Low $\delta^{18}$O zircon grains in the Neoarchean Rum Jungle Complex, northern Australia: An indicator of emergent continental crust

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ABSTRACT

The timing of widespread continental emergence is generally considered to have had a dramatic effect on the hydrological cycle, atmospheric conditions, and climate. New secondary ion mass spectrometry (SIMS) oxygen and laser-ablation–multicollector–inductively coupled plasma–mass spectrometry (LA-MC-ICP-MS) Lu-Hf isotopic results from dated zircon grains in the granitic Neoarchean Rum Jungle Complex provide a minimum time constraint on the emergence of continental crust above sea level for the North Australian craton. A 2535 ± 7 Ma monzogranite is characterized by magmatic zircon with slightly elevated $\delta^{18}$O (6.0‰–2.5‰ relative to Vienna standard mean ocean water [VSMOW]), consistent with some contribution to the magma from reworked supracrustal material. A supracrustal contribution to magma genesis is supported by the presence of metasedimentary rock enclaves, a large population of inherited zircon grains, and subchondritic zircon Hf ($\varepsilon_{Hf} = -6.6$ to $-4.1$). A separate, distinct crustal source to the same magma is indicated by inherited zircon grains that are dominated by low $\delta^{18}$O values (2.5‰–4.8‰, n = 9 of 15) across a range of ages (3536–2598 Ma; $\varepsilon_{Hf} = -18.2$ to +0.4). The low $\delta^{18}$O grains may be the product of one of two processes: (1) grain-scale diffusion of oxygen in zircon by exchange with a low $\delta^{18}$O magma or (2) several episodes of magmatic reworking of a Mesoarchean or older low $\delta^{18}$O source. Both scenarios require shallow crustal magmatism in emergent crust, to allow interaction with rocks altered by hydrothermal meteoric water in order to generate the low $\delta^{18}$O zircon. In the first scenario, assimilation of these altered rocks during Neoarchean magmatism generated low $\delta^{18}$O magma with which residual detrital zircons were able to exchange oxygen, while preserving their U-Pb systematics. In the second scenario, wholesale melting of the altered rocks occurred in several distinct events through the Mesoarchean, generating low $\delta^{18}$O magma from which zircon crystallized. Ultimately, in either scenario, the low $\delta^{18}$O zircons were entrained as inherited grains in a Neoarchean granite. The data suggest operation of a modern hydrological cycle by the Neoarchean and add to evidence for the increased emergence of continents by this time.

INTRODUCTION

Ever since Logan (1857) identified a fundamental difference between Laurentian and Huronian series rocks in Canada, and Stockwell (1961) dated the age of the former at ca. 2.5 Ga, Archean Earth has widely been regarded as a significantly different planet to its younger equivalent. This difference is primarily manifest as a unique dome-and-keel pattern of Archean granite-greenstone terranes (Macgregor, 1951; Hickman, 1984) with basaltic carapaces erupted largely under submarine conditions (Arndt, 1999; Kump and Barley, 2007). Lack of widespread subaerial exposure of crustal blocks until the end of the Neoarchean reflects hotter geotherms and more ductile continental lithosphere that was generally unable to support large mountain belts (Arndt, 1999; Rey et al., 2003; Cruden et al., 2006; Flament et al., 2011). Only when crustal radiogenic heat production decreased (e.g., Bodorkos and Sandiford, 2006), and geothermal gradients fell with secular cooling of the mantle (e.g., Labrosse and Jaupart, 2007; Brown, 2008), did the continental crust stiffen and emerge above sea level (Taylor and McLennan, 1985; Flament et al., 2008, 2011). Although there is considerable evidence for emergent continental crust at various times through the Archean (e.g., from the Paleoarchean to Neoarchean sedimentary basins of the Kaapvaal and Pilbara cratons; McLennan et al., 1983; Nocita and Lowe, 1990; Nelson et al., 1999; Van Kranendonk et al., 2002; Hessler and Lowe, 2006), the timing of widespread continental emergence in the latest Neoarchean into the early Paleoproterozoic is only loosely constrained by poorly dated supracrustal successions and by geochemical and isotopic proxies (e.g., Taylor and McLennan, 1985; Eriksson et al., 1999; Farquhar et al., 2000; Anbar et al., 2007).

Constraining the timing of continental emergence is important because newly exposed continental crust would have had a dramatic effect on the hydrological cycle, as well as on global atmospheric conditions, climate, and biological evolution. Newly exposed Neoarchean crust would have affected
changes to the atmosphere and hydrosphere and climate through increased
drawdown of CO₂ via continental weathering. In combination with a change
from dominantly submarine to subaerial volcanism (e.g., Kump and Barley,
2007), a decrease in overall magmatism and associated volcanic degassing
at the close of the Archean (Condie et al., 2009), and an increase in photo-
synthesis prompted by increased areas of continental shelves and erosive
supply of nutrients to the oceans (e.g., Campbell and Allen, 2008), CO₂
drawdown via weathering of newly exposed crust contributed to oxygena-
tion of the atmosphere (Farquhar et al., 2000; Anbar et al., 2007), which in
turn supported the evolutionary development of eukaryotic life (e.g., Margu-
lis et al., 1976; Martin and Müller, 1998; Van Kranendonk, 2012).

An important indicator of continental emergence is the interaction of
continental crust and its derived weathering products with meteoric water,
which can be recorded in the oxygen isotopic signature of zircon (e.g.,
Tang et al., 2008). Meteoric water is characterized by low Δ₁⁸O (typically
0‰ to −55‰; Valley et al., 2005) as a result of preferential evaporation
of ¹⁸O at Earth’s surface. Oxygen diffusion in zircon is regarded to be
prohibitively slow in most crustal environments, including during high-
temperature metamorphism and anatexis (Peck et al., 2003; Moser et al.,
2008). However, in a restricted range of environments involving high-tem-
perature hydrothermal fluids (e.g., Bindeman et al., 2008), alteration of the
primary oxygen isotopic character of zircon can indicate the interaction
between zircon crystals and fluids.

In this paper, we present data from a Neoarchean granite from the Rum
Jungle Complex of northern Australia that contains evidence of fraction-
ated zircon oxygen isotopes indicative of an active hydrological cycle
affecting emergent continental crust by ca. 2535 Ma. The data presented
are interpreted as evidence of the minimum time of continental emergence
of the North Australian craton. The data also highlight the potential for
similar samples to yield valuable information on fluid-rock interaction
and the development of continental emergence through the Archean-Proter-
ozoic transition.

**GEOLOGICAL SETTING**

Exposed Neoarchean basement of the North Australian craton lies
within the Paleoproterozoic Pine Creek Orogen (Fig. 1). The basement
is dominated by ca. 2545–2521 Ma granite and granitic gneiss of the Rum
Jungle Complex (Cross et al., 2005), the ca. 2520 Ma Nanambu Complex,
and the ca. 2527–2510 Ma Kukalak Gneiss (Page et al., 1980; Hollis et al.,
2009; Carson et al., 2010; Kosticin et al., 2012), and ca. 2640 Ma Arrarra
Gneiss and ca. 2670 Ma Njibinjibinj Gneiss (Hollis et al., 2009; Carson et
al., 2010). Assuming that these form a continuous basement, largely under
cover of younger rocks, this represents an extent of at least 22,000 km² of
Neoarchean crust (see Hollis et al., 2009).

The Rum Jungle Complex outcrops in the Rum Jungle and Waterhouse
domes and is separated from overlying sedimentary and volcanic rocks
of the ca. 2020 Ma Woodcutters Supergroup by a major unconformity
(Needham et al., 1988). The Rum Jungle Complex consists mainly of
syenogranite, monzogranite, and quartz monzonite (Drüppel et al., 2009),
intruded by pegmatites, dolerite, and quartz tourmaline veins (Lally,
2002). The Rum Jungle Complex includes enclaves of amphibolite-facies
metasedimentary rocks of the Stanley Metamorphics, which include bio-
tite gneiss, biotite-muscovite gneiss, biotite granofels, feldspathic gneiss,
quartz-muscovite schist, chlorite schist, actinolite schist, and banded iron-
stone, which were deformed and metamorphosed to amphibolite facies
prior to being incorporated into the Rum Jungle Complex, and which are
variably retrogressed (Rhodes, 1965; Lally, 2002). There are no available
constraints on the pressure-temperature conditions of metamorphism.
The timing of deformation and metamorphism also remains unconstrained and
could be as young as the emplacement age of the main population of late
Neoarchean granites themselves.

Five granites and one diorite from the Rum Jungle Complex yield
secondary ion mass spectrometry (SIMS; sensitive high-resolution ion
microprobe [SHRIMP]) U-Pb zircon magmatic crystallization ages in the
range 2545–2521 Ma (Cross et al., 2005). Here, we present data from one
of these (sample 2001082534), a fine- to medium-grained, equigranular
monzogranite (Fig. 1; GDA94 UTM zone 52, 710747mE, 8543205mN).
This is the only one of the six dated samples of the Rum Jungle Complex
that contains inherited zircon. It belongs to the felsic group of Drüppel et
al. (2009; see also Northern Territory Geological Survey, 2012), which
are rich in K and large ion lithophile elements (LILEs), are depleted in
Sr, Eu, and high field strength elements (HFSEs, e.g., Nb and Ti), and
have anomalously high Th and U. These rocks are thought to have formed
by intracrustal melting (Drüppel et al., 2009). Analytical methodologies
for sample preparation, zircon U-Th-Pb and O SIMS analysis, and zircon
Lu-Hf laser-ablation–multicollector–inductively coupled plasma–mass
spectrometry (LA-ICP-MS) analysis are described in Appendix 1.¹

**ZIRCON ISOTOPIC RESULTS**

Zircons are dominated by euhedral to subrounded prisms and their
broken equivalents that range from clear and colorless to turbid and

¹GSA Data Repository Item 2014079, Appendix 1: zircon analytical techniques, is available
at www.geosociety.org/pubs/ft2014.htm, or on request from editing@geosociety.org.

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[Figure 1. Location of the Rum Jungle Complex within the Pine Creek Orogen. Inset map shows the location within Australia.]
Low $\delta^{18}$O zircon grains in the Neoarchean Rum Jungle Complex

**U-Pb Results**

Fifty-one analyses were made on 46 zircon grains from sample 2001082534 (Cross et al., 2005). Fourteen analyses are discordant above an arbitrary threshold of 10% or have high common Pb contents of >8% $^{206}$Pb, and are thus not considered further. A further 10 analyses are interpreted as mixtures of different age components and are also not considered further. The remaining 27 analyses are characterized by a dominant population between 2695 Ma and 2515 Ma, and a range of discrete older grains that extend up to ca. 3535 Ma (Fig. 3A; Table 1). The 10 youngest grains are clear, colorless, euhedral to subrounded, prismatic grains with faint to well-developed oscillatory or sector zoning (Fig. 2). Twelve analyses of these 10 grains yield a weighted mean $^{207}$Pb/$^{206}$Pb age of 2535 ± 7 Ma (95% confidence, mean square of weighted deviates [MSWD] = 0.92), interpreted as the age of magmatic crystallization. This age is consistent with other ages for the volumetrically dominant component of the Archean basement to the North Australian craton (2545–2510 Ma; Cross et al., 2005; Hollis et al., 2009). The range of older dates is interpreted to reflect a substantial component of zircon inheritance in this sample. These grains are morphologically diverse, ranging from clear to patchy brown, prismatic to rounded, and equant to elongate. They are usually oscillatory zoned, although a few are homogeneous or sector zoned (Fig. 2).

**Oxygen Isotopic Data**

Oxygen isotopic ratios were measured for 26 zircons across a range of ages (Fig. 3B; Table 1). Eleven grains of the 2535 ± 7 Ma magmatic population fall within a limited range of $\delta^{18}$O = 6.0‰–7.5‰ (relative to Vienna standard mean ocean water [VSMOW]), indicative of a contribution from reworked, or assimilated, supracrustal rocks. Inherited grains
(3536–2632 Ma) span a broad range in δ18O from 2.5‰ to 6.5‰. The majority of these grains (n = 9 of 15, 3536–3037 Ma) have δ18O values (2.5‰–4.8‰) significantly below what would be expected for zircon grown in equilibrium with a mantle-derived melt (5.3‰ ± 0.6‰; Valley et al., 2005; Fig. 3B; Table 1).

Lu-Hf Results

Hf isotopic ratios were measured for 23 zircons. The 2535 ± 7 Ma magmatic population is characterized by a weak spread in subchondritic Hf values (176Hf/177Hf = 0.280052–0.281064, εHf = −4.1 to −6.6; Fig. 3C; Table 1), consistent with derivation from melting of significantly older (Paleoarchean) sources with crustal residence ages of older than ca. 3.3 Ga (assuming initial 176Lu/177Hf = 0.015). The 15 inherited grains analyzed (3536–2632 Ma) range from strongly radiogenic (close to depleted mantle) to highly unradiogenic (176Hf/177Hf = 0.280581, εHf = −18.2, at 2695 Ma). Three inherited grains have a two-stage model age similar to that of the 2535 Ma population (ca. 3.3 Ga; Fig. 3C) and may have been derived from comparable sources. The 10 other analyses have two-stage model ages ranging from 4.3 to 3.0 Ga (Table 1).

DISCUSSION

Low δ18O zircon (δ18O < 5.3‰ ± 0.6‰, i.e., less than that in equilibrium with mantle-derived melt) is rare, particularly in Archean rocks (e.g., Valley et al., 2005; data compiled in Van Kranendonk and Kirkland, 2013). The sample analyzed here (sample 2001082534) is unusual amongst dated samples of the Archean basement of the North Australian craton (e.g., Hollis et al., 2009), and unique amongst the dated samples of the Rum Jungle Complex (Cross et al., 2005), in that it contains inherited zircons. These inherited grains are also unusual in being dominated by low δ18O values (n = 9/15, δ18O = 2.5‰–4.8‰). Therefore, although the data set presented here is small, and restricted to a single sample, the data nonetheless provide a potentially significant insight into otherwise elusive environmental processes operating in the Archean.

The zircon U-Pb,Lu-Hf, and O isotopic systematics of zircon grains from sample 2001082534 indicate diverse crustal sources that contributed to the granitic magma. The zircon population can be divided into two broad components based on age and isotopic signature: (1) a ca. 2535 Ma magmatic zircon component (n = 12), grown within the magma, which is characterized by elevated δ18O values of 6.0‰–7.5‰ and a subchondritic zircon Hf mixing trend (Fig. 3C; 176Hf/177Hf = 0.280052–0.281064, εHf = −4.1 to −6.6); and (2) an inherited zircon component, identified by a large proportion (9 of 15) of xenocrystic grains that have low δ18O values of 2.5‰–4.8‰. A further six inherited grains have slightly higher δ18O values of 5.2‰–6.5‰ and may represent a distinct inherited component to the granitic magma. Of these six grains, three that have mantle-like to slightly higher δ18O values (5.2‰–6.5‰) have Hf isotopic compositions (εHf = −4.1 to −6.6). Such values are consistent with assimilation of Paleoarchean or older sedimentary protoliths into the granitic magma.

Regarding the second distinct crustal source, nine of the 15 analyzed inherited zircons (60%) have δ18O values significantly lower than those expected for zircon in equilibrium with mantle-derived melt (2.5‰–4.8‰). These low δ18O values indicate that the zircon grains either crystallized from, or diffusively exchanged oxygen with, a low δ18O melt or fluid. As the Rum Jungle Complex granite is interpreted to have had an elevated bulk δ18O composition (source 1 listed earlier), the low δ18O zircons indicate a distinct source or sources.

Two questions should be addressed in relation to this second source: (1) What was the nature of the fluid responsible for generating a low δ18O source, or sources? (2) Did the zircons crystallize from, or did they diffusively exchange oxygen with, that low δ18O source?

Nature of the Fluid that Generated a Low δ18O Source

Low δ18O zircon that is produced by crystallization from, or diffusive exchange with, a melt or fluid requires interaction with a source having δ18O at least as low as, and probably much lower than, the minimum δ18O value found in zircon (Bindeman, 2011). In the case examined here, this source must have been lower than 2.5‰, the lowest value analyzed herein (Table 1). One possibility is that the fluid involved was seawater (assuming seawater δ18O ~ 0‰ during the Archean; e.g., Gregory and Taylor, 1981; Gregory, 1991). However, this is considered unlikely, because very large volumes of seawater, with continued replenishment, would be required to achieve the observed degree of isotopic exchange. Similarly low δ18O zircons (2.4‰–4.4‰) are known from remelting of basaltic oceanic crust that has been hydrothermally altered by seawater (e.g., Peck, 2000). However, in the case of the inheritance in the granite studied here, a much more extensive isotopic exchange with seawater would be required (e.g., Eiler, 2001) to reduce the relatively δ18O heavy metasedimentary rocks (possibly the Stanley Metamorphics) to the low δ18O values implied by the range of inherited zircon ages.

Rather, we consider that hydrothermal exchange of much lower δ18O meteoric fluids (δ18O = 0‰ to −55‰; Valley et al., 2005) with supracrustal rocks in a near-surface environment presents the most viable method of producing the observed low δ18O values in the source. This conclusion is supported by previous studies that have deduced a meteoric origin of fluids that generated low δ18O sources, which in turn yielded low δ18O zircon (e.g., 2‰–4‰ for Eo- to Neoarchean Greenland gneisses—Hiess et al., 2011; 2‰–3‰ for Neoproterozoic Dabie-Sulu granites—Wang et al., 2011; 2‰–4‰ for Tertiary granitic rocks, Scotland—Gilliam and Valley, 1997).

How and When Did the Zircons Obtain Their Low δ18O Signature?

Low δ18O values in zircon are usually explained as the result of crystallization from magmatic rocks produced by melting of crust that was previously altered by low δ18O fluids (e.g., Gregory and Taylor, 1981; Gilliam and Valley, 1997; King et al., 2000; Valley et al., 2005; Bindeman, 2008; Hiess et al., 2011). Alternatively, hydrothermal zircon can grow directly from solutions with a low δ18O component (Kirkland et al., 2009). A third alternative is that intracrystalline diffusion of oxygen in zircon can occur under hydrothermal supersolidus conditions, as indicated by the experimental data of Watson and Cherniak (1997; see also Cherniak and Watson, 2003), although evidence for oxygen diffusion has not been observed in natural samples, which instead more commonly show evidence of dissolution and reprecipitation (e.g., Bindeman et al., 2008). In the case of the Rum Jungle Complex, the timing of alteration to form the low δ18O source is important in understanding the process by which the zircon obtained low δ18O values. Next, we assess whether alteration could have occurred after, during, or before granite emplacement.
(1) Interaction of meteoric fluids with the granite after granite emplacement and crystallization is considered unlikely, because the oxygen isotopic systematics of the 2535 Ma magmatic zircon population form a coherent population and are undisturbed. Alteration via this mechanism would require these magmatic grains to be more resilient to alteration, whereas fracturing and metamictization of the older, inherited grains (resulting from alpha recoil damage) preferentially would have resulted in oxygen diffusion in these grains. In this scenario, one would expect there to be a correlation between alpha dose and δ¹⁸O. However, as shown in Figure 4, there is no such correlation. Alpha doses and grain densities (Table 1) were calculated using the method of Murakami et al. (1991), who compared radiation doses to transmission electron microscopy (TEM) diffraction patterns and outlined three stages of zircon structure, ranging from crystalline to completely amorphous. Each stage is defined by characteristic radiation doses. Calculations indicate that the majority of grains analyzed from the sample studied here have radiation doses in the range that is consistent with a highly crystalline structure (i.e., <3 × 10¹⁵ alpha events/mg). Also, the inherited grains with low δ¹⁸O all show a high degree of U-Pb concordance (>95%), consistent with low, or no, alteration. Furthermore, there is no correlation between age and uranium content (Table 1), which implies that radiogenic-Pb loss and disturbance have not demonstrably affected the zircon population. Finally, calculated ε²⁰⁶Pb values are sensitive to disturbance of U-Pb systematics (which might also indicate disturbance of the O isotopic system), resulting in erratic or scattered ¹⁷⁷Hf/¹⁷⁶Hf arrays. This is not the case for this sample (i.e., clustered ε²⁰⁶Pb of −4.1 to −6.6), which is inconsistent with the generation of low δ¹⁸O values by postmagmatic alteration of zircon.

(2) Alteration of the supracrustal rocks to low δ¹⁸O values by meteoric water before granite emplacement could either have occurred by (a) generation of a low δ¹⁸O source prior to ca. 3.5 Ga (the age of the oldest low δ¹⁸O grain), from which all of the low δ¹⁸O inherited zircons were then grown during subsequent melting events, or (b) diffusive exchange of oxygen in the inherited zircons with a low δ¹⁸O melt into which they were entrained after ca. 3.0 Ga (the age of the youngest low δ¹⁸O grain), but before emplacement of the 2535 Ma granite. The latter possibility is considered along with item 3 next.

A key observation regarding this scenario is that the low δ¹⁸O zircon values occur in inherited grains with a wide range of ages (3536–3037 Ma). Therefore, if these grains crystallized directly from either a low δ¹⁸O melt or from a hydrothermal fluid, then this must have occurred at different times, over the course of ~500 m.y. (between 3.5 and 3.0 Ga, i.e., the ages of the low δ¹⁸O inherited zircons). Particularly given the rarity of low δ¹⁸O zircon in Archean rocks in general (e.g., data compiled in Van Kranendonk and Kirkland, 2013), this is most likely to have occurred by magmatic reworking of the same older than 3.5 Ga low δ¹⁸O source. This source must have been originally formed by interaction with and alteration by meteoric water, and it was then melted and remelted at various times through the Paleoproterozoic to Mesoarchean. This reworking of the same source suggests an isolated geological system over at least 500 m.y. The resulting low δ¹⁸O zircons, crystallized from low δ¹⁸O magma during several reworking events, were then delivered as inherited zircons into the Rum Jungle Complex through a combination of erosion, deposition in a sedimentary environment, and assimilation into the granite.

(3) Alteration of metasedimentary rocks by meteoric water during intrusion of granitic magmas could have occurred by magma intrusion resulting in fracturing of the host rocks and associated infiltration and circulation of meteoric groundwater heated by the intruding granite. Metasedimentary supracrustal rocks (perhaps the Stanley Metamorphics) were altered to low δ¹⁸O bulk compositions by the circulating, heated meteoric water through a process of repeated intrusion, alteration, and wholesale melting and assimilation of altered rocks (e.g., Bindeman, 2008). Generation of low δ¹⁸O magmas by this process has been suggested for a range of modern and ancient felsic magmatic rocks in varied environments, including near-surface magmatic-hydrothermal systems (e.g., Yellowstone Plateau volcanic field—Hildreth et al., 1984; Bindeman and Valley, 2000, 2001; Bindeman et al., 2001, 2008; Heise volcanic field, Idaho—Bindeman et al., 2007; Timber Mountain/Oasis Valley caldera complex—Bindeman and Valley, 2003; Dabie-Sulu orogen—Zheng et al., 2004; Tang et al., 2008; West Greenland gneisses—Hiess et al., 2011).

These processes of alteration and crustal cannibalization may have occurred at any time between ca. 3.0 Ga (the age of the youngest low δ¹⁸O inherited grain) and 2535 Ma (the age of the Rum Jungle Complex granite), but they are most likely to have occurred during emplacement of the Neoarchean magmas, because, locally, this is the only known magmatic heating event in the period 3.0–2.5 Ga.

In this scenario, detrital zircon captured from assimilated metasedimentary rocks diffusively exchanged oxygen with a low δ¹⁸O magma on a time scale of <1 m.y. while not affecting the U-Pb system of the magma and magmatic zircons, which requires much higher temperatures and longer time scales (Cherniak and Watson, 2001, 2003). Recharge of the system with granitic magmas having more elevated δ¹⁸O bulk compositions (generated by deeper-level melting in the mid- to upper crust) resulted in assimilation of existing low δ¹⁸O magmas and their altered, low δ¹⁸O inherited zircon component, while accounting for crystallization of the distinct 2535 Ma elevated δ¹⁸O magmatic zircon population.

Supporting this model is new evidence of low δ¹⁸O zircon from the Billabong Complex, Tanami region, located ~800 km to the south of the Rum Jungle Complex (Whelan et al., 2013). SIMS oxygen data for the Billabong Complex reveal a significant proportion (~30%) of low δ¹⁸O magmatic and inherited zircon in the range ca. 2550–2510 Ma (δ¹⁸O = 2.0‰–4.7‰; Whelan et al., 2013). These data indicate that high-crustal-level hydrothermal-meteoric systems may have been widespread during Neoarchean magmatism in the North Australian craton.

![Figure 4. Alpha recoil events (dose) vs. δ¹⁸O for zircon from sample 2001082534. See Table 1 for tabulated alpha recoil data. Magmatic zircon grown during granite crystallization is shown in gray, and inherited grains are shown in black.](image-url)
### Table 1. Tabulated U-Pb-Th and O SIMS and Lu-Hf LA-ICP-MS Data for Sample 2001082534, Rum Jungle Complex

<table>
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<th>U (ppm)</th>
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<th>% common 206Pb</th>
<th>206Pb/207Pb ± σ</th>
<th>207Pb/206Pb ± σ</th>
<th>206Pb/206Pb age (Ma) ± σ</th>
<th>Disc %</th>
<th>Hf 176/Hf 177 ± σ</th>
<th>ε Hf</th>
<th>TDM (Ma) ± σ</th>
<th>δ 18O (‰) ± σ</th>
<th>No. alpha events/mg (×10¹⁵)</th>
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Inherited analyses |

| A51.1 | 170 | 0.99 | 1.28 | 0.1741 | 1.3 | 0.482 | 2.9 | 2598 | 21 | 2 | 0.281040 | 0.000036 | 3.5 | 3253 | 6.31 | 0.08 | 2.31 | I: crystalline | 4.58 |
| A37.3 | 313 | 0.22 | 2.00 | 0.1777 | 0.8 | 0.503 | 3.3 | 2632 | 14 | 0 | 0.281143 | 0.000015 | 4.0 | 3030 | 5.50 | 0.11 | 3.81 | II: intermediate | 4.43 |
| A13.2 | 335 | 0.17 | 0.56 | 0.1846 | 0.7 | 0.478 | 2.8 | 2695 | 12 | 6 | 0.280581 | 0.000013 | 18.2 | 4252 | 5.15 | 0.09 | 4.18 | I: crystalline | 4.39 |
| A46.1 | 94 | 0.53 | 0.50 | 0.2066 | 0.1 | 0.562 | 2.8 | 2903 | 15 | 5 | 0.280731 | 0.000017 | 8.1 | 3776 | 6.28 | 0.06 | 7.59 | II: intermediate | 4.36 |
| A09.1 | 525 | 0.39 | 0.95 | 0.2096 | 0.9 | 0.533 | 2.8 | 2930 | 15 | 5 | 0.280731 | 0.000017 | 8.1 | 3776 | 6.28 | 0.06 | 7.59 | II: intermediate | 4.36 |
| A53.1 | 130 | 0.52 | 3.93 | 0.2278 | 1.3 | 0.613 | 3 | 3037 | 21 | 1 | 0.280977 | 0.000020 | 3.0 | 3172 | 3.12 | 0.06 | 2.06 | II: intermediate | 4.36 |
| A03.1 | 142 | 0.01 | 2.07 | 0.2292 | 0.8 | 0.611 | 3 | 3047 | 12 | 1 | 0.280681 | 0.000014 | 7.2 | 3827 | 2.50 | 0.06 | 2.07 | II: intermediate | 4.36 |
| A44.1 | 158 | 0.65 | 0.29 | 0.2363 | 0.9 | 0.618 | 2.9 | 3095 | 14 | 0 | 0.280969 | 0.000013 | 6.6 | 3423 | 6.24 | 0.11 | 1.22 | I: crystalline | 4.68 |

**Note:** Data use scheme of Murakami et al. (1991). SIMS—secondary ion mass spectrometry; LA-ICP-MS—laser-ablation—inductively coupled plasma—mass spectrometry; $T_{DM}$—depleted mantle model age.
The proposed scenario requires that the Rum Jungle Complex was emplaced at a shallow crustal level in order to access low δ18O meteoric waters. Although there are no existing pressure-temperature constraints on the depth of emplacement, the geochemistry of the granites indicates they were formed by melting at pressures lower than the garnet stability field (<10 kbar; Drüppel et al., 2009). Therefore, they may have been emplaced at the shallow depths required to drive a meteoric-hydrothermal system (e.g., Bindeman, 2011). It may be possible to obtain a maximum constraint on emplacement depth by metamorphic studies of metasedimentary xenoliths of the Stanley Metamorphics within the Rum Jungle Complex. This model could be tested further by analyzing the whole-rock oxygen isotopic composition of the Stanley Metamorphics, which form xenoliths within, and wall rocks to, the Rum Jungle Complex.

**Diffusive Exchange of Oxygen in Zircon in a Hydrothermal-Magmatic Environment**

Diffusive exchange of oxygen in zircon with a low δ18O melt is one of the two proposed models that could explain the occurrence of variably low δ18O inherited zircon from a range of ages in the Rum Jungle Complex. However, oxygen diffusion profiles in zircon have, to date, not been demonstrated in natural samples. In order for this to be a viable mechanism, a long-lived, high-temperature (supersolidus) hydrothermal system within several kilometers of the surface is required, as oxygen diffusion in zircon is slow, even under prolonged exposure to high-temperature conditions, but particularly in the absence of fluid water (Page et al., 2007; Lancaster et al., 2009; Bowman et al., 2011). Examination of oxygen zoning profiles in low δ18O zircon would be a useful further test.

Experimental data indicate that with water present, temperatures of ~700 °C are required to induce grain-scale diffusion for 120-µm-diameter meteoric water circulation, in the region. Ma, 2534 ± 6 Ma, 2531 ± 3 Ma, 2525 ± 5 Ma, 2521 ± 4 Ma; Cross et al., 2009; MacFarlane et al., 1994; Murikami et al., 2001). Much of this evidence is gleaned from elevated δ18O (6.0‰–7.5‰) and evolved εHf (−4.1 to −6.6) of the 2535 Ma magmatic zircon population, and consistent with the presence of metasedimentary enclaves and inherited older zircons in the granite. A second source is interpreted to be a granitic magma, which was generated by melting of older than 3.3 Ga supracrustal rocks, as gleaned from elevated δ18O (6.0‰–7.5‰) and evolved εHf (−4.1 to −6.6) of the 2535 Ma magmatic zircon population, and consistent with the presence of metasedimentary enclaves and inherited older zircons in the granite. A second source is interpreted to be a granitic magma, which was generated by melting of hydrothermally altered supracrustal rocks, which were then assimilated by the intrusive Rum Jungle Complex monzogranite, based on the low δ18O composition of most of the inherited zircon grains in the granite.

**Implications for Studies of Fluid-Rock Interaction in the Archean**

The data presented here have implications for investigating the antiquity of emergence of the continents. In this study, the data provide a minimum constraint on the timing of emergence of Neoarchean crust of the North Australian craton at ca. 2535 Ma, the age of granite emplacement and inferred hydrothermal circulation of meteoric water under shallow crustal conditions. This constitutes the earliest evidence for emergence of Neoarchean crust of the North Australian craton.

However, this is not the earliest evidence for emergence of continental crust on a global scale, which has been established for rocks at least as old as 3.5 Ga (Buick et al., 1995). Elevated freeboard existed at various times throughout the Archean, as evidenced by Archean continental and shallow-marine successions (e.g., Burke et al., 1986; Nocita and Lowe, 1990; Hessler and Lowe, 2006), evaporitic sediments (e.g., Buick and Dunlop, 1990; Lowe and Fisher-Worrell, 1999; Sugitani et al., 2003), subaerial volcanism (Blake, 1993; Li et al., 2013), and paleosols (e.g., MacFarlane et al., 1994; Murikami et al., 2001). Much of this evidence is from Palearchean to Neoarchean rocks of the Kaapvaal and Pilbara cratons. However, continental emergence probably occurred only locally, and diachronously, and over a long time period, with emergent crust constituting perhaps only a small proportion of Earth’s surface area by the end of the Archean (Taylor and McLennan, 1985; Stevenson and Patchett, 1990; Arndt, 1999; Vlaar, 2000; Flament et al., 2008).

An understanding of how and when continental emergence progressed is important, as widespread emergence of continents provided a means to draw down atmospheric CO2, with concomitant increases in atmospheric oxygen (e.g., at ca. 2.5–2.3 Ga; Holland, 2002; Bekker et al., 2004; Anbar et al., 2007). However, these types of data are only available for a few cratons, such that the full picture of continental emergence across the Neoarchean-Paleoproterozoic transition remains uncertain.

Targeting the oxygen isotopic composition of zircons in Archean–Paleoproterozoic granites may provide a fruitful direction for further investigation of the antiquity and progress of continental emergence in different cratonic blocks. Assuming that postmagmatic alteration can be discounted, recognition of low δ18O of inherited zircon having a range of ages necessitates the interpretation of hydrothermal alteration of the protolith. Several well-studied Phanerozoic examples indicate that extensional, rift-related silicic magmatism is conducive to extensive alteration of magmatic and associated sedimentary rocks by hydrothermal meteoric fluids and that these processes can be reflected in depleted 18O isotopic compositions of the magmatic rocks and their zircon cargo (Eiler, 2001; e.g., the British Tertiary igneous province—Gilliam and Valley, 1997; Monani and Valley, 2001; Mesozoic granitoids of eastern China—Wei et al., 2002; Yellowstone intracaldera volcanic rocks—Bindeman and Valley, 2001; Bindeman et al., 2008; Timber Mount caldera complex, Nevada—Bindeman et al., 2006). In such environments, magmatism provides the heat source for circulation of meteoric hydrothermal fluids, and a shallow crustal level of emplacement allows water recharge. Low δ18O detrital or xenocrystic zircon can be expected to be captured by melts in such environments. The same may be true of Archean examples. However, these may be only rarely recorded in the rock record, given the poor preservation potential of such high-level magmatic systems.

High-crustal-level granites generated in extensional tectonic settings are known from several Archean cratons (e.g., Witwatersrand Basin—Moore et al., 1993; Pilbara craton, Australia—Brauhart et al., 1998, 2000; Yilgarn craton, Australia—Hallberg, 1986). Targeting of the oxygen isotopic composition of inherited zircon in granites within these extensional geological domains, where assimilation of supracrustal material has occurred, may provide more insight into the prevalence of emergent crust through the Archean.

**CONCLUSIONS**

Low δ18O zircons are rare, particularly in Archean rocks, but are present as 3.54–3.03 Ga inherited grains within a 2535 ± 7 Ma monzogranite of the Rum Jungle Complex, northern Australia. The zircon U-Pb, Lu-Hf, and O isotopic compositions of magmatic and inherited grains indicate that at least two distinct sources contributed to the magmatic magma of the Rum Jungle Complex. The first source is interpreted to be a granitic magma, which was generated by melting of older than 3.3 Ga supracrustal rocks, as gleaned from elevated δ18O (6.0‰–7.5‰) and evolved εHf (−4.1 to −6.6) of the 2535 Ma magmatic zircon population, and consistent with the presence of metasedimentary enclaves and inherited older zircons in the granite. A second source is interpreted to be a low δ18O magma formed by melting of hydrothermally altered supracrustal rocks, which were then assimilated by the intrusive Rum Jungle Complex monzogranite, based on the low δ18O composition of most of the inherited zircon grains in the granite.

We propose that magmatism at shallow crustal levels provided the mechanism for generating low δ18O magma by interaction with hydrothermal-
meteoric water. This low ð18O magma was either generated prior to 3536 Ma and then periodically remelted through the Paleoarchean to Mesoproterozoic, producing low ð18O zircon by crystallization from melt, or low ð18O zircons were generated by diffuse re-equilibration with a low ð18O magma during the Neoarchean at ca. 2535 Ma. These low ð18O zircons were ultimately entrained as inherited zircon in the Rum Jungle Complex monzogranite.

These data provide a minimum timing constraint for the emergence of continental crust of the North Australian craton by the end of the Archean (at 2535 Ma). Searching for the signatures of hydrothermal alteration in inherited zircon from other high-crustal-level Archean granites may yield further insights into fluid-rock interactions and the emergence of continental crust through time.

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