Zircon Lu- Hf systematics and the evolution of the Archean crust in the southern Superior Province, Canada

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Abstract. A combined $Lu - Hf$ and $U - Th - Pb$ isotopic study was made of 25 zircons and 2 whole rocks from the late Archean crust $(2,888 - 2,668$ Ma) in the southern Superior Province, Canada. The relative abundances of U, Th, Lu and Hf in zircons from the low grade Michipicoten and Gamitagama greenstone belts show variable patterns which in part reflect the bulk compositional differences of their parent rocks. Zircons from the high grade lower crustal regions adjacent to these belts (Kapuskasing Structural Zone) are distinguished from the low grade zircons by their strong depletions of Lu and Hf. The low Hf contents imply that the growth of metamorphic zircon involves a significant fractionation of the Zr/Hf ratio.

Initial Hf isotope ratios for Hf in zircons from the low grade rocks are correlated with silica enrichment of their host rocks, e_{Hf} varies from +9.2 to -1.3 and data from similar rock types exhibit correlations of e_{Hf} with time. Whole rock basalt analyses yield e_{Hf} values of +8.7 and + 11.3 suggesting their derivation from a depleted mantle. The basalt data fall on an evolution trend which implies that differentiation from a chondritic mantle occurred at 3,100-2,900 Ma. Low e_{Hf} values (-1.3 to +1.4) for rhyolites and granites are consistent with a derivation involving remelting of old crust similar to a 2,888 Ma granite with e_{Hf} of +0.5. Significantly higher values (+1.4 to +3.9) are found in zircons from $2,748 - 2,682$ Ma dacites and tonalites suggesting that their parent rocks had higher Lu/Hf ratios. This may indicate that their parent rocks were mafic. However, there is some evidence that the possible lower crustal source reservoirs of these rocks may have undergone processes early in their histories which increased their Lu/ Hf ratios. This would give rise to the higher e_{Hf} values observed in their derivatives.

introduction

Isotopic evolution studies of ancient rocks focus on the change of isotope ratios through time and, as such, require the age of a rock and the isotopic composition of the rock at that age to be known precisely. In a given isotopic system the age and initial ratio are usually determined from an isochron defined by the analysis of a number of co-genetic rocks. In the three systems most frequently used for Archean rocks, problems are often encountered in obtaining

meaningful isochrons. The most frequent causes of these problems are metamorphic resetting for Rb-Sr, lack of sufficient parent/daughter ratio differences for Sm-Nd and parent mobility for $U-Pb$. For a wide variety of rocks, primary ages are best determined without the use of isochrons by using zircons. The $U-Pb$ system in zircons can give precise results $(+1-3 \text{ Ma})$, although, because of the radiogenic nature of the Pb, the data do not yield information about initial Pb ratios. As a result of the chemical affinity of Hf for Zr, zircons also contain substantial amounts of Hf, one of whose isotopes, 176Hf, is also radiogenic. Since zircons are relatively low in the parent Lu, their Hf isotopic compositions change extremely slowly with time (Patchett et al. 1981). Therefore zircons have the unique advantage that an age and initial ratio can be obtained from analysis on a single mineral. When the precise age control of the U-Pb system is combined with the initial 176 Hf/ 177 Hf ratio derived from the same crystals, zircon becomes a mineral with great promise for determining the sources of ancient rocks. There is, of course, a potential danger in using the zircon crystal system in this way. The age discordance often observed in the $U-Th-Pb$ system in zircons is attributed to loss of radiogenic Pb due to radiation damage of the crystal lattice. Migration of other ions within this lattice may be possible. The ease with which this occurs for Hf in zircons is not well understood but the process should yield upwardly biased $176Hf/177Hf$ ratios because zircon contains the most primitive $176Hf^{177}Hf$ of any mineral phase in a rock. Patchett (1983) indicated that, for one of two analyses investigated, an increase in initial ¹⁷⁶Hf/¹⁷⁷Hf ratios could be correlated with grossly discordant (45%) U-Pb data. It was later found that some of the $U-Pb$ discordance could be attributed to the addition of more recent overgrowths (Kinny et al. 1984); the Hf isotope ratio increase may have also resulted from this effect.

Isotopic studies of late Archean $(2,800-2,700 \text{ Ma})$ rocks of the Superior Province have yielded some paradoxical results. Pb isotopic studies of mafic rocks of this age in the Abitibi Subprovince indicate that the 238 U/204Pb ratios (μ_1) of the sources of these rocks are nearly uniform. Tilton (1983) showed that komatiites, tholeiites and associated crustally derived ores from Munroe Township have similar μ_1 values and suggested that this indicated their derivation from either an undepleted source or a source that had been depleted shortly before emplacement of the lavas. A combined Pb and Nd isotope study of komatiites

Fig. 1. Geological map of the southern Superior Province area showing the Michipicoten and Gamitagama belts (A), and the Kapuskasing Structural Zone (B). Sampling localities are indicated

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MAFIC VOLCANIC ROCKS

WWW PARAGNEISS, MAFIC GNEISS

SAMPLE LOCATION

from Alexo Township by Dupré et al. (1984) gave a μ_1 value nearly identical to the Munroe Township komatiites. The Alexo rocks also have a low Th/U ratio and a positive e_{Nd} value, an observation which was interpreted by the authors to indicate a depleted source. More recently, Shirey and Carlson (1986) have suggested that the mantle underlying the whole Superior Province is characterized by μ_1 values similar to those in the Abitibi komatiites. Sr isotopic data from Proterozoic carbonatite complexes in this region suggest the development of this depleted mantle between 3,100 Ma and 2,800 Ma (Bell et al. 1982).

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This apparent province-wide mantle Pb isotopic homogeneity is in contrast to the more numerous Pb isotopic data from late Archean stratiform ore deposits which have been interpreted to indicate sources with widely heterogeneous μ_1 values set at 4,100 Ma (Thorpe 1982). Support for the existence of this type of heterogeneity comes from Nd isotopic studies of Archean alkalic, basaltic and komatiitic lavas. This work suggests the existence of variably depleted (or slightly contaminated) mantle source regions (Basu et al. 1984; Cattell et al. 1984). It is uncertain whether or not ore deposit Pbs, carbonatite and komatiites share common sources. However, the accumulated data suggest that the rocks in some of the Superior Province greenstone belts may be characterized by variable and less depleted sources or a mantle whose derivatives have been modified by old continental crust. These rocks are in areas which were not studied by Tilton (1983) and Dupré et al. (1984).

The purpose of the present study is to assess the usefulness of applying yet another isotopic system to the problem of crustal growth in the Superior Province. Precise $U-Pb$ ages and initial $^{176}Hf/^{177}Hf$ ratios have been determined for zircons from a contiguous greenstone-granite area **-**

the Michipicoten and Gamitagama greenstone belts. This area was selected not only because its ores indicate a variable initial Pb isotopic composition but also because the lower crustal regions of the belts are clearly exposed. The problem of possible Hf migration in zircons was mentioned earlier. We hoped to assess the possibility of post crystallization disturbances of the zircons used in this study by undertaking $U-Th-Pb$ analysis in conjunction with $Lu-$ Hf measurements.

Regional geology and geochronology

The Michipicoten and Gamitagama greenstone belts are complexly deformed supracrustal assemblages in the eastern Wawa Subprovince (Fig. 1). The Michipicoten belt consists of mafic to felsic volcanics with associated greywacke, conglomerate and banded iron formation (Goodwin 1962; Attoh 1980; Sage 1980). The Gamitagama belt consists predominantly of mafic volcanics and the Gamitagama Lake Complex, a late Archean calcalkaline intrusion with associated potassic intrusions. Metamorphic grade of the belts is low greenschist to amphibolite facies. The two belts are separated by granite terrain but are believed to have originally been continuous (Ayres 1969). Three volcanic cycles have been recognized. Previous zircon geochronology established that felsic members of cycle I and cycle III have primary ages between 2,749 and 2,696 Ma, respectively (Smith 1981; Turek et al. 1982; Turek et al. 1984). A thin middle volcanic horizon of mafic volcanics (cycle II), stratigraphically overlying the predominant iron formation horizon, has not been dated. Felsic subvolcanic stocks, spatially associated with volcanic rocks of each cycle, have been found to be coeval with their host extrusive rocks and are thus believed to represent the ancient magma chambers of the extrusives.

Foliated syntectonic tonalites at the margin of the Michipicoten belt have been dated by zircon $U-Pb$ at $2,699-2,680$ Ma. Lithologically diverse post-tectonic plutons of the Gamitagama Lake Complex were emplaced at 2,668 Ma (Krogh and Turek 1982). Thus the age of deformation and regional metamorphism falls between 2,699 and 2,668 Ma.

Rocks to the east of the belts consist mainly of massive to migmatitic tonalite and granodiorite of the Wawa domal gneiss terrain. The greenschist grade metamorphism of the belts increases gradually eastward to upper amphibolite and granulite facies of the Kapuskasing Structural Zone (KSZ). Consequently, it is believed that this 120 km exposure represents an oblique cross section through 20 km of Archean crust, probably exhumed during the Proterozoic (Percival and Card 1983).

It is not known whether the earliest crust in the area was mafic or sialic. However, the oldest dated rock, a granite from the Hawk Lake Granite Complex which is located near the boundary between the greenstone and granitic terrain, yields an age of 2,888 +4 Ma (Turek et al. 1984). Older rocks may also occur in the lower crustal regions toward the KSZ. However, the $U-Pb$ system in zircons from this region appears to have been severely affected by the high-grade metamorphism, and yields ages from 2,650 to 2,627 Ma (Percival and Krogh 1983). These ages are significantly younger than the metamorphism indicated for the upper crustal rocks and probably reflect later blocking of the $U-Pb$ systems at deep crustal levels. For simplicity, samples from the mid-crustal and lower crustal areas east of the greenstone belts, are referred to in the tables and diagrams as "eastern gneisses". Tonalitic boulders from a conglomerate in the Michipicoten belt may have had a similar provenance and are included in this category.

Sample selection and analytical techniques

Zircon crystals from a variety of rocks from the greenstone belts were selected for study (Fig. 1). These are mainly primary zircons from terrains of low metamorphic grade. Also, zircons from areas where U-Pb ages reflect the age of metamorphism of the belts were analyzed to determine their Lu-Hf characteristics. The clearest possible crystals, weighing from 0.3 to 5 mg were washed, spiked with a mixed 233 U 236 U 230 Th 205 Pb tracer, then dissolved in high pressure bombs following the technique of Krogh (1973). Extraction of Pb in HBr medium preceded aliquoting and spiking with a mixed 176 Lu 180 Hf tracer. U and Th were extracted on a $HNO₃$ anion column. Separation of Zr and Hf from Lu employed column A of Patchett and Tatsumoto (1980). Hf was purified from Zr using the liquid cation exchanger, bis-(2-ethylhexyl) orthophosphoric acid (HDEHP) on a Teflon¹ support column. Whole rock Zr-Hf separations were done in $2N H_2SO_4$ medium using an anion column.

Mass spectrometric techniques followed those described elsewhere (Patchett and Tatsumoto 1980). Hf isotopic data are normalized to $179 \text{Hf}/177 \text{Hf} = 0.7325$. The mean value of $176 \text{Hf}/177 \text{Hf}$ in 12 runs of the JMC-475 standard analyzed during this study was $0.282202 + 9$. Pb isotopic data were corrected for mass fractionation by $0.10 \pm 0.02\%$ /amu based on repeated analyses of SRM 982. When dealing with zircons, exact duplicate analyses are not possible due to crystal heterogeneity. However, some measure of reproducibility is provided by $#22a$ and b which were selected from the same population. Although slight differences are apparent in their U -Th-Pb systems, their measured and calculated initial 176 Hf/ 177 Hf ratios are identical within error (Table 1). Regression lines on the concordia diagrams were calculated using the method of York (1969). Errors quoted on the ratios and those indicated on the diagrams are at the 95% confidence limit.

Hf isotope evolution

¹⁷⁶Lu decays to ¹⁷⁶Hf with a half-life of 3.57×10^{10} a. The Hf isotope evolution of terrestrial rocks is normally compared to chondrites which are presumed to represent undifferentiated solar system material. Thus the Hf isotope reference curve begins with a

¹⁷⁶Hf/¹⁷⁷Hf of 0.27978 \pm 9 and evolves with a ¹⁷⁶Lu/¹⁷⁷Hf = 0.0334 (equivalent to $Lu/Hf = 0.24$) over a time period of 4,550 Ma to give a present day $176Hf/177Hf=0.28286$. Analogous to Nd isotope notation (Lugmair et al. 1976; DePaolo and Wasserburg 1976), deviations from the chondritic growth curve of initial 176 Hf/ 177 Hf ratios of a given age T are expressed in parts per 10⁴ (Patchett 1983). Thus

$$
e_{\text{Hf}}{}^{T} \text{sample} = \left[\frac{\left(\frac{176}{H} \text{H} \text{f} \right)^{177} \text{H} \text{f} \right)^{T} \text{sample}}{\left(\frac{176}{H} \text{H} \text{f} \right)^{177} \text{H} \text{f} \right)^{T} \text{cm}} - 1 \right] \cdot 10^{4}
$$

where

$$
\begin{aligned} &(^{176}\text{Hf}/^{177}\text{Hf})^T\text{CHON} = (^{176}\text{Hf}/^{177}\text{Hf})^0\text{CHON} - (^{176}\text{Lu}/\\ &^{177}\text{Hf})^0\text{CHON}(e^{\lambda T} - 1) \\ &(^{176}\text{Hf}/^{177}\text{Hf})^0\text{CHON} = 0.28286 \quad (^{176}\text{Lu}/^{177}\text{Hf})^0\text{CHON} = 0.0334 \end{aligned}
$$

Fractionation of Lu/Hf during magmatogenesis is not fully understood; however, partition coefficients (D) for the rare earth elements (REE) and for Hf have been measured by Fujimaki et al. (1984). *DL,/Dar* for olivine, orthopyroxene, clinopyroxene, garnet and plagioelase are approximately 2.5, 4, 2.9, 28 and 1, respectively. This can be compared to D_{Sm}/D_{Nd} of 1.1, 1.6, 1.5, 4 and 0.8 for the same minerals. Thus the Lu/Hf of the depleted mantle has been increased by as much as two times that of Sm/Nd, whereas both ratios decrease in the crust compared to chondritic values. The average Lu/Hf enrichment factor, f , of a sample relative to chondrites, over a time interval T_0-T , can be computed with an expression analogous to Nd notation (DePaolo and Wasserburg 1976) :

$$
f = e_{\text{Hf}}^T / Q \cdot (T_0 - T)
$$

where

$$
Q = \frac{\lambda \cdot (1^{16} \text{Lu}/1^{17} \text{Hf})^0 \text{CHON} \cdot 10^4}{(1^{16} \text{Hf}/1^{17} \text{Hf})^0 \text{CHON}} = 0.0229 \text{ Ma}^{-1}
$$

Results

Zircon Lu, Hf, U and Th contents and U- Th-- Pb discordance

 U -Th-Pb isotope results for 25 zircon samples from the Michipicoten and Gamitagama belts and associated granitic terrain are presented in Table 1. The $U - Pb$ analyses shown on the concordia diagrams in Fig. 2 have been combined with previously determined age data (Smith 1981; Krogh and Turek 1982; Turek et al. 1984) and result in improvement in age precision in some cases. Apparent $^{232}Th/^{208}Pb$ ages are also given in Table 1. As in previous studies most of these ages are less than their apparent $207Pb/206Pb$ ages. Four samples ($\# 3$, 7, 19 and 22a) have anomalously old $^{232}Th/^{208}Pb$ ages. The reason for this is unknown but can be accounted for by small amounts of Th loss (maximum $<$ 10% for $\#$ 19). This apparent loss may be analytical (i.e., leaching during zircon wash or insoluble fluoride formation). Alternatively the old Th/Pb ages may indicate the presence of excess radiogenic Pb in these crystals. Although rarely reported, the addition of radiogenic Pb has been substantiated in Archean gneissic zircons from Enderby Land, Antarctica (Williams et al. 1984).

The Lu-Hf isotopic data for the zircons and two maflc whole rocks are given in Table 2. The relative abundances of U, Th, Lu, and Hfin the zircons are plotted on triangular diagrams in Fig. 3. For some zircons the Lu and Hf contents appear to be representative of the bulk chemistry of their parent magmas. For instance the low Lu contents of the syntectonic granodiorites and tonalites $(+18-20)$,

¹ Any use of trade names in this report is for descriptive purposes only and does not imply endorsement by the US Geological Survey

Field numbers appear after sample numbers

Measured ratios

a Calculated from displacement of data from concordia curve along their respective discordancy lines ^a Field numbers appear after sample numbers
b Measured ratios
c Corrected for blank; other ratios corrected for blank and initial Pb (Turek et al. 1984)
d Calculated from displacement of data from concordia curve along t c Corrected for blank; other ratios corrected for blank and initial Pb (Turek et al. 1984)

 $D_{ecav_const.}$ 2^{232} Th=4.948 x 10⁻¹¹a⁻¹ (LeRoux and Glendenin 1963), 2^{238} U=1.55125 x 10⁻¹ λ ²³5U=9.8485 × 10⁻¹ (Jaffey et al. 1971); b lanks 0.01-0.02 ng for U, " Calculated from displacement of data from concorda curve aroug tuen respective uncordancy mixes
Decay constants used: λ^{232} Th = 4.948 x 10⁻¹¹a⁻¹ (LeRoux and Glendenin 1963), $\lambda^{238}U = 1.55125 \times 10^{-10}a^{-1}$, λ 0.02-0.05 ng for Th, 0.03-0.15 ng for Pb; errors on U/Pb and Th/Pb ratios are 0.5% (2 σ).

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 λ

Fig. 2a-e. U-Pb concordia diagrams for the zircons for which the Lu-Hf analyses were made. Unless otherwise indicated the discordancy lines have been generated by combining the data for each sample with that of previous studies, a Eastern gneisses, primaryages: *line* 1 4+ 1, 2,888 Ma (II); *line* 2 ~ 2, 2,860 Ma (V). Metamorphic ages: *line 3* tonalite boulders from a Michipicoten belt conglomerate, 4+ 3 and 4+ 4, 2,650 Ma (Table 1); *line 4* Kapuskasing area tonalite, $\# 5$ and $\# 6$, 2,650 Ma (Table 1); *line* 5 Kapuskasing zone mafic gneiss, #7, 2,650 Ma (IV). b Volcanic rocks and subvolcanic granitoids: *line 1* cycle I rocks: $\# 8$, $\# 9$ (shown on inset), $\# 10$ and $\# 11$, reference line is 2,747 Ma for $\# 8$, all other units are within error of this age (I, II, V); *line 2* cycle II, $\# 12$, 2,731 Ma (II); *line 3* cycle III rocks: $\# 13$, $\# 14$ and $\# 15$, reference line is $2,710$ Ma for $\# 14$, all other units are within error of this age (I, II) . c Syntectonic granitoids: *line* $1 + 18$, 2,699 Ma (II); *line 2 4+* 19, 2,690 Ma (II); *line 3 4+* 20, 2,682 Ma (II). Post-tectonic granitoids: *line 4* Gamitagama Lake Complex plu-

may result from the low availability of Lu in these magmas; most Arehean tonalites have heavy REE depletions. Low Hf contents of zircons from a diorite-gabbro magma (424) and ± 25) are consistent with the results of earlier studies showing that zircons from more basic granitoids are characterized by low Hf contents and higher Zr/Hf ratios (e.g., Lyakhovich and Shevaleevskii 1962). The low Hf concentrations are reflected in the high 17^{6} Lu/ 17^{7} Hf compared to zircons from more felsic rocks and consequently result in a relatively large correction for in situ decay (over 0.03%).

Zircons from the high grade KSZ show depletions of both Lu and Hf $(4, 5, 6, \text{ and } 7)$. The age data for these zircons indicate resetting of the U -Th-Pb system during the \sim 2,650 Ma metamorphism. The lowest Hf content, 1,790 ppm, is from equant multifaceted crystals from a mafic gneiss $(4, 7)$. These crystals are believed to have grown during the metamorphism (Percival and Krogh 1983). In zircons, Zr^{+4} and Hf^{+4} participate in isovalent isomorphism and a decrease in Hf is expected to be accompanied by an increase in Zr. Therefore the low abundance of Hf in \pm 7 may represent a significant fractionation of Zr/ Hf. Available evidence suggests that fractionation of Hf from Zr is linked with the lower mobility of Hf due to its more basic properties (Vlasov 1966). The transport of these elements is most likely to be in aqueous fluorine-rich solutions where the Hf fluoride complexes are believed to be less stable relative to Zr fluoride complexes (Gerasimovskiy et al. 1972). Thus the low Hf content of $# 7$ might result from liberation of Zr and Hf during metamorphic recrystallization of the gneiss, at which time Zr was preferentially mobilized to form zircon while a significant fraction of the Hf leached was precipitated in situ as isomorphous inclusions in minerals such as pyroxenes and amphiboles.

Zircons from a gneissic tonalite ($\# 5$ and $\# 6$) are predominantly brown, rounded and unzoned also indicating metamorphic growth (Percival and Krogh 1983). Their U and Th contents are normal, however they have low abundances of Lu and Hf in common with $# 7$. The Lu and Hfcontents of these tonalites are clearly different from those of the syntectonic tonalites. Their $U-Th-Pb$ ages have been reset, and although they have similar discordance, their calculated e_{Hf} values vary widely. We conclude that their low Hf contents may be metamorphic and their Lu-Hf systems have probably been disturbed.

Zircons in two tonalite boulders $(4, 3, 3, 4)$ from a conglomerate within the Michipicoten belt show a variable response to metamorphism. Fine-grained $(<50 \mu m)$ low-colour crystals from one boulder $(4, 3)$ plot close to concordia near 2,650 Ma and have a low Hf concentration similar to the above tonalites. Coarser-grained $(75-125 \text{ µm})$ pink crystals from another boulder $(4, 4)$ have more discordant ratios, but give a higher $^{207}Pb/^{206}Pb$ age. This indicates that these zircons are either primary or have suffered less metamorphic disturbance. The Hf content of these zircons is more normal. In spite of these differences both analyses give unusually high $176 \text{Lu}/177$ Hf and identical e_{HF} values.

tons, $\# 21$, $\# 22$, $\# 23$, $\# 24$ and $\# 25$, reference line is 2,668 Ma for $\# 24$ (III); $\# 26$ is from the Michipicoten belt. Data sources: I = Smith 1981; II = Turek et al. 1984; III = Krogh and Turek 1982; IV = Percival and Krogh 1983; V = unpublished data

Table 2. Lu-Hf isotopic data

Conc. (ppm)			Atomic ratios				
\ddagger	Lu	Hf	176 Lu 177Hf	$^{176}\mathrm{Hf}$ 177 Hf	$^{176}\mathrm{Hf}$ $^{177}Hf_0$	T(Ma)	${e_{\rm{Hf}}}^T$
	Eastern gneisses						
$\mathbf{1}$	84.0	9550	0.001246	0.281025(10)	0.280953(10)	2888 (4)	$+0.5(0.4)$
2	15.3	3240	0.000671	0.281119(18)	0.281080(18)	2860 (20)	$+4.4(0.6)$
3	48.8	4090	0.001688	0.281283(40)	0.281194(40)	2652(3)	$+3.4(1.4)$
4	152	10580	0.002037	0.281287(43)	0.281179(43)	2652(3)	$+2.9(1.5)$
5	6.94	4890	0.000201	0.281479(55)	0.281468(55)	2650(2)	$+13$ (2)
6	12.8	4430	0.000408	0.281146(40)	0.281124(40)	2650(2)	$+0.9(1.4)$
7	3.44	1790	0.000272	0.281147(71)	0.281133(71)	2650(2)	$+1.2(2.5)$
		Volcanic rocks and subvolcanic granitoids					
8	74.2	9230	0.001139	0.281142(38)	0.281080(38)	2748 (5)	$+1.7(1.3)$
9	70.4	8055	0.000213	0.281008(28)	0.280996(28)	2747(2)	$-1.3(1.0)$
10	90.1	11360	0.000611	0.281108(20)	0.281075(20)	2747 (8)	$+1.4(0.7)$
11	65.3	12940	0.000716	0.281138 (38)	0.281099(38)	2742 (8)	$+2.2(1.3)$
12	48.5	10040	0.000685	0.281342(15)	0.281305(15)	2731(1)	$+9.2(0.5)$
13	62.0	9060	0.000970	0.281222(24)	0.281170(24)	$2717(11)$ +	$+3.9(0.9)$
14	61.0	14280	0.000607	0.281096(36)	0.281063(36)	2710 (14)	$+0.1(1.3)$
15	39.0	-10710	0.000515	0.281174(24)	0.281146(24)	2711(3)	$+3.1(0.9)$
$16*$	0.4282	2.047	0.029650	0.282899(36)	0.281268(37)	2760 (36)	$+8.7(1.3)$
$17*$	0.5458	3.413	0.022673	0.282604 (22)	0.281387(26)	2695 (54)	$+11.3(0.8)$
		Syntectonic and post-tectonic granitoids					
18	32.2	10450	0.000437	0.281171(29)	0.281147(29)	2699 (2)	$+2.9(1.0)$
19	27.5	8810	0.000443	0.281180(17)	0.281156(17)	2690 (4)	$+3.0(0.6)$
20	31.6	10090	0.000444	0.281202(14)	0.281178(14)	2682(5)	$+3.6(0.5)$
21	4.78	5260	0.000129	0.281352(100)	0.281345(100)	2668 (2)	$+9$ (4)
22a	56.8	7640	0.001055	0.281330(18)	0.281274(18)	2668(2)	$+6.6(0.6)$
22 _b	53.0	7000	0.001072	0.281324(19)	0.281267(19)	2668(2)	$+6.4(0.7)$
23	80.6	10800	0.001058	0.281173(55)	0.281117(55)	2668(2)	$+1.0(1.9)$
24	50.1	5410	0.001312	0.281312(25)	0.281242(25)	2668(2)	$+5.5(1.0)$
25	51.4	5960	0.001222	0.281344(35)	0.281279(35)	2668(2)	$+6.8(1.2)$
26	42.6	8580	0.000703	0.281166(8)	0.281129(8)	2670 (10)	$+1.4(0.3)$

Notes: Data corrected for blanks of less than 0.25 ng for Lu, and 0.3-1.0 ng for Hf; 0=initial ratios corrected for U-Pb zircon age T using decay constant: λ^{176} Lu = 1.94 × 10⁻¹¹y⁻¹ (Patchett et al. 1981); $*$ 16 and 17 are whole rock analyses; 2 σ errors in parentheses refer to the last digits, errors on ¹⁷⁶Hf/¹⁷⁷Hf ratios represent in-run precisions, errors on the calculated ¹⁷⁶Hf/¹⁷⁷Hf₀ and e_{Hf} values include in-run precisions and uncertainties in $176Lu/177H$ ratios; estimated errors on Lu and Hf concentrations are 2-5% and 0.5% on 1^{76} Lu/ 1^{77} Hf; errors on the whole rock determinations are 0.2% on Lu and Hf concentrations and 0.1 to 0.3% on 1^{76} Lu/ 1^{77} Hf; 4+ U-Pb zircon data from this study in combination with more discordant data from Turek et al. (1982) results in a significantly higher concordia age than previously reported for this rock

An analysis of euhedral zircons from a gneissic tonalite from the Hawk Lake Granitic Complex $(4, 2)$, also shows low Lu and Hf contents but indicates non-metamorphic $207Pb/206Pb$ and Th/Pb ages (Table 1). However, previous U/Pb analyses from this unit indicated some later disturbances with more discordant zircons (Smith 1981).

The above results indicate that Lu and Hf contents of zircons vary both with rock composition and metamorphic recrystallization. Low Hf contents can be expected in primary zircons from mafic rocks and in zircons that have experienced metamorphic growth or resetting. Figure 3b indicates that primary zircons in the low-grade rocks may be distinguished from the zircons from the metamorphically disturbed eastern gneisses. Note that a post-tectonic granodiorite $(4, 21)$ has low Lu and Hf contents and also plots near the metamorphic zircons but has no apparent U/Pb age disturbance other than recent Pb loss.

Xenocrystic zircon cores from a granodiorite (419)

have U/Pb ratios which scatter outside analytical error on a concordia diagram (Turek et al. 1984). The cores indicated an age ≥ 20 Ma older than the magmatic population. To avoid this problem the crystals chosen for this study were all of the euhedral magmatic variety. The $U-Pb$ analysis of these crystals gives data concordant and colinear with the magmatic fractions from the previous study. There is no indication from the e_{Hf} value of $\#$ 19 of a significant lowering of the initial Hf ratio due to the presence of older zircon material.

The $U-Pb$ analyses for zircons from the low grade rocks give ages which are less than 14% discordant. An exception is the result for a rhyolite (49) which is 32% discordant, but the sample has the lowest measured 176Hf/ ¹⁷⁷Hf. On the basis of these results we believe that zircons from the low grade terrain that yield primary ages provide reliable primary estimates of the e_{Hf} values of their host rocks. However, the Lu--Hf systems of the zircons from

Fig. 3. Hf-U-Th and Hf-Lu-Th diagrams for zircons. Sym $bols: \bigcirc$ Hawk Lake Granitic Complex; \bigcirc KSZ; \bigcirc tonalite boulders; \triangle dacites; ∇ rhyolites; \circ subvolcanic granitoids; \circ syntectonic granitoids; \bigcirc post-tectonic granitoids

higher grade rocks with non-primary $U-Pb$ ages may have been open and their calculated e_{Hf} values should be considered as maximum estimates of the primary values.

Initial 176Hf/177Hfratios of Superior Province rocks

Eastern gneisses. Analysis of zircons from the $2,888 \pm 4$ Ma granite phase of the Hawk Lake Granitic Complex (41) yields an e_{Hf} value of $+0.5$, which lies within error on the chondrite growth curve. As discussed above, previous U-Pb analyses from a tonalitic phase of the complex are scattered (Smith 1981). The zircons chosen for the present study $(+ 2)$ are much more concordant and this datum, combined with another more recently determined analysis which also consisted of clear hand picked grains (P. Smith and M. Tatsumoto, unpublished data 1986) gives an upper intercept age of 2,860 Ma (Fig. 2a). Using this age the e_{Hf} value is $+4.4$. The cause of the discordia non-linearity may be multi-stage alteration in the more discordant zircons (e.g., Nunes and Thurston 1980), however the presence of a multiple-age population cannot be ruled out. Therefore the Lu- Hf data for this unit must be interpreted with caution.

In the eastern gneisses that register metamorphic $U-Pb$ ages ($\# 3$, $\# 4$ from a tonalite boulder and $\# 5$, $\# 6$, and $\#7$ from the KSZ), e_{Hf} values range from $+0.9$ to $+3.4$ with an exceptionally high value of $+13$ for $\# 5$. Most of these values are similar to the upper crustal dacites and tonalites to be discussed later, and it is possible that some of the Hf ratios have remained close to their primary values. However, it is difficult to assess this possibility without additional data on ages or whole rock Hf isotope ratios.

Volcanic rocks and subvolcanic granitoids. Zircons from four felsic rocks from cycle I have $U-Pb$ ages that agree within experimental error at 2,747 Ma (Fig. 2b). Two dacites $(48$ and $\# 10$) and a granodiorite ($\# 11$) yield e_{Hf} values between +1.4 and +2.2. The similarity of the e_{Hf} value for the granodioritic stock $(+11)$ with the dacites of cycle I

suggests that the stock is co-genetic as well as coeval with the volcanics. A rhyolite ($# 9$) has a significantly lower e_{Hf} of -1.3 . A tholeitic pillow basalt ($\# 16$) which stratigraphically underlies these volcanics has been dated by the Pb-Pb method at $2,760 \pm 36$ Ma (Smith et al. 1986). Using this age an e_{Hf} value of +8.7, determined from a whole rock analysis, is significantly higher than the values from the felsic rocks.

Cycle II in the Michipicoten belt is represented by a quartz-diorite stock ($\#12$) emplaced at 2,731 \pm 1.7 Ma (Fig. 2b). A zircon which has only a 1.8% U-Pb discordancy age yields an e_{Hf} of $+9.2$.

Cycle III volcanics dated at 2,710 Ma are represented by a dacitic flow (413) and a rhyolite breccia (414) from the Michipicoten belt (Fig. 2b). Of equivalent age in the Gamitagama belt is a crystal tuff (4.15) of rhyodacitic composition. The dacite and the rhyodacite have e_{Hf} values of $+3.9$ and $+3.1$, respectively, and are equal within experimental error. The rhyolite yields a significantly lower e_{Hf} value of $+0.1$. Also believed to be cycle III is a pillow basalt from the Gamitagama belt (417) dated by the Pb isochron method at $2,695 \pm 54$ Ma (Smith et al. 1986). The e_{Hf} value from a whole rock sample is $+11.3$.

Syntectonic and post-tectonic granitoids. The syntectonic granitoids $(+ 18-20)$ occur near the margin of the Michipicoten belt and were emplaced between 2,699 and 2,682 Ma. e_{Hf} values in these rocks lie in a narrow range from $+2.9$ to $+3.6$ (Fig. 2c). The post-tectonic Gamitagama Lake Complex varies in composition from gabbro to quartzmonzonite. Two phases of the complex were dated at $2,668 \pm 2$ Ma by Krogh and Turek (1982). Zircon U-Pb dates on these units, together with results for three additional phases, agree with this value (Table 1, Fig. 2c). Hf in zircons from the gabbro (425) , diorite (424) , and quartzmonzonite (\neq 22) phases has a narrow e_{Hf} range of $+5.5$ to +6.8. e_{Hf} for the granodiorite ($\#$ 21), although less well determined, is within error of these values. e_{Hf} for the granite ($\#$ 23) is significantly lower ($+1.0$). A post-tectonic rapikivi granite $(4, 26)$ in the Michipicoten belt has a similarly low e_{Hf} of $+1.4$.

Discussion

*Sources of e*_{Hf} variation

This Hf isotopic study indicates that many of the differences in trace element chemistry of greenstone belt rocks cannot be the result of short-term processes such as fractional crystallization or partial melting but rather must be ascribed to radiogenic growth in different source reservoirs separated for a long time. The range of e_{Hf} values from $+11.3$ to -1.3 for the diverse rocks of the Michipicoten and Gamitagama greenstone belts is evidence for at least two isotopically distinct source regions for these rocks. The data are plotted on the Hf evolution diagram (Fig. 4); all the points except one lie either within error of, or are above, the chondritic Lu--Hf growth curve defined by Patchett and Tatsumoto (1980). In general there is an inverse correlation between silica content and e_{Hf} values. The correlation between the isotopic and petrochemical compositions will be refined when detailed trace element studies on these rocks become available.

Evidence for depleted mantle sources for Archean green-

Fig. 4. e_{Hf}^T vs T diagram for zircons from the Michipicoten and Gamitagama greenstone belts and surrounding granitic terrain. Also shown are the whole rock basalt analyses (16 and 17) and trajectories proportional to their measured Lu/Hf ratios *(dotted lines). Horizontal line* corresponds to the chondritic growth curve $(e_{HF} = 0)$. Evolution paths are shown for hypothetical reservoirs (depleted mantle, lower crust and upper crust), as discussed in the text. Zircons with metamorphic U-Pb ages are not shown. Error bars are $\pm 2 \sigma$

stone rocks has been suggested by Nd isotopic studies. Mafic volcanic rocks from the contemporaneous Abitibi belt yield e_{Nd} values ranging from $+4$ to $+1$ (Cattell et al. 1984; Dupré et al. 1984). The Michipicoten and Gamitagama tholeiites, which have e_{Hf} values of $+8.7$ and $+11.3$, respectively, are consistent with the Nd data. Although the values representing the depleted mantle necessarily are obtained from whole rock analyses and cannot be considered of the same quality as data for zircon, the zircon results for the cycle II quartz-diorite give an e_{Hf} value of +9.2, within error of the tholeiitic basalt value. Also substantiating these high enrichments are duplicate Lu -Hf analyses for zircons from the Uchi greenstone belt (Patchett et al. 1981) dated at $2,730 + 1.3$ Ma (Nunes and Thurston 1980). These zircons are identical in age to the quartz-diorite dated at $2,731 \pm 1$ Ma.

The e_{Hf} values of the more differentiated rocks are significantly lower than those derived from the depleted mantle. Particularly striking are the large differences between the data for felsic volcanics and the basalts. Direct derivation of the felsic volcanics from the basalts is clearly not possible. Rather, the lower values of the felsic rocks are best interpreted to reflect a derivation involving older continental crust. Old crust with the essential non-radiogenic isotopic composition could be derived from the reprocessing of sediments. Patchett et al. (1984) have demonstrated that coarse to medium clastic sediments have low Lu/Hf. They suggested that this is due to the chemical resistance of zircon and the resultant concentration of this mineral in the sediments. Subducted trench sediments containing aged unradiogenic zircons, if incorporated into the depleted mantle, could give lower e_{Hf} values in rocks subsequently derived from that mantle. Although this is a possibility, a more probable alternative is the introduction of old crust via direct reheating of older basement material. The granite from the Hawk Lake Granitic Complex (41) provides a suitable non-radiogenic source. Moreover, the rocks that are geographically closest to $\#$ 1 have the lowest e_{Hf} values. The e_{Hf} value of rhyolite $\# 9$ is consistent with a derivation by anatexis of $# 1$. An upper crustal derivation for $# 9$ is supported by Pb isotopic evidence where high apparent μ_1 values have been found for the rhyolite and associated iron formation (Smith and Farquhar 1983). This model is also supported by the similarity of U, Th, Lu, and Hf abundance patterns for the basement granite and the rhyolite in Fig. 3.

Dacitic rocks from cycles I and III have intermediate e_{HF} values between the basalts and the rhyolites. In addition, the younger syntectonic tonalites and granodiorites have similar e_{Hf} values which possibly indicate a related source. A number of workers have suggested that the geochemical character of tonalites and associated rocks can be accounted for by partial melting of eclogite or garnet amphibolite of basaltic composition, at mantle or lower crustal depths, leaving residual garnet (Arth and Hanson 1972; Barker and Arth 1976; Glikson 1979). If early formed, foundered or subducted basaltic crust was melted to produce the later tonalitic rocks, the basalts comprising this crust must have maintained moderately high e_{Hf} values prior to melting. Either these basalts were not much older than the melts or their Lu/Hf ratios were low enough to maintain their e_{Hf} values above that of chondrites during the period prior to melting. The very high positive e_{Hf} value of the cycle I tholeiite precludes an origin of the tonalitic rocks by partial melting of these basalts. Older basalts are not recorded in the greenstone belts. However, basalts having ages and e_{Hf} values similar to the 2,860 Ma tonalite $(4, 2)$, and having Lu/Hf ratios like those of $\# 16$ and $\#$ 17, would be suitable precursors of the tonalitic rocks. The higher positive e_H values observed in the tonalitic rocks relative to the other felsic rocks may result from the fact that the source regions for these rocks had more mafic characteristics with higher average e_{Hf} values and Lu/ Hf ratios.

Another explanation for the e_{Hf} values of the tonalites is that they were derived from source regions which were modified early in their histories by processes that led to increases in their Lu/Hf ratios. What little evidence we have points to the lower crust as the most likely reservoir in which this enrichment might take place. It seems clear that this segment of the lithosphere has been depleted to varying degrees in mobile elements such as K, Rb, U and Th either by crustal anatexis (e.g., Nesbitt 1980) or $CO₂$ rich fluid metasomatism (e.g., Lambert and Heier 1968). Less is known about how the concentrations of Zr, Hf and Lu vary as a result of these deep seated processes. The study by Fujimaki et al. (1984) indicates that residual garnet, stable at lower crustal depths, may retain a large fraction of available Lu. On the other hand the REE and Zr appear to have been extremely mobile in some Australian granulites (Windrim et al. 1984). In these rocks Zr/Hf ratios ranged up to 144, compared to the average value of \sim 40 for many igneous and metamorphic rocks (Brooks 1970; Ehmann et al. 1975). Allen et al. (1985) noted the differences in Hf concentrations and Zr/Hf ratios between prograde charnokites and retrograde gneisses in southern India, These changes were ascribed to the effects of fluoride bearing fluid phases which preferentially dissociated Hf into the gneisses as the solution became more alkaline. In the KSZ, depletion of Hf and enrichment of Zr appear to have occurred. Truscott and Shaw (1986) have determined an average Hf concentration of 2.7 ppm and a Zr/Hf ratio of \sim 90 from rocks from the KSZ. The low Hf concentrations of the KSZ zircons show that fractionation of Zr/Hf in the lower crust can take place by the growth of metamorphic zircon. These zircons could have grown from a Zr rich, Hf poor fluid phase migrating from greater depths. Supporting evidence comes from another isotopic system. A whole rock Pb isotopic analysis of a syntectonic tonalite (\pm 21) has ²⁰⁶Pb/²⁰⁴Pb = 15.41, ²⁰⁷Pb/²⁰⁴Pb = 14.97 and $^{208}Pb/^{204}Pb = 39.83$ (P. Smith and R. Farquhar, unpublished data 1984). This composition also suggests that this rock has a lower than average U/Pb, and higher than average Th/U, features which are again characteristic of rocks in the lower crust (Gray and Oversby 1972).

Sparse as it is, the data we have suggests that an enhancement of the Lu/Hf ratio in certain areas of the lower crust may result from the preferential retention of Lu and/ or the loss of Hf via fluid metasomatism or crustal anatexis. Any increase in this ratio could lead to a higher e_{Hf} in tonalites derived from this reservoir only if the increase took place sufficiently early in the reservoir's history. The 2,888 Ma granite $(4, 1)$ is evidence that this may have occurred. The granite, which cannot have been derived directly from the mantle, is the product of an early intracrustal fractionation which might have given rise to a (lower crustal?) reservoir enriched in Lu relative to Hf. Alternative mechanisms to explain the e_{Hf} values of the tonalite magmas, such as mixing (discussed later), are possible. However, we stress that detailed whole rock Lu-Hf studies of granulite terrains are needed before more quantitative assessments can be made or before questions such as the proportions of recycled material in the rocks can be addressed.

Time trends

If we accept as a working hypothesis the view that the observed e_{Hf} distributions on Fig. 4 are the result of the extraction of the various rock types from different reservoirs, from time to time, then an analysis of the time trends is relevant. There are trends on two scales: (1) short-term differences or those indicated by rocks of various compositions comprising a single greenstone belt cycle; and (2) long-term differences evolved in similar rock types over the total life span of the greenstone belts.

A typical short-term trend in e_{Hf} is shown by cycle I volcanics in the Michipicoten belt, where the rocks are all within error of 2,748 Ma in age. The relative ages of the members of this group have been deduced stratigraphically. The earliest member consists of a tholeiitic pillow basalt with an e_{Hf} of +8.7 which is overlain by a dacitic tuff having an e_{Hf} of +2.0. The cycle is capped by a rhyolite with an e_{Hf} of -1.3 . The trend in this cycle involves a progressive change from depleted (mantle) to more enriched (crustal) source reservoirs. These features could be accommodated in a growth model of a cycle that involved decreasing depth of melting with time. The later felsic rocks could be produced by assimilation or intra-crustal melting of old crust. Renewed deeper melting and a return to depleted mantle signatures marks the beginning of another cycle. The granite phase of the Gamitagama Lake Complex has a lower e_{HF} value compared to earlier phases and thus the posttectonic granitoids show a similar time trend toward lower (crustal) e_{Hf} values.

Inspection of Fig. 4 shows that when rocks of similar composition, but different age, are considered separately, long-term age trends are apparent. For separate rock types e_{HF} values decrease with increasing age. Points for the two basalts, together with samples ± 2 and ± 12 , lie on a trend that corresponds to a rate of increase in e_{Hf} of about 0.05 e_{Hf} units/Ma. If this trend represents the depleted mantle sampled at different times, then the intersection of the trend with the chondritic growth curve at 2,900-3,100 Ma may date the time of mantle depletion. Individual model source ages analogous to those calculated using the Sm-Nd method cannot be of assistance in determining the age of depletion for the basalts because, as noted by Unruh et al. (1984) for lunar mare basalts, the present day Lu/Hf ratios of these rocks are less than chondritic (Fig. 4). However, the trend intersection age agrees with a 3,070 Ma model Nd isotope age derived from Abitibi komatiites with presumed unfractionated Sm/Nd ratios (Dupré et al. 1984). Furthermore, the enrichment factors (f) of $1-2$ implied by the trend are not incompatible with theoretical factors calculated for a residual mantle using Lu and Hf distribution coefficients and assuming a wide range of the degree of partial melting.

The $2,748 - 2,682$ Ma dacites and tonalites also indicate a roughly positive trend when their e_{Hf} is plotted against time. If the rocks were entirely derived from a high Lu/Hf source as discussed earlier, then their growth in 176 Hf/ 177 Hf, the positive trend on Fig. 4, provides us with a rough estimate of the Lu/Hf ratio in that source (0.06). On the basis of our isotopic results alone, it is impossible to decide whether the observed distribution of e_{Hf} values for the tonalitic rocks is due to deep seated fractionation of Lu/Hf, or simply the result of crustal mixing. It is possible to derive the observed trend of e_{Hf} values by the remelting of basalts,

as discussed above, with the local incorporation of sediments or felsic materials. Since the Lu/Hf ratios in these materials would be substantially lower than those in the basalts, e_{Hf} values would be reduced. However the rough time trend in e_{Hf} values on Fig. 4 then requires that the mixing ratios of basalt to upper crustal material over the time range sampled (66 Ma) must be approximately the same. We regard this as a less likely scenario than the derivation of the tonalites from a deep seated source depleted in Hf.

Although at this time we do not favour mixing of old crust into the depleted mantle to explain the time trends, the data are insufficient to rule out this process. For example, it could be argued that the old crust affected all rocks (including the basalts) such that the amount of assimilation of the low e_{Hf} source material in all rocks decreased with time. This has been observed in modern island arc rocks where observed decreases in contamination with time have been attributed to buffering of later derived magmas from the crust by lining conduits with more recent magma (Myers et al. 1985). An alternative possibility is the gradual removal of old crust from the magma generation area by rifting (e.g., Nohda and Wasserburg 1981).

Volcanism in this area has been described as being bimodal in composition (Ayres 1983). The participation of old crust in the generation of the felsic rocks in this greenstone terrain, as inferred by our Hf isotope measurements, supports this idea and suggests analogies to Cenozoic anorogenic and continental margin volcanism. Distinctive Pb and Sr isotopic signatures for bimodal volcanism in the San Juan volcanic field have been interpreted by Lipman et al. (1978) to reflect the lower crust for felsic volcanics and mantle keel for basalts.

The Hf isotopic results for the Michipicoten and Gamitagama greenstone belts contrast with available Sr initial isotopic data on Archean rocks. No differences have been discerned among felsic and mafic volcanic rock types with respect to their initial ${}^{87}Sr/{}^{86}Sr$ ratios (Hart and Brooks 1977; Wetherill et al. 1981). The Hf data also contrast with a recent $Sm-Nd$ study of greenstone belt rocks from the Wabigoon Subprovince in the western Superior Province (Shirey and Hanson 1983). In this region, a variety of crustal rocks have homogeneous mantle-like e_{Nd} values. On the other hand Pb isotope analyses for Superior Province ore deposits, many of which are in the Wawa Subprovince, suggest that large differences in source μ_1 values may have existed.

Conclusions

(1) The abundances of Lu, Hf, U, and Th in zircons from various rock types from the southern Superior Province show considerable variation which can be linked with host rock composition. In some cases the Lu/Hf ratio can be comparatively high for zircons, leading to relatively large in situ decay corrections to the ^{176}Hf ¹⁷⁷Hf ratios in Archean zircons. No correlation between zircon U-Pb discordance and e_{Hf} was found.

(2) Zircons from the KSZ have low concentrations of Lu and Hf. The low Hf contents indicate that growth of metamorphic zircon in the lower crust can lead to fractionation of Zr from Hf.

(3) The 176 Hf/ 177 Hf ratios in the zircons are interpreted to result from long-lived heterogeneities in the sources of

Michipicoten and Gamitagama rocks. Initial Hf ratio differences exist among the phases of each volcanic cycle and within the post-tectonic granitoids. Rhyolites and potassic granitoids have the lowest e_{Hf} values (-1.3 to +1.4), suggesting that their Hf ratios are dominated by a continental crust component exemplified by the 2,888 Ma granite from the Hawk Lake Granitic Complex. Dacites, granodiorites and tonalites including the later syntectonic granitoids have significantly higher e_{Hf} values (+1.4-+3.9) indicating that their parent rocks in the lower crust had higher Lu/Hf ratios. The higher Lu/Hf ratios for these precursors may stem from the fact that they are more mafic or may reflect early deep-seated processes which have led to the enhancement of the Lu/Hf in the lower crust. Greenstone belt tholeiites have the highest e_{Hf} values (+8.7 and +11.3) and indicate derivation from a depleted mantle.

(4) The syntectonic granitoids surrounding the Michipicoten belt have e_{Hf} values similar to the earlier dacites. This suggests a genetic link between these rock types.

(5) The rocks of this area show time progressive increases in their e_{Hf} values over their \sim 220 Ma life span. The preferred interpretation for the basalt trend is that it reflects an early mantle depletion at 3,100-2,900 Ma. The dacite-tonalite trend is interpreted to record an early fractionation of the Lu/Hf ratio in the lower crust. On the other hand, if all the rocks (including the basalts) have been affected by mixing processes to some degree, then the overall time trends towards higher e_{Hf} values could reflect systematic increases in the proportion of the depleted mantle contributions over crustal contributions.

(6) Lu–Hf studies in zircons, dated accurately by $U-$ Pb, provide a sensitive technique for the study of greenstone belt evolution. Results of this Hf isotopic study provide the first evidence of distinct isotopic differences between mafic and felsic rocks and of time correlations of e_{HF} in Archean rocks. This adds support to more uniformitarian ideas with respect to greenstone belt evolution.

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