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Lu–Hf systematics of the ultra-high temperature Napier Metamorphic Complex in Antarctica: Evidence for the early Archean differentiation of Earth's mantle

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Abstract

The Napier Complex of the East Antarctic Craton comprises some of the oldest rocks on Earth (~3.8 billion years old), overprinted by an ultra-high temperature (UHT) metamorphic event near the Archean–Proterozoic boundary. Garnet, orthopyroxene, sapphirine, osumilite, rutile and a whole rock representing a fully equilibrated assemblage from this UHT granulite belt have yielded a Lu–Hf isochron age of 2403±43 Ma, the first ever determined on a UHT mineral assemblage. Preservation of the UHT mineral assemblage in the rock analyzed, without any significant retrogression, suggests rapid cooling with closure likely to have occurred for the Lu–Hf system at post-peak UHT conditions near a temperature of ~800 °C. This mineral–whole rock isochron yields an initial $^{176}Hf/^{177}Hf$ ratio corresponding to an ε_{Hf} value of −14±1, acquired during UHT metamorphism. Such a low value demonstrates that overall UHT granulites evolved in a low Lu/Hf environment, probably formed when the rocks were first extracted from a highly depleted mantle. Zircon ε_{Hf} values we have measured "see through" the UHT metamorphism and show that the source materials for the magmas that formed the Napier Complex were extremely depleted (>+5.6 ε_{Hf} at 3.85 Ga) relative to the chondritic uniform reservoir (CHUR). These results also suggest significant depletion of the early Archean mantle, in agreement with the early differentiation of the Earth that the latest core formation models require.

Keywords: UHT granulite; Lu–Hf isotope; zircon; Archean; Napier Complex; Antarctica

1. Introduction

Evidence that at least portions of the Earth's mantle were already chemically depleted by melting before the formation of the oldest surviving crust has come chiefly from Sm–Nd isotopic studies of the oldest cratons (e.g., Itsaq in Greenland) [1–3]. However, this interpretation

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has been questioned because of increasing recognition that the Sm–Nd system can be perturbed by some younger metamorphic and metasomatic events [4,5]. It is generally thought that the Lu–Hf system is not as easily reset as the Sm–Nd system because (i) the two most important minerals for this method, garnet and zircon, act as protective armor against the migration of ions in or out of the system during younger deformational events, (ii) Hf has a considerably smaller diffusivity in silicate minerals than do Nd or Pb, and (iii) Hf is present in zirconium minerals – zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) – at the wt.% level of concentration, tightly bound in the crystal lattice such that its isotopic compositions are not easily reset. Lutetium occurs in significant amounts in minerals with an affinity for the heavy rare earth elements (HREE), such as garnet and zircon. However, zircon has an even greater affinity for Hf over Lu by several orders of magnitude, overall resulting in low Lu/Hf values, usually <0.001, so that correction for in situ radiogenic growth is negligible. Even singularly, therefore, zircon can provide unique information about the geochemical evolution of both the continental crust and mantle during the Archean. Furthermore, the short half-life of radioactive ^{176}Lu permits rapid ingrowth of radiogenic ^{176}Hf at a rate that is three times faster than the ingrowth of radiogenic ^{143}Nd from the alpha decay of ^{147}Sm. Hence, the Lu–Hf isotopic system is particularly well suited for isochron dating of rocks with garnet, pyroxene, rutile and zircon in their primary mineral assemblages, usually with a wide range in Lu/Hf values.

We have conducted Lu–Hf systematics of mineral separates and whole-rock samples from Bunt Island, and zircon grains from Gage Ridge in the Napier Complex of the East Antarctic Craton (Fig. 1) in order to constrain Archean crustal and mantle evolution and to assess the robustness of the Lu–Hf isochron dating method during ultra-high temperature (UHT) metamorphism.

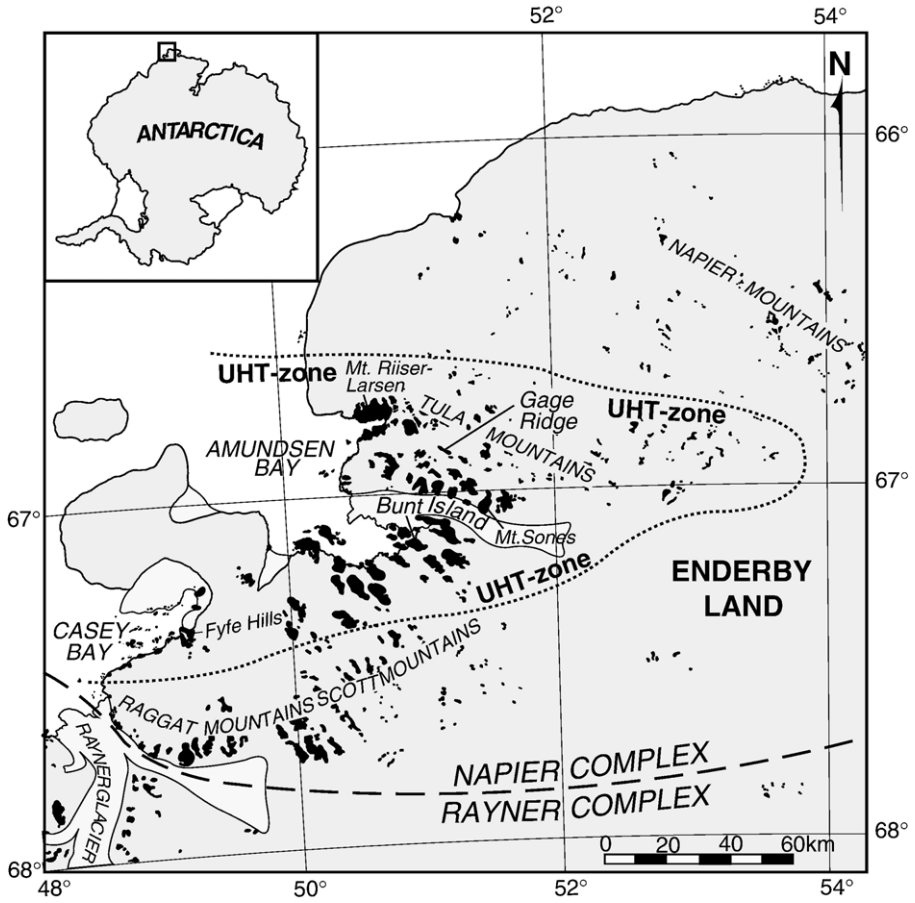

Fig. 1. Outcrop map of the western Napier Complex, Enderby Land, East Antarctica. Areas of outcrop are indicated in black. The approximate extent of UHT mineral assemblages (UHT-zone) is indicated by the short dashed line, after Harley and Motoyoshi [9], and the southwestern boundary between the Napier and Rayner Complexes is indicated by the long dashed line, after Sheraton et al. [8].

2. General geology

The Napier Complex in northern Enderby Land is one of the most famous regional UHT metamorphic terranes in the world, typified by the occurrence of sapphirine+quartz and garnet+osumilite, and close association between mafic and felsic rocks in what is thought to be tectonic interleaving [6,7]. The UHT mineral assemblages imply peak metamorphic conditions of $T \approx 1050–1120$ °C and $P \approx 7–11$ kbar, followed by a period of near-isobaric cooling [7–9]. The complex is dominated by ca. 2990–2800 Ma tonalitic to granitic orthogneiss [10]. However, granitic to tonalitic orthogneisses – remnants of early Archean crust [10–12] – with SHRIMP zircon U–Pb concordia upper intercept crystallization ages at ca. 3800–3900 Ma, have been identified in the Fyfe Hills, Mt. Sones and Gage Ridge [10,13] (Fig. 1). SHRIMP dating [10,13] revealed the presence of some rare, reversely discordant grains with apparent $^{207}Pb/^{206}Pb$ ages >4.1 Ga among the predominant 3.8-Ga zircon population. Because of their low U concentrations and reverse discordance, however, Kelly and Harley [7] argued that Pb diffusion and localized Pb enrichment might have played a role in the development of the observed pattern, and therefore that the >4.1 Ga ages might be slightly older than the actual age. Three major tectonothermal events affected the complex between ca. 2990 and 2450 Ma, after which the area has essentially remained undisturbed, except for reworking of its eastern and western margins during the ~1 Ga Grenville event [7,8,14]. Although the precise timing of peak UHT metamorphic conditions and duration of the event in the Napier Complex have been the subject of considerable debate, it is generally agreed that this occurred at or prior to ca. 2500 Ma, which straddles the ca. 2590 to 2450 Ma range obtained by a variety of methods on both metamorphic and plutonic rocks [7,15–17]. The debate has focused on whether SHRIMP zircon U–Pb ages of 2490–2450 Ma represent a protracted period of peak UHT metamorphic conditions [16,17] or are the result of post-UHT zircon growth associated with cooling of the complex through ~800 °C [7].

3. Sample description

Our UHT samples from Bunt Island preserve high-grade mineral assemblages including garnet, orthopyroxene, sapphirine, quartz and osumilite, as summarized in Table 1, and described in detail by Osanai et al. [6]. The samples we have studied were collected from one outcrop that exhibits thin layering (a few cm-scale) with different constituent minerals. The granulites have coarse-grained (1 mm–2 cm) granoblastic to porphyroblastic polygonal to lobate textures. Rutile is always present as a minor phase, both as acicular inclusions in orthopyroxene, osumilite, quartz, sapphirine and garnet, and as a separate phase along grain boundaries. Zircon is an accessory mineral, abundant especially in sample Bunt 01-2, and occurs as inclusions with quartz in orthopyroxene, osumilite, sapphirine and especially garnet, and at grain boundaries. Garnets (usually 1–5 mm in size) have compositions of pyrope (50–55%)–almandine (45–50%)–grossular (1–2%) solid solutions [6], and occur as polygonal to lobate shapes in osumilite-bearing granulites. These garnets often are anhedral porphyroblast (1–2 cm) containing lobate/ovoid inclusions of rutile, zircon, quartz, orthopyroxene, and occasional spinel. No optical growth zoning patterns are observed in the garnet, except for the thin rims adjacent to orthopyroxene ([18]; Osanai et al., unpublished data). The garnet in the mafic granulite is present both as interstitial grains (0.1–1 mm in width) and exsolution lamellae in orthopyroxene, consistent with near-isobaric cooling at high pressure [18]. Orthopyroxene in two samples (Bunt 01-2 and -5) is replaced by cordierite-bearing symplectite, also thought to have formed during retrogression. Lamellar intergrowth of sapphirine and quartz in orthopyroxene is particularly well developed in Bunt 01-2 and -5. Phlogopite is present as a rare interstitial phase in Bunt 01-6.

Table 1
Rock types and mineral assemblages of the studied samples from Bunt Island in the Napier Complex, East Antarctica

Sample no.	Bunt 01-2	Bunt 01-5	Bunt 01-7	Bunt 01-6
Rock type	Osumilite-bearing granulite	Osumilite-bearing granulite	Osumilite-bearing granulite	Mafic granulite
Osumilite	+	+	+	
Sapphirine	+	+	+	
Sillimanite	−	−	−	
Garnet	+	+	+	+
Orthopyroxene	+	+	+	+
Clinopyroxene				+
Cordierite	−	−	−	
Phlogopite				−
K-feldspar	+	+	+	−
Plagioclase	+	+	+	−
Quartz	+	+	+	−
Rutile	−	−	−	−
Zircon	−	−	−	−
Spinel	−		−	−
Opaque phases				−

(+) present; (−) minor or local.

The four individual zircon grains among the minerals studied were obtained from a massive granitic orthogneiss (Sample 78285013) from Gage Ridge (Fig. 1). The orthogneiss is composed primarily of mesoperthite and quartz, but has a trace of orthopyroxene and accessory zircon. The zircon was dated previously by the U–Pb method [10], and analyzed for trace element concentrations [7], which provided the critical background necessary for the Lu–Hf systematics reported here. The zircons are medium to dark brown, well rounded, elongate, and zoned (Fig. 2). Under cathodoluminescence and backscattered electron imaging, each of the grains shows a core with micrometer-scale oscillatory zoning surrounded by a narrow, relatively homogeneous rim (Fig. 2), believed to represent subsolidus metamorphic crystal growth or recrystallization. The elongate shape and oscillatory zoning of the zircon cores are

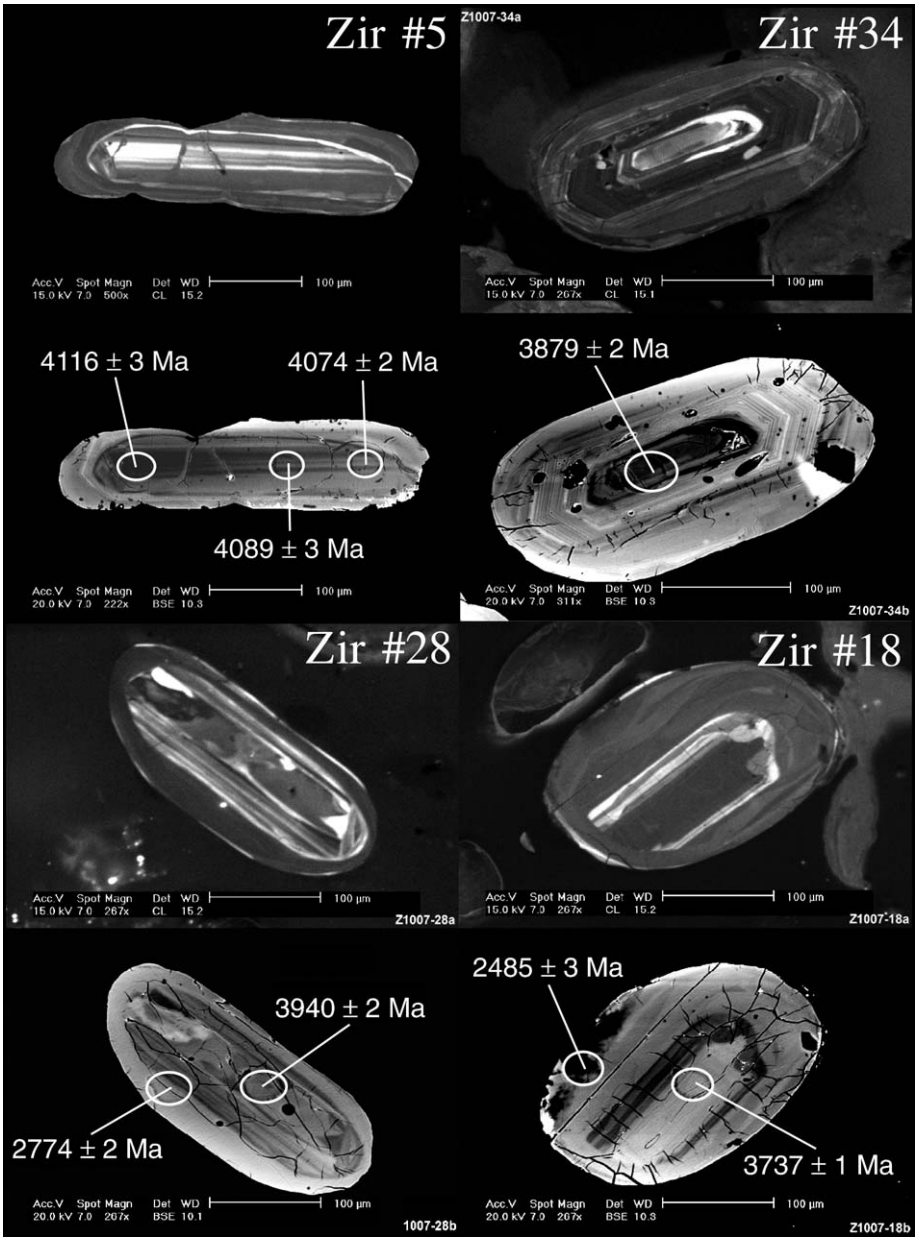

Fig. 2. SEM images (cathodoluminescent – CL, and backscattered electron – BSE) for zircon grains from the Gage Ridge orthogneiss. All scale bars are 100 μm. All ages are $^{207}Pb/^{206}Pb$ ages with errors at 1σ level [7,10].

interpreted to be the result of magmatic crystallization, which has been supported by a preservation of magmatic REE patterns [7]. The magmatic zircon cores yield $^{207}Pb/^{206}Pb$ ages between 4116 and 3737 Ma (Fig. 2) with 3% normal to 4% reverse discordance, and produce an upper intercept with the concordia curve at 3850 Ma. This value is interpreted to represent the crystallization age of the early Archean igneous precursors for the orthogneisses [10]. The overgrowth rim of relatively stubby zircon gives a younger $^{207}Pb/^{206}Pb$ age of 2485 Ma with 4% normal discordance, recording subsolidus growth during the UHT metamorphism in the complex. The strongly elongate (450×150 μm) and zoned Zir #5 with no younger growth yields a weighted spot $^{207}Pb/^{206}Pb$ age of 4093±53 Ma with a reverse discordance of ~4%, and is the most pristine sample used for our Hf isotopic study of the early Archean mantle.

4. Analytical procedures

Measurements have focused on zircon, garnet, orthopyroxene, osumilite, rutile and sapphirine, and whole rock samples. Mineral separates were prepared from samples free of any visible surface weathering following established procedures [19]. Hafnium was isolated at the University of Michigan using a two-stage separation column procedure before analysis on a multi-collector ICP–MS (Nu-Plasma HR). Our sample dissolutions are carried out in concentrated HF and HNO_3 (10:1) in steel-jacketed Teflon® bombs at oven temperatures of 240 °C for at least 2 days. Upon driving off the HF and HNO_3 solution, the samples are completely dissolved in 6N HCl on a hot plate, and are then aliquotted and spiked with a $^{176}Lu-^{178}Hf$ solution. After spike-sample homogenization, each sample is dried down (but not baked) on a hot plate. 4 M HF is added to the residue, and then the closed beaker is left on a hot plate overnight in order to bring the maximum amount of Hf back into solution, while at the same time entraining REE with fluoride salts. The Hf in solution and the fluorides containing the REE and other minor and trace elements (e.g., Ti, Cr, Zr, Nb, etc.) are then separated from each other by centrifuging and pipetting. This first-order separation of REE from Hf eliminates the potential isobaric interferences from Lu and Yb on the critical radiogenic ^{176}Hf during mass spectrometric analysis. The solution containing Hf is loaded on an anion-exchange column (AG1-X8, 200−400 mesh) for further purification. The sample matrix and any residual trace of REE are removed by 4 M HF eluant, while Hf, and the closely related elements Zr, Ti, Nb, Cr, etc., adhere to the resin as fluoride complexes until eluted with a mixture of 6 M HCl–1 M HF. Although the elements accompanying Hf after the first elution (Zr, Ti, Cr, etc.) do not behave as ionization suppressor for Hf [20], the presence of significant amounts of Ti and Cr in the Hf fraction reduces the transmission of Hf significantly during mass spectrometric analyses on the Nu-Plasma and can lead to a drastic decrease in analytical sensitivity. Therefore, Ti and Cr are separated from Hf on a second-stage cation-exchange column (Ln Resin LN-B25-A, 100 −150 mesh) using 2 M HCl–0.1 M HF mixture. This step is necessary only for isotopic composition measurements, and it was not applied to the spiked samples. Although we were not able to get rid of Ti completely, its concentration in the sample was reduced dramatically, and no difficulties were noted during the analyses on the Nu-Plasma.

For the spiked aliquot, the sample matrix and residual traces of REE are combined with the REE in fluoride residue produced in the first separation step to maximize the Lu yield. The mixture is treated with 6 M HCl, evaporated to dryness, and taken up in 2.5 M HCl. The treatment with 6 M HCl is necessary here to completely convert fluorides into chlorides for full recovery of the REE. The sample is loaded on to a cation-exchange column (AG50W-X8, 200–400 mesh) where washing with 2.5 M HCl leaves a rather pure REE fraction on the column [21]. Further addition of 6 M HCl in appropriate amounts strips dominantly the heavy REE fraction, which is analyzed directly on the Nu-Plasma for Lu without further separation. Measured values for $^{176}Hf/^{177}Hf$ of the JMC-475 Hf standard yielded a mean of 0.282125±0.000024 (N=32, $2\sigma_m$). The total procedural blank level was about 30 pg for Hf. The results are presented in Table 2.

5. Result and discussion

Because our results include calculations for which a ^{176}Lu decay constant ($\lambda^{176}Lu$) has to be adapted, this section begins with justification for the value used. Several $\lambda^{176}Lu$ values ($1.86–1.98\times10^{-11}$ yr^{-1}) are reported in the literature, determined using the Lu–Hf isochron method on samples dated previously using other methods for which the decay constants are known [22–28]. The calibration experiments on terrestrial minerals dated by U–Pb systematics have yielded $\lambda^{176}Lu$ values of 1.865×10^{-11} yr^{-1} [22] and 1.867×10^{-11} yr^{-1} [23], whereas whole-rock meteorite isochrons have given values from 1.93×

Table 2
Lu–Hf isotope data for the UHT rocks from the Napier Complex, East Antarctica

Sample no.	[Lu] (ppm)	[Hf] (ppm)	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	2σ	Age±2σ [1.87][a] $(\varepsilon Hf)_i$	Age±2σ [1.93][b] $(\varepsilon Hf)_i$	Age±2σ [1.98][c] $(\varepsilon Hf)_i$
Bunt Island								
Bunt 01-2								
Grt	3.53	4.54	0.1103	0.285520	0.000005	2203±44	2128±42	2072±41
Opx	0.28	4.84	0.0083	0.281244	0.000006	(−17.2±1.2)	(−17.2±1.2)	(−17.2±1.2)
Spr	0.02	5.34	0.0005	0.280902	0.000011	MSWD=5.9		
Os	0.06	2.11	0.0039	0.281069	0.000009			
WR[d]	0.74	2.55	0.0409	0.282711	0.000009			
Bunt 01-5								
Grt	13.81	2.88	0.6798	0.301423	0.000003	1584±55	1531±54	1490±52
Opx	0.31	3.03	0.0145	0.281508	0.000004	(−25.8±11.7)	(−25.8±11.7)	(−25.7±11.7)
Spr	0.08	6.16	0.0018	0.280960	0.000010	MSWD=545		
WR	0.19	1.54	0.0173	0.281682	0.000016			
Bunt 01-6								
Grt	22.25	3.48	0.9052	0.306580	0.000004	1489±55	1439±53	1401±52
Opx	0.43	6.54	0.0093	0.281262	0.000003	(−27.9±11.0)	(−27.9±11.0)	(−27.8±11.0)
Opx(h)[e]	0.55	1.51	0.0521	0.282875	0.000008	MSWD=1958		
R–Opx(h)	0.22	5.01	0.0062	0.280992	0.000006			
Rut[d]		181.59		0.280848	0.000027			
WR	0.69	4.45	0.0219	0.281811	0.000009			
Bunt 01-7								
Grt[d]	2.12	7.88	0.0381	0.282691	0.000006	2403±43	2322±41	2260±40
Grt(h)[e]	2.92	5.65	0.0732	0.284219	0.000003	(−13.6±1.0)	(−13.6±1.0)	(−13.5±1.0)
R–Grt(h)[d]	0.67	11.38	0.0084	0.281309	0.000008	MSWD=7.2		
Opx	0.10	1.95	0.0070	0.281203	0.000005			
Os	0.03	4.19	0.0011	0.280905	0.000010			
Rut	37.46	1574.90	0.0035	0.281019	0.000109			
WR	0.76	3.15	0.0344	0.282455	0.000009			
Gage Ridge								
Sample No. 78285013								
Zir #5	73.93	10,054.50	0.0010	0.280453	0.000011	(2.7±0.4)	(5.8±0.4)	(8.4±0.4)
Duplicate				0.280440	0.000014			
Zir #18	80.41	12,280.49	0.0009	0.280491	0.000013	(4.3±0.5)	(7.4±0.5)	(10.0±0.5)
Zir #28	64.00	13,995.53	0.0006	0.280505	0.000010	(5.6±0.4)	(8.7±0.4)	(11.3±0.4)
Zir #34	78.75	13,049.26	0.0009	0.280433	0.000007	(2.5±0.3)	(5.6±0.3)	(8.2±0.3)

Normalized for mass fractionation to $^{178}Hf/^{177}Hf=1.46718$. $^{176}Hf/^{177}Hf$ of JMC-475 Hf standard=0.282125±0.000024 ($N=32$, 2σ).
Errors for [Hf], [Lu], and $^{176}Lu/^{177}Hf$ are ~1% (2σ).
$(\varepsilon_{Hf})_i$ for zircons are calculated with the concordia upper intercept age of 3.85 Ga [10].
Data regression was done using ISOPLOT after method of Ludwig [47].
Grt=garnet, Opx=orthopyroxene, Os=osumilite, Rut=rutile, Spr=sapphirine, Zir=zircon, WR=whole rock, R=residue.
[a] Calculated with the $\lambda^{176}Lu$ value (1.865×10^{-11} yr^{-1}) of Scherer et al. [22], and the CHUR parameters ($^{176}Lu/^{177}Hf=0.0332$, $^{176}Hf/^{177}Hf=0.282772$) of Blichert-Toft and Albarède [30].
[b] Calculated with the $\lambda^{176}Lu$ value (1.93×10^{-11} yr^{-1}) of Sguigna et al. [29], and the CHUR parameters of Blichert-Toft and Albarède [30].
[c] Calculated with the $\lambda^{176}Lu$ value (1.983×10^{-11} yr^{-1}), and the CHUR parameters ($^{176}Lu/^{177}Hf=0.0332$, $^{176}Hf/^{177}Hf=0.28277$) of Bizzarro et al. [27].
[d] Not included in age calculation.
[e] Dissolved in PFA Teflon® beakers on a hot plate set at 150 °C.

10^{-11} yr^{-1} [24–26] to 1.983×10^{-11} yr^{-1} [27]. Most recently, Amelin [28] determined $\lambda^{176}Lu$ based on Lu–Hf and U–Pb analyses of phosphate minerals from meteorites, obtaining two sets of decay constant: 1.864×10^{-11} yr^{-1} for an ordinary chondrite (Richardton), and 1.832×10^{-11} yr^{-1} for a primitive achondrite (Acapulco).

For comparison and ramification assessment, the $\lambda^{176}Lu$ values of 1.865×10^{-11} yr^{-1} [22], 1.93×10^{-11} yr^{-1} [26,29], and 1.983×10^{-11} yr^{-1} [27], are utilized to determine the ages in this study (Table 2). In addition, two slightly different Lu–Hf chondritic uniform reservoir (CHUR) parameters, based on two separate analyses of chondritic meteorites [27,30], were

applied in order to estimate the ε_{Hf} values, defined as the deviation of the $^{176}Hf/^{177}Hf$ ratio of a sample from the CHUR in parts per 10^4.

5.1. Bunt Island: granulites

Bunt 01-7 gives a well-defined Lu–Hf mineral–whole rock isochron age of 2403±43 Ma (MSWD=7.2) using λ^{176}Lu of Scherer et al. [22], and a *y*-intercept of 0.280869±28 (ε_{Hf}=−14±1) (Fig. 3a). Although the mean square weighted deviate (MSWD) of 7.2 for our data array is higher than the value of 2.5 used to distinguish between an isochron and an errorchron [31], the array is considered to be an isochron for two reasons. First, the error for the determined age is less than 2 percent, and second, the data yield an age of 2390±18 Ma (ε_{Hf}=−13.4±0.3) with an MSWD=0.18 in a calculation that disregards the osumilite data point. This sample gives an age of 2322±41 Ma using the λ^{176}Lu value of Sguigna et al. [29], and 2260±40 Ma using the value of Bizzarro et al. [27] (Table 2). The λ^{176}Lu value given by Scherer et al. [22] is preferred because it yields ε_{Hf} values that are not extreme and unrealistic (see below); moreover it has recently been confirmed by careful examination of phosphates in meteorites [28]. Another outcome of that choice is that the Lu–Hf age calculated for the primary phase assemblage not disturbed by retrogression approaches the range for the published SHRIMP zircon U–Pb ages at 2490–2450 Ma [7,16].

It is not within the scope of this paper to determine the actual timing of peak UHT metamorphic conditions or even the duration of metamorphism in the Napier Complex. Two possible interpretations are therefore considered for the Lu–Hf isotopic data. If the SHRIMP zircon U–Pb ages record the time of peak UHT conditions [16], then the result suggests that the Lu–Hf system also went through its closure temperature

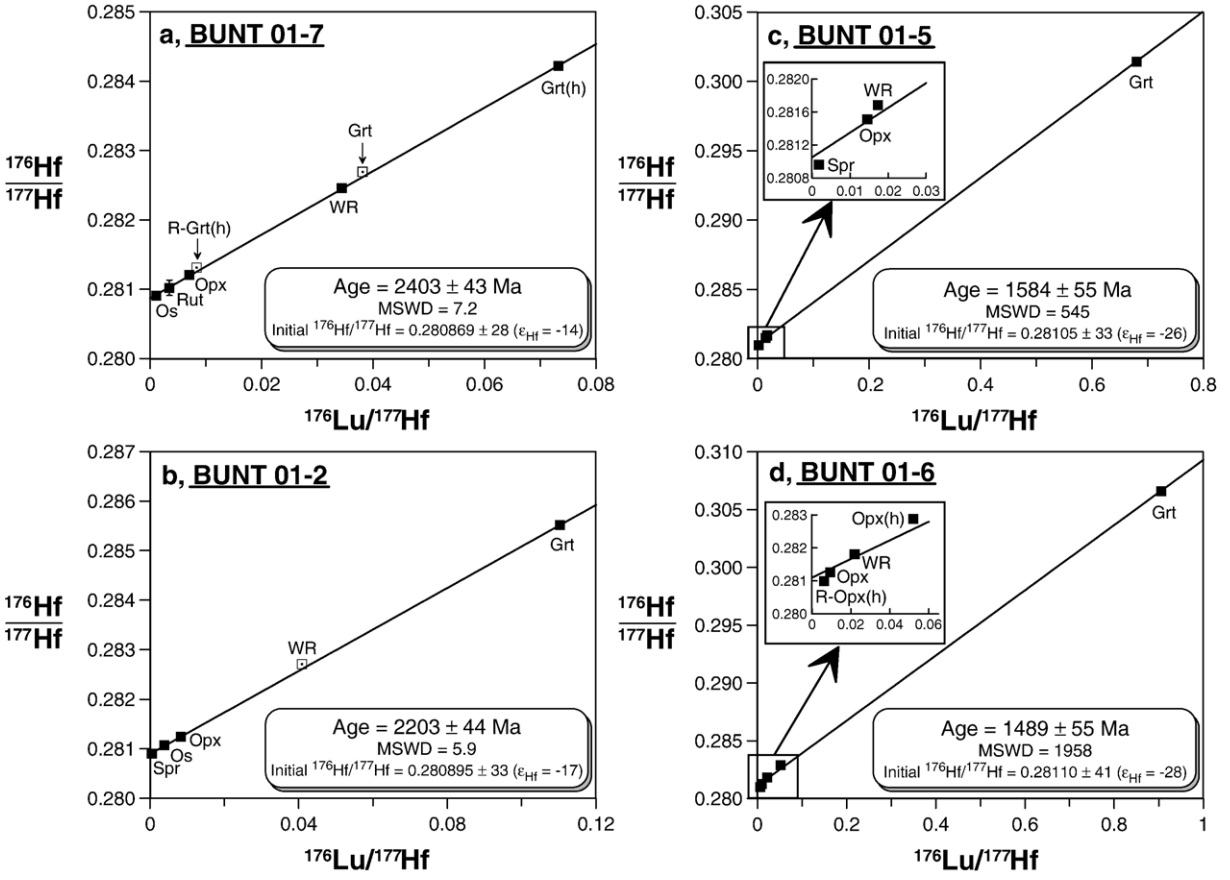

Fig. 3. $^{176}Hf/^{177}Hf$ vs. $^{176}Lu/^{177}Hf$ isochron diagrams for granulites from Bunt Island. Only the data represented by solid symbols have been used in the regression. The decay constant used to calculate the age is $\lambda^{176}Lu = 1.865 \times 10^{-11}$ yr^{-1}, after [22]. All error bars are 2σ uncertainties and are given only where they exceed the size of the symbol in the plot. Grt=garnet; Opx=orthopyroxene; Os=osumilite; Rut=rutile; Spr=sapphirine; WR=whole rock, R=residue.

close to peak UHT conditions. If, on the other hand, the U–Pb zircon ages do not record the time of peak UHT conditions, but are instead timing the post-peak zircon growth during cooling through ~800 °C [7], then the result means that the Lu–Hf system constrains only cooling, not the time of peak UHT conditions. We do not rule out a possibility that the Lu–Hf closure temperature in the minerals studied – even in this case of the mm-scale grain sizes and anhydrous mineralogy – might be lower than that for U–Pb in zircon, considering that the Lu–Hf isochron age obtained from this UHT granulite assemblage is close only to the lowest or youngest of the published zircon U–Pb ages. In any case, this observation indicates that the Lu–Hf dating method can be useful in the study of high-grade metamorphic rocks still retaining their original mineral assemblages. The late prograde and peak chronological history of granulites – and even of eclogites and mantle peridotite xenoliths – is often more acutely obscured by diffusional resetting in the other available chronological systems.

The garnet in sample Bunt 01-7 (Grt in Table 2) has a relatively low $^{176}Lu/^{177}Hf$ ratio of 0.038, not much higher than the whole rock value of 0.034. This can be accounted for by the abundant rutile, quartz and zircon inclusions in the mineral. For comparison, the garnet fraction dissolved in a Teflon® beaker on a hot plate (Grt(h) in Table 2) – an approach that does not completely dissolve the accessory phases – has a $^{176}Lu/^{177}Hf$ ratio of 0.073, which is a factor of two greater than the ratio for the garnet fraction dissolved in a Teflon® bomb, supporting our inclusion–control interpretation. The $^{176}Hf/^{177}Hf$ ratios of the Grt and the residue after Grt(h) dissolution – labeled R-Grt(h) in Table 2 – are slightly displaced above the isochron formed by the other minerals and whole rock fraction (Fig. 3a), which may be due to inherited zircon inclusions in the garnet.

Bunt 01-2 gives a mineral–whole rock isochron age of 2203±44 Ma (MSWD=5.9) using the $\lambda^{176}Lu$ in [22] and a *y*-intercept of 0.280895±33 ($\varepsilon_{Hf}=-17\pm1$) (Fig. 3b), which is appreciably younger than the age for the peak UHT metamorphism determined from sample Bunt 01-7. However, this younger age is consistent with the ~2.2 Ga Sm–Nd mineral isochron age of sapphirine–quartz gneiss from the Mt. Riiser–Larsen area (Fig. 1) [32] and the chemical Th–U–total Pb isochron method (CHIME) ages on monazite [15,33] for a few granulites in the Napier Complex. Taking into consideration the presence of secondary cordierite in sample Bunt 01-2, we interpret the 2.2 Ga ages to date retrograde metamorphism in the region. Concordance of the reported ages at ~2.2 Ga obtained by a variety of other methods on retrogression assemblages with this Lu–Hf age based on the $\lambda^{176}Lu$ value of Scherer et al. [22] and a simple mineral assemblage provides additional support for this value of 1.865×10^{-11} yr^{-1}. The slight displacement of the whole rock sample above the isochron formed by the constituent minerals may be due to abundant inherited zircon grains, which is supported by the SHRIMP $^{207}Pb/^{206}Pb$ age of 2424± 36 Ma for a stubby zircon from the same sample (Osanai et al., unpublished data). Zircon grains in this sample typically occur as inclusions in garnet, which might armor the U–Pb system, and possibly Lu–Hf system, against re-equilibration with fluids during the retrograde metamorphic event.

Minerals and the whole rock from sample Bunt 01-5 define a poorly constrained slope corresponding to an errorchron of 1584±55 Ma (MSWD=545), using the $\lambda^{176}Lu$ in [22], with a *y*-intercept of 0.28105±33 ($\varepsilon_{Hf}=-26\pm12$) (Fig. 3c). Sample Bunt 01-6 yields an errorchron of 1489±55 Ma (MSWD=1958) with a *y*-intercept of 0.28110±41 ($\varepsilon_{Hf}=-28\pm11$) (Fig. 3d). The ca. 1500–1600 Ma ages for these two samples are not easily ascribed to a well documented tectonic event, though two recent studies have hinted at resetting in that age range. Depth-profiling studies [34] discovered layers in some zoned zircons with an age of ca. 1600 Ma, and xenotime CHIME dating [15] yielded similar results. Although the time for the resetting is not well constrained owing to poor co-linearity of data points and consequent high MSWD, significant partial resetting of the Lu–Hf system can still be inferred in some areas of the Napier Complex during Proterozoic deformation. This interpretation is consistent with the reaction textures observed in these samples, such as widespread cordierite-bearing symplectite, and presence of garnet as an exsolved phase. The negative ε_{Hf} values for the Bunt Island granulites (e.g., −14±1 for the 2.4-Ga sample Bunt 01-7), based on the mineral isochrons (Table 2) suggests that overall UHT granulites in the Napier Complex evolved in a low Lu/Hf environment, probably formed when the rocks were first extracted from a depleted mantle (see below). This result is consistent with published ε_{Nd} values of −4 to −9 for some Napier felsic gneisses with whole-rock Sm–Nd isochron ages at ~2.5 Ga [35,36], and maintains the well known relationship of $\varepsilon_{Hf}\approx2\varepsilon_{Nd}$ [3,24,37].

5.2. Gage Ridge: zircons

Individual zircon grains from Gage Ridge have yielded a remarkably uniform range of $^{176}Hf/^{177}Hf$ values between 0.280433±7 and 0.280505±10 (Table

2). Because of their exceedingly low Lu/Hf values (<0.001; Table 2), the grains are effectively recording the initial Hf isotope composition of the magmatic systems from which the gneiss protoliths crystallized. Although new growth of zircon after magmatic crystallization (rim or new grains) may have a different Hf isotopic composition compared to the magmatic zircon core [38,39], errors in the initial $^{176}Hf/^{177}Hf$ ratios for whole grains due to the overgrowth rims will be negligible for two reasons. First, Hf concentrations in the zircon are on the order of 1.0–1.4%, and therefore, it is unlikely that the Hf and Zr required to form the rim would have diffused long distances through anhydrous granulite to the nucleation sites around the zircon cores. Even in the case of the Zir #18 which has a ~2.5-Ga metamorphic rim, ghost igneous zoning is still preserved in the rim (Fig. 2), suggesting that rims formed by recrystallization of the pre-existing zircon. From another perspective, orthogneiss from which the zircon grains obtained is composed primarily of mesoperthite and quartz with a trace of orthopyroxene and accessory zircon. Garnet has not been identified in the thin section [7], which otherwise might have served as a potential source for the elements required to grow the rim. Second, the rims are volumetrically minor compared to the cores, or in some cases, do not exist at all (e.g., Zir #5) (Fig. 2). No significant differences in Hf isotopic ratios have been observed between zircon grains with rims and those without.

From the two types of U–Pb ages reported in the literature – $^{207}Pb/^{206}Pb$ ages for individual grains, and the concordia upper intercept age of 3850 Ma for all the zircon grains [10], we have adapted the latter in the calculations of the ε_{Hf} values for the zircons. This has been done largely to eliminate from consideration the reversely discordant apparent $^{207}Pb/^{206}Pb$ ages >4.1 Ga [7], thought to have been caused by a small degree of Pb migration and its localization in the rim region. The most important result to emerge from our study is that all the early Archean zircon grains studied exhibit positive ε_{Hf} values from 2.5±0.3 to 5.6±0.4, if we adopt the $\lambda^{176}Lu$ value from Scherer et al. [22] for reasons given earlier (Table 2). When other decay constants are used in the calculation instead, the ε_{Hf} values remain positive, actually shifting to even bigger values than the ones adapted here (Table 2; Fig. 4a, b). These results indicate that (1) the source of the crustal materials that formed the Napier Complex at 3.85 Ga were depleted relative to the CHUR; and (2) the depleted mantle reservoir has been in existence since very early in Earth's history, in agreement with the early differentiation of the Earth that the latest core formation models require [40,41].

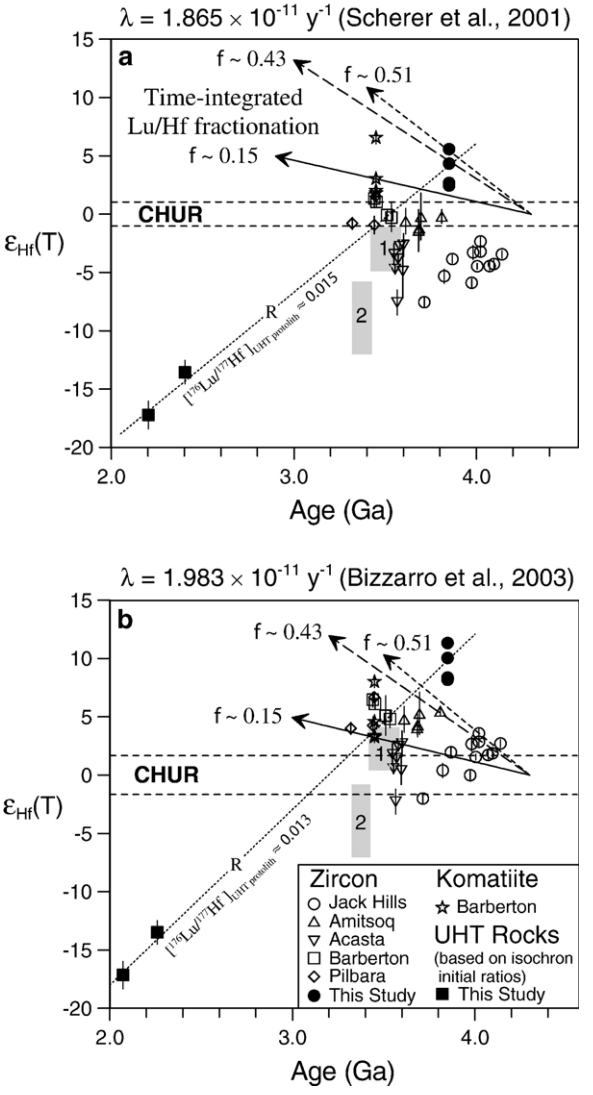

Fig. 4. Zircon and isochron *y*-intercept ε_{Hf} isotopic values (this study) plotted against the concordia upper intercept ages of 3.85 Ga for these grains [7] from the Gage Ridge orthogneiss. The UHT granulites were dated by the Lu–Hf isochron method (this study). Error bars are 2σ. Dashed lines represent the uncertainty of the CHUR values. Calculated with the (a) $\lambda^{176}Lu$ value of Scherer et al. [22] and the CHUR parameters of Blichert-Toft and Albarède [30], and (b) λ and CHUR in Bizzarro et al. [27]. Data for zircons and komatiites from other areas are taken from [38,42,43]. Data for the Jack Hills are ε_{Hf} and $^{207}Pb/^{206}Pb$ ages of individual zircon grains. The grey boxes labeled 1 and 2 represent distinct zircon populations from the Jack Hills [42]. Other data correspond to the weighted average ε_{Hf} of zircon populations from distinct rock samples calculated with the corresponding U–Pb upper intercept age of concordia diagram. Time-integrated Lu/Hf fractionation line of *f*, the chondrite-normalized Lu/Hf ratio ≈ 0.15 of the present-day depleted Earth mantle assuming a starting point for mantle depletion at 4.3 Ga, is shown for a comparison with two reference lines of $f \approx 0.43$ and ≈0.51. Dotted line R is the best-fit line through the Napier data points, corresponding to the evolution of the UHT protolith with $^{176}Lu/^{177}Hf \approx 0.013$–0.015.

Moreover, the results demonstrate that even the oldest silicic rocks in the complex are not likely to have formed from remobilized older crustal materials, but were instead juvenile products of mantle melting. In addition, zircons with metamorphic rims have a similar ε_{Hf} value to the zircons without a rim (Table 2; Figs. 2 and 4), which suggests that the rims formed by recrystallization rather than by new growth.

In order to characterize the Lu–Hf isotopic evolution of the very early Archean mantle, available Hf isotope data for pre-3.5 Ga single zircon grains [38,42] and deep-seated 3.45 Ga komatiites [43] have been plotted, along with our new Napier Complex data as a function of age in Fig. 4. Only zircons for which integrated U–Pb and Hf isotope data are available were selected, thus avoiding the possibility that the original isotopic signature was perturbed by younger geological events. For comparison, the terrestrial depleted mantle ε_{Hf} evolution line for $f_{Lu/Hf} \approx 0.15$ (where $f_{Lu/Hf} = [^{176}Lu/^{177}Hf]_{mantle}/[^{176}Lu/^{177}Hf]_{CHUR} - 1$) – derived from the mid-ocean ridge basalts today, and Proterozoic and Phanerozoic juvenile mantle-derived rocks – is also shown, assuming a starting point for mantle depletion at 4.3 Ga [5,27]. The zircons studied have ε_{Hf} values (+2.5 to +5.6), which is rather high compared to what would be expected for typical depleted mantle at 3.85 Ga, at least according to currently accepted models. This fractionation is similar to the one estimated for the MORB source region at present ($f_{Lu/Hf} \approx 0.43$) [5], and corresponds to a highly depleted mantle value in the early Archean as invoked previously in a number of studies (e.g., [2,5,44]). Development of such a depleted mantle in the early Archean is supported by duplicate analyses (Table 2) of the magmatic zircon (Zir #5), which does not have a metamorphic rim. The depleted values of $f_{Lu/Hf} \approx 0.51$ calculated for the samples are further justification to adopt the decay constant by Scherer et al. [22] as it yields the least extreme ε_{Hf} values for the Napier zircons (Table 2; Fig. 4). If the CHUR parameters suggested by Salters and White [37] are used – i.e., higher $^{176}Hf/^{177}Hf$ and Lu/Hf values than the parameters actually used in Table 2 – then the ε_{Hf} values of the zircon grains studied are adjusted downward by only ~0.2 ε units. Even when we apply the recent CHUR values by Patchett et al. [45], the ε_{Hf} values result in an increase of only ~0.1 ε units. This observation leaves the Napier Complex (not previously studied using the Lu–Hf system) secure in supporting presence of early Archean mantle with the characteristics of strong depletion. Using the $\lambda^{176}Lu$ value by Scherer et al. [22], we find that depleted (upper mantle) materials and complementary domains of enriched materials have existed since the earliest Archean. The enriched materials might be either continental crust or the hypothetical reservoir residing in the deep mantle that has been proposed by Boyet and Carlson [46] on the basis of a $^{142}Nd/^{144}Nd$ positive anomaly in most terrestrial rocks relative to the chondritic meteorites.

The initial $^{176}Hf/^{177}Hf$ ratios based on the mineral isochrons of the UHT granulites from Bunt Island plot on the extrapolation of the variation line defined by the zircon grains from Gage Ridge (Fig. 4a, b). This supports the above suggestion that overall UHT granulites evolved in a low Lu/Hf environment, $^{176}Lu/^{177}Hf \approx 0.014$ (Fig. 4a, b), formed when the rocks were first extracted from a highly depleted mantle.

6. Conclusions

(1) Mineral Lu–Hf isochrons constructed from the original UHT phase assemblage record ages close to those obtained using the SHRIMP zircon U–Pb method. The significance of both sets of ages in the Napier Complex depends on whether they are thought of as dating peak UHT conditions or post-peak cooling through ~800 °C.
(2) ε_{Hf} values indicate that metamorphic zircon rims in the case considered here represent recrystallization of earlier magmatic zircon, not new growth.
(3) The $\lambda^{176}Lu$ value given by Scherer et al. [22] yields calculated ages which are most consistent with the zircon U–Pb ages, and is therefore recommended for future Lu–Hf studies.
(4) Magmatic zircons from the Napier felsic rocks yield ε_{Hf} values that are positive, indicating that these rocks were derived from depleted mantle sources at 3.85 Ga. The extent of depletion involved is higher than has been predicted by extrapolation from the Lu–Hf isotopic evolution inferred for the source of Proterozoic and Phanerozoic basalts, judging from an $f_{Lu/Hf}$ value of 0.51.

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