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# Lu–Hf systematics of the ultra-high temperature Napier Complex, East Antarctica: Evidence for the early Archean differentiation of Earth’s mantle

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**Summary** The Napier Complex 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 an equilibrated assemblage from this belt yield a Lu–Hf isochron age of  $2,403 \pm 43$  Ma. Preservation of the UHT mineral assemblage in the rock analyzed 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. Zircon  $\epsilon_{\text{Hf}}$  values measured “see through” the UHT metamorphism and show that the source of magmas that formed the Napier Complex was extremely depleted ( $> +5.6 \epsilon_{\text{Hf}}$  at 3.85 Ga) relative to the chondritic uniform reservoir (CHUR). These results suggest significant depletion of the early Archean mantle, in agreement with the early differentiation of the earth that the latest core formation models require.

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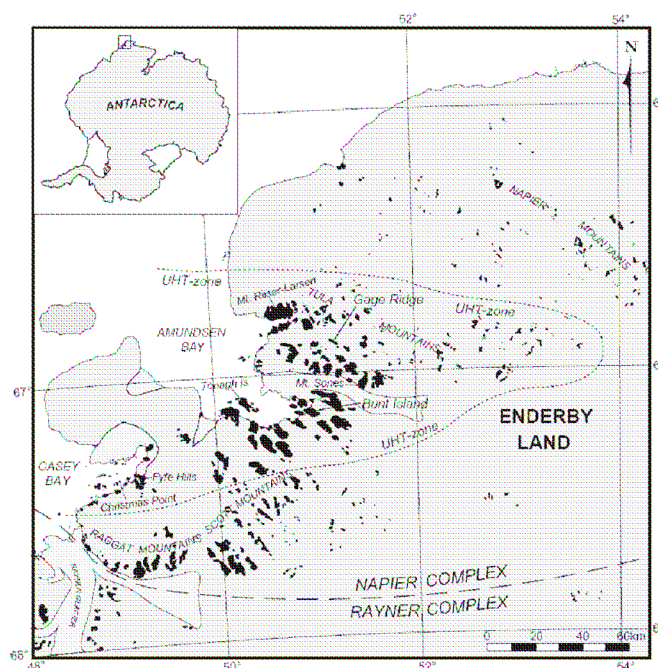
## Introduction

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) (Hamilton et al., 1978; Bennett et al., 1993; Vervoort et al., 1996). However, this interpretation has been questioned because of increasing recognition that the Sm–Nd system can be perturbed by some younger metamorphic

and metasomatic events. 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 ( $\text{ZrSiO}_4$ ) and baddeleyite ( $\text{ZrO}_2$ ) – at the weight-percent level of concentration, tightly bound in the crystal lattice such that its isotopic compositions are not easily reset. 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 (Figure 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.

## 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. (2001). The samples we have studied were collected from one outcrop that exhibits thin



**Figure 1.** Outcrop map of the western Napier Complex, 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 (2000).

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

**Table 1 Rock types and mineral assemblages**

Sample no.	Bunt 01-2	Bunt 01-5	Bunt 01-7	Bunt 01-t
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.

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 (Harley and Black, 1997), and analyzed for trace element concentrations by Kelly and Harley (2005), 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. 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, believed to represent subsolidus metamorphic crystal growth or recrystallization. The elongate shape and oscillatory zoning of the zircon cores are interpreted to be the result of magmatic crystallization, which has been supported by a preservation of magmatic REE patterns.

## Result and discussion

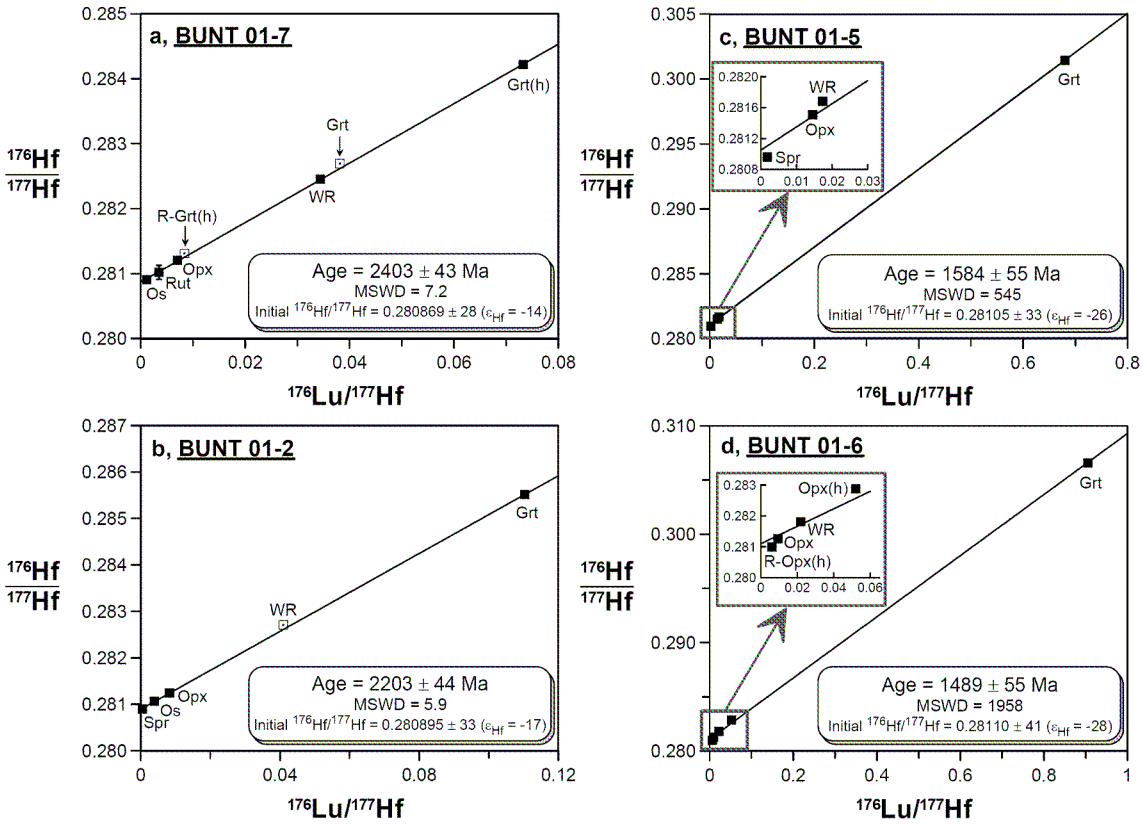
### *Bunt Island: granulites*

Bunt 01-7 gives a well-defined Lu–Hf mineral-whole rock isochron age of  $2,403 \pm 43$  Ma (MSWD = 7.2) using  $\lambda^{176}\text{Lu}$  of Scherer et al. (2001), and a y-intercept of  $0.280869 \pm 28$  ( $\epsilon_{\text{Hf}} = -14 \pm 1$ ) (Figure 2a). 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, 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  $2,390 \pm 18$  Ma ( $\epsilon_{\text{Hf}} = -13.4 \pm 0.3$ ) with an MSWD = 0.18 in a calculation that disregards the osumilite data point. It is not within the scope of this short extended abstract 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 (e.g., Carson et al., 2002), then the result suggests that the Lu–Hf system also went through its closure temperature 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  $\sim 800^\circ\text{C}$ , 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

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, 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. 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 (Harley, 1985). 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.

The four individual zircon grains among the minerals studied were obtained from a massive

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



**Figure 2.**  $^{176}\text{Hf}/^{177}\text{Hf}$  vs.  $^{176}\text{Lu}/^{177}\text{Hf}$  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  $\lambda^{176}\text{Lu}=1.865\times 10^{-11}\text{ yr}^{-1}$ , after Scherer et al. (2001). All error bars are  $2\sigma$  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 = sapphire; WR = whole rock, R=residue.

obscured by diffusional resetting in the other available chronological systems.

Bunt 01-2 gives a mineral-whole rock isochron age of  $2,203 \pm 44$  Ma (MSWD = 5.9) using the  $\lambda^{176}\text{Lu}$  in Scherer et al. (2001) and a y-intercept of  $0.280895 \pm 33$  ( $\epsilon_{\text{Hf}} = -17 \pm 1$ ) (Figure 2b), 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  $\sim 2.2$  Ga Sm–Nd mineral isochron age of sapphirine-quartz gneiss from the Mt. Riiser-Larsen area (Fig. 1) and the chemical Th–U–total Pb isochron method (CHIME) ages on monazite for a few granulites in the Napier Complex. Taking into consideration the presence of secondary cordierite in sample Bunt 01-2, we interpret the  $\sim 2.2$ -Ga ages to date retrograde metamorphism in the region.

Minerals and the whole rock from sample Bunt 01-5 define a poorly constrained slope corresponding to an errorchron of  $1,584 \pm 55$  Ma (MSWD = 545), with a y-intercept of  $0.28105 \pm 33$  ( $\epsilon_{\text{Hf}} = -26 \pm 12$ ) (Figure 2c). Sample Bunt 01-6 yields an errorchron of  $1,489 \pm 55$  Ma (MSWD = 1958) with a y-intercept of  $0.28110 \pm 41$  ( $\epsilon_{\text{Hf}} = -28 \pm 11$ ) (Figure 2d). The ca. 1,500 – 1,600 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.

#### Gage Ridge: zircons

Individual zircon grains from Gage Ridge have yielded a remarkably uniform range of  $^{176}\text{Hf}/^{177}\text{Hf}$  values between  $0.280433 \pm 7$  and  $0.280505 \pm 10$ . Because of their exceedingly low Lu/Hf values ( $<0.001$ ), 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, errors in the initial  $^{176}\text{Hf}/^{177}\text{Hf}$  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 percent, 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. 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 thin section, 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. No significant differences in Hf isotopic ratios have been observed between zircon grains with rims and those without.

The most important result to emerge from our study is that all the early Archean zircon grains studied exhibit positive  $\epsilon_{\text{Hf}}$  values from  $2.5 \pm 0.3$  to  $5.6 \pm 0.4$ , if we adopt the  $\lambda^{176}\text{Lu}$  value from Scherer et al. (2001). 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. 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  $\epsilon_{\text{Hf}}$  value to the zircons without a rim, which suggests that the rims formed by recrystallization rather than by new growth.

## Summary

(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  $\sim 800^\circ\text{C}$ .

(2)  $\epsilon_{\text{Hf}}$  values indicate that metamorphic zircon rims in the case considered here represent recrystallization of earlier magmatic zircon, not new growth.

(3) The  $\lambda^{176}\text{Lu}$  value given by Scherer et al. (2001) 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  $\epsilon_{\text{Hf}}$  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  $f_{\text{Lu/Hf}}$  value of 0.51.

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