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Magmatic and Inherited Zircon Ages from a Diorite Xenolith of the Popes Harbour Dyke, Nova Scotia: Implications for Late Ediacaran Arc Magmatism in the Avalon Terrane of the Northern Appalachians

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Abstract: The Meguma terrane is a unique unit of the Northern Appalachians as it is only identified in Nova Scotia. It was thrust over the Avalon terrane during the Early Devonian Acadian Orogeny. The Avalon and Meguma terranes are exotic to North America and likely originated along the margin of Gondwana. The precise relationship between the terranes is uncertain and very little is known about the basement rocks of each terrane. Hosted within the Late Devonian lamprophyric Popes Harbour dyke of the Meguma terrane are xenoliths of meta-sedimentary and meta-igneous rocks that are from the basement of the Avalon terrane. The xenoliths offer a glimpse into the nature of the lower crust of the Northern Appalachians. In this study, we present in situ zircon U-Pb age dates from a rare dioritic xenolith in order to assess its origin. The results show that the majority of zircons ages are between ~580 Ma and ~616 Ma with smaller groups at 750–630 Ma, ~2100 Ma, and <570 Ma. The zircon $^{206}Pb/^{238}U$ weighted-mean age of the rock is 603 ± 5.3 Ma and contemporaneous, with granitic intrusions of the Avalon terrane located within the Antigonish and Cobequid highlands of Nova Scotia. The diorite is compositionally similar to granitoids from an active continental margin. The discovery of Early Paleoproterozoic (~2100 Ma) zircons and the absence of Late Paleoproterozoic (1900–1700 Ma) and Mesoproterozoic (1600–1000 Ma) zircons suggests that the parental magma either encounters only Early Paleoproterozoic and Late Neoproterozoic rocks during emplacement or is derived by the melting of Paleoproterozoic rocks and/or the melting and mixing of Paleoproterozoic and Late Neoproterozoic rocks. Therefore, it is possible that Paleoproterozoic rocks may exist within the basement of the Avalon terrane.

Keywords: Avalonia; dioritic granulite xenolith; Gondwana; sub-Meguma crust; Neoproterozoic

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1. Introduction

The northern Appalachian orogen, largely confined to the current northeastern margin of North America, is a collage of allochthonous terranes sequentially accreted from west to east [1]. The Meguma terrane is the easternmost (most outboard) terrane, which is juxtaposed against the adjacent Avalon terrane along the Cobequid–Chedabucto fault zone, an east–west dextral strike slip zone of Late Paleozoic age [2]. Both of these exotic peri-Gondwanan terranes were accreted to Laurentia (North America) during continental collision in the early to middle Paleozoic [3]. The accretion of these terranes resulted in the Middle Paleozoic Acadian Orogeny and closure of the Rheic Ocean. The last major movement along the Cobequid–Chedabucto fault to affect the accreted terranes occurred at 370–350 Ma [4]. Avalonia and Meguma are believed to have been proximal to the northern margin of Gondwana in the late Neoproterozoic; although, the precise origin and location of the terranes is debated [5–19]. However, there are differences in their present distribution.

The Meguma terrane outcrops only in the southern mainland of Nova Scotia, whereas the West Avalon terrane extends discontinuously from eastern Newfoundland to southeastern New England. The Meguma terrane is the only major terrane in the northern Appalachian orogen that has no obvious correlatives elsewhere in the Appalachians [11,19–21].

The two terranes differ by their early Paleozoic stratigraphy. The Meguma comprises most of the ~10 km-thick succession of the Cambro–Ordovician siliciclastic turbidites (Meguma Group) that contains Gondwana fauna [22]. These rocks are locally overlain unconformably by Silurian shallow marine and continental sedimentary and volcanic rocks [23]. The youngest of these rocks contains Early Devonian fossils [24,25]. The Cambrian to Lower Devonian rocks were metamorphosed from lower greenschist to amphibolite facies conditions during the Acadian orogeny at about 405–370 Ma [26]. These processes were accompanied and followed by intrusions of voluminous granitoid rocks of the South Mountain Batholith and associated plutons that were emplaced at a depth of ~10–12 km around 380–370 Ma [27–29]. The granitic intrusions, which imposed a distinct contact metamorphic aureole, were followed by rapid exhumation and subsequent deposition of Upper Devonian (late Fammenian ~365–360 Ma) to early Carboniferous continental and shallow marine sediments that straddle the Cobequid–Chedabucto fault zone and overstep the terrane boundary with Avalonia [2]. In contrast, the early Paleozoic rocks of West Avalonia (i.e., North American portion) are characterized by platformal successions of Cambrian–Early Ordovician siliciclastic rocks [30], which lie on top of various Late Neoproterozoic, arc-related volcano sedimentary units or associated magmatic arc granitoid rocks. However, the basements of both terranes upon which the Late Neoproterozoic and younger units rest is not exposed. According to detrital zircon studies, the Cambro–Ordovician sedimentary rocks of Avalonia and Meguma appear to have different provenance [31–33], whereas Siluro–Devonian sedimentary rocks of both terranes display similar age characteristics [34].

The only window into the basement rocks of the Meguma and Avalon terranes are xenoliths within the Late Devonian (~370 Ma) Popes Harbour lamprophyric dyke [35–37]. The xenoliths are nearly all derived from the Avalonian crust and consist of meta-sedimentary and meta-igneous lithologies that underwent granulite facies metamorphism [35,38]. The meta-igneous (granite–granodiorite, gabbro, granitic pegmatite) xenoliths from the Popes Harbour dyke are of particular significance because they are rare compared with the meta-sedimentary xenoliths [35,37,38]. Furthermore, the igneous xenoliths are representative of pre-Appalachian magmatic activity that may correlate with pre-rift, active-margin magmatism of Gondwana (i.e., 640–540), rift-related magmatism (~485 Ma), or post-rift magmatism (485–420 Ma) in Avalonia [15,39–44]. Consequently, there is also a possibility that the diorite contains inherited zircons that could reveal the existence of older rocks than those exposed on the surface [45–48].

In this study, we report new in situ zircon laser ablation–inductively coupled plasma mass spectrometry (LA-ICP-MS) geochronology results from a rare dioritic xenolith collected from the Late Devonian Popes Harbour lamprophyric dyke. Our results show that the diorite is compositionally similar to Cordilleran granitoids and has an Ediacaran age. Moreover, Rhyacian, Tonian, and Cryogenian inherited zircons were identified within the diorite, which may provide additional information on the nature and origin of the Avalon terrane.

2. Geological Background

The Popes Harbour dyke (44°46′47.55″ N, 62°38′56.88″ W) is located in Eastern Nova Scotia within the community of Tangier, ~70 km east of Halifax (Figure 1). The dyke is 12–15 m wide and is one of many Late Devonian (~370 Ma) lamprophyric dykes, known as the Weekend dyke swarm, that intrude the Halifax Group and Goldenville Group of the Meguma Supergroup [21,35,36,49,50]. The dykes are perpendicular to the eastern coast of Nova Scotia and are generally a few metres in width. The dyke swarm width is ~200 km with nearly all dykes exposed along the coast [49].

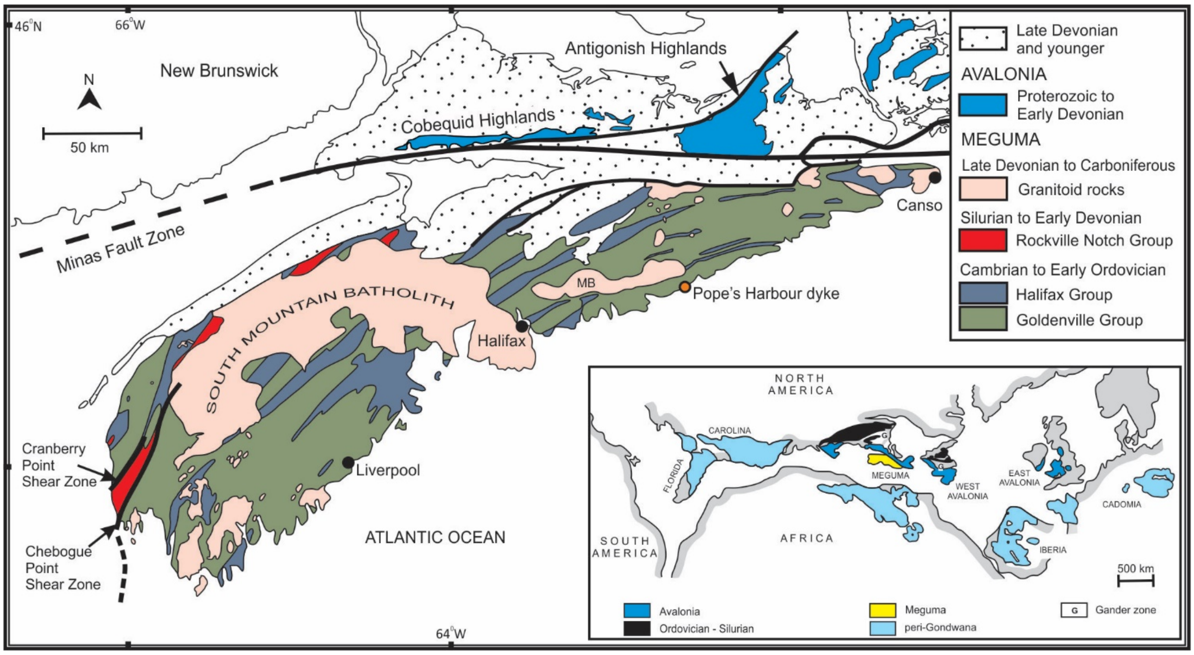

Figure 1. Simplified bedrock geological map of southern Nova Scotia showing the distribution of Late Devonian and older rock units of Avalonia and Meguma and the location of the Popes Harbour dyke. MB—Musquodoboit Batholith. Inset shows the Early Mesozoic reconstruction of Pangea and the locations of Meguma, Avalonia, and other peri-Gondwana terranes [33].

Xenoliths are observed only within the Popes Harbour dyke and are composed of sedimentary (sillimanite and/or kyanite-bearing quartz-poor metapelites, quartzite) and igneous (amphibolite, gabbro, diorite, granite–granodiorite, granitic pegmatite, orthopyroxene-bearing tonalite) rocks that underwent granulite facies conditions [35,51]. The meta-sedimentary xenoliths are more abundant, but there is textural evidence that some disaggregated as xenocrysts of garnet and aluminosilicate (sillimanitized kyanite and sillimanite) minerals are observed in the dyke. The igneous xenoliths tend to be mafic, but there are intermediate to silicic examples [35,38].

Compositionally, the meta-igneous and meta-sedimentary xenoliths are different from the overlying rocks of the Meguma terrane [38]. The Sr-Nd isotopic data for the meta-igneous xenoliths have chondritic to moderately radiogenic Sr and Nd values ($^{87}Sr/^{86}Sr_{370\ Ma}$ = 0.70285 to 0.70500; $\varepsilon Nd_{(370\ Ma)}$ = −2.03 to +5.33), whereas the meta- sedimentary xenoliths are moderately unradiogenic to chondritic ($^{87}Sr/^{86}Sr_{370\ Ma}$ = 0.70458 to 0.70916; $\varepsilon Nd_{(370\ Ma)}$ = −2.03 to +1.53). However, these values assume an initial age of 370 Ma which is certainly not the case. It is likely the meta-sedimentary rocks are no younger than ~410 Ma and the meta-igneous rocks cannot be younger than ~420 Ma as this is the youngest magmatic age in western Avalonia prior to the Acadian Orogeny [33,52,53]. In comparison, the Sr-Nd isotopes of the Meguma terrane sedimentary rocks from Clarke and Halliday [54,55] are unradiogenic ($^{87}Sr/^{86}Sr_{500\ Ma}$ = 0.7113 to 0.7177; $\varepsilon Nd_{(500\ Ma)}$ = −8.8 to −11.3). Consequently, Eberz et al. [38] concluded that xenoliths are representative of the Avalon terrane and that they form the structural basement to Meguma.

3. Petrography

The diorite xenolith of this study is coarse grained and granular and composed primarily of plagioclase feldspar, pyroxene, quartz, and accessory amounts of titanite, cordierite, apatite, and opaque minerals (Figure 2). The primary mineralogy and textures of the rock are mostly preserved, but it is clear that the rock was altered and that some minerals show evidence of the effects of metamorphism (i.e., polygonal to sub-round mineral shapes). The plagioclase is 60–70 vol% of the mineral mode and is identified by polysynthetic twinning and straight grain boundaries. All plagioclase crystals show a patchwork of alteration to clay minerals. Clinopyroxene is the most abundant mafic mineral (≤10 vol.%) and is anhedral–subhedral. It is interstitial to the plagioclase (Figure 2b). Quartz is rounded to sub-round in shape and represents ~10 vol.% of the mineral mode. Subhedral to anhedral titanite (≤5 vol%) is common and appears to have crystallized at the same time as the clinopyroxene, since they share grain boundaries and are both interstitial to plagioclase. A minor amount (<2 vol%) of anhedral cordierite is present and was identified in cross-polarized light, since it has low first order bluish-grey colour (Figure 2a). Apatite is small (≤20 μm) and rounded–hexagonal in shape. The crystals are usually found surrounded by feldspar. Rounded–irregular-shaped opaque minerals, likely to be Fe-Ti oxide minerals, are not abundant, but are either interstitial–primary minerals or are inclusions within the titanite.

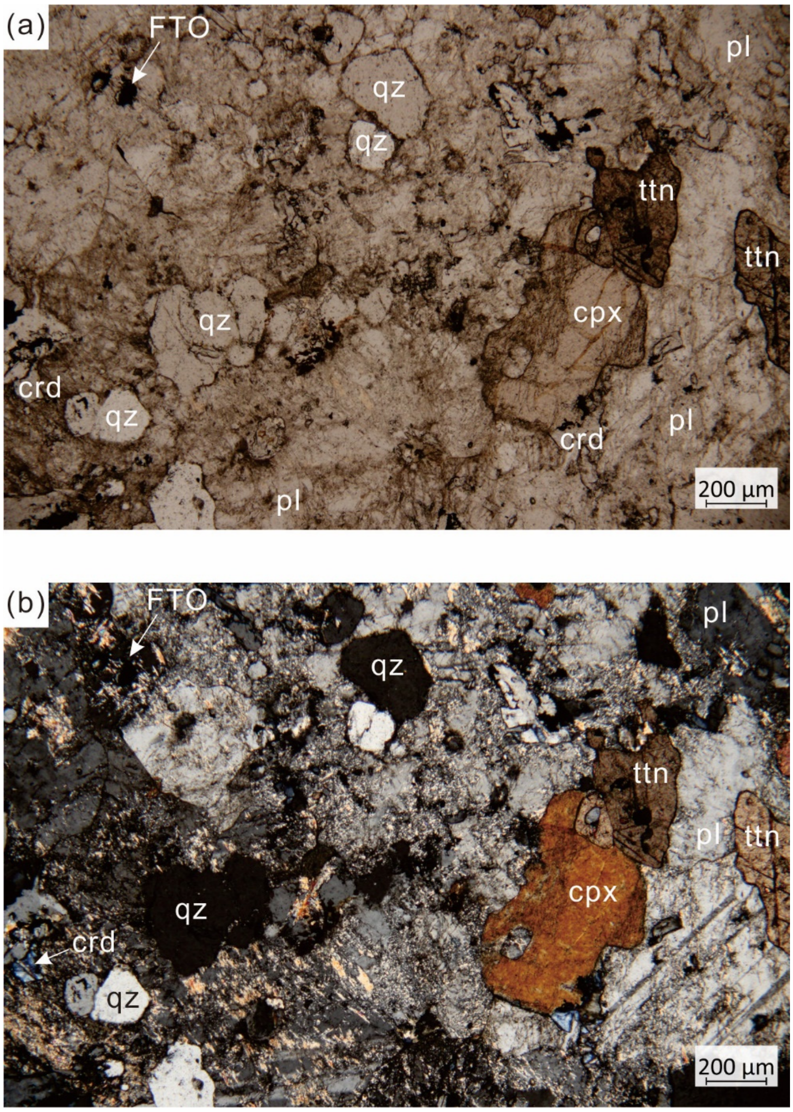

Figure 2. Photomicrograph of the diorite xenolith. (**a**) Plane-polarized light and (**b**) cross-polarized light images of diorite showing quartz (qz), plagioclase (pl), clinopyroxene (cpx), titanite (ttn), apatite (ap), Fe-Ti oxide (FTO) minerals, and cordierite (crd).

4. Methods

The dioritic xenolith (~3 kg) was collected from the Popes Harbour dyke, Nova Scotia, located at 44°46′47.55″ N, 62°38′56.88″ W [35]. Zircons were separated using magnetic and heavy-liquid techniques at the Yu-Neng Rock and Mineral Separation Company (Lanfang, Hebei, China). Cathodoluminescence (CL) images were taken at the Institute of Earth Sciences, Academia Sinica (Taipei, Taiwan), and used to examine the internal structures of individual crystals and to select suitable locations for in situ U-Pb analyses. Zircon U-Pb isotopic analyses were performed by laser ablation–inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Department of Geosciences, National Taiwan University, Taipei using an Agilent 7500s Q-ICP-MS and a Photon Machines Analyte G2 193 nm laser ablation system. A spot size of 35 μm with laser repetition rate of 5 Hz was used and the laser energy density was 3.83 to 5.33 J/cm^2. Calibration was performed by using the zircon standards GJ-1 (608.5 ± 0.4 Ma), 91,500 (1065 Ma); zircon Plešovice (337.1 ± 0.4 Ma) was used as a secondary standard for data quality control [56–58]. Measured (U,Th)/Pb isotope ratios were calculated using the GLITTER 4.4.4 software and the relative standard deviations of reference values for GJ-1 were set at 2% [59]. The common Pb-correction of Andersen [60] was used to process the data, whereas the weighted mean ages, Concordia plots, and probability density plots were created using Isoplot v. 4.1 [61].

5. Results

A total of 60 spot analyses on 51 individual zircons were analyzed from the dioritic xenolith (Supplementary Table S1). Individual zircon grains are mostly ellipsoidal–round in shape with a few that have irregular–sub-round shapes (Figure S1). All crystals are ~100 μm to ~150 μm along the long axis of the crystals. The cathodoluminescence (CL) images of the zircons show complex structures with a few showing oscillatory zonation and the majority showing darker cores and brighter rims. We analyzed the darker cores and lighter rims between different zircons and within the same zircon and found no consistent age relationship. In general, the brighter regions tend to yield younger ages, although this not always the case (Figure S1). We think that the prevalence of the dark core–bright rim structure is a consequence of crystal regrowth during magmatism and possibly the effects of deformation that affected Avalonia during the Acadian Orogeny. The zircons can be divided into a predominantly Neoproterozoic age group and a Paleoproterozoic age group.

The Neoproterozoic group (56 spots) has 7 age clusters with the complete $^{206}Pb/^{238}U$ age spectrum from 406 ± 10 Ma (1σ) to 752 ± 16 Ma (1σ) that have Th/U ratios from 0.07 to 1.17 (Figure 3). All but two analyses (GXN39 and GXN52) were within ~11% discordance (i.e., [1 − ($^{206}Pb/^{238}U$ age/$^{207}Pb/^{235}U$ age)] × 100) or better (Figures S2). However, for younger (≤ 1000 Ma) zircons, the $^{206}Pb/^{238}U$ ratio retains nearly all of the chronometric information, and therefore we will focus on these ages [62]. There are seven spots that have Tonian to Cryogenian ages. Two zircons have $^{206}Pb/^{238}U$ ages of 752 ± 16 Ma (1σ) and 717 ± 17 Ma (1σ) and five have $^{206}Pb/^{238}U$ ages of 692 ± 15 Ma (1σ), 677 ± 14 Ma (1σ), 671 ± 15 Ma (1σ), 646 ± 15 Ma (1σ), and 637 ± 14 Ma (1σ). The majority of the zircon crystals (42) have Ediacaran ages, but 5 clusters can be identified based on distinct age gaps within the data set. The oldest of the clusters consists of six zircons with $^{206}Pb/^{238}U$ ages ranging from 619 ± 15 Ma (1σ) to 630 ± 14 Ma (1σ). The largest (13) cluster has $^{206}Pb/^{238}U$ ages ranging from 606 ± 15 Ma (1σ) to 616 ± 14 Ma (1σ). The second largest (12) cluster has $^{206}Pb/^{238}U$ ages ranging from 591 ± 13 Ma (1σ) to 601 ± 13 Ma (1σ). The remaining two clusters (5 and 6 spots, respectively) have $^{206}Pb/^{238}U$ ages ranging from 581 ± 12 Ma (1σ) to 587 ± 13 Ma (1σ) and from 546 ± 13 Ma (1σ) to 570 ± 13 Ma (1σ), but the ages of the younger grouping are more dispersed. The youngest spot analyses have Cambrian ages (515 ± 12 Ma, 1σ to 530 ± 13 Ma, 1σ) with one Early Devonian age (406 ± 10 Ma, 1σ).

The four Paleoproterozoic zircon grains have $^{207}Pb/^{206}Pb$ ages of 2354 ± 16 (1σ), 2072 ± 18 (1σ), 2076 ± 18 (1σ), and 2034 ± 18 (1σ) and their Th/U ratios are 0.31, 0.36, 1.19, and 0.91. Their discordance is within 11% or better (i.e., [1 − ($^{206}Pb/^{238}U$ age/$^{207}Pb/^{206}U$ age)] × 100) and they do not indicate a coherent age. The Paleoproterozoic ages are very likely indicative of inheritance from the sub-Meguma basement and suggest that Paleoproterozoic rocks may be present within the Avalon terrane.

Of the 51 zircons, 7 were analyzed for core–rim variability. Two zircons (spots 4 and 5 and spots 15 and 16) yielded core–rim ages within error of each other (515 ± 12 Ma and 522 ± 13 Ma, and 677 ± 14 Ma and 692 ± 15 Ma), whereas the remaining grains have bimodal ages (Table S1). Spots 11 and 12 have the largest spread in $^{206}Pb/^{238}U$ ages with 1972 ± 37 ($^{207}Pb/^{206}Pb$ age = 2076 ± 18) and 671 ± 15 Ma, whereas spots 45 and 58 have the smallest spread in $^{206}Pb/^{238}U$ ages (634 ± 15 and 600 ± 14 Ma). The age dichotomy within the bimodal-age zircons is likely related to younger crystal growth on an older inherited zircon.

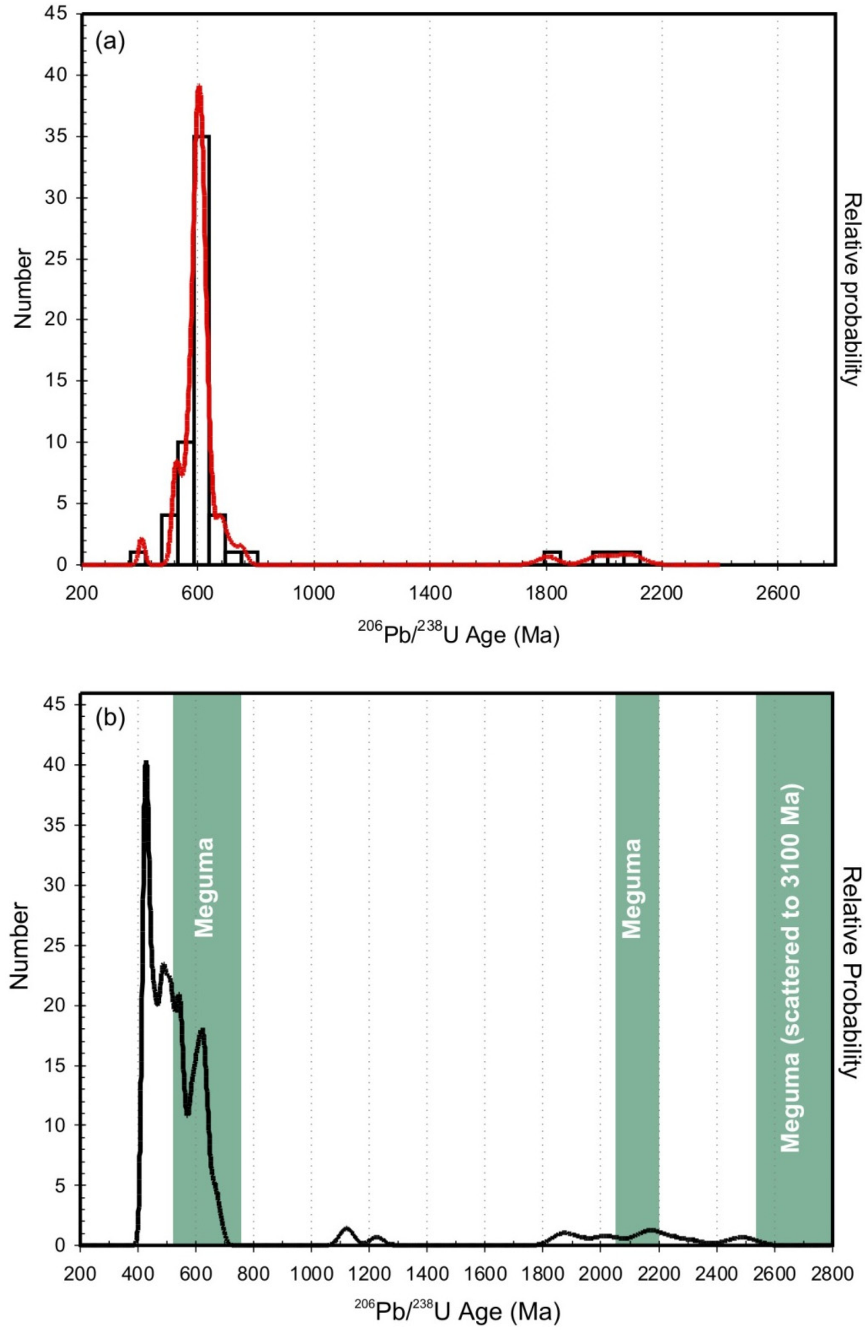

Figure 3. (**a**) Frequency distribution of all zircon $^{206}Pb/^{238}U$ ages from the diorite xenolith. (**b**) Zircon $^{206}Pb/^{238}U$ age groupings from the meta-sedimentary xenoliths are from Shellnutt et al. [33].

6. Discussion

6.1. Age of the Dioritic Xenolith and Correlation with Magmatism in Avalonia

The zircon age distribution from the dioritic xenolith is complex. It is clear that the majority of zircon $^{206}Pb/^{238}U$ ages (30) are between 581 ± 12 Ma and 616 ± 14 (Figure 4) and that older (18) and younger (12) age populations are identified. It is possible that some ages could reflect analytical overlap of a single spot between a younger rim and an older core (e.g., spots, 4–5, 11–12), but we do not think that this is significant as there is one example of a zircon that has a bright CL rim and dark CL core, yet the ages are within uncertainty and the analytical spot size is small enough to minimize the analytical overlap. There is a 10-million-year age gap between the youngest (581 ± 12 Ma) age of the majority group and the oldest (570 ± 13 Ma) age of the younger group. We interpret this age gap as significant and a break between the likely magmatic zircons and the zircons that record metamorphism or recrystallization. In other words, we think that the magmatic age of the diorite is >580 Ma. Some of the younger $^{206}Pb/^{238}U$ ages (i.e., ≤570 Ma) are from the bright CL image rims of zircons rather than the darker core regions, but this is true for all zircons and there are many cases where the bright CL image rims are older than the darker CL image core regions (Figure S1). This suggests that some of the younger ages may be indicative of new growth or recrystallization of the rim. One of the best examples of the regrowth relationship is between spots 7 (569 ± 15 Ma) and 8 (629 ± 13 Ma). Moreover, the age of the youngest zircon of the study is from a bright rim and is 406 ± 10 Ma. This Early Devonian age is within error of the early stages of the Acadian Orogeny and is probably indicative of the diorite deformation age before it was incorporated as a xenolith in the Popes Harbour dyke at ~370 Ma [36,52]. We do not know whether the age spread of the younger zircons (i.e., 570–515 Ma) is entirely related to Acadian Orogeny deformation or whether it is related to contact metamorphism, associated with the emplacement of younger (i.e., <570 Ma) intrusions, since Late Ediacaran–Late Silurian granitic plutons are common throughout the Avalon terrane of Nova Scotia [40,42,63,64].

The older zircon group ranges from 619 ± 15 Ma to 752 ± 16 Ma, but there are Paleoproterozoic zircons as well. The significance of the Paleoproterozoic zircons will be discussed later. We do not think that the Tonian–Cryogenian (752–637 Ma) and Paleoproterozoic ages are representative of the emplacement age of the diorite for the following reasons: (1) there are too few zircons in the rock of these ages, (2) there are no coherent groups of ages, and (3) some of the zircons with older ages have younger rims, suggesting they may be inherited. Tonian–Cryogenian rocks are identified in Avalonia and include the Burin gabbro–quartz diorite–trondhjemite complex (763 ± 3 Ma), Economy River orthogneiss (734 ± 2 Ma), Stirling belt rhyodacite (681 +6/−2 Ma), Connaigre Bay rhyolite (683 ± 1.6 Ma), and Furby's Cove (673 ± 3) intrusive suite, and there are a number of plutons with reported ages between 621 ± 3 Ma and 631 ± 2.9 Ma [40,44,63,65–68]. The rock ages match those of the older zircon group reported here and indicate that the older zircon group is likely representative of inheritance.

The age gap between our division of the older group and the majority group is only 3 million years (i.e., 619 ± 15 Ma and 616 ± 14 Ma). The placement of the 619 ± 15 Ma zircon into the older group rather than the majority group is somewhat problematic as it is only 3 million years younger than the next oldest age (i.e., 622 ± 13 Ma) that we consider to be part of the older group. The inclusion or exclusion of the 619 ± 15 Ma age in the majority group does not affect the weighted mean $^{206}Pb/^{238}U$ age. For example, ages from 581 ± 12 Ma to 616 ± 14 Ma yield a weighted mean $^{206}Pb/^{238}U$ age of 600 ± 4.8 Ma, whereas the inclusion of the 619 Ma age only slightly increases the age by 0.5 Ma (Figure 4a,b). If we now look at the youngest zircons of the majority cohort, we can see that there are five ages between 580 Ma and 590 Ma (i.e., 581 ± 15 Ma to 587 ± 13), with the oldest zircon of this group only 4 million years younger than the next oldest zircon (i.e., 591 ± 13 Ma). We are uncertain whether the 4-million-year age gap is significant or not. However, if we exclude the five youngest zircons (i.e., 587–581 Ma) and the 619 Ma age, then the weighted mean $^{206}Pb/^{238}U$ age is 603 ± 5.3 Ma (Figure 4c). If we include the 619 Ma age, then the weighted mean $^{206}Pb/^{238}U$ age is 604 ± 5.3 Ma (Figure 4d). The ~3-million-year age difference between the two weighted mean ages of the majority group may not be meaningful, but we prefer the 603 ± 5.3 Ma age as the probability of correlation (0.998) is the highest amongst the four weighted mean ages presented here (Figure 4). Moreover, our reasoning follows that of White et al. [44] in the exclusion of 586–588 Ma zircon ages from the Sandy Gunns Lake pluton of the Antigonish Highlands (Avalon terrane), which yielded a zircon age of 603.7 ± 1.8 Ma.

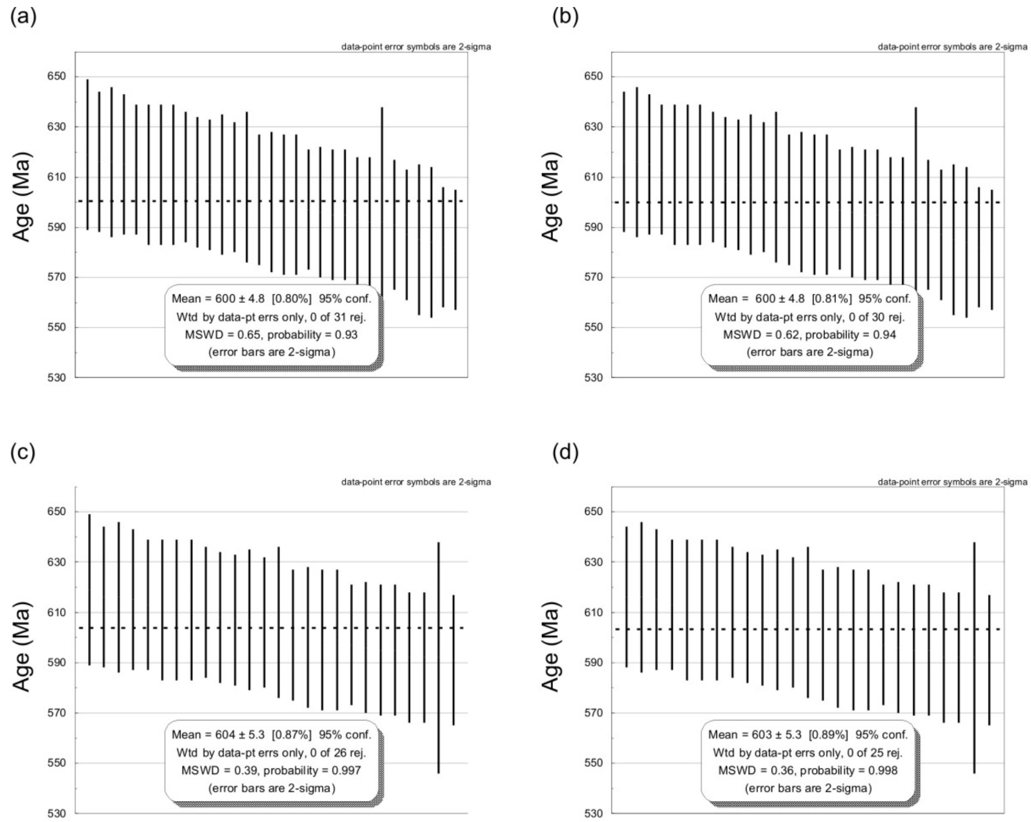

Figure 4. A comparison of zircon $^{206}Pb/^{238}U$ ages-weighted mean ages that include or exclude the youngest and oldest zircons of the main population. (**a**) All zircons from ~581 to ~619 Ma. (**b**) All zircons from ~581 Ma to ~616 Ma. (**c**) All zircons from ~591 Ma to ~619 Ma. (**d**) All zircons from ~591 Ma to ~616 Ma. Data uncertainty is reported at 2-sigma values. MSWD—mean standard of weighted deviates.

The preferred weighted mean $^{206}Pb/^{238}U$ age (603 ± 5.3 Ma) of the diorite from this study is significant as it contemporaneous with granitic magmatism throughout West Avalonia and may also be consistent with interpretations presented by Shellnutt et al. [33] on the detrital zircon ages from the meta-sedimentary xenoliths from the Popes Harbour dyke. The age of the diorite is within uncertainty of zircon $^{206}Pb/^{238}U$ weighted mean ages of six silicic plutons of West Avalonia from the Antigonish Highlands and the Cobequid Highlands to the north and west of the Popes Harbour dyke. The Sandy Gunns Lake, Ohio, Antigonish Harbour, and Greendale plutons have ages of 603.7 ± 1.7 Ma, 606.4 ± 0.6 Ma, 606.6 ± 1.6 Ma, and 609.2 ± 5.3 Ma, respectively [44]. There are other plutons in the Antigonish Highlands that have zircon ages from 612.7 ± 2.4 Ma to 617.7 ± 1.6 Ma. In the Cobequid Highlands, a mylonitic granite (605 ± 5 Ma) and the Debert River granite (609 ± 4 Ma; 612 ± 4 Ma) both have ages within uncertainty of the diorite weighted mean age [39]. Therefore, it is likely that the diorite xenolith of this study represents a contemporaneous but spatially distinct intrusion from those of the Antigonish and Cobequid highlands. Alternatively, it could be a displaced member of one of the ~600 Ma plutons; however, the fault movement along the Cobequid–Chedabucto fault system occurred ~20 million years after the Popes Harbour dyke was emplaced. Therefore, it is possible that the diorite xenolith is representative of a pluton beneath the Meguma terrane that was contemporaneous with regional ~600 Ma magmatism across Avalonia.

Shellnutt et al. [33] reported the detrital zircon $^{206}Pb/^{238}U$ ages from the meta-sedimentary granulite xenoliths also from the Popes Harbour dyke. The majority (~90%) of ages range from the Cryogenian to Early Devonian and have distinct clusters at 680–660 Ma, ~630 Ma, ~600 Ma, ~580 Ma, 550–450, and 430–420 Ma with two smaller Paleoproterozoic (~1980 Ma to ~2620 Ma) and Mesoproterozoic (~1100 Ma to ~1200 Ma) populations. There is a distinct cluster of detrital zircons ages at ~600 Ma that is contemporaneous with the age of the diorite in this study, but, more importantly, it was suggested that the protoliths of the meta-sedimentary granulites could be correlative with the Late Silurian (Pridolian) Stonehouse Formation of the Arisaig Group (Antigonish Highlands), since they are both a unit of Avalonia, have similar detrital zircon age distributions, and have similar depositional ages [7,33,69]. Furthermore, the diorite of this study is compositionally magnesian, metaluminous, and calcic and similar to some of the contemporaneous plutons from the Antigonish Highlands. Frost et al. [70] suggest that magnesian, metaluminous/peraluminous, and calcic/calc–alkalic granitoids are typical of Cordilleran batholiths (i.e., volcanic arc granites). Specifically, calcic plutons (i.e., diorite xenoliths) are typical of the outboard portions of Cordilleran batholiths, whereas the calc–alkalic rocks (i.e., Antigonish Highlands) are typical of the main portion of Cordilleran batholiths. Furthermore, the presence of cordierite in the diorite suggests that it may be similar to the cordierite-bearing peraluminous granitoids (CPG) of Barbarin [71], which are interpreted as being associated with collisional geodynamic settings. However, the cordierite in the diorite is likely a consequence of deformation rather than crystallization. Furthermore, the rocks are metaluminous and contain clinopyroxene and titanite. Therefore, it is likely that, due to the presence of clinopyroxene, titanite, and the metaluminous composition, the diorite is more similar to the amphibole-rich calc–alkaline granitoids (ACG) of active continental margins. In other words, the classification schemes of Frost et al. [70] and Barbarin [71] indicate that the diorite is similar to volcanic arc granite. If this is the case, then it is likely that it was generated within the same Neoproterozoic subduction zone (i.e., Andean-type margin) system that is interpreted for the ~600 Ma Avalonian granites from the Antigonish and Cobequid highlands. We cannot be certain that the diorite xenolith was not modified after deformation, but from a spatial perspective, the diorite was likely emplaced farther from the volcanic arc front that produced the ~600 Ma granitoids of the Antigonish Highlands [39,44] and consistent with an outboard location of a Cordilleran Batholith.

6.2. Paleoproterozoic Rocks in the Avalon Terrane

The four Paleoproterozoic ($^{207}Pb/^{206}Pb$ ages = 2354 $\pm$ 16 Ma to 2034 $\pm$ 18 Ma) zircons identified in this study are clearly not representative of emplacement ages as rocks of this age not known within the Avalon terrane of Nova Scotia and Newfoundland [72]. Currently, the oldest known rocks are the Economy River orthogneiss (734 $\pm$ 2 Ma) and the Burin gabbro–quartz diorite–trondhjemite (763 $\pm$ 3 Ma) complex [65,68]. The Mesoproterozoic Sailor Brook gneiss (1217 Ma), Brook syenite (1080 +5/−3 Ma), Red River anorthosite (1095.3 $\pm$ 1.5 Ma), and Otter Brook orthogneiss (978 +6/−5 Ma) of the Blair River Complex in Northern Cape Breton are the oldest rocks in Nova Scotia, but their correlation with Avalonia is debated and the Red River anorthosite may be Late Silurian in age [46,73–75]. Nevertheless, rocks that are >800 Ma have not definitively been identified within Avalonia, and yet detrital zircons with Paleoproterozoic (1800 Ma to 2500 Ma) and older ages are common in Silurian–Devonian sedimentary rocks of Avalonia and within Cambrian–Ordovician sedimentary rocks of the Meguma Supergroup [7,11,34,76]. Moreover, Paleoproterozoic detrital zircons ($^{207}Pb/^{206}Pb$ ages = 1981 $\pm$ 18 Ma to 2407 $\pm$ 20 Ma) were identified within the meta-sedimentary xenoliths of the Popes Harbour dyke [33]. Therefore, it is clear that there is Paleoproterozoic material within Avalonia, but the nature of this material, beyond zircon, is less certain.

Paleoproterozoic detrital zircons identified within sedimentary rocks of the Avalon terrane must be, by definition, derived from a precursor rock whether it is an igneous, metamorphic, or sedimentary rock. Thus, they cannot provide further constraints on the origin of the zircons. In contrast, the Paleoproterozoic zircons identified within the dioritic xenolith implies that they must be inherited from the country rock into which the magma intruded or was derived. Consequently, this opens the door to the possibility that the diorite either encountered or was derived from a >600 Ma Avalonian sedimentary rock that contained Paleoproterozoic zircons or inherited zircons from a rock that is Paleoproterozoic in age. Detrital zircon studies from Avalonian sedimentary rocks show that there can be age variability between regions (i.e., East Avalonia vs. West Avalonia), but also within different formations of the same group from the same region [77,78]. The primary difference in detrital zircon age peaks between and within Avalonian sedimentary rocks is the presence or absence of Mesoproterozoic (1000–1200 Ma, 1400–1600 Ma) and Late Paleoproterozoic (1700–1900 Ma) ages [7,76,78–82]. Therefore, the presence or absence of a characteristic age peak within the diorite xenolith may be able to help to constrain its source petrogenesis.

The absence of Mesoproterozoic (1000 Ma to 1600 Ma) zircons in the dioritic xenolith indicates that either the magma did not encounter a rock with Mesoproterozoic zircons, or, for some reason, it managed to incorporate only Neoproterozoic (i.e., Tonian and Cryogenian) and Paleoproterozoic (i.e., Rhyacian) zircons, while avoiding Mesoproterozoic zircons—an unrealistic prospect. Alternatively, it is possible that Mesoproterozoic zircons are within the diorite xenolith, but we did not find one; that is, absence of evidence is not evidence of absence. However, the amount of Mesoproterozoic zircons found within Avalonian sedimentary rocks, when present, is often ~5% or greater which is similar to or slightly less than the proportion of Paleoproterozoic (i.e., 1900–2400 Ma) zircons that are found within the same rock. In our study, we analyzed fifty-one individual zircons and identified four Paleoproterozoic zircons (~8%) that are within ~10% discordance. Thus, we would expect to randomly discover 2 or more Mesoproterozoic zircons. If the dioritic magma inherited zircons from a sedimentary rock then it must have been from a formation that had very few or no Mesoproterozoic zircons such as the Mall Bay Formation, Random Formation, Briscal Formation, and Crown Hill Formation of the Avalon terrane of Newfoundland [81,82]. However, this would necessarily imply that the diorite was emplaced close enough to the surface (i.e., hypabyssal intrusion), where it would encounter a sedimentary rock that has pre-600 Ma detrital zircons with limited Mesoproterozoic zircons. Although the above explanation is plausible, there is a simpler explanation.

Granitic magmas at Cordilleran settings are typically derived either by melting of crust or by mixing/mingling of melts derived from the crust and mantle [71,83–86]. Moreover, granitic magmas are commonly emplaced in the lower upper crust to middle crust rather than the uppermost crust [83,86]. In other words, the parental magma of the diorite xenolith could only inherit zircons or crustal material that was within the magma generation and transportation zone as opposed to sedimentary rocks that are directly related to the surficial extent of weathering and the exposure of the watershed region. Therefore, the absence of Mesoproterozoic-inherited zircons in the diorite could be due to the absence of Mesoproterozoic rocks in the melt and transportation region, a likely scenario if the melt region was relatively small. More importantly, this hypothesis implies that there must be Paleoproterozoic rocks within the lower crust of the Avalon terrane. The Tonian–Cryogenian zircons are likely derived from silicic igneous or metamorphic rocks of the same age that represent a period of subduction-related magmatism along the margin of Gondwana [8,10,15]. A situation of two or more distinct periods of magmatism within the same collisional setting is not uncommon [87–89]. If this hypothesis is correct, then the Paleoproterozoic-inherited zircons were either incorporated into the dioritic magma as xenocrysts or, possibly, as residual phases from a Paleoproterozoic source rock.

The survival of relict zircon within a hydrous granitic melt is dependent on a number of factors, including the initial radius (>120 μm) of the protolith zircon, the duration of the magmatic event, and the volume of local melting in which the protolith zircon interacts [90]. Furthermore, Watson [90] states that only the largest relict zircons will survive magmatic temperature events that exceed 850 °C. All of the Paleoproterozoic zircons of this study are >100 μm in width and have bright rims that are likely regions of new crystal growth, suggesting that the original zircon core was larger than it is now. Apatite saturation (820 °C), rutile saturation (832 °C/859 °C), and SiO_2 concentration (861 °C) temperature estimates of the diorite suggest that the magma temperature was unlikely to be significantly higher than 850 °C [91–94]. The implication is that the Paleoproterozoic zircons may represent inherited residual zircons after melting of a Paleoproterozoic source rock. Moreover, if there were small Late Paleoproterozoic zircons in the melt zone, it could potentially explain their absence, since they would have dissolved.

The possible existence of Paleoproterozoic rocks within the Avalon terrane has potential implications for its original location next to Gondwana (Figure 5). There is debate regarding the original geographic location of Avalonia, as positions closer to the Amazon Craton [8,9,72] or the West African Craton [5,14] are advocated, and Baltica [18] is suggested as well. Detrital zircon age data from northern South America (i.e., Colombia, Venezuela, Guyana, Suriname), Morocco, and Portugal show similar, but variable age distribution patterns. Relevant to this study is the fact that all regions have rocks and/or detrital zircons with Paleoproterozoic (2200–1800 Ma) and Mesoproterozoic (1600–1000 Ma) aged populations. However, Late Paleoproterozoic (1900–1700 Ma) rocks and detrital zircons are more abundant in northern South America and southern West Africa [95–100] than from northern West Africa, Portugal, and Baltica [101–109]. The lack of Late Paleoproterozoic-inherited and detrital zircons in the diorite and meta-sedimentary xenoliths of the Popes Harbour dyke is more supportive of a crustal source that has fewer Late Paleoproterozoic rocks. Furthermore, sedimentary rocks with Mesoproterozoic (1200–900 Ma) detrital zircons and few to no Late Paleoproterozoic (1900–1700 Ma) detrital zircons are present in West Avalonia and the Moroccan Mesetas [108]. It is difficult to be certain and more data is needed, but our study suggests that the diorite was derived, at least in part, by melting of crust that had fewer Late Paleoproterozoic rocks, which is supportive of a paleogeographic location closer to the northern West African craton than the Amazon craton or the southern West African craton.

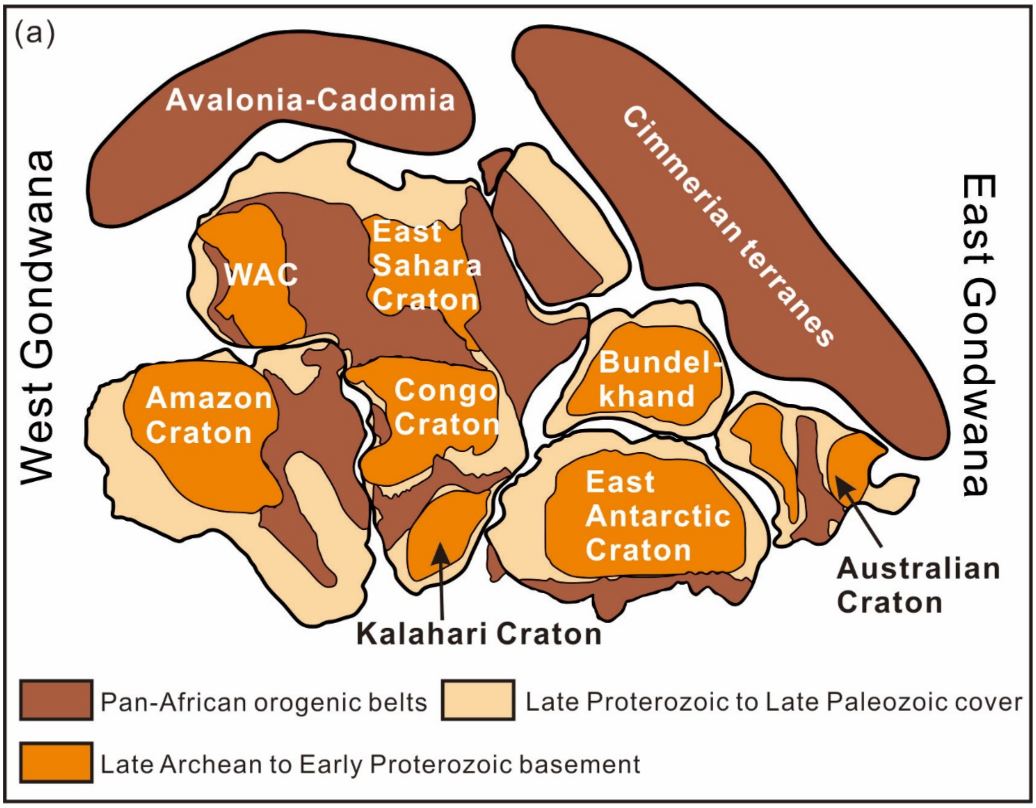

Figure 5. *Cont.*

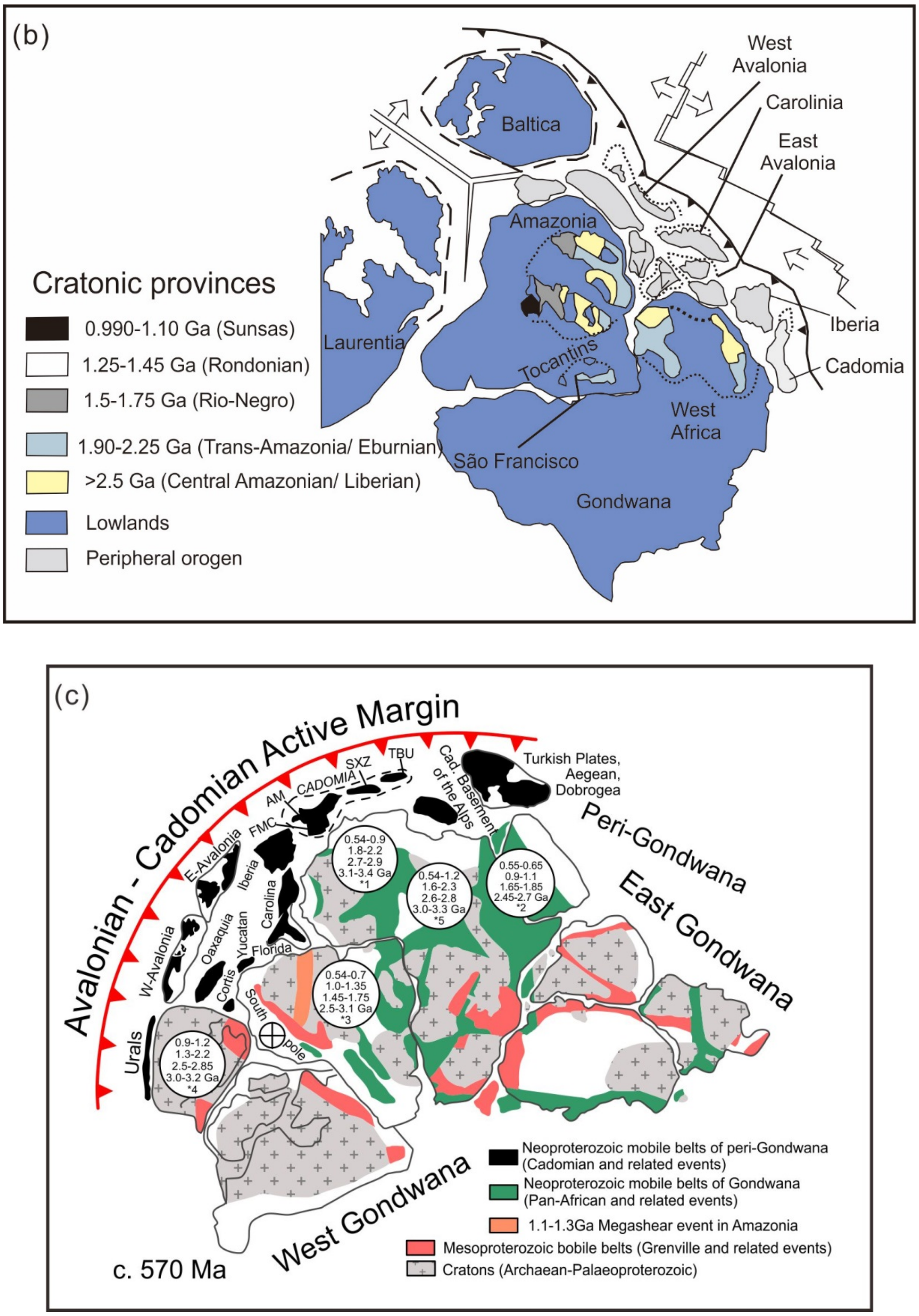

Figure 5. *Cont.*

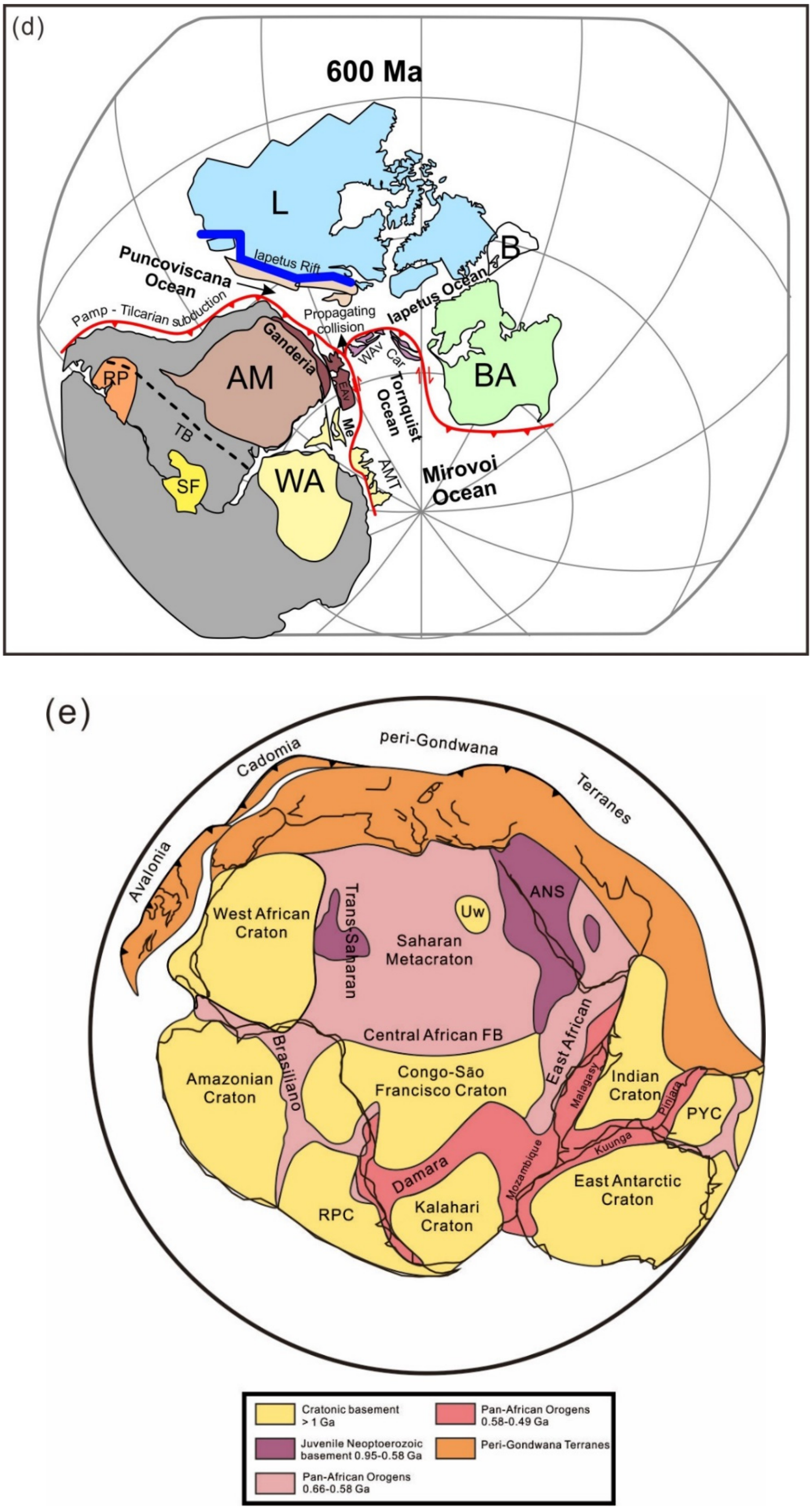

Figure 5. Late Neoproterozoic palinspastic reconstructions of Gondwana showing different locations of West Avalonia. (**a**) Late Neoproterozoic reconstruction of Gondwana from Hefferan et al. [5] with

Greater Avalonia along the margin of the West African Craton; (**b**) Ediacaran (635–590 Ma) reconstruction of Gondwana by Nance et al. [9] showing West Avalonia close to the Amazon Craton; (**c**) Ediacaran (570 Ma) reconstruction of Gondwana by Linnemann et al. [8] showing the location of West Avalonia near the Amazon Craton. W-Avalonia—West Avalonia; E-Avalonia—East Avalonia; FMC—French Massif Central; AM—Armorican Massif; SXZ—Saxo–Thuringian zone of the Bohemian Massif; TBU—Teplá–Barrandian unit of the Bohemian Massif. (**d**) Ediacaran (600 Ma) reconstruction of Gondwana by van Staal et al. [72] showing West Avalonia proximal to the Amazon Craton. WAv—West Avalonia; EAv—East Avalonia; Me—Meguma; Car—Carolinia; AMT—Amorican terrane assemblage; BA—Baltica; AM—Amazonia; WA—West Africa craton; RP—Rio de la Plata; TB—Transbrasiliano suture; SF—São Francisco craton; L—Laurentia; B—Barentsia. (**e**) Cambrian reconstruction of Gondwana from Avigad et al. [14] with Avalonia proximal to the West African Craton. ANS—Arabian–Nubian Shield; PYC—Pilbara–Yilgarn Craton.

7. Conclusions

The results of this study show that the majority of zircon ages from the diorite xenolith are between ~580 Ma and ~616 Ma with smaller groups at 750–630 Ma, ~2100 Ma, and <570 Ma. We interpret the zircon $^{206}Pb/^{238}U$-weighted mean age of the rock to be 603 ± 5.3 Ma. Our interpretive age is contemporaneous with granitic intrusions of the Avalon terrane located within the Antigonish and Cobequid highlands of Nova Scotia. The diorite and contemporaneous granitoids of the Antigonish Highlands are compositionally similar to Cordilleran Batholiths or volcanic arc granites, and are consistent with an origin from the active margin of Gondwana. The discovery of Early Paleoproterozoic (~2100 Ma) zircons and the absence of Late Paleoproterozoic (1900–1700 Ma) and Mesoproterozoic (1600–1000 Ma) zircons in the diorite xenolith suggests that the parental magma either encountered only Early Paleoproterozoic and Late Neoproterozoic rocks during emplacement, or was derived by melting of Paleoproterozoic rocks or melting and mixing of Paleoproterozoic and Late Neoproterozoic rocks. Furthermore, the absence of Late Paleoproterozoic (1900–1700 Ma) zircons in the dioritic and meta-sedimentary granulite xenoliths from the Popes Harbour dyke suggests that this part of Avalonia was likely located closer to the West African margin of Gondwana rather the Amazonian margin of Gondwana.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min12050575/s1, Figure S1: Cathodoluminescence images of the zircons from the diorite xenolith.; Figure S2: Concordia diagram of the Paleoproterozoic zircons. Figure S3: Concordia diagram of the Neoproterozoic zircons. Figure S4: Concordia diagram of the main group of zircons. Figure S5: Concordia diagram of the < 570 Ma zircons. Table S1: The results presented in this file are the common lead corrected zircon U-Pb geochronology of the diorite xenolith; Table S2: Whole rock composition of the diorite xenolith.

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