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The Geon 14 Arc-Related Mafic Rocks from the Central Grenville Province

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Draft

Abstract

The late Paleoproterozoic to Mesoproterozoic (~1.7-1.2 Ga) evolution of the active southeastern margin of Laurentia terminated with the Grenvillian continental collision and the development of a large, hot, long-duration orogen at ~1.09-0.98 Ga. As a result, much of the hinterland of the Grenville Province consists of Paleo- and Mesoproterozoic rocks, mostly preserved as an imbricate stack of high-grade gneisses, that represent a potential repository of active-margin processes. This study presents geochronologic, geochemical, and isotopic analyses of two granulite-facies suites of ca. 1.45-1.40 Ga mafic tholeiites from the Canyon domain (Manicouagan area, central Grenville Province). One suite consists of 1439^{+76}_{-68} Ma high-FeTi mafic sills with ϵNd values of -0.4 (T_{DM} 2.57-2.72 Ga), indicate derivation from variably depleted to enriched MORB-type mantle sources, probably in an extensional back-arc setting, before intrusion in a ca. 1.5 Ga supracrustal metasedimentary sequence. The other, previously dated, 1410 ± 16 Ma Mafic to intermediate unit exhibits ϵNd values of 0.0 to +0.9 (T_{DM} 2.02-2.25 Ga), and variably enriched MORB to arc geochemical signatures, for which formation in a transitional back-arc to arc setting is suggested.

Integrated with published information, the new data support a model of a long-lived continental-margin arc and intermittent back-arc development on southeast Laurentia during the mid-Mesoproterozoic (ca. 1.5-1.4 Ga), in which repeated short periods of extension and crustal thinning in the back-arc or intra-arc regions were followed by compression and crustal thickening.

Keywords: Laurentia, Mesoproterozoic arc, back-arc, central Grenville Province, mafic tholeiites.

Introduction

Convergent plate boundary zones are major sites of formation, consumption, and recycling of Earth's continental crust (Clift and Vannucchi 2004; Cawood et al. 2009), so the study of magmatic processes in such zones can provide crucial understanding on the evolution of continental crust through time. This study is concerned with crust of Mesoproterozoic age preserved within the Grenville Province, part of the late Mesoproterozoic to early Neoproterozoic Grenville Orogen that is exposed on the southeast margin of the Canadian Shield and beyond. The Grenville Province (*fig. 1a*) has been modelled as a part of a large hot long-duration orogen (LHO; Jamieson et al. 2002; Beaumont et al. 2006; Rivers 2008; Rivers et al. 2012) that incorporated and reworked the long-lived Paleo- to Mesoproterozoic active margin of southeastern Laurentia (Rivers and Corrigan 2000). Continental outgrowth along the active margin started during late Paleoproterozoic accretionary orogenesis (e.g., Penokean, Makkovikian, and Labradorian orogenies; ca. 1.90-1.62 Ga; Hoffman 1988). In the eastern Grenville Province, it was followed by the development of early-Pinwarian (>1.5 Ga) supracrustal sequences (e.g., Wakeham Group) deposited on the southeastern Laurentian margin in a setting variably interpreted as a passive margin (Gower 1996; Gower and Krogh 2002) or an active margin intra-arc or back-arc setting (Rivers and Corrigan 2000; Wodicka et al. 2003; Corriveau et al., 2007; Rivers et al. 2012). Prolonged, extensive and widespread Mesoproterozoic (1.5-1.23 Ga) juvenile crust formation (and reworking), is inferred to have involved distinct phases of arc and back-arc activity along the entire stretch of the Laurentian continental margin, with 1.28-1.23 Ga accretionary activity limited to the southwestern Grenville Province. This was followed by the final continental collision during the Grenvillian Orogeny (1.09-0.98 Ga; *sensu stricto* of Rivers, 2008) (van Breemen and Davidson 1988; Gower et al. 1990; Gower and Tucker 1994; Tucker and Gower 1994; Nadeau and van Breemen 1994;

Gower 1996; Rivers 1997; Rivers and Corrigan 2000; Gower and Krogh 2002; Slagstad et al. 2004, 2009; Bonnet et al. 2005; van Breemen and Corriveau 2005; Whitmeyer and Karlstrom 2007; Hynes and Rivers 2010; Rivers et al. 2012; and references therein). As a result, it is reasonable to assume that the Grenville Province contains a record of crustal addition, loss, and recycling in rocks that were formed and accreted to the south-eastern margin of Laurentia from 1.9-1.1 Ga. An outline of the orogen-wide development of active-margin arcs and back-arcs, outboard island arcs, oceanic back-arc basins, and accretion of arc terranes was reported previously (Rivers and Corrigan 2000), but at the time details were sparse, especially from the central Grenville Province.

A major issue confronting any study of the high-grade gneissic rocks in the hinterland of the Grenville Province is that many primary characteristics of the protoliths may be obscured by high-grade metamorphism and deformation related to subsequent arc formation, accretionary orogenesis, and finally by the Grenvillian continental collision. High-grade metamorphism also has the potential to modify the isotopic and geochemical compositions of these rocks, which are presently mostly preserved in upper amphibolite to granulite-facies gneiss complexes. Given the low strain and good preservation of primary features in the study area, described in more detail below, we assume that their geochemical and isotopic signatures are preserved, and hence their study has the potential to provide insights on the processes operating on the ancient active continental margin of southeastern Laurentia. This assumption is evaluated in the course of the analysis.

Geon 14 mafic magmatism in the central Grenville Province constitutes an important part of the pre-Grenvillian evolution of the southeastern Laurentian margin, as revealed by recent studies by several workers. In particular, there is now good evidence for the deposition of a large

widespread Mesoproterozoic supracrustal sequence (the Complexe de la Plus Value or PLV; Moukhsil et al. 2012, 2013a) before ca. 1.5 Ga (Lasalle et al. 2013), and the development of continental margin volcanic arc on the southeastern Laurentian margin during Geon 14 (Dunning and Indares 2010; Valverde Cardenas et al. 2012; Augland et al. 2015), all of which are of special interest in this study. In this paper, we have examined two contrasting suites of ca. 1.4 Ga mafic rocks, one occurring as sills in the recently recognized ca. 1.5 Ga supracrustal sequence of the PLV, and the other from the ca. 1.4 Ga mafic to intermediate unit, both occurring in the Canyon domain of the central Grenville Province. Here we report the field and petrographic observations, major and trace element chemistry, Sm-Nd isotopes, and CA-TIMS U-Pb geochronology for these mafic rocks in order to characterize their age and tectonic setting.

Geological Context

The central Grenville Province: Manicouagan area

The first-order orogenic architecture of the Grenville Province is divided into the Parautochthonous Belt in the north and the structurally overlying Allochthonous Belt in the south (fig. 1a; Rivers et al. 1989), and the Manicouagan area exposes high-grade gneiss complexes in which these first-order divisions can be observed. The Parautochthonous Belt is represented by the Gagnon terrane, a Paleoproterozoic continental margin sequence that overlies an Archean basement, and both were metamorphosed and deformed during the Rigolet phase (~1005- 980 Ma) of the Grenvillian Orogeny, with the grade of metamorphism ranging from greenschist-facies (near the Grenville Front) to high-pressure granulite- and eclogite-facies conditions to the south (Rivers 2008, and references therein).

The Gagnon terrane is tectonically overlain by the allochthonous terranes of the Manicouagan Imbricate Zone (MIZ; Indares et al. 1998), which mainly consists of Labradorian

(~1.65 Ga) anorthosite-mangerite-charnockite-granite (AMCG) rocks and Pinwarian (~1.45 Ga) granitoids. The MIZ, part of the Allochthonous high-pressure belt, was metamorphosed at 750-920 °C and 1700-1900 MPa conditions from ca. 1060-1040 Ma (Indares 1997, 2003; Indares et al. 1998; Cox and Indares 1999a, b; Cox et al. 1998; Yang and Indares 2005) during the Ottawa phase of the Grenvillian Orogeny (Rivers 2008; Rivers et al. 2012). To the southeast of the MIZ, the late Paleoproterozoic to mid-Mesoproterozoic supracrustal and plutonic rocks comprising the Island domain, Canyon domain, Gabriel Complex, and Banded Complex (Hynes et al. 2000; Indares and Dunning 2004; Dunning and Indares 2010) were subjected to Ottawa mid-pressure granulite-facies metamorphism at 800-900 °C and 600-1100 MPa conditions from ca. 1080-1040 Ma (Dunning and Indares 2010; Lasalle et al. 2013; Lasalle et al. 2014; Lasalle and Indares 2014; Patrick and Indares 2017), and belong to the mid-pressure belt of Rivers (2008). In addition, the Hart Jaune terrane to the southeast of MIZ consists of 1.47 Ga mafic granulites (Hynes et al. 2000) that lack evidence for high-grade Ottawa metamorphism (Indares and Dunning 2004) and therefore, the terrane represents part of the Ottawa Orogenic Lid (OOL) of Rivers (2008).

On the basis of numerous Nd model ages, the Manicouagan area in the central Grenville Province has also been identified by Dickin and co-workers to be a junction of several crustal domains or terranes (*fig. 1b*; Dickin and Higgins 1992; Dickin 2000; Martin and Dickin 2005; Thomson et al. 2011). The most recent work by these authors shows four crustal terranes with distinct ages of formation: Archean (~2.7 Ga, restricted to the Parautochthonous Belt), Makkovikia (2.0-1.8 Ga), Labradoria (1.75 Ga), and Quebecia (1.55 Ga). Labradoria and Quebecia were interpreted as juvenile arc terranes accreted to the Laurentian margin at around

1.65 and 1.45 Ga, respectively. In this study, we re-examine this interpretation in the light of the currently available detrital zircon data from the central and eastern Grenville Province.

The rocks for this study come from the mid-pressure Canyon domain (Hynes et al. 2000; Dunning and Indares 2010), which is described in more detail below.

Geology of the study area: Canyon domain

The Canyon domain, first defined by Hynes et al. (2000), is situated in the southern Manicouagan Reservoir area (fig. 2) and structurally overlies mid-pressure and high-pressure Labradorian units to the north (Indares et al. 2000; Dunning and Indares 2010). ‘Canyon domain’ is a working term, used here to characterize a thrust package of supracrustal units and associated plutonic rocks (Dunning and Indares 2010; Indares and Moukhsil 2013) with distinct boundaries in the east (Berthé anorthosite) and in the west (Tétépiska anorthosite), but a poorly defined intrusive boundary in the south with the Bardoux and Castoréum Plutonic Suites. Following a regional mapping campaign led by the Ministère de l'Énergie et des Ressources naturelles du Québec (MERNQ; see Moukhsil et al. 2012), detailed field investigations have led to characterization of the domain into distinct lithologic units (see Indares and Moukhsil 2013), which are described briefly below in their geochronological order.

The Complexe de la Plus Value (PLV)

The oldest unit is a supracrustal sequence formally named the Complexe de la Plus Value (PLV) by Moukhsil et al. (2012) in the Lac du Milieu area located east of fig. 2. In the study area the PLV occurs in the southern part of the Canyon domain near the Manic 5 reservoir, and consists of a layered sequence of granulite-facies gneissic rocks with inferred protoliths of greywacke, pelite, quartzite, calc-silicate, and mafic compositions. The upper age limit for the deposition of the PLV was initially determined to be 1482 ± 21 Ma (U-Pb igneous zircon

crystallization age of granite from the Bardoux Plutonic Suite intruding the PLV in the Lac du Milieu area, [Moukhsil et al. 2012](#)), but has recently been more precisely constrained by [Augland et al. \(2015\)](#) to be 1497 ± 5 Ma based on TIMS U-Pb zircon dating of an augen granite with arc signature from the Bardoux Plutonic Suite in the Lac Okaopéo area south of our study area. The upper limit of deposition of the PLV has been constrained by detrital zircons studies ([Lasalle et al. 2013](#)) of two aluminous paragneisses from the Canyon domain, in which igneous cores of the youngest detrital zircon are ~ 1500 Ma, and the metamorphic grains and rims yield ages ranging between ~ 1450 and 1000 Ma, suggesting that the PLV was deposited at ~ 1.5 Ga, and underwent Pinwarian and Grenvillian metamorphisms. In addition, the core of a metamorphic monazite from an aluminous paragneiss in the PLV has yielded an age of 1445 ± 27 Ma ([Lasalle et al. 2014](#)).

The PLV is intruded by several plutonic suites in which it occurs as enclaves, e.g., granite and charnockite of the Bardoux Plutonic Suite (1497 Ma; [Augland et al. 2015](#)), felsic orthogneisses (including both older and younger tonalites of the Hulot Complex; ~ 1370 - 1440 Ma; [Gobeil et al. 2002, 2005](#); [Augland et al. 2015](#)), granite, monzonite, and tonalite of the Castoréum Plutonic Suite (1393 ± 8 Ma, [Moukhsil et al. 2013b](#); [Augland et al. 2015](#)), and undeformed mangerite of the Okaopéo Plutonic Suite (1014.6 ± 2.1 Ma; [Augland et al. 2015](#)). Furthermore, the PLV has been intruded by numerous younger dykes including those of gabbro-norite composition (1383.4 ± 1.1 Ma; [Augland et al. 2015](#)) in the Hulot Complex and many discordant felsic pegmatites and ultrapotassic dykes of late Grenvillian age (~ 980 - 990 Ma; [Dunning and Indares 2010](#)) in the Canyon domain.

The PLV in the Canyon domain has a high-grade metamorphic signature as revealed by the dominant metamorphic assemblage of Grt+Sill+Kfs $\pm$ Bt+Liq (abbreviations after [Whitney](#)

and Evans 2010) in aluminous rocks that were metamorphosed under the peak metamorphic conditions of 600-1100 MPa and 800-900 °C (Lasalle and Indares 2014; Patrick and Indares 2017) during the Ottawa phase of the Grenvillian Orogeny as indicated by monazite ages of ~1081-1038 Ma and metamorphic zircon ages of ~1076-1044 Ma (Dunning and Indares 2010; Lasalle et al. 2013, 2014).

The Mafic to intermediate unit (MIU)

The Mafic to intermediate unit (MIU) was first described from the type location (#395), near its boundary with the PLV, as an exposure of dark and light grey layers with the latter dated at 1410 ± 16 Ma (fig. 4a in Dunning and Indares 2010). At that location, the layers are massive, medium-grained, and lack coarse plutonic texture, and the layering was interpreted as an original feature indicative of a supracrustal volcanoclastic origin, with the rocks being meta-tuffs. The dark grey layers were also observed to contain leucocratic melts with $\text{Grt} \pm \text{Opx}$, and to occur as lenses or rafts within the light grey components. On the basis of lithology and age, Dunning and Indares (2010) tentatively correlated this unit with the Montauban Group to the southwest, which consists of remnants of an island arc accreted to the Laurentian margin (Nadeau and van Breemen 1994; Sappin et al. 2009). Later geochemical and isotopic data from a sample collected from the light grey layer of the unit was interpreted to indicate an origin in a mature continental arc setting (Valverde Cardenas et al. 2012). Subsequently, another exposure of the same belt to the north was discovered to consist of relict plutonic textures and original compositional layering (fig. 2a in Indares and Moukhsil 2013), which were interpreted as part of the mafic to intermediate unit formed as a shallow-depth layered intrusion. Based on pronounced compositional layering between different mafic parts and from the overall association of the unit, Indares and Moukhsil (2013) named it as the Layered Mafic Suite (LMS). This name was not

intended to imply that the whole unit consisted of layered intrusions in the classical sense, and both the names have been alternatively used in recent literatures (e.g., Lasalle et al. 2013, 2014; Patrick and Indares 2017). This unit at the type location has been pervasively cross-cut by late Grenvillian granite pegmatites dated at 995 ± 3.5 Ma (Dunning and Indares 2010).

The Quartzofeldspathic unit

The MIU is in local contact with a supracrustal sequence named the Quartzofeldspathic unit (QFU; Indares and Moukhsil 2013). Although of uncertain origin, the QFU contains (i) mafic rafts that exhibit geochemical signature similar to modern mature continental arcs (Valverde Cardenas et al. 2012), (ii) patches of a bimodal hydrothermally altered volcanic sequence (Hindemith and Indares 2017; Patrick and Indares 2017) named the Layered Bimodal Suite (LBS) that formed at 1238 ± 13 Ma (Indares and Moukhsil 2013; Lasalle et al. 2013), and (iii) an apparently younger magmatic complex named the Vein Complex (VC), which was thought to have formed due to felsic intrusion within the MIU (Indares and Moukhsil 2013). The age of the QFU and the mafic rafts within it were inferred to be ~ 1.4 Ga based on the presence of transposed felsic pegmatites in the unit that also occur in the PLV and MIU, but are absent from the LBS. Together these five units, the PLV, MIU, QFU, LBS, and VC constitute the major units exposed in the central and northern part of the Canyon domain (fig. 2).

Previous interpretations on tectonic evolution

Based on the inferred depositional age of PLV at >1500 Ma, and the intrusion of Bardoux suite at ca. 1497 Ma in an arc setting, the PLV was compared with the Wakeham Group farther east by Augland et al. (2015), who proposed that the former was deposited in a back-arc or intra-arc setting, consistent with the interpretations of Larbi et al. (2003), Corriveau and Bonnet (2005), Bonnet et al. (2005) and Corriveau et al. (2007). A recent seismic study has revealed that

the Wakeham Group continues to the southeast under Paleozoic cover on Anticosti Island (*fig. 1*; Pinet 2016), considerably enlarging the known extent of this unit.

On the basis of geochemical and Hf isotope data, the tectonic settings of the central Grenville Province have been deduced to have evolved from a ca. 1500 Ma continental margin arc to a ca. 1434 Ma distal-arc or microcontinent-arc setting followed by crustal shortening due to terrane accretion and subsequent arc formation at ca. 1413 Ma (Augland et al. 2015). Additionally, the voluminous metaluminous Renwick mangerite with a within-plate signature was emplaced at 1402 ± 72 Ma and is in thrust contact with the PLV (Moukhsil et al. 2012, 2013a). Another age of 1403^{+32}_{-25} Ma obtained by Indares and Dunning (2004) from a granodiorite body in the northeastern part of the Canyon domain near the Banded Complex, and is apparently part of the Renwick mangerite.

Field Relations of the mafic rocks

The mafic samples in the **PLV** come from concordant layers up to a few tens of centimeters thick that show sharp contacts with the layering in the paragneiss (*fig. 3a*). There is no evidence of intrusive or tectonic contact between the mafic layers and the PLV paragneiss, and therefore, the layers could be interpreted to be *in situ*. Alternatively, they could have intruded the paragneiss sequence as concordant sills. The mafic gneisses commonly contain thin leucocratic films or veins parallel to or crosscutting the layering (*fig. 3b*), and in places leucocratic pods enclose clusters of coarse-grained ferromagnesian minerals. These features are consistent with derivation by partial melting, either of the mafic layers, or of the host paragneiss, or both, and the latter case raising the possibility of melt injection within the mafic sills. Our samples for this study were collected from well preserved homogeneous regions within the mafic

layers that lacked leucocratic veins (*fig. 3c*), and hence are most likely to represent the original compositions.

As described above, the *Mafic to intermediate unit* at the type outcrop #395 was initially interpreted to be supracrustal in origin (Dunning and Indares 2010), but following recognition at a different location (#210) farther north that the unit also included components of shallow mafic intrusions that gave it a ‘layered’ appearance, it was renamed the Layered Mafic Suite (LMS; Indares and Moukhsil 2013). Follow-up fieldwork in 2011 at the extension of the type outcrop for the unit (#395) led to the identification of a wider range of lithologic types, varying from dark through intermediate to light grey in colour (D, I, and L, respectively; *fig. 3d*), which are documented in more detail in this study. The dark grey components are locally observed to be intruded by the light grey components, and feature sharp to diffuse, cusped and lobate contacts (*fig. 3e*). Elsewhere the dark and intermediate grey components are enclosed within the light grey components and exhibit evidence for partial disintegration, brecciation, and rounded to sub-rounded margins (*fig. 3d, f*). Moreover, the dark and intermediate grey components are commonly associated with thin leucocratic films or pods, in the absence of which the contacts range from sharp to diffuse. These contact relationships, together with the variable colour (and hence composition) of the mafic components ranging from dark grey through intermediate to light grey (*fig. 3d*), along with the presence of leucocratic films and pods in them, are indicative of multiple injections of different magma batches, complex magma mingling, and possible mixing in a sub-volcanic or shallow plutonic settings, such as has been documented in many intrusive complexes elsewhere (e.g., Vernon et al. 1988; Sutcliffe 1989; Sutcliffe et al. 1989; Castro et al. 1990; Lindline et al. 2004; Barbarin 2005). However, in addition to the original igneous complexity, dark grey components contain occasional garnet- and pyroxene-bearing

leucocratic veins (Dunning and Indares 2010) that are inferred to be the result of localized dehydration melting along the margins of dark and light grey (hornblende-rich) rocks (fig. 3d and e). Such melts are mostly small-volume and in-situ, and have not migrated significantly. As such, these mafic rocks are not similar to the migmatites reported from the amphibolitized margins of Fe-Ti gabbros from the Baie du Nord segment of the MIZ (fig. 3c in Cox et al. 1998), and from the mafic migmatites in the Kapuskasing Structural Zone (fig. 2 in Hartel and Pattison 1996). The samples collected for this study are massive and come from parts of the exposures free from leucocratic veins and visible hydrothermal alteration (fig. 3e).

Ideally, an appropriate informal name for this ca. 1.41 Ga unit should take into consideration its compositional range, intrusive mode of occurrence, and shallow plutonic origin. The name Layered Mafic Suite is no longer appropriate due to the lack of layering in the type outcrop and its unintended link with classical layered mafic intrusions. The original name, Mafic to intermediate unit, although coined to describe rocks that were inferred to be of volcanoclastic origin, is permissive of either a volcanoclastic or plutonic origin and sufficiently general to accommodate the observed major features of the unit described herein, and so is retained in this study pending more detailed evaluation of the unit as a whole. Thus henceforth in this paper we extend the original meaning of the term 'Mafic to intermediate unit' (MIU), for which an age of ca. 1.41 Ga has been determined for a mafic light grey component (Dunning and Indares 2010), to include rocks of a somewhat wider range of compositions that are deduced to be part of a shallow plutonic, mixed intrusive unit. At the extension of outcrop #395 from which the samples in this study come, there are no known rocks of supracrustal origin.

Sampling and Analytical techniques

The rocks in our study area in the central Grenville Province have undergone relatively low-strain mid-pressure granulite-facies metamorphism. In order to minimize the effects of metamorphism, we have taken special care to collect samples from the most lithologically coherent and unmelted parts of representative units in large exposures. For analytical purposes, we have only sampled rocks that were free of leucosomes and cross-cutting veins, and all samples were cut to remove weathered portions before proceeding to standard thin section preparation and crushing to produce powders for analysis.

Detailed petrographic study was carried out on 7 selected polished thin sections using an optical microscope and 5 samples were chosen for SEM mineralogical mapping using a Quanta 650 FEG-SEM. The Energy Dispersive Scanning (EDS) system in the SEM was used to semi-quantitatively identify and calculate modal abundances of mineral phases. Analyses were carried out under 25 kv acceleration potential and 10 nA beam current condition to obtain BSE images and EDS analyses. False colour mineralogical maps (*fig. 4*) showing the relationships and the distribution of the phases were produced by post-processing the BSE and EDS data using Mineral Liberation Analysis software on the SEM.

Fresh interiors of selected samples were used for standard crushing in a steel-plated jaw crusher and powdering in an agate ball mill. A portion of the powdered samples was selected for separation of zircon and CL imaging and U-Pb geochronology. CL imaging (*fig. 5*) of selected zircon grains was carried out using a CL detector attached to the FEI Quanta 400 SEM using a 15 kV acceleration potential and a 10 nA beam current. The procedure followed for U-Pb chemical abrasion thermal ionization mass spectrometry (CA-TIMS) analyses is given in the appendix.

305 In order to carry out whole rock Sm-Nd isotope ratio analyses of four samples by TIMS,
306 whole rock powders were dissolved in Savillex© Teflon beakers using an 8 ml (4:1) mixture of
307 29 M HF – 15 M HNO₃. Prior to acid digestion, a mixed ¹⁵⁰Nd/¹⁴⁹Sm spike was added to each
308 sample with both sample and spike being weighed on a high-precision balance. After five days of
309 digestion, the solution was evaporated to dryness and then taken back up in 6 M HCl for 2-3
310 days. The sample was dried down and then re-dissolved in 1.0 ml of 2.5 M HCL. Samples were
311 then loaded into a column containing cation exchange resin AG-50W-X8, H⁺ form, 200-400
312 mesh where a Sr fraction could be isolated followed by collection of bulk rare earth elements
313 (REE). This solution was then dried and taken up in 0.18 M HCl and loaded on a second column
314 containing Eichrom© Ln resin (50-100 mesh) to isolate Sm and Nd separately from the other
315 REEs. Sm and Nd concentrations and the Nd isotopic compositions were determined using a
316 multi-collector Finnigan Mat 262 mass spectrometer in static mode for concentration
317 determination, and dynamic mode for isotopic composition determination. Sm and Nd were
318 loaded onto a double rhenium filament assembly and instrumental mass fractionation of Sm and
319 Nd isotopes was corrected using a Raleigh law relationship relative to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and
320 ¹⁵²Sm/¹⁴⁷Sm = 1.783. The measured values were adjusted to the JNdi-1 standard (¹⁴³Nd/¹⁴⁴Nd =
321 0.512115, Tanaka et al. 2000). Our current measurement of JNdi-1 yields a mean ¹⁴³Nd/¹⁴⁴Nd =
322 0.512098. We also analyzed USGS whole rock reference material BCR-2 with each analysis
323 comprising a separate dissolution, providing the best estimate of the reproducibility of an
324 individual whole-rock analysis. The mean values of BCR-2 are as follows, where the relative two
325 standard deviations of the mean (n = 11) are given in parentheses in percent; ¹⁴³Nd/¹⁴⁴Nd =
326 0.512636 (0.0021%); ¹⁴⁷Sm/¹⁴⁴Nd = 0.1383 (0.389%); Nd ppm=27.7 (0.7%); Sm = 6.33 (0.6%).

Six selected mafic samples, one from the PLV and five from the MIU, were crushed and powdered using standard clean laboratory protocols, and were analyzed for whole rock major and trace element concentrations at the Activation Laboratories (Actlabs) Ltd. in Ontario, Canada. The standard analytical protocol involved fusing a measured weight of rock powder with lithium metaborate/ tetraborate to produce homogeneous glass beads that were analyzed using Perkin Elmer Sciex inductively coupled plasma mass spectrometry (FUS-ICP/MS) for trace elements. The details of all analytical protocols can be found on the Actlabs website (www.actlabs.com). The detection limits for the analyses are typically in the range of 0.01-0.001 % for major elements and 1-30 ppm for trace elements.

Results

Petrography

The mafic gneissic layers in the **PLV** are coarse-grained, heterogeneous, and display two different textural types. Type-I (#11-383c and M5-383E1; *fig. 4a*) is composed of Grt+Pl+Cpx+Opx+Qtz+Bt+Ilm±Hbl. Garnet porphyroblasts are extensively corroded and partially replaced by Pl+Cpx+Bt±Hbl±Opx. The matrix is composed of subgranoblastic Pl+Cpx+Opx+Qtz+Bt+Ilm±Hbl, with trace amounts of rutile, apatite, titanite, magnetite, sulphides, zircon, K-feldspar, allanite, monazite, and barite. K-feldspar is commonly associated with plagioclase, hornblende, and biotite. The samples with this textural type contain large, partly resorbed quartz grains (*fig. 4b*) of various shapes (sub-rounded to stretched ribbons) and sizes (up to 3.6 mm long ribbons) mantled by plagioclase, clino-, and orthopyroxene. Quartz grains in some of the PLV samples with Type-I texture are large and highly corroded indicating chemical disequilibrium with the matrix composition. Such large partially resorbed quartz grains in mafic rocks are generally interpreted to be xenocrystic (e.g., Kuno 1950; Sato 1975;

350 Koyaguchi 1986), and may provide a substrate in a hybrid melt to nucleate pyroxenes (e.g.,
 351 Hibbard 1981; Vernon 1990; Lindline et al. 2004). Their occurrences in mafic magmas may be
 352 indicative of mingling with felsic melts that were either produced during emplacement and
 353 stagnation of mafic magma in a crustal magma chamber, or they may have been derived by wall-
 354 rock assimilation during the ascent of mafic magma through continental crust. The preservation
 355 of quartz xenocrysts in the mafic sills indicates that homogenization of the contaminant with the
 356 mafic melt was incomplete (Hibbard 1981; Vernon 1990; Lindline et al. 2004). Type-II (#11-
 357 383e1; *fig. 4c*) is composed of large garnet porphyroblasts embedded in a matrix of
 358 Pl+Cpx+Opx+Hbl+Bt+Ilm. Garnet is variably corroded and replaced by Hbl+Cpx+Pl+Opx with
 359 the relict shape still preserved in some cases. This type does not have large quartz grains as
 360 observed in type-I, and contains allanite as an accessory phase. The mineral assemblage for the
 361 peak metamorphic stage in both the textural types in the PLV comprises Grt+Pl+Cpx+Opx,
 362 which was retrogressed under hydrous condition forming hornblende and biotite replacing
 363 garnet.

364 The main lithological components of the *MIU* analyzed in this study come from the dark,
 365 intermediate, and light grey components, which are Grt-Cpx-rich (*fig. 4d*), Hbl-Grt-Cpx-rich (*fig.*
 366 *4e*), and Pl-Hbl-rich (*fig. 4f*), respectively. The dark grey component is characterized by
 367 granoblastic idiomorphic garnet (1–5.5 mm) and clinopyroxene, along with orthopyroxene,
 368 ilmenite, hornblende, and minor plagioclase. Large apatite crystals, present both as inclusions (in
 369 garnet and clinopyroxene) as well as in the matrix, form a characteristic accessory phase in these
 370 samples. The intermediate grey component is composed of porphyroblastic garnet (0.8–3.7 mm)
 371 and clinopyroxene embedded in a matrix of Hbl+Pl+Opx+Ilm. Biotite constitutes an important
 372 minor phase. The light grey component contains large sub-idiomorphic garnet porphyroblasts

embedded in an overall coarse, crudely foliated matrix composed of subgranoblastic Hbl+Pl+Bt+Ap+Ilm+Ttn. The large garnet poikiloblasts indicate their formation favoured by vapour-absent dehydration reactions under upper amphibolite to granulite-facies conditions (e.g., Hartel and Pattison 1996; Pattison 2003; Pattison et al. 2003). Cpx is extremely rare in the matrix in the investigated sample and occurs as very small grains at two locations. Thin rims of Pl±Hbl±Bt wrap around large (6-15 mm) corroded poikiloblastic garnet, which contains inclusions of Plg+Cpx+Ilm+Ttn+Ap. Titanite in the matrix is less abundant and smaller in size than those within garnet. All the samples in the MIU contain accessory allanite, magnetite, and zircon. The petrographic evidences in the mafic rocks from the MIU are suggestive of different basaltic bulk compositions, and support the field interpretation of mingling between heterogeneously sourced magmatic components.

All the mafic rocks in our study have the mineral assemblage Grt+Pl+Hbl±Cpx±Opx that is indicative of mid-pressure granulite-facies metamorphism (e.g., Pattison 2003), which is consistent with the estimated *P-T* range for the peak metamorphism determined from the host paragneiss samples in the PLV mentioned earlier. The peak AFM mineral assemblage for dark grey samples comprises Grt+Cpx+Opx, whereas textures and abundance of hornblende in intermediate and light grey samples indicate hornblende could have been part of peak assemblage in these samples. Both the PLV and the MIU were retrogressed under variable hydrous conditions leading to the development of rims of hornblende and biotite around garnet porphyroblasts and pyroxenes, and in the matrix. Moreover, modal estimation of minerals in SEM-MLA provides variable amounts of chlorite-sericite-magnetite-carbonate-sulphides that are suggestive of hydrothermal alteration. The abundances of carbonates, magnetite, and sulphides

395 (total ~1.5 %) is highest in the dark grey rocks in the MIU, whereas sericite and chlorite (total
 396 ~5%) are most commonly developed after plagioclase and garnet in the light grey rocks.

397 **U-Pb isotope analyses**

398 One sample (#11-383C) from the mafic layers in the **PLV** was chosen for zircon U-Pb
 399 analysis. Zircon in this sample display three different morphologies— prisms, round to sub-round
 400 grains, and flat grains. The prisms show complex internal CL structures (*fig. 5*) e.g., relict
 401 prisms, xenocrystic and composite cores, sector zoning, local internal dissolution indicated by
 402 dark convolute structures, bright areas of recrystallization, and thin but well developed
 403 metamorphic rims. A few prisms are much larger than average (not shown in the figure) and are
 404 thought to be xenocrystic. The round to sub-round zircon have internal convolute structures in
 405 dark zones with low CL response that indicate dissolution, and bright areas with high CL
 406 response indicating local recrystallization, relict prisms, radial fractures, and sector zoning.
 407 These round to sub-round zircon grains are interpreted to be corroded and recrystallized prisms.
 408 The flat grains also show complex internal structures with well-developed metamorphic rims.
 409 We carried out five analyses of the euhedral clear prisms, comprising three single-grain analyses
 410 and two multigrain analyses composed of 3-4 grains each. The data are presented in *table 1* and
 411 plotted on a Concordia diagram (*fig. 5*). The data points defined a discordia line that intersects
 412 the Concordia at an upper intercept of 1439^{+76}_{-68} Ma, interpreted as the crystallization age, and a
 413 lower intercept of 1029^{+33}_{-47} Ma, interpreted as the age of growth of metamorphic rims.

414 **Sm-Nd isotopes**

415 Four samples were selected for Nd isotope analyses (*table 2*; *fig. 6*), two from the mafic
 416 layers in the PLV (#RS383E, 11-383c) and two from the representative dark grey rocks in the
 417 MIU (#11-395dx, 11-395d1). The samples from the PLV possess initial Nd isotopic ratios

($^{143}\text{Nd}/^{144}\text{Nd}$)_{ini} of 0.510807 and 0.510805, yield $\epsilon\text{Nd}_{1.4\text{ Ga}}$ values of -0.4, and T_{DM} model ages of 2.57 and 2.72 Ga, respectively. The samples from the dark grey rocks possess initial Nd isotope ratios of 0.510637 and 0.510595, and yield $\epsilon\text{Nd}_{1.4\text{ Ga}}$ values of -3.7 and -4.6, respectively. These two samples have yielded anomalously old model ages, which are not considered to be meaningful.

The high Sm/Nd ratios (>30), and shallow slopes, and anomalously old Archean model ages (>3.7 Ga) in the dark grey rocks suggest that their Sm-Nd isotope systematics have been modified, possibly by hydrothermal processes unrelated to regional high-grade orogenic metamorphism. For instance, [Rosing \(1990\)](#) showed that even a small change in the Sm/Nd ratio due to fluid-rock interaction may result in significant deviation of the calculated initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio and model age, and that such deviation may be modified exponentially by the time interval between crystallization and secondary disturbance leading to anomalously old model ages. The effect of secondary alteration on Sm-Nd isotopes similar to the dark grey rocks has also been demonstrated on Na- and K-metasomatized igneous clasts from the Paleoproterozoic Bonnetia volcanic arc terrane in Yukon ([Nielsen et al. 2013](#); their fig. 11 and 12).

Geochemistry

Both the PLV and the MIU have been subjected to Grenvillian mid-pressure granulite-facies metamorphism, and both the suites record evidence for partial melting and low-grade hydrothermal alteration. Therefore, it is necessary to assess the effects of partial melting and hydrothermal alteration on the major and trace element composition of the mafic rocks.

Effects of metamorphism and hydrothermal alteration

Effects on major elements

The mafic rocks in our study exhibit alteration index $[A.I = 100 \times (MgO + K_2O) / (MgO + K_2O + Na_2O + CaO)]$ (Ishikawa et al. 1976) between 33-48 (median value 37) and peraluminous index $(P.I = Al_2O_3 / (CaO + Na_2O + K_2O)_{mol.})$ between 0.56-0.89 (median value 0.62) (table 3), which are similar to fresh MORB and arc-related mafic volcanic rocks ($A.I = 36 \pm 8$ and 34 ± 10 , respectively, and $P.I = 0.8 \pm 0.2$; Laflèche et al. 1992). However, the mafic rocks from the PLV and the dark and intermediate grey rocks from the MIU exhibit $Al_2O_3 / Na_2O > 10$ suggesting Na-loss (Spitz and Darling 1978), and high chlorite-carbonate-pyrite index or CCPI > 90 suggesting carbonate-sericite-chlorite-sulphide alteration $[CCPI = 100 \times (MgO + FeO_t) / (MgO + FeO_t + K_2O + Na_2O)]$ (Large et al. 2001). However, caution should be taken with CCPI index since it is strongly correlated with magmatic fractionation and primary compositional variations in mafic rocks (Large et al. 2001). The alteration index K/Na in the mafic rocks vary between 0.2-0.9, suggesting them to be mostly unaltered ($K/Na = 2.0-0.5$) with four samples being moderately Na-altered ($K/Na = 0.5-0.1$) (Nielsen et al. 2013). Overall, the major element data suggest that the mafic rocks in our study are mostly unaltered except mobility in alkalis.

Effects on trace elements

One sample from the PLV (RS383E1) exhibit depletions in LREE relative to MREE $[(La/Sm)_{CN} \leq 1]$; subscript 'CN' stands for chondrite-normalized], strong negative Eu^* anomalies (0.38), high Ti/Eu (~ 11000), strong depletions in Zr and Hf, enrichments in Nb and Ta compared to La, and strong fractionation in Zr/Hf ratio (26). Two dark grey samples from the MIU also exhibit evidence for LREE depletions, strong -ve Eu^* anomalies (0.30-0.32), high Ti/Eu ($> 11,000$), and disturbance in Nd isotopic systematics due to fluid-rock interaction. These three samples are moderately altered with low K/Na and high CCPI values as is the sample RS209-1

from QFU. The mobility in HFSE, REE, and Eu^{2+} in these samples depends on the pH, chemistry, pressure-temperature, and redox condition of hydrothermal fluids (Jiang et al. 2005). Recently, argillic and carbonate alteration of various degrees by high-temperature CO_2 -rich fluids have been shown to have affected the ca. 1.24 Ga andesitic volcanic rocks from the LBS in the study area (Hindemith et al. 2017). Despite widely accepted notion that the REE and HFSE are ‘conservative’ elements (Pearce 1983; Tatsumi et al. 1986; Pearce and Peat 1995), several recent studies have shown that these elements can be mobile in magmatic, metamorphic, and submarine-hydrothermal environments (e.g., Ludden et al. 1982; Sorensen and Grossman 1989; Rubin et al. 1993; Jenner 1996; Woodhead et al. 2001; Kamber et al. 2002).

The rest of the samples with negative Eu^* anomalies ($\text{Eu}/\text{Eu}^* < 1$) indicate that they have not been subjected to partial melting and melt loss, since mafic restitic compositions would show positive Eu^* anomalies or decrease in original negative anomalies inherited from their protoliths (Rudnick 1992). The K/Rb ratios (150-775) in the mafic rocks mostly fall within the range of igneous fractionation trend (fig. 7a; Shaw 1968; Rudnick et al. 1985), which along with their $\text{Eu}/\text{Eu}^* < 1$ (fig. 7b) suggest that most of these samples have not been modified by partial melting or alteration. The increasing K/Rb ratios at $\text{K}_2\text{O} < 1$ wt% in the altered samples from the PLV and the dark grey rocks from the MIU indicate Rb loss (Rudnick 1992). However, LILE and LFSE are well known to be fluid-mobile under low-grade conditions, and hence will not be used in our study.

Th, although stable below amphibolite-facies conditions, can be mobile during high-grade metamorphism in a water-dominated system (Jenner 1996). In Th/U vs. La/Th diagram, the moderately altered samples plot within the field of igneous rocks because of loss in La. Some of the least altered mafic samples exhibit La/Th ratios (25-52; fig. 7c) higher than common

igneous rocks ($\text{La/Th} \leq 21$; Rudnick et al. 1985; Sun and McDonough 1989) suggesting Th mobility relative to La. However, their La/Th ratios do not correlate with any of the alteration indices; and moreover, the mafic samples in our study plot well within the permissible range of other least altered mafic granulites (e.g., Blein et al. 2003; Bonnet et al. 2005; Montreuil and Constantin 2010), for which Th has been successfully used as a tool in petrotectonic discrimination (e.g., Montreuil and Constantin 2010). High La/Th (>20) is common in many modern back-arc basin basalts e.g., the East Scotia and the Lau Basin Spreading Centres (Taylor and Martinez 2003; and references therein). Therefore, variability in Th in the least altered mafic rocks in our study is considered to be source characteristics and a result of the processes involved in the magma genesis (Valverde Cardenas et al. 2012).

Dehydration melting in mafic migmatites have been shown to produce leucosomes that are not significantly different in composition than their original protoliths (Sawyer 1991), and many recent studies have shown that such process have minor effect on immobile element remobilization in mafic gneisses (e.g., Smith et al. 2001; Blein et al. 2003). Although the large leucocratic portions were not sampled for this study, the field observation suggests that the small-volume in-situ melts, where melting occurred, are locally restricted in a way suggestive of the overall preservation of the bulk rock compositions (Vielzeuf et al. 1990). As for example, poikiloblastic garnet-bearing mafic migmatites in the marginal gabbro from the Baie du Nord segment in the MIZ have been shown have broadly retained their protolith compositions that are identical to the main unaltered Fe-Ti gabbro (Cox et al. 1998). Several recent studies of high-grade gneisses in the Grenville Province have demonstrated that high-grade metamorphism and hydrothermal alteration can be effectively isochemical for immobile-incompatible major and

trace elements e.g., HFSE and REE (Blein et al. 2003; Bonnet et al. 2005; Dickin and McNutt 2007; Sappin et al. 2009; Yardley 2012; Corriveau and Spry 2014).

In summary, since the mafic samples analyzed in this study were selected from the most homogeneous and least altered parts of outcrops in which no visible signs of partial melting or hydrothermal alteration were recognized, they are inferred to represent original protolith chemistry. This is also supported by lack of evidence for partial melting in hand specimens and on the thin-sections. Combined mineralogical, isotopic, and geochemical evidence suggest that the mafic samples are mostly unaltered to moderately altered in few cases, and that their immobile major and trace elements contents are largely unaffected by metamorphic or hydrothermal processes.

Major and trace elements

The major and trace element geochemistry of the mafic rocks from the PLV and the MIU are listed in table 3. All the oxide values are reported as weight percentages and the trace element concentrations are reported in ppm.

All the samples in the **PLV** have fairly restricted major element compositions with low SiO₂ (44-46), high TiO₂ (2.64-3.44) and FeO_(total) (17-19) characterizing them as ‘ferro-basalt’ or ‘FeTi basalt’ (fig. 8a) according to the classification of Byerly et al. (1976). They also display average Al₂O₃ (12.7-14), low MgO (~6), Mg# (0.37-0.40), Ni (40-70), Cr (50-70), and high Sc (~55) and V (435-742). Based on the immobile major and trace elements they are classified as tholeiitic (fig. 8b) sub-alkaline (fig. 8c) basalt. Note that the moderately altered sample RS383E1 has shifted to higher TiO₂ and lower Zr/TiO₂ side compared to the other samples.

The dark, intermediate, and light grey rocks from the **MIU** have distinct major elements concentrations. The dark grey rocks have very low SiO₂ (~40) along with high TiO₂ (~3.5-4) and

531 $\text{FeO}_{(\text{total})}$ (20-23) characterizing them as high Fe-Ti basalt (*fig. 8a*) of Byerly et al. (1976). These
 532 samples also have average Al_2O_3 (12-14), low MgO (6), Mg# (0.32-0.35), and high Sc (~63) and
 533 V (470-620). The intermediate grey sample is also a high FeTi basalt and it exhibits low SiO_2
 534 (43), high TiO_2 (3), $\text{FeO}_{(\text{total})}$ (20), average Al_2O_3 (12), and relatively higher MgO (7), Mg#
 535 (0.39), Sc (60), and V (803). The light grey rocks have relatively higher SiO_2 (46-47) and Al_2O_3
 536 (18-20), along with lower TiO_2 (~1.8), $\text{FeO}_{(\text{total})}$ (~12), MgO (3.56-4.64), Mg# (0.35-0.42), Sc
 537 (19-34), and V (134-302). The Ni and Cr contents are below the detection limit of ICP-MS for
 538 the dark and light grey rocks. All the three components are classified as tholeiitic (*fig. 8b*) sub-
 539 alkaline (*fig. 8c*) basalt to basaltic andesite.

540 In the chondrite-normalized REE diagrams, the samples from the **PLV** show low to
 541 moderate REE fractionation (*fig. 9a*) as indicated by $(\text{La/Yb})_{\text{CN}} = 2.0\text{-}2.6$, and high -ve Eu^*
 542 anomalies [$\text{Eu}/\text{Eu}^* = 0.67\text{-}0.86$; Eu^* refers to the value obtained by linear interpolation between
 543 adjacent elements]. Their overall REE patterns are very similar to E-MORB (although exhibiting
 544 much higher abundances than E-MORB) except for the -ve Eu^* anomalies. The moderately
 545 altered sample #RS383E1, however, is slightly depleted in LREE [$(\text{La}/\text{Sm})_{\text{CN}} = 0.8$] and
 546 relatively enriched in MREE [$(\text{Gd}/\text{Yb})_{\text{CN}} = 2.0$] with strong -ve Eu^* anomaly (0.38). In the **MIU**,
 547 the dark grey rocks are moderately fractionated in REE [$(\text{La}/\text{Yb})_{\text{CN}} = 1.9\text{-}3.5$] with flat LREE
 548 [$(\text{La}/\text{Sm})_{\text{CN}} = 0.8\text{-}1.3$], slightly enriched MREE [$(\text{Gd}/\text{Yb})_{\text{CN}} = 1.6\text{-}1.9$] (*fig. 9b*), and strong
 549 negative Eu^* anomalies ($\text{Eu}/\text{Eu}^* = 0.30\text{-}0.58$). Note that the two moderately altered samples (11-
 550 395dx and d1) are similar to #RS383E1 in the PLV. The intermediate grey sample is moderately
 551 fractionated in REE [$(\text{La}/\text{Yb})_{\text{CN}} = 3.6$] with enrichments in both LREE [$(\text{La}/\text{Sm})_{\text{CN}} = 1.7$] and
 552 MREE [$(\text{Gd}/\text{Yb})_{\text{CN}} = 1.6$], and weaker negative Eu^* anomaly ($\text{Eu}/\text{Eu}^* = 0.89$) compared to the
 553 dark grey rocks (*fig. 9c*). The light grey rocks are the most fractionated in REE [$(\text{La}/\text{Yb})_{\text{CN}} = 5\text{-}7$]

with enrichment in both LREE $[(La/Sm)_{CN} = 1.7-2.3]$ and MREE $[(Gd/Yb)_{CN} = 1.6-2.1]$, weak negative Eu* anomalies $(Eu/Eu^* = 0.83-0.85)$, and similar REE patterns to the intermediate grey sample (*fig. 9c*).

In primitive mantle-normalized multi-element diagram, the least altered samples from the PLV and the dark grey rocks from the MIU display distinct but small depletions in Th, Nb, Zr, and Ti (*fig. 9d and e*). The moderately altered dark grey rocks in the MIU show patterns similar to the PLV sample #RS383E1, such as depletions in Zr, Hf, Ti, and variable enrichment in Nb (*fig. 9d and e*). The intermediate and light grey samples in the MIU exhibit depletions in all HFSE and are variably depleted or enriched in Th (*fig. 9f*). Their multi-element patterns match well with two mafic samples from the ~1.4 Ga QFU (Valverde Cardenas et al. 2012) and the average composition of the Andean arcs (Kelemen et al. 2004).

Discussion

Significance of the U-Pb isotope data

The age data obtained in this study along with other recent studies from the Canyon domain are presented in *fig. 10*. In this study, sample #11-383c from the **PLV** has yielded an imprecise upper intercept age of 1439^{+76}_{-68} Ma (*fig. 5*). Considering the lower limit of uncertainty, there is a small overlap of about 11 Ma between the upper age bracket for PLV deposition of ~1.5 Ga and the age of emplacement of the dated mafic layer. However, our preferred interpretation, which is consistent with the interpreted field relationships, is that the mafic layers in the PLV are younger than the paragneiss sequence, and intruded the PLV at 1439^{+76}_{-68} Ma as concordant sills. Despite large uncertainties, this age is comparable with the age of emplacement of the ‘older tonalites’ in the Lac Okaopéo area farther south at 1434^{+7}_{-11} Ma

(Augland et al. 2015), and with the age of the core of a metamorphic monazite at 1445 ± 27 Ma (Lasalle et al. 2014).

The crystallization age of the *MIU* has been previously determined to be 1410 ± 16 Ma based on CA-TIMS U-Pb dating of zircon from a light grey layer (#04-395z; Dunning and Indares 2010). This correlates well with the age bracket of a pre-Grenvillian metamorphic event in the PLV between 1408 ± 24 Ma and 1391 ± 33 (Lasalle et al. 2013) determined from zircon rims in two metapelite samples. This post-Pinwarian metamorphic event (including uncertainties) in the PLV was previously attributed to the emplacement of the mafic rocks in the adjacent MIU (Indares and Moukhsil 2013; Lasalle et al. 2013), but can now also be related to the intrusion of the mafic sills in the PLV (this study), since the ages of the two units overlap within uncertainties.

The PLV was metamorphosed during the Ottawa phase of the Grenvillian Orogeny, as revealed by (i) monazite ages between ca. 1081-1038 Ma determined by TIMS (Dunning and Indares 2010), (ii) ages of BSE-dark grains or cores of monazites between ca. 1082-1059 Ma determined by LA-ICP-MS analyses (Lasalle et al. 2014), and (iii) metamorphic zircon ages between ca. 1076-1044 Ma determined by LA-ICP-MS analyses (Lasalle et al. 2013). Modelling of *P-T* paths for several paragneiss samples in the PLV has provided an estimated peak Ottawa metamorphic conditions of 600-1100 MPa and 800-900 °C, with retrograde conditions of 600-800 MPa and 800-865 °C (Lasalle and Indares 2014; Patrick and Indares 2017).

The PLV was also affected by the Rigolet phase as supported by (i) one concordant TIMS analysis of metamorphic monazite at 1001 ± 3 Ma (Dunning and Indares 2010), and (ii) the ages between ca. 1014-980 Ma obtained from BSE-bright metamorphic rims of monazites from the matrix of aluminous paragneiss samples (Lasalle et al. 2014). In this study, the CL images of

zircon from the mafic sills in the PLV (*fig. 5, i and ii*) reveal multiple metamorphic rims around prismatic igneous cores. Our data yield a lower intercept metamorphic age of 1029^{+33}_{-47} Ma, overlapping within uncertainties with the previous results, but also allowing for the possibility that the PLV could have been affected by Rigolet metamorphism. In the Lac Okaopéo area to the south, similar age of metamorphism was recorded from the main Pb-loss event in zircon at 1027 ± 25 Ma from the Bardoux pluton, and in one case an age of 1002 ± 2 Ma was yielded by a metamorphic zircon in the 1383.4 Ma metagabbro (Augland et al. 2015). The age of intrusion of the non-metamorphic Okaopéo plutonic suite at 1014.6 ± 2.1 Ma within the PLV was interpreted to provide a minimum age for the metamorphism of the PLV in the Lac Okaopéo area (Augland et al. 2015).

The late-Grenvillian ages documented in the PLV and metagabbro were ascribed to the thermal and/or fluid effects of several small granitic pegmatite intrusions and/or fluid-assisted greenschist-facies metamorphism during the Rigolet phase (Lasalle et al. 2014; Augland et al. 2015). However, the ca. 996.7-1005.4 Ma magmatic monazite in REE-rich pegmatitic granite dykes derived from partial melting of metasedimentary units at depth (Turlin et al. 2017) may suggest that the Canyon domain and the Lac Okaopéo area were subjected to short-lived, high-grade Rigolet metamorphism, which could have overprinted the peak Ottawa metamorphism.

Significance of the Sm-Nd isotope data

The mafic sills emplaced into the *PLV* have low $\epsilon_{\text{Nd}_{1.4\text{Ga}}}$ values (-0.4) that are just below the CHUR evolution line (*fig. 6*), which could indicate derivation from a non-depleted primitive mantle source. However, there is no evidence for such a mantle source at this time in rocks preserved in the Grenville Province. Therefore, depleted mantle modified by crustal components,

or enriched mantle, seem more plausible sources to explain the observed isotopic compositions of the mafic sills. From ca. 1.65-1.13 Ga, magmas derived from the SCLM to the southeast of the Superior Province were shown to be depleted suggesting the involvement of relatively young depleted mantle and crust with very short crustal residence time (Emslie and Hegner 1993). Such depleted mantle-derived melts could have interacted with enriched crustal components to produce the observed isotopic composition in the mafic sills. In this context, it is noteworthy that Emslie et al. (1997) postulated a role for either melting of, or contamination by, depleted old Labradorian SCLM to explain the source characteristics of the Michael Gabbro (1426±6 Ma; Schärer et al. 1986) and the Shabogamo Gabbro (1445±4 Ma; Krogh 1993), which were subsequently interpreted to have been emplaced in a back-arc setting inboard from, and parallel to, the Laurentian margin (Rivers and Corrigan 2000). Although comparable in terms of T_{DM} ages, these gabbroic dykes exhibit more enriched ϵNd values (-4.0 to -6.0) than the mafic sills in the PLV (ϵNd -0.4).

Two other analyses, one from the light grey sample dated at 1.41 Ga from the *MIU* and a mafic sample from the *QFU*, yielded ϵNd values of +0.0 to +0.9 at 1.4 Ga with model T_{DM} ages of 2.02-2.25 Ga (fig. 10; table 3) that were interpreted to indicate derivation from depleted mantle after crustal contamination (Valverde Cardenas et al. 2012).

The study area in the Manicouagan lies immediately to the north of the Quebecia terrane (fig. 1b; Nd model age of 1.55 Ga; Dickin and Higgins 1992; Dickin 2000), and is located within their Makkovikian model-age crust (Nd model ages range from 1.7-2.0 Ga; Thomson et al. 2011; Vautour 2015), which was suggested to have been reworked during the Labradorian Orogeny in a continental margin arc setting. The Nd data of the mafic rocks in our study correlate well with the data from the Makkovikian and older model-age crust (Dickin and Higgins 1992; Thomson et

al. 2011; Vautour 2015), supporting the interpretation of Thomson et al. (2011) that the Geon 14 arc-related rocks in the Canyon domain were formed on older crust that have Laurentian affinity, and that they are not part of an accreted terrane (Quebecia?) such as the Montauban arc located farther southwest in Portneuf – St. Maurice domain (Corrigan and van Breemen 1997; Sappin et al. 2009).

Petrogenesis

It is necessary to assess the possible effects of magmatic petrogenetic processes such as fractional crystallization, Fe-Ti enrichment, and degrees of crustal contamination before discussing the likely petrotextonic affinities of the mafic rocks in our study. The operating premise of this part of the study is that critical use of isotope, major, and trace elements (REE, and HFSE) data from the samples in the PLV and MIU that are inferred to be least altered and represent their original protolith chemistry can provide insights into the petrogenetic processes, origin, and tectonic setting of the mafic units.

Fractional crystallization and Fe-Ti-P enrichment

The high-grade mafic rocks of both the PLV and MIU have major and trace elements suggestive of their protoliths to be tholeiitic basalts in composition. They exhibit low MgO, Mg#, Ni, Cr, and –ve Eu anomalies that are indicative of their derivation from evolved magmas after fractional crystallization of early olivine, clinopyroxene, and plagioclase at source. The least altered mafic rocks of the PLV and the dark and intermediate grey rocks in the MIU display high TiO₂, FeO_(total), and P₂O₅ at very low contents of SiO₂, characterizing them as high Fe-Ti (and –P) mafic tholeiites, formally known as “ferrobasalt” or “high Fe-Ti basalt” (Byerly et al. 1976), which in the terrestrial record is now well-known to be spatially restricted to extensional tectonic settings in both oceanic and continental environments. Peng et al. (2013) discussed the

different processes suggested by various authors to be responsible for the enrichment of Fe-Ti content in mantle-derived mafic magmas. In both oceanic and continental extensional settings, the mechanism of Fe-Ti-P enrichment in tholeiitic basalt has been explained by a combination of high degrees (up to 74%) of plagioclase, clinopyroxene, and olivine fractionation and accumulation of Fe-Ti oxides and apatite in a closed system under low fO_2 conditions, suggesting generation of such basalt in a shallow level extensional setting (Clague and Bunch 1976; Byerly et al. 1976; Brooks and Nielsen 1978; Sinton et al. 1983; Juster et al. 1989; Brooks et al. 1991). The high Fe-Ti-P mafic rocks in our study indicate early olivine, clinopyroxene, and plagioclase fractionation with decreasing MgO along a tholeiitic trend. They are rich in Fe-, Ti-, and P-bearing phases such as ilmenite, titanite, and apatite. Moreover, they exhibit high REE contents with marked negative Eu* anomalies, features characteristic of ferrobasalts that have experienced up to 90% fractional crystallization in back-arc spreading centres (Pearce et al. 1994). In summary, we postulate that the mafic rocks in this study have experienced significant early olivine, clinopyroxene, and plagioclase fractionation coupled with Fe-Ti oxide and apatite saturation following the “Fenner” trend under low fO_2 conditions in a shallow level closed magma chamber. This is compatible with the generation of high Fe-Ti-P mafic rocks in an extensional setting.

In modern oceanic environments, high Fe-Ti-P basalts have been documented at the propagating tips of spreading centres along many mid-ocean ridges e.g., Galapagos spreading centre (Byerly et al. 1976; Juster et al. 1989) and East Pacific Rise (Clague and Bunch 1976; Pearce et al. 1986), in oceanic back-arc basins e.g., Lau Basin (Pearce et al. 1994), and along spreading centres propagating into an island arc crust e.g., Josephine Ophiolite (Harper 2003). In continental settings, such magmas are documented in modern continental rifts e.g., Afar Rift

(Barberi et al. 1974) and the Red Sea (Cocherie et al. 1994), ancient plume-related continental rifts e.g., the Mesoproterozoic high Fe-Ti-P rocks of western Shandon in the North China Craton (Peng et al. 2013), in ancient intra-cratonic rifts e.g., Broken Hill Block of Australia (Rutherford et al. 2006; Raveggi et al. 2007), and in almost all major Proterozoic anorthosites or AMCG complexes worldwide (Ashwal 1978, 1982; Philpotts 1981; also for examples relevant to SE Laurentian margin see Duchesne 1990; Owens and Dymek 1992; McLelland et al. 1994; Dymek and Owens 2001; Hébert et al. 2005; Charlier et al. 2006, 2008). Considering the active continental margin setting at 1.4 Ga along the southeastern margin of Laurentia, we infer that the high Fe-Ti-P mafic rocks in our study were formed in a continental margin back-arc or intra-arc extensional setting as has also been suggested for the Renzy terrane in the western Grenville Province that has an inferred minimum age of ca. 1.40 Ga (Montreuil and Constantin 2010).

Crustal contamination

In the PLV, the mafic sills exhibit major and trace element compositions, e.g., HFSE depletion relative to REE (fig. 9), low to moderate LREE enrichment, and relatively higher SiO₂ compared to other Fe-Ti-P metabasalts from the study area, and slightly enriched εNd values, all of which suggest that their source was variably modified by crustal components, either in a subduction-related process or by crustal assimilation. Th is considered to be a reliable indicator of crustal input when compared with other incompatible elements such as Nb (Pearce and Peat 1995; Pearce 2008). On the Th/Yb vs. Nb/Yb diagram (fig. 11a, Pearce and Peat 1995; Pearce 2008), the mafic sills from the PLV plot on the mantle array between N-MORB and E-MORB precluding significant input from felsic upper crust or substantial melting of subducted sediments in an arc source. Therefore, their mantle source could have been modified by minor input from subduction-related fluids causing the low Th and variable enrichments in the LILE. Melts

derived from such fluid-metasomatized mantle were probably subjected to contamination by old mafic granulitic lower crust during ascent through attenuated continental crust prior to emplacement within the PLV sequence. The low Th in these samples and the presence of xenocrystic zircon may also support the involvement of attenuated continental lower mafic crust (e.g., Peng et al. 2013).

The least altered dark and intermediate grey rocks from the *MIU* exhibit very low SiO₂ and low to moderate LREE enrichment, precluding significant contamination by upper crust or subduction components (Zheng and Hermann 2014; Dai et al. 2015). Their chondrite-normalized REE patterns and small –ve Nb anomalies may suggest an enriched E-MORB-type source similar to the source for the PLV samples. Although the light grey rocks display a higher proportion of SiO₂ and LREE enrichment at low positive εNd values, assimilation and fractional crystallization (AFC; DePaolo 1981a) processes involving upper crust would significantly increase SiO₂ content and decrease εNd values, which is not the case for these rocks. Therefore, a Paleoproterozoic juvenile mafic crust is probably a more suitable candidate as a potential contaminant of the mafic rocks in the MIU, as suggested by several authors for other mafic rocks of this age elsewhere in the Grenville Province (e.g., Dickin and Higgins 1992; Sappin et al. 2009). The mafic samples from the QFU, however, exhibit higher SiO₂ contents (~53%) at εNd of 0.0. Moreover, their variably enriched Th contents (in table 3 and fig. 9f) may suggest increased crustal input through subduction-processes and/or crustal contamination. In all these mafic samples from the MIU and QFU, their variable SiO₂ contents, depletions in HFSE compared to REE in the primitive mantle-normalized multi-element plots (fig. 9), and variably depleted to enriched Th contents that exhibit a trend from an enriched MORB-like mantle towards continental arc or lower crust (fig. 11a), all suggest variable degrees of addition of

subduction components and/or contamination by juvenile mafic crust in their mantle sources. As such, the mingling of mafic magmas derived from heterogeneous mantle sources in a shallow magma chamber, while undergoing variable degrees of contamination by heterogeneous crustal components, is considered to be the most plausible interpretation for the mixed intrusive nature of the MIU.

Tectonic setting

The least altered mafic rocks from the PLV and the dark grey samples from the MIU exhibit values of Zr/Y (2-3), Zr/Yb (21-30), Zr/Hf (34-38), Ti/Y (245-297), and Ti/Zr (93-129) ([table 3](#)) that are comparable to those of average N-MORB (2.6, 24, 36, 272 and 103, respectively; average N-MORB values from [Sun and McDonough 1989](#)). The intermediate grey sample exhibits somewhat higher values in Ti/Y (457) and Ti/Zr (187). The light grey rocks (except RS395A2) from the MIU and the mafic rocks from QFU exhibit slightly wider range of values in Zr/Y (2-5), Zr/Yb (19-46), Zr/Hf (29-39), Ti/Y (201-314), and lower Ti/Zr (47-99).

On the Th/Yb–Nb/Yb diagram ([fig. 11a](#)) of [Pearce \(2008\)](#), the samples from the PLV and the dark and intermediate grey sample from the MIU plot along the mantle array, whereas the light grey rocks show a trend of increasing Th/Yb towards continental arc or crust. When considered together, the mafic components (dark, intermediate and light grey) from the MIU, along with the mafic rocks from QFU, exhibit a trend (grey shaded area in [fig. 11a](#)) from ocean floor basalt to continental margin arc basalt, suggesting a range of melt sources present at this time. In order to further constrain the tectonic setting(s) of their formation, the mafic samples in our study have been plotted on several REE- and HFSE-based tectonic discrimination diagrams ([fig. 11 b-d](#)), where the mafic sills intruding the PLV straddle the depleted to enriched MORB fields with a weak trend towards arc, whereas the mafic rocks from the MIU and QFU define a

clear trend from MORB to calc-alkaline arc basalt, a result of variable enrichment from crustal components. The moderately altered samples are slightly scattered due to alteration biases for the elements used in these diagrams, which shifts the positions of the samples away from the Hf and Zr corners with a slight bias towards the Nb, Y, and Th corners; however, this has not affected the plots significantly and less weightage is given to these moderately altered samples.

Therefore, we infer that the high Fe-Ti-P mafic sills in the *PLV* exhibit evidence for a variably depleted to enriched MORB source that formed in an extensional setting on an active continental margin, with minor input from subduction components and contamination by older mafic granulitic lower crust. Considered collectively with the geochronological data, this is most compatible with continental intra-arc or back-arc rifting at or before 1439^{+76}_{-68} Ma.

In the *MIU*, the mafic rocks formed at ca. 1410 Ma, and the mafic rocks in the QFU with an inferred age of 1.4 Ga, were derived from mantle sources with a range of tectonic affinities from enriched MORB to continental arc, and were further variably modified by subduction and/or crustal contamination by Paleoproterozoic juvenile mafic crust. Such diverse geochemical signatures are characteristic of many modern and ancient active continental margin back-arc basins, and have recently been reported for post-Pinwarian mafic rocks in the western Grenville Province (e.g., Renzy terrane with an inferred minimum age of 1.40 Ga; Montreuil and Constantin 2010). The increasing influence of arc or crustal components in the MIU and QFU suggests that the margin evolved from continental intra-arc or back-arc extension to crustal shortening before ca. 1410 Ma, resulting in increasing proximity of the back-arc source to the arc itself.

Tectonic Model and Implications

Recent studies by several workers in the central Grenville Province have led to the availability of a large amount of high-quality data enabling a refinement of the Mesoproterozoic tectonic evolution of the study area. Of particular importance are the following observations:

1. The ages obtained from the fragmental igneous cores of detrital zircon in the aluminous paragneisses and quartzite of the PLV range between ~1.5-2.7 Ga, with the dominant peak at ~1.7-1.9 Ga, and subsidiary peaks at ~1.5 Ga and ~2.5-2.7 Ga, indicating the major supply of the detritus was derived from the nearby Labradorian and Makkovikian crust (Lasalle et al. 2013; Moukhsil et al. 2013a). This age distribution is very similar to that of the eastern part of the Wakeham Group (WG; Wodicka et al. 2003; van Breemen and Corriveau 2005), suggesting that the provenance of detritus in both basins was from the Laurentian margin. This is difficult to reconcile with the accretion model of the Labradoria terrane at 1.65 Ga and the Quebecia terrane at 1.45 Ga (Dickin and Higgins 1992; Martin and Dickin 2005).
2. The similar ages of detrital clastic sources in the PLV and WG, together with their similar depositional ages of ≥ 1.5 Ga, support the previously proposed back-arc or intra-arc settings for the WG related to an early phase of the accretionary Pinwarian Orogeny (Rivers and Corrigan 2000; van Breemen and Corriveau 2005; Corriveau and Bonnet 2005; Rivers et al. 2012; Lasalle et al. 2013; Augland et al. 2015).
3. The presence of ~1500 Ma detrital zircon in both the PLV and the WG suggests that part of the detritus in both the basins was derived from early-Pinwarian crust of felsic composition, which was most probably part of the continental-margin arc. Intra-arc

volcanism of that age has been well documented farther east in both the Musquaro sector of the Wakeham Group and in the La Romaine supracrustal belt, a southeastern extension of the Wakeham Group (*fig. 1a*; Corriveau and Bonnet 2005; Bonnet et al. 2005).

4. The PLV and its proposed correlatives have been recognized over a large area in the central Grenville Province (Manicouagan area) and extended accross the Makkovikia, Labradoria, and Quebecia terranes, whereas the WG is restricted to the Labradoria terrane in the east (*fig. 1*).
5. The Bardoux Plutonic Suite, emplaced at ca. 1497 Ma within the PLV, also covers a wide area spanning the Labradoria, Makkovikia, and the Quebecia Nd model-age terranes, and is suggested to have formed in a continental margin arc setting (Augland et al. 2015). The documentation of several felsic to mafic metavolcanic rocks, subvolcanic plutons, and pillow lavas in the western WG with evolved geochemical signatures (Martignole et al. 1994), together with evidence for associated syn-volcanic hydrothermal activity, suggests development of a continental back-arc to intra-arc basin related to the early Pinwarian arc (Corriveau and Bonnet 2005). Metavolcanic rocks of comparable age to the Bardoux Plutonic Suite have also been reported from the eastern WG (Lac Musquaro area; *fig. 1a*), for which a depositional age between ca. 1.52-1.50 Ga has been determined (van Breemen and Corriveau 2005). These metavolcanic rocks formed between 1511 ± 13 and 1491 ± 7 Ma (van Breemen and Corriveau 2005), and were approximately coeval with several granitic orthogneisses emplaced between 1505 ± 12 and 1494 ± 12 Ma (SHRIMP U-Pb of zircon; O. van Breemen and L. Corriveau, unpublished, cited in Corriveau and

Bonnet 2005) that exhibit evolving geochemical signatures suggestive of within-plate to continental margin arc settings (Corriveau and Bonnet 2005). Moreover, the earlier 1.53 Ga tonalitic intrusions (SHRIMP U-Pb zircon; O. van Breemen and L. Corriveau, unpublished, cited in Corriveau et al. 2003) that have volcanic arc granite or syn-collisional granite geochemical signatures were interpreted to be representative of an early Pinwarian intra-arc setting in the La Romaine supracrustal belt (Corriveau and Bonnet 2005; Bonnet et al. 2005) farther east (fig. 1a).

The above observations suggest that there is compelling temporal and tectonic correlation between the PLV in the central Grenville Province and the WG in the eastern Grenville Province. As suggested previously by Augland et al. (2015) for the Lake Okaopéo area immediately south of the Manic 5 reservoir, it is reasonable to assume that the PLV was formed in an early Pinwarian active margin arc/back-arc setting similar to that of the WG, and that these terranes were not accreted to the continental margin. Indeed, although preserved as physically separate entities over ~200 km apart and lying on substrates with different model ages, both the PLV and WG are extensive units (figs. 1 and 2), and it appears feasible that they may be remnants of a single elongate back-arc basin or two coeval back-arc basins. Therefore, based on the above observations and integrating our results with those of Augland et al. (2015) from the nearby Lac Okaopéo area located immediately south of the Manic 5 reservoir, and also taking into account the conclusions of Schellart (2008a, b) on back-arc extension and trench migration in active arc systems, the evolution of the study area in the central Grenville Province is proposed:

1. Ca. **1500 Ma**: The early-Pinwarian (>1500 Ma) continental-margin arc undergoes back-arc or intra-arc extension, forming a short-lived basin in which the PLV was deposited within a short time interval at ca. 1500 Ma (fig. 12a; Lasalle et al. 2013).

Back-arc extension gives way to compression and possible inversion (?) of the back-arc basin (*fig. 12b*), leading to intrusion of the Bardoux Plutonic Suite within the PLV at 1497 ± 5 Ma (*Augland et al. 2015*). The dominantly volcanic arc to subordinate within-plate type geochemical signatures and positive ϵ_{Hf} values (4.7-2.3) of the granitoids composing this suite have been interpreted to indicate contamination of juvenile mantle-derived felsic magma with older Makkovikian model-age crust, as indicated by their T_{DM} model ages (1.9-2.05 Ga; *Augland et al. 2015*). Although we do not see any direct evidence of an early-Pinwarian arc in the study area, remnants of it have been reported from farther east in the Grenville Province in Labrador and Québec (*Tucker and Gower 1994; Gower and Krogh 2002; Corriveau and Bonnet 2005; Wodicka et al. 2003*). Furthermore, the close temporal (*fig. 10*) and spatial relationships between the youngest age of deposition of the PLV and the intrusion of the arc-related Bardoux granitoids into the PLV supports the interpretation that the PLV was deposited in an arc-related setting. We further suggest that the within-plate character and juvenile mantle signature exhibited by some samples from the Bardoux Plutonic Suite provide cryptic evidence of earlier extension within the early-Pinwarian (>1.5 Ga) arc through which the granitoid magmas were intruded. These geochemical features are widespread in the Wakeham group, where an evolution of geochemical signatures from within-plate to continental margin arc has been reported (*Corriveau and Bonnet 2005*).

2. Ca. **1440-1430 Ma**: Limited back-arc extension coeval with Geon 14 arc formation was postulated to have occurred along much of the length of the Grenville Province by *Rivers and Corrigan (2000)*. This is compatible with our data from the central

Grenville Province in which the 1439^{+76}_{-68} Ma high Fe-Ti-P mafic sills in the PLV with variably depleted to enriched MORB signatures were contaminated by minor subduction components and old mafic granulitic lower crust as they intruded the sequence in an extensional back-arc rift setting (*fig. 12c*). The source for these mafic rocks must have evolved in a shallow magma chamber before being emplaced within the PLV. This interpretation is compatible with the geochemical signature of the coeval ‘older tonalites’ of the Hulot Complex, which intruded the PLV at 1434^{+7}_{-11} Ma farther south in Lac Okaopéo area, (Augland et al. 2015). These were interpreted to have been derived from juvenile mantle-derived magma ($\epsilon\text{Hf} = +8$ to $+10$) contaminated by Labradorian (~ 1.6 Ga) crust in a distal arc or microcontinent-arc setting (Augland et al. 2015). Some of their samples of the ‘older tonalites’ plot in the within-plate field in the Rb-(Ta+Yb) diagram (*fig. 3* in Augland et al. 2015; Moukhsil et al. 2013b) and show a trend towards peralkaline granite (Lars Augland, personal communication, 2016), which may suggest the influence of an extensional setting farther inboard, possibly related to thinning of the Labradorian arc crust. Rims of detrital zircon in the PLV dated at ~ 1450 Ma (Lasalle et al. 2013) and the cores of metamorphic monazite in the PLV dated at ~ 1445 Ma (Lasalle et al. 2014) may record these igneous events.

3. Ca. **1410 Ma**: The mafic rocks from the MIU emplaced at 1410 ± 16 Ma (Valverde Cardenas et al. 2012) and the inferred 1.4 Ga mafic rocks from the QFU, both of which indicate enriched MORB and arc sources that developed in an inboard back-arc environment and were variably modified by subduction components and/or contamination by Paleoproterozoic crust (*fig. 12d*). The geochemical and isotopic

characters displayed by the arc to transitional-arc and non-arc compositions of these rocks support the presence of multiple sources that are typical of a back-arc setting developed inboard from, but in close proximity to, the continental-margin arc. Farther south from the Canyon domain in the Lac Okaopeó area, the ‘younger tonalites’ of the Hulot Complex, dated at 1413 ± 12 Ma and exhibiting more radiogenic Hf isotopic signatures ($\epsilon_{\text{Hf}} = 6.27\text{--}8.04$), were inferred to have formed in an arc setting as a result of increased proximity of the arc source due to shortening (and thickening?) of the Laurentian margin (Augland et al. 2015). Therefore, considering the ages with their uncertainties, and the probable proximity of the MIU and the ‘younger tonalites’, a tectonic setting possibly reflecting processes such as roll-forward (slab advance) of the subducting slab, or shortening of the proximal (outboard) part of the back-arc basin, and coeval extension within the distal part of the basin seems most plausible. Both this igneous activity and the associated inferred tectonic activity could explain the growth of zircon in the PLV as metamorphic grains and rims between $\sim 1391\text{--}1408$ Ma (Lasalle et al. 2013). This outboard shortening of the active margin could be temporally related to the post-Pinwarian island arc/back-arc accretion (e.g., the ca. 1.45–1.39 Ga Montauban Group and La Bostonnais complex; Nadeau and van Breemen 1994; Sappin et al. 2009), and arc/back-arc development on the thin Laurentian margin (e.g., the ca. 1.40–1.35 Ga Bondy Gneiss Complex; Blein et al. 2003).

The end of the Pinwarian orogeny (1.52–1.46 Ga) in southeastern Laurentia was characterized by AMCG magmatism (Gower and Krogh 2002), with the granodiorite in the Banded Complex (1403^{+32}_{-25} Ma; Indares and Dunning 2004) and the Renwick mangerite

(1402 ± 72 Ma; Moukhsil et al. 2012, 2013a) possibly being a local representative of this suite.

Both the mantle and crustal signatures of the component parts of these complexes interpreted to have formed in a continental back-arc setting (Rivers and Corrigan 2000; Rivers et al. 2012).

Most of the post-Pinwarian interval up to the onset of the Grenvillian Orogeny was characterized by short-lived compressional arc to extensional intra-arc or back-arc settings, involving both continental and oceanic arcs, and marginal basin settings. In the study area, we have documented two important magmatic events during Geon 14 that characterize the evolution from an extension to compression in a back-arc and related compressional arc developed on attenuated Laurentian margin. Such an oscillating structural evolution between extension and compression in continental margin arcs over time scales of a few 10s of Ma, and the associated isotopic 'pull-up' and 'pull-down' of ϵNd values, is typical of modern continental arcs (e.g., DeCelles et al. 2009).

An important feature of the Geon 14 magmatism in the central Grenville Province was the emplacement of mantle-derived high Fe-Ti-P mafic tholeiites that were variably contaminated by crustal sources. The repetitive intrusion of small volumes of high Fe-Ti-P magma is compatible with limited extension in a long-lived arc/back-arc regime (e.g., Montreuil and Constantin 2010). Back-arc or intra-arc extension appears to have played an important role in the subduction-related processes on the southeastern margin of Laurentia during and after the Pinwarian Orogeny (e.g., Blein et al. 2003; Slagstad et al. 2004, 2009; Corriveau and Bonnet 2005; Sappin et al. 2009; Montreuil and Constantin 2010), suggesting that a large part of the margin would have been dominated by thin, thermally weak, and rheologically soft crust that underwent repetitive arc formation and accretion followed by intra-arc or back-arc extension. This process of repetitive arc formation and accretion followed by intra-arc or back-arc extension

appears to have continued throughout the remainder of the Mesoproterozoic up to the beginning of the Grenvillian Orogeny (Rivers and Corrigan 2000).

Conclusions

The tectonomagmatic and related metamorphic events during Geon 14 in the central Grenville Province constitute an important part of the pre-Grenvillian evolution of the southeastern margin of Laurentia. In the last decade significant efforts have been directed to deciphering the details of these events that have been obscured by later high-grade metamorphism and associated deformation during the Grenvillian Orogeny. This study represents an attempt to see through this Grenvillian veil and interpret the geochemistry and tectonic significance of two suites of mafic rocks presently preserved as mid-pressure granulites. Specifically, analysis of the suite of mafic sills emplaced into the metasedimentary Complexe de la Plus Value (PLV), and of the mafic intrusive rocks comprising the mafic to intermediate unit (MIU) has provided more detailed information about the pre-orogenic magmatism and hence the inferred architecture of this part of the Laurentian margin during Geon 14, and its possible implications for the pre-Grenvillian and Grenvillian orogenic evolution of SE Laurentia. The main conclusions of the study are:

1. The 1439^{+76}_{-68} Ma mafic sills intruded the PLV supracrustal sequence (>1500 Ma) during limited extension of arc/back-arc crust, resulting in thinning of the Laurentian continental margin. These mafic sills were derived from variably depleted to enriched MORB-type mantle and were modified by minor subduction components and contamination by old mafic granulitic lower crust.

2. The mafic intrusive rocks in the MIU, characterized as arc to transitional-arc and non-arc types, were formed at ca. 1410 Ma in a back-arc setting where shortening of the Laurentian crust increased the proximity of the back-arc to the more outboard arc source as suggested by increased crustal input from subduction components and/or contamination. The various magmatic components in the unit were mingled in a shallow closed magma chamber before their final emplacement.
3. Repetitive intrusion of the high Fe-Ti-P mafic rocks during Geon 14 in the central Grenville Province suggests that arc/back-arc extension was an important process in an overall compressional arc regime on SE Laurentia during the Mesoproterozoic. Such a tectonic setting resulted in prolonged but limited extension of thin, hot, and ductile crust.

These conclusions are compatible with both the general model of an active margin on SE Laurentia during the Mesoproterozoic, suggested previously by others, and with more recent work in the central Grenville Province, but provide significant new details and refinements for the region.

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Table captions

Table 1: U–Pb data for mafic sample #11-383c in the Complexe de la Plus Value (PLV), Canyon domain.

Table 2: Sm–Nd isotope data for the mafic rocks from the Canyon domain. See footnote of the table for data sources and other details.

Table 3: Major and trace element data for the mafic rocks from the Canyon domain. See footnote of the table for data sources and other details.

Figure Captions

Fig. 1. (a) Schematic map of the Grenville Province showing principal crustal age (U–Pb) domains in the pre-Grenvillian Laurentian crust (simplified from [Rivers et al. 2012](#)), with the southern continuation of the Wakeham Group under Paleozoic rocks on Anticosti Island after [Pinet \(2016\)](#); (b) Schematic map of the Grenville Province showing principal crustal blocks or terranes based on crustal formation ages (Nd model ages; modified from [Thomson et al. 2011](#) and [Vautour 2015](#)). A, Anticosti Island; AB, Allochthon Boundary; BG, Bondy Gneiss Complex; B, Bardoux Plutonic Suite; LJ, Lac Joseph allochthon, largely composed of metasedimentary rocks with a Makkovikian model age; M, Manicouagan Impact Crater; Mo, Montauban; Mq, Lac Masquaro; R, Musquaro-La Romaine extension; TLB, Trans-Labrador batholith; W, Wakeham Group.

Fig. 2. Simplified geological map of the study area in the Canyon domain located to the south of Manicouagan Impact Crater (compiled after [Indares and Dunning 2004](#); [Dunning and Indares 2010](#); [Moukhsil et al. 2013a, b](#); and [Augland et al. 2015](#)). Note that the boundaries of the Banded Complex, Canyon domain, and the Island domain ([Dunning and Indares 2010](#)) are not well defined.

Fig. 3. Field photographs of the mafic rocks in the Complexe de la Plus Value (PLV; a-c) and in the intrusive rocks of the Mafic to intermediate unit (MIU; d-f). (a) A typical outcrop (#11-383c) of PLV showing mafic layers interpreted as intrusive sills within the paragneiss; (b) Close up of a mafic sill in the PLV showing contact with layered paragneiss and injection of leucocratic veins (partial melts from the paragneiss indicated by arrows) that are oriented parallel and transverse to paragneiss layering; (c) Outcrop of a homogeneous mafic sill interlayered with paragneiss but mostly free from injected leucocratic veins; (d) Outcrop of MIU showing different mafic components ranging from dark (D) to intermediate (I) to light grey (L) along with leucocratic films and pods; (e) Light grey component intruding and mingling with the dark grey component within the MIU showing a sharp to diffuse cusped-lobate contact between them, and some parts of the dark grey component are partially disaggregated within the light grey component indicating contemporaneity of, and mingling between, the two phases; (f) Disintegration of rounded to sub-rounded fragments of the more mafic dark and intermediate grey components within the less mafic light grey component, indicative of the effects of magma mingling.

Fig. 4. SEM-MLA mineralogical maps and photomicrograph of mafic rocks in the Complexe de la Plus Value (PLV; a-c) and the intrusive rocks of the Mafic to intermediate unit (MIU; d-f) from the Canyon domain. (a) Type-I texture in sample #11-383c in the PLV showing poikiloblastic garnet in a heterogeneous matrix composed of plagioclase, orthopyroxene, clinopyroxene, biotite, ilmenite, and quartz. Note the presence of large quartz grains and their association with orthopyroxene in the matrix; (b) Photomicrograph in plane-polarized light showing large ribbon shaped quartz xenocryst partially mantled partially by pyroxenes and plagioclase observed in Type-I; (c) Type-II texture in sample #11-383E1 in the PLV showing

large garnet porphyroblasts in a matrix of plagioclase, hornblende, clinopyroxene, ilmenite and minor biotite (note the abundance of hornblende, larger garnet, and absence of large quartz grains in this sample); (d) Dark grey component of MIU (#11-395d1) with large subidiomorphic garnet and clinopyroxene with ubiquitous ilmenite, apatite, orthopyroxene, and minor hornblende and plagioclase; (e) Intermediate grey component of MIU (#11-395a1) with medium grained garnet porphyroblasts in a matrix of hornblende, plagioclase, clinopyroxene, orthopyroxene, biotite and ilmenite; (f) Light grey component of MIU (#11-395) showing large poikiloblastic garnet porphyroblasts rimmed by plagioclase with subordinate amount of hornblende and biotite; matrix composed of plagioclase, hornblende, and biotite that wraps around garnet. Each MLA map is ~4cm in length (standard size of a thin section).

Fig. 5. U-Pb concordia diagram with CL images of representative prismatic zircon from mafic sill #11-383c in the Complexe de la Plus Value (PLV).

Fig. 6. ϵNd vs. time plot showing the mafic sills in the Complexe de la Plus Value (PLV) and the intrusive rocks of Mafic to intermediate unit (MIU) in the Canyon domain (this study) plotted at 1.4 Ga. Data for the mafic rocks from the QFU with an inferred ~1.4 Ga age are from [Valverde Cardenas et al. \(2012\)](#); evolution lines and fields for Quebecia, Makkovikia, and the Gagnon terrane are from [Thomson et al. \(2011\)](#); depleted mantle evolution line after [DePaolo \(1981b\)](#).

Fig. 7. (a) K_2O vs. Rb plot (modified after [Rudnick et al. 1985](#)); (b) Eu/Eu^* vs. K/Rb plot (modified after [Rudnick 1992](#)) and (c) Th/U vs. La/Th plot (modified after [Rudnick et al. 1985](#)); for the mafic rocks from the Complexe de la Plus Value (PLV) and the intrusive rocks of the Mafic to intermediate unit (MIU) in the Canyon domain. Data for the mafic gneisses from Bondy gneiss complex ([Blein et al. 2003](#)), mafic rocks from the QFU ([Valverde Cardenas et al. 2012](#)),

and the Renzy terrane amphibolites (Montreuil and Constantin 2010), all with a known or inferred age of ~1.4 Ga are also shown.

Fig. 8. Rock-type classification diagrams for mafic samples from the Complexe de la Plus Value (PLV) and the intrusive rocks of the Mafic to intermediate unit (MIU) in the Canyon domain. (a) FeO_t vs. TiO_2 diagram showing high Fe-Ti basalt fields (after Byerly et al. 1976); (b) $\text{Al-Fe}_{\text{tot}}+\text{Ti-Mg}$ diagram (after Jensen and Pyke 1982); (c) Zr/TiO_2 vs. Nb/Y diagram (after Winchester and Floyd 1976; modified by Pearce 1996). Symbols as in fig. 7.

Fig. 9. Chondrite-normalized REE (a-c) and primitive mantle-normalized REE and HFSE (d-f) patterns for the mafic samples in the Complexe de la Plus Value (PLV) and for the intrusive rocks in the Mafic to intermediate unit (MIU). (a) Mafic sills in the PLV; (b) Dark grey rocks, and (c) Intermediate and light grey rocks in the MIU. Multi-element (REE and HFSE) diagrams for the mafic rocks in (d) PLV; (e) Dark grey rocks, and (f) Intermediate and light grey rocks in the MIU. Normalizing values for chondrite and primitive mantle are from Sun and McDonough (1989). Also shown for comparison the patterns of N-MORB and E-MORB (Sun and McDonough 1989), average Andean arc (Kelemen et al. 2014), and the inferred ~1.4 Ga mafic rocks from the QFU (Valverde Cardenas et al. 2012).

Fig. 10. Summary of U-Pb ages from the Canyon domain and the Lac Okaopéo area. Data points are colour coded and sources are mentioned on the figure. Vertical error bars indicate uncertainties associated with ages; the upper age limit of detrital zircon from the PLV is ~1500 Ma and the downward-pointing arrow indicates the oldest detrital grain at ~2700 Ma (from Lasalle et al. 2013).

Fig. 11. (a) Th/Yb vs. Nb/Yb (after [Pearce 2008](#)); (b) La/10–Y/15–Nb/8 (after [Cabanis and Lecolle 1989](#)); (c) Th–Hf/3–Nb/16 (after [Wood 1980](#)); and (d) Zr/4–Nb*2–Y (after [Meschede 1986](#)) diagrams showing data plots for the mafic sills in the Complexe de la Plus Value (PLV) and the intrusive rocks of the Mafic to intermediate unit (MIU) in the Canyon domain. Data for the average lower and upper continental crust (LCC and UCC) after ([Rudnick and Gao 2014](#)), rest of the data source and symbols are as in fig. 7 and 9. Vectors at bottom right in (a) indicate trends of subduction zone enrichment (S), crustal contamination (C), within-plate enrichment (W), and fractional crystallization (f).

Fig. 12. Schematic cross-sections illustrating the proposed tectonic model for the Geon 14 evolution of the southeastern Laurentian margin in the Canyon domain of central Grenville Province (modified from [Hanmer et al. 2000](#); [Blein et al. 2003](#)). Data compiled from [Dunning and Indares \(2010\)](#); [Moukhsil et al. \(2012, 2013a, b\)](#); [Lasalle et al. \(2013\)](#); and [Augland et al. \(2015\)](#).

Table 1: U–Pb data for the sample of mafic sill in the Complexe de la Plus Value (PLV), Canyon domain.

		Concentration		Measured	Corrected atomic ratios (c)								Age [Ma]			
Sample #11-383c	Weight	U	Pb rad	total common Pb	$^{206}\text{Pb}/$ ^{204}Pb	$^{208}\text{Pb}/$ ^{206}Pb	$^{206}\text{Pb}/$ ^{238}U	2σ	$^{207}\text{Pb}/$ ^{235}U	2σ	$^{207}\text{Pb}/$ ^{206}Pb	2σ	$^{206}\text{Pb}/$ ^{238}U	$^{207}\text{Pb}/$ ^{235}U	$^{207}\text{Pb}/$ ^{206}Pb	
		[mg]	[ppm]	[ppm]	[pg]			+/-		+/-		+/-				
Fraction		a	b													
Z1	1 euh prm	0.002	303	57.4	5.6	996	0.0573	0.1938	78	2.1362	120	0.07994	36	1142	1161	1196
Z2	1 best prm	0.002	273	52.2	9.3	559	0.0536	0.1961	152	2.1664	202	0.08012	54	1154	1170	1200
Z3	1 euh prm	0.002	202	45.2	9.7	449	0.098	0.2196	140	2.5749	236	0.08504	66	1280	1294	1316
Z4	4 best euh prm	0.006	47	9.2	5.6	653	0.0589	0.1999	90	2.2271	184	0.08079	56	1175	1190	1216
Z5	3 clr euh prm	0.004	49	8.7	2.1	1228	0.0473	0.1838	100	1.9325	170	0.07628	58	1087	1092	1102

Notes:

All zircon grains was chemically abraded (Mattinson 2005) prior to dissolution. Z, zircon; 2, 4, number of grains in analysis; prm, prism; sml, small; euh, euhedral; clr, clear.

- Weights of grains were estimated, with potential uncertainties of 50% for these small samples.
- Radiogenic lead
- Atomic ratios corrected for fractionation, spike, laboratory blank of 1-2 picograms (pg) common lead, and initial common lead at the age of the sample calculated from the model of Stacey and Kramers (1975), and 0.3 pg U blank. Two sigma uncertainties are reported after the ratios and refer to the final digits.

Table 2: Sm-Nd isotope data for the mafic rocks from the Canyon domain.

Sample	Geol. Domain	Nd (ppm)	Sm (ppm)	Sm/Nd	¹⁴⁷ Sm/ ¹⁴⁴ Nd _{calc}	¹⁴³ Nd/ ¹⁴⁴ Nd _{meas}	2σ	¹⁴³ Nd/ ¹⁴⁴ Nd _{ini}	εNd ₀	εNd _{1.4 Ga}	T _{DM}
RS383E ⁺⁺	PLV	34.13	9.25	0.27	0.1638	0.512314	8	0.510807	-6.2	-0.4	2573
383c	PLV	30.64	8.58	0.28	0.1693	0.512362	7	0.510805	-5.2	-0.4	2723
395-d1	MIU	56.22	16.86	0.30	0.1813	0.512304	7	0.510637	-6.4	-3.7	
395-dx	MIU	52.70	16.81	0.32	0.1928	0.512368	7	0.510595	-5.1	-4.6	
RS395a ₂ ⁺	MIU	44.38	9.856	0.22	0.1342	0.512106	3	0.510871	-10.2	0.9	2015
RS209-1 ⁺	QFU	20.99	5.15	0.25	0.1482	0.512191	6	0.510828	-8.6	0.0	2247

Notes:

1. calc = calculated, meas = measured, ini = initial, T_{DM} = depleted mantle model age.
2. T_{DM} values are calculated based on present day (¹⁴⁷Sm/¹⁴⁴Nd)_{DM} = 0.2137 and (¹⁴³Nd/¹⁴⁴Nd)_{DM} = 0.513160 (Goldstein et al. 1994) of depleted mantle based on the assumption that this mantle was separated from the CHUR at 4.55 Ga with a linear evolution, and present day εNd value of +10.
3. T_{DM} = 1/λ × ln[1+{(¹⁴³Nd/¹⁴⁴Nd)_{sample} - 0.513160}/{(¹⁴⁷Sm/¹⁴⁴Nd)_{sample} - 0.2137}]
4. εNd and T_{CHUR} values are calculated based on chondrite uniform reservoir (CHUR) values of ¹⁴⁷Sm/¹⁴⁴Nd = 0.1960 ± 4 and ¹⁴³Nd/¹⁴⁴Nd = 0.512630 ± 11 (2⁻) (Bouvier et al. 2008), and λ ¹⁴⁷Sm = 6.539 (± 0.061) × 10⁻¹² Yr⁻¹ (Begemann et al. 2001). 2⁻ = 2 standard error of the mean × 10⁻⁶.
5. (¹⁴⁷Sm/¹⁴⁴Nd)_{calc} = Sm/Nd × [0.53151+0.14252 (¹⁴³Nd/¹⁴⁴Nd)_{meas}]
6. The results of isotopic measurements for Nd reference material JNdi-1 (Nd) = 512098 ± 6 (2σ, n = 15).
7. Samples with superscript + are from Valverde Cardenas et al. (2012); superscript ++ indicates previously analyzed samples published here; all samples recalculated based on the values of CHUR and DM used here.
8. All model ages and εNd values are calculated using U-Pb crystallization ages (t) determined for the mafic sill in PLV (this study), the light grey rock in MIU (Dunning and Indares 2010), and an estimated age of 1.4 Ga for the QFU (Valverde Cardenas et al. 2012; Indares and Moukhsil 2013).

9. Sm and Nd concentrations were obtained by FUS-MS and have detection limits of 0.1 ppm.

Draft

T_{CHUR}
1495
1526
1292
1399

Draft

Table 3: Major and trace element data for the mafic rocks from the Canyon domain.

Suite	PLV	PLV	PLV	PLV	MIU	MIU	MIU	MIU	MIU	MIU	MIU	QFU	QFU
Sample	11-383c	RS383E ⁺⁺	RS399 ⁺⁺	RS383E1 ⁺⁺	11-395dx	11-395d1	11-395d4	RS395A1	11-395	11-395g2	RS395A2 ⁺	RS206C1 ⁺	RS209-1 ⁺
SiO ₂	46.21	45.03	43.76	44.36	40.55	40.36	40.38	42.58	46.55	46.54	46.08	53.38	52.95
Al ₂ O ₃	13.35	13.14	14.01	12.69	13.53	12.30	14.07	12.56	19.05	20.34	18.09	14.55	15.83
Fe ₂ O _{3(T)}	19.44	20.30	19.75	20.72	23.75	25.44	22.01	21.85	13.26	13.06	13.35	14.34	12.83
MnO	0.30	0.30	0.28	0.32	0.41	0.45	0.33	0.27	0.18	0.16	0.19	0.22	0.19
MgO	5.72	6.03	6.53	6.6	5.86	6.04	5.96	7.08	4.64	3.56	4.82	4.73	8.13
CaO	9.60	10.05	10.27	10.08	10.63	11.49	10.71	10.72	8.83	8.56	9.08	8.15	8.15
Na ₂ O	1.66	1.17	1.00	1.54	0.95	0.59	1.32	1.14	3.01	3.00	3.02	0.78	0.74
K ₂ O	0.89	0.90	0.67	0.59	0.40	0.13	0.84	0.89	1.91	2.06	1.83	0.77	0.23
TiO ₂	2.65	2.84	2.64	3.44	3.70	4.05	3.52	2.99	1.78	1.83	1.82	2.12	0.94
P ₂ O ₅	0.48	0.49	0.44	0.32	0.45	0.70	0.45	0.27	0.52	0.78	0.50	0.45	0.07
LOI	-0.64	-0.87	-0.28	-0.6	-0.67	-0.96	-0.55	—	0.87	0.13	0.45	—	-0.02
Total	99.66	99.38	99.07	100.06	99.56	100.59	99.04	100.35	100.6	100.02	99.23	99.49	100.04
FeO _t	17.49	18.27	17.77	18.64	21.37	22.89	19.8	19.66	11.93	11.75	12.01	12.9	11.54
#Mg	0.37	0.37	0.40	0.39	0.33	0.32	0.35	0.39	0.41	0.35	0.42	0.40	0.56
Sc	50	52	50	58	63	66	60	60	29	19	34	43	37
V	460	446	435	742	616	470	623	803	282	134	302	260	229
Cr	50	52	71	—	—	—	—	60	—	—	—	40	288
Co	130	233	177	203	189	148	171	278	66	53	158	297	168
Ni	40	50	64	70	—	—	—	100	—	—	—	30	81
Cu	80	26	45	35	20	20	20	70	20	—	—	10	34
Zn	130	158	133	209	130	170	180	210	90	140	190	180	161
Y	58	57	49	70	91	104	86	39	34	31	43	60	28
Zr	170	183	154	50	152	216	164	96	112	425	135	272	57
Hf	4.5	5.1	4.5	2.0	4.1	5.2	4.8	2.9	3.1	8.5	4.0	6.9	2.0
Ga	19	19	23	18	18	15	28	21	24	25	25	21	21
Ge	2	—	—	—	4	3	3	2	2	2	1	2	—
Nb	14	13	9	27	34	27	27	9	9	10	11	14	4
Ta	2.0	1.0	0.5	1.5	3.7	2.5	3.4	0.8	1.0	1.0	0.5	0.9	0.3
Rb	48	40	17	9	11	2	9	29	64	62	101	40	10
Ba	310	269	141	198	111	22	115	147	1000	1085	614	556	63
Sr	134	122	221	156	110	73	163	149	897	949	606	212	132
Pb	—	—	—	—	—	—	—	7	—	7	21	8	—
Th	0.5	0.6	0.4	1.0	1.1	1.1	2.4	0.6	1.0	2.8	1.6	3.2	3.2
U	0.5	0.5	0.3	0.7	0.6	0.6	1.2	0.3	0.4	0.6	0.7	1.3	1.6

Table 3: Continued

Suite	PLV	PLV	PLV	PLV	MIU	MIU	MIU	MIU	MIU	MIU	MIU	QFU	QFU
Sample	11-383c	RS383e ⁺⁺	RS399 ⁺⁺	RS383e1 ⁺⁺	11-395dx	11-395d1	11-395d4	RS395A1	11-395	11-395g2	RS395A2 ⁺	RS206C1 ⁺	RS 209-1 ⁺

Cs	0.6	—	—	—	—	—	—	0.4	0.5	0.6	1.3	0.4	—
La	16.7	17.4	19.1	16.0	23.2	27.1	39.2	19.3	25.2	32.5	29.4	41.3	12.6
Ce	45.4	49.1	51.2	48.8	68.0	75.8	112.0	54.5	60.7	78.0	73.4	91.5	34.2
Pr	6.8	7.1	6.9	7.9	11.1	11.6	16.8	7.5	8.6	9.7	10.2	11.8	4.7
Nd	32.8	33.1	32.0	41.6	55.6	57.9	76.1	31.7	40.3	42.7	45.3	49.7	20.8
Sm	9.3	9.2	8.5	13.7	18.4	18.1	19.1	7.5	9.4	9.0	10.2	10.9	5.4
Eu	2.08	2.28	2.48	1.78	1.90	1.95	3.47	2.19	2.33	2.41	2.85	2.71	1.10
Gd	9.6	10.1	9.1	14.8	20.5	19.6	17.4	7.6	7.9	8.3	9.6	10.7	5.4
Tb	1.7	1.9	1.7	2.7	3.3	3.3	2.7	1.3	1.2	1.3	1.5	1.9	1.0
Dy	10.7	10.8	9.5	14.5	18.4	19.3	15.3	7.0	6.8	6.8	7.7	10.6	5.5
Ho	2.2	2.2	1.9	2.6	3.5	3.8	3.0	1.3	1.4	1.3	1.4	2.0	1.1
Er	6.3	6.7	5.8	7.4	9.9	10.9	8.8	3.9	3.8	3.6	4.2	6.2	3.3
Tm	0.93	1.02	0.87	1.05	1.42	1.61	1.28	0.61	0.55	0.54	0.62	0.94	0.50
Yb	5.9	6.2	5.4	6.2	8.9	10.3	8.0	3.8	3.6	3.3	3.8	5.9	3.0
Lu	0.97	0.88	0.79	0.84	1.36	1.59	1.26	0.56	0.55	0.53	0.55	0.85	0.40
ΣREE	151.4	158.0	155.2	179.9	245.5	262.9	324.4	148.9	172.4	200.0	200.8	247.0	98.9
Eu/Eu*	0.67	0.72	0.86	0.38	0.30	0.32	0.58	0.89	0.83	0.85	0.88	0.77	0.62
Ti/Eu	7638	7467	6382	11586	11674	12451	6081	8185	4580	4552	3828	4690	5123
Zr/Hf	38	36	34	26	37	42	34	33	36	50	34	39	29
Ti/Y	274	297	321	293	244	233	245	457	314	354	251	210	201
Zr/Y	2.9	3.2	3.1	0.7	1.7	2.1	1.9	2.4	3.3	13.7	3.1	4.5	2.0
Ti/Zr	93	93	103	412	146	112	129	187	95	26	81	47	99
Zr/Yb	29	30	29	8	17	21	21	25	31	129	35	46	19
(La/Nb) _{PM}	1.2	1.3	2.2	0.6	0.7	1.0	1.5	2.3	2.9	3.4	2.7	3.1	3.5
(Nb/Th) _{PM}	3.3	2.7	2.9	3.2	3.7	2.9	1.3	1.9	1.1	0.4	0.8	0.5	0.1
(La/Yb) _{CN}	2.0	2.0	2.6	1.8	1.9	1.9	3.5	3.6	5.0	7.1	5.5	5.1	3.0
(Gd/Yb) _{CN}	1.3	1.3	1.4	2.0	1.9	1.6	1.8	1.6	1.8	2.1	2.1	1.5	1.5
(La/Sm) _{CN}	1.2	1.2	1.4	0.8	0.8	1.0	1.3	1.7	1.7	2.3	1.9	2.4	1.5
A.I	37.0	38.0	39.0	38.0	35.0	34.0	36.0	40.0	36.0	33.0	35.0	38.0	48.0
CCPI	91	93	94	93	96	98	93	93	78	77	79	92	96
P.I	0.63	0.62	0.67	0.59	0.63	0.56	0.62	0.56	0.83	0.89	0.77	0.52	0.57
K ₂ O/Na ₂ O	0.5	0.8	0.7	0.4	0.4	0.2	0.6	0.8	0.6	0.7	0.6	1.0	0.3
Al ₂ O ₃ /Na ₂ O	8.0	11.2	14.0	8.2	14.2	20.8	10.7	11.0	6.3	6.8	6.0	18.7	21.4

Notes:

1. The oxide concentrations are reported in wt%, whereas trace element concentrations are reported in ppm.
2. The deviation of Eu from the rest of the REE can be expressed as Eu anomaly (Eu/Eu*), where Eu* refers to the value obtained by linear interpolation between adjacent elements.
3. $FeO_t = 0.8998 \times Fe_2O_3$; $Ti = 5995 \times TiO_2$
4. #Mg is calculated as $\#Mg = MgO / (MgO + Fe_2O_{3\ total})$ in moles.
5. Superscript + indicates 1.41 Ga arc rocks from Valverde Cardenas et al. (2012). QFU, Quartzofeldspathic unit (see Indares and Moukhsil 2013 for definitions).
6. Superscript ++ indicates previously analyzed unpublished data.
7. Subscript 'PM' indicates primitive mantle-normalized and 'CN' indicates chondrite-normalized values of Sun and McDonough (1989).
8. A.I, alteration index; P.I, peraluminous index; CCPI, chlorite-carbonate-pyrite index; see text for details.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 6

Fig. 7

Fig. 8

Fig. 9

- X - Youngest detrital zircon in PLV
- - Igneous zircon
- ◇ - Metamorphic zircon
- - Metamorphic monazite
- △ - Metamorphic titanite

- ▲ ● Dunning and Indares 2010
- ◆ × Lasalle et al. 2013
- Lasalle et al. 2014
- ◆ ● Augland et al. 2015
- ◆ ● This study

Fig. 10

Fig. 11

Fig. 12

Appendix

CA-TIMS U-Pb in zircon (after Sparkes and Dunning 2014)

The zircon grains analyzed in sample 11-383c were selected from mineral concentrates using tweezers under the microscope according to criteria of clarity, similarity of crystal form and lack of inclusions. All grains were chemically abraded using the Mattinson (2005) chemical abrasion thermal ionization mass spectrometry (CA-TIMS) technique. The selected crystals of zircon were annealed at 900 °C for 36 hours prior to etching in concentrated HF acid in a pressure bomb at 200 °C for a few hours. This procedure is designed to remove any altered domains from the crystal that may have undergone lead loss. It is a remarkably effective and simple procedure and has now largely replaced physical abrasion (Krogh 1982) for zircon analysis.

Single grains or a small number of zircon grains were grouped into fractions of like morphology to allow precise measurement of all Pb masses on the mass spectrometer. At an age of ca. 1000 Ma, for clear high quality zircon, this amounts to 2-5 grains of zircon per fraction. These etched zircon fractions were washed in distilled HNO₃, then doubly distilled H₂O, prior to loading in Krogh-type TEFLON dissolution bombs. A mixed ²⁰⁵Pb/²³⁵U tracer was added in proportion to the sample weight, along with ca. 15 drops of distilled HF, then the bomb was sealed and placed in an oven at 210 °C for 5 days. Ion exchange chemistry was carried out according to the procedure of Krogh (1973), with modified columns and reagent volumes scaled down to one tenth of those reported in 1973. The purified Pb and U were collected in a clean beaker in a single drop of ultrapure H₃PO₄.

Lead and uranium were loaded together on outgassed single Re filaments with silica gel and dilute H₃PO₄. Mass spectrometry was carried out using a multi-collector MAT 262. The

Faraday cups were calibrated with NBS 981 lead standard and the ion-counting secondary electron multiplier (SEM) detector was calibrated against the Faraday cups by measurement of known lead isotopic ratios. The small amounts of Pb were measured by peak jumping on the SEM, with measurement times weighted according to the amounts of each mass present. U was measured by peak jumping on the SEM. A series of sets of data were measured in the temperature range 1400 to 1550 °C for Pb and 1550 to 1640 °C for U, and the best sets combined to produce a mean value for each ratio. The measured ratios were corrected for Pb and U fractionation of 0.1% /amu and 0.03%/amu respectively as determined from repeat measurements of NBS standards. The ratios were also corrected for laboratory procedure blanks (1-2 picograms - Pb, 0.3 picogram - U) and for common lead above the laboratory blank with lead of the composition predicted by the two-stage model of [Stacey and Kramers \(1975\)](#) for the age of the sample. Ages are calculated using the decay constants recommended by [Jaffey et al. \(1971\)](#).

The uncertainties on the isotopic ratios and ages were calculated using an unpublished program and are reported as two sigma in [table 1](#). Ages are reported as the weighted average of the $^{206}\text{Pb}/^{238}\text{U}$ ages calculated using ISOPLOT, and are reported at the 95% confidence interval.

As a check on the accuracy of the entire laboratory procedure, nine U-Pb analyses of the TEMORA zircon standard ([Black et al. 2003](#)) were carried out overlapping in time with the measurement of these samples, using the same detector and measurement conditions. These were reported by [Sparkes and Dunning \(2014\)](#). Eight of nine analyses overlap and yielded a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 416.84 Ma (MSWD = 0.18), in close agreement with the published value (416.75 Ma, [Black et al. 2003](#)).

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