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# Zircon U-Pb, Hf and O isotope constraints on growth versus reworking of continental crust in the subsurface Grenville orogen, Ohio, USA

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## Highlights

- Zircon U-Pb, O & Hf isotope data from six basement samples from Ohio are presented.
- Juvenile crust formation with a Hf- $t_{DM}$  of c. 1650 Ma is suggested.

- The possibility of a Mazatzal Province protolith is synthesized.
- Zircon recrystallisation in the presence of heavy  $\delta^{18}\text{O}$  fluids is argued for.
- Hydrothermal recrystallisation in Lu-Hf zircon host-rock equilibrium is debated.

## Abstract

Combined U-Pb, O and Hf isotope data in zircon allows discrimination between juvenile and reworked crust, and is therefore a useful tool for understanding formation and evolution of the continental crust. The crustal evolution of basement rocks in central North America (Laurentia) is poorly constrained, as it is almost entirely overlain by Palaeozoic cover. In order to improve our understanding of the evolution of this region we present U-Pb, O and Hf isotope data from zircon in drill-core samples from the subsurface basement of Ohio. The Hf isotope data suggests juvenile crust formation at  $\sim 1650$  Ma followed by continued reworking of a single reservoir. This 1650 Ma reservoir was tapped at  $\sim 1450$  Ma during the formation of the Granite-Rhyolite Province and subsequently reworked again during the Grenvillian orogeny. The  $\sim 1650$  Ma crust formation model age for the suite of samples along with the presence of  $\sim 1650$  Ma magmatic rocks suggests an eastward extension of the Mazatzal Province (or Mazatzal-like crust) and makes it a possible protolith to the subsurface basement of Ohio and surrounding Mesoproterozoic (i.e. Grenville-age) rocks. The eastward extension of this  $\sim 1650$  Ma crustal reservoir into Ohio requires a revision of the crustal boundary defined by Nd isotopic data to be located further east, now overlapping with the Grenville front magnetic lineament in Ohio. In fact, the easternmost sample in this study is derived from a more depleted reservoir. This limits the extent of  $>1.5$  Ga basement in subsurface Ohio and constrains the location of the crustal boundary. Further, syn-orogenic magmatism at  $\sim 1050$  Ma suggests a potential extrapolation of the Interior Magmatic Belt into Ohio. Oxygen isotopic data in zircon suggests that during Grenvillian metamorphism, zircon recrystallisation occurred in the presence of heavy  $\delta^{18}\text{O}$  fluids resulting in zircon with elevated  $\delta^{18}\text{O}$  values.

## Keywords

Grenville; crustal growth; U-Pb; oxygen; Lu-Hf

## 1 Introduction

The Precambrian covers nearly 90% of Earth's history, yet only 6% of the Earth's surface outcrops are Precambrian basement rocks (Goodwin, 1996). This makes geological interpretation and modelling of the Precambrian evolution difficult and hampers our understanding of the large-scale crustal evolution of continents. For example, the Grenville Province in North America is one of the most studied Precambrian orogens on Earth. It is, however, poorly known in its entirety since it only crops out in limited areas south of Canada; the Adirondack Mountains (Daly & McLelland, 1991), the Llano Uplift (Mosher et al., 1998), the Franklin and Van Horn Mountains (Bickford et al. 2000) and the Sierra del Cuervo (Fig. 1, Rivers et al., 2012). Inliers of Grenvillian lithotectonic units also occur in the southern and central Appalachian orogen (Sinha et al., 1996; Hatcher et al., 2004). Current knowledge about the orogen is largely based on data from the Canadian Shield and our understanding of the vast unexposed subsurface Grenville Province is based on geophysical surveys and few basement penetrating deep drill cores (e.g. Rivers et al., 2012). Recent work on the evolution of rocks affected by Grenvillian orogenesis in the mid-continent have focused on zircon U-Pb and Sm-Nd analyses on the few available exposed outcrops (i.e. Daly & McLelland 1991; McLelland et al., 1993; Van Schmus et al., 1996; Rohs & Van Schmus, 2007; Fisher et al., 2010; Fig. 1).

The term Grenville is commonly used for both the Grenville orogenic province in North America and for a time-period connected to a global event of coeval orogenesis during which Rodinia was assembled (Cawood et al., 2007). Here, we follow the nomenclature of Rivers (2008), and the term Grenville only refers to the orogenic province. The Grenville Province in North America is mainly exposed in eastern Canada from the Labradorian coast, southwest to the Great Lakes where it is covered by Phanerozoic rocks in the east central U.S. (Fig. 1).

To assess the extent and crustal characteristics of Grenvillian rocks in the subsurface of the central US, we present new *in situ* zircon U-Pb, Lu-Hf, and O isotope data for six deep drill core samples that were selected due to their proximity to the proposed western extent of the Grenvillian orogen (i.e. the Grenville front magnetic lineament), in Ohio, USA. In order to understand the evolution of the Grenville in North America it is necessary to establish the pre-Grenvillian crustal components of Laurentia. We explore the involvement of juvenile versus reworked Paleoproterozoic continental crust, and present a tentative model for the isotopic geochemical evolution of basement crust in Ohio, and its implications for the general evolution of the Grenville orogen.

## 2 Geological setting

The Grenville Province consists of a number of orogenic thrust stacks along the present-day eastern margin of North America and formed during the Mesoproterozoic in a continent-continent collisional orogenic system superimposed on an accretionary orogenic system (Tollo et al., 2004; Rivers et al., 2012). Worldwide, Grenvillian-age orogenic provinces are found on a number of continents including Amazonia, Baltica, Australia and Antarctica and are all related to the assembly of Rodinia (e.g. Li et al. 2008). Recent work has suggested that the southern and central portion of Grenville in eastern Laurentia was accreted when the proto-North-American plate collided with another continent at the Laurentian margin (e.g. Loewy et al., 2003; Fisher et al. 2010). Key elements of pre-Grenvillian basement are summarised below (Fig. 1).

### 2.1 Penokean Province (1.9 to 1.8 Ga)

During middle Palaeoproterozoic, igneous and metasedimentary rocks formed the Penokean Province through oceanic arcs (Pembine-Wausau terrane), microcontinent accretion (Marshfield terrane), and subsequent deformation of both the associated Archaean basement and Palaeoproterozoic supracrustal rocks of the adjacent Superior craton. The Penokean Province extends from central Minnesota eastward to Ontario, Canada where it pinches out at the Grenville Front in Ontario (Davidson, 1995;

Holm, 1999). Whole-rock Nd model ages of the Penokean belt are quite uniform at about 2.1 Ga (Barovich et al., 1989; Holm et al., 2005) and Hf model ages of A-type granites intruding the Penokean Province range from 2.2–2.1 Ga (Goodge & Vervoort, 2006).

## 2.2 Ga Yavapai Province (1.8 to 1.7)

Juvenile crust assembly in volcanic arcs between 1.8–1.7 Ga were subsequently accreted along the southeastern margin of Laurentia forming the Yavapai Province, which currently extends from Arizona to the mid-continent (Karlstrom & Humphreys, 1998; Van Schmus et al., 2007; Whitmeyer & Karlstrom, 2007). Whole-rock Nd model ages for the Yavapai Province range between 2.0–1.8 Ga (DePaolo, 1981). Numerous granitoids intruded the Penokean and Yavapai provinces between 1.72–1.68 Ga.

## 2.3 Mazatzal Province (1.7 to 1.6 Ga)

The 1.7–1.6 Ga Mazatzal Province contains juvenile crust that formed in continental arcs and back-arcs (Shaw & Karlstrom, 1999) and whole-rock Nd isotopic data yield depleted mantle model ages of 1.8–1.7 Ga (Bennett & DePaolo, 1987; Wooden & DeWitt, 1991; Aleinikoff et al., 1993). The Mazatzal Province is adjacent to the Yavapai Province and extends from the southwestern U.S.A. through the mid-continent to the related Labradorian orogen in Canada (Whitmeyer & Karlstrom, 2007).

## 2.4 Granite-Rhyolite Province (1.5 to 1.3 Ga)

During early to middle Mesoproterozoic (ca. 1.55–1.35 Ga) the Granite Rhyolite Province formed through anatectic melting and addition of juvenile melts to the southern margin of Laurentia (Van Schmus et al., 1996). Van Schmus et al. (1996) outlined a crustal boundary across the mid-continent extending from Mexico to Ontario. It separates Nd- $t_{DM}$  > 1.5 Ga crust from Nd- $t_{DM}$  < 1.5 Ga crust, which suggests a possible crustal boundary between >1.5 Ga Laurentia and juvenile crust accreting onto the southeastern margin of the Mazatzal Province (Laurentia). The Granite-Rhyolite Province and Palaeoproterozoic crust farther west were intruded by A-type granites between 1.48 Ga and 1.35 Ga

(Van Schmus et al., 1996). The older components within the Granite-Rhyolite Province have been correlated to parts of the Central Gneiss Belt in Canada (Easton, 1986; Slagstad et al., 2004; Slagstad et al., 2009). Based on their bulk geochemical composition, these rocks are regularly labelled A-type despite increasing evidence of an orogenic origin (Karlstrom et al., 2001). They have been linked to the final stages of assembly and subsequent break-up of a ca. 1.5 Ga supercontinent (Windley, 1993). The supercontinent break-up initiated the opening of a Grenvillian-age ocean and was succeeded by an early oceanic closure linked to the first stages of the assembly of the supercontinent Rodinia (Cawood et al., 2007).

## 2.5 Rocks of the subsurface Grenville orogen in the mid-continent

Early attempts to date the magmatic and metamorphic evolution of the southern extension of the Grenville Province in Ohio proved difficult. Geochronology on metamorphic and/or severely altered/weathered drill core samples predominantly indicated cooling and/or mixed ages of unclear geological significance. For example, whole-rock Rb-Sr dates range from ca. 600 to ca. 1300 Ma that probably represent resetting of the Rb-Sr system by thermal or geochemical events (Vargo, 1972; Faure and Barbis, 1983; Mensing and Faure, 1983; Lucius and von Frese, 1988). More recent work on the evolution of exposed Grenvillian aged rocks have focused on zircon U-Pb and whole-rock Sm-Nd analyses (i.e. Daly & McLelland 1991; McLelland et al., 1993; Van Schmus et al., 1996; Rohs & Van Schmus, 2007; Fisher et al., 2010). The Adirondacks have Nd-model ages between 1.55 and 1.0 Ga (the majority between 1.4 and 1.3 Ga; Daly & McLelland 1991; McLelland et al., 1993; Fisher et al., 2010). The Llano Uplift and the Franklin- and Van Horn Mountains yield zircon U-Pb ages between 1.28 and 1.07 Ga and corresponding Nd model ages from 1.44 to 1.11 Ga (Van Schmus et al., 1996; Fisher et al., 2010, and refs. therein). The Central Appalachian basement hosting allochthonous Grenville inliers give Nd model ages that range from 1.52 to 1.25 Ga (Pettingill et al., 1984; Owens & Samson, 2004). The Nd model ages of southern Appalachian granites range from 1.75 to 1.34 Ga (Fullagar et al., 1997; Carrigan et al., 2003; Ownby et al., 2004; Berquist 2005), except for the Roan Mountain (Fisher et al., 2010 and refs. therein) that give igneous crystallization ages between 1.3 and 1.2 Ga (Carrigan et al., 2003; Ownby et al., 2004). Nd model ages of Roan Mountain range from 2.32



to 1.65 Ga (Carrigan et al., 2003; Ownby et al., 2004), but Alenikoff et al. (2103) showed that the Carvers Gap granulite from the Roan Mountains is not of igneous origin but rather a 1.0 Ga metasedimentary rock probably derived from 1.8 Ga Amazonian crust. Overall, Grenvillian crustal blocks exposed in the eastern and southern parts of Laurentia yield Nd model ages with a peak between 1.5 to 1.3 Ga (Owens & Samson, 2004).

In the Granite-Rhyolite Province, the Nd isotope signatures are thought to reflect juvenile magmatism in the eastern portion and increasing influx of Paleoproterozoic crust towards the west (Van Schmus et al., 1996). These Nd signatures were used to delineate a boundary between  $>1.55$  Ga Nd- $t_{DM}$  and  $<1.55$  Ga Nd- $t_{DM}$  basement rocks (Fig. 1; Van Schmus et al., 1996; Fisher et al., 2010). The southern and central Appalachian basement overlaps the Granite-Rhyolite Province with respect to Nd, but the southern and central Appalachian basement is unique from the Llano Uplift, Adirondack and Granite-Rhyolite Province as it has a higher  $^{207}\text{Pb}/^{204}\text{Pb}$  ratio for a given  $^{206}\text{Pb}/^{204}\text{Pb}$  ratio, suggesting a more ancient crust in the southern and central Appalachian basement (Fisher, et al., 2010). This was taken as evidence that the southern and central Appalachian basement was not derived from the Granite-Rhyolite Province and is thought to be exotic to pre-Grenvillian Laurentia.

## 2.6 Precambrian geology of Ohio

The Precambrian basement complex in Ohio consists of three known geologic provinces: the Grenville Province in eastern Ohio and the Granite-Rhyolite Province and East Continent Rift Basin in western Ohio (Fig. 2A). The Precambrian basement complex is overlain by approximately 800 to 4300 m of Phanerozoic sedimentary rocks and glacial deposits. The term Grenville front is used to separate the Grenville Province to the east from the Granite-Rhyolite Province to the west (Bass, 1960). This interpretation is based on sparse deep-wells and regional magnetic and gravity data in an attempt to extrapolate the outcropping Grenville Front in Ontario, Canada into the subsurface of Ohio (Fig. 2B). Baranoski et al. (2009) proposed the use of the term Grenville front magnetic lineament due to the absence of published drill-core data from subsurface Ohio and a lack of a direct correlation to its

Canadian counterpart at the surface. Baranoski et al. (2009) show an interpretation that the Grenville Province in Ohio is partially allochthonous west of the Grenville front magnetic lineament.

### 3 Methods

Zircon separates were obtained by using heavy liquids except for the samples from the Scioto drill core that contained enough rock to use a Wilfley shaking table. Magnetic minerals were removed using a hand magnet. Zircon grains of different size and shape were hand-picked from the heavy mineral separates, selecting both euhedral, subhedral and anhedral grains. The crystals were mounted on tape together with the zircon standard 91500 (Wiedenbeck et al., 2004) and cast into epoxy. After hardening, the epoxy mount was polished to expose a cross section through the grains. Back-scattered electron imaging (BSE) was used to investigate internal growth patterns in the individual crystals, and for guidance of analytical work, using a standard Hitachi S-4300N electron microscope at the Department of Geology, Lunds University. Thin sections were cut from each core and all samples were examined both macroscopically in small pieces of hand sample and microscopically in thin sections.

#### 3.1 Zircon U-Pb dating

Secondary ion mass spectrometer (SIMS) U-Th-Pb analyses were carried out using a large geometry Cameca IMS1280 instrument at the Swedish Museum of Natural History. Instrument set up broadly follows that described by Whitehouse et al. (1999), Whitehouse and Kamber (2005) and references therein. An  $O_2^-$  primary beam with 23 kV incident energy (-13kV primary, +10 kV secondary) was used for sputtering. For this study, the primary beam was operated in aperture illumination (Köhler) mode yielding a ca. 15-20  $\mu m$  spot. Presputtering with a 25  $\mu m$  raster for 120 seconds, centering of the secondary ion beam in the 3000  $\mu m$  field aperture, mass calibration optimisation, and optimisation of the secondary beam energy distribution were performed automatically for each run, Field aperture and energy adjustment with the  $^{90}Zr_2^{16}O^+$  species at nominal mass 196 was used. Mass calibration of all

peaks in the mono-collection sequence was performed at the start of each session; within run mass calibration optimisation scanned only the zircon matrix peak, namely  $^{90}\text{Zr}_2^{16}\text{O}^+$ . A mass resolution ( $M/\Delta M$ ) of ca. 5400 was used to ensure adequate separation of Pb isotope peaks from nearby  $\text{HfSi}^+$  species. Secondary ion signals were detected using the axial ion-counting electron multiplier. All analyses were run in fully automated chain sequences.

Data reduction assumes a power law relationship between  $\text{Pb}^+/\text{U}^+$  and  $\text{UO}_2^+/\text{U}^+$  ratios with an empirically derived slope in order to calculate actual Pb/U ratios based on those in the 91500 standard. U concentrations and Th/U ratio are also referenced to the 91500 standard. Common Pb corrections are made only when  $^{204}\text{Pb}$  counts statistically exceed average background and assume a  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of 0.83 [equivalent to present day Stacey and Kramers (1975) model terrestrial Pb]. Decay constants follow the recommendations of Steiger and Jäger (1977) and decay constant errors are ignored. All age calculations were done in Isoplot 3.70 (Ludwig, 2008) and results are presented in supplementary table A.1.

### 3.2 Zircon O-isotope analyses

The zircon mount was repolished before oxygen isotope analysis to eliminate U-Pb craters, followed by gold (Au) coating. Oxygen isotopes were measured at the same spot sites as for U-Pb using a Cameca IMS1280 multicollector ion microprobe at the Swedish Museum of Natural History. The instrument setup and analytical procedures were similar to those of Whitehouse and Nemchin (2009), using a ca. 2 nA  $\text{Cs}^+$  primary ion beam together with a normal incidence low energy electron gun for charge compensation, medium field magnification (ca. 80x) and two Faraday detectors (channels L'2 and H'2) at a common mass resolution of ca. 2500. Measurements were performed in pre-programmed chain analysis mode with automatic field aperture and entrance slit centring on the  $^{16}\text{O}$  signal. The magnetic field was locked using nuclear magnetic resonance (NMR) regulation for the entire analytical session. Each data-acquisition run comprised a 20 x 20  $\mu\text{m}$  pre-sputter to remove the Au layer followed by the centering steps and 64 seconds of data integration performed using a non-

rastered, ca., 10 x 10  $\mu\text{m}$  spot. Field aperture centering values reported in supplementary table A.2 are well within those for which no bias has been observed during tests on standard mounts (Whitehouse and Nemchin, 2009). A total of 80 unknowns (20/sample) were measured during one analysis session. In the measurement chain, every set of four unknowns was followed by two bracketing analyses on the Geostandards 91500 zircon. A  $\delta^{18}\text{O}$  value of +9.86‰ (SMOW, Wiedenbeck et al., 2004) was assumed for the 91500 zircon in data normalisation. Small linear-drift corrections were applied to each session. Results and standards are presented in supplementary table A.2. Standard results compared to reference value +9.86‰ are shown in supplementary figure A.1. Long term external reproducibility is 0.30 ( $\pm 1\sigma$ ).

### 3.3 Zircon Hf-isotope analyses

Following U-Pb and O isotope work, Hf-analyses were done in situ at the Memorial University, St Johns, Newfoundland, Canada, using a ThermoScientific Neptune Multicollector (MC) ICP-MS connected to a GeoLas Laser ablation system. The MC-LA-ICP-MS cup configuration and operational parameters are summarized in Fisher et al., (2011). Laser repetition rate of 10 Hz was applied and laser flux was maintained at 5 J/cm<sup>2</sup>. Ablation was conducted with He carrier gas in the ablation cell and with Ar makeup carrier gas added afterwards via T-piece just before the torch. The gas background was measured for 30 s in the beginning of each run and used for blank corrections. Blank corrected signal intensities were corrected for isobaric interferences of Yb and Lu on <sup>176</sup>Hf.  $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$  (Patchett & Tatsumoto, 1980) and the exponential law were used for mass bias correction of Hf.  $^{173}\text{Yb}/^{171}\text{Yb} = 1.1301$  and  $^{176}\text{Yb}/^{171}\text{Yb} = 0.7938$  (Segal et al., 2003) and the exponential law were used for mass bias correction of Yb. No invariant ratio for Lu is available as Lu only has two naturally occurring isotopes (<sup>175</sup>Lu and <sup>176</sup>Lu). Therefore it was assumed that the mass bias for Lu is equal to that of Yb, and a  $^{176}\text{Lu}/^{175}\text{Lu} = 0.2656$  was used to determine the magnitude of the <sup>176</sup>Lu interference (Chu et al., 2002).

Zircon phases dated by U-Pb analyses were also used for Hf-analysis. Some extra spots, in other

grains, were added. A spot size between 49 and 69  $\mu\text{m}$  was used as close to U-Pb craters as possible. Cracks, inclusions and texturally complex BSE zones were avoided as much as possible. Four zircon reference samples were used for data quality control, Plesovice (Sláma et al., 2008), R-33 (Black et al., 2004), FC-1 and Temora (Woodhead and Hergt, 2005; Fisher et al. 2011) yielded  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282508 \pm 0.000038$  (2SD, n=10),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282753 \pm 0.000071$  (2SD, n=15),  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282181 \pm 0.000064$  (2SD, n=17) and  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.282662 \pm 0.000047$  (2SD, n=9) respectively. These ratios are within the range to slightly outside the available published solution mode data (Sláma et al., 2008) of Plesovice =  $0.282482 \pm 0.000013$ ; (Woodhead & Hergt 2005; Fisher et al. 2011) of FC-1 =  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.282184 \pm 0.000016$  and (Woodhead & Hergt 2005) of Temora =  $^{176}\text{Hf}/^{177}\text{Hf}$  of  $0.282686 \pm 0.000024$ . R-33 has the greatest variance ( $^{176}\text{Hf}/^{177}\text{Hf}$  of  $\pm 0.000071$ ) of the measured reference materials and was used in uncertainty propagation when external (standard) errors > individual sample data-point error. Secondary standard analyses are shown in Supplementary figure A.2.

The depleted mantle model of Griffin et al. (2002) was used, assuming a present day  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$  and  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$ . The  $^{176}\text{Lu}$  decay constant of Scherer et al. (2001) and Söderlund et al. (2004) were used in all calculations and results are presented in supplementary table A.3. Values for chondritic uniform reservoir (CHUR) are from Bouvier et al., (2008).

## 4 Samples and analytical results

Eight samples from six different drill cores that penetrate the Precambrian basement of Ohio were analysed. Five of the cores drilled into the subsurface continuation of the Grenville Province. One core in Logan County drilled into the presumed unmetamorphosed foreland, west of the Grenville front. Drill core specifications are listed in table 1.

The U-Th-Pb, O and Hf data are listed in supplementary tables A.1, A.2 and A.3 respectively. Zircon images are shown in figure 3. Extended petrographic sample descriptions are found in supplementary

material. Petrographic images of macroscopic samples and photomicrographs are shown in supplementary figure A.3. Tera-Wasserburg plots are shown in figure 4. Core drill sites are shown in figure 2A. Uncertainties are presented at the  $2\sigma$ -level. Decay constant errors are ignored.

#### 4.1 Rhyolite, west of the Grenville front (Logan County)

The core sampled is a felsic aphanitic rock with small anhedral phenocrysts of varying mineralogy. Quartz is the dominant mineral with prominent silt sized grains. Altered subhedral K-feldspar phenocrysts up to 5 mm are also present. Fine-grained opaque phases occur both in the aphanitic matrix and as inclusions in chlorite, biotite and feldspars. Thin bands of mica with kinematic indicators such as  $\delta$ - and  $\sigma$  structures resembling flow-structures occur around phenocrysts. Small cracks within the rock are filled with mica and quartz. Based on its location west of the Grenville front magnetic lineament (Fig. 2) and the lack of higher-grade metamorphic recrystallization (coarsening) of the very fine-grained matrix it is assumed to be affiliated with unmetamorphosed rocks of the Granite Rhyolite Province in the Grenville orogen foreland (cf. Baranoski et al. 2009). Zircon grains occur as texturally simple, perfectly euhedral and transparent crystals, with no morphological signs of secondary alteration or growth after igneous crystallization (Fig. 3). The zircon grains are oscillatory zoned in BSE images (Fig. 3). Minor inclusions of apatite, feldspars and/or pyrite are found in most zircon grains.

Eight concordant analyses in oscillatory-zoned texturally simple zircon grains define a concordia age of  $1471 \pm 3$  Ma (MSWD + equivalence=1.1; Fig. 4A), which we interpret as the igneous crystallisation age. U and Th/U range between 141–363 ppm and 0.11–0.22 respectively.  $\delta^{18}\text{O}$  from ten spots range from 8.1–11.8‰. Eight spots were measured for Hf-isotope compositions and yield  $\epsilon\text{Hf}_{1471 \text{ Ma}}$  8.2–10.4 (n=8) and a weighted mean of  $9.0 \pm 0.9$  (MSWD=0.4). There is no correlation between  $\delta^{18}\text{O}$  and  $\epsilon\text{Hf}$ .

## 4.2 Grenville Province

### 4.2.1 Deformed pegmatite (Fayette County)

The sample selected is a pinkish meta-pegmatite from a sequence of impure marble intercalated with hornblende amphibolite. The sample contains feldspar (predominantly plagioclase), quartz, muscovite, garnet and apatite. Muscovite is well developed along with plagioclase, defining a tectonic fabric. Muscovite and feldspars are often surrounded by dynamically recrystallised quartz. Six zircon grains were retrieved from the sample, but only three of these were successfully recovered for final analyses. Texturally they are all simple, with slight or no signs of secondary alteration growth or inclusions (Fig. 3).

Only three grains were recovered from the sample and the reliability of these grains is uncertain. Five analyses yielded a U and Th/U range between 51-87 ppm and 0.56-0.63, respectively. Texturally identical domains spread along concordia between ca. 1580-1680 Ma (Fig. 4B). Analyses 3a and 3b from the same grain and textural domain yield dates of  $1577 \pm 25$  Ma and  $1676 \pm 23$  Ma respectively. The cause of the data spread is unclear, but is probably due to ancient Pb-loss during a metamorphic event in which case the older date represents the minimum igneous age. The weighted mean  $^{207}\text{Pb}/^{206}\text{Pb}$  age is  $1643 \pm 54$  Ma (MSWD=3.5; Fig. 4B), and the excess spread is due to the probable ancient Pb-loss. The two oldest and concordant data points yield a concordia age of  $1671 \pm 17$  Ma, but such data filtering seems unjustified at this stage. The  $^{207}\text{Pb}/^{206}\text{Pb}$  weighted mean yield an age of  $1643 \pm 54$  Ma, but lack statistical validity. Nevertheless, the data suggest a minimum age of 1.57 Ga, although an older igneous crystallisation age is likely. One of the two successful Hf-data points came from the same location as the oldest and concordant U-Pb spot at 1681 Ma, while the other overlap two concordant, but contrasting, U-Pb spots (1577 and 1676 Ma) from a homogenous zircon domain (Fig. 3). Ascribing a crystallisation age for this sample is non-trivial but for simplicity, 1643 Ma is used in the  $\epsilon\text{Hf}_t$  calculations.  $\delta^{18}\text{O}$  range from 4.6–6.0‰ with a weighted mean of  $5.4 \pm 0.7\%$  (MSWD=1.8).

Hf-isotope compositions for three spots only yielded useful data in two spots (Fig. 3) with  $\epsilon\text{Hf}_{1643 \text{ Ma}} = 2.5 \pm 1.5$  and  $5.7 \pm 2.2$  respectively.

#### 4.2.2 Isotropic granite (Morrow County)

The sample is a coarse-grained isotropic dark red granite. Feldspars (both microcline and plagioclase) and quartz are the dominant minerals. Plagioclase is variably altered, especially the larger grains. Biotite and muscovite are present. Biotite grains are sub- to anhedral and show signs of alteration. Apatite occurs mostly as inclusions in feldspar. Oxides are present in small cracks and around most of the euhedral zircon grains. Other accessory minerals are chlorite and epidote.

Three distinct zircon domains are recognized. The texturally oldest domain is dark, often cracked, and shows oscillatory zoning. It is partially or entirely replaced by a BSE-bright unzoned secondary domain. The third and texturally youngest phase occurs as BSE-dark unzoned discordant  $<10\mu\text{m}$  wide envelopes around most grains. These were too thin for analyses. The grains are similar to those from the Scioto core rocks (4.2.5 below), both in size, morphology and internal textural characteristics (Fig. 3).

Twenty-eight U-Pb analyses from the two oldest domains form two concordant clusters that correlate with the textural context. Zoned core analyses cluster at ca. 1450 Ma and the secondary domain at 1030 Ma (Fig. 4C). U and Th/U range between 272–1417 ppm and 0.27–0.44 respectively in the oldest domain, and between 1019–6080 ppm and 0.03–0.37 respectively in the secondary domain. Three analyses overlap the concordia with intermediate dates between the two main clusters. Four imprecise data are weakly discordant or just overlapping the concordia at ca. 0.9 Ga. Fourteen concordant data points of the oldest domain with U  $\sim 500$  ppm and Th/U  $\sim 0.3$  yield a  $^{207}\text{Pb}/^{206}\text{Pb}$  weighted mean age of  $1451 \pm 10$  Ma (MSWD = 4.6; Fig. 4D). They scatter along the concordia with insufficient equivalence for calculating a concordia age, thus the weighted mean  $^{207}\text{Pb}/^{206}\text{Pb}$ -date is assumed to be the best estimate of the crystallisation age. Four concordant analyses from the secondary domain yield a concordia age of  $1029 \pm 6$  Ma (MSWD + equivalence=1.8; Fig. 4E), which is interpreted as the age of zircon recrystallization due to dissolution-reprecipitation processes, possibly a catalytic agent by



partial melting of the host-rock. This resulted in increasing U=1141–2001 ppm and lower Th/U=0.031–0.23 in the secondary domain. Spot 12b is concordant with a  $^{207}\text{Pb}/^{206}\text{Pb}$  1188  $\pm$  24 Ma date, and might either be a mixture of domains or represent incomplete Pb-loss during recrystallisation.

$\delta^{18}\text{O}$  for 15 spots in the oldest domain range between 6.3 and 8.0‰ including two spots that are <1% discordant.  $\delta^{18}\text{O}$  for three of the four concordant spots in the secondary domain range between 7.1–7.4‰ with a weighted mean of 7.3  $\pm$  0.4‰ (MSWD=0.24).

The oldest domain range yield  $\epsilon\text{Hf}_{1451\text{ Ma}}$  6.9–9.9 and a weighted mean of 8.5  $\pm$  0.8 (MSWD=0.54; n=9).  $\epsilon\text{Hf}_{1029\text{ Ma}}$  for the secondary domain range from -2.9–3.7 and yield a weighted mean of 2.9  $\pm$  0.9 (MSWD=0.19; n=8/9).

#### 4.2.3 Dark fine-grained mafic schist (Lake County)

This sample is a fine-grained dark grey mafic schist. Minerals are anhedral and consist of plagioclase (commonly sericitised), chlorite, actinolite, biotite and opaque phases. Accessory minerals are calcite (in fractures), zircon, muscovite and epidote and an abundance of apatite needles. The rock is silica-undersaturated with no quartz and has probably experienced low greenschist facies metamorphism.

The zircon population contains grains characterised by BSE-bright weakly and irregularly zoned zircon interpreted as primary igneous zircon, sometimes with thin rims (<10  $\mu\text{m}$ ) of a secondary zircon domain (Fig. 3). The secondary zircon domain was not analysed.

Thirteen spots in the primary domain have U between 91–433 ppm and Th/U between 0.29–0.61 respectively. One spot, n3421-08a with high common Pb ( $^{206}\text{Pb}/^{204}\text{Pb} = 176$ ) was discarded. The remaining twelve spots yield a concordia age of 1231  $\pm$  21 Ma (MSWD + equivalence=1.9) and a weighted average  $^{207}\text{Pb}/^{206}\text{Pb}$  age of 1228  $\pm$  10 Ma (MSWD=1.7; Fig. 4F), which are interpreted as the igneous crystallisation age. The  $\delta^{18}\text{O}$  for seventeen spots range from 6.05‰–7.49‰ with a weighted mean of 6.6  $\pm$  0.2‰ (MSWD=1.2).

The primary domain has  $\epsilon\text{Hf}_{1228 \text{ Ma}}$  that range from 5.7–11 and yield a weighted mean of  $7.9 \pm 1.1$  (MSWD=2.0; n=12/12).

#### 4.2.4 Altered and deformed meta-granitic rock (Erie County)

The sample is a relict medium-to coarse-grained foliated quartz-feldspar granite. The rock consists of a fine grained alteration matrix, pervasively altered feldspars, quartz, opaque phases, chlorite and minor amounts of fresh feldspar. Accessory minerals include muscovite, zircon, apatite and epidote.

Remnants of relict BSE-dark cores are present in some zircon grains (e.g. grain 5 in Fig. 3). In most grains, however, these cores are absent. A secondary domain of BSE-bright zircon (replacements) either dominate the entire crystal section, or occur as discordant mantles around texturally older cores (e.g. grain 8 in Fig. 3). A third domain occurs as thin (<10  $\mu\text{m}$  wide) BSE-dark discordant rims around the secondary domain.

Cores were not analysed due to their metamict appearance. In the secondary zircon domain, U and Th/U range between 416–1577 ppm and 0.11–0.22 respectively and yield normal and reverse discordant data with a weighted mean  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $1050 \pm 6 \text{ Ma}$  (MSWD=0.7; Fig. 4G). The date is interpreted to represent zircon re-crystallisation during the Grenville orogeny.

$\delta^{18}\text{O}$  in 20 spots from the secondary domain range between 6.79‰–9.42‰, and  $\epsilon\text{Hf}_{1050 \text{ Ma}}$  range between -0.4–4.7 with a weighted mean of  $2.0 \pm 1.1$  (MSWD=1.8; n=11).

#### 4.2.5 Transition from veined banded orthogneiss to undeformed isotropic red granite (Scioto County)

This drill core covers a 6 metre rock sequence with a transition from non-veined, coarse-grained meta-intrusion that grades downward into a compositionally banded orthogneiss with an increasing amount of deep red near-isotropic coarse-to medium-grained granitic vein material. The lowermost 0.6 metres of the core is dominated by the coarse-to medium-grained deep red isotropic granitic material similar in appearance to the veins in the upper portion of the core. The transition between non-veined compositionally banded gneiss and near-isotropic red granitic material takes place over a distance of about 0.3 m. The granitic material appears intermingled with the gneissic banding along the contact. The compositional banding, the gneissic foliation and the veined banding are at low angle to the length-axis of the core, which significantly accentuates the extent of the individual lithologies in the core.

Three samples were taken from this core in a ca. 1 m thick transition zone (sub-parallel with the core): a banded gneiss (sample 6A), a banded gneiss with veins of isotropic red granite (6B), and isotropic granite (6C). The red isotropic granite is similar in appearance to the granite sampled further to the northwest (see 4.2.2, granite in Morrow County).

Sample 6A is a medium- to coarse-grained banded gneiss of intermediate composition. The gneissic banding is defined by alternating felsic (plagioclase-rich) and mafic (biotite-hornblende-rich) layers. The sample contains feldspar, quartz, hornblende, biotite and opaque phases. Accessory minerals are apatite, chlorite, sphene, zircon, calcite, epidote and muscovite. Biotite and hornblende define a tectonic fabric. K-feldspar is perthitic and about ten percent of the plagioclase is sericitised.

Myrmekite intergrowths are also present. The microscopic texture is overall typically granoblastic indicating widespread static recrystallisation after ductile deformation. Biotite is partially replaced by chlorite. Sample 6B is from the veined boundary between orthogneiss and isotropic granite. It is medium-to coarse grained compositionally banded veined gneiss with red non-strained granitic veins composed of feldspars, hornblende, quartz and biotite. The accessory minerals are mainly opaque

phases, apatite, zircon, sphene, muscovite, epidote and various iron oxides. Sample 6C is a medium- to coarse-grained red near-isotropic to isotropic granite. It contains feldspar, quartz, hornblende and biotite. Accessory minerals include opaque phases, apatite, sphene, zircon, epidote and muscovite. The amount of perthitic feldspar increases, and sericitisation and saussuritisation decrease from 6A to 6C. Myrmekite intergrowth is present in all samples but not abundant.

The zircon populations in the three different samples are texturally identical and the zircon characteristics of the samples are described together. All grains are nearly transparent with a slight to distinct red to orange colour, mostly on the surface and around cracks. The majority of the grains are cracked. Three distinct textural domains are recognised in BSE images: (1) a dark, texturally old inner core, sometimes showing igneous oscillatory zoning; (2) The cores have been partially or entirely replaced by BSE-bright unzoned domains. Inclusions of quartz, pyrite, apatite, biotite and feldspars are present in most of the BSE bright domains; (3) The third and texturally youngest phase occurs as a BSE-dark unzoned euhedral discordant phase. The third phase has been dated in Scioto 6A and 6C to  $982 \pm 9$  Ma (MSWD+equivalence=1.9; Fig 4J) and  $959 \pm 15$  Ma (MSWD+equivalence=0.8; Fig 4K), respectively, and is interpreted to represent a third event of zircon growth spatially associated with granitic vein material in the core samples. This domain is too thin for Hf-isotope analyses and is not considered any further in this paper.

Overall, 34 spots from 32 grains in the two oldest zircon domains from all three samples were analysed. U concentrations vary between 17–5066 ppm. Twenty of the dated grains are discordant, 17 spots are 5.7–34% normal discordant and 3 are 0.9–2.3% reverse discordant (Fig. 4H). With one exception, grains with over 2200 ppm U are discordant. The data fall along a discordia with an upper intercept of  $1012 \pm 21$  Ma (MSWD = 5). All but three of the concordant data spots are from sample 6B (Fig. 4I; Table A.1). Many of the analyses from BSE-bright non-zoned domains are associated with large  $^{207}\text{Pb}/^{206}\text{Pb}$  analytical uncertainties and large fractions of common Pb ( $^{206}\text{Pb}/^{204}\text{Pb} < 350$ ; Table A.1). Only one spot in the texturally oldest domain of a grain from 6B (n3428-05a; Table A.1) is concordant. This grain yields a  $^{207}\text{Pb}/^{206}\text{Pb}$  date of  $1404 \pm 17$  Ma. Ten concordant spots from the non-zoned BSE-bright second generation are not sufficiently equivalent for the calculation of a concordia

age, but yield a weighted average  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $1022 \pm 7$  Ma (MSWD = 2; Fig. 4I). This age is interpreted to represent the timing for crystallisation of secondary zircon during the Grenvillian orogeny.

Thirty-eight  $\delta^{18}\text{O}$  analyses of mainly non-zoned BSE-bright second generation zircon grains range from 8.2–14.8‰. Spots associated with these are discordant U/Pb and also have the highest and lowest  $\delta^{18}\text{O}$ . Excluding O isotope values associated with discordant U/Pb spots reduces the range to between 9.6‰ and 12.2‰ for 28 spots. Twenty-one grains were analysed for Hf-isotope composition.  $\epsilon\text{Hf}_{1022 \text{ Ma}}$  (n=20) for second generation zircon range from 0.2 to 6.1 with a weighted mean of  $3.0 \pm 0.7$  (MSWD=1.5). The single spot from the  $1404 \pm 17$  Ma texturally oldest domain has an initial  $\epsilon\text{Hf}_{1404 \text{ Ma}} = 8.2 \pm 2.5$ .

## 5 Discussion

### 5.1 Hf constrains on subsurface evolution of Ohio

The ~1.64 Ga age of the Fayette sample represents the earliest recorded igneous event among these samples (Fig. 4). The Fayette sample has  $\epsilon\text{Hf}$  values ca. 6 units below the DM curve in  $\epsilon\text{Hf}$ -time space at a poorly constrained mean value of ~5 (Fig. 5). Even though the age is poorly constrained, the combined U-Pb-Hf data indicates the involvement of a >1.6 Ga crustal component during igneous crystallization that was present east of the Grenville front magnetic lineament. The oscillatory-zoned cores of Morrow, Logan and one spot from Scioto (n3428-5a) have igneous ages of ca. 1400–1450 Ma. Their  $\epsilon\text{Hf}_i$  values range between 8.5 and 9.0. They plot ca. 3–3.5  $\epsilon$ -units below the DM curve yielding a more depleted signature than the sample from Fayette. In  $\epsilon\text{Hf}$ -time space the Lake sample is ca. four  $\epsilon$ -units below the DM curve with a  $\epsilon\text{Hf}_{1228 \text{ Ma}}$  value of 7.9 indicating the involvement of a more depleted reservoir (Fig. 5). The 2.0  $\epsilon\text{Hf}_{1050 \text{ Ma}}$  value of Erie is the most evolved of the samples with values >11  $\epsilon$ -units below the DM curve. The recrystallised zircon domains in Morrow and the unzoned BSE-bright second-generation zircon domains in Scioto have  $\epsilon\text{Hf}_i$  values similar to Erie >11  $\epsilon$ -units below the DM curve (Fig. 5). These recrystallised domains plot with and slightly above the Erie

sample. Included with the ca. 1450 Ma population, these indicate an evolution corresponding to  $^{176}\text{Lu}/^{177}\text{Hf} \approx 0.01$  and further define an evolutionary array with a Hf- $t_{\text{DM}}$  of ca. 1650 Ma (Fig. 5). For simplicity in subsequent text, we call this array the Grenvillian array.

Recent studies, by Zeh et al. (2010) suggest that zircon can lose Pb through various processes under metamorphic conditions. These processes lead to zircon domains with different appearance and generally lower U-Pb ages and Th/U ratios than their unmetamorphosed igneous counterparts (Harley et al., 2007). However, in situ modified metamorphic zircon grains will not lose its isotopic composition with regard to Hf (Zeh et al., 2010). This contrasts with zircon grains that have been dissolved and re-precipitated from a fluid or melt (Gerdes and Zeh, 2009; Zeh et al., 2010). In short, zircon grains can lose Pb while retaining its Hf isotope composition during solid-state recrystallization, which would be represented by the Pb-loss trend in figure 5. Conversely, during dissolution-reprecipitation processes in the presence of a fluid and/or melt, zircon-rock Hf isotope exchange is more likely to occur. The recrystallised zircon domains in Morrow and Scioto seem to have equilibrated with a host rock during the Grenvillian orogeny with  $^{176}\text{Lu}/^{177}\text{Hf} \approx 0.01$ . As the rocks in this study are heavily altered granitoids and not derived from anatexis, the simplest interpretation is that these zircon domains (re)-crystallised in equilibrium with their host rocks in the presence of a fluid.

Almost all samples east of the Grenville front fall on the same crustal evolution array with a  $^{176}\text{Lu}/^{177}\text{Hf}$  value that corresponds to 0.01 (Fig. 5). This array represents a possible reservoir with a Hf- $t_{\text{DM}}$  at  $1640 \pm 40$  Ma, which is similar to the Fayette sample age (Fig. 5). This interpretation is strengthened further by a closer look at the Morrow and Scioto samples, where both cores and rims (texturally second domain in Scioto) plot on this array. One analysis, the Morrow-8b deviate to a lower  $\epsilon\text{Hf}_t$  value (-2.9), corresponding to a  $^{176}\text{Lu}/^{177}\text{Hf}$  value of ca. 0.0001 suggesting Grenvillian aged Pb-loss without changing the Hf-isotopic composition (Fig. 5). An alternative explanation to the anomalously low  $\epsilon\text{Hf}$  value could be a 3D effect from drilling through the rim and analysing large portions of core material. Furthermore, it is apparent from the Hf data for the Erie and Scioto samples, and for the rims of the Morrow sample, that these rocks were derived from a crustal source with an

extended crustal residence time. It is also noteworthy that the spread in  $\epsilon_{\text{Hf}}$  is greater in the samples with Grenvillian crystallisation ages than in the older samples, ranging up to 7  $\epsilon$ -units.

Two samples, Fayette and Lake deviate from the main trend and have  $\epsilon_{\text{Hf}}$ -values not corresponding to the Grenvillian array. As previously mentioned Fayette has a mean  $\epsilon_{\text{Hf}_i}$  value of 5, suggesting the possible involvement of an older component ( $>2.0$  Ga as a conservative estimate). This is discussed in section 5.4. The Lake sample on the other hand, has a mean  $\epsilon_{\text{Hf}_i}$  value of 7.9, ca. 3  $\epsilon$ -units higher than the Grenvillian array at the corresponding time. This indicates a more depleted source, which fits with an event that generated depleted melts with  $\epsilon_{\text{Hf}_i} \geq 12.5$  at ca. 1230 Ma. These mixed with an existing crustal component  $\epsilon_{\text{Hf}_i} \leq 5$ . A potential candidate for the enriched component could be the existing crust as defined by the array (Fig. 5). Given such a model and assuming a Hf-concentration ratio between the primitive melt and a reworked crustal component of 1:2, the juvenile component contribute up to 75%, and since the Lake sample is mafic schist, a predominantly juvenile component might be expected.

Similar trends of juvenile 1.2 Ga input have been recorded in e.g. the Baltic Shield (Pedersen et al., 2009; Petersson et al. 2013), in Mexico (Weber et al., 2010) and in the Gardar Province of south Greenland (Blaxland et al., 1978; Upton et al., 2003). This event is roughly coeval with emplacement of the Harp ( $1271 \pm 1$  Ma; Cadman et al., 1993), Mackenzie ( $1267 \pm 2$  Ma; Le Cheminant & Heaman 1989) and Sudbury ( $1238 \pm 4$  Ma; Krogh et al., 1987) dyke swarms. Although a genetic relationship between these events remains unclear.

## 5.2 O-isotope constrains on subsurface evolution of Ohio

There is no simple correlation between  $\delta^{18}\text{O}$  and age or geographical location. However, there is a negative correlation between Th/U and  $\delta^{18}\text{O}$  (Fig. 6a). It has been argued that heavy  $\delta^{18}\text{O}$  signatures commonly represent the influence of sedimentary components to the crystallising magma (Hawkesworth & Kemp 2006) or reaction with metamorphic fluids (Valley et al., 2005). The  $\delta^{18}\text{O}$  of the Fayette sample is within the mantle value ( $5.3 \pm 0.3\%$ ) indicating no influence of reworked sediment components or heavy  $\delta^{18}\text{O}$  metamorphic fluids. As the Fayette pegmatite intrudes a marble

the mantle like  $\delta^{18}\text{O}$  value suggests intrusion without assimilation. The  $\delta^{18}\text{O}$  values of the cores of Morrow (6.8‰) and Lake (6.6‰) are slightly heavier than a mantle value, while Logan and Scioto samples have the heaviest  $\delta^{18}\text{O}$  signatures with values ranging between 8.1–11.8‰ and 8.2–14.8‰ respectively. Notably, the 7.1–7.4‰  $\delta^{18}\text{O}$  values of the rims in Morrow are equal to a mean of the larger spread in the cores (6.3–8.0‰) possibly reflecting a homogenisation related to a partial melting event, without the addition of further components. Crystallisation and recrystallisation of zircon during the Grenvillian orogeny probably occurred in the presence of heavy  $\delta^{18}\text{O}$  fluids suggested by the negative correlation for Th/U and  $\delta^{18}\text{O}$  (Fig. 6a). It is also noticeable that  $\delta^{18}\text{O}$  signatures of subsurface Ohio rocks are increasing towards heavier values with decreasing age. This increase in heavy  $\delta^{18}\text{O}$  also correlates in time with the onset of high-grade metamorphism related to the Grenvillian continent-continent collision (Fig. 6b). Given the slow diffusion of O in zircon, O-isotope exchange might only be anticipated to any significant degree in dissolution-reprecipitation processes, while solid-state recrystallisation processes might be less affected, if at all (Valley, 2003). Peck et al., (2004) analysed some of the heaviest  $\delta^{18}\text{O}$  magmatic zircon worldwide in the Grenvillian Frontenac terrane and proposed hydrothermally altered basalts and sediments as a source for the heavy oxygen. We propose that the increase in heavy oxygen signatures in subsurface Ohio, at the onset of the Grenville continent-continent collision, is a function of reaction with hydrothermal fluids during dissolution-reprecipitation processes. The origin of the heavy oxygen is difficult to assess, but might possibly stem from interaction with a sediment-rich component. The Logan sample, in the unmetamorphosed foreland, has very heavy  $\delta^{18}\text{O}$  signatures with values between 8.1 and 11.8‰. Metamorphic fluids during the Grenville orogeny cannot explain these signatures in these simple igneous textured grains. These signatures are more readily explained by reworking of a sedimentary component or altered basalt. Such a reworked component must have been relatively juvenile to explain the homogeneity of the Logan sample  $\epsilon\text{Hf}$  (c.f. Fig 8C in Iizuka et al 2013). The location of the Logan sample in the unmetamorphosed foreland suggests a different geologic evolution than its counterparts on the opposite side of the Grenville magnetic lineament.



### 5.3 Coupled U-Pb–Lu–Hf–O isotope constraints on subsurface evolution of Ohio

The oxygen isotope data from the Grenvillian aged zircon grains and zircon domains are not compatible with closed system reworking of older protoliths. This is seen in the markedly heavier oxygen signatures in these zircon domains, interpreted as addition of heavy  $\delta^{18}\text{O}$  during the Grenvillian orogeny from a fluid component. A heavy  $\delta^{18}\text{O}$  fluid provides a likely candidate to explain the trends seen in the isotopic data. The presence of such fluid component during reworking provides an explanation for the excess spread in Hf-isotope signatures of the Grenvillian aged zircon grains and zircon domains. It seems reasonable that the fluids that affected the  $\delta^{18}\text{O}$  signatures of the zircon also led to Hf exchange between fluids, zircon and rock matrix. This is interpreted as the most likely cause behind the excess spread in  $\epsilon\text{Hf}$  amongst the Grenvillian aged zircon and zircon domains.

Alternatively, the spread in Hf-isotope signatures among the Grenvillian aged samples might reflect mixing between an unknown ancient component and juvenile additions during the Grenvillian orogeny. Irrespective of the nature of the more depleted component in this scenario, the reworked crustal component must be  $>1.65$  Ga. If the enriched component were reworked sediments, an inverse correlation between  $\epsilon\text{Hf}$  and  $\delta^{18}\text{O}$  would be expected. However, this is not observed. At the time of the Grenville orogeny the difference in  $\epsilon\text{Hf}$  between the depleted mantle and a reworked  $\geq 1.65$  Ga Palaeoproterozoic crustal component is at least 15 units. From this perspective, the sample spread in relation to the external analytical precision is surprisingly limited, and reworking of a single reservoir provides a simpler explanation of the data. Furthermore, the homogeneity in Hf-isotopic signatures between Ohio and the Adirondack Mountains (Bickford et al., 2010; Valley et al., 2010) seen in figure 5 might provide further support for sequential tapping of a comparatively homogenous source. This is in agreement with Goodge and Vervoort (2006) who point out that the majority of the  $\sim 1.4$  Ga Laurentian A-type granites intruding the mid-continent contain reworked crustal contributions in excess of 90%.

## 5.4 Speculation on older crustal component within the orogen.

In Ohio, the closest Archaean crust is the Superior province, and the Marshfield terrane located in parts of Wisconsin and Illinois (Fig. 7). Early stages of the Penokean orogeny include the accretion of the Pembine-Wausau arc terrane at the southern margin of the Superior craton followed by the accretion of the Archaean micro-continent, Marshfield terrane (Whitmeyer & Karlstrom, 2007). As mentioned above (Section 2.1) the Penokean Province includes igneous and metasedimentary rocks extending from Minnesota, northeast to Canada where it pinches out at the Grenville deformation front in northern Ontario (Davidson, 1995; Holm, 1999). The Penokean Province consistently yields Nd- $t_{DM}$  of ca. 2.1 Ga (Barovich et al., 1989; Holm et al., 2005). Hoffman, (1988) interpreted Nd model ages of the Penokean Province as hybrid ages, due to mixing of Archaean crust and juvenile accreted crust. A-type granites intruding the Penokean Province indicate a similar evolution as the Fayette sample, as both have Hf- $t_{DM}$  of ca. 2.1 Ga assuming an average crustal  $^{176}\text{Lu}/^{177}\text{Hf}$  of 0.015 (Fig.5). Interestingly the  $\delta^{18}\text{O}$  values of the Fayette sample are mantle-like with a mean value of  $5.3\pm0.3\%$  indicating no influence of reworked sedimentary components in the source. Combined U-Pb-O-Hf isotopes suggest reworking of older crustal components that have preserved mantle like  $\delta^{18}\text{O}$  values. Both volcanic and plutonic rocks from the Superior Province are known to have mantle like  $\delta^{18}\text{O}$  values with a limited range  $5.7\pm0.6\%$  (Peck et al., 2000; Valley et al. 2005) allowing the possibility for the Superior Province or the Marshfield terrane as zircon sources in the Fayette sample. Importantly however, if any Archaean component is present, it likely contributes very minor amounts as e.g. the  $\sim 1.45$  Ga do not show evidence of any significant contribution of  $>1.65$  Ga crustal components.

## 5.5 Implications for the Grenville Province

The age of the Fayette sample corresponds to the Labradorean stage of geological evolution and is unknown in this part of the orogen. It is possible that these zircon grains are xenocrystic in the pegmatite. Even so, the zircon grains must have been drawn from an existing basement rock and to that end the combined U-Pb, O and Hf data remain valid for an older crustal component within the orogen. Although poorly constrained, the age of the Fayette sample together with the Hf-isotopic

signatures of these samples may provide some constraints on the crustal architecture of the North American continent with an eastward shift of the Nd  $t_{DM}$ -line by Van Schmus et al. (1996; Fig. 7) and with that a revised location of the eastern limit of the Mazatzal Province at ca. 1.6 Ga. The size and proportions of the Mazatzal and Labradorian crust in the mid-continent is defined by sparse amounts of Nd model ages (e.g. Van Schmus et al., 1996, 2007). With these new data an eastward shift of the crustal boundary of a 1.5 Ga Laurentia is suggested to between the Erie and the Lake samples (Fig. 2 & 7). It is noteworthy that all samples except for the Lake sample, are quartz-rich felsic rocks but the Lake sample, east of our revised crustal boundary, has a Si-undersaturated intermediate and juvenile composition. Nd isotopes from southern Appalachians suggest the presence of a Meso- and Paleoproterozoic basement in the Blue Ridge (Fullagar, 2002; Carrigan et al. 2003), and a ca. 1.7 Ga basement to the Inner Piedmont Province is indicated by Pb isotope data (Stuckless et al. 1986). Fisher et al. (2010) identified a change in Pb isotope signatures across the geophysical anomaly termed the New York-Alabama Lineament (NY-AL; Fig. 7; King & Ziez, 1978) and suggested a possible upper crustal suture of Grenvillian age separating the Granite-Rhyolite Province from the basement of the southern and central Appalachians. The NY-AL lineament is parallel but slightly offset to the southwest of our revised location of the eastern limit of the Mazatzal Province in Ohio at ca. 1.6 Ga. Both our revised extent of Paleoproterozoic basement and the isotope anomaly of the NY-AL supports the collisional model presented by Tohver et al. (2004, 2005).

The cores of the Morrow and Logan samples have ages of approximately 1450 Ma, an age well known in the mid continent among A-type granites correlated to the Mazatzal orogen and the break-up of an early supercontinent (e.g. Windley, 1993; Whitmeyer & Karlstrom, 2007), and the Canadian part of the Grenville province (e.g. Rivers et al., 2012). Goodge & Vervoort (2006) show that the ~1.4 Ga A-type granites of the mid-continent have Hf- $t_{DM}$  ages spanning from 2.0–1.65 Ga and crustal residence times matching the formation age of the basement they intrude. In Yavapai/Mazatzal rocks in New Mexico, Rämö et al., (2003) recorded juvenile additions that imply subcontinental enrichment at 1650 Ma; a metasomatic event at 1460 Ma followed by magmatic underplating at ca. 1220 Ma. Holm et al. (1998, 2007) and Romano et al. (2000) have recorded 1.65–1.63 Ga reactivation along the Yavapai

Province northern boundary east of the Cheyenne belt in the western Great Lakes area and connected it to the Mazatzal orogeny. With ca. 1.65 Ga juvenile crust (Karlstrom & Bowring, 1988, Hoffman, 1989; Windley, 1993; Rämö et al., 2003; Whitmeyer & Karlstrom, 2007) and crustal residence times of ca. 200 m.y. the Mazatzal Province is the most likely candidate as the source of the Grenvillian rocks in Ohio's subsurface.

The Hf- $t_{DM}$  of the Grenvillian array (as defined in Fig. 5) and the age of the Fayette sample are coeval with the Mazatzal orogenic juvenile crust (Karlstrom & Bowring, 1988, Hoffman, 1989; Windley, 1993); and related to the final stages of assembly of a ca. 1.5 Ga supercontinent (Windley, 1993). Volcanogenic greenstone successions including basalt, basaltic andesite, dacitic tuff and rhyolite with ages from 1.68 to 1.65 Ga constitute the oldest rocks in the Mazatzal Province (Karlstrom et al., 2004). According to Nd and Pb isotopic data from Bennet and DePaolo, (1987), Wooden and DeWitt, (1991) and Aleinikoff et al., (1993) these rocks have mantle derivation ages of 1.8–1.7 Ga. The data for this paper is compatible with an eastward extension of the Mazatzal Province, thus redefining the source of Ohio's subsurface basement (Fig. 7). The eastern terranes of Grenville have been suggested to be rifted Laurentian fragments reconnected to the main continent during the Appalachian orogeny (Carrigan et al., 2003). Both the Blue Ridge of Virginia and the Mars Hill terrane have been shown to have >1.5 Ga basement components (Fig. 7. Carrigan et al., 2003; Hatcher et al., 2004). According to Davidson (1995) older rocks (ca. 1.75–1.45 Ga) that have been reworked during the Grenville orogen are typically parautochthonous. Subsurface Mazatzal Province is thousands of kilometres west of the Appalachians thus to be a candidate for an origin, must either be far travelled fragments or initially exotic to Laurentia and accreted during the Appalachian orogeny (Whitmeyer & Karlstrom, 2007). In any case, the proximity between Ohio and the subsurface Mazatzal Province shortens this distance markedly making such a scenario more likely. However, the possibility of an exotic terrane in Ohio cannot be excluded. The distribution of 1.66–1.65 Ga Mazatzal rocks indicates that a large region was affected by subduction related magmatism (Anderson & Cullers, 1999). Furthermore, extensive plutonism and intense metamorphism occurred in southern Labrador nearly coeval with the Mazatzal orogeny (Gower et al., 1992; Dickin, 2000). In any case, the reservoir in Ohio, as defined by the

Grenvillian array has at a later stage been sequentially reworked during different orogenic events. Mueller et al. (2008) shows that Grenvillian detrital zircon grains from a Pleistocene beach ridge in northern Florida, with an origin in the southern Appalachians, have a  $t_{DM}$  of ca. 1.6 Ga, i.e. coeval with the Hf- $t_{DM}$  of our drill core samples from Ohio. In addition, sediments from the Little Willow- and the Big Cottonwood-Formations in Wasatch Range, Utah, contain Grenvillian aged detrital zircon with isotopic signatures suggesting that these sediments are derived from Yavapai/Mazatzal terranes and the Wyoming Craton (Spencer et al., 2012). These zircon grains have almost identical Hf signatures to the subsurface zircon grains from the Ohio basement. When incorporating data from the Arnold Hill-, Palmer Hill- and Hawkeye granites from the Adirondack Mountains (Valley et al., 2010) on the same plot, they also plot on the same crustal array as our samples (Fig. 5). The similarities between these three models imply the possibility for a common evolution such as a shared protolith. Bickford et al., (2010) present Hf isotopic compositions of zircon from the previously dated (McLelland et al., 2004) AMCG suite of the Adirondacks (New York) which, when recalculated using current depleted mantle values of Griffin et al. (2002) and applying a Hf- $t_{DM}$  evolution corresponding to  $^{176}\text{Lu}/^{177}\text{Hf} = 0.01$  yield Hf-isotopic signatures matching the samples defining the Grenvillian array (Fig. 5).

The Grenvillian aged samples, Scioto, Erie and the zircon rims of Morrow, suggests syn-orogenic magmatism, a common feature in the Interior Magmatic Belt to the north (Rivers et al. 2012). This suggests an extrapolation of this belt into subsurface Grenville Province of Ohio. Another example of rocks related to the Interior Magmatic Belt is the Hawkeye granites of the Adirondack Mountains (Rivers et al. 2012) that, as previously mentioned, indicate a similar crustal evolution trend as the Ohio drill-core samples.

When adding the mean Hf values of granites intruding the Laurentian basement from Goodge & Vervoort (2006) to our  $\epsilon\text{Hf}$ -time plot (Fig. 5), the samples from the southern Granite-Rhyolite Province are the only samples corresponding to the Grenvillian array. The Mazatzal Province underlies the majority of the Granite-Rhyolite Province, especially the southern Granite-Rhyolite Province (Fig. 7). Unfortunately the Mazatzal was not included in the Goodge & Vervoort (2006) dataset, but the geographical location of the Mazatzal at  $\sim 1.6$  Ga (Whitmeyer & Karlstrom, 2007) and

the juvenile character of the 1.68–1.65 Ga rock that constitute the oldest in the Mazatzal Province (Karlstrom et al., 2004) opens the possibility of the Mazatzal Province as a protolith to the subsurface basement in Ohio (Fig. 7).

## 6 Conclusions

All samples, except Lake and Fayette, indicate continuous reworking of a single crustal reservoir with extended reservoir times. A Hf- $t_{DM}$  of ca. 1650 Ma indicates little or no addition of juvenile material (Fig. 5). The igneous crystallisation age of Fayette (ca. 1650 Ma) is coeval with the protolith of the crustal reservoir, and the poorly constrained Hf isotopic signature of this rock might indicate the involvement of an even older crustal component within the Grenville orogen. The data presented in the paper suggest a revision of the current Nd  $t_{DM}$ -line of Van Schmus et al. (1996) and imply a 1.5 Ga crustal boundary of Laurentia east of the current Grenville front magnetic lineament (Fig. 7) of Ohio. Rocks to the west of our revised crustal boundary are more felsic than the compositionally intermediate sample (Lake) to the east, which has a more juvenile Hf-signature.

The ca. 1650 Ma protolith and the igneous crystallisation ages of approximately 1450 Ma for the Morrow cores and the Logan sample is consistent with the Mazatzal Province being a possible protolith. The Hf- $t_{DM}$  is coeval with the Mazatzal crust and 1450 Ma is an age well known in the mid-continent from anorogenic rocks connected to the Mazatzal orogen and the break-up of a ca. 1.5 Ga supercontinent.

Syn-orogenic magmatism at ca. 1050 Ma suggests an extrapolation of the outcropping Interior Magmatic Belt of Ontario to incorporate the subsurface basement rocks of Ohio.

Zircon in the subsurface Precambrian rocks of Ohio were partly recrystallised, during the Grenville continent-continent collision, in the presence of heavy  $\delta^{18}O$  fluids, increasing the  $\delta^{18}O$  value of recrystallised zircon.

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## Figure captions

**Fig. 1.** Crustal provinces of the Mid-Continent showing the crustal distribution today, redrawn after Goodge and Vervoort (2006). The dashed black “Van Schmus line” divides the continent between rocks with Sm-Nd  $t_{DM}$  ages >1.5 Ga and  $t_{DM}$  ages <1.5 Ga (Van Schmus et al., 1996).

**Fig. 2a.** Schematic outline for the principal bedrock units of the subsurface Precambrian of Ohio including well locations and U-Pb ages. Dashed yellow line depicts interpreted Grenville magnetic lineament. Modified from Baranoski et al. (2009) **b.** Composite aeromagnetic map of the Ohio region including well locations. Simulated flight altitude 305-meters above ground, spectral colour display, and sun angle zero degrees. Compiled from various sources and processed by USGS Reston, Virginia. Dashed yellow line depicts interpreted Grenville magnetic lineament. Modified from Baranoski et al. (2012).

**Fig. 3.** Back Scattered Electron (BSE) images for selected zircon grains from our samples. Analysis sites for ion microprobe age determinations are marked with white ellipses. Spot numbers with corresponding  $^{207}\text{Pb}/^{206}\text{Pb}$  ages (Ma) are given for each spot. In most instances, these analysis sites are

identical to those for the O- and Hf-isotope analyses. Note however, that the Hf analysis spot radius is about two to three times the size of the U-Pb spots which are all 15 $\mu$ m, while the O spot size is even smaller (10 $\mu$ m) and located inside those for U-Pb.

**Fig. 4.** Tera-Wasserburg U-Pb diagrams for the analysed zircon spots from Ohio subsurface basement rocks. Insets contain assigned age with errors 2 $\sigma$ .

**Fig. 5.**  $\epsilon_{\text{Hf}}$  versus  $^{207}\text{Pb}/^{206}\text{Pb}$  ages for all samples in this study. Ages represent interpreted igneous or recrystallised crystallisation ages for individual populations. Individual zircon spot  $\epsilon_{\text{Hf}}$  values are indicated by the small squares, while the weighted mean for each population is given by the large squares. For clarity, error bars are left out for individual spots and the error bars for the weighted means are smaller than their symbol sizes, except for Fayette (2SOM  $\pm 3$ ). Depleted Mantle evolution curve was calculated using mean present day values of  $^{176}\text{Lu}/^{177}\text{Hf} = 0.0384$  and  $^{176}\text{Hf}/^{177}\text{Hf} = 0.28325$ , after Griffin et al. 2002 and is indicated by the red line. The solid heavy black line represents a regression ( $R^2=0.98$ ) for the average data of Scioto, Morrow, Erie and Logan, which corresponds to a single crustal reservoir with  $^{176}\text{Lu}/^{177}\text{Hf} = 0.01$  and  $t_{\text{DM}} = 1640 \pm 40$  Ma. Thin, hatched curves represent the error envelope of the regression and the squared light-grey field gives the model age envelope. The thick hatched line give a possible crustal evolution model for an older Archaean host-rock. Yellow line indicates possible Pb-loss. Beige ellipse indicates the Lyon Mountain granite in the Adirondack Mountains from Valley et al., (2010), and the pink ellipse indicates the AMCG suite of Adirondack (New York) from Bickford et al. (2010). Small grey circles indicate Goodge & Vervoort (2006) data of granites intruding different Laurentian provinces. O isotope data is given in the legend.

**Fig. 6 a.** Linear regression showing the negative relationship between  $\delta^{18}\text{O}$  and Th/U. The relationship ( $R^2=0.6$ ) demonstrating the effect of heavy  $\delta^{18}\text{O}$  metamorphic fluids on zircon during recrystallisation. A decrease in Th/U value indicates an increased metamorphism due to the larger difference in ionic radii between  $\text{Th}^{4+}$  and  $\text{Si}^{4+}$  than  $\text{U}^{4+}$  and  $\text{Si}^{4+}$ . **b.**  $\delta^{18}\text{O}$  versus  $^{207}\text{Pb}/^{206}\text{Pb}$  date diagram, showing the correlation between the influxes of heavy  $\delta^{18}\text{O}$  and the onset of high-grade continent-continent-collisional metamorphism (marked by blue box) in the Grenville orogen.

**Fig. 7.** Crustal provinces of the Mid-Continent showing the crustal distribution today, redrawn after Goode and Vervoort (2006) and the distribution of the Mazatzal Province at ca. 1.65 Ga, redrawn after Whitmeyer & Karlstrom (2007). Dashed red line indicated the revised location of the Mazatzal eastern extension at ca. 1.65 Ga.

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Sample	Core no.	X-coord. 83 (UTM zone 17)	Y-coord. 83 (UTM zone 17)	Sample depth interval (meters)	Rock description
Logan	645	1614624.94	290219.16	1005–1006	Rhyolite
Fayette	750	1709645.48	546845.74	1435–1435.5	Meta-pegmatite
Scioto 6A	2958	1876804.97	215544.30	1710.5–1711	Vained and banded orthogneiss
Scioto 6B	2958	1876804.97	215544.30	1711–1711.5	Boundary between 6A & 6B
Scioto 6C	2958	1876804.97	215544.30	1711.5–1712	Undeformed isotropic granite
Morrow	2935	1854064.88	329468.44	1247–1250	Isotropic granite
Erie	2864	2009312.10	599301.02	1357–1357.5	Altered and deformed metagranite
Lake	2904	2335029.49	762090.37	1849.5–1852	Dark fine-grained mafic schist



Figure 1

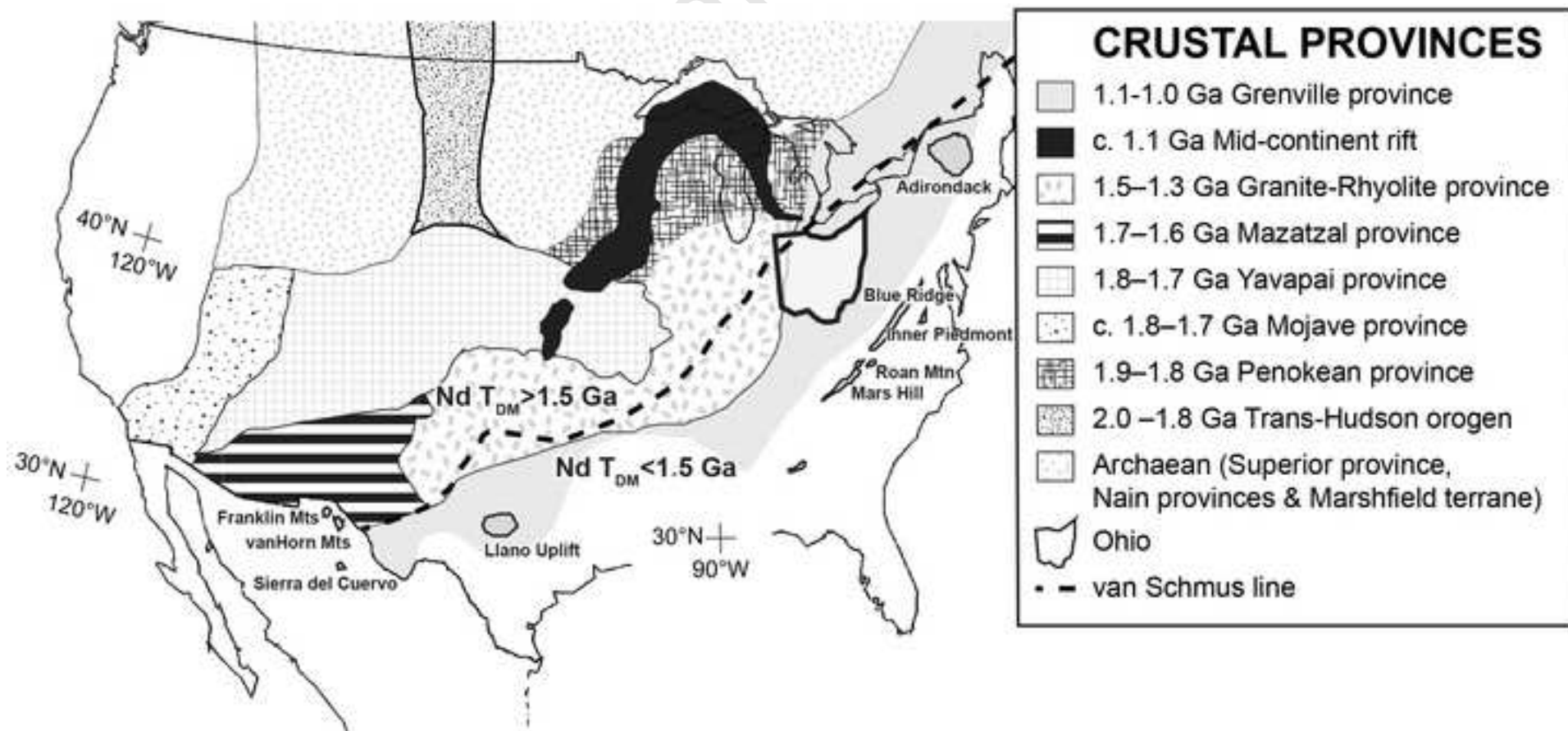
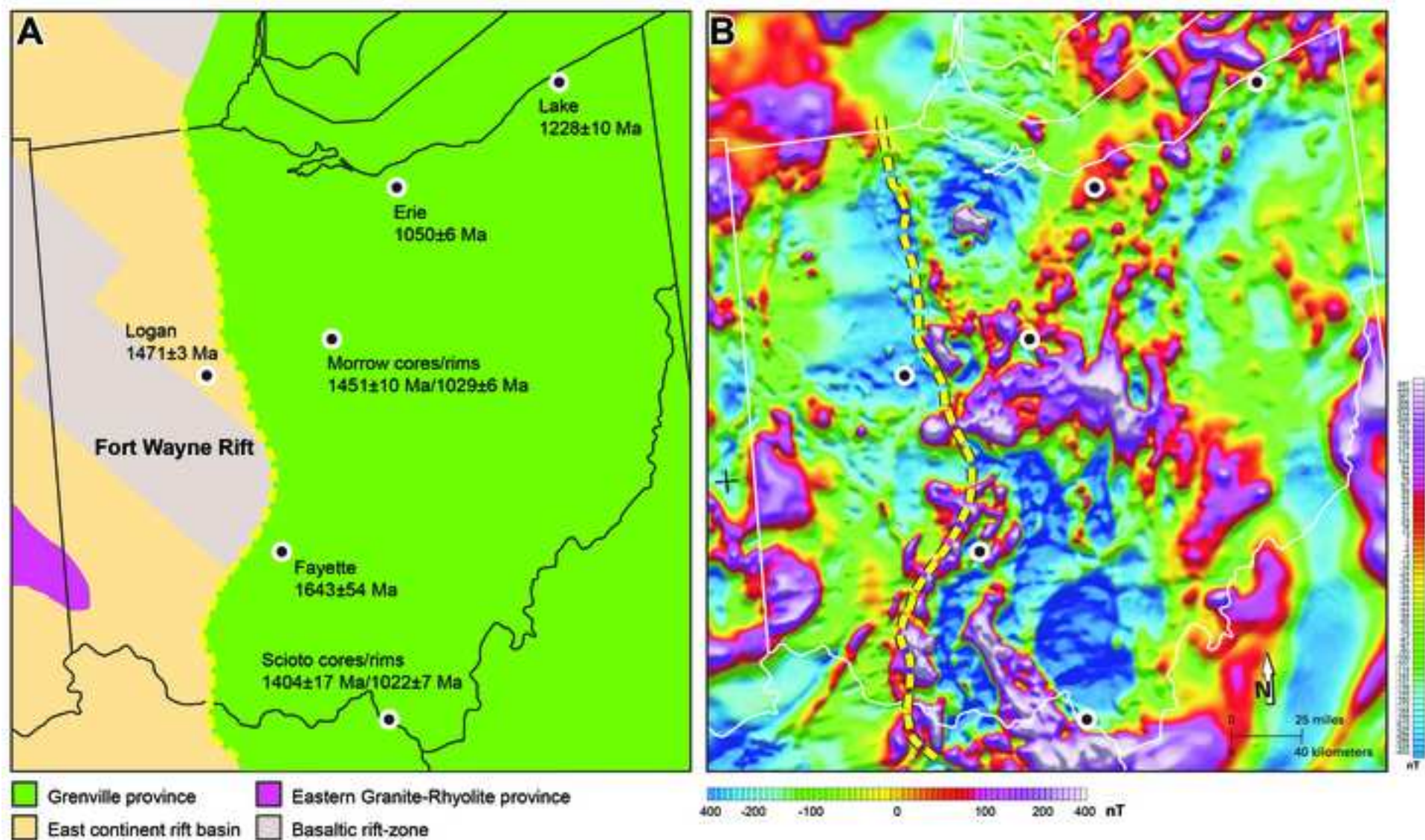
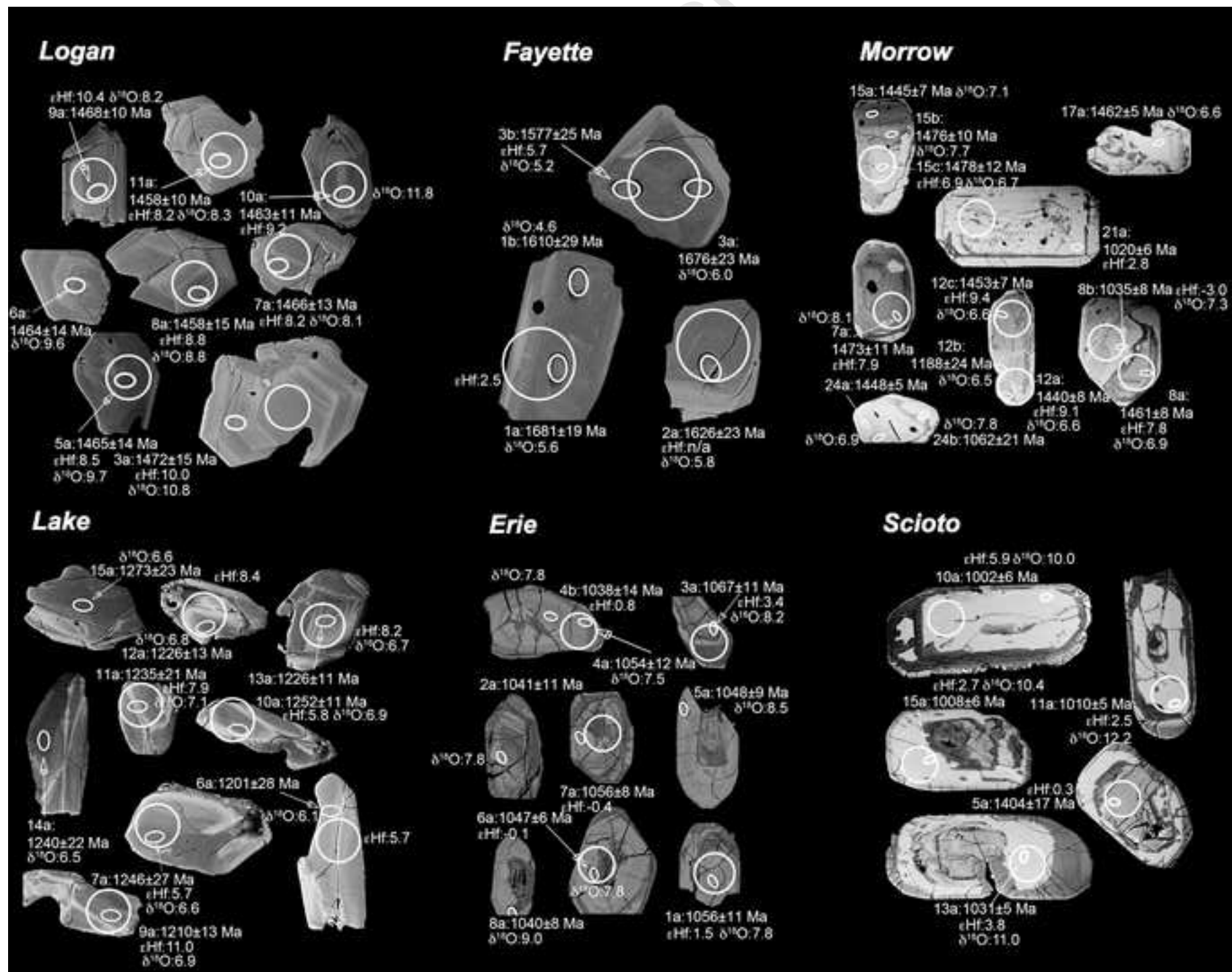


Figure 2







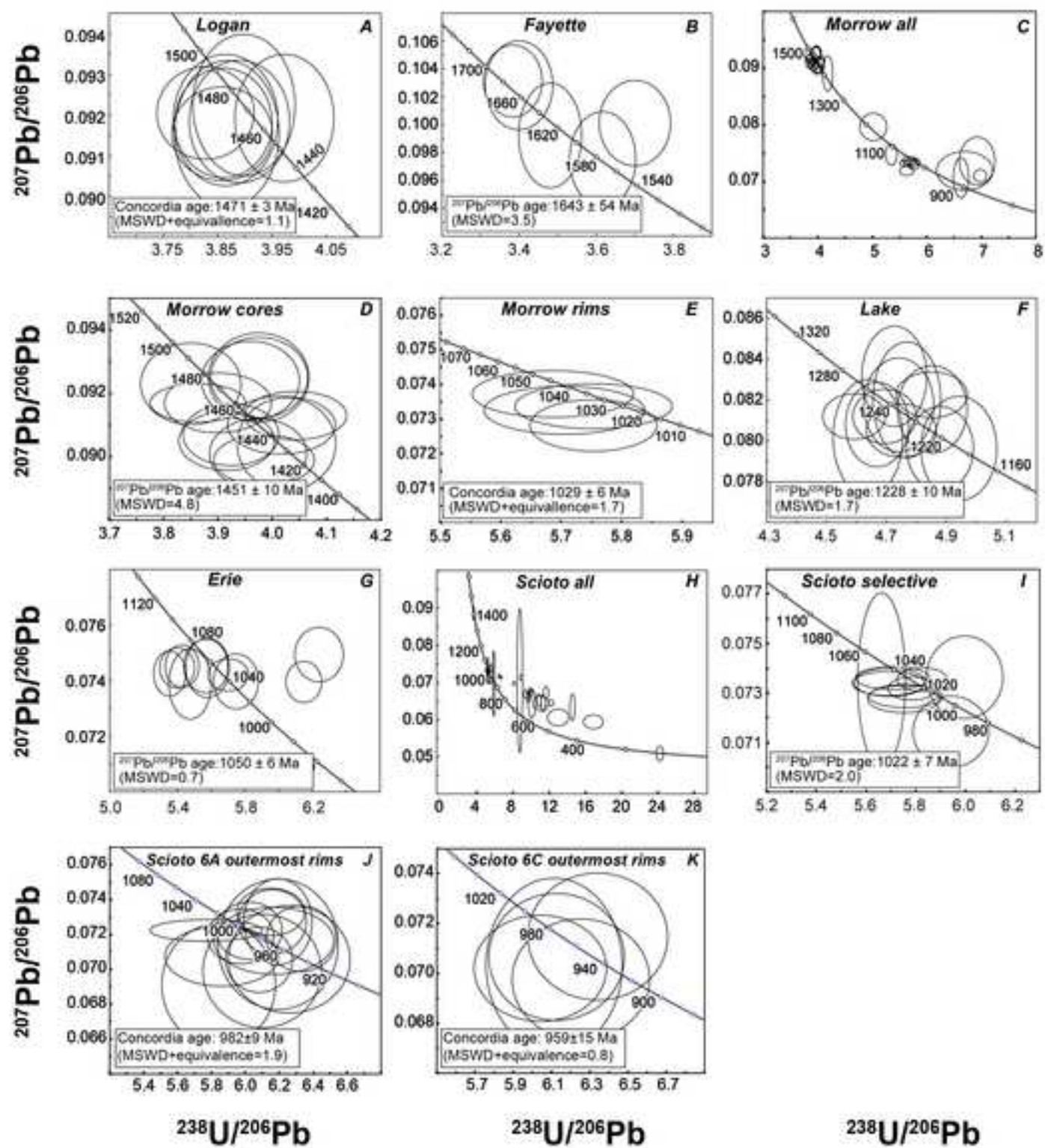


Figure 5

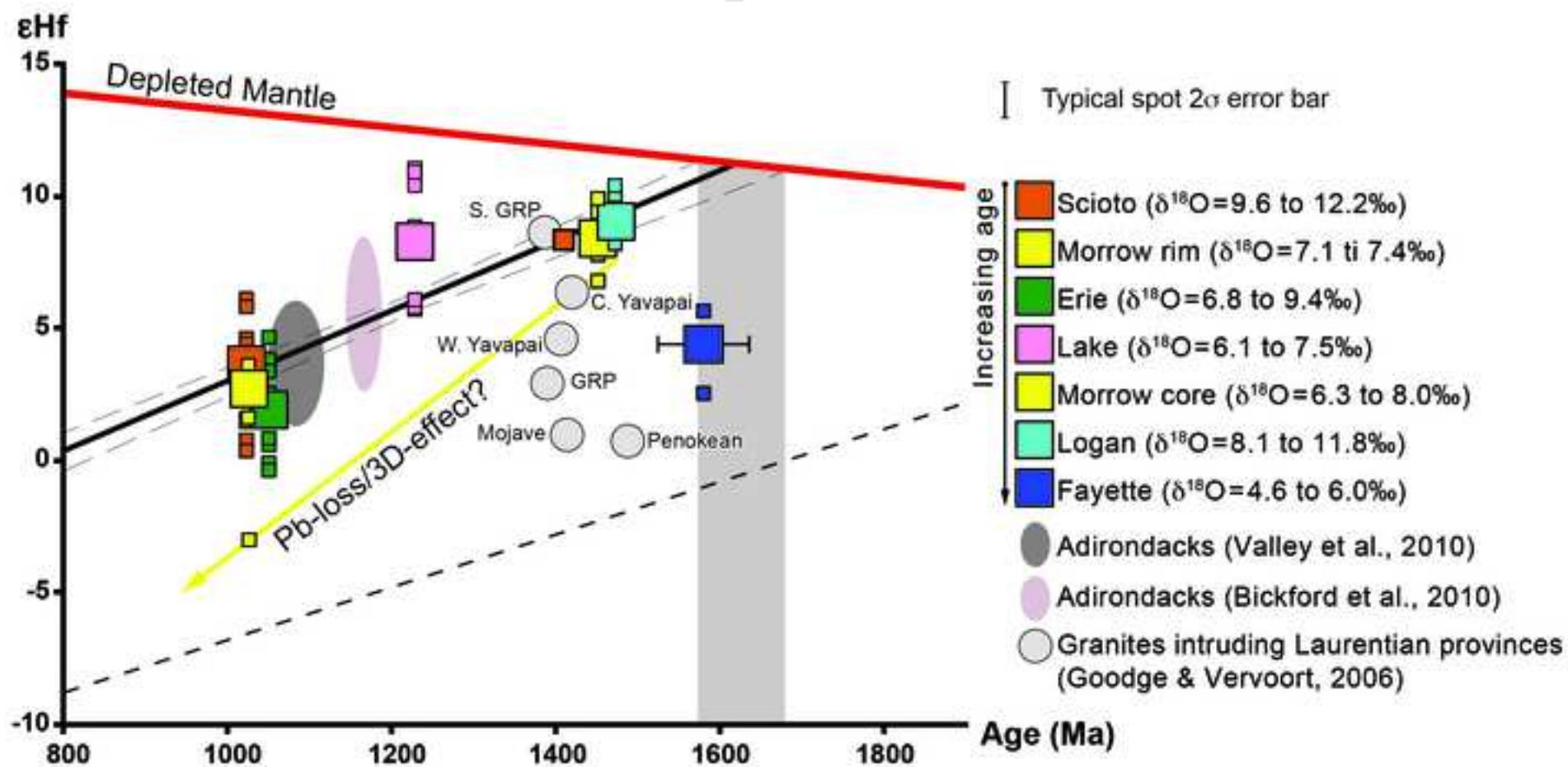


Figure 6

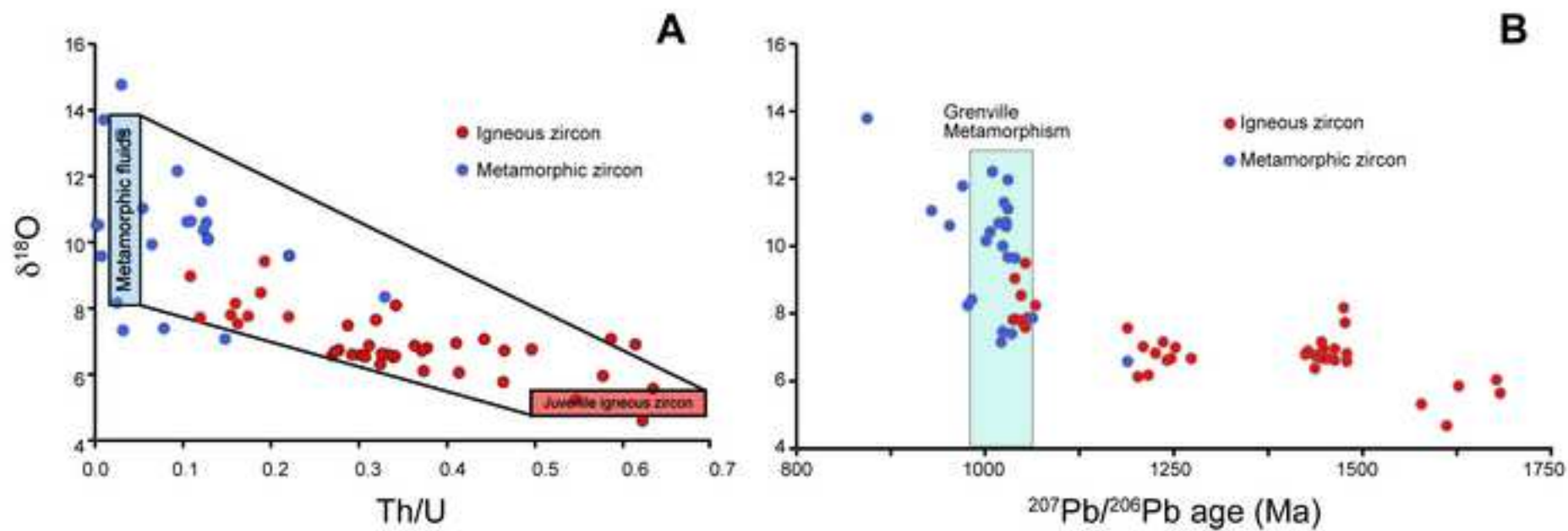


Figure 7

