Gondwana margin evolution from zircon REE, O and Hf signatures of Western Province gneisses, Zealandia

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Abstract: U–Th–Pb dated zircons from Western Province paragneisses and orthogneisses were analysed for rare earth element (REE) concentrations, as well as oxygen and hafnium isotopic compositions. Experiments performed in situ using a sensitive high-resolution ion microprobe (SHRIMP) and laser ablation multicollection inductively coupled plasma mass spectrometer (LA-MC-ICPMS) allow better understanding of crustal growth on the Zealandia margin of Gondwana from the micron scale. Paragneiss zircons were probably derived from similar sources to those that supplied the regional Ordovician Greenland Group and correlative southern Australian and Antarctic meta-sedimentary rocks. Detrital zircon grains record variable REE patterns relating to magmatic and metamorphic crystallization processes operating prior to and following Ordovician deposition. δ18O and εHf(T) values trace major phases of juvenile crust formation and subsequent reworking in provenance sources, signifying an increase in the recycling of compositionally diverse, evolved crustal materials through time. Orthogneiss zircons relate to two episodes of magmatism that record similar REE concentration patterns. Devonian zircons have elevated δ18O and un-radiogenic εHf(T); Cretaceous zircons record more primitive δ18O and radiogenic εHf(T). Both orthogneiss suites require thorough mixing of mantle-derived magmas with a component of Greenland Group rocks. The relative proportion of this crustal contamination is c. 20–50% for the Devonian orthogneisses and c. 10–40% for the Cretaceous orthogneisses. Orthogneiss protolith materials were largely hybridized prior to and during zircon crystallization, suggesting that plutonic assembly occurred over restricted structural levels. These results demonstrate the ability of zircon to retain detailed petrogenetic information through amphibolite-facies metamorphism with excellent fidelity.

Supplementary material: Analytical methods and data are available at www.geolsoc.org.uk/SUP18755

Gneiss and zircon

Unravelling the petrogenetic history of high-grade metamorphic terrains enables more complete understanding of Earth’s crustal evolution. Paragneisses are derived from the metamorphism of sedimentary protoliths and, depending on the intensity of that metamorphism, can contain detrital minerals from multiple sources of different ages. Orthogneisses are metamorphic rocks of igneous parentage, generated from magmas containing materials from mantle, crustal and subducted reservoirs in varying proportions. Gneissic lithologies have often been subject to multiple overprinting metamorphic and tectonic events, typically leading to ambiguous bulk geochemical signatures that obstruct a clear picture of their primary formation processes. A major key to unlocking such complex geology is the mineral zircon (tetragonal ZrSiO₄), which is capable of retaining trace elemental and isotopic signatures characteristic of its formation environment despite, in many cases, multiple protracted high-pressure and high-temperature metamorphic events.

Zircon as a tracer of crustal evolution

Zircon rare earth elements (REE) can serve as geochemical and geological process indicators, for
example the redox-sensitive elements Ce and Eu can track the evolution of magmatic oxidation states and feldspar crystallization, while the relative abundance of lighter and heavier REE indicates the partitioning behaviour of a melt–crystal system, which can involve multiple phases that are stable over a range of pressure and temperature conditions (Hoskin & Schaltegger 2003). Oxygen isotopes, specifically $\delta^{18}O$, in zircon are sensitive to fluid–rock interaction and can be used to distinguish between melts that are derived from the mantle or magmas equilibrated at similar temperatures, and those that include recycled weathered and hydrothermally altered protolith materials (Valley 2003). Hafnium isotopes, through the in-growth of radiogenic $^{176}$Hf from $^{176}$Lu decay, can be used to trace the involvement of magmas derived from mantle that is representative of evolution from a chondritic uniform reservoir (CHUR), mantle that has been previously depleted by crustal extraction, an dritic uniform reservoir (CHUR), mantle that has been representative of evolution from a chondritic uniform reservoir (CHUR), mantle that has been previously depleted by crustal extraction, an evolved crustal composition or some combination of these sources (Kinny & Maas 2003).

**Background geology, geochronology and geochemistry**

In this paper we apply an integrated zircon *in situ* (sensitive high-resolution ion microprobe, SHRIMP, and laser ablation multicollection inductively coupled plasma mass spectrometer, LA-MC-ICPMS) rare earth element, oxygen and hafnium isotopic approach to determine the petrogenesis of a suite of U–Th–Pb SHRIMP dated amphibolite-facies gneisses from the Western Province of New Zealand (Fig. 1). The gneiss protoliths formed during the Palaeozoic and Mesozoic, when proto-New Zealand, along with southeastern Australia and East Antarctica, was located on the southeastern margin of the Gondwana supercontinent (Mortimer 2004; Fig. 2). Coeval and in some cases possibly contiguous lithologies from these landmasses subsequently separated during the middle Cretaceous with the opening of the Tasman Sea (Eagles et al. 2004; Kula et al. 2007).

In the central part of South Island’s West Coast, the Buller Terrane dominates the basement rocks NW of the Alpine Fault and the Rakaia Terrane prevails SE of the fault (Fig. 1). The Buller Terrane includes the Greenland Group, a southern Australian Ordovician meta-sedimentary correlative, that is intruded by Late Devonian–Early Carboniferous and Early Cretaceous granitic plutons (Nathan et al. 2002; Cox & Barrell 2007). Immediately NW of the Alpine Fault is a fault-bounded and variably mylonitized belt of high-grade metamorphic and igneous rocks. We have focused our study on six garnet–biotite ± sillimanite ± kyanite paragneiss and eight biotite orthogneiss units from this belt, mostly from the Fraser and Granite Hill complexes (Rattenbury 1987, 1991; Kimbrough et al. 1994; Suggate & Waight 1999; Jongens 2006).

This study builds on that of Hiess et al. (2010), who presented SHRIMP U–Th–Pb geochronology of zircon and monazite from these samples to constrain the ages of protolith rocks and metamorphic overprints. Hiess et al. (2010) concluded that many of these Fraser Complex and Granite Hill Complex gneisses are more highly metamorphosed equivalents of the meta-sedimentary and igneous rocks of the Buller Terrane. All ages reported in this paper are a sample’s zircon U–Pb age. Most ages date the formative intrusive crystallization event, but some ages record subsequent metamorphic recrystallization.

The paragneiss detrital zircon ages for any one sample vary and typically cluster around several time intervals that are interpreted to be the intrusion ages of the various source rock components. The clusters match that of widespread Ordovician quartz-rich turbidite meta-sedimentary rocks of the Greenland Group from the Buller Terrane (Laird 1967; Cooper 1975, 1989; Nathan 1976; Pickett & Wasserburg 1989; Cooper & Tulloch 1992; Ireland 1992; Roser et al. 1996; Ireland & Gibson 1998; Nebel-Jacobsen et al. 2011). These rocks have the characteristic signature of a dominant Early Palaeozoic–Late Neo-proterozoic (480–550 Ma) population, a second peak of Early Neo-proterozoic–Late Mesozo-proterozoic ‘Grenvillian’ age (960–1270 Ma), a minor peak around 1600 Ma, and then scattered ages out to Early Archaean (Ireland & Gibson 1998).

The orthogneiss zircons record bimodal clusters of ages representing emplacements of the Late Devonian Karamea Suite (Grindley 1978; Tulloch 1983, 1988; Tulloch et al. 1991, 2009; Cooper & Tulloch 1992; Muir et al. 1994, 1996a, b; Rattenbury et al. 1998) and the Cretaceous Separation Point and Rahu Suits (Tulloch 1983, 1988; Waight et al. 1997, 1998a–c). Paragneiss and orthogneiss monazite ages indicate Devonian and Cretaceous.

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**Fig. 1.** Geological map of Western Province basement granitic, gneissic and meta-sedimentary rocks and key faults in central Westland modified after Nathan et al. (2002) and Cox & Barrell (2007) showing sample locations. The 10 km grid is in NZTM2000 coordinates. The inset map shows the New Zealand basement terranes in the central South Island after Mortimer (2004), the outline of the South Island, the trace of the Alpine Fault and the study area enlarged in the main map.
thermal pulses related either to primary crystallization during granitoid intrusion or to the regional metamorphism caused by their intrusion (Ireland & Gibson 1998). Further details about the background geology and geochronology related to these samples can be found in Hiess et al. (2010) and references within.

Various combinations of REE, O and Lu–Hf analytical techniques have been applied to zircons from the Western Province and Median Batholith of New Zealand (Herd 2007; Bolhar et al. 2008a, b; Scott et al. 2009; Nebel-Jacobsen et al. 2011; Tulloch et al. 2011), eastern Australia (Kemp et al. 2006, 2007, 2008, 2009; Ickert 2010; Jeon et al. 2012), western Antarctica (Flowerdew et al. 2006, 2007; Yakymchuk et al. 2013) and elsewhere worldwide to provide new insight into crustal formation and evolution processes.

This study targets high-grade metamorphic rocks for which their inferred less metamorphosed equivalent meta-sedimentary and plutonic rocks have previously been extensively interrogated for their geochronology, geochemistry and isotopic compositions. Existing whole-rock and our mineral-specific approaches can be compared to test the survival of petrogenetic signatures in zircon through amphibolite-facies metamorphic conditions, and these results used to build a more complete model of magmatic, sedimentary, metamorphic and tectonic evolution for the Gondwana margin in Zealandia.

Analytical methods
A detailed descriptive of all analytical methods employed, primary data and their statistical
treatment is outlined in the Supplementary Materials. In summary, following previously published U–Th–Pb geochronology with SHRIMP RG at the Australian National University (Hiess et al. 2010), mounted, polished and extensively imaged paragneiss and orthogneiss sample zircon grains (Figs 3–6) were analysed for both REE concentrations (127 analyses) and then oxygen isotopic compositions (151 analyses) with the Korea Basic Science Institute SHRIMP IIe/MC following established methods of Hoskin (1998) and Ickert et al. (2008). Hafnium isotopic compositions (185 analyses) were later determined with a 193 nm excimer laser ablation system coupled to a Nu Plasma multicollector ICPMS at the University of Melbourne with procedures following Woodhead et al. (2004). Primary O and Hf isotopic data for every reference material and sample analysis are presented in the Supplementary Materials. Great care was taken to correlate the same growth domains with each analytical technique for a given spot. Analyses were made within clear grains from all samples and are located on recrystallized or homogenized textures, or within grains that contain recrystallized domains from core to rim to provide a range of materials representative of each rock sample (Hiess et al. 2010; Figs 3–6).

Results
Summaries of paragneiss and orthogneiss zircon descriptions, U–Pb ages, δ18O and εHf(T) isotopic compositions, U, Th and REE concentrations are presented in Tables 1 and 2, respectively.

Paragneiss zircon REE
Each of the four paragneiss samples contains zircon grains with variable CI carbonaceous chondrite normalized REE concentration profiles (Fig. 7). The 76 analyses demonstrate a wide range of positive Ce/Ce* and negative Eu/Eu* anomalies that vary within and between samples. Fifty-six analyses (74%) are heavy-REE (HREE) enriched. Twenty analyses (26%) have distinctively flatter HREE patterns with (Lu/Gd)N ratios of 17 or less. These flatter HREE analyses can be identified in each sample and are located on recrystallized or homogenized textures, or within grains that contain these textures (Figs 3 & 4; Table 1). Analyses with flatter HREE profiles are not otherwise associated by age, geochemical or isotopic characteristics. Sample A553 from Crooked River (Fig. 7d) contains zircon grains with the highest proportion (c. 64%) of flat HREE analyses. This sample also recorded a strong Cretaceous overprint in its zircon U–Pb ages (Hiess et al. 2010) that was absent from all the other paragneiss samples. The nearby sample A552 (Fig. 1) contains zircon grains with the fewest flat HREE analyses (Fig. 7c).

Paragneiss zircon δ18O
Paragneiss δ18O zircon compositions (76 grain analyses, four rock samples) demonstrate a secular trend that indicates progressively more isotopic variation in zircons towards younger age (Fig. 8). Seven Archaean and Palaeo-proterozoic age domains record δ18O from 2.2 ± 0.7 to 6.9 ± 0.7‰, 40 Meso-proterozoic and Neo-proterozoic domains range from δ18O 1.9 ± 0.7 to 12.2 ± 0.7‰, and 29 Phanerozoic domains range from δ18O 1.5 ± 0.7 to 12.7 ± 0.7‰. Fourteen 18O/16O analyses record relatively primitive δ18O values that range between 4.5 and 6.4‰. When considering conservative ion microprobe analytical uncertainties, for example as in Valley et al. (2005) and Kemp et al. (2006), these analyses lie within a compositional field that is close to zircon derived from Earth’s mantle or melts equilibrated at similar temperatures, with a δ18O of 5.3 ± 0.3‰ (Valley et al. 1998). Ten 18O/16O analyses record lower δ18O from 1.5 to 4.4‰ and 52 18O/16O analyses record higher δ18O from 6.5 to 12.7‰ whose upper limit increases through the Proterozoic and Phanerozoic. Sample A552 contains the highest proportion of low δ18O zircon grains (n = 8). Sample A553 contains five Cretaceous analyses with δ18O ranging from 8.9 to 10.6‰, made on recrystallized textures, or on zircon grains containing recrystallized domains.

Paragneiss zircon εHf(T)
Paragneiss zircon hafnium isotopic compositions (112 grain analyses, six rock samples) range from εHf(T) = −25.4 to +10.9 units (Fig. 9), with 35 analyses (31%) greater than CHUR and 77 analyses (69%) less than CHUR, as defined by Bouvier et al. (2008), at initial ages. Of the 13 18O/16O analyses that record primitive δ18O compositions (4.5–6.4‰), nine lie within, and four lie outside, analytical uncertainty of two 176Lu/177Hf arrays corresponding to slopes of 0.021 and 0.017 that intersect the depleted mantle curve at c. 1800 and c. 3400 Ma respectively. These arrays are taken from Figure 1 of Kemp et al. (2006) and were interpreted to reflect the model ages of two major episodes of crustal extraction from the depleted mantle. Most analyses fall in an age range from 400 to 1000 Ma and εHf(T) ranges from −15 to +10 units, lying beneath the 176Lu/177Hf = 0.021 array. Sample A552 contains the highest proportion of old, juvenile grains. Sample A553 contains three Cretaceous zircon grain analyses with εHf(T) ranging from −6.6 to −4.7 units, made on recrystallized textures, or on grains containing recrystallized domains.
Fig. 3. Zircon cathodoluminescence images of paragneiss samples A546 and A550. Elliptical spots indicate SHRIMP analysis sites for U–Pb, REE and δ18O. Circular spots indicate LA-MC-ICPMS site for εHf(T).
Fig. 4. Zircon cathodoluminescence images of paragneiss samples A552 and A553. Elliptical spots indicate SHRIMP analysis sites for U–Pb, REE and $\delta^{18}O$. Circular spots indicate LA-MC-ICPMS site for $\varepsilon_{Hf}$. 

ZIRCON REE–O–HF, WESTERN PROVINCE GNEISS 329
Orthogneiss zircon REE

Zircon grains of different U–Pb ages from the two Devonian and four Cretaceous orthogneiss samples (26 Cretaceous, 22 Jurassic to Devonian, three inherited Cambrian to Palaeo-proterozoic analyses) have been analysed for REE and demonstrate relatively similar CI normalized REE concentration profiles (Fig. 10). All 51 patterns rise steeply from La to Lu, while positive Ce and negative Eu.

Fig. 5. Zircon cathodoluminescence images of Devonian orthogneiss samples A549, A556 and A557. Elliptical spots indicate SHRIMP analysis sites for U–Pb, REE and δ18O. Circular spots indicate LA-MC-ICPMS site for εH(T).
anomalies are generally pronounced and relatively consistent within individual samples. The two Devonian samples (A557, Bonar Creek, 386.5 ± 7.5 Ma, Fig. 10e; A556, Tuke River, 370.6 ± 9.9 Ma, Fig. 10d) have relatively similar mean compositions with $\left(\frac{\text{Sm}}{\text{La}}\right)_N$ of 32 and 51, $\left(\frac{\text{Lu}}{\text{Gd}}\right)_N$ of $\pm 1$.

Fig. 6. Zircon cathodoluminescence images of Cretaceous orthogneiss samples A548, A554 and A558. Elliptical spots indicate SHRIMP analysis sites for U–Pb, REE and $\delta^{18}$O. Circular spots indicate LA-MC-ICPMS site for $\varepsilon_{H(T)}$. ZIRCON REE–O–HF, WESTERN PROVINCE GNEISS 331.
### Table 1. Paragenesis zircon grain descriptions, 206Pb/238U age, 207Pb/206Pb age, δ18O, δHf(T), and REE concentrations and REE concentrations

| Sample | Parent | δ18O VSMOW | δHf(T) (‰) | Sm/Ce | Eu*6 | La | Gd | Ce*6 | Lu | Gd | YT | Er | Sm | Eu | Ce | Pr/Sm | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er | Tb | Dy | Ho | Er |
|--------|--------|-------------|-------------|--------|------|----|----|------|----|----|----|----|----|----|----|----|-------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---
| 11.1 p c re | 339.6 | 50 | 1.5 | 0.7 | −3.7 | 2.3 | 417 | 13 | 0.03 | 0.1 | 15 | 0.2 | 0.3 | 0.7 | 3 | 7 | 17 | 20 | 16 | 15 | 28 | 23 | 118 | 10 | 37 | 0.5
| 12.1 a m re | 380.5 | 8.5 | −10.6 | 2.2 | 267 | 48 | 0.18
| 13.1 r m to | 383.1 | 8.3 | −2.7 | 1.7 | 568 | 7 | 0.01
| 14.1 ow m t | 468.4 | 10.1 | −5.6 | 1.6 | 641 | 44 | 0.72
| 15.1 f m re | 491.7 | 10.5 | −5.8 | 1.7 | 800 | 237 | 0.31
| 16.1 ow m re | 500.6 | 10.7 | −2.7 | 1.8 | 520 | 322 | 0.64
| 17.1 ro c re | 512.0 | 11.4 | −7.3 | 1.7 | 420 | 49 | 0.12
| 18.1 ow m re | 522.7 | 11.0 | −8.7 | 2.1 | 77 | 1.0 | 0.3
| 19.1 f m re | 568.0 | 14.6 | −3.6 | 1.3 | 700 | 238 | 0.35
| 20.1 ow m re | 625.8 | 13.5 | 0.1 | 1.8 | 310 | 130 | 0.43
| (Continued)
| Spot | Grain | Age (Ma) | Error, 1 SD | $\delta^{18}$O (‰) | Error, Initial | U (ppm) | Th (ppm) | Th/U | Ce | Pr | Nd | Sm | Eu | Gd | Tb | Dy | Ho | Er | Trm | Yb | Lu | (Sm/La)$_N$ | (Lu/Gd)$_N$ | Ce | Eu |
|------|-------|----------|-------------|-----------------|-----------------|--------|--------|-----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| 5.1  | ro c os | 923.0 | 93.0 | 5.1 | 1.7 | 44 | 15 | 0.36 | 13.1 | ro c os | 1011.1 | 16.4 | 7.3 | 1.6 | 446 | 112 | 0.26 | 15.1 | p m os | 1016.6 | 20.0 | 7.2 | 1.4 | 513 | 232 | 0.47 |
| 4.1  | p m os | 1016.6 | 43.1 | 5.6 | 1.9 | 292 | 199 | 0.71 | 6.1  | ov m os | 1251.9 | 51.4 | –6.9 | 1.7 | 210 | 160 | 0.79 |

Mt Elliot paragneiss A560 (42.52570°S, 171.82040°E, 200 m)

206 Pb/238U age or 207Pb/206Pb age, U and Th concentrations from Hiess et al. (2010).

$\delta^{18}$O = [(sample/mean) - 1] × 1000/VMOW. VMOW: $\delta^{18}$O = 0.0020052 (Baertschi 1976).

Initial $^{176}$Hf/$^{177}$Hf ratios for each spot calculated using their individual SHRIMP measured $^{206}$Pb/$^{238}$U or $^{207}$Pb/$^{206}$Pb ages from Hiess et al. (2010). Subscript N indicates elemental concentrations normalized to CI carbonaceous chondrite abundances of McDonough & Sun (1995). Ce and Eu anomalies were calculated in this manner, for example Ce/Ce* = Ce$_{N}$/[sqrt(La$_N$ × Tb$_N$)].
Table 2. Orthogneiss zircon grain descriptions, U–Pb ages, $^{18}$O and $\epsilon_{HFT}$ compositions, and REE concentrations

| Spot | Grain | Age (Ma)$^1$ | Error, 1 SE (Ma) | $^{18}$O error, 1 SE (‰) | $\epsilon_{HFT}$, Initial$^2$ | Error, 2 SE | U (ppm) | Th (ppm) | Th/U | La (ppm) | Ce (ppm) | Pr (ppm) | Nd (ppm) | Sm (ppm) | Eu (ppm) | Gd (ppm) | Tb (ppm) | Dy (ppm) | Ho (ppm) | Er (ppm) | Yb (ppm) | Lu (ppm) | Sm$^\text{Lan}$ | Eu$^\text{HF}$ | Ce$^\text{HF}$ | Eu$^\text{HF}$ |
|------|-------|-------------|-----------------|--------------------------|-----------------------------|-------------|--------|--------|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-------|--------|--------|--------|
| 1.0  | ov m  | 106.8 2.0   | 6.2 0.6         | 3.5 3.8                  | 596 186 0.32               |             |        |        |      |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| 1.1  | p ed  | 110.3 2.1  | 6.0 0.6         | 1.0 3.9                  | 534 531 1.03               |             |        |        |      |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| 1.2  | p ed  | 116.2 2.2  | 5.9 0.6         | 0.2 2.4                  | 626 362 0.60               |             |        |        |      |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| 1.3  | p m  | 116.3 2.2  | 6.8 0.6         | 1.4 2.2                  | 703 354 0.52               |             |        |        |      |        |        |        |        |        |        |        |        |        |        |        |        |        |        |
| 1.4  | p co | 117.4 2.3  | 6.3 0.6         | 2.1 2.5                  | 239 222 0.96               |             |        |        |      |        |        |        |        |        |        |        |        |        |        |        |        |        |        |

Solitude Creek orthogneiss AS46 (42.99129°S, 170.94165°E, 470 m)

$^1$Weighted mean $^{209}$Pb/$^{206}$U age = 114.5 ± 2.0 Ma (95% c.l.), n = 11/15, MSWD = 1.2

$^2$Mean $^{18}$O = 6.2 ± 0.7% (1 SD), n = 5/6

$^3$Mean $\epsilon_{HFT}$ = −12.2 ± 2.1 (1 SD), n = 4/5

Clarke River orthogneiss AS49 (42.39921°S, 171.85563°E, 253 m)

$^1$Weighted mean $^{209}$Pb/$^{206}$U age = 378.1 ± 6.8 Ma (95% c.l.), n = 13/16, MSWD = 1.2

$^2$Mean $^{18}$O = 8.1 ± 1.3% (1 SD), n = 8/11

$^3$Mean $\epsilon_{HFT}$ = −9.7 ± 2.3 (1 SD), n = 8/11

Mt Elliot orthogneiss AS51 (42.52570°S, 171.82040°E, 200 m)

$^1$Weighted mean $^{209}$Pb/$^{206}$U age = 127.0 ± 6.9 Ma (95% c.l.), n = 7/15, MSWD = 5.1

$^2$Mean $^{18}$O = 5.8 ± 0.9% (1 SD), n = 2/6

$^3$Mean $\epsilon_{HFT}$ = 3.4 ± 2.1 (1 SD), n = 2/5

Hokitika Gorge orthogneiss AS54 (42.95660°S, 171.01540°E, 78 m)

$^1$Weighted mean $^{209}$Pb/$^{206}$U age = 116.0 ± 2.3 Ma (95% c.l.), n = 14/15, MSWD = 1.8

$^2$Mean $^{18}$O = 8.5 ± 0.6% (1 SD), n = 5/6

$^3$Mean $\epsilon_{HFT}$ = −0.5 ± 2.6 (1 SD), n = 5/6

Mean: (Sm/Lu)$_{Gd}$ = 35, Ce/Ce* = 307, Eu/Eu* = 0.3, n = 6

$^1$Mean: (Sm/La)$_{Gd}$ = 52, Ce/Ce* = 107, Eu/Eu* = 0.4, n = 6

(Continued)
Table 2. Continued

| Spot      | Grain1 | Age (Ma)2 | Error, 1 SD | δ18O VSMOW (‰) | Eror, 1 SD | εHf Initial3 | Error, 2 SE | U (ppm) | Th/U | La (ppm) | Ce (ppm) | Pr (ppm) | Nd (ppm) | Sm (ppm) | Eu (ppm) | Gd (ppm) | Tb (ppm) | Dy (ppm) | Ho (ppm) | Er (ppm) | Yb (ppm) | Lu (ppm) | (Sm/La)N | (La/Lu)N | Ce/Ce*4 | Eu/Eu*5 |
|-----------|--------|------------|-------------|----------------|------------|--------------|-------------|---------|------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| 9.1 p ed os | 04 | 114.9 2.5 9.3 0.8 | -2.6 3.2    | 3334 | 843 0.26 0.1 | 51 0.0 0.2 | 0.6 0.5 | 5 | 17 | 55 | 103 | 111 | 130 | 282 | 270 | 113 | 66 | 269 | 0.3 |
| 8.1 p c os | 05 | 115.3 2.5 9.0 0.8 | -2.0 3.6    | 1360 | 869 0.66 0.0 | 111 | 0.2 | 0.4 | 1.4 | 1.5 | 12 | 33 | 102 | 179 | 175 | 187 | 367 | 327 | 422 | 36 | 379 | 0.3 |
| 10.1 p m os | 10 | 120.4 2.6 8.0 0.8 | -2.1 2.5 | 2268 | 913 0.42 0.1 | 191 | 0.3 | 0.5 | 2.4 | 1.3 | 19 | 52 | 165 | 253 | 237 | 242 | 457 | 385 | 385 | 225 | 27 | 296 | 0.2 |
| 5.1 p c os | 04 | 370.9 7.9 9.0 0.8 | -0.6 3.0 | 813 | 289 0.37 0.0 | 40 | 0.1 | 0.3 | 2.3 | 0.8 | 17 | 32 | 102 | 154 | 148 | 151 | 298 | 273 | 549 | 28 | 92 | 0.1 |

Mikono River orthogneiss A555 (43.03080°S, 170.89150°E, 300 m)

2Weighted mean 206Pb/238U age = 114.2 ± 2.4 Ma (95% c.l.), n = 11/13, MSWD = 1.4
3Mean δ18O = 6.0 ± 0.8‰ (1 SD), n = 9/10
4Mean εHf = −8.2 ± 2.4 (1 SD), n = 7/8
5Mean (Sm/La)N = 256, (Lu/Gd)N = 44, Ce/Ce* = 184, Eu/Eu* = 0.4, n = 8
6Mean (Sm/La)N = 256, (Lu/Gd)N = 30, Ce/Ce* = 61, Eu/Eu* = 0.4, n = 9
7Mean (Sm/La)N = 51, (Lu/Gd)N = 33, Ce/Ce* = 51, Eu/Eu* = 0.2, n = 9
8Mean (Sm/La)N = 33, (Lu/Gd)N = 33, Ce/Ce* = 51, Eu/Eu* = 0.2, n = 9
9Mean (Sm/La)N = 256, (Lu/Gd)N = 44, Ce/Ce* = 184, Eu/Eu* = 0.4, n = 8

Take River orthogneiss A556 (43.03700°S, 170.87450°E, 155 m)

2Weighted mean 206Pb/238U age = 370.6 ± 9.9 Ma (95% c.l.), n = 12/15, MSWD = 3.7
3Mean δ18O = 9.0 ± 0.9‰ (1 SD), n = 8/9
4Mean εHf = −14.4 ± 2.6 (1 SD), n = 8/10
5Mean (Sm/La)N = 256, (Lu/Gd)N = 30, Ce/Ce* = 61, Eu/Eu* = 0.4, n = 9

Bonacci Creek orthogneiss A557 (43.08450°S, 170.63910°E, 450 m)

2Weighted mean 206Pb/238U age = 386.5 ± 7.5 Ma (95% c.l.), n = 13/15, MSWD = 1.6
3Mean δ18O = 7.8 ± 0.8‰ (1 SD), n = 8/9
4Mean εHf = −6.2 ± 2.5 (1 SD), n = 9/10
5Mean (Sm/La)N = 32, (Lu/Gd)N = 33, Ce/Ce* = 51, Eu/Eu* = 0.2, n = 9

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Whataroa Quarry orthogneiss A558

$^{238}\text{U}$ age: 90.0 ± 1.9 Ma (95% c.l.), $n = 14/18$, MSWD = 1.2

Mean $\delta^{18}\text{O} = 6.5 \pm 0.7\%$ (U), $n = 14/18$

Mean $\delta^{18}\text{O}_{\text{SMOW}} = 8.0 \pm 2.4\%$ (SD), $n = 14/18$

Mean $(\text{Sm}/\text{La})_{\text{N}} = 25$, $(\text{Lu}/\text{Gd})_{\text{N}} = 43$, Ce/Ce* = 73, Eu/Eu* = 0.2, $n = 13$

Habit: ov, oval; p, prismatic; f, fragment; eq, equant. Analysis site: i, inheritance; c, core; m, middle; ed, edge; og, overgrowth. Zonation: os, oscillatory; h, homogeneous; t, turbid; re, recrystallized.

$^{18}\text{O}$ calculated from spots in bold used to define weighted mean ages in Hiess (2010).

Mean REE ratios are calculated from all spots.
Fig. 7. Paragneiss zircon REE concentrations normalized to CI carbonaceous chondrite abundances of McDonough & Sun (1995). Grey patterns relate to the HREE depleted profiles \((\text{Lu}/\text{Gd})_n\) from 0.3 to 17 so they can be better discriminated from the more typical black HREE enriched profiles.

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**Fig. 8.** Paragneiss zircon $\delta^{18}O$ compositions against corresponding $^{206}\text{Pb} / ^{238}\text{U}$ or $^{207}\text{Pb} / ^{206}\text{Pb}$ crystallization ages (Hiess et al. 2010). Global compilation (Valley et al. 2005) and Archaean tonalite–trondhjemite–granodiorite (TTG) from Greenland (Hiess et al. 2009; Hiess et al. 2011) plotted for comparison. Fields for mantle zircon from Valley et al. (1998), Hadean and Archaean ‘supracrustal zircon’ from Cavosie et al. (2005) and Archaean ‘low $\delta^{18}O$ zircon’ from Hiess et al. (2011). All errors are 1 SD.

**Fig. 9.** Paragneiss zircon $\varepsilon_{\text{Hf}(T)}$ compositions against corresponding $^{206}\text{Pb} / ^{238}\text{U}$ or $^{207}\text{Pb} / ^{206}\text{Pb}$ crystallization ages (Hiess et al. 2010). CHUR parameters from Bouvier et al. (2008) and primitive zircon $^{176}\text{Lu} / ^{177}\text{Hf}$ arrays from Kemp et al. (2006). $\varepsilon_{\text{Hf}(T)}$ and age errors are 2 SE and 1 SD, respectively.
33 and 30, Ce/Ce* of 51 and 61, and Eu/Eu* of 0.2 and 0.1 respectively. Three older Cretaceous samples (A551, Mt Elliot, 127.0 ± 6.9 Ma, Fig. 10a; A554, Hokitika Gorge, 116.0 ± 2.3 Ma, Fig. 10b; A555, Mikonui River, 114.2 ± 2.4 Ma, Fig. 10c) share similar mean compositions with (Sm/La)$_N$ of 270, 354 and 256, (Lu/Gd)$_N$ of 52, 35 and 44, Ce/Ce* of 107, 307 and 184, and Eu/Eu* of 0.4, 0.3 and 0.4, respectively, while the youngest Cretaceous sample (A558, Whataroa Quarry, 92.0 ± 1.9 Ma, Fig. 10f) is distinct with a mean (Sm/La)$_N$ of 25, (Lu/Gd)$_N$ of 43, Ce/Ce* of 73 and Eu/Eu* of 0.2.

Devonian zircon $\delta^{18}O$ and $\varepsilon_{Hf(T)}$ from orthogneiss

Devonian zircon grains from three orthogneiss samples with overlapping weighted mean age uncertainties (Fig. 11) record relatively high mean $\delta^{18}O$ values ranging from 7.8 ± 0.8 to 9.0 ± 0.9‰ and relatively un-radiogenic mean $\varepsilon_{Hf(T)}$ values ranging from −14.4 ± 2.6 to −6.2 ± 2.5 units. Of these three samples, the marginally oldest, A557 from Bonar Creek at 386.5 ± 7.5 Ma records the relatively more primitive compositions ($\delta^{18}O = 7.8 ± 0.8‰; \varepsilon_{Hf(T)} = −6.2 ± 2.5$ units;

Fig. 10. Orthogneiss zircon REE concentrations normalized to CI carbonaceous chondrite abundances of McDonough & Sun (1995).
The marginally youngest sample, A556 from Tuke River at 370.6 ± 9.9 Ma records the relatively more evolved compositions (d18O = 9.0 ± 0.9‰; ɛHf(T) = −14.4 ± 2.6 units; Fig. 11c, d), while the intermediate aged sample A549 from Clarke River at 378.1 ± 6.8 Ma records intermediate compositions (d18O = 8.1 ± 1.3‰; ɛHf(T) = −9.7 ± 2.3 units; Fig. 11a, b). These subtle age differences have been identified as statistically significant in recent high-precision isotope dilution – thermal ionization mass spectrometry (ID-TIMS) studies of regional plutonic rocks (Tulloch et al. 2009; Turnbull et al. 2013). Each sample contains inherited Phanerozoic crystals with evolved and/or primitive compositions. No correlation exists between Th/U (as an indicator of magmatic evolution) and d18O or ɛHf(T) for any Devonian sample (Fig. 12).

**Fig. 11.** Devonian orthogneiss zircon d18O and ɛHf(T) compositions against corresponding 206Pb/238U crystallization ages (Hiess et al. 2010). Individual analyses in black with 1 SD age and d18O errors, 2 SE ɛHf(T) errors. Weighted mean (95% confidence limits) ages and mean (1 SD) isotopic compositions for samples in white. Fields for mantle zircon from Valley et al. (1998). CHUR parameters from Bouvier et al. (2008).

**Cretaceous zircon d18O and ɛHf(T) from orthogneiss**

Cretaceous zircon grains from five orthogneiss samples (Fig. 13) have weighted mean ages spanning from 92.0 ± 1.9 to 127.0 ± 6.9 Ma. Four mean d18O compositions cover a limited and primitive range from 5.8 ± 0.9 to 6.5 ± 0.7‰, with one higher composition at 8.5 ± 0.9‰ (A554, Hokitika Gorge, 116.0 ± 2.3 Ma; Fig. 13e). Four mean ɛHf(T) values are more radiogenic than, or lie within uncertainty of CHUR, ranging from −12 ± 2.1 to +8.0 ± 2.4 units, with one un-radiogenic composition of −8.2 ± 2.4 units (A555, Mikonui River, 114.2 ± 2.4 Ma; Fig. 13h). There is a less clear correlation between age, oxygen and hafnium isotopic composition within the Cretaceous as compared with the Devonian orthogneiss samples. One subtle
trend however, is that zircon from the oldest (A551, Mt Elliot, 127.0 ± 6.9 Ma) and youngest (A558, Whataroa Quarry, 92.0 ± 1.9 Ma) samples tends to be more primitive with $\delta^{18}O$ of 5.8 ± 0.9 and 6.5 ± 0.7‰ (Fig. 13c, i), and $\varepsilon_{Hf(T)}$ of +3.4 ± 2.2 and +8.0 ± 2.4 units (Fig. 13d, j), respectively, while the intermediate aged samples (A554, Hokitika Gorge, 116.0 ± 2.3 Ma; A548, Solitude Creek, 114.5 ± 2.0 Ma; A555, Mikonui River, 114.2 ± 2.4 Ma) located within relatively close proximity to each other (Fig. 1) are generally subtly more evolved with $\delta^{18}O$ of 8.5 ± 0.9, 6.2 ± 0.7 and 6.0 ± 0.8‰ (Fig. 13e, a, g), and $\varepsilon_{Hf(T)}$ of −0.5 ± 2.6, −1.2 ± 2.1 and −8.2 ± 2.4 units (Fig. 13f, b, h), respectively. All samples except A548 contain inherited Phanerozoic crystals with evolved and/or primitive compositions. No correlation exists between Th/U and $\delta^{18}O$ or $\varepsilon_{Hf(T)}$ for any Cretaceous sample (Fig. 12).

Discussion

Paragneisses petrogenesis from zircon $\delta^{18}O$ and $\varepsilon_{Hf(T)}$

The U–Pb age spectra of Western Province paragneiss zircon grains have previously been correlated with Ordovician Greenland Group meta-sedimentary rocks from the Buller Terrane and other voluminous sedimentary units within the Lachlan and Adelaidean fold belts of SE Australia and the Wilson and Bowers terranes of Antarctica (Chen & Williams 1990; Ireland 1992; Gibson & Ireland
Fig. 13. Cretaceous orthogneiss zircon $\delta^{18}O$ and $\varepsilon_{Hf(T)}$ compositions against corresponding $^{206}\text{Pb}/^{238}\text{U}$ crystallization ages (Hiess et al. 2010). Individual analyses in black with 1 SD age and $\delta^{18}O$ errors, 2 SE $\varepsilon_{Hf(T)}$ errors. Weighted mean (95% confidence limits) ages and mean (1 SD) isotopic compositions for samples in white. Fields for mantle zircon from Valley et al. (1998). CHUR parameters from Bouvier et al. (2008).
These arrays were interpreted to reflect the model wana margin meta-sediments of Eastern Australia. These common Gondwana margin age signatures are complemented here by the similar zircon oxygen and hafnium isotopic profiles observed between the Western Province paragneisses and those of Palaeozoic sedimentary rocks of the Lachlan fold belt; compare Figures 8 and 9 here with Figures 2 and 1 of Kemp et al. (2006).

Both the oxygen (Fig. 8) and hafnium (Fig. 9) spectra in the Western Province zircon grains indicate that they represent detritus from a broad mixture of lithologies. Approximately 18% of the zircon grains have δ18O from 4.5 to 6.4‰ and represent mantle-derived zircon with δ18O of 5.3 ± 0.3‰ (Valley et al. 1998) or zircon sourced from other relatively primitive magmas which indicate no significant high-δ18O or low-δ18O input. However, supracrustal materials or fluids have contributed to the majority of zircon compositions. Approximately 13% of the zircon grains have δ18O from 1.5 to 4.4‰, indicating low-δ18O input to magma protoliths, for example hydrothermally altered rocks with δ18O < 4.5‰ (Eiler 2001). While approximately 68% the zircon grains have δ18O from 6.5 to 12.7‰, indicating high-δ18O input to magma protoliths for example 18O-enriched pelagic or continental sediments and rocks (Eiler 2001). The increasing upper limit to δ18O compositions through the Proterozoic and Phanerozoic is interpreted to reflect global trends of increasing magmatic variability in 18O/16O owing to maturation of the crust, changes in the composition of sediments and shifts in the rates and styles of recycling for surface materials into crustal magmas (Valley et al. 2005).

The variability observed in εHf(T) also indicates that the zircon grains were derived from a mixture of juvenile and reworked, mantle and crustal reservoirs with Lu/Hf compositions both higher (n = 35; 31%) and lower (n = 77; 69%) than that of CHUR at their time of formation. Zircon domains with the most primitive ε18O compositions (4.5–6.4‰; n = 13) record a broad range of ages (453–2987 Ma) and initial ε18O compositions (−25.4 ± 1.8 to +10.3 ± 1.9 units). Nine of these analyses (c. 69%) lie within the uncertainty of two 176Lu/177Hf arrays suggested by Kemp et al. (2006) for comparative zircon data from Gondwana margin meta-sediments of Eastern Australia. These arrays were interpreted to reflect the model ages of two major episodes of crustal growth at c. 1800 and c. 3400 Ma. Nebel-Jacobsen et al. (2011) obtained a range of Lu–Hf model ages from 0.9 to 3.7 Ga with age maxima at c. 1.5 and c. 2.4 Ga for detrital zircons from the Buller and Takaka terranes.

The calculation of model-age arrays with small populations is highly influenced by the selection or rejection of individual analyses and the choice of 176Lu/177Hf ratio used to define unique model ages. It can be argued that the distribution of primitive and evolved zircon within our entire dataset with respect to their U–Pb ages, δ18O, εHf(T) and potential model ages could simply reflect preservation or sampling biases, obstructing a constant production and reworking of juvenile magmas through geological time as opposed to strongly episodic behaviour. A compilation of published zircon εHf(T) compositions from Zealandia, Antarctica and southeastern Australia is presented in Figure 14. Paragneiss-derived grain analyses from this study (Fig. 14a) are broadly distributed within similar fields to those of detrital and inherited grains from other regions within Gondwana (Kemp et al. 2006; Flowerdew et al. 2007; Nebel-Jacobsen et al. 2011), reinforcing their shared provenance and proximity on the former passive margin (Fig. 2).

**Paragneisses and orthogneiss petrogenesis from zircon RIE**

The RIE patterns observed in paragneiss zircon grains attest to variable source lithologies involved in their genesis (Fig. 7). The application of RIE in detrital zircon as provenance indicators has previously been tested and found to be of limited use (Hoskin & Ireland 2000). In this study positive Ce and negative Eu anomalies are highly variable within paragneiss samples and may reflect the range of oxidation states and degrees of feldspar crystallization present in the source magmas of the detrital grains. Distinctively flatter HREE profiles were measured for 26% of analyses and occur in varying proportions for each sample. The flatter HREE profiles are located on recrystallized or homogenized grain textures, or within grains that contain these textures (Figs 3 & 4; Table 1). These analyses can be attributed to the crystallization or recrystallization of zircon in competition with

Fig. 14. Compilation of published single-grain zircon εHf(T) compositions from Zealandia, Antarctica and southeastern Australia (a) covering the interval 0–4000 Ma and (b) expanded for the interval 0–500 Ma. Data are sourced from Halpin et al. (2005), Flowerdew et al. (2006, 2007), Kemp et al. (2006, 2007, 2009), Bolhar et al. (2008b), Goodge et al. (2008), Scott et al. (2009), Will et al. (2010), Nebel-Jacobsen et al. (2011), Tulloch et al. (2011) and Yakymchuk et al. (2013).
phases that preferentially incorporate HREE from the melt, for example, garnet in higher-pressure environments. The HREE-depleted paragneiss zircon formed within the garnet-bearing host rock, during Devonian and Cretaceous regional plutonism, high-pressure metamorphism and localized crustal melting. The strong Cretaceous overprinting recorded in zircon U–Pb of sample A553 from Crooked River (Hiess et al. 2010) is reflected in the dominantly flat zircon HREE profiles recorded in this sample.

Both Devonian and Cretaceous orthogneiss zircon REE patterns (Fig. 10) are similar to igneous grains sourced from typical continental crust (Hoskin & Schaltegger 2003; Hoskin 2005). The lack of flatter HREE profiles within the orthogneiss samples can be attributed to the absence of garnet in their modal assemblages. The similarities within and differences between (Sm/La)$_{ec}$, (Lu/Gd)$_{Nc}$, Ce/Ce* and Eu/Eu* values from the Devonian and Cretaceous suites reflect their distinct mineralogy and chemistry.

**Orthogneiss petrogenesis from zircon $\delta^{18}O$**

The three Devonian orthogneiss samples record mean zircon grain $\delta^{18}O$ values of 9.0 ± 0.9, 8.1 ± 1.3 and 7.8 ± 0.8‰ (Fig. 11c, a, e) that indicate the incorporation of high-$\delta^{18}O$ materials within their protoliths. These zircon grain $\delta^{18}O$ values translate to estimated whole-rock $\delta^{18}O$ values of 10.8 ± 0.9, 9.9 ± 1.3 and 9.6 ± 0.8‰ based on the 70 wt% SiO$_2$ average composition for non-metamorphosed correlative granitoid Karamea Suite plutons (Tulloch et al. 2009) and zircon–whole-rock $\delta^{18}O$ fractionation relationships of Valley et al. (2005). Whole-rock $\delta^{18}O$ values of 9.9–10.5‰ have been demonstrated as an indicator of S-type granites (O’Neil & Chappell 1994–1999). Whole-rock $\delta^{18}O$ values ranging from 13.7 to 16.2‰ (Tulloch et al. 2009) consistent with those of other siliciclastic sediments. A significant process driving $^{18}O$-enrichment in the Devonian magmas is interpreted to be the deep melting and assimilation of Buller Terrane mature crustal basement rocks by primitive arc-derived magmas. This is based on the age of inherited zircons and the isotopic compositions contained within Karamea Suite rocks (Pickett & Wasserburg 1989; Muir et al. 1994, 1996a, b; Tulloch et al. 2009).

Recent tectonic models for Karamea Suite magma genesis are based on intra-arc extension of previously over-thickened lithosphere, allowing mantle-derived magmas to intrude into, melt, and hybridize with, meta-sedimentary crust (Tulloch et al. 2009). A subtle trend between the three Devonian zircon grain O–Hf compositions suggests that magmas may have initially been more mafic (A557), with the influence of crustal assimilation becoming more significant through time (A549 and A556).

Cretaceous orthogneiss sample A554 from Hokitika Gorge contains zircon grains with a high mean $\delta^{18}O$ composition of 8.5 ± 0.9‰ (Fig. 13e), consistent with the range of zircon grain values observed in the three Devonian orthogneiss samples (Fig. 11a, c, e). This sample records a single inherited zircon at 370 Ma with a $\delta^{18}O$ of 9.0 ± 0.8‰ indicating the incorporation of evolved Devonian source material. The sample is presently located within a few kilometres of outcropping exposure of Karamea Suite granitoids (Fig. 1). However, these gneissic rocks have been tectonically displaced to their current position by ductile mylonite shearing and late brittle faulting, so this proximity could be coincidental.

The remaining four Cretaceous orthogneiss samples are, however, distinctively more primitive with respect to their zircon grain oxygen isotopic compositions, recording mean zircon $\delta^{18}O$ compositions of 5.8 ± 0.9, 6.0 ± 0.8, 6.2 ± 0.7 and 6.5 ± 0.7‰ (Fig. 13c, g, a, i). These lower zircon $\delta^{18}O$ values translate to estimated whole-rock $\delta^{18}O$ values of 7.6 ± 0.9, 7.8 ± 0.8, 8.0 ± 0.7 and 8.3 ± 0.7‰ based on a 70 wt% SiO$_2$ average composition for nonmetamorphosed correlative granitoid Hohonu Batholith plutons of the Separation Point and Rahu Suites (Tulloch & Kimbrough 1989; Waight et al. 1999a–c) and zircon–whole-rock $\delta^{18}O$ fractionation relationships of Valley et al. (2005). Whole-rock $\delta^{18}O$ values of <10‰
have been demonstrated as an indicator of I-type granites (O’Neil & Chappell 1977) and are thus suggestive of an I-type affinity. This is consistent with previous classification of the coeval I-type Separation Point and I-S type Rahu Suites (Tulloch 1983, 1988; Waight et al. 1997, 1998a–c).

The more primitive magmas that sourced the Cretaceous zircon grains probably incorporated relatively smaller amounts of $^{18}$O-enriched crustal material components during their formation. The protoliths to these more mafic and juvenile Cretaceous orthogneiss samples thus perhaps relate to the Mid Cretaceous Tasman Sea extensional rift event, where magmatism was dominated by the upwelling of largely uncontaminated, mantle-derived melts (Tulloch & Kimberg 1989; Waight et al. 1998a–c). This mafic O–Hf zircon grain signature is exemplified in the oldest (A551) and youngest (A558) Cretaceous orthogneiss samples, perhaps signalling early and late flare-ups of asthenosphere-derived basaltic magma. Four of the Cretaceous samples (A551, A554, A555 and A558) record seven Carboniferous to Cambrian inherited zircon grain analyses with $\delta^{18}$O values ranging from $6.2 \pm 0.8$ to $9.7 \pm 0.8$%; (Fig. 13c, e, g, i), indicating a subtle input of older and slightly $^{18}$O-enriched material to Cretaceous magmatism. This probably reflects the incorporation of surrounding plutonic or meta-sedimentary crustal rocks by assimilation during magma transport and emplacement.

**Orthogneiss petrogenesis from zircon $\varepsilon_{Hf(T)}$**

The mean Devonian zircon grain $\varepsilon_{Hf(T)}$ values of $-14.4 \pm 2.6$, $-9.7 \pm 2.3$ and $-6.2 \pm 2.5$ units (Fig. 11d, b, f) indicate the incorporation of older crustal components with less radiogenic Hf isotopic compositions than CHUR at initial ages, consistent with the recycling of evolved supracrustal rocks like the Buller Terrane Greenland Group meta-sediments in their source magmas. Correspondingly, mean zircon grain $\varepsilon_{Hf(T)}$ values of $+8.0 \pm 2.4$, $+3.4 \pm 2.2$, $-0.5 \pm 2.6$ and $-1.2 \pm 2.1$ units (Fig. 13j, d, f, b) indicate that the majority of Cretaceous magmas are more juvenile, with Hf isotopic compositions than are more radiogenic than, or similar to CHUR at initial ages.

Zircon grains of sample A555, from the Mikonui River record the least radiogenic Cretaceous orthogneiss composition (mean of $-8.2 \pm 2.4$ $\varepsilon_{Hf(T)}$ units; Fig. 13h) and are more consistent with the range of zircon grain values observed in the three Devonian orthogneiss samples (Fig. 11b, d, f). This sample records a single Carboniferous inherited zircon at 312 Ma with an $\varepsilon_{Hf(T)}$ of $-6.2 \pm 2.8$ units indicating the presence of older un-radiogenic source material. This sample also crops out within a few kilometres of Karamea Suite granitoids (Fig. 1); however, the same caveats for coincident tectonic juxtaposition as sample A554 (see above) apply here. Three other Cretaceous orthogneiss samples (A551, A554 and A558) record five Carboniferous, Devonian or Cambrian inherited zircon grains with $\varepsilon_{Hf(T)}$ values of $+6.4 \pm 2.3$, $+2.2 \pm 2.7$, $+0.5 \pm 2.8$, $-0.6 \pm 3.0$ and $-5.2 \pm 2.6$ units (Fig. 13d, f, j), also indicating the incorporation of older, compositionally mixed materials during Cretaceous magmatism.

Devonian and Cretaceous orthogneiss zircon grain populations record $\varepsilon_{Hf(T)}$ compositions that are comparable with other correlative magmatic suites from Zealandia (Bolhar et al. 2008b; Scott et al. 2009; Tulloch et al. 2011), Antarctica (Yakymchuk et al. 2013) and Australia (Kemp et al. 2007, 2009; Fig. 14b). The up to 30 e-unit range of compositions encountered at a given time attest to variation in the makeup of juvenile and reworked sources, both along and across the axis of the active margin (Yakymchuk et al. 2013).

**Protolith mixing to generate Karamea, Separation Point, Rahu and other Gondwana igneous suites**

Binary mixing lines constructed with whole-rock strontium–neodymium and strontium–oxygen isotopic pairs have been used to model the potential sources for magmas of the regional Devonian and Cretaceous plutonic suites (Pickett & Wasserburg 1989; Muir et al. 1996b; Waight et al. 1998b, c; Tulloch et al. 2009). Buller Terrane Greenland Group meta-sediments are used to anchor the evolved, crustal end of the mixing arrays while various regional mafic lithologies and reservoirs can be used at the primitive, mantle end. Sample isotopic signatures can be reconciled by crustal end-member proportion of c. 30–60% for the Karamea and c. 20–40% for the Separation Point and Rahu suites. Assimilation fractionation curves (DePaolo 1980) yield similar results, while scattered analyses within individual suites have been cited as evidence for multiple source components (Keay et al. 1997) and further complication arises from the difficulty in assigning precise end-member compositions and model parameters for a given sample.

Oxygen and hafnium isotopes in zircon have also been used to construct binary mixing and assimilation fractional crystallization models applied to correlative intrusive and extrusive units in eastern Australia (Kemp et al. 2007, 2008) and western Antarctica (Yakymchuk et al. 2013) with distinct sources and mixing arrays in each example. Here we apply O–Hf binary mixing to the New Zealand Western Province paragneiss and orthogneiss zircon suites to further explore their petrogenetic
models (Fig. 15). A depleted mantle end-member is used for each example with present day $^{176}\text{Hf} / ^{177}\text{Hf}$ of 0.28326, hafnium concentration of 0.157 ppm and oxygen concentration of 44.14 wt% taken from Workman & Hart (2005). A δ$^{18}\text{O}_{\text{Zr}}$ of $5.3 \pm 0.3\%$ is from Valley et al. (1998). CHUR parameters are from Bouvier et al. (2008) and corrected for linear Hf isotopic evolution.

**Insights to paragneiss and orthogneiss genesis from zircon O––Hf**

The paragneiss zircon grain dataset (Fig. 15a) demonstrates mixing between the steadily evolving radiogenic depleted mantle and a range of unradiogenic crustal rock and fluid reservoirs through time. The arrays are highly scattered, reflecting the variable nature of local crustal compositions but clearly diverge towards more common high-δ$^{18}\text{O}$ end-members, or less common low-δ$^{18}\text{O}$ end-members. These crustal reservoirs have become progressively more fractionated but have persisted from the Archaean to Phanerozoic.

Devonian (Fig. 15b) and Cretaceous (Fig. 15c) orthogneiss zircon grain populations are represented as crystallization products of binary mixtures between the depleted mantle and Greenland Group meta-sediments corrected to 370 and 115 Ma. The Greenland Group δ$^{18}\text{O}_{\text{Zr}}$ end-member is taken as the least radiogenic sample NE-19 of Pickett & Wasserburg (1989) from 10 reported to date (Pickett & Wasserburg 1989; Waight et al. 1998c; Tulloch et al. 2009) using the crustal array correlation of $\varepsilon_{\text{Hf}} = 1.35 \times e_{\text{Nd}} + 2.82$ from Vervoort & Blichert-Toft (1999). A Greenland Group δ$^{18}\text{O}_{\text{WR}}$ of 13.8% is based on the average δ$^{18}\text{O}_{\text{WR}}$ of 15.4 of Tulloch et al. (2009), a grand mean SiO$_2$ of 66.75 wt% from 79 Greenland Group greywacke and argillite samples (Nathan 1976; Roser et al. 1996) and zircon-whole-rock fractionation factors of Valley et al. (2005). A Greenland Group oxygen concentration of 48.74 wt% is based on the same 79 Greenland Group samples (Nathan 1976; Roser et al. 1996).

A highly significant variable in the construction of these mixing arrays is the Hf concentration of the crustal end-member (Kemp et al. 2007, 2008; Yakymchuk et al. 2013). Oxygen is widely distributed through a rock’s modal assemblage and the relative differences in oxygen concentration between the crust and mantle are not large. However, hafnium is very depleted in mantle rocks and enriched in crustal rocks, where it is strongly partitioned into the mineral phase zircon (Hoskin & Schaltegger 2003). During the assimilation or partial melting of crustal rocks by mantle-derived magmas, existing crustal zircon may dissolve preferentially and/or incompletely. This reduces the amount of Hf incorporated into the crustal melt and subsequently available to be sequestered by any newly precipitated zircon. The presence of inherited zircon in all orthogneiss samples except Cretaceous A548 from Solitude Creek confirms that this incomplete mixing process is present to some degree in the majority of Western Province plutonic systems.

For each plot one mixing curve is derived based on the highest Hf concentration for the Greenland Group meta-sediments reported to date of 9.1 ppm from sample 33-RO (Pickett & Wasserburg 1989). This case assumes complete zircon dissolution (no inheritance) within a Hf-rich Greenland Group source rock. A second curve is computed at a lower Hf concentration that captures most of the data points into an envelope of realistic values. This is 1.0 ppm for the Devonian (Fig. 15b) and 0.3 ppm for the Cretaceous (Fig. 15c). Inheritance-free sample A548 and sample A555 with very minor inheritance plot close to the 9.1 ppm curve, in part confirming the validity of this approach (Fig. 15c). Only Devonian sample A556 fails to plot within the mixing envelope and indicates that our presently defined Greenland Group end-member composition may not be representative of slightly less radiogenic crustal samples that were involved in its magmatism (Fig. 15b). All analyses indicate a bulk mixing crustal proportion of c. 20–50% for the Devonian and c. 10–40% for the Cretaceous samples. This is in general accord with earlier mixing models for magmas of the Kara-mea, Separation Point and Rahu Suites (Pickett & Wasserburg 1989; Muir et al. 1996b; Waight et al. 1998a–c; Tulloch et al. 2009).

Zircon grains from each Devonian or Cretaceous orthogneiss sample have subtly different δ$^{18}\text{O}$ and δ$^{18}\text{O}_{\text{Hf(T)}}$ composition when considering quoted uncertainties. This evidence points towards some combination of slightly unique magmatic processes occurring and/or a distinctive makeup of protolith
components by proportion or chemistry in each rock. Such local variations are consistent with
the construction of these large, composite intrusive bodies from multiple magma batches, crystallizing
as discrete plutons.

The spectrum of igneous O and Hf isotopic compositions within any individual orthogneiss sample is,
however, relatively restrictive when excluding analytical uncertainties. This is significant considering analyses took place on multiple crystals and across all grain structural levels from core to rim (Figs 5 & 6; Hiess et al. 2010). Three Devonian orthogneiss samples have a within-sample variability (Δ) of Δ18O ranging from 1.8 to 2.7‰ and ΔHf(T) ranging from 3.9 to 6.0 units (Fig. 11); five Cretaceous orthogneiss samples have Δ18O ranging from only 0.5–1.3‰ and ΔHf(T) ranging from only 1.7–4.8 units (Fig. 13). Additionally, the analyses within each sample show no clear correlation between their O–Hf isotopic compositions (Fig. 15b, c). This indicates that, during each sample’s protracted, oscillatory-zoned zircon crystallization history, no strong linear magmatic compositional evolution occurred within the plutonic environment.

This lack of melt compositional fractionalation during the orthogneiss zircon grain formation is similarly reflected within individual samples by their lack of variation in REE patterns (Fig. 10), by the lack of correlation or significant variability between U–Pb age and δ18O or εHf(T) (Figs 11 & 13) or between Th/U and δ18O or εHf(T) (Fig. 12). This suggests that zircon crystallization did not involve progressive interaction of end-member components, nor heterogeneous open system processes, nor transient zircon crystallization over a significant range of pressures and temperatures. The source components for each samples magma batch were thus highly homogeneous prior to the onset of, and throughout zircon crystallization, which occurred over a limited structural level within the crust.

Conclusions

(1) SHRIMP and LA-MC-ICPMS were used to determine the REE concentrations, oxygen and hafnium isotopic compositions within U–Th–Pb dated zircon grains from paragneisses and orthogneisses of the Western Province, Zealandia.

(2) Paragneiss zircons were probably derived from similar sources to those that supplied the widespread regional Ordovician Greenland Group and correlative Gondwana margin units located in southeastern Australia and Antarctica. The detrital zircon grains record variable elemental and isotopic signatures related to phases of crust formation and the recycling of reworked materials in source terranes, followed by overprinting metamorphism within the garnet-bearing host rock.

(3) Orthogneiss magmatic zircon formed during Devonian and Cretaceous igneous events involving the effective mixing of regional Greenland Group rocks with primitive magmas. These plutonic systems were assembled incrementally and confined to restricted structural levels, with relative crustal metasedimentary rock contributions for the Devonian and Cretaceous of c. 20–50% and c. 10–40% respectively.

(4) Zircon grains can be used to trace a range of crustal processes operating along active margins, retaining detailed petrogenetic information through amphibolite-facies metamorphism with excellent fidelity.

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