

# New Cryogenian, Neoproterozoic, and middle Paleozoic U–Pb zircon ages from the Caledonia terrane, southern New Brunswick, Canada: better constrained but more complex volcanic stratigraphy

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## ABSTRACT

New U–Pb zircon ages from volcanic, plutonic, and sedimentary units in the Avalonian Caledonia terrane of southern New Brunswick provide better timing constraints in this geologically complex area. Previous ca. 620 Ma ages from the Broad River Group are now corroborated by additional dates from felsic tuff in the Gordon Falls Formation and rhyolite in the former Fairfield (now East Branch Black River) Formation of  $620 \pm 5$  Ma and  $622 \pm 1.9$  Ma, respectively. Combined with ages ranging from ca. 625 Ma to 615 Ma from cross-cutting plutons, the data suggest that the minimum age of the Broad River Group is about 615 Ma. A quartz-feldspar porphyry dyke in mafic volcanic rocks of the previously undated Long Beach Formation yielded an igneous crystallization age of  $685 \pm 10$  Ma, the oldest unit yet dated in the Caledonia terrane but similar in age to porphyry in the Stirling belt in the Avalonian Mira terrane of Nova Scotia. The age of the Coldbrook Group was constrained previously by U–Pb (zircon) ages of volcanic rocks between 560 and 550 Ma as well as by similar ages from comagmatic plutons. Five additional samples from both volcanic and plutonic units lie in the same range of 560–550 Ma, including errors, demonstrating that the Coldbrook Group and related plutons formed in less than 10 million years. Such a large volume of mainly felsic magma erupted and emplaced in a short time span suggests a “supereruption/supervolcano” environment such as the late Cenozoic southwestern USA but not yet recognized at ca. 560–550 Ma elsewhere in Avalonia. Two units yielded Paleozoic ages: felsite of the Bloomsbury Mountain Formation with a zircon population at  $427 \pm 9$  Ma, indicating a Silurian maximum emplacement age, and dacite of the Grassy Lake Formation with several zircon grains at  $382.8 \pm 8.3$  Ma, indicating a maximum age of middle Devonian, the first rocks of this age to be identified in the Caledonia terrane.

## RÉSUMÉ

De nouveaux âges U – Pb sur zircon provenant d'unités volcaniques, plutoniques et sédimentaires dans le terrane avalonien Calédonie du sud du Nouveau-Brunswick fournissent de meilleures contraintes temporelles dans cette région géologiquement complexe. Les âges d'environ 620 Ma précédemment obtenus du Groupe de Broad River sont maintenant appuyés par des dates supplémentaires provenant du tuf felsique dans la Formation de Gordon Falls et de la rhyolite dans l'ancienne Formation de Fairfield (maintenant East Branch Black River) de  $620 \pm 5$  Ma et  $622 \pm 1,9$  Ma, respectivement. Combiné avec des âges allant de 625 Ma à 615 Ma à partir de plutons encaissés, les données suggèrent que l'âge minimum du Broad River Group est d'environ 615 Ma. Un dyke de porphyre de quartz-feldspath dans des roches volcaniques mafiques de la Formation de Long Beach non datée a donné un âge de cristallisation ignée de  $685 \pm 10$  Ma, la plus ancienne unité encore datée dans le terrane de Calédonie mais similaire en âge au porphyre dans la ceinture de Stirling dans le terrane avalonien Mira de la Nouvelle-Écosse. L'âge du Groupe de Coldbrook était auparavant limité par les âges U – Pb (zircon) des roches volcaniques entre 560 et 550 Ma, ainsi que par les âges similaires des plutons co-magmatiques. Cinq échantillons supplémentaires provenant des unités volcaniques et plutoniques se situent dans la même période de 560 à 550 Ma, y compris les erreurs, démontrant que le Groupe de Coldbrook et les plutons associés se sont formés en moins de 10 millions d'années. Un volume aussi important de magma principalement felsique ayant entré en éruption et mis en place dans un court laps de temps suggère un environnement de "super-éruption / supervolcan" tel que le sud-ouest du Cénozoïque supérieur aux États-Unis, mais pas encore reconnu entre 560–550 Ma ailleurs dans la zone d'Avalonia. Deux unités ont donné des âges paléozoïques: la felsite de la Formation de Bloomsbury Mountain avec une population de zircon à  $427 \pm 9$  Ma, indiquant un âge de mise en place maximal du Silurien, et la dacite de la Formation de Grassy Lake avec plusieurs grains de zircon à  $382,8 \pm 8,3$  Ma, indiquant un âge maximal du Dévonien moyen, premières roches de cet âge identifiées dans le terrane de Calédonie.

[Traduit par la rédaction]

## INTRODUCTION

The Caledonia terrane is a large area of mainly Neoproterozoic rocks that forms the Avalonian part of southern New Brunswick, extending from the Saint John area to the northeast through the Caledonia Highlands (Fig. 1). Based on mapping, petrological studies, and limited geochronology, Barr and White (1999a, b) divided the Neoproterozoic rocks of the Caledonia terrane into ca. 630–615 Ma and ca. 560–550 Ma suites, each of which includes both volcanic and plutonic rocks, as well as less abundant epiclastic sedimentary rocks. The younger suite is overlain by the Cambrian to early Ordovician Saint John Group, a package of non-marine grading to marine sedimentary rocks (Tanoli and Pickerill 1988; Landing 1996; Landing and Westrop 1998). All these rocks were subsequently overlain by Carboniferous and Triassic successions forming part of the Maritimes and Fundy basins.

At the time of the work by Barr and White (1999a, b; 2004), the inferred ages of igneous rock units in the Caledonia terrane were based on a small number of dated rocks (Fig. 1), especially in comparison to the extent and geological complexity of the terrane. Ages reported from apparently younger Ordovician and Devonian volcanic rocks (Grassy Lake and Fairfield formations; Fig. 1) were

especially poorly constrained (Barr *et al.* 1994). The ages presented here are part of an on-going study (e.g., Barr *et al.* 2019) to provide more and better age data for rock units in the Caledonia terrane. In particular, additional units were sampled for dating, and some previously dated units were resampled and zircon grains were chemically abraded prior to analysis by isotope dilution thermal ionization mass spectrometry (ID-TIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The overall goal of this geochronological work is to provide a better understanding of the tectonic history of the Caledonia terrane, thus enabling more detailed understanding of tectonic relationships among the various Avalonian terranes.

## GEOLOGICAL SETTING

## Broad River Group

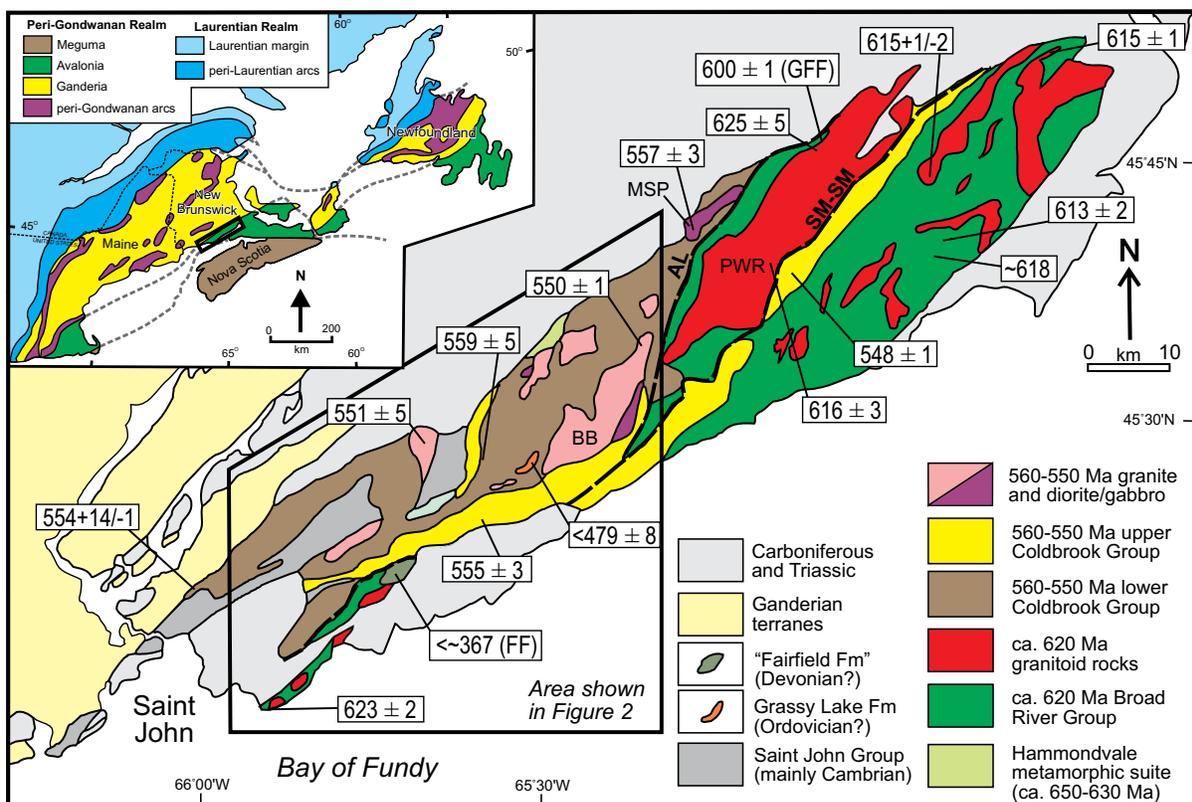
The ca. 630–615 Ma volcanic and sedimentary rocks of the Caledonia terrane, known as the Broad River Group, are exposed mainly in the eastern highlands and in small faulted slivers along the Bay of Fundy coast (Fig. 1). The Broad River Group consists dominantly of intermediate and felsic crystal and lithic-crystal tuff, with less abundant

intermediate and felsic flows, mafic tuff and flows, and epiclastic sedimentary rocks. Barr and White (1999a, b) divided the group into eleven lithological units, which were subsequently modified and given formation status (Barr and White 2004). Although internally varied, each formation has distinctive components which distinguish it from other formations in the group, but in general, stratigraphic relations among the formations are not known, except in rare, less deformed, areas where bedding and evidence of younging direction have been preserved. The Broad River Group has undergone pervasive regional metamorphism and contains mineral assemblages typical of the greenschist facies. Locally, the rocks have been affected also by contact metamorphism. In most places the volcanic or sedimentary protolith can be inferred, and the protolith names are, therefore, used in describing and naming the rocks. Based on rock types and geochemistry, Barr and White (1999a, b) inferred that the Broad River Group and related plutons formed in an Andean-type convergent margin subduction zone.

Previous direct controls on the age of the Broad River Group were from a rhyolite flow and felsic tuff in the southeastern part of the Caledonia terrane which yielded U–Pb ages of ca. 618 Ma and  $613 \pm 2$  Ma, respectively (Bevier and Barr 1990; Barr *et al.* 1994). A third sample, felsic tuff from near the northern margin of the terrane (Fig. 1), yielded a younger age of  $600 \pm 1$  Ma. Because of this younger age, Barr and White (2004) re-assigned these rocks to the Coldbrook Group, on the basis that the age might reflect inherited zircon rather than the igneous crystallization age.

### Point Wolfe River and related plutons

The Point Wolfe River pluton, largest in the Caledonia terrane, extends for nearly 50 km through the central and eastern highlands (Fig. 1). The northwestern margin of the Point Wolfe River pluton, where it is in contact with mainly tuffaceous rocks of the Broad River Group, is irregular and intrusive, whereas the southern margin is faulted, mainly



**Figure 1.** Simplified geological map of the Caledonia terrane of southern New Brunswick after Barr and White (1999b), showing the distribution of U–Pb (zircon) ages available prior to the current study. Sources are referenced in the text. Box outlines the area shown in Figure 2. Inset map shows subdivisions of the northern Appalachian orogen modified from Hibbard *et al.* (2006). Abbreviations: AL, Arnold Lake high-strain zone; BB, Bonnell Brook pluton; GFF, Gordon Falls Formation; MSP, Mechanic Settlement pluton; PWR, Point Wolfe River pluton; SM-SM, Stewart Mountain-St. Martins high-strain zone. Note that the Fairfield Formation (FF) is abandoned as a result of the new age presented here.

against younger rhyolite and basalt of the Coldbrook Group. The plutonic rocks are typically protomylonitic near the faulted contact, which is the St. Martins-Stewart Mountain shear zone of Park *et al.* (2008, 2017). Barr and White (1999a, b) divided the Point Wolfe River pluton into six mappable lithologic units. An intrusive sequence from more mafic to more felsic rocks was inferred, although contact relations to confirm this assumption are limited. U–Pb dating from the two largest units of the Point Wolfe River pluton (Pollett River granodiorite and Old Shepody Road granite) gave ages of  $625 \pm 5$  Ma and  $616 \pm 3$  Ma, respectively (Bevier and Barr 1990). Although these ages do not overlap, even considering error limits, the close spatial association and petrological similarities of the units suggest that they are comagmatic (Barr and White 1999a). Granitoid plutons apparently similar to those of the Point Wolfe River suite occur throughout the Broad River Group southeast of the St. Martins-Stewart Mountain shear zone (Fig. 1). Units dated previously by U–Pb (zircon) are the Millican Lake pluton at Cape Spencer ( $623 \pm 2$  Ma; Watters 1993), granodiorite of the Kent Hills pluton in the northeastern highlands ( $615 \pm 1$ – $2$  Ma; Barr *et al.* 1994), and gabbro of the Caledonia Mountain pluton, also in the northeastern highlands ( $615 \pm 1$  Ma; Barr *et al.* 2000).

### Hammondvale Metamorphic Suite

The Hammondvale Metamorphic Suite occurs in a narrow fault-bounded block along the northwestern margin of the Caledonia terrane (Fig. 1). It consists of albite- and garnet-porphyroblastic mica schist, as well as minor marble, calc-silicate rocks and quartzite. Peak pressure conditions during metamorphism were 12.4 kbar at 430°C, and peak temperature conditions were 580°C at 9.0 kbar (White *et al.* 2001). Muscovite  $^{40}\text{Ar}/^{39}\text{Ar}$  muscovite ages from three samples range up to  $618 \pm 15$  Ma, a minimum age for the high-P/low-T metamorphism in this unit. Based on detrital zircon ages, the maximum depositional age is about 650 Ma (Satkoski *et al.* 2010). The Hammondvale Metamorphic Suite has been interpreted to be a fragment of an accretionary complex formed on the margin of the Caledonia terrane during the subduction event that produced the Broad River Group and related plutons, suggesting that subduction was to the southeast in present-day coordinates (White *et al.* 2001).

### Coldbrook Group

The Coldbrook Group consists of two main groups of lithologies: (1) dacitic and rhyolitic flows and tuffs which extend from the city of Saint John through much of the northwestern part of the Caledonia terrane, and (2) basaltic and rhyolitic units which dominate in the southern part of the group (Fig. 1). The basaltic and rhyolitic units,

together with associated epiclastic sedimentary rocks, are interpreted to be the youngest units in the group because they are overlain by Cambrian rocks in several areas (Fig. 1). Furthermore, the gabbroic and granitic intrusions with which they have been inferred to be comagmatic (Barr and White 1999a) intruded the dacitic flows and tuffs but not the basalt and rhyolite formations (Fig. 1).

The Coldbrook Group is generally less deformed and metamorphosed than the Broad River Group, and it is likely that the Broad River Group experienced a low-grade metamorphic and deformational event prior to deposition of the Coldbrook Group (Barr and White 1999a; Park *et al.* 2008). However, at least in part, this difference is related to geographic distribution, as the northwestern part of the Caledonia terrane is generally less deformed than the coastal and eastern parts, and some of that deformation may be as young as Silurian to Carboniferous, although it began in the Neoproterozoic (Park *et al.* 2008, 2017). Contacts of the Coldbrook Group with the older Broad River Group appear to be everywhere faulted, but an originally unconformable relationship is inferred. Barr and White (1999a) suggested that the Coldbrook Group and related plutons formed during extension and rifting within the former active margin represented by the Broad River Group.

Prior to the present study, the age of the Coldbrook Group was constrained by U–Pb (zircon) ages of  $554 \pm 14$ – $1$  Ma from a dacitic tuff in the lower Coldbrook Group and  $559 \pm 5$ ,  $555 \pm 3$ , and  $548 \pm 1$  Ma from rhyolite at widely separated outcrops of the upper Coldbrook Group (Bevier and Barr 1990; Barr *et al.* 1994; Miller *et al.* 2000), as well as by ages from cross-cutting plutons as shown on Figure 1.

### Bonnell Brook and related plutons

The Bonnell Brook and related plutons occur widely throughout the central and western parts of the Caledonia terrane, north and west of the St. Martins-Stewart Mountain and Arnold Lake shear zones (Fig. 1). In contrast to the older plutons, these plutons are bimodal, and consist mainly of syenogranite and monzogranite, with less abundant dioritic to gabbroic rocks. The largest component of the Bonnell Brook and peripheral plutons is relatively homogeneous medium-grained equigranular syenogranite (to monzogranite) composed of perthitic orthoclase, quartz, and plagioclase, and containing less than 3% biotite, amphibole, titanite, and allanite (Guy 1998). Also present locally, especially around the northern margins of the pluton, is fine-grained syenogranite to monzogranite that consists of mainly plagioclase microphenocrysts in a granophyric groundmass. Especially where granophyric or fine-grained, the syenogranite contains miarolitic cavities. Based on these textural features, the Bonnell Brook pluton is interpreted to be a high-level intrusion, with shallower parts exposed towards the northern part of the map area. A dome-like

body of spherulitic rhyolite located north of the largest body of the Bonnell Brook pluton is interpreted to be the highest level (sub-volcanic) part of the pluton. It is texturally very similar to the granophyric unit of the main pluton, except it contains subhedral plagioclase microphenocrysts rimmed by spherulites instead of granophyre.

Areas of diorite to quartz diorite are present mainly on the southeastern margin of the Bonnell Brook pluton, inferred to be the deeper part, and are intruded by dykes of the syenogranite, clearly showing the relative ages of the two lithologies. The dioritic rocks consist mainly of plagioclase and hornblende with minor interstitial quartz, K-feldspar and relict clinopyroxene in the cores of some hornblende grains. These dioritic rocks are similar to dioritic parts of the mainly gabbroic (to ultramafic) Mechanic Settlement pluton (Grammatikopoulos *et al.* 1995).

Age constraints on these plutons (Fig. 1) include U–Pb (zircon) ages of  $550 \pm 1$  Ma from the main Bonnell Brook syenogranite,  $551 \pm 5$  Ma from the Upham Mountain syenogranite, and  $557 \pm 3$  Ma from quartz diorite associated with the Mechanic Settlement pluton (Grammatikopoulos *et al.* 1995; Barr and White 1999a).

### Saint John Group

Volcanic and non-marine coarse clastic sedimentary rocks of the upper part of the Coldbrook Group are overlain by the Saint John Group, a lower Cambrian through lower Ordovician Paleozoic platformal sedimentary sequence which contain a typical “Avalonian” fauna (e.g., Tanoli and Pickerill 1988; Landing 1996; Landing and Westrop 1998; Palacios *et al.* 2011). Following the terminology of Tanoli and Pickerill (1988), the lowermost formation, Ratcliffe Brook, consists of siliciclastic sedimentary units including coarse conglomerate, feldspathic quartz sandstone, arkosic sandstone, siltstone and minor mudstone. In contrast to the underlying similar redbeds of the Coldbrook Group, all units of the Saint John Group contain notable quantities of detrital white mica, and the coarser lithic clasts are recognizable rock types derived from the underlying Coldbrook Group and related intrusions as well as mylonite. Tanoli *et al.* (1985) first suggested that Neoproterozoic redbed units contain little or no detrital muscovite whereas overlying Cambrian rocks contain abundant detrital muscovite, a difference supported by subsequent studies (Reynolds *et al.* 2009; Satkoski *et al.* 2010). However, Barr and White (1999a) were not aware of this difference during their mapping and did not distinguish between muscovite-present and muscovite-absent redbeds in their separation of the Ediacaran and Cambrian redbed units, so some areas of muscovite-bearing redbeds were incorrectly assigned to the Seely Beach Formation of the Coldbrook Group on their maps and vice versa (Barr and White 1999b, 2004). Hence, for simplicity at page scale, all Seely Beach Formation of Barr and White (2004) is included

with the Saint John Group on Figure 2.

The oldest direct radiometric age constraint on the Saint John Group is an age of  $530.7 \pm 0.9$  Ma (U–Pb zircon; Isachsen *et al.* 1994) later revised to  $528.1 \pm 0.9$  Ma (Compston *et al.* 2008) for an ash layer from the Ratcliffe Brook Formation well above its base (Palacios *et al.* 2011).

### Grassy Lake Formation

Barr and White (2004) assigned the name Grassy Lake Formation to an area of flows and tuffs in the west-central Caledonia terrane (Fig. 1). The rocks are mainly dark-grey, light grey, or pinkish-grey dacitic to rhyolitic flows and tuffs. Flow-banding is present in flows and fine-grained crystal (welded) tuffs. The crystals include feldspar and embayed quartz, in a cryptocrystalline to spherulitic felsic groundmass. Locally, lithic lapilli tuff is abundant. All these rocks are similar to those in the surrounding units of the Coldbrook Group and the Grassy Lake Formation was recognized as a separate formation only because U–Pb (zircon) dating indicated a maximum age of  $479 \pm 8$  Ma (Barr *et al.* 1994). The extent of the formation and contact relationships with surrounding rocks of the Coldbrook Group remain uncertain because of limited outcrop. However, they were inferred by Barr and White (1999a, b) to be unconformable because of the age contrast.

### Fairfield Formation

Like the Grassy Lake Formation, the Fairfield Formation (Barr and White 2004) was separated from the older units by Barr and White (1999a, b; their unit D<sub>F</sub>) on the basis of radiometric dating which suggested a poorly constrained maximum age of 367 Ma (Barr *et al.* 1994). The formation consists of pink to red rhyolitic flows and red felsic lithic tuff with tuffaceous siltstone and sandstone. In the dated area these rocks are surrounded by tuffaceous rocks of the Broad River Group, and in postulated faulted contact with rhyolite of the Coldbrook Group (Fig. 1). Outcrops of similar rocks west and north of St. Martins were assigned also to the Fairfield Formation based on lithologic similarity.

### West Beach Formation

Basaltic rocks that occur in small fault-bounded areas along the coast of the Bay of Fundy were assumed to be Carboniferous by Barr and White (1999a, b; their unit Cb) based on lithological similarities to the ‘Mispec Formation’ or ‘West Beach Formation’ in the Saint John area (Alcock 1938; Rast *et al.* 1978; Strong *et al.* 1979). McLeod (1987) had identified them as Carboniferous or older. Currie (1992) included similar rocks in the Saint John area in the ‘Lorneville beds’ and inferred an “Eo-Cambrian” age. However, Park *et al.* (2014) demonstrated that these rocks in the Saint John

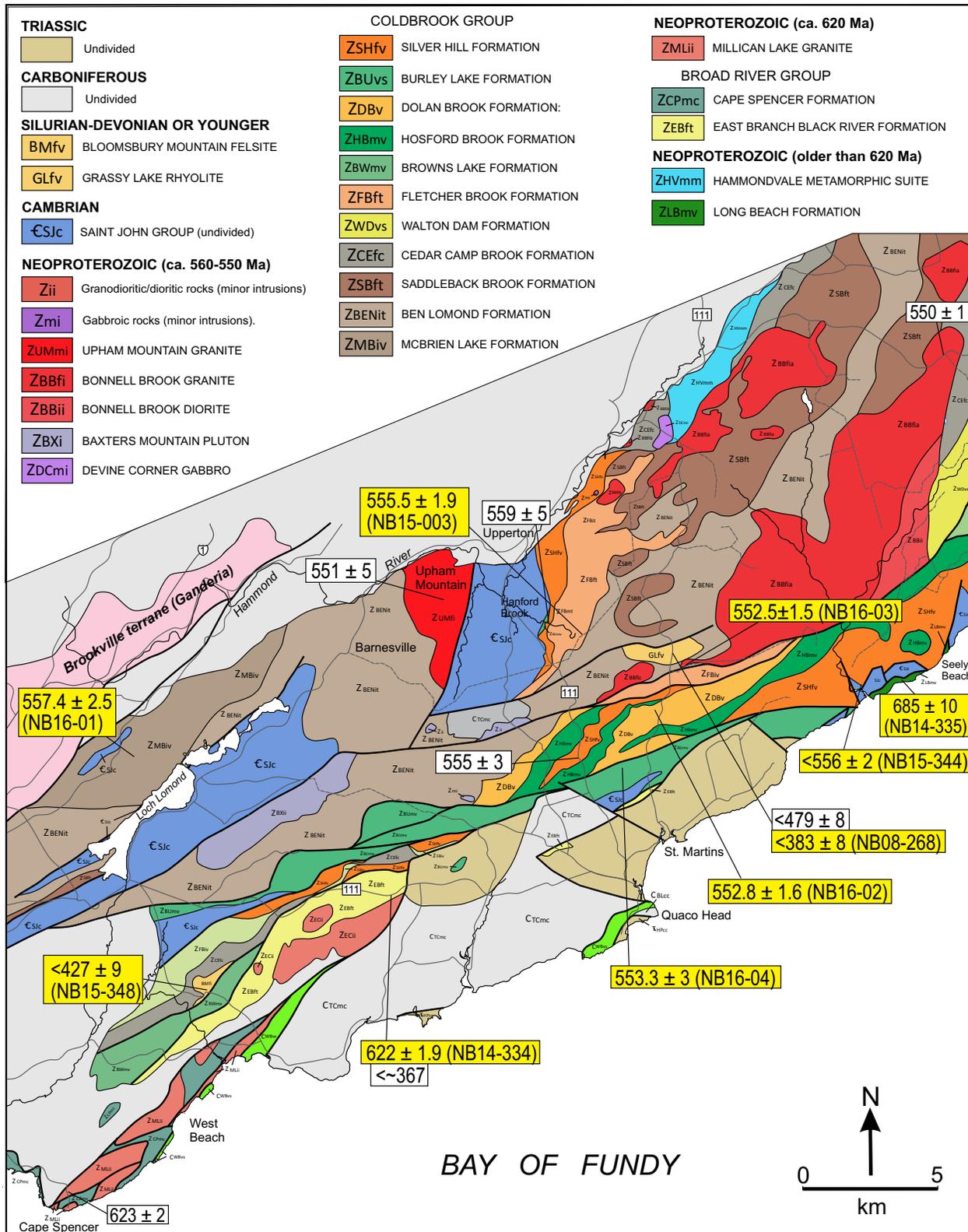


Figure 2. Geological map of the western part Caledonian Highlands mainly from Barr and White (2004) with modifications based on more recent work (e.g., Johnson *et al.* 2016; Park *et al.* 2017). Locations and ages of previously dated samples are shown in white boxes (as in Fig. 1), together with locations and ages obtained in the present study (in yellow boxes).

area (Taylors Island Formation) are Late Devonian to Early Carboniferous (Famennian to Tournaisian) and intruded by granitoid plutons of Early Carboniferous age.

## ANALYTICAL TECHNIQUES

Samples for this study were processed under clean conditions at Memorial University. The highest quality zircon grains were selected for analyses after examination under the microscope. Zircon grains were chemically abraded (cf. Mattinson 2005), whether analysed by ID-TIMS or by laser ICP-MS. They were annealed for 36 hours at 1000°C. This was followed by etching in concentrated HF in a TEFLON pressure-dissolution bomb in an oven at 200°C for 5 hours. This procedure eliminates radiation-damaged, altered or metamict zones in zircon that cannot be restored with annealing, thus virtually eliminating secondary lead loss. For simple grains of one age, this results in concordant or near-concordant analyses by either instrument technique. For zircon grains with cores and overgrowths of different ages, this technique will eliminate secondary lead loss that would cause data points to fall below the correct mixing line. Typical zircon grains for each sample were also mounted in epoxy and imaged by CL (Deben cathodoluminescence detector) using the JSM-7100F field emission SEM from the TERRA Facility – CREAT (Memorial University Earth Sciences Department) in order to describe their internal morphologies and to interpret their growth history. The current used varied from 10 to 15 kV.

The protocol used for CA-TIMS dating is detailed by Sparkes and Dunning (2014). The isotopic ratios were measured by either simultaneous measurement on multiple Faraday cups or, for small samples, by peak-jumping on one secondary electron multiplier using a Finnigan multicollector MAT 262 V TI mass spectrometer at the Earth Sciences Department of Memorial University. Several fractions, generally composed of 1 to 5 grains, were analysed for each sample. The data are listed in Table A1 in the Appendix.

In the case of samples with complicated zircon age patterns revealed by TIMS analysis, zircon grains representative of the population were selected under the microscope and were prepared following the same annealing and etching protocols as for the CA-TIMS analyses. The prepared grains were then mounted in epoxy in grain mounts and polished followed by imaging, then analysis by LA-ICP-MS. The U–Pb age measurement with LA-ICP-MS was done on a GeoLas ArF 193nm excimer laser ablation system (Coherent, Göttingen, Germany) coupled to an Element XR (Thermo Fisher Scientific, Bremen, Germany). An in-house made teardrop-shaped ablation chamber was used. The chamber had space for a 1-inch mount containing the samples and a 10 mm mount containing the standards.

Zircon 91500 (Wiedenbeck *et al.* 1995) was used as primary standard and the zircons Plešovice (Sláma *et al.* 2008) and 02123 (Ketchum *et al.* 2001) were used as secondary standards. The ICP-MS was tuned to high sensitivity and a low oxide ratio ( $\text{ThO}^+/\text{Th}^+ < 0.3\%$ ). Data evaluation was done with Iolite applying an exponential-linear downhole U/Pb fractionation correction model. Although  $^{235}\text{U}$  was measured it was recalculated from the  $^{238}\text{U}$  signal during data evaluation using a  $^{238}\text{U}/^{235}\text{U}$  ratio of 138.81. The laser ablation settings were: crater size of 20  $\mu\text{m}$ , repetition rate of 5 Hz, fluence of 4  $\text{J}/\text{cm}^2$ , 200 pulses and 1L/min He for the carrier gas flow. The ICP-MS settings were: 0.93 L/min for the sample gas flow, 0.9 L/min for the auxiliary gas flow, 16 L/min for the plasma gas flow, the plasma power was 1550 W. The measured isotopes and dwell times were  $^{202}\text{Hg}$  (10 ms),  $^{204,206,207,208}\text{Pb}$  (10, 50, 50, 10 ms),  $^{232}\text{Th}$  (10 ms) and  $^{235,238}\text{U}$  (50, 10 ms). The determined weighted average  $^{206}\text{Pb}/^{238}\text{U}$  ages for the secondary standards were  $340.5 \pm 1.7$  Ma (MSWD = 2.8,  $n = 55$ ) and  $299.2 \pm 2.0$  Ma (MSWD = 2.0,  $n = 25$ ) for Plešovice and 02123, respectively. The data are listed in Table A2 in the Appendix.

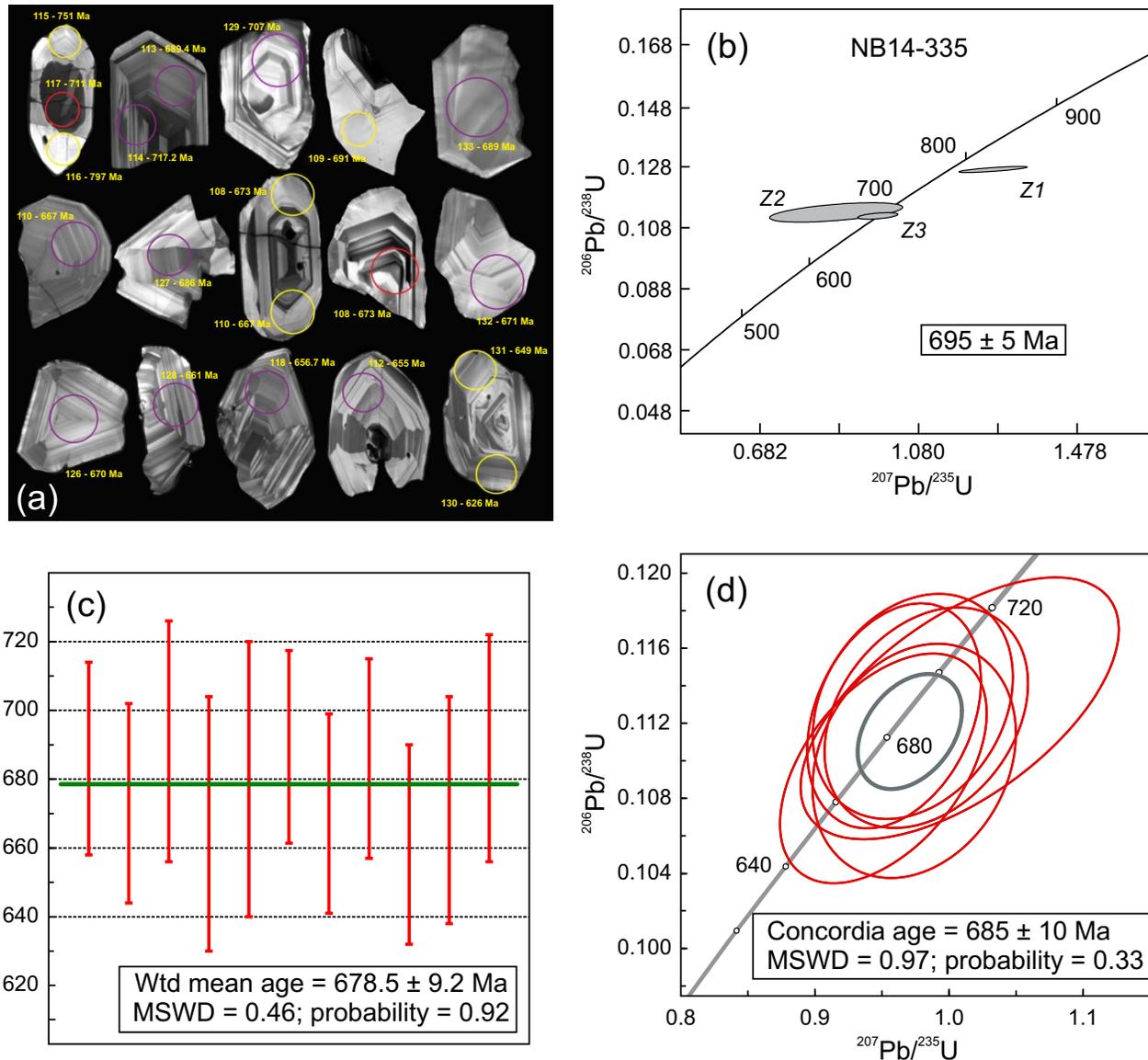
All U–Pb isotopic ratios are reported with  $2\sigma$  uncertainties and all calculated ages using ISOPLOT are reported at the 95% confidence interval.

## SAMPLE DESCRIPTIONS AND RESULTS

### Long Beach Formation – quartz-feldspar porphyry (sample NB14-335)

A quartz-feldspar porphyry dyke is exposed in a roadside outcrop of mafic volcanic rocks along the new Fundy Trail Parkway east of St. Martins. These deformed and metamorphosed mafic rocks form the headland between Big Salmon River and Long Beach and are separated from Cambrian and Coldbrook Group rocks by a south-dipping reverse fault (Park *et al.* 2017). The mafic rocks previously had no direct age constraints but were assigned to the West Beach Formation (Barr and White 2004), one of several such enclaves of fault-bounded mafic rocks along the coast of the Bay of Fundy between Saint John and Alma. Based on new mapping (Park *et al.* 2017) and the age reported here, these rocks have been assigned to a new unit, the Long Beach Formation (Fig. 2).

Dated porphyry dyke sample NB14-335 consists of plagioclase and quartz phenocrysts in a fine-grained groundmass of feldspar, quartz, and sericite. The quartz phenocrysts are embayed and contain prominent deformation lamellae. Plagioclase phenocrysts are broken and deformed. The sample yielded abundant euhedral zircon grains with igneous zoning (e.g., Fig. 3a). Four zircon fractions were analysed via CA-TIMS, two of which are concordant with  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $700 \pm 15$  Ma (Z2, 1 small



**Figure 3.** Age data for sample NB14-335, quartz-feldspar porphyry dyke in the Long Beach Formation. (a) Cathodoluminescence images of zircon grains showing spots analyzed by LA-ICP-MS and ages obtained. (b) Concordia diagram for TIMS data (Table A1). (c) Weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of 11 analyses. (d) Concordia diagram for 6 overlapping analyses.

low-U prism) and  $694 \pm 5$  Ma (Z3). Together these data yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $695 \pm 5$  Ma (MSWD = 0.69). One analysis (Z4) of a clearly inherited zircon grain is at  $828 \pm 5$  Ma and not shown on the diagram, and the fourth analysis (Z1) is discordant (Fig. 3b). Because of the importance of these unexpectedly old ages, zircon grains from this sample were also analysed by LA-ICP-MS to test for the potential presence of younger grains missed in selecting grains for TIMS work. The zircon grains are of high quality and euhedral to subhedral (Fig. 3a). Obvious

bright-CL overgrowths on darker, but euhedral cores, are of the same age generation of zircon, and are likely due to influx of new magma of different chemistry into the magma chamber, growing new layers on the same crystals, a common feature in felsic igneous rocks. One exception in the CL images is in the grain (upper left in Fig. 3a) with an anomalously older 797 Ma rim (analysis 116), which seems to overgrow a corroded core. One grain (lower right, Fig. 3a) gave a young age of  $626 \pm 26$  Ma (analysis 130) but another part of the same growth zone gave an age of  $649 \pm 27$  Ma

(analysis 131). A weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age using 11 analyses of clear igneous growth-zoned areas gives  $679 \pm 9$  Ma with an excellent MSWD of 0.46 (Fig. 3c). However, only 6 grains overlap tightly enough to calculate an acceptable concordia age which is  $685 \pm 10$  Ma with MSWD = 0.97 (Fig. 3d).

The igneous crystallization of the porphyry is best reported as  $685 \pm 10$  Ma, as this age covers the range of the 3 different ages calculated from the different combinations of data described above. This age makes this porphyry the oldest rock yet dated in the Caledonia terrane, and provides a minimum age for the even older mafic volcanic rocks of the Long Beach Formation that it intruded.

#### East Branch Black River Formation (formerly Fairfield Formation) – rhyolite (sample NB14-334)

Sample NB14-334 was collected from the same outcrop as the sample dated by Barr *et al.* (1994) which yielded a poorly constrained Devonian age and was assigned to the Fairfield Formation (Fig. 1). Like the original sample, it consists of micro- to cryptocrystalline flow-banded rhyolite with microspherulites in a sericitic quartz and feldspar groundmass. It contains scattered microphenocrysts of plagioclase. The sample yielded abundant clear euhedral prisms which display simple igneous growth zoning, with some very luminescent cores or rims (Fig. 4a).

Six zircon fractions were analysed via CA-TIMS, most consisting of 1 or 2 grains. These six analyses yielded 2 discrete ages: two grains yielded  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $632 \pm 4$  and  $634 \pm 6$  Ma and are likely inherited. Four overlapping younger concordant analyses yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $622 \pm 1.9$  Ma with MSWD = 1.18 (Fig. 5a), interpreted to be the igneous crystallization age of the rhyolite.

This age is consistent with U–Pb ages from the Broad River Group and related plutons (Figs. 1, 2). Given the uncertainty of the previously reported age, the name Fairfield Formation is abandoned here, and the rocks formerly included in that unit are considered part of the surrounding East Branch Black River Formation of the Broad River Group (Fig. 2). The new age is consistent with the observation that the East Branch Black River Formation is intruded by the Millican Lake plutons, one of which yielded an age of  $623 \pm 2$  Ma (Watters 1993) and supports the interpretation that the plutons are comagmatic with associated volcanic rocks of the Broad River Group (Barr and White 1999a). However, this sample also demonstrates the difficulty of correlating rock units in the Caledonia terrane based on rock type or chemistry – the dated flow-banded rhyolite sample is to all appearances identical to flow-banded rhyolite in the Coldbrook Group which yields ages of ca. 555 Ma, and the samples are chemically similar as well (Barr and White 1999a).

#### Gordon Falls Formation – felsic tuff (sample SH15-137)

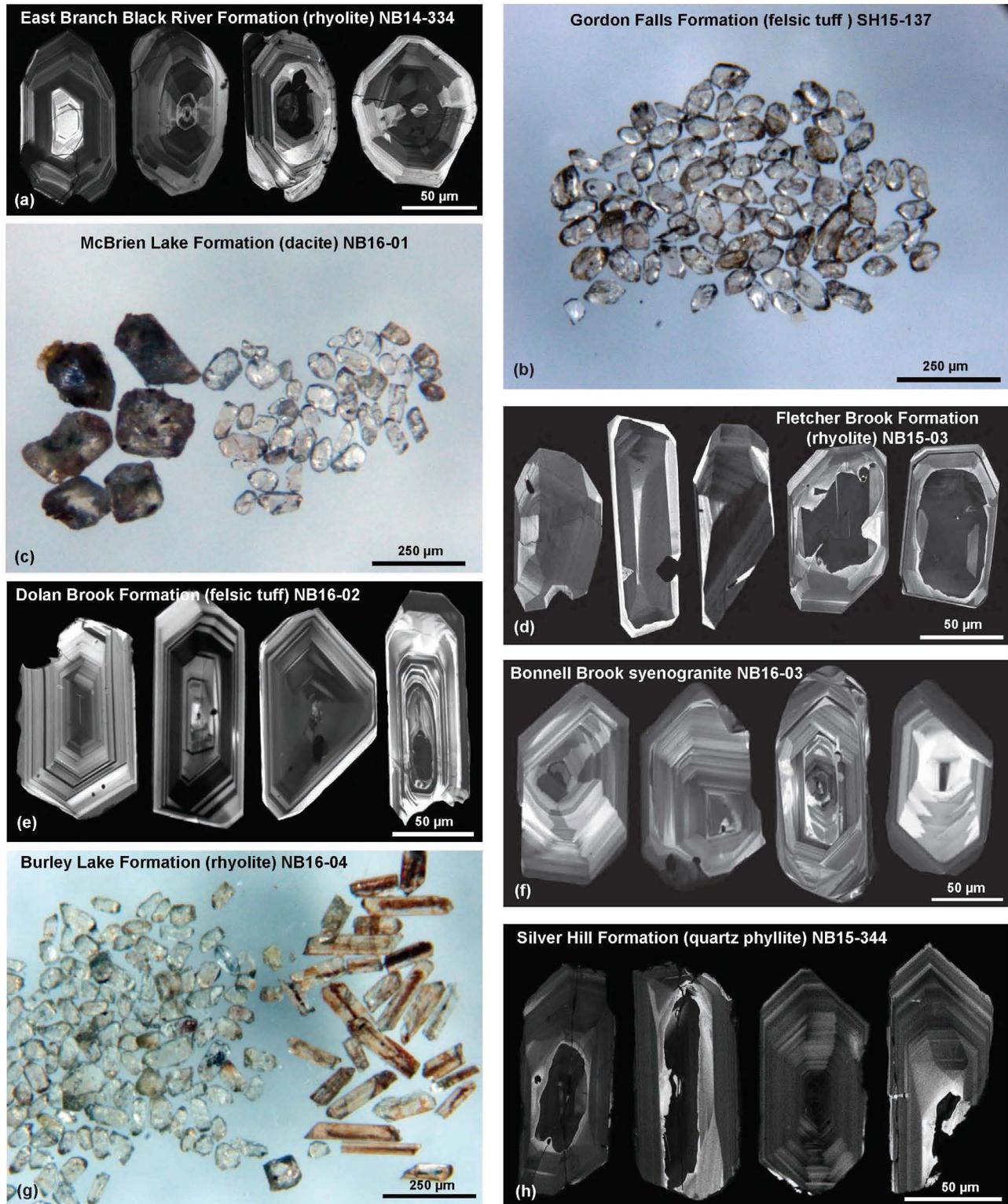
The Gordon Falls Formation of Barr and White (2004) occurs in a small fault-bounded sliver on Pollett River near the northern margin of the Caledonia terrane, sandwiched between the ca. 625 Ma Pollett River granodiorite on the south and Carboniferous sedimentary rocks to the north (Figs. 1, 6). It consists mainly of dacitic to rhyolitic crystal tuff, with minor lithic-crystal tuff and siliceous felsite with abundant pyrite (Barr and White 1999a). Bevier and Barr (1990) reported a U–Pb date of  $600 \pm 1$  Ma for a dacitic tuff sample from Gordon Falls, which seems incompatible with the age of 625 Ma obtained from the adjacent Pollett River granodiorite, although the contact is faulted. This line-of-reasoning led Barr and White (2004) to re-assign the unit to the Coldbrook Group on the basis that the age might reflect zircon inheritance.

Sample SH15-137 was collected from the same outcrop as the previously dated sample to try to resolve the uncertainty. Like the sample dated by Barr *et al.* (1994), it is a deformed felsic crystal tuff that consists of relict plagioclase augen in a strongly foliated groundmass of polycrystalline quartz, feldspar lenses, epidote, and sericite. The sample contained abundant small euhedral to subhedral zircon prisms (Fig. 4b). Two analyses of 8 and 2 prisms yielded overlapping concordant points with ages of  $620.5 \pm 5.5$ , and  $617.5 \pm 2.5$  Ma, indicating an age of  $620 \pm 5$  Ma based on the higher quality analysis (Fig. 5b). This age is interpreted to be the eruption age of the tuff, superseding the previously reported younger age by Barr *et al.* (1994). The younger age may be the result of minor lead-loss from a multiple-grain fraction that dragged that point down along concordia from 620 Ma. The new ca. 620 Ma is more consistent with the geological setting of the Gordon Falls Formation.

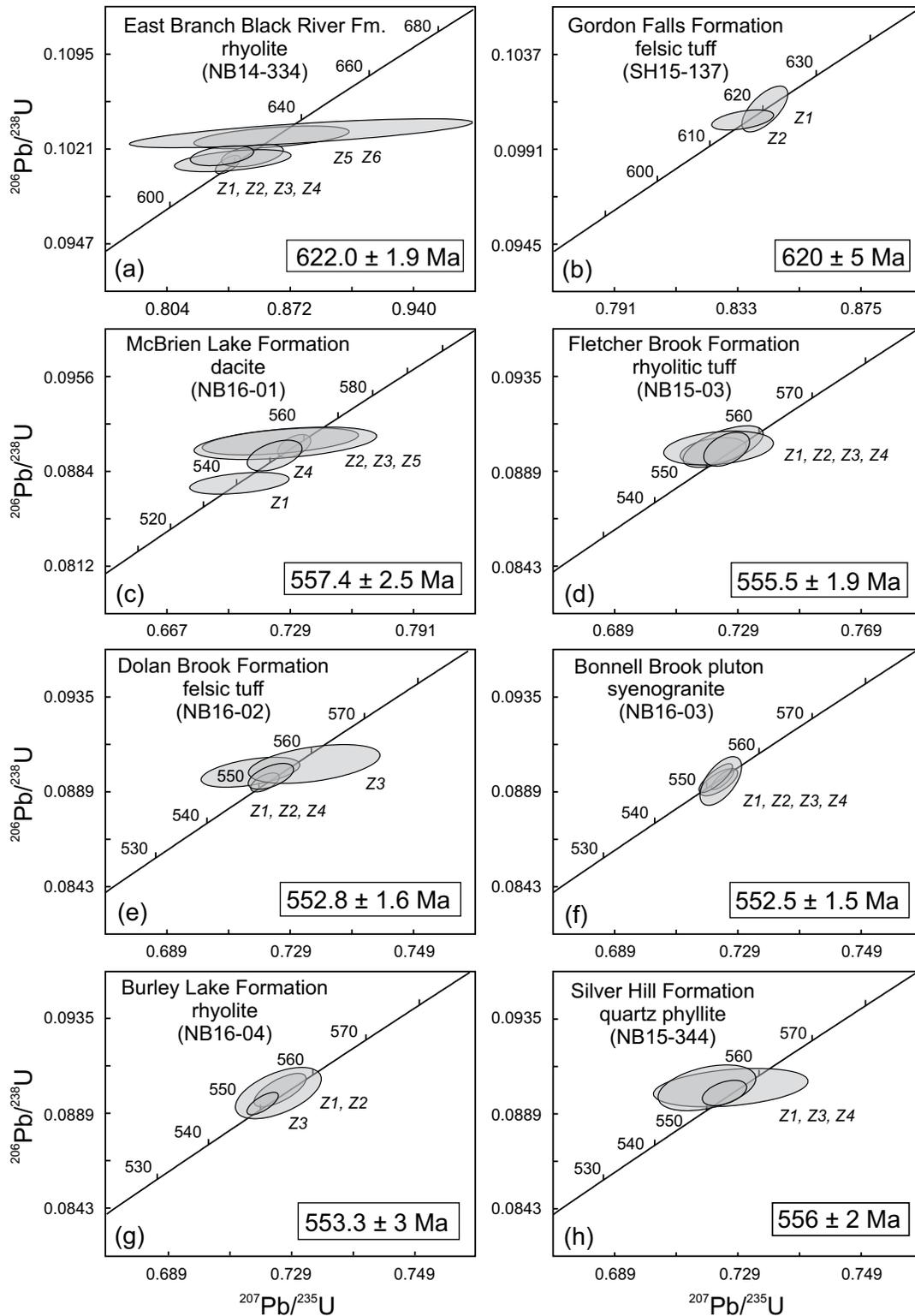
#### McBrien Lake Formation – dacite (sample NB16-01)

The McBrien Lake Formation is interpreted to be the oldest unit in the Coldbrook Group (Barr and White 2004). It consists mainly of grey-green dacitic flows best exposed in the western part of the Caledonia terrane, where dated sample NB16-01 was collected (Fig. 2). The unit extends into the city of Saint John where a flow-banded, welded, dacitic tuff sample previously yielded a U–Pb (zircon) age of  $554 +14/-1$  Ma (Barr *et al.* 1994; location shown on Figure 1, west of the area of Figure 2). Similar flows occur in places in the overlying Ben Lomond Formation, a mainly tuffaceous unit in which many of the clasts resemble the flows of the McBrien Lake Formation (Barr and White 1999a).

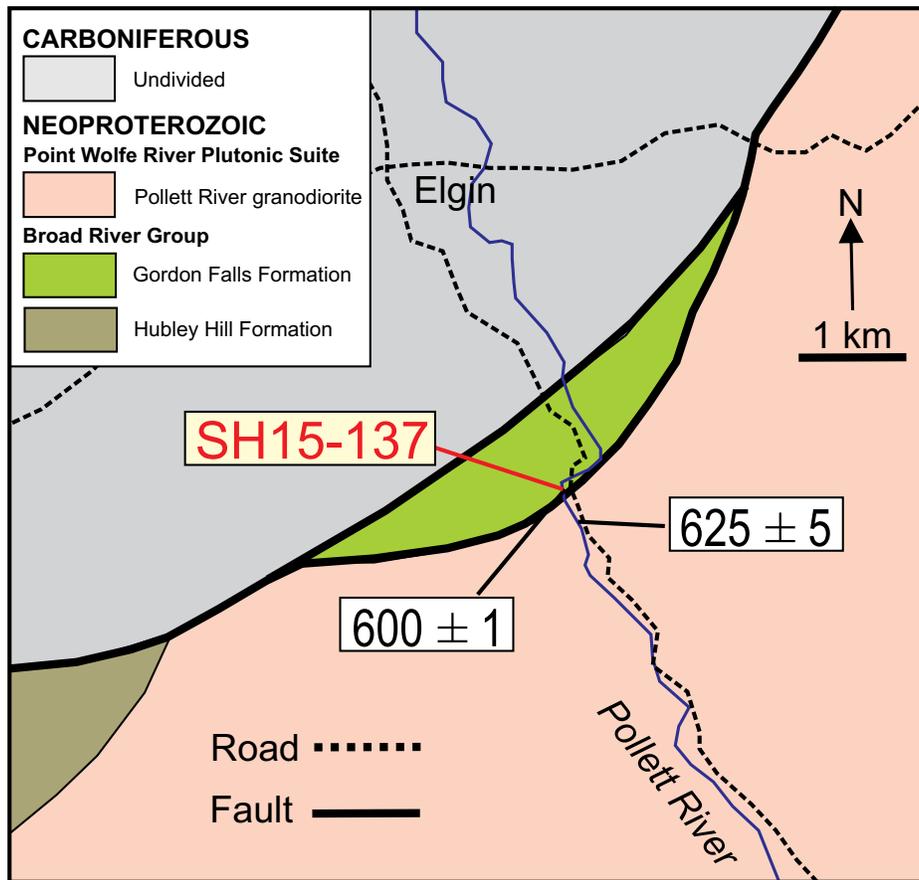
Dated sample NB16-01 is from a dacite flow, and consists of skeletal, needle-like plagioclase in a spherulitic groundmass with scattered flakes of altered biotite. Secondary minerals include abundant sericite, epidote, chlorite, and carbonate minerals. The sample yielded abundant small euhedral



**Figure 4.** Zircon images from samples (a) NB14-334 (rhyolite, East Branch Black River Formation, formerly Fairfield Formation), (b) SH15-137 (felsic tuff, Gordon Falls Formation), (c) NB16-01 (dacite, McBrien Lake Formation), (d) NB15-003 (rhyolitic tuff, Fletcher Brook Formation), (e) NB 16-02 (felsic tuff, Dolan Brook Formation), (f) NB16-03 (Bonnell Brook syenogranite), (g) NB16-04 (rhyolite, Burley Lake Formation), and (h) NB15-344 (quartz phyllite, Silver Hill Formation).



**Figure 5.** Concordia diagrams for samples (a) NB14-334 (rhyolite, East Branch Black River Formation, formerly Fairfield Formation), (b) SH15-137 (felsic tuff, Gordon Falls Formation), (c) NB16-01 (dacite, McBrien Lake Formation), (d) NB15-003 (tuff, Fletcher Brook Formation), (e) NB 16-02 (felsic tuff, Dolan Brook Formation), (f) NB16-03 (Bonnell Brook syenogranite), (g) NB16-04 (rhyolite, Burley Lake Formation), and (h) NB15-344 (quartz phyllite, Silver Hill Formation).



**Figure 6.** Geological map of the Gordon Falls Formation after Barr and White (2004) showing the location of dated sample SH15-137.

zircon prisms (Fig. 4c) and 5 analyses were carried out (Table A1). Analysis Z1 plots below the rest, interpreted to be due to lead loss. The other 4 (Z2–Z5) are all concordant and overlap, and these yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $557.4 \pm 2.5$  Ma (MSWD = 1.04, Fig. 5c), interpreted to be the igneous crystallization age of the flow.

#### Fletcher Brook Formation – rhyolitic tuff (sample NB15-003)

The mainly tuffaceous Fletcher Brook Formation is interpreted to underlie the Silver Hill Formation and overlie the Ben Lomond Formation in the north-central part of the Coldbrook Group (Fig. 2). The formation contains a wide variety of rock types, including amygdaloidal basalt, andesitic to basaltic lapilli tuff, pyroclastic breccia and debris flows, laminated felsic ash tuff, vari-coloured dacitic lithic lapilli tuff, andesitic to dacitic flows, and locally spherulitic felsic tuff with prominent eutaxitic banding. Dated felsic tuff sample NB15-003 from the latter rock type contains embayed quartz, feldspar, and felsic rock fragments in a

cryptocrystalline groundmass. It yielded small zircon grains that look like simple igneous prisms of one morphology and age. Some display very luminescent outer growth zones in CL (Fig. 4d). Four fractions were analyzed, each consisting of 1, 2, or 3 grains and these tightly overlap on concordia and provide a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $555.5 \pm 1.9$  Ma (MSWD = 0.081, Fig. 5d). This age is interpreted to be the igneous crystallization age of the tuff.

#### Dolan Brook Formation – felsic tuff (sample NB16-02)

The Dolan Brook Formation is located at the southwestern margin of the Bonnell Brook pluton, and in a smaller area to the west. Like the Fletcher Brook Formation, it is a lithologically varied unit that includes interlayered basalt and rhyolite as well as a variety of mafic to felsic lithic lapilli tuffs and laminated ash tuff. Some of the dacitic tuffs are similar to those in stratigraphically lower formations of the Coldbrook Group such as Ben Lomond Formation, and the amygdaloidal basalt and rhyolite components resemble those in the Burley Lake, Fletcher Brook, and Silver Hill

formations. Hence the stratigraphic significance of this heterogeneous unit is uncertain.

Dated sample NB16-02 is a felsic lithic crystal tuff with scattered crystals of embayed quartz and feldspar in a cryptocrystalline quartz and feldspar (ash) groundmass with abundant sericite. Lithic clasts are mainly rhyolitic, some with flow banding. The sample yielded abundant small euhedral, high-quality igneous prisms (Fig 4e) and 4 analyses were carried out of small fractions of 3 or 4 crystals each. These yielded a simple data set of four overlapping concordant points with a range of  $^{206}\text{Pb}/^{238}\text{U}$  ages from 551.8 to 557.0 (Fig. 5e). One analysis, Z3, is of distinctly poorer quality and shifted slightly to the right; it was not used in the age calculation. Analyses Z1, Z2, and Z4 yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $552.8 \pm 1.6$  Ma (MSWD = 1.07), interpreted as the crystallization age of the tuff.

#### Bonnell Brook pluton – syenogranite (sample NB16-03)

Sample NB16-03 is fine-grained granite from the chilled margin of the Bonnell Brook syenogranite, very close to its contact with the Ben Lomond Formation of the Coldbrook Group (Fig. 2). It consists of large subhedral crystals of quartz, K-feldspar, and rare altered biotite in a groundmass that varies from granophyric to spherulitic. Secondary minerals include sericite, chlorite, and epidote.

This sample yielded abundant simple prisms with excellent igneous growth zoning (Fig. 4f) similar in size and morphology to those in the sample from the Dolan Brook Formation (Fig. 4e). The zircon grains are smaller than those typical of granite, consistent with the fact that this part of the Bonnell Brook pluton is high-level. Four analyses, of 3 to 6 crystals per fraction, yielded tightly overlapping concordant points, with  $^{206}\text{Pb}/^{238}\text{U}$  ages between only 551.9 and 553.1 Ma (Fig. 5f). The weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age using all four analyses is  $552.5 \pm 1.5$  Ma (MSWD = 0.094). This age corroborates the age of  $550 \pm 1$  Ma obtained previously from the interior part of the pluton (Barr *et al.* 1994) and supports the interpretation of Barr and White (1999a) that the Bonnell Brook pluton intruded comagmatic rocks of its own volcanic carapace.

#### Burley Lake Formation – rhyolite (sample NB16-04)

The Burley Lake Formation north of St. Martins (Fig. 2) consists of basalt, rhyolite, and interlayered clastic sedimentary rocks, overlain by sedimentary rocks of the Saint John Group. Sample NB16-04 is cryptocrystalline to microcrystalline flow-banded rhyolite from that formation. Texture varies from eutaxitic to spherulitic, with lithophysae filled with larger quartz crystals.

The sample yielded small clear euhedral zircon prisms and a small number of larger elongate zircon grains with hematitized cores (Fig. 4g). Only the small clear prisms

were analysed and three analyses yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $553.3 \pm 3$  Ma (MSWD = 0.053, Fig. 5g), interpreted to be the igneous crystallization age of the rhyolite.

#### Silver Hill Formation – quartz phyllite (sample NB15-344)

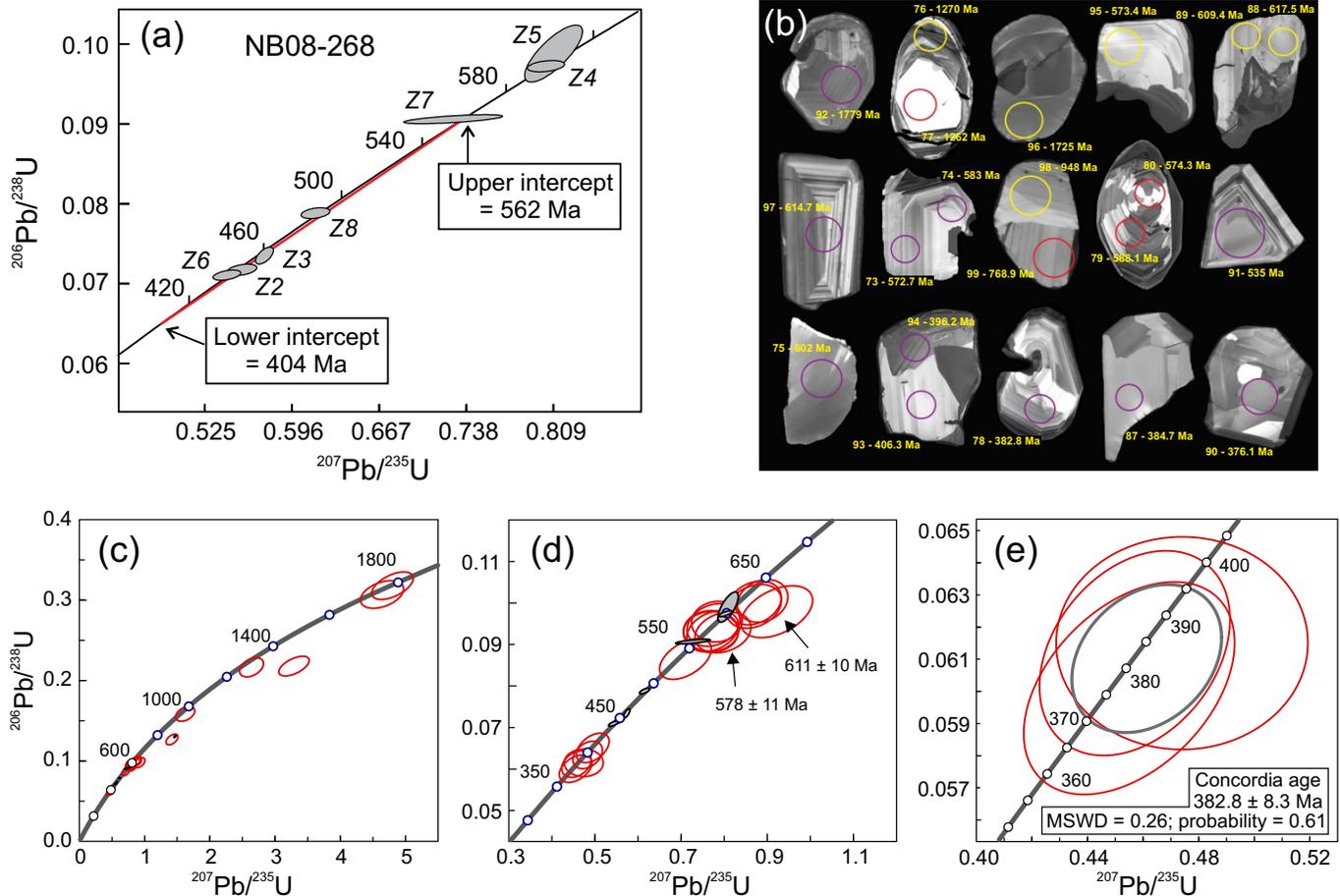
New roadcuts along the Fundy Trail Parkway east of Big Salmon River display complex structural relationships between deformed rhyolite of the Silver Hill Formation (Coldbrook Group) and quartz arenite, sandstone, siltstone, and shale of the Ratcliffe Brook Formation (Saint John Group) (Park *et al.* 2017). Sample NB15-344 consists of quartz-rich phyllite composed mainly of quartz, chlorite, and sericite. Its close association with deformed and recrystallized rhyolite suggests that, like the rhyolite, it is part of the Silver Hill Formation (Park *et al.* 2017).

The sample yielded some rounded zircon grains but a high proportion of clear euhedral prisms. Most grains are sharp and euhedral and have continuous growth zoning (Fig. 4h). Four zircon fractions were dated, three of which (Z1, Z3, Z4) are excellent pristine analyses of 1 or 2 grains each. The fourth grain (Z2) is significantly down a line towards 347 Ma, with large uncertainty. Its position on concordia is interpreted to be due to lead-loss not removed by chemical abrasion. The remaining 3 analyses from euhedral grains yield a weighted average  $^{206}\text{Pb}/^{238}\text{U}$  age of  $556 \pm 2$  Ma (MSWD = 0.22) (Fig. 5h).

The age of  $556 \pm 2$  Ma is interpreted to be the maximum age of deposition of the phyllite protolith, and is similar to ages of volcanic rocks from the older parts of the Coldbrook Group (Fig. 9). These rocks are likely the main source of detritus in the phyllite. A quartz arenite sample from the overlying Ratcliffe Brook Formation but from a location farther east in the Caledonia terrane yielded a similar weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  date of  $553.3 \pm 5.3$  Ma (MSWD = 0.33) (Satkoski *et al.* 2010).

#### Grassy Lake Formation – rhyolite (sample NB08-268)

The Grassy Lake Formation was identified as separate from the Coldbrook Group based on a poorly constrained age of less than  $479 \pm 8$  Ma (Barr *et al.* 1994). Otherwise, field evidence did not provide any reason to separate this dacitic-rhyolitic tuffaceous unit from the surrounding Ben Lomond Formation of the Coldbrook Group. At that time the age of the Ben Lomond Formation was already constrained by the ca. 550 Ma U–Pb age (Bevier and Barr 1990) of the Bonnell Brook pluton which intruded it. Attempts to better constrain the age of the Grassy Lake Formation by additional sampling at that time were thwarted by absence or scarcity of zircon grains, and additional field work over the years has not provided any additional constraints on relations with the surrounding Coldbrook Group rocks.



**Figure 7.** Age data for sample NB08-268 from the Grassy Lake Formation. (a) Concordia diagram for TIMS data (Table A1). (b) CL images of zircon grains showing spots analyzed and ages obtained by LA-ICP-MS. (c) Concordia diagram for LA-ICP-MS analyses showing multiple concordant ages between Mesoproterozoic and Paleozoic. (d) Concordia diagram for Neoproterozoic and Paleozoic analyses by LA-ICP-MS, together with three TIMS analyses (in grey). Three laser spot analyses combined with the TIMS analysis at 609 Ma give a  $^{206}\text{Pb}/^{238}\text{U}$  age of  $611 \pm 10$  Ma with MSWD = 0.20. Five laser spot analyses (analyses 73, 74, 79, 80, 95, Table A2) on 3 entire growth-zoned igneous crystals gave ages between 573–588 Ma and yielded a weighted average age of  $578 \pm 11$  Ma with MSWD = 0.33. (e) Concordia diagram for the youngest 3 laser spot analyses from 3 whole zircon grains. Calculated concordia age is  $382.8 \pm 8.3$  Ma for these three overlapping analyses.

To further pursue the unresolved problem of the age of the Grassy Lake Formation, sample NB08-268 was collected from an outcrop 200 m north of the sample dated previously by Barr *et al.* (1994) but similar in rock type to the previously dated sample. It consists of grey microcrystalline to cryptocrystalline rhyolite with flow-banding and spherulitic layering. Scattered phenocrysts are mainly of plagioclase. Secondary minerals include sericite, chlorite, and epidote.

Eight zircon fractions were analysed by TIMS from sample NB08-268 (Fig. 7a). The two youngest fractions (Z2, Z6) are overlapping and concordant at  $442 \pm 3$  and  $446 \pm 3.5$  Ma. A line can be calculated (60% probability of fit) with an upper intercept of ca. 560 and lower intercept at 404 Ma, but the lower intercept is too imprecise ( $\pm 65$  Ma) to be

useful. It could be that the ca. 442–446 Ma age of duplicated concordant analyses represents the age of the rock, and that is why there is no lower point. In any case, the Grassy Lake Formation cannot be older than the igneous growth-zoned rims that are a significant part of the grains in the CL image (Fig. 7b). If the grains that have yielded  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $446 \pm 3.5$  and  $442 \pm 3$  Ma are devoid of older cores, then this is the true age of eruption of this rock. However, if they contain small older cores which we cannot know from our data, then the true age of the rims (and the rock) is younger than 443 Ma.

To attempt to better constrain the age of this rock, zircon grains from this sample were also analysed by LA-ICP-MS (Fig. 7b) and yielded multiple concordant ages (Fig. 7c).

One subhedral grain is concordant at  $1779 \pm 68$  Ma, whereas two analyses on another grain gave  $^{206}\text{Pb}/^{238}\text{U}$  ages of  $1262 \pm 51$  and  $1270 \pm 54$  Ma (Fig. 7c). Three igneous growth-zoned grains gave spot ages of  $602 \pm 30$  Ma,  $609 \pm 25$ ,  $617.5 \pm 25$ , and  $614.7 \pm 25$  Ma, and combined with the TIMS analysis at  $609 \pm 16$  Ma, this group of grains gives a  $^{206}\text{Pb}/^{238}\text{U}$  age of  $611 \pm 10$  Ma (Fig. 7d) with  $\text{MSWD} = 0.20$ . Five laser spot analyses (#73, 74, 79, 80, 95) on 3 entire growth-zoned igneous crystals gave ages between 573 – 588 Ma and yielded a weighted average age of  $578 \pm 11$  Ma (Fig. 7d) with  $\text{MSWD} = 0.33$ . Because the two Ediacaran age clusters are from well-preserved igneous grains that have been chemically abraded it is possible to say that the Ediacaran clusters of data do not significantly overlap, and the data set shows no evidence of zircon grains with ages of ca. 555 Ma, the age of the Coldbrook Group.

The five youngest analyses, from 4 crystals, are  $406 \pm 18$  to  $376 \pm 16$  Ma. These ages all overlap, and an age of  $389 \pm 14$  Ma can be calculated from all 5 analyses. However, the youngest 3 analyses (#78, 87, 90), from 3 excellent whole zircon grains, are tightly clustered, have smaller than average errors and a calculated concordia age for these is  $382.8 \pm 8.3$  Ma (Fig. 7e). This is interpreted to be the best estimate of the age of the youngest igneous zircon in the rock, and hence is a maximum age for the Grassy Lake Formation. The combined U–Pb zircon TIMS and laser data set are consistent, with TIMS ages matching or falling in between the clusters of ages identified by laser.

#### Bloomsbury Mountain Formation – felsite (sample NB15-348)

The Bloomsbury Mountain Formation is a dome of brown to pink felsite that was assigned to the Coldbrook Group by Barr and White (1999a, b, 2004). It was sampled for dating because of the possibility that this dome-like undeformed rock might be younger than other units in the Coldbrook Group, and also because gold anomalies had been recognized by prospectors in the area. Viewed in thin section, sample NB15-348 is homogeneous and consists mainly of spherulitic material, with rare feldspar crystals, and is interpreted to be a shallow intrusive rock. It yielded not-perfectly-euhedral zircon grains and every grain imaged has a corroded core, with a significant part of the grain composed of younger overgrowths with sharp igneous growth zones in the overgrowth (Fig. 8a). The less luminescent cores also have igneous growth zones. The linear data array for the 4 analyses from ca. 561 to 443 Ma intersects concordia at 417 Ma (with large uncertainties of ca. 100 myrs), indicating a likely Silurian–Devonian age and that the magma may have formed as a melt of a single-age Proterozoic igneous rock. The different distances that the analyses plot down the discordia line (Fig. 8b) likely correlate with the proportion of those growth-zoned igneous overgrowths. The age of sample NB15-348 is not

really pinned down by the TIMS analyses; it is younger than (or equal to)  $443 \pm 5$  Ma (the youngest  $^{206}\text{Pb}/^{238}\text{U}$  age). The most conservative interpretation is that  $443 \pm 5$  Ma is the oldest possible crystallization/eruption age, but a younger age, like the projected 417 Ma lower intercept, cannot be ruled out.

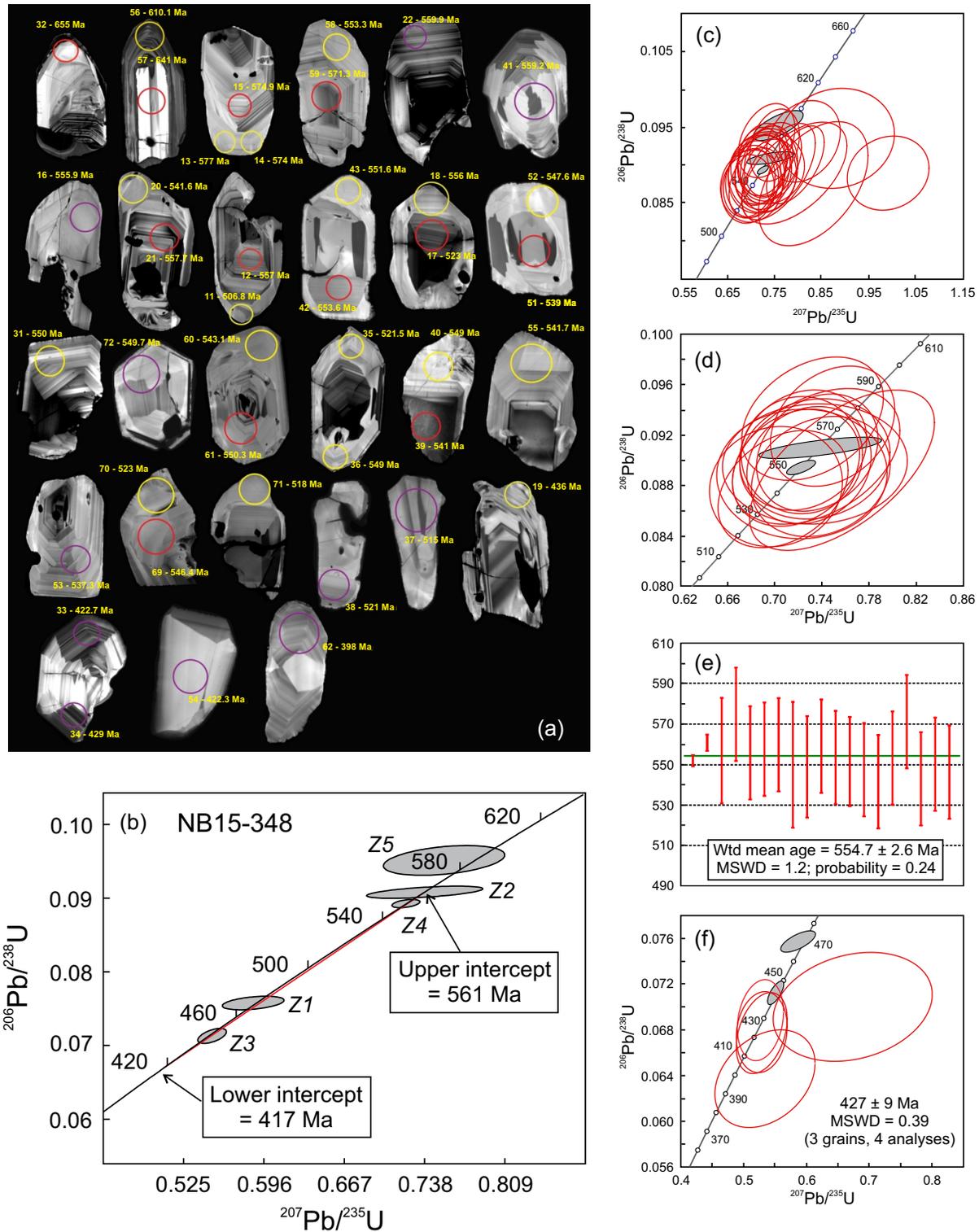
To further investigate the age of the felsite, zircon grains were analysed by LA-ICP-MS. Relatively few analyses are concordant, and most are ca. 555 Ma (Fig. 8c), as are 2 of the TIMS analyses (in grey). The 19 best analyses give a weighted mean age of  $554.7 \pm 2.6$  Ma (Fig. 8d, e). These include both core and rim analyses (see CL image) so many of these overgrowths are likely due to magma chamber complexity in refilling, corrosion, and new growth in cycles.

While the 555 Ma age cluster is dominant, one grain has 2 spot ages of  $574 \pm 26$  and  $574.9 \pm 23$  Ma (analyses 14, 15), which overlap with the older age cluster in sample NB08-268, so perhaps these 2 rocks have sampled most of the same ages of rocks, in different proportions, although we are wary of subdividing too much with analyses of such low precision compared to TIMS (all uncertainties are propagated at 2 standard error of the mean). Two analyses are  $655 \pm 35$  Ma (rim) and  $641 \pm 27$  Ma (core). That core has an igneous rim at  $610 \pm 25$  Ma, an interesting age match with 4 zircon analyses from NB08-268 and not surprising given that these rocks unconformably overlie or intruded the ca. 625–615 Ma Broad River Group and associated plutons.

The five youngest analyses, from 4 grains, range from 436 to 398 Ma (Fig. 8f). They all overlap (barely) and each looks like a simple one-age zircon crystal. Three of these grains give 4 spot analyses (#19, 33, 34, 54) from which an acceptable age of  $427 \pm 9$  Ma ( $\text{MSWD} = 0.39$ ) can be calculated. This is likely the true age (within uncertainties) of the youngest group of igneous zircon grains in the rock and hence provides a maximum age of emplacement for the felsite. The single  $398 \pm 21$  Ma analysis (#62) is 24 million years younger than the next youngest. Again, the combined TIMS and laser ICP-MS data set makes sense and they are consistent, with TIMS ages matching or falling in between the clusters identified by laser, and the calculated TIMS lower intercept age of ca. 417 (albeit  $\pm 100$  Ma) in agreement with the youngest age group identified by laser analysis.

## DISCUSSION AND CONCLUSIONS

Two new CA-ID-TIMS ages presented here resolve two long-standing uncertainties in the Caledonia Highlands: the ages of the (1) Fairfield and (2) Gordon Falls formations. The new age of  $622.0 \pm 1.9$  Ma from rhyolite of the Fairfield Formation is consistent with field relations that suggest that it is part of the Broad River Group and not a younger Devonian unit; hence it is now included in the East Branch Black River Formation of that group (Fig. 2). Similarly, the



**Figure 8.** Age data for sample NB15-348 from the Bloomsbury Mountain felsite. (a) Cathodoluminescence images of zircon grains showing spots analyzed and ages obtained by LA-ICP-MS. (b) Concordia diagram for TIMS data (Table A1). (c) Concordia diagram for LA-ICP-MS analyses (from Table A2) and TIMS data (grey). (d) Concordant analyses at ca. 555 Ma, including 2 of the TIMS analyses (in grey). (e) Weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age for the 19 best analyses, including both core and rim analyses. (f) Concordia diagram for five youngest spot analyses from 4 grains and two TIMS analyses (in grey).

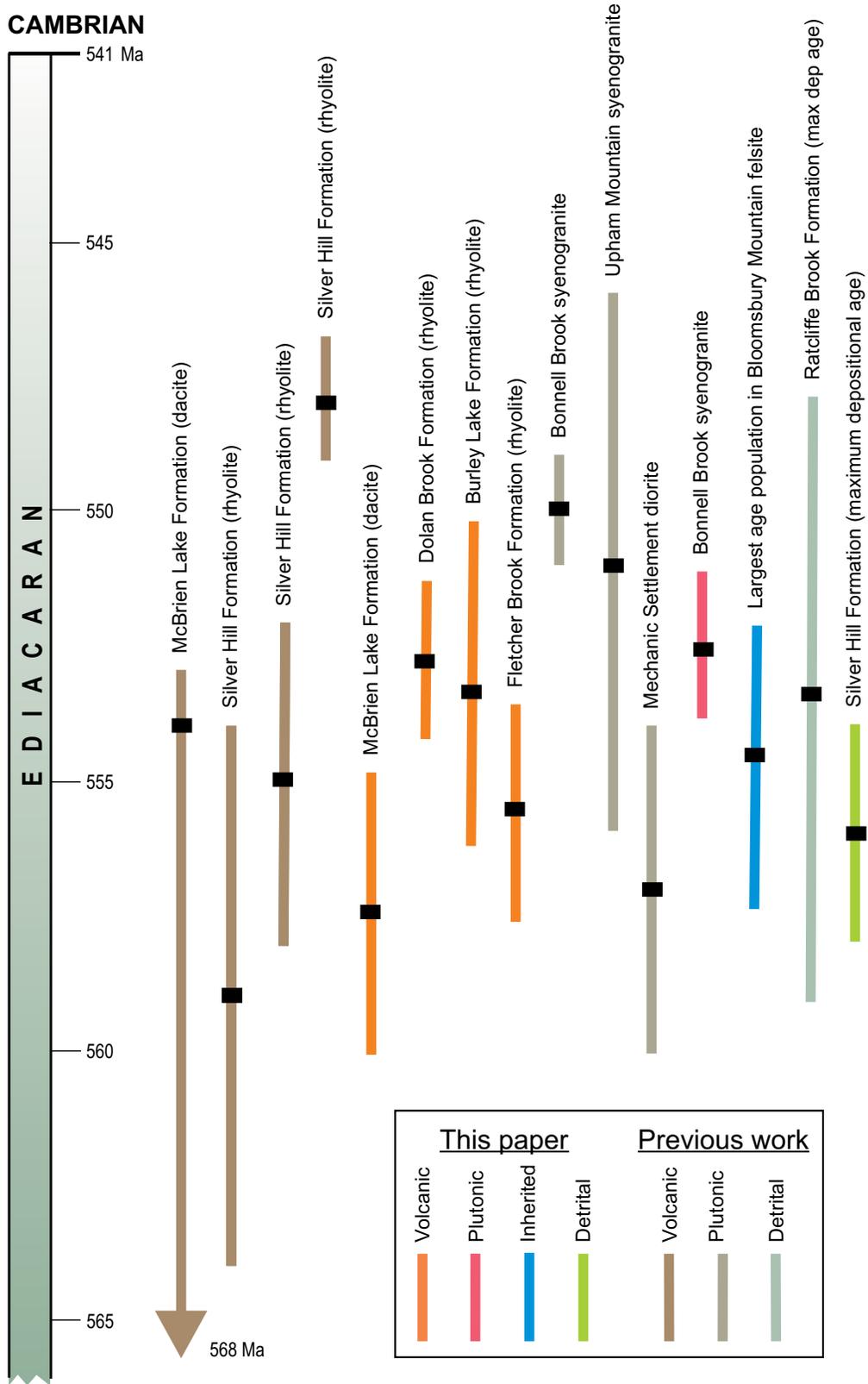


Figure 9. Compilation of ages from the Coldbrook Group and related samples plotted with errors, including previously published ages (Fig. 1) and the new data presented in this paper.

# CALEDONIA HIGHLANDS “Stratigraphic” Summary

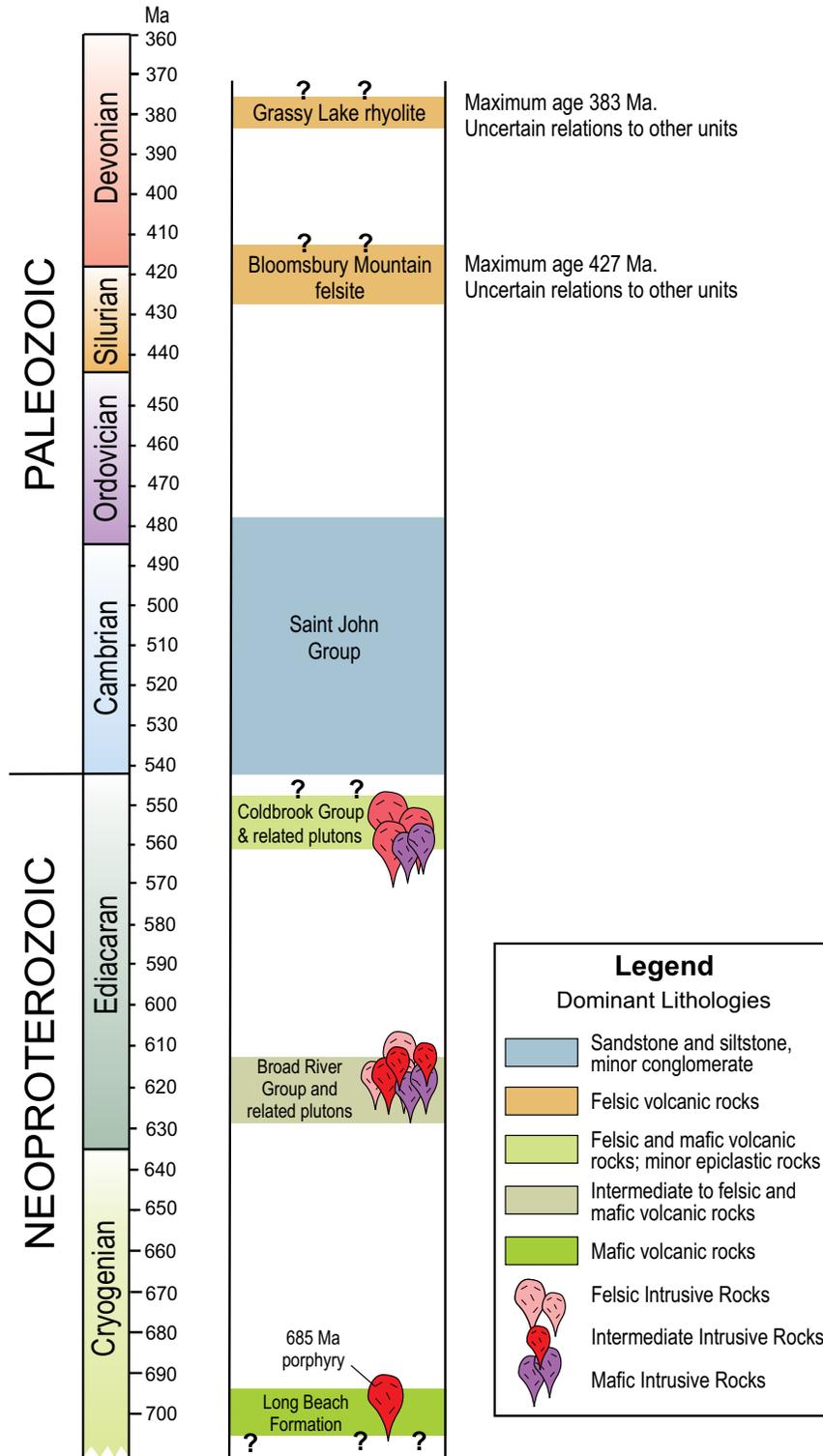


Figure 10. Summary of pre-Carboniferous rock units in the Caledonia terrane based on the results of this study and previous work as described in the text.

new age of  $620 \pm 5$  Ma from felsic tuff of the Gordon Falls Formation is more consistent with field relations which suggest that it is also part of the Broad River Group (Fig. 1). These additional two ages also provide better constraint on the age of the volcanic rocks of the Broad River Group, previously constrained mainly by ages from cross-cutting plutons (Fig. 10).

However, the new data also demonstrate that igneous rocks in the Broad River Group are not the oldest in the Caledonia terrane. The age of  $685 \pm 10$  Ma from quartz-feldspar porphyry in the Long Beach Formation provides a minimum age for that formation (Fig. 10). The close association of the high-level intrusion and volcanic rocks of the formation suggest that they are comagmatic and hence that the formation has a similar Cryogenian age. More dating is needed to constrain the extent of rocks of this age in the Caledonia terrane because the Long Beach Formation is fault bounded. The age of the porphyry is similar to that of dated porphyry in the Stirling belt of the Avalonian Mira terrane in Cape Breton Island, which yielded an age of  $681 +6/-2$  Ma (Bevier *et al.* 1993). This potential correlation is of particular importance because the Stirling belt hosts the Mindamar Zn-Pb-Cu-Ag-Au deposit, volcanic exhalative type of deposit, located in what appears to be a stratigraphically controlled position between dated 680 Ma rhyolite porphyry, quartz-carbonate rocks, and overlying tuffaceous sedimentary rocks (Barr *et al.* 1996). Mineralized volcanic and plutonic rocks of similar age also occur in the southwestern part of the Newfoundland Avalon terrane (Swinden and Hunt 1991; O'Brien *et al.* 1992).

New CA-ID-TIMS ages reported here from 4 volcanic samples from the Coldbrook Group (McBrien Lake, Fletcher Lake, Dolan Brook, and Burley Lake formations) overlap within error and hence do not better constrain the stratigraphic order of the units as inferred from field observations. The data do not show a clear division into lower and upper parts as suggested previously based on field relations (e.g., Barr and White 1999a). However, the more precise age from the McBrien Lake Formation ( $557.4 \pm 2.5$  Ma compared to the previous age of  $554 +14/-1$  Ma; Barr *et al.* 1994) better constrains the maximum eruptive age of the Coldbrook Group to less than 560 Ma, as the McBrien Lake Formation is the lowermost unit based on mapping (Barr and White 2004). The cross-cutting Bonnell Brook granite and related plutons provide a minimum age for the Fletcher Brook and underlying formations (Fig. 2). Syenogranite sample NB16-03 yielded an age of  $552.5 \pm 1.5$  Ma, consistent within error with the previous age of  $550 \pm 1$  Ma for another sample from the northeastern part of the pluton (Fig. 2). The youngest zircon populations in quartz phyllite sample NB15-344 ( $556 \pm 2$  Ma) and the Ratcliffe Brook Formation quartz arenite ( $553.3 \pm 5.3$  Ma) reported previously by Satkoski *et al.* (2010) provide further evidence of the age, as does age of  $554.7 \pm 2.6$  Ma from the largest

inherited zircon population in the Bloomsbury Mountain felsite (Fig. 8e). Taken in combination with previously dated samples, the age of the Coldbrook Group and associated plutons is now well constrained to between 560 and 550 Ma, including errors (Fig. 9).

The range of ages from the rhyolite unit mapped throughout the highlands as Silver Hill Formation (Barr and White 2004) suggests that more than one rhyolite formation may be present, although the ages are not precise enough to demonstrate this difference with certainty, especially as the outlying younger age of  $548 \pm 1$  Ma (Bevier and Barr 1990) has not been corroborated by more recent work. Given the large lateral extent and thickness of the Coldbrook Group, as well as the area of related plutons, as mapped by Barr and White (1999a, b, 2004), a large volume of mainly felsic magma was erupted and intruded in less than 10 million years, and perhaps much less than that time. Such an environment invokes comparison with supereruptions documented at more recent volcanoes such as Yellowstone and elsewhere in the southwestern USA (Wilson 2008; Best *et al.* 2013). The existing chemical data from the Coldbrook Group and related plutons suggest that they were emplaced in an extensional setting (Barr and White 1999a; Guy 1998), although more modern chemical studies are needed to confirm that interpretation. Although large volumes of felsic magma occur in other parts of Avalonia, such as the Marystown Group in Newfoundland (Sparkes and Dunning 2014; Sparkes *et al.* 2016), they have ages of ca. 575 Ma and therefore are older than the Coldbrook Group.

The extent and exact age of the two youngest units in the Caledonia terrane remain difficult to pin down based on both field relations and CA-ID-TIMS and LA-ICP-MS ages. Most evidence points to Silurian-Devonian age for the Bloomsbury Mountain felsite and a maximum Devonian age (ca. 383 Ma) for the Grassy Lake Formation (Fig. 10). The Bloomsbury Mountain felsite appears to be a high-level intrusion and hence its younger age (maximum 427 Ma) compared to its ca. 560–550 Ma host rocks is feasible, although it is the only unit of this age known in the terrane. The Grassy Lake Formation is more difficult to explain because of its similarity to the surrounding ca. 555 Ma volcanic rocks of the Coldbrook Group. Furthermore, field relations suggest that it, or rocks like it, were intruded by the ~552 Ma Bonnell Brook pluton. The absence of evidence from zircon inheritance for interaction with the ca. 620 Ma and 555 Ma rocks which form most of the Caledonia terrane is puzzling, as is the disturbed character of the zircon grains in sample NB08-268 compared to the other analyzed samples. More mapping and sampling are needed in the Grassy Lake area to look for field, petrographic, or chemical evidence that can distinguish this apparently Devonian volcanic unit from similar rocks of the surrounding Coldbrook Group.

The results presented here clearly demonstrate the need for accurate and precise U–Pb zircon age constraints in

order to understand the geological history of complex geological areas such as the Caledonia terrane and other parts of Avalonia.

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## APPENDIX

### U–Pb zircon data

**Table A1.** CA–TIMS U–Pb zircon data, Caledonia terrane.

Fraction	Concentration		Measured		Corrected Atomic Ratios *						Age (Ma)				
	Weight (mg)	U (ppm)	Pb (rad)	TC Pb <sup>1</sup>	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>206</sup> Pb	<sup>206</sup> Pb/ <sup>238</sup> U	<sup>207</sup> Pb/ <sup>235</sup> U	2σ	<sup>207</sup> Pb/ <sup>206</sup> Pb	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	<sup>207</sup> Pb/ <sup>235</sup> U	<sup>207</sup> Pb/ <sup>206</sup> Pb	
<b>Long Beach Formation Quartz-feldspar porphyry dyke (NB14-335) (UTM:313362E, 5033179N, Grid Zone 20T)</b>															
Z1 2 clr 2:1 prm	0.003	58	9.2	5.2	286	0.3586	0.1289	82	1.2669	700	0.07131	360	781	831	966
Z2 1 clr prm	0.002	23	3.1	2.3	124	0.3339	0.1148	260	0.8730	1366	0.05517	802	700.4	637	419
Z3 2 clr euh prm	0.003	34	4.5	3.1	253	0.3062	0.1136	88	0.9777	412	0.06241	244	693.8	692	688
Z4 4 clr prm	0.006	48	7.1	5.1	511	0.1833	0.1370	76	1.2786	166	0.06769	76	828	836	859
<b>East Branch Black River Formation (formerly Fairfield) Rhyolite (NB14-334) (UTM: 288307E, 5023664N, Grid Zone 20T)</b>															
Z1 1 lrg euh prm	0.002	190	23.0	15	136	0.3336	0.1012	70	0.8403	264	0.06023	172	621.4	619	612
Z2 1 clr euh prm	0.002	158	18.3	5.9	273	0.2640	0.1016	64	0.8344	144	0.05957	94	623.7	616	588
Z3 4 lrg clr prm	0.006	179	21.8	6.8	1020	0.3374	0.1009	58	0.8376	56	0.06021	32	619.6	618	611
Z4 2 sml clr prm	0.003	143	17.5	2.0	1405	0.3319	0.1016	72	0.8511	140	0.06075	88	623.8	625	631
Z5 2 sml clr prm	0.003	65	8.1	12	120	0.3404	0.1030	72	0.8617	350	0.06067	228	632	631	628
Z6 2 sml clr prm	0.003	35	4.3	13	70	0.3319	0.1033	92	0.8780	774	0.06162	504	634	640	661
<b>Gordon Falls Formation Tuff (SH15-137) (UTM: 337138E, 5071739N, Grid Zone 20T)</b>															
Z1 8 sml euh prm	0.008	75	9.3	9.5	415	0.3732	0.1011	90	0.8423	64	0.06045	42	620.5	620	620
Z2 2 sml clr euh prm	0.002	109	13.7	3.2	447	0.3913	0.1005	40	0.8347	86	0.06023	56	617.5	616	612
<b>McBrien Lake Formation Dacite (NB16-01) (UTM: 275648E, 5030513N, Grid Zone 20T)</b>															
Z1 2 clr sml prm	0.002	41	3.8	2.7	186	0.1964	0.0875	68	0.7035	204	0.05831	156	541	541	541
Z2 1 clr sml prm	0.001	41	4.1	2.2	123	0.2128	0.0905	100	0.7266	376	0.05821	278	558.7	555	538
Z3 3 sml clr prm	0.003	83	8.6	3.3	453	0.2754	0.0903	72	0.7310	68	0.05870	52	557.4	557	556
Z4 1 sml clr prm	0.001	116	11.5	3.2	222	0.2266	0.0896	96	0.7212	112	0.05838	82	553.2	551	544
Z5 1 sml clr prm	0.001	48	4.6	2.2	141	0.1558	0.0907	84	0.7241	322	0.05792	236	559.5	553	527
<b>Fletcher Brook Formation Rhyolitic tuff (NB15-003) (UTM: 298036E, 5035971N, Grid Zone 20T)</b>															
Z1 2 clr euh prm	0.002	103	9.9	1.9	618	0.1927	0.0899	54	0.7205	88	0.05812	68	555.0	551	534
Z2 1 clr euh prm	0.001	113	11.0	3.0	232	0.1991	0.0901	68	0.7222	146	0.05817	114	555.8	552	536
Z3 3 clr euh prm	0.003	312	30.5	1.8	3040	0.2045	0.0900	68	0.7248	60	0.05842	50	555.5	554	545
Z4 3 clr euh prm	0.003	82	8.1	1.8	806	0.2082	0.0901	82	0.7237	106	0.05824	68	556.3	553	539
<b>Dolan Brook Formation Tuff (NB16-02) (UTM: 301590E, 5032110N, Grid Zone 20T)</b>															
Z1 4 sml clr prm	0.004	98	9.8	12	205	0.2349	0.0899	60	0.7161	132	0.05781	94	554.6	548	522
Z2 4 clr euh prm	0.004	133	13.2	2.2	1370	0.2315	0.0894	38	0.7208	38	0.05850	26	551.8	551	549
Z3 3 sml clr prm	0.003	106	10.7	13	159	0.2364	0.0903	76	0.7368	174	0.05921	126	557	561	575
Z4 3 sml clr euh prm	0.003	146	14.4	3.5	730	0.2223	0.0897	52	0.7227	60	0.05847	42	553.5	552	547

Table A1. Continued.

Fraction	Concentration			Measured		Corrected Atomic Ratios *						Age (Ma)			
	Weight (mg)	U (ppm)	Pb rad	TC Pb <sup>1</sup>	<sup>206</sup> Pb/ <sup>204</sup> Pb	<sup>208</sup> Pb/ <sup>206</sup> Pb	<sup>206</sup> Pb/ <sup>238</sup> U	2σ	<sup>207</sup> Pb/ <sup>235</sup> U	2σ	<sup>207</sup> Pb/ <sup>206</sup> Pb	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	<sup>207</sup> Pb/ <sup>235</sup> U	<sup>207</sup> Pb/ <sup>206</sup> Pb
<b>Bonnell Brook Syenogranite (NB16-03) (UTM: 303187E, 5034281N, Grid Zone 20T)</b>															
Z1 3 sml clr euh prm	0.003	204	18.9	2.6	1323	0.1439	0.0896	58	0.7208	44	0.05836	22	553.1	551	543
Z2 5 sml clr euh	0.005	353	32.9	3.5	2810	0.1510	0.0895	40	0.7230	30	0.05859	16	552.6	552	552
Z3 6 sml clr euh prm	0.006	71	6.6	3.4	721	0.1520	0.0894	96	0.7224	56	0.05858	52	552.3	552	552
Z4 5 sml clr euh prm	0.005	194	18.2	3.8	1432	0.1591	0.0894	54	0.7218	50	0.05857	30	551.9	552	551
<b>Burley Lake Formation Rhyolite (NB16-04) (UTM: 299417E, 5028954N, Grid Zone 20T)</b>															
Z1 5 sml euh prm	0.005	60	6.3	3.0	575	0.3033	0.0900	66	0.7252	70	0.05843	40	555.7	554	546
Z2 2 clr sml euh prm	0.002	88	8.5	3.0	351	0.1951	0.0899	102	0.7247	114	0.05847	78	554.9	553	547
Z3 4 sml clr euh prm	0.004	71	6.8	2.7	615	0.1849	0.0894	44	0.7196	42	0.05839	24	551.8	550	545
<b>Silver Hill Formation Quartz phyllite (NB15-344) (UTM: 311644E, 5033065N, Grid Zone 20T)</b>															
Z1 1 clr sml euh prm	0.001	147	14.6	2.2	395	0.2188	0.0902	76	0.7262	206	0.05842	156	556.5	554	545
Z2 2 clr sml euh Z3 1	0.002	136	10.7	2.8	474	0.1627	0.0746	30	0.5828	106	0.05670	96	463	466	480
Z3 1 clr sml euh prm	0.001	128	12.7	2.5	307	0.2268	0.0902	90	0.7185	130	0.05780	96	556.5	550	522
Z4 2 clr sml euh prm	0.002	188	18.6	2.0	1058	0.2231	0.0899	50	0.7242	58	0.05842	44	555.0	553	545
<b>Grassy Lake Formation Rhyolite (NB08-268) (UTM: 302562E, 5034881N, Grid Zone 20T)</b>															
Z1 3 sml sharp euh prm	0.003	94	13.6	1.5	1571	0.2032	0.1307	126	1.4673	146	0.08143	50	792	917	1232
Z2 3 sml sharp 2:1 prm	0.003	80	5.8	2.2	508	0.1207	0.0716	58	0.5553	100	0.05624	94	446	448	462
Z3 2 sml sharp prm abr	0.002	148	11.3	1.5	941	0.1543	0.0734	88	0.5737	60	0.05668	56	457	460	479
Z4 3 sml clr euh prm	0.003	47	5.2	2.5	366	0.2612	0.0974	58	0.8029	124	0.05977	86	599	598	595
Z5 2 clr sml euh prm	0.002	108	12.4	1.1	1251	0.2771	0.0990	296	0.8091	192	0.05927	112	609	602	577
Z6 2 clr tiny euh prm	0.002	240	17.7	8.5	269	0.1557	0.0709	52	0.5430	92	0.05552	84	442	440	433
Z7 1 clr euh prm	0.001	133	14.1	1.6	67	0.2995	0.0907	46	0.7274	328	0.05817	244	560	555	536
Z8 2 clr euh prm	0.002	198	16.3	6.6	315	0.1555	0.0788	56	0.6152	96	0.05663	84	489	487	477
<b>Bloomsbury Mountain Felsite (NB15-348) (UTM: 278716E, 5019226N, Grid Zone 20T)</b>															
Z1 2 tiny clr euh	0.002	34	2.9	1.0	50	0.2536	0.0757	76	0.5866	224	0.05618	198	471	469	459
Z2 1 tiny clr euh	0.001	85	8.3	3.8	147	0.1862	0.0910	68	0.7381	420	0.05886	312	561	561	562
Z3 2 tiny clr euh	0.002	130	10.2	3.3	372	0.2255	0.0712	84	0.5503	104	0.05605	88	443	445	455
Z4 1 clr euh prm	0.001	240	22.8	3.4	420	0.1775	0.0894	46	0.7216	100	0.05853	74	552	552	550
Z5 2 clr euh prm	0.002	58	6.3	3.9	196	0.2690	0.0953	168	0.7553	440	0.05746	312	587	571	509

Notes: Z = zircon, 1, 2 = number of grains, lrg = large, clr = clear, sml = small, prm = prism, euh = euhedral. All zircon was chemically abraded (cf. Mattinson 2005). Weights were estimated. TCPb<sup>1</sup> = Total common Pb. \*Atomic ratios corrected for fractionation, spike, laboratory blank of 1–2 picograms of common lead, and initial common lead at the age of the sample calculated from the model of Stacey and Kramers (1975), and 0.3 picogram U blank. Two sigma uncertainties are reported after the ratios and refer to the final digits. All <sup>206</sup>Pb/<sup>238</sup>U ages used in the age calculations are reported to one decimal place.

**Table A2.** Chemical abrasion laser ICP-MS data, Caledonia terrane.

Spot #	Concentrations			U/Th	Isotopic Ratios							Age (Ma)			
	Pb (ppm)	U (ppm)	Th (ppm)		<sup>207</sup> Pb/ <sup>235</sup> U	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	2σ	rho	<sup>207</sup> Pb/ <sup>206</sup> Pb	2σ	<sup>207</sup> Pb/ <sup>235</sup> U	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	2σ
<b>Bloomsbury Mountain Felsite (Sample: NB15- 348)</b>															
11	14.6	93.8	59.5	1.572	0.712	0.054	0.0818	0.0036	0.2626	0.0636	0.0036	540	32	506.8	22
12	25.3	143.9	89.5	1.601	0.735	0.058	0.0903	0.0044	0.3827	0.0589	0.0034	555	34	557.0	26
13	11.7	97.0	48.6	2.013	0.881	0.100	0.0936	0.0054	0.0911	0.0684	0.0084	633	53	577.0	32
14	21.5	138.8	78.9	1.734	0.810	0.064	0.0932	0.0044	0.2384	0.0633	0.0039	598	35	574.0	26
15	31.2	193.9	117.1	1.653	0.732	0.049	0.0933	0.0040	0.3342	0.0569	0.0026	558	27	574.9	23
16	19.5	93.1	75.3	1.227	0.734	0.052	0.0901	0.0039	0.1091	0.0595	0.0031	553	30	555.9	23
17	19.4	124.1	82.2	1.514	0.690	0.048	0.0845	0.0039	0.3533	0.0592	0.0027	528	29	523.0	23
18	93.3	408.0	402.0	1.010	0.793	0.050	0.0901	0.0042	0.5739	0.0633	0.0022	590	29	556.0	25
19	20.6	160.9	91.4	1.758	0.664	0.100	0.0700	0.0039	0.2264	0.0680	0.0110	509	61	436.0	23
20	23.7	165.7	95.0	1.736	0.695	0.045	0.0877	0.0037	0.1875	0.0575	0.0025	533	27	541.6	22
21	81.1	277.0	319.7	0.863	0.723	0.042	0.0904	0.0038	0.0089	0.0583	0.0020	550	24	557.7	23
22	38.3	242.3	151.0	1.601	0.724	0.044	0.0908	0.0039	0.1798	0.0585	0.0023	554	27	559.9	23
31	70.2	311.0	310.0	1.012	0.757	0.064	0.0892	0.0052	0.5909	0.0601	0.0034	568	37	550.0	31
32	14.7	187.8	61.4	3.110	0.927	0.074	0.1070	0.0060	0.2849	0.0636	0.0043	663	39	655.0	35
33	51.7	300.1	233.3	1.285	0.524	0.032	0.0678	0.0029	0.1299	0.0560	0.0024	426	22	422.7	18
34	55.1	423.0	281.0	1.607	0.522	0.029	0.0688	0.0029	0.2020	0.0550	0.0015	425.3	19	429.0	17
35	21.3	148.7	94.7	1.593	0.672	0.041	0.0843	0.0036	0.1596	0.0578	0.0021	519	25	521.5	21
36	12.6	107.5	58.1	1.844	0.723	0.059	0.0889	0.0042	0.0200	0.0589	0.0042	548	35	549.0	25
37	24.1	141.8	102.7	1.375	0.764	0.076	0.0832	0.0041	0.2805	0.0656	0.0056	571	44	515.0	25
38	41.9	238.3	171.0	1.372	0.840	0.079	0.0842	0.0042	0.1797	0.0711	0.0056	615	43	521.0	25
39	15.8	99.1	66.1	1.530	0.831	0.095	0.0876	0.0067	0.4513	0.0675	0.0067	608	53	541.0	40
40	48.9	250.0	214.0	1.182	0.791	0.091	0.0890	0.0055	0.5360	0.0620	0.0051	584	50	549.0	33
41	26.5	166.6	102.5	1.616	0.736	0.042	0.0906	0.0038	0.2362	0.0587	0.0017	557	24	559.2	23
42	11.4	91.7	46.6	1.972	0.734	0.064	0.0897	0.0039	0.0490	0.0588	0.0043	551	38	553.6	23
43	46.7	246.0	182.3	1.352	0.718	0.044	0.0894	0.0038	0.2435	0.0579	0.0020	547	25	551.6	22
51	18.2	109.8	78.7	1.393	0.700	0.054	0.0873	0.0039	0.0595	0.0582	0.0037	533	33	539.0	23
52	31.9	192.0	132.0	1.488	0.739	0.048	0.0887	0.0039	0.1944	0.0596	0.0026	559	28	547.6	23
53	27.3	129.7	113.7	1.141	0.692	0.046	0.0869	0.0037	0.0675	0.0572	0.0026	530	27	537.3	22
54	44.5	362.1	225.9	1.596	0.524	0.032	0.0677	0.0029	0.3509	0.0555	0.0020	426	21	422.3	18
55	42.4	231.0	171.0	1.405	0.707	0.045	0.0877	0.0038	0.3163	0.0580	0.0023	541	27	541.7	23
56	14.1	335.0	49.7	7.030	0.876	0.047	0.1046	0.0046	0.1919	0.0602	0.0014	639	26	641.0	27
57	17.0	265.0	61.2	4.880	0.832	0.047	0.0993	0.0042	0.2905	0.0604	0.0017	613	26	610.1	25
58	30.2	160.7	120.0	1.357	0.729	0.043	0.0896	0.0038	0.1555	0.0584	0.0020	553	26	553.3	23
59	39.9	198.5	152.8	1.286	0.749	0.043	0.0927	0.0039	0.2788	0.0582	0.0018	568	24	571.3	23
60	10.1	64.3	40.8	1.581	0.701	0.046	0.0879	0.0039	0.0780	0.0582	0.0027	536	28	543.1	23
61	19.9	101.3	73.0	1.493	0.725	0.049	0.0891	0.0040	0.1298	0.0583	0.0027	552	29	550.3	23
62	11.2	146.3	64.3	2.272	0.529	0.063	0.0637	0.0035	0.3138	0.0582	0.0062	427	42	398.0	21
69	15.2	91.0	54.8	1.689	0.710	0.049	0.0885	0.0039	0.0375	0.0580	0.0030	539	29	546.4	23
70	18.1	128.8	79.3	1.625	0.673	0.057	0.0846	0.0043	0.5061	0.0572	0.0041	528	39	523.0	25
71	17.4	132.8	72.6	1.833	0.697	0.047	0.0837	0.0039	0.1333	0.0603	0.0030	533	28	518.0	23
72	23.2	108.4	82.5	1.329	0.990	0.071	0.0890	0.0040	0.1370	0.0792	0.0045	693	36	549.7	23

Table A2. Continued.

Spot #	Concentrations			Isotopic Ratios								Age (Ma)			
	Pb (ppm)	U (ppm)	Th (ppm)	U/Th	<sup>207</sup> Pb/ <sup>235</sup> U	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	2σ	rho	<sup>207</sup> Pb/ <sup>206</sup> Pb	2σ	<sup>207</sup> Pb/ <sup>235</sup> U	2σ	<sup>206</sup> Pb/ <sup>238</sup> U	2σ
<b>Grassy Lake Formation Rhyolite (Sample: NB08- 268)</b>															
73	69.1	346.0	283.0	1.220	0.797	0.053	0.0929	0.0040	0.2407	0.0597	0.0028	594	30	572.7	24
74	51.4	259.6	201.6	1.287	0.775	0.050	0.0947	0.0042	0.2281	0.0577	0.0024	581	28	583.0	25
75	11.1	136.5	45.8	3.000	0.922	0.068	0.0979	0.0051	0.4356	0.0645	0.0032	660	36	602.0	30
76	109.0	645.0	67.5	9.380	3.290	0.190	0.2179	0.0100	0.5777	0.1055	0.0031	1476	46	1270.0	54
77	30.4	124.0	46.8	2.430	2.639	0.150	0.2164	0.0097	0.3950	0.0881	0.0027	1306	42	1262.0	51
78	14.3	182.6	80.9	2.241	0.457	0.028	0.0612	0.0026	0.3280	0.0532	0.0019	380	19	382.8	16
79	24.9	117.4	95.1	1.222	0.783	0.048	0.0955	0.0040	0.0593	0.0587	0.0022	585	28	588.1	24
80	43.1	145.2	167.8	0.864	0.773	0.049	0.0932	0.0040	0.3010	0.0593	0.0023	577	28	574.3	23
87	10.0	72.1	54.8	1.322	0.474	0.037	0.0615	0.0027	0.0020	0.0551	0.0034	388	25	384.7	17
88	62.3	256.0	211.0	1.236	0.889	0.048	0.1005	0.0042	0.1917	0.0629	0.0015	644	26	617.5	25
89	79.7	346.3	301.1	1.149	0.869	0.052	0.0992	0.0043	0.2644	0.0625	0.0019	633	28	609.4	25
90	21.8	159.3	130.5	1.258	0.455	0.031	0.0601	0.0027	0.4281	0.0544	0.0024	378	22	376.1	16
91	45.5	232.1	202.9	1.149	0.710	0.049	0.0865	0.0040	0.4878	0.0577	0.0026	542	29	535.0	24
92	48.4	228.0	59.8	3.824	4.800	0.260	0.3179	0.0140	0.5441	0.1084	0.0022	1781	45	1779.0	68
93	47.3	292.2	237.0	1.237	0.495	0.031	0.0651	0.0029	0.4498	0.0551	0.0020	408	21	406.3	18
94	12.9	290.0	63.3	4.730	0.483	0.028	0.0634	0.0027	0.3488	0.0546	0.0017	399	19	396.2	16
95	34.4	96.0	130.3	0.736	0.769	0.052	0.0930	0.0040	0.0165	0.0594	0.0030	575	30	573.4	24
96	83.9	154.3	116.6	1.321	4.640	0.270	0.3070	0.0140	0.4019	0.1064	0.0032	1753	48	1725.0	68
97	149.7	696.3	594.9	1.167	0.870	0.051	0.1000	0.0043	0.2456	0.0604	0.0020	635	28	614.7	25
98	28.9	164.4	72.4	2.270	1.622	0.120	0.1585	0.0075	0.4062	0.0722	0.0037	974	47	948.0	42
99	190.0	615.0	440.0	1.441	1.420	0.075	0.1267	0.0054	0.4978	0.0750	0.0014	895	32	768.9	31
<b>Long Beach Formation quartz-feldspar porphyry (Sample: NB14- 335)</b>															
107	49.9	155.7	156.4	1.004	0.983	0.062	0.1123	0.0048	0.3090	0.0629	0.0024	690	32	686.0	28
108	97.4	317.0	350.0	0.908	0.974	0.062	0.1100	0.0051	0.2307	0.0621	0.0025	689	32	673.0	29
109	13.0	53.8	34.2	1.561	1.210	0.110	0.1131	0.0061	0.1433	0.0765	0.0062	797	50	691.0	35
110	76.7	227.0	292.0	0.808	1.030	0.085	0.1091	0.0065	0.5999	0.0668	0.0037	721	40	667.0	37
111	56.3	189.0	198.0	0.962	1.063	0.096	0.1113	0.0069	0.2950	0.0690	0.0054	732	47	680.0	40
112	34.5	119.9	126.0	0.959	1.059	0.098	0.1070	0.0057	0.4435	0.0710	0.0050	725	47	655.0	33
113	85.7	243.0	297.0	0.826	0.973	0.061	0.1129	0.0049	0.2609	0.0616	0.0024	687	31	689.4	28
114	79.0	201.2	239.4	0.843	1.039	0.058	0.1177	0.0050	0.3291	0.0638	0.0018	721	29	717.2	29
115	25.0	50.5	61.8	0.826	1.980	0.160	0.1236	0.0068	0.0237	0.1151	0.0084	1098	55	751.0	39
116	24.5	49.9	35.9	1.423	2.620	0.260	0.1318	0.0072	0.0910	0.1460	0.0130	1288	75	797.0	41
117	188.9	451.0	677.0	0.677	1.260	0.085	0.1167	0.0056	0.3520	0.0772	0.0035	826	38	711.0	33
118	51.2	154.0	168.0	0.972	0.911	0.054	0.1073	0.0047	0.4104	0.0618	0.0020	656	29	656.7	27
126	88.4	224.5	306.2	0.737	0.951	0.063	0.1096	0.0050	0.4814	0.0627	0.0025	675	33	670.0	29
127	133.2	377.0	471.0	0.823	0.959	0.053	0.1124	0.0049	0.3113	0.0619	0.0017	684	26	686.0	29
128	72.5	242.7	228.8	1.059	1.072	0.071	0.1080	0.0050	0.1883	0.0724	0.0035	737	35	661.0	29
129	38.6	154.9	128.8	1.197	1.026	0.091	0.1160	0.0053	0.5391	0.0630	0.0042	711	45	707.0	31
130	107.9	277.0	409.0	0.675	0.922	0.057	0.1021	0.0045	0.2498	0.0658	0.0026	661	30	626.0	26
131	50.7	189.7	190.5	0.995	0.943	0.065	0.1059	0.0047	0.2865	0.0645	0.0030	671	34	649.0	27
132	19.9	95.1	72.5	1.310	1.061	0.092	0.1098	0.0057	0.3465	0.0688	0.0046	728	46	671.0	33
133	26.4	123.5	87.7	1.404	1.008	0.097	0.1128	0.0057	0.6023	0.0629	0.0051	706	48	689.0	33