# Creation of a continent recorded in zircon zoning

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## ABSTRACT

We have discovered a robust microcrystalline record of the early genesis of North American lithosphere preserved in the U-Pb age and oxygen isotope zoning of zircons from a lower crustal paragneiss in the Neoarchean Superior province. Detrital igneous zircon cores with  $\delta^{18}$ O values of 5.1%-7.1% record creation of primitive to increasingly evolved crust from  $2.85 \pm 0.02$  Ga to  $2.67 \pm 0.02$  Ga. Sharp chemical unconformity between cores and higher  $\delta^{18}O$ (8.4% - 10.4%) metamorphic overgrowths as old as  $2.66 \pm 0.01$  Ga dictates a rapid sequence of arc unroofing, burial of detrital zircons in hydrosphere-altered sediment, and transport to lower crust late in upper plate assembly. The period to  $2.58 \pm 0.01$  Ga included ~80 m.y. of high-temperature (~700-650 °C), nearly continuous overgrowth events reflecting stages in maturation of the subjacent mantle root. Huronian continental rifting is recorded by the youngest zircon tip growth at  $2512 \pm 8$  Ma (~ 600 °C) signaling magma intraplating and the onset of rigid plate behavior. This >150 m.y. microscopic isotope record in single crystals demonstrates the sluggish volume diffusion of U, Pb, and O in zircon throughout protracted regional metamorphism, and the consequent advances now possible in reconstructing planetary dynamics with zircon zoning.

**Keywords:** zircon, U-Pb, oxygen isotopes, ion probe, lower crust, Kapuskasing, Archean.

# INTRODUCTION

The integration of U-Pb and O isotope data for igneous zircons is a powerful methodology for revealing continental lithosphere-hydrosphere interaction through time (e.g., Valley et al., 1994; Rumble et al., 2002; Valley et al., 2005). For metamorphosed zircon, however, questions remain as to whether primary zircon oxygen isotopic compositions reequilibrate due to rapid, wet ( $P_{\rm H_{2}O}$  >70 bar) volume diffusion without affecting U-Pb ratios, a scenario suggested by experimental data (Watson and Cherniak, 1997). We have investigated detrital zircons with primary mantle-like oxygen isotope compositions that underwent tens of millions of years of high-grade regional metamorphism and zircon overgrowth in an <sup>18</sup>O/<sup>16</sup>O-enriched sedimentary matrix in the lower crust of the Neoarchean Superior province. Our aim was to test whether U-Pb age and oxygen isotopic zoning in such zircons can be primary, and interpretable as a record of thermotectonic processes operating at length scales more than 10 orders of magnitude larger than the crystals; i.e., the genesis and evolution of the ancient core of the North American plate.

# TECTONIC SETTING

The Superior province of the Canadian shield is the largest Archean tectosphere fragment, and peneplanation after the Paleoproterozoic Kapuskasing uplift event has exposed an oblique crustal cross section through its southern subduction-accretion margin (Fig. 1) (Percival and West, 1994). The Abitibi and Wawa subprovinces in the southern Superior province (Fig. 1, inset) were among the last to be accreted (2750–2670 Ma; Corfu and Davis, 1992) during northward subduction in the Kenoran orogeny. At the south end of the 300-km-long Kapuskasing uplift, a more



Figure 1. Inset: Geology of southern Superior province of the Canadian shield; Kapuskasing uplift is indicated. Bedrock geology map of the Borden Lake belt in southern Kapuskasing uplift is modified after Percival and West (1994) and shows amphibolite-granulite transition (dashed line), paleopressures, and zircon sample location site 32.

or less continuous metamorphic and structural gradient representing a 15-km-thick section of accreted crust consists of a series of metaplutonic and metasupracrustal belts. The largest and most extensive of the latter is the Borden Lake belt (Fig. 1) (Bursnall et al., 1994), a 5 km  $\times$  25 km east-striking synformal structure consisting mostly of multiply deformed mafic gneiss interlayered with narrow, discontinuous units of garnetiferous paragneiss (metawacke and metaconglomerate). The Borden Lake belt strikes at a high angle across the amphibolite-granulite transition and has a maximum age of 2667  $\pm$  2 Ma for conglomerate deposition (Krogh, 1993). Here we report zircon data for a sample of metawacke at the high-grade end of the Borden Lake belt (site 32, Fig. 1).

## Metamorphism

The metamorphic ages of zircon in the high-grade end of the Borden Lake belt have not been previously investigated. The age of peak metamorphism of surrounding gneisses has been estimated as ca. 2.66 Ga based on the age of widespread zircon growth in granulite facies metabasalts (Krogh and Moser, 1994). Deep crustal metamorphism followed polyphase compressional folding at all levels and was broadly coeval with orogen-parallel ductile flow in the middle and lower crust between 2660 Ma and 2630 Ma. This is a Superior province-wide event that, in the Kapuskasing cross section, appears to young with depth (Krogh, 1993; Moser et al., 1996). Paleopressures gradually increase to the east across the granulite facies domain, reaching maximum values of 1.1 GPa and peak temperatures of ≥850 °C (Mäder et al., 1994; Pattison, 2003). Water activity during metamorphism has been estimated as between 0.1 and 0.5 (Mäder et al., 1994). Granulite facies gneisses are cut locally by meter-scale tonalitic melt pods and granitic pegmatite dikes dated as 2640 ± 2 Ma and 2584 ± 2 Ma, respectively (Krogh, 1993).

## Primary Oxygen Isotope Compositions

Igneous zircon crystals from the upper crust of the Superior province (most samples are from the regions west and east of the Kapuskasing uplift) have remarkably uniform  $\delta^{18}$ O values compared to Proterozoic and younger crust (Peck et al., 2000; Valley et al., 2005), and average ~5.7% ± 0.6% (King et al., 1998) (i.e., close to mantle values). Zircons from late tectonic sanukitoid-like plutons yield higher values of 6.5% ± 0.4% (King et al., 1998). In contrast, paragneiss units, including those within the Borden Lake belt, have enriched whole-rock values between 8.5% and 12.0% (Li et al., 1991).

# SAMPLE DESCRIPTION

An ~15 kg sample of homogeneous garnet-biotite-hornblende paragneiss was taken from a well-exposed outcrop of granulitegrade paragneiss and mafic gneiss near the eastern termination of the Borden Lake belt (site 32, Fig. 1). The gneiss contains ~2% of centimeter-thick, discontinuous garnet-quartz plagioclase biotite leucosome. The paleopressure at site 32 is ~1 GPa based on the regional gradient (Fig. 1). A large yield of high-quality nonparamagnetic zircon was obtained from this sample and is made up of small, light pink, rounded to elongate detrital grains and large transparent brown prisms often containing pink to colorless cores. Brown zircon overgrowths are generally absent in paragneiss at the western low-grade end of the Borden Lake belt, and detrital grains are rounded; therefore some component of rounding of the cores is presumed to be due to mechanical erosion prior to metamorphism. (For methods, see the GSA Data Repository Appendix 1<sup>1</sup>.)

# RESULTS

#### Detrital Zircon Cores

The cathodoluminescence (CL) structures of detrital cores are characterized by oscillatory planar growth bands consistent with crystallization from magma. The bulk of the zircon cores (n = 42 of 47) range in  $^{207}$ Pb/ $^{206}$ Pb age from 2827 ± 16 to 2672 ± 20 Ma (all measurement uncertainties given at 2 standard deviations; age range based on most precise data) with a mean of all analyses equal to 2711 Ma (Fig. 2) (Table DR1; see footnote 1). The low average discordance (~2%; see Table DR1) for these analyses is consistent with prior isotope dilution-thermal ionization mass spectrometry studies in the region, and lower intercepts of discordant arrays are near 0 Ma; thus there is no evidence of ancient Pb loss, and <sup>207</sup>Pb/<sup>206</sup>Pb ion probe ages are treated as close approximations of true U-Pb isotopic age. These ages correspond to known ages of crust formation preceding and during the Kenoran orogeny. The  $\delta^{18}$ O values of zircon cores range from 5.1% to 7.1% (Fig. 2) regardless of size, tend to be negatively correlated with age, are similar to laser fluorination data for zircons throughout the Superior province, and partially overlap mantle zircon values of 5.3% ± 0.3% (Valley et al., 2005).

A small group (n = 5 of 47) of anomalous zircon cores have muted CL intensity and blurred to locally disrupted planar growth banding quite distinct from the CL characteristics of the main population (cf. cores of grains 6 and 4; Figs. 3A, 3B). These cores have higher  $\delta^{18}$ O domains and four of the five yield lower <sup>207</sup>Pb/<sup>206</sup>Pb spot ages coeval with metamorphism. Multispot analyses are available for three of these cores (labeled as recrystallized; Fig. 2) and reveal significant age and  $\delta^{18}$ O heterogeneity. For example, the core in grain 6 (Fig. 3B) features patchy domains at the edge and center with low  $\delta^{18}$ O values (6.3%–7%) and old <sup>207</sup>Pb/<sup>206</sup>Pb ages within the range typical for the main population. Darker CL domains



Figure 2. Summary of spatially correlated U-Pb and O isotopic measurements for 47 detrital cores and 26 metamorphic rims (Table DR1; see footnote 1). Age ranges for events depicted by solid bars are discussed in text. Note small time gap between end of sedimentation in Borden Lake belt and onset of lower crustal metamorphism of same sediments. Note also that previous laser fluorination analyses of Superior province magmatic zircon regionally gave average  $\delta^{16}$ O of 5.7% ± 0.6‰ and values as high as 6.5‰ ± 0.4‰ for late sanukitoid magmas (King et al., 1998).

in the core, however, have anomalous, higher  $\delta^{18}$ O values (by 2%c-3%c) and younger <sup>207</sup>Pb/<sup>206</sup>Pb ages overlapping that of the metamorphic overgrowths. Based on CL patterns of the other cores with anomalously high  $\delta^{18}$ O values, we anticipate that detailed multispot analysis will reveal similar domainal isotope heterogeneity.

#### **Metamorphic Zircon Rims**

The optically brown, dark CL, metamorphic rims exhibit concentric but discontinuous and weak internal CL banding. The banding is mostly concentric to the core-rim boundary but is sometimes truncated at low angles by outer, younger growth zones (Fig. 3; Fig. DR1 [see footnote 1]). The core-rim boundary can parallel the planar CL zoning in the core or truncate it as a curved nonconformable surface. Transparent brown zircon grains are euhedral and as much as four times larger than pink detrital grains, suggesting that the brown zircon represents new growth as opposed to in situ recrystallization of preexisting grains. Metamorphic rims do not contain thorite or coffinite inclusions, or patchy domains of different age and trace element (CL) composition that might suggest dissolution-reprecipitation processes (e.g., Geisler et al., 2007). Metamorphic zircon rims (n = 26) around detrital cores are uniformly higher in [U] than the cores by 5-10 times, and have Th/U ratios ≤0.1 (Table DR1). All but two rims have <sup>207</sup>Pb/<sup>206</sup>Pb ages ranging from  $2659 \pm 8$  Ma to  $2594 \pm 6$  Ma with a ca. 2622 Ma peak (Fig. 2). One rim tip (grain 6, Fig. 3B) has a much younger <sup>207</sup>Pb/<sup>206</sup>Pb age of  $2512 \pm 8$  Ma and is concordant. All metamorphic rims are significantly enriched in <sup>18</sup>O/<sup>16</sup>O compared to detrital cores, with  $\delta^{18}$ O values ranging from 8.4% to 10.4%. This variation is sometimes observed at roughly equal radial distances within a single metamorphic overgrowth (e.g.,

<sup>&</sup>lt;sup>1</sup>GSA Data Repository item 2008059, Appendix 1, Table DR1, and Figure DR1, including methods, U-Pb and O isotopic data, and scanning electron microscope and cathodoluminescence images, is available online at www. geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



Figure 3. A: Composite cathodoluminescence (CL) image (i.e., grayscale values of metamorphic rim inverted; see Fig. DR1 [see footnote 1] for original) of grain 4 showing locations and results of U-Pb and oxygen isotopic spot analyses. B: Composite (rim grayscale inverted) CL image of grain 6 showing patchy resetting of U-Pb age to metamorphic values and domainal enrichment of  $\delta^{18}$ O associated with darkening and/or disruption of CL in core (these changes may be due to recrystallization). Note concentric age and oxygen banding in metamorphic rim. Crystal growth spans  $\geq$ 150 m.y. C:  $\delta^{18}$ O results from grain 4 indicating that no discernible isotopic exchange has occurred between core and rim (see text). D: Stages of continental plate creation and local destruction corresponding to zircon growth zone sequences and sequence boundaries.

grain 6; Fig. 3B). These higher  $\delta^{18}$ O values reflect growth of zircon rims in approximate isotope exchange equilibrium with the <sup>18</sup>O/<sup>16</sup>O-enriched metasediment rock matrix, as indicated by  $\delta^{18}$ O values of garnet in this paragneiss sample (9.2%c–9.8%c, laser fluorination;  $\Delta^{18}$ O(zircon-garnet) ~0%c; Table DR1). Ti-in-zircon thermometry yields apparent temperatures (Valley et al., 2006) ranging from 706 °C in inner rims to 662 °C, with a lowest temperature of ~600 °C in the youngest zircon (Fig. 3B; grain 6, outer tip). Individual crystals record segments of the overall >150 m.y. growth history of the population.

#### Oxygen δ<sup>18</sup>O Transects Across Core-Rim Boundaries

Detailed multispot oxygen isotope analyses in several grains using a small, 7 µm beam diameter (e.g., grain 4; Fig. 3A) reveal sharp compositional discontinuities between detrital cores and metamorphic rims. For example, grain 4 displays core values of 5.9% (n = 7 spots), rim values of 8.8‰ (n = 14 spots), and intermediate  $\delta^{18}$ O values from ion microprobe pits that straddle the core-rim boundary observed in CL (Fig. 3C). This indicates that the width of any oxygen isotopic gradient between these two domains, which formed by volume diffusion, is  $\leq 7$  µm (i.e., the diameter of the ion beam pits). Note that the slightly higher  $\delta^{18}$ O at the center of the core comes from a domain that yields a premetamorphic <sup>207</sup>Pb/<sup>206</sup>Pb age of 2699 ± 28 Ma and is bounded by a CL zoning discontinuity.

# DISCUSSION

Our data indicate that the oxygen isotope gradient between the unrecrystallized zircon cores that make up ~90% of our sample population and their metamorphic rims exists at the micron scale, and that oxygen volume diffusion is very slow in metamorphosed zircon (Valley et al., 1994; Peck et al., 2003; Page et al., 2007). The majority of the high-quality zircons in our sample are highly retentive of age and oxygen isotope information and their isotopic zoning can be interpreted in terms of chemical and thermal change during the evolution of the sample and the surrounding lithosphere.

In the Kapuskasing uplift, zircon growth zoning tracks a primordial cycle of lithosphere genesis and local destruction that can be subdivided into four stages (Fig. 3D). Offboard genesis of the primitive crust of the Superior province during Stage I is represented by the detrital cores, the ages of which (2.87-2.67 Ga) overlap arc igneous rocks of the southern Superior province, whereas their planar growth zoning and mantle-like  $\delta^{18}$ O values (Fig. 2) indicate crystallization from juvenile magmas prior to and during the Kenoran orogeny. The provenance area was therefore a mixture of juvenile and slightly evolved crust consistent with regional evidence for primitive to slightly evolved sources for Superior province sediments (e.g., Longstaffe and Schwarcz, 1977). Higher  $\delta^{18}$ O values, to 7.0%, in the younger cores suggest increasing contribution of sediment recycling, as seen with Hf isotopes for detrital Superior province zircons (Davis et al., 2005) and <sup>18</sup>O/<sup>16</sup>O-enriched, late sanukitoid plutons (King et al., 1998). The minor <sup>18</sup>O/<sup>16</sup>O-enriched domain at the center of the igneous core of grain 4 (Fig. 3A) has a premetamorphic <sup>207</sup>Pb/<sup>206</sup>Pb age and is interpreted to be an inherited xenocryst from a previous, more evolved episode of arc magmatism.

Rapid exposure and erosion of arc-hosted zircon bearing rocks, transport and deposition of detrital zircons, and then burial to the lower crust occurred in Stage II, creating the chemical and isotopic unconformity separating the detrital cores from the metamorphic rims. The initial unconformity was created by mechanical erosion of the igneous crystals during uplift, transport, and sedimentation in arc-proximal sequences of interlayered wacke and conglomerate, resulting in some rounded tips and edges and locally truncated igneous CL zoning (e.g., Fig. DR1). The youngest detrital zircon age of 2671 ± 12 Ma is a maximum age of deposition, consistent with the previous estimate of sedimentation of  $2667 \pm 2$  Ma (Krogh, 1993). The mechanical unconformity was locally amplified by metamorphism that deepened reentrant surfaces on the already rounded grains (e.g., grain 6; Fig. 3B). This presumably occurred as the sediments were infolded with basement metabasalt of the present Borden Lake belt and underwent prograde metamorphism as they moved into the lower crust during the latest stages of orogeny and perhaps gravity-driven overturn of upper crust.

A lower age bracket of 2659 ± 8 Ma for arrival of Borden Lake metasediments in the lower crust, and the beginning of Stage III, is derived from the oldest nucleation of high-temperature <sup>18</sup>O/<sup>16</sup>O-enriched metamorphic zircon in equilibrium with the bulk rock. The precise mechanism of dark zircon formation is currently being investigated in more detail; however, the greater size and distinctive chemistry of the brown zircon rims, the absence of patchy subdomains of mineral phase and isotopic heterogeneity, the significant, concentric changes in U-Pb ages, oxygen isotope values, and trace elements (as seen in CL images) together indicate protracted radial growth of zircon rather than short-lived in situ recrystallization. Growth would have occurred intermittently around detrital cores for as much as ~80 m.y., during which apparent Ti-in-zircon temperatures vary between 706 °C and ~660 °C. The tectonic significance of Stage III growth events is least well understood, but is broadly seen as relating to coeval postorogenic heating, extension of crust, and the growth and/or periodic destabilization of its underlying mantle lithosphere root (e.g., Moser et al., 1996). Metamorphic growth events appear to have been most frequent ca. 2620 Ma, when temperatures were above 650 °C, and these events coincided with boudinage in the lower crust and crustal-scale fluid flow along brittle structural breaks at higher levels (Krogh, 1993).

The fourth and final stage marks the first evidence of rigid plate behavior and is manifest in a discontinuous growth domain at the tip of grain 6 (Fig. 3B) that is the youngest and coolest event so far detected, with a concordant age of  $2512 \pm 8$  Ma at apparent Ti temperature of 600 °C. This final, minor zircon growth episode is coeval with the initiation of lithosphere rifting and passive margin development 200 km to the south (the 2.5-2.3 Ga Huronian Supergroup). It is also coeval with the emplacement of the Matachewan radiating diabase dike swarm that extends throughout the southern half of the Superior province, but not below midcrustal depths in the Kapuskasing uplift cross section (Percival, 1983). Growth of lower crustal zircon at 2.51 Ga has also been detected in kimberlite xenoliths in the Abitibi subprovince and attributed to contact metamorphism of the lower crust due to subcrustal mafic intraplating during dike swarm emplacement (Moser and Heaman, 1997). The minor growth of ~600 °C zircon tips thus reflects the thermal perturbation of the deep crust caused by the igneous intraplate prior to final ≥2.43 Ga cooling (Hanes et al., 1994). Stage IV rifting signals the onset of behavior of the Superior lithosphere as a conventional, rigid continental plate.

# CONCLUSIONS

Our observations of the zircon 'run products' of a natural diffusion experiment in the lower crust demonstrate that extremely sluggish rates of volume diffusion of oxygen operate in unrecrystallized zircon during protracted regional high-grade metamorphism, and that remarkably complete microrecords of geodynamic events can be preserved. These findings amplify the already considerable power of zircon geochronology for reconstructing planetary evolution and, in our case, allow for more detailed exploration of the formation, evolution, and local destruction of Earth's primordial continental lithosphere.

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