.0039	13.464	0.094	2727.0	5.2	1.5	0.9089
dwd3215	DD78-24	0.027	86	0.35	195.6	90.71	0.5257	0.0016	13.641	0.118	2726.4	10.9	0.1	0.7693
dwd3191	DD81-32	0.062	43	0.64	2.1	8090	0.5271	0.0013	13.724	0.038	2732.1	1.7	0.1	0.9300
3. Northeast Kakagi Lake–Savatt Lake volcanic belt														
dwd3188	DD90-60	0.010	87	0.67	3.1	1763	0.5134	0.0030	13.120	0.079	2701.2	1.9	1.4	0.9820
dwd3217	DD78-18	0.054	384	0.85	615.5	222	0.5132	0.0025	13.179	0.072	2709.5	5.6	1.8	0.7897
dwd3189	DD90-62	0.007	221	0.65	2.9	3436	0.5259	0.0017	13.690	0.044	2731.8	2.6	0.3	0.8800
dwd3194	JH82-4	0.018	13	0.51	0.8	1979	0.5242	0.0019	13.660	0.053	2733.3	2.1	0.7	0.9445
dwd3216	DD78-32	0.035	100	0.39	388.2	70.21	0.4953	0.0025	12.979	0.158	2742.7	15.3	6.6	0.7133
dwd3181	DD84-2	0.028	97	0.52	0.7	13367	0.2846	0.0057	7.605	0.153	2774.9	2.0	47.1	0.9982
dwd3208	OGS88-1	0.003	74	0.98	2.4	1039	0.6533	0.0020	23.553	0.078	3255.7	2.2	0.6	0.9111
Central Wabigoon subprovince														
4. Marmion Terrane														
dwd439	DD85-2	0.068	148	1.00	19.2	3207	0.51537	0.0018	13.0782	0.047	2689.7	2.1	0.5	0.9336
dwd483	S78-20	0.100	102	0.88	20.7	3043	0.51727	0.0018	13.1748	0.047	2695.8	2.1	0.4	0.9342
dwd490	DD81-7	0.015	56	0.34	5.35	1036	0.53191	0.0026	14.0212	0.071	2752.3	2.3	0.1	0.9592
dwd454	DD85-18	0.042	110	0.44	810.3	60.23	0.57185	0.0028	16.8272	0.243	2931.7	17.2	0.7	0.8462
dwd3182	DD88-15	0.016	70	0.47	0.7	12019	0.5743	0.0022	16.924	0.069	2934.0	1.5	0.4	0.9738
dwd491	DD84-6	0.027	34	0.58	6.35	1180	0.57747	0.0028	17.2532	0.087	2956.2	2.2	0.8	0.9622
dwd384	DD85-17	0.240	52	0.46	19.45	5351	0.58756	0.0035	18.0129	0.110	2997.8	2.1	0.8	0.9774
5. North-central area														
dwd3180	DD96-10	0.075	124	1.09	4.0	14276	0.5184	0.0012	13.213	0.035	2696.8	1.5	0.2	0.9433
dwd3190	98KYT-37	0.008	133	0.72	8.7	770	0.5191	0.0017	13.310	0.046	2706.8	2.2	0.5	0.9207
dwd3024	DD96-11	0.010	28	0.71	1.3	1410	0.5286	0.0018	13.819	0.051	2738.9	2.0	0.2	0.9448
6. Winnipeg River subprovince														
dwd3193	DD96-14	0.007	224	0.49	2.7	3585	0.5126	0.0016	13.252	0.043	2720.5	2.2	2.4	0.9150
dwd3207	C83-32HS	0.004	310	0.49	1.5	8579	0.6346	0.0022	21.924	0.080	3188.4	1.5	0.8	0.9672
dwd3206	C83-32HS	0.007	380	0.56	5.4	4843	0.5927	0.0023	20.961	0.083	3225.3	2.2	8.7	0.9388
7. Bird River subprovince														
dwd3185	DD95-20	0.013	331	0.53	1.3	21839	0.5253	0.0012	13.600	0.035	2722.7	1.6	0.0	0.9256
8. English River subprovince														
dwd3192	C87-39	0.017	267	0.62	6.4	4319	0.5108	0.0013	12.949	0.036	2688.0	1.7	1.3	0.9284
dwd3218	C88-29	0.010	397	0.83	3.8	6486	0.5201	0.0039	13.290	0.100	2701.2	2.9	0.1	0.9721
dwd3187	97GRS700	0.022	72	0.55	0.8	13045	0.5249	0.0030	13.613	0.080	2725.6	1.7	0.3	0.9843
Sachigo subprovince														
9. Igneous rocks														
dwd304	DD82-1	0.085	151	0.47	196.3	371	0.5201	0.0021	13.322	0.052	2705.0	4.3	0.2	0.7844
dwd3068	88GRS501	0.010	22	0.79	0.9	1544	0.5251	0.0016	13.672	0.044	2732.0	2.1	0.5	0.9208
dwd458	DD85-26	0.004	287	0.25	5.5	1527	0.5553	0.0028	15.589	0.078	2855.3	2.7	0.4	0.9441
dwd457	DD85-21	0.023	72	0.42	5.6	2184	0.5585	0.0020	15.810	0.057	2868.9	2.7	0.4	0.8961
dwd3183	DD87-20	0.010	289	0.58	1.4	16218	0.5768	0.0042	17.114	0.120	2945.0	3.9	0.4	0.9428
dwd449	DD85-23	0.041	97	0.91	15.0	2205	0.5866	0.0020	17.791	0.064	2980.5	2.1	0.2	0.9309
dwd456	DD85-27	0.035	159	0.68	8.0	5803	0.5873	0.0020	17.911	0.064	2989.3	2.1	0.5	0.9344
dwd455	DD85-22	0.048	139	0.54	8.7	6011	0.5628	0.0020	16.834	0.060	2958.2	2.1	3.4	0.9347

Table 3 (Continued)

Analysis no.	Sample	Wt. (mg)	U (ppm)	Th/U	PbCom (pg)	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{238}\text{U}$	2 sig	$^{207}\text{Pb}/^{235}\text{U}$	2 sig	$^{207}\text{Pb}/^{206}\text{Pb}$	2 sig	Disc. (%)	Correl. coeff.
10. Quartz arenite detrital zircons														
dwd3071	88GRS114	0.020	12	0.49	1.8	1014	0.5530	0.0026	15.504	0.075	2853.1	1.9	0.7	0.9697
dwd3090	88GRS408	0.008	7	1.05	1.2	380	0.5559	0.0025	16.086	0.108	2904.7	6.3	2.3	0.8314
dwd3091	88GRS398	0.008	13	0.49	0.5	1448	0.5653	0.0024	16.488	0.065	2917.4	4.4	1.2	0.7783
dwd3072	88GRS114	0.010	73	1.01	0.6	10146	0.5867	0.0020	17.791	0.066	2980.1	1.5	0.2	0.9681
dwd3070	88GRS114	0.020	63	0.74	6.8	1543	0.5857	0.0028	17.773	0.087	2981.2	1.7	0.4	0.9773
11. Quetico subprovince detrital zircons														
dwd3205	Q-10	0.001	318	0.90	0.6	3181	0.5155	0.0016	13.166	0.043	2700.3	2.1	0.9	0.9210
dwd3204	Q-10	0.002	182	0.83	0.5	4711	0.5161	0.0018	13.180	0.048	2700.1	1.8	0.8	0.9515
dwd3201	Q-10	0.009	152	1.11	3.2	2642	0.5129	0.0016	13.110	0.043	2701.5	1.9	1.5	0.9390
dwd3195	DD88-18	0.005	64	1.21	1.0	2112	0.5200	0.0016	13.323	0.043	2705.5	2.1	0.3	0.9225
dwd3173	Q10-98	0.005	49	0.56	4.3	369	0.5159	0.0016	13.241	0.049	2708.3	3.1	1.2	0.8671
dwd3167	Q4-98	0.009	27	0.95	1.2	1257	0.5246	0.0022	13.526	0.060	2715.8	1.9	-0.1	0.9653
dwd3171	Q10-98	0.020	56	0.91	0.6	11207	0.5223	0.0024	13.490	0.064	2718.9	2.3	0.5	0.9572
dwd3197	DD88-18	0.003	45	0.62	1.0	849	0.5217	0.0032	13.524	0.084	2724.7	3.4	0.8	0.9446
dwd3198	DD88-18	0.003	59	0.41	1.4	848	0.5269	0.0029	13.783	0.107	2739.6	8.3	0.5	0.7604
dwd3199	DD88-18	0.003	49	0.37	1.0	951	0.5278	0.0027	13.829	0.069	2742.4	3.5	0.5	0.9097
dwd3202	Q-10	0.005	120	0.74	0.6	6889	0.5367	0.0018	14.356	0.051	2776.4	1.5	0.3	0.9654
dwd3196	DD88-18	0.004	25	0.62	0.9	770	0.5386	0.0023	14.531	0.068	2790.5	2.6	0.6	0.9408
dwd3203	Q-10	0.003	84	0.64	0.5	3600	0.5435	0.0019	14.849	0.050	2810.9	2.7	0.6	0.8835
dwd3168	Q4-98	0.006	68	0.38	1.9	1667	0.5626	0.0018	16.117	0.055	2888.1	1.7	0.5	0.9541
dwd3175	Q10-98	0.003	106	0.22	0.4	6531	0.5750	0.0014	16.956	0.045	2935.1	1.7	0.3	0.9143
dwd3174	Q10-98	0.004	95	0.77	0.5	7074	0.5949	0.0016	18.621	0.055	3031.1	1.6	0.9	0.9449
dwd3169	Q4-98	0.003	33	0.55	0.5	2254	0.6423	0.0022	22.856	0.081	3235.2	2.1	1.5	0.9298

Ab—abraded; zr—zircon grain; eq—equant; elong—elongate; clr—colourless; brn—brownish; crk—cracked; subrnd—subrounded; incl—inclusions, Pbcom is total measured common Pb assuming the isotopic composition of laboratory blank:  $^{206}\text{Pb}/^{204}\text{Pb}$ —18.221;  $^{207}\text{Pb}/^{204}\text{Pb}$ —15.612;  $^{208}\text{Pb}/^{204}\text{Pb}$ —39.360 (errors of 2%). Th/U calculated from radiogenic  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio and  $^{207}\text{Pb}/^{206}\text{Pb}$  age assuming concordance. Disc.—per cent discordance for the given  $^{207}\text{Pb}/^{206}\text{Pb}$  age. Uranium decay constants are from Jaffey et al. (1971).

Lu/Hf value for the protolith. In the present case we calculate two ‘end-member’ mantle extraction ages based on the average Lu/Hf ratios of crustal mafic rocks (0.022, see discussion in Amelin et al., 1999) and Precambrian granitoid rocks (0.0093, Vervoort and Patchett, 1996). Values of  $^{176}\text{Lu}/^{177}\text{Hf}$  deter-

mined from sedimentary rocks in the Superior province are 0.012–0.015, which probably represents a good approximation to the Superior province crustal average and lies well within the range of these end member values (Stevensen and Patchett, 1990).

Model age calculations also depend on the parameters chosen to define the depleted mantle growth curve. Vervoort and Blichert-Toft (1999) suggested a model based on rocks with a wide range of ages whose  $\epsilon_{\text{Hf}}$  values were calculated using the Siguina et al. (1982) decay constant. The linear growth curve adopted for the present work is based on the  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio suggested by Vervoort and Blichert-Toft (1999) for present day depleted mantle ( $\epsilon_{\text{Hf}} = 18$ ), and the mean  $\epsilon_{\text{Hf}}$  value measured on rocks assumed to have formed from late Archean depleted mantle beneath the western Superior province ( $3.5 \pm 0.2$ , see Section 5). The first parameter falls near the upper (most depleted) limit of  $^{176}\text{Hf}/^{177}\text{Hf}$  values for ‘normal’ mid-ocean ridge segments (Nowell et al., 1998). The second parameter is the best approximation for the mantle beneath the western Superior province and is therefore the most appropriate for defining mantle extraction ages in this region. This model implies a time integrated  $^{176}\text{Lu}/^{176}\text{Hf}$  ratio of the MORB source of 0.0409. Alternative models and

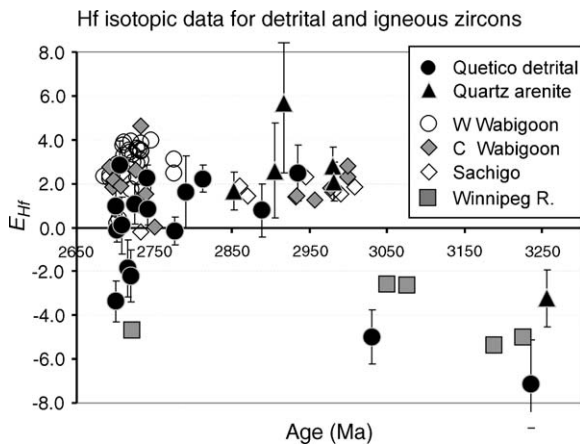


Fig. 5. Age vs.  $\epsilon_{\text{Hf}}$  for middle and late Archean igneous rocks compared to detrital zircons from >2.8 Ga quartz arenites and 2.7 Ga Quetico turbidities.

implications for early growth of the continental crust are discussed below.

#### 4.2. Results from western Superior province terranes

##### 4.2.1. Western Wabigoon subprovince

The western Wabigoon subprovince contains the Kakagi Lake–Savant Lake volcanic belt (KSVB, Fig. 1). Values of  $\epsilon_{\text{Hf}}$  for the central and southwestern part of KSVB show a high level of consistency (Fig. 3). All samples within the age range 2710–2732 Ma from this area are tightly grouped and give an average  $\epsilon_{\text{Hf}}$  of  $3.5 \pm 0.2$  (95% confidence error, MSWD of 0.9). Late-tectonic plutons younger than 2710 Ma in some cases appear to have slightly lower  $\epsilon_{\text{Hf}}$  values and were omitted from this average. These plutons might be expected to show contamination from older crust because 2710 Ma marks the beginning of regional deformation and deposition of orogenic sandstones, which commonly contain Mesoproterozoic detrital zircon. This supports previous suggestions that early volcanic rocks in this region mostly developed in a juvenile oceanic arc environment (Davis et al., 1988). Small amounts of enrichment appear in late plutons such as the Ottertail, Taylor Lake, Heronry and High Lake stocks.

Values of  $\epsilon_{\text{Hf}}$  show less consistency for rocks in the northwestern part of the belt (Fig. 3). Zircon samples from a 2745 Ma old felsic volcanic rock in the lower Handy Lake group and from a 2772 Ma old felsic volcanic rock in the Fourbay Lake Group have depleted Hf signatures (+4 and +3, respectively), which are similar to the arc-related volcanic rocks in the southwestern part of the belt. Evidence for slight but consistent enrichment is found from three 2732–2735 Ma rocks in this area. One is a subvolcanic quartz porphyry overlying the 2745 Ma volcanic unit within the Handy Lake Group (+1). The other two are a rhyolite (+2) and a shallow pluton (+1) associated with the South Sturgeon Lake volcanic assemblage. This assemblage is part of a caldera complex that may have formed in a back-arc environment and was host to significant volcanogenic massive sulphide mineralization at 2732 Ma (Davis et al., 1985). A younger 2704 Ma sub-volcanic porphyry near the top of the Handy Lake Group shows more enrichment and agrees with a similar-aged granitoid clast in a conglomerate

along the nearby Kashaweogama Fault at +0. This was probably eroded from a nearby pluton within the lower basaltic sequence of the Jutten Group. A quartz arenite unit within the upper part of the Jutten Group contains relatively old detrital zircons with ages ranging from 2.95 Ga to 3.3 Ga. Hf analysis of one 3256 Ma old detrital zircon from this unit gave an enriched  $\epsilon_{\text{Hf}}$  value  $-3$ , indicating possible mantle extraction ages in the range 3.4–3.5 Ga (Fig. 5). Such zircons are likely derived from rocks of the Winnipeg River subprovince (see Section 5).

##### 4.2.2. Central Wabigoon subprovince

Tomlinson et al. (2001, 2003) suggested that the south-central part of the Wabigoon subprovince comprises a distinct terrane, which they called the Marmion terrane. This is based on evidence from zircon ages and Nd isotopes that the area is largely composed of juvenile and reworked 3.0 Ga crust (Davis and Jackson, 1988; Henry et al., 1998; Tomlinson et al., 2003). Evidence from Hf isotopes supports this view. Two of the oldest volcanic rocks from the Lumby Lake greenstone belt and a quartz diorite phase of the Marmion batholith give 3.0 Ga ages and show the most primitive  $\epsilon_{\text{Hf}}$  values (Fig. 4). These average to  $2.7 \pm 0.4$ . Seven younger plutons and a rhyolite in the age range 2.70–2.98 Ga show more enriched  $\epsilon_{\text{Hf}}$  and give scattered values. Such a pattern would be expected for contamination from a crustal source that was not significantly older than 3.0 Ga.

Zircons from three Neoproterozoic felsic volcanic units in the Obonga Lake greenstone belt show variably depleted signatures for Hf (Figs. 3 and 4). This accords with Nd isotopic values for the corresponding whole rocks (Tomlinson et al., 2002). A 2739 Ma old foliated pluton intruded by the Roaring River complex (Stern et al., 1990) and quartz monzonite from the pluton itself show slightly enriched  $\epsilon_{\text{Hf}}$  values of about +2. Zircon from a 3075 Ma old tonalite at Caribou Lake on the northern boundary of the Wabigoon subprovince shows a markedly enriched  $\epsilon_{\text{Hf}}$  value of  $-2.6$ , indicating a mantle extraction age in the range 3.3–3.4 Ga (Fig. 4). In contrast to the western Wabigoon subprovince, the central part contains rocks from different sources with a variety of crustal pre-histories.

##### 4.2.3. Winnipeg River subprovince

Zircon  $\epsilon_{\text{Hf}}$  data from rocks in the Winnipeg River subprovince show distinctly more enriched values than

from most other samples in the western Superior province. One of the oldest units, the Cedar Lake gneiss, was dated at 3180 Ma by Corfu (1988). Subsequent U–Pb dating of this unit by SHRIMP has shown that it contains a variety of zircons with ages extending back to 3250 Ma (Melnyk et al., submitted). Two single zircons from the 3180 Ma sample dated by Corfu (1988) gave  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of 3188 Ma and 3225 Ma. Both zircons have similar  $\varepsilon_{\text{Hf}}$  values of about  $-5$  (Fig. 4). This indicates substantial enrichment, with a mantle extraction age in the range 3.5–3.7 Ga. A 3050 Ma old sample from the Tannis Lake gneiss also gave an enriched zircon  $\varepsilon_{\text{Hf}}$  value of  $-2.3$  (Fig. 4) with a likely mantle extraction age in the range 3.2–3.4 Ga. These results are in broad agreement with Nd analyses from the same units, which gave mantle extraction ages of  $3.4 \pm 0.2$  Ga (Henry et al., 2000). Ages of up to 3320 Ma have now been measured by U–Pb SHRIMP on zircons from a phase the Tannis Lake gneiss (Melnyk et al., submitted). Tonalite gneiss aged 2721 Ma near the southern boundary of the subprovince gave an enriched  $\varepsilon_{\text{Hf}}$  value of  $-5$  (Fig. 3), suggesting a mantle extraction age for the crustal protolith in the range 3.1–3.3 Ga.

#### 4.2.4. Sachigo subprovince

The most northerly sample in this study is a 2709 Ma old shoshonitic rhyolite from the Oxford Lake Group in Manitoba. This gives a slightly enriched  $\varepsilon_{\text{Hf}}$  value of  $+2.5$  (Fig. 3). Zircons from the North Caribou block in the Sachigo subprovince of Ontario show fairly uniform  $\varepsilon_{\text{Hf}}$  signatures of around  $+2$  for different ages except for a Neoproterozoic tuff with  $\varepsilon_{\text{Hf}}$  of 0 (Fig. 4). Corfu and Stott (1993b, 1996) found juvenile Hf values for Mesoproterozoic rocks in the Uchi subprovince on the southern margin of the North Caribou block with a pattern of progressive scatter toward more enriched values in younger rocks. They suggested that these areas represent 3.0 Ga crust that was progressively reworked with addition of considerable mantle-derived material at around 2.7 Ga. Given the small number of analyses, the present data may be consistent with this suggestion (Fig. 4).

Hf isotopic analyses were also carried out on single detrital zircons in quartz arenite units from the Sachigo subprovince. Five detrital zircons were analyzed from three units within the North Caribou block. Some of these analyses are relatively imprecise because

of small sample size but they give  $\varepsilon_{\text{Hf}}$  values within error of the scatter of igneous rocks from the same area (Fig. 5). This supports previous suggestions based on age data that the quartz arenites had a local provenance.

#### 4.2.5. Quetico metasedimentary subprovince

The Quetico subprovince represents a major E–W trending belt of metasedimentary and plutonic rocks that stretches across the western Superior province. About half the detrital zircon ages from this area are in the narrow age range of 2710–2700 Ma while others give scattered older ages, most of which are younger than 3.0 Ga. Quetico sandstones from the Rainy Lake area at the western end of the subprovince are an exception. They contain Meso- to Paleoproterozoic detrital zircons with ages as old as 3.45 Ga (Fralick and Davis, 1999). Hf measurements on two detrital zircons with ages of 3031 Ma and 3235 Ma from this area gave enriched  $\varepsilon_{\text{Hf}}$  values of  $-4.7$  and  $-6.3$ , respectively (Fig. 5). The oldest indicates a mantle extraction age in the range 3.6–3.8 Ga. Both values are even more enriched than those found in rocks of similar age in the Winnipeg River subprovince. Neoproterozoic zircons show a spread from slightly enriched to an  $\varepsilon_{\text{Hf}}$  value of  $-3.0$  (Fig. 5).

## 5. Discussion

### 5.1. Terrane analysis and tectonic history

Hf isotopic data from zircons confirm and expand on previous conclusions from Nd whole rock isotopic work (Henry et al., 1998, 2000), while adding the ability to reveal magmatic pre-histories of single detrital zircons. Based on these data, there appear to be at least three distinct terrane types in the western Superior province.

Juvenile 2.7–2.75 Ga terranes (e.g. western Wabigoon, Shebandowan subprovinces) probably formed largely in oceanic environments during the most intense phase of igneous activity in the region.

Juvenile 3.0 Ga terranes (e.g. North Caribou, Marmion terranes) were reworked by continental arc and plume-related activity over a 300 m.y. time span, culminating in extensive granitoid magmatism at around 2.7 Ga.

An older terrane, whose deep crustal level is exposed in the Winnipeg River subprovince, shows a protolith history that extends to 3.5 Ga. It was reworked during the Mesoarchean but seems to have largely escaped the most intense period of arc-related volcanism that occurred in most other areas in the age span 2.71–2.75 Ma. This terrane was again magmatically reworked during the main period of regional deformation that occurred in the time span 2.71–2.65 Ma and affected the entire region.

Volcanic and plutonic rocks in the age range 2720–2730 Ma are present in most terranes. To test whether such rocks are autochthonous or whether they may have formed in an oceanic environment and been structurally juxtaposed against older units,  $\varepsilon_{\text{Hf}}$  values were compared for zircons from a number of terranes in this age range (Fig. 3). A single zircon Hf analysis from a 2722 Ma volcanic unit in the Shebandowan greenstone belt, the western extension of the Wawa subprovince, shows  $\varepsilon_{\text{Hf}}$  of +4. This is indistinguishable from the +3.5 value of many similar aged rocks in the western Wabigoon subprovince and is certainly indicative of minimal older crustal contamination. In contrast, the 2721 Ma tonalite gneiss from the Winnipeg River subprovince shows  $\varepsilon_{\text{Hf}}$  of –4.9, the most enriched value found from any Neoproterozoic rock in this study, with a 3.1–3.3 Ga range of mantle extraction ages that is comparable to U–Pb zircon ages of the oldest gneisses in this terrane. Zircons from a 2723 Ma old rhyolite in the Separation Lake greenstone belt give a less enriched  $\varepsilon_{\text{Hf}}$  value of –1 with mantle extraction ages in the range 2.9–3.1 Ga. This belt appears to be an eastern attenuated extension of the Bird River granite-greenstone subprovince and lies between the Winnipeg River and the English River subprovinces. The enriched Hf result could indicate that the Separation Lake belt volcanics are contaminated by much older Winnipeg River-type crust, which now lies to the south, or that they are correlative with rocks in the Uchi subprovince to the north. Finally, 2726 Ma old zircon from a rhyolite in the Melchett Lake greenstone belt, an unusual exposure of volcanic rocks within the eastern English River subprovince, shows a primitive  $\varepsilon_{\text{Hf}}$  value of +3.8. The relationship of the Melchett Lake belt to the younger (<2704 Ma) surrounding metasedimentary rocks of the English River subprovince is unclear. If it represents exposed basement to these rocks then they were probably deposited onto oceanic or oceanic arc-related crust.

If it is allochthonous, then it may have been transported from terranes with similar age and provenance to the south. These data show that near contemporaneous magmatism was occurring in quite different tectonic environments over the time span 2720–2730 Ma. Evidence for autochthonous development of Neoproterozoic sequences in different Superior province terranes has been found in other U–Pb studies (Ayer et al., 2002).

Both the North Caribou block of the Sachigo subprovince and the Marmion terrane in the south-central part of the Wabigoon subprovince appear to consist largely of depleted mantle-derived 3.0 Ga rocks and younger rocks derived from their reworking. Similarities in Nd and Hf isotopes, age distributions and lithological associations are close enough to warrant the suggestion that these two terranes are correlative. They could either represent rifted fragments of the same continent or the Marmion terrane might be a fragment of the North Caribou terrane that was transported southward during accretion of the Superior province. Re-assembly of near-contiguous rifted fragments during accretion seems less likely, given the destructive nature of plate collision processes and evidence for large-scale oblique convergence, which would offset once contiguous rifted fragments (Percival et al., 1994). The reflection seismic profile from line 1A across the central Wabigoon subprovince suggests that the south-central part contains a relatively thin upper crustal sheet overlying a more reflective middle crust (see southern part of section 1D in Fig. 2 of White et al., 2003). If so, the Marmion terrane may represent a klippe derived from the North Caribou terrane that was thrust over the accretionary margin. Emplacement of this terrane as a high-level thrust sheet at about 2700 Ma could have provided a major source of sediment into the Quetico basin, which is consistent with Mesoarchean ages and moderately enriched Hf signatures from some of its detrital zircons.

The  $\varepsilon_{\text{Hf}}$  values of zircons in rocks from the Winnipeg River terrane generally show greater enrichment than those from other areas. Other distinctive features of the Winnipeg River subprovince are its relatively high metamorphic grade and plutonic character indicating that it was exhumed from depth, its much older U–Pb ages, and the fact that it shows very few ages corresponding to the main 2.71–2.75 Ga period of calc-alkaline and tholeiitic magmatism that preceded accretion. Most rocks within the Winnipeg River sub-

province are either younger than 2.71 Ga or older than 2.8 Ga. This led Davis and Smith (1991) to suggest that the subprovince represents an accreted fragment of sialic crust that underthrust the Wabigoon subprovince. If so, it probably did not represent a continental terrane extensive enough to bring the accretionary process to an end. This is because the beginning of large scale melting and recumbent isoclinal folding (2716 Ma, Melnyk et al., submitted) predates what is thought to be the time of accretion of oceanic arcs in the Shebandowan subprovince further south (<2700 Ma, Corfu and Stott, 1998). The seismic reflection profile also suggests that Winnipeg River crust was thrust southward over a slab of oceanic crust (White et al., 2003). The Winnipeg River subprovince may represent part of a small continental fragment that accreted early, as suggested in the model of Stott and Corfu (1991).

The enriched hafnium isotopic signature of a single 3256 Ma zircon from the Jutten quartz arenite (−3.2) in the northeastern part of KSVB suggests that its source was from rocks of the Winnipeg River subprovince. The Jutten sequence overlies 2884 Ma rhyolite (Skulski et al., 1999) and its youngest dated zircon gives 2948 Ma. It is likely that most such quartz arenites in the Superior province were deposited before 2800 Ma since no detrital zircons younger than this have thus far been found in any of them despite the fact that younger rocks are voluminous in the region. Thus, Hf data support the suggestion of Skulski et al. (1999) that part of the Savant Lake area represents an early shelf sequence related to rocks of the Winnipeg River subprovince while rocks further south (2745 Ma lower Handy Lake and 2775 Ma Fourbay Lake units) were deposited in an oceanic environment. Hf in zircon from the 2.73 Ga South Sturgeon Lake assemblage (Beidelman Bay pluton and felsic volcanic) shows slightly enriched signatures (+1 and +1.8, respectively). Nd in whole rocks from the same area shows a similar level of enrichment (Bernier et al., 1999). These zircons agree in age and  $\epsilon_{\text{Hf}}$  with a coeval part of the Savant Lake group (+1.1), which suggests that the sequences are correlative. Since the South Sturgeon Lake assemblage is host to a number of major VMS deposits, this part of the Savant Lake group may be a useful exploration target. It is likely that these rocks evolved in a back-arc environment and their less depleted Hf and Nd may be due either to contamination with older crust (either Winnipeg River or Marmion-type terrane) or the influence

of a plume source. The most enriched Hf values ( $\epsilon_{\text{Hf}}$  of about 0) are from zircons in 2.70 Ga rocks. This period of magmatism is suggested to mark suturing between the older continental margin sequence and the oceanic rocks (Skulski et al., 1999).

Mesoarchean rocks are also found at Caribou Lake on the northern margin of the central Wabigoon subprovince (Davis et al., 1988) and in the Onaman-Tashota granite-greenstone belt east of Lake Nipigon (Stott and Davis, 1999). Zircon aged 3075 Ma from Caribou Lake shows similar  $\epsilon_{\text{Hf}}$  enrichment to the 3050 Ma zircon from gneiss at Tannis Lake near Kenora (Fig. 4). This supports the suggestion of Tomlinson et al. (2001, 2003) that rocks of the Winnipeg River terrane extend across much of the northern Wabigoon subprovince. The Jutten Group is at lower metamorphic grade than rocks of the Winnipeg River subprovince, which attain granulite facies at its eastern end near the Miniss River fault. This suggests that the Winnipeg River subprovince represents a deep crustal level of the Winnipeg River terrane that was differentially uplifted along the Miniss River fault. This uplift probably began as early as 2700 Ma, as suggested by detrital zircons from the western Quetico subprovince with Paleoproterozoic ages and enriched  $\epsilon_{\text{Hf}}$  signatures.

Erosion of the Winnipeg River terrane at 2700 Ma may account for the difference in the age distribution of detrital zircons from sandstones in the Quetico versus the English River subprovince. Turbidities in the English River subprovince were probably deposited in the time span 2700–2705 Ma based on ages of youngest detrital zircons and crosscutting plutons (Corfu et al., 1995; Davis, 1995), while lithologically similar rocks in the Quetico subprovince were deposited shortly after 2700 Ma (Davis, 1995; Davis et al., 1990). The age distribution of detrital zircons from the English River subprovince is similar to that of igneous rocks in the adjacent Wabigoon, Uchi and Sachigo subprovinces. It reflects the preponderance of igneous activity in these areas over the 2.71–2.75 Ga time span with sparser but near continuous activity back to 3.0 Ga. In contrast, about half of the Quetico detrital zircon population is within the narrow age span 2700–2710 Ma. Plutonic rocks within this time span make up a significant proportion of the Winnipeg River subprovince and probably formed from extensive melting of older rocks. Uplift and exposure of these rocks to erosion at 2700 Ma might have contributed much

of the 2.70–2.71 Ga, isotopically enriched detrital zircon.

### 5.2. Hf and O isotopes in zircon

Hf isotopic signatures of zircon from plutons younger than about 2710 Ma scatter toward slightly more enriched values than older rocks from juvenile terranes. Many of these plutons are from the sanukitoid magmatic suite, which is thought to have formed from melting of mantle that had been metasomatized during previous subduction (Shirey and Hanson, 1984). The resulting magmas were modified by fractional crystallization and crustal assimilation (Stern et al., 1990; Stevenson et al., 1999). Emplacement of these plutons is usually approximately coeval with regional folding. The degree of Hf isotopic enrichment does not seem to be obviously correlated with the degree of fractionation or the crustal pre-history of the terranes in which the rocks were emplaced. King et al. (1998) noted that many late plutons show O isotopic ratios slightly higher than mantle values. They suggested that either crustal assimilation or dewatering of subducted sediments may have raised the O isotopic signature of the metasomatized mantle source from which the primary magmas of the plutons were derived. Hf isotopes provide a potential method for evaluating these possibilities. Fig. 6 shows  $\delta^{18}\text{O}$  plotted against  $\varepsilon_{\text{Hf}}$  for zircons analysed by King et al. (1998). This includes data from some

pre-2.71 Ga TTG rocks, which show mantle-like  $\delta^{18}\text{O}$  values around 5.5‰ and depleted  $\varepsilon_{\text{Hf}}$  values. Rocks with both elevated  $\delta^{18}\text{O}$  values and slightly enriched  $\varepsilon_{\text{Hf}}$  are largely from the late-tectonic sanukitoid suite. Although the relatively large errors in  $\varepsilon_{\text{Hf}}$  make it difficult to establish a well-constrained trend (correlation coefficient of 0.79), there appears to be an inverse correlation between  $\delta^{18}\text{O}$  and  $\varepsilon_{\text{Hf}}$ . The best-fit line follows the equation  $\varepsilon_{\text{Hf}} = -1.2 \times \delta^{18}\text{O} + 9.9$ . This correlation suggests that the increase in  $\delta^{18}\text{O}$  was more likely due to crustal assimilation rather than dewatering of sediments because Hf resides mostly in zircon and should be immobile during hydrothermal processes. Stevenson et al. (1999) also suggested on geochemical, Nd and Pb isotope grounds that crustal assimilation played a major role in the magmatic evolution of the sanukitoid suite. If the most differentiated plutons (quartz monzonite) represent 50% contamination, this would imply a contaminant with  $\delta^{18}\text{O}$  of about 9‰ and a  $\varepsilon_{\text{Hf}}$  value of about 0. This is consistent with  $\delta^{18}\text{O}$  values measured on orogenic sandstones in metasedimentary subprovinces such as the Pontiac (Feng et al., 1990) as well as Hf isotopic measurements on bulk zircon from these rocks (Stevenson and Patchett, 1990). It would also be consistent with lesser amount of contamination from more  $\delta^{18}\text{O}$  enriched intravolcanic metasedimentary units (Feng et al., 1990) with an older mantle extraction age. Sanukitoid plutons are often spatially associated with such units.

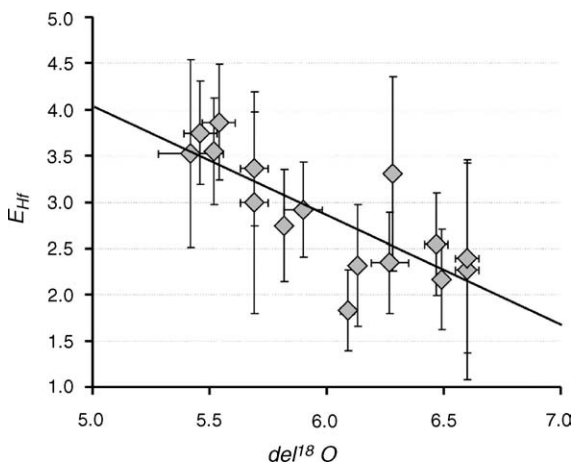


Fig. 6.  $\varepsilon_{\text{Hf}}$  vs.  $\delta^{18}\text{O}$  for zircons from plutons in the western Superior Transect area along with the best fit correlation line. Data with  $\delta^{18}\text{O} > 5.5$  are mostly from ca. 2.70 Ga rocks of the sanukitoid suite.

### 5.3. Implications for development of the Neoproterozoic depleted mantle: choice of the $^{176}\text{Lu}$ decay constant

Fourteen Neoproterozoic units in the western Wabigoon subprovince that show no evidence of crustal contamination define a consistent  $\varepsilon_{\text{Hf}}$  value of  $3.5 \pm 0.2$  (MSWD of 0.86, average age of 2724 Ma). This likely represents the sub-oceanic depleted mantle at this time. Omitted from the western Wabigoon data set are five relatively young plutons that may have been affected by older crust (see previous section) and one 2720 Ma old rhyolite from the Lake of the Woods area that appears somewhat enriched. Measured  $\varepsilon_{\text{Hf}}$  from a 2.72 Ga volcanic unit in the Shebandowan belt is consistent with this value, as is the average  $\varepsilon_{\text{Hf}}$  value of  $4.0 \pm 0.4$ , adjusted for the presently assumed constants, that was measured for units in the southern Abitibi subprovince

by Corfu and Noble (1992). These areas are now about 1000 km apart but considering that they probably formed in an oceanic environment before accretion, they may have originally been much more widely separated. This suggests that the Neoproterozoic depleted mantle source was quite uniform with respect to its Hf isotopic composition.

The absolute value of the Hf isotopic anomaly depends strongly on the choice of  $^{176}\text{Lu}$  decay constant. Until recently, a value of  $1.931 \pm 0.027 \times 10^{-5} \text{ m.y.}^{-1}$ , based on  $\gamma$ - $\gamma$  coincidence counting (Siguigna et al., 1982) was widely used. However, radioactive counting experiments over the past two decades have not produced consistent values (Scherer et al., 2003). The analytical precision and accuracy of the  $^{238}\text{U}$  and  $^{235}\text{U}$  decay constants ( $\pm 0.2\%$ , Jaffey et al., 1971; Mattinson, 1987) are much better established than that of  $^{176}\text{Lu}$ , making comparative U–Pb and Lu–Hf dating an attractive calibration method. The value of  $1.865 \pm 0.015 \times 10^{-5} \text{ m.y.}^{-1}$  used in this work is based on U–Pb and Lu–Hf dating of the same mineral phases in terrestrial rocks (Scherer et al., 2001). More recently, Bizzarro et al. (2003) have proposed a higher value of  $1.983 \pm 0.033 \times 10^{-5} \text{ m.y.}^{-1}$  based on comparative U–Pb and Lu–Hf dating of meteorites. The ca. 6% difference between terrestrial and meteoritic samples has been reproduced by other measurements on similar samples (Scherer et al., 2003; Söderlund et al., 2003; Blichert-Toft et al., 2002), implying that there is some hidden bias with either the terrestrial or meteoritic samples. The effects of using different proposed decay constants on the calculated chondritic growth curve for Hf become progressively greater with age and result in major differences for calculated  $\varepsilon_{\text{Hf}}$  values from Archean samples. For example, The Scherer et al. (2001) value produces  $\varepsilon_{\text{Hf}}$  values that are 2.2 units lower at 2700 Ma than the Siguigna et al. (1982) value and 3.9 units lower than that of Bizzarro et al. (2003). We follow Scherer et al. (2001) in this work because it is presently the best-replicated value. It is in tight agreement with several other determinations on a variety of different aged minerals and whole rocks including rocks comparable in age to those of the present study (Scherer et al., 2003; Söderlund et al., 2003). The consistency of this choice with other data and observations is discussed below.

Fig. 7 shows estimates of  $\varepsilon_{\text{Hf}}$  for depleted mantle at 2.7 Ga and 3.0 Ga based on the current Superior

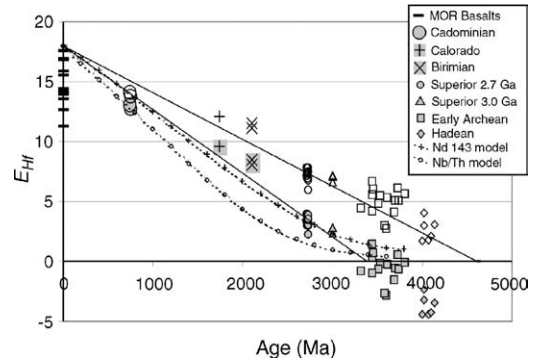


Fig. 7. Comparison of data calculated assuming a  $^{176}\text{Lu}$  decay constant of  $1.865 \times 10^{-5} \text{ m.y.}^{-1}$  (lower data set, Scherer et al., 2001), and a decay constant of  $1.983 \times 10^{-5} \text{ m.y.}^{-1}$  (upper data set, Bizzarro et al., 2003). Linear depleted mantle growth models are shown for each proposed value assuming a present day  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio of 0.28325 ( $\varepsilon_{\text{Hf}} = +18$ ), based on the upper limit of MORB basalts, and  $^{176}\text{Hf}/^{177}\text{Hf}$  measured for 2.7 Ga zircons in mantle-derived rocks from this study. Data from mantle-derived samples in other areas are shown for comparison (MOR—Nowell et al., 1998; Cadominian—Samson et al., 2003; Colorado—Vervoort and Blichert-Toft, 1999; Birimian—Blichert-Toft et al., 1999; early Archean—Amelin et al. (2001); Vervoort and Blichert-Toft, 1999; Hadean—Amelin et al., 1999). Also shown are depleted mantle evolution models based on  $^{143}\text{Nd}$  isotopes (Nagler and Kramers, 1998) and time integrated Nb/Th ratios (Collerson and Kamber, 1999), both curves adjusted to have the same present day value as  $\varepsilon_{\text{Hf}}$ .

province data, as well as a previously published reference data set from zircon that ranges in age over most of the geologic time scale. These data are shown calculated using both the Scherer et al. (2001) and the Bizzarro et al. (2003) decay constants. The reference data are not comprehensive but were chosen for comparison purposes from previous studies and compilations (Amelin et al., 1999, 2000; Vervoort and Blichert-Toft, 1999) as generally representing the most depleted results on zircon. Scattered data from some of the early Archean rocks and Hadean detrital zircons may include effects of recycling.

The Superior province data for depleted mantle are approximately consistent with the roughly linear distribution of post-Archean data no matter which decay constant is used (Fig. 7) but the choice of decay constant greatly affects the intersection age with the chondritic line (horizontal axis). Using the Scherer et al. (2001) decay constant, a linear depleted mantle growth model based on  $\varepsilon_{\text{Hf}}$  of +3.5 at 2.7 Ga and a depleted mantle estimate of +18 at 0 Ma (Vervoort and

Blichert-Toft, 1999) intersects the chondritic evolution line at an age of 3380 Ma. Linear models such as this assume that formation of the continental crust and associated mantle depletion occurred during one event whereas it is likely to have occurred progressively but with the bulk of crust-mantle extraction completed by the end of the Archean (Condie, 1997). The mean  $\varepsilon_{\text{Hf}}$  value of  $+2.7 \pm 0.4$  Ma measured from three 3.0 Ga old units in the south-central Wabigoon subprovince falls above the extrapolated line suggesting a lower degree of mantle depletion at this time and an earlier age for the beginning of mantle differentiation. A growth line between Superior province  $\varepsilon_{\text{Hf}}$  values at 3000 Ma and 2700 Ma would intersect the chondritic line at 3920 Ma. Despite their simplistic assumptions, these models show that the Scherer et al. (2001) decay constant value produces results that are broadly consistent with the preserved early rock record. Rocks older than 3.5 Ga are extremely rare and the oldest rock yet dated is about 4.0 Ga (Bowring and Williams, 1999; Stern and Bleeker, 1998). In contrast, data based on the Bizzarro et al. (2003) decay constant value imply sizeable amounts of mantle depletion during the early Archean and Hadean. A one stage linear model based on this decay constant gives a chondritic intersection age of 4.6 Ga (Fig. 7).

Comparison of mantle evolution curves for Nd and Hf isotopes provides one independent way to test for a realistic choice of decay constant. The  $^{147}\text{Sm}$  decay constant is considered to be accurate and both parent–daughter pairs generally show a strong geochemical coherence so the isotopic systems should produce mantle evolution curves of the same shape. The average  $^{143}\text{Nd}$  mantle evolution curve suggested by Nagler and Kramers (1998) is compared to  $\varepsilon_{\text{Hf}}$  data on Fig. 7 where its vertical axis (not numbered) has been scaled so  $\varepsilon_{\text{Hf}}$  and  $\varepsilon_{\text{Nd}}$  match at 0 Ma. The depleted mantle  $\varepsilon_{\text{Hf}}$  data show good agreement with the Nd curve for Mesoproterozoic and younger rocks when they are calculated using the Scherer et al. (2001) decay constant value but poor agreement when calculated using the Bizzarro et al. (2003) value. Thus, despite evidence for the existence of Paleoproterozoic and Hadean mantle depletion (Boyet et al., 2003; Caro et al., 2003; Bennett et al., 1993; Jacobsen and Dymek, 1988), the depleted mantle Nd isotopic record from middle Archean time to the present supports the Scherer et al. (2001) decay constant value.

Another comparative approach can be made using trace element ratios such as Nb/Th that are sensitive to crust-mantle differentiation. Because Th is preferentially enriched in the continental crust, the depleted mantle residue develops a supra-chondritic Nb/Th ratio, which has been used as a proxy for the degree of mantle depletion (Collerson and Kamber, 1999; Kamber et al., 2003a). For a two-component system (enriched crust and depleted mantle), the integral of the Nb/Th secular variation curve for rocks derived from depleted mantle should be similar to the time-integrated history of mantle depletion as recorded by the growth of  $^{176}\text{Hf}$  and  $^{143}\text{Nd}$  isotopic anomalies. The integral curve presented in Fig. 7 is based on Nb/Th ratios compiled by Collerson and Kamber (1999) minus the bulk silicate Earth ratio of 6.96 suggested by Kamber et al. (2003b). As with Nd, the curve is scaled to give the same value as the  $\varepsilon_{\text{Hf}}$  curve at 0 Ma. This curve appears somewhat inconsistent with data calculated using either the Scherer et al. (2001) or Bizzarro et al. (2003)  $^{176}\text{Lu}$  decay constant values, although it is closer to those using the Scherer et al. (2001) value. Agreement would be improved if the bulk earth value of Nb/Th were somewhat lower than that estimated by Kamber et al. (2003b). Long-term storage of Nb in a high Nb/Th reservoir such as subducted ocean crust could also explain the difference. This would tend to offset the effect of transferring Th to the continental crust and delay substantial Nb/Th fractionation in the Neoproterozoic and Paleoproterozoic mantle. In this case Nb/Th evolution could have been largely controlled by re-mixing of subducted ocean crust into the depleted mantle reservoir by convection or plumes. This mechanism was discussed by Kamber et al. (2003b), although they concluded that it had little effect on the continental growth curve.

Hf data from Hadean zircons analyzed by Amelin et al. (1999) show negative  $\varepsilon_{\text{Hf}}$  values when calculated using the Scherer et al. (2001) decay value (Fig. 7). This implies that at least some of the zircons had significantly older protoliths, which must have been felsic in order for their Hf model ages to be less than the age of the Earth. This is consistent with observations that some  $>4.0$  Ga zircons contain K-feldspar and quartz inclusions, significantly older cores, and high  $\delta^{18}\text{O}$  ratios (Maas et al., 1992; Wilde et al., 2001; Mojzsis et al., 2001). The Bizzarro et al. (2003) value would give depleted mantle signatures for these zircons.  $^{143}\text{Nd}$  and

$^{142}\text{Nd}$  isotopes in rocks from Isua (Boyet et al., 2003; Caro et al., 2003) as well as Pb isotopic data in galena (Appel et al., 1978; Frei and Rosing, 2001; Kamber et al., 2003b) suggest that depleted mantle existed during the Hadean and that it had a highly enriched crustal complement. By the end of the Hadean, such early crust must have been mostly recycled into the mantle, erasing its effect on Neoproterozoic and younger rocks (Kamber et al., 2003b). Formation of a depleted mantle with high Lu/Hf occurred on the Moon following solidification of its magma ocean, as shown by Archean-aged basalts with Hf isotopes that are much more radiogenic than in coeval terrestrial rocks (Unruh et al., 1984; Beard et al., 1998). A similar mantle residue produced from solidification of a terrestrial magma ocean would have rapidly produced high  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  values before foundering of the early crust. If the Scherer et al. (2001) decay constant value is correct, there remains no memory of this period of early differentiation in mantle beneath the Superior province. Hadean crust appears to have been recycled into the mantle with great efficiency resulting in a uniform isotopic composition that persisted to the Neoproterozoic.

## 6. Conclusions

The southwest part of the Wabigoon subprovince is largely composed of juvenile 2.7 Ga crust. The southern part of the central Wabigoon may be correlative with rocks of the North Caribou terrane in the Sachigo subprovince. Both consist of juvenile 3.0 Ga crust that was subsequently reworked by arc and plume magmatism. The Winnipeg River subprovince appears unique in the western Superior province in containing an isotopic record of early Archean crust that extends back to at least 3.5 Ga. Younger rocks from the Winnipeg River subprovince contain a significant component of recycled ancient crust. The northern Wabigoon subprovince also contains rocks with middle to early Archean magmatic provenance and, along with evidence from Nd isotopes, this may indicate that the Winnipeg River terrane extends across the northern part of the Wabigoon subprovince. Juvenile rocks show reproducible depleted mantle  $\epsilon_{\text{Hf}}$  values indicating that the Hf method on zircon, like U–Pb dating, is robust. The ability to determine initial Hf isotopic compositions on single detrital zircons is a

unique advantage of the method and shows that some of the early quartz arenite sequences and late orogenic sediments were derived from recycled crust with a history extending to the early Archean.

Results of multi-collector ICP-MS Hf isotopic analyses on zircon are broadly consistent with previous Nd isotopic studies and TIMS-based Hf studies in the Superior province. They support previous suggestions that the western Superior region was assembled by a process that involved recycling of older crust in the north and accretion of juvenile oceanic terranes, and possibly Paleoproterozoic sialic fragments, from the south.

Uncertainty in the  $^{176}\text{Lu}$  decay constant is a major problem for using Hf isotopic data to study early crust-mantle differentiation. Calculating data from mantle-derived rocks using the  $^{176}\text{Lu}$  decay constant of Scherer et al. (2001) gives  $\epsilon_{\text{Hf}}$  compositions for the depleted mantle reservoir of  $3.5 \pm 0.2$  at 2.72 Ga and  $2.7 \pm 0.4$  at 3.0 Ga. Linear models for mantle depletion using these parameters suggest that significant continental crust formation began in the early Archean, not the Hadean. The higher Bizzarro et al. (2003) decay constant indicates significant mantle depletion early in the Hadean, consistent with  $^{143}\text{Nd}$  and  $^{142}\text{Nd}$  isotopic evidence from the oldest rocks, but less consistent with post-Archean Nd mantle evolution than the Scherer et al. (2001) value. The Bizzarro et al. (2003) value implies long-term persistence of Hadean mantle depletion, whereas the Scherer et al. (2001) value can only be consistent with Hadean mantle depletion if the earliest enriched crust became remixed with its mantle source early in the Archean, leaving little or no evidence of its existence in younger rocks. Both cases support suggestions by Armstrong (1991) that large amounts of enriched crust existed near the beginning of Earth's history. Continuing Hf isotopic work on precisely dated zircon will be a powerful tool for resolving regional and global problems in Earth history, but establishing a precise and unambiguous value for the  $^{176}\text{Lu}$  decay constant is essential to its effective use in studying early crust-mantle differentiation.

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