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Development of High-Silica Adakitic Intrusions in the Northern Appalachians of New Brunswick (Canada), and Their Correlation with Slab Break-Off: Insights into the Formation of Fertile Cu-Au-Mo Porphyry Systems

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Abstract: High-silica adakites exhibit specific compositions, as follows: $SiO_2 \geq 56$ wt.%, $Al_2O_3 \geq 15$ wt.%, Y ≤ 18 ppm, Yb ≤ 1.9 ppm, $K_2O/Na_2O \geq 1$, MgO < 3 wt.%, high Sr/Y (≥10), and La/Yb (>10). Devonian I-type adakitic granitoids in the northern Appalachians of New Brunswick (NB, Canada) share geochemical signatures of adakites elsewhere, i.e., $SiO_2 \geq 66.46$ wt.%, $Al_2O_3 > 15.47$ wt.%, Y ≤ 22 ppm, Yb ≤ 2 ppm, $K_2O/Na_2O > 1$, MgO < 3 wt.%, Sr/Y ≥ 33 to 50, and La/Yb > 10. Remarkably, adakitic intrusions in NB, including the Blue Mountain Granodiorite Suite, Nicholas Denys, Sugar Loaf, Squaw Cap, North Dungarvan River, Magaguadavic Granite, Hampstead Granite, Tower Hill, Watson Brook Granodiorite, Rivière-Verte Porphyry, Eagle Lake Granite, Evandale Granodiorite, North Pole Stream Suite, and the McKenzie Gulch porphyry dykes all have associated Cu mineralization, similar to the Middle Devonian Cu porphyry intrusions in Mines Gaspé, Québec. Trace element data support the connection between adakite formation and slab break-off, a mechanism influencing fertility and generation of porphyry Cu systems. These adakitic rocks in NB are oxidized, and are relatively enriched in large ion lithophile elements, like Cs, Rb, Ba, and Pb, and depleted in some high field strength elements, like Y, Nb, Ta, P, and Ti; they also have Sr/Y ≥ 33 to 50, Nb/Y > 0.4, Ta/Yb > 0.3, La/Yb > 10, Ta/Yb > 0.3, Sm/Yb > 2.5, Gd/Yb > 2.0, Nb + Y < 60 ppm, and Ta + Yb < 6 ppm. These geochemical indicators point to failure of a subducting oceanic slab (slab rollback to slab break-off) in the terminal stages of subduction, as the generator of post-collisional granitoid magmatism. The break-off and separation of a dense subducted oceanic plate segment leads to upwelling asthenosphere, heat advection, and selective partial melting of the descending oceanic slab (adakite) and (or) suprasubduction zone lithospheric mantle. The resulting silica-rich adakitic magmas ascend through thickened mantle lithosphere, with minimal affect from the asthenosphere. The critical roles of transpression and transtension are highlighted in facilitating the ascent and emplacement of these fertile adakitic magmas in postsubduction zone settings.

Keywords: high-silica adakite; New Brunswick; northern Appalachians; slab break-off; fertile Cu-Au-Mo porphyry systems

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1. Introduction

Devonian intrusions, many of which are subvolcanic, are widespread in the northern Appalachians, including various types in New Brunswick. They were emplaced during the later stages of or immediately following the Acadian Orogeny in the various zones of the Appalachians; the Canadian Appalachians are categorized into distinct tectono-stratigraphic zones and subzones primarily dating from the Early Paleozoic and older [1], which are present from the north to the south of New Brunswick, the Humber, Dunnage,

Gander, Avalon, and Meguma (Figure 1). Many of these intrusions are oxidized I-type granitoids that, according to their geochemical characteristics, are adakites (Figure 2) [2]. Adakites commonly have $SiO_2 \geq 56$ wt.%, $Al_2O_3 \geq 15$ wt.%, Y ≤ 18 ppm, Yb ≤ 1.9 ppm, $K_2O/Na_2O \geq 1$, MgO < 3 wt.%, high Sr/Y (≥20), and La/Yb (>10), as well as being enriched in large ion lithophile elements (LILEs), such as Cs, Rb, Ba, and Pb, and depleted in high field strength elements (HFSEs), such as Nb, Ta, P, and Ti, and heavy rare earth elements and Y (HREEs) [3]. Adakitic volcanic and subvolcanic rocks were first recognized on the Island of Adak in the Andrean of Islands (Aleutians chain) by Kay [4]. Since the 1990s, adakites displaying comparable geochemical attributes have gained international attention with and are recognized in magmatic suites from recent to Archean (TTGD) [5]. According to Condie [6], although adakitic rocks and TTG (tonalite–trondhjemite–granodiorite) share some similar geochemical characteristic, they are not the same. While both TTGs and adakites commonly have strongly fractionated rare earth element (REE) patterns, TTGs possess lower concentrations of Sr, Mg, Ni, Cr, and Nb/Ta compared to most adakites. Condie [6] suggested that adakites were likely derived from slab melts, whereas high-aluminum TTGs originated from the partial melting of the lower crust in arc systems, or in the root zones of oceanic plateaus. Lentz and Yousefi [5], utilizing GEOROC data, proposed the division of adakites into two compositional types, namely high-SiO_2 adakites (HSAs) where SiO_2 > 60 wt.% and low-SiO_2 adakites (LSAs) where SiO_2 < 60 wt.%. However, a redefinition designating HSAs as SiO_2 > 63 wt.% and LSAs as having SiO_2 contents of 57–63 wt.% is proposed. Additionally, basaltic andesite adakites (BAAs) have SiO_2 content of 52–57 wt.%, akin to high-Mg adakites (MgO > 3 wt.%), are also recognized. Some geochemical characteristics, in particular the proportions of trace elements, indicate that the conditions of formation of these adakites are not typical of ensimatic or ensialic arcs. A review has been conducted on the adakitic data in the GEOROC database, and is presented in a separate paper [7]. Based on key trace element ratios—Sr/Y > 20, Nb/Y > 0.4, Ta/Yb > 0.3, La/Yb > 10, Gd/Yb > 2, and Sm/Yb > 2.5—the high-silica adakitic rocks in NB are related to slab failure. The theory of slab failure is emphasized in specific investigations carried out in New Brunswick, as demonstrated by the research conducted by Yousefi et al. [2] focusing on Eagle Lake Granite in southwestern NB, as well as ongoing work by Bustard et al. [8] on dykes along the gold-bearing Melanson Brook Fault in northern NB, and are related to slab failure/break-off at the end of the Acadian Orogeny.

As mentioned above, several of the adakitic intrusions in NB have associated Cu-Au-Mo mineralization, including Blue Mountain Granodiorite Suite (400.7 ± 0.4 Ma, U-Pb zircon [9]), Nicholas Denys (381 ± 4 Ma, U-Pb zircon [10]), Sugar Loaf, Squaw Cap (415 ± 0.5 Ma, U-Pb zircon [11]), North Dungarvan River (376 ± 4 Ma, ^{40}Ar-^{39}Ar muscovite [12]), Magaguadavic Granite (396 ± 1 Ma, U-Pb zircon [13]), Hampstead Granite, Tower Hill (401 ± 4 Ma, Rb-Sr muscovite [14]), Watson Brook Granodiorite (382.1 ± 2.8 Ma, Rb-Sr biotite), Rivière-Verte Porphyry, Eagle Lake Granite (360 ± 5 Ma, U-Pb zircon [15]), Evandale Granodiorite (391.2 ± 3.2 Ma, U-Pb zircon [16]), North Pole Stream Suite (406.1 ± 1.9 Ma, ^{40}Ar/^{39}Ar muscovite [17]), Beech Hill (343 ± 33 Ma, Rb-Sr muscovite [18]), Pabineau Falls Granite (390 ± 1 Ma, U-Pb zircon [19]), and the McKenzie Gulch Porphyry dykes (386.2 ± 3.1 and 386.4 ± 3.3 Ma, U-Pb zircon [20]); the location of these intrusions is also presented in the study of Azadbakht [18]. These are comparable to the Cu porphyry intrusions at Mines Gaspé, Québec, where the Porphyry Mountain and Copper Mountain intrusions at Mines Gaspé date from 384.8 ± 2.8 Ma and 384.9 ± 2.5 Ma (Middle Devonian), respectively [21]; the ages of the Porphyry Mountain and Copper Mountain intrusions were refined by Marcelissen et al. [22] using U-Pb zircon geochronology and are 378.80 ± 0.37 Ma and 377.60 ± 0.45 Ma, respectively. These ages suggest the rapid cooling of the granite suite to temperatures below 500 °C in less than 2 million years. Furthermore, temperatures between 600 °C and 500 °C may have persisted for an extended duration of 5 to 15 million years within the hybrid suite. Cu porphyry intrusions can be found in various regions globally, including the Devonian-age Deboullie pluton in Maine [23].

An important point is that the emplacement of this volume of fertile acidic-to-intermediate magma into the crust during a slab failure event is related to transpressional-to-transtensional extension during the post-collisional orogenic phase; this allows fertile magmas to traverse the subduction-altered lithosphere, ultimately ascending into the upper crust. When oxidized melts from the slab interact with the subduction-altered lithospheric mantle, magmas maintain their oxidized state, potentially fostering conditions conducive to the genesis of porphyry Cu-Au mineralization. Investigating the oxidative evolution of granitic rocks across geological times, with a focus on ancient granitic terrains, such as those hosting porphyry copper deposits, opens a captivating aspect for geological inquiry [24]. Based on the work of Sun et al. [25], most of the global copper–gold ore deposits, such as those of the epithermal-to-porphyry-type spectrum, are linked to convergent margin magmas, and are commonly associated with magmas characterized by a high oxygen fugacity (fO_2). Polymetallic Cu porphyry deposit systems exhibit an association with oxidized I-type intrusions in NB [18]. In these granitoids, the mineral chemistry of accessory phases, such as zircon, titanite, magnetite, and apatite, can be used to assess relative fertility, in order to elucidate petrogenetic and metallogenetic processes. Mineral-specific compositional systematics are utilized as an indicator for exploration, in the context of porphyry Cu ± Mo ± Au deposits. Hence, it was imperative for this study to examine the fertility of the adakitic granitoids in NB, utilizing mineral data as fertility indices. According to Ishihara [26], oxidized systems are referred to as magnetite series; these intrusions are characterized by higher concentrations of magnetite, as well as biotite and hornblende. The higher magnetic susceptibility of rocks in oxidized systems is confirmed in several studies [2,15,18]. More importantly, as stated by Ishihara [26], Au-Ag, Cu, Pb-Zn, and Mo mineralization are commonly related to these magnetite series magmatic systems. Such mineralization is associated with the emplacement of Devonian oxidized I-type magmatic systems across New Brunswick. Along the continental margin arc and island-arc settings associated with subduction, the down-going oceanic slab typically undergoes seawater alteration and oxidation prior to subduction. This is most easily achieved via heat-driven seawater hydrothermal alteration along a spreading ridge; this is a process that results in the extensive hydration and oxidation, mobilization of metals, and fixing of seawater-derived S in the form of sulfide and sulfate. Mafic-to-intermediate magmas derived from the partial melting of such seawater-altered oceanic crust and (or) suprasubduction zone mantle could exhibit elevated Fe^{3+}/Fe^{2+} values. These magmas may ascend without undergoing crustal contamination in arc and possibly back-arc basin settings, where ascent is facilitated by extensional tectonic conditions (cf. [26]). If magma ascent occurs within a compressional arc-related tectonic setting, they may undergo reduction if they ascend through and interact with the continental crust containing varying amounts of reduced carbon- and sulfur-bearing sedimentary rocks. This process leads to the formation of magmas belonging to the reduced ilmenite series (cf. [26]). This research presents a detailed analysis of late-to-post-collisional Devonian adakitic intrusions in New Brunswick, offering insights into their geochemical characteristics, petrogenesis, and tectonic context as it relates to mineralization.

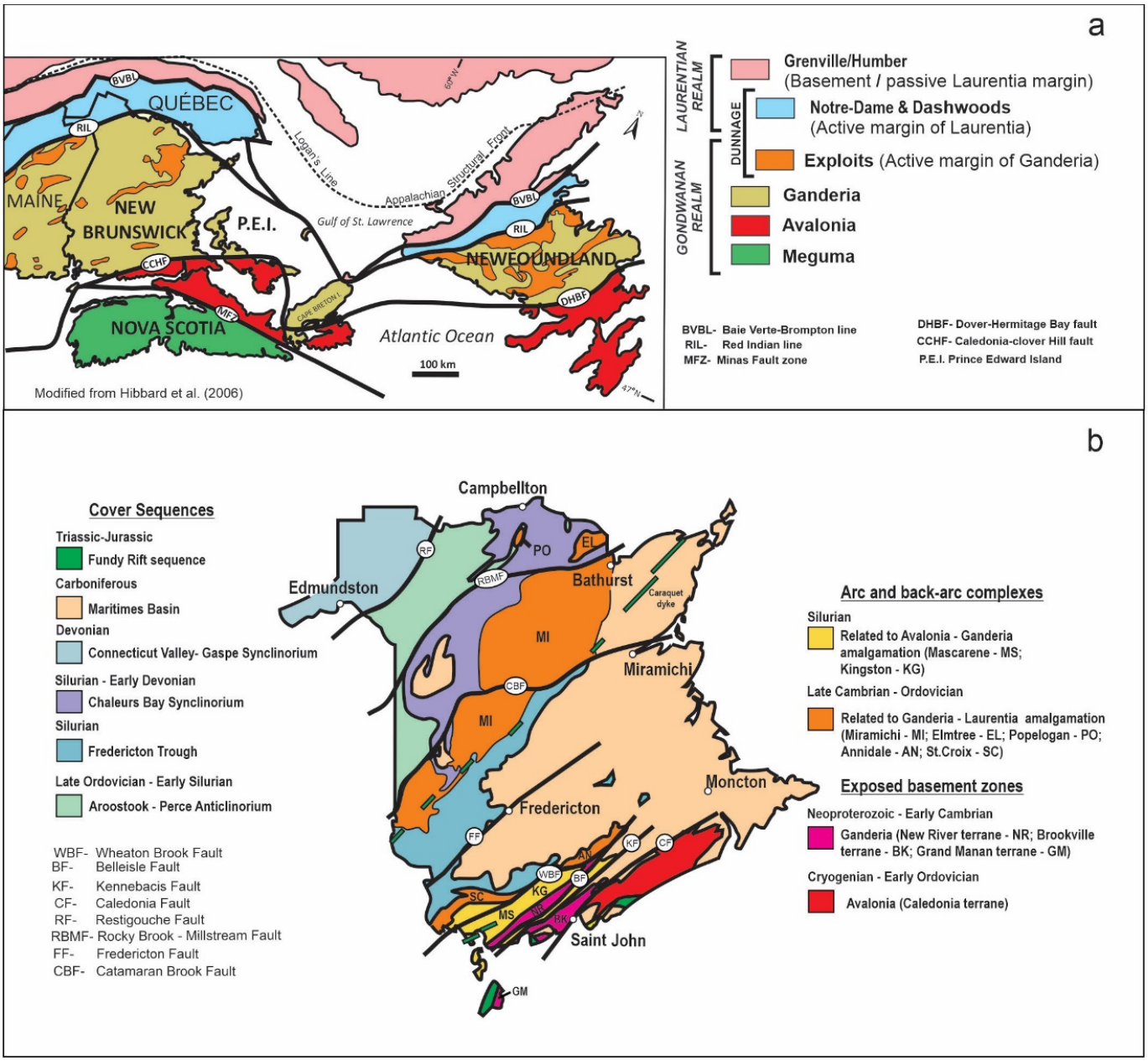


Figure 1. (**a**) Major tectonic zones of the Canadian Appalachians; (**b**) Tectonic zones and cover sequences of New Brunswick (modified from [27]).

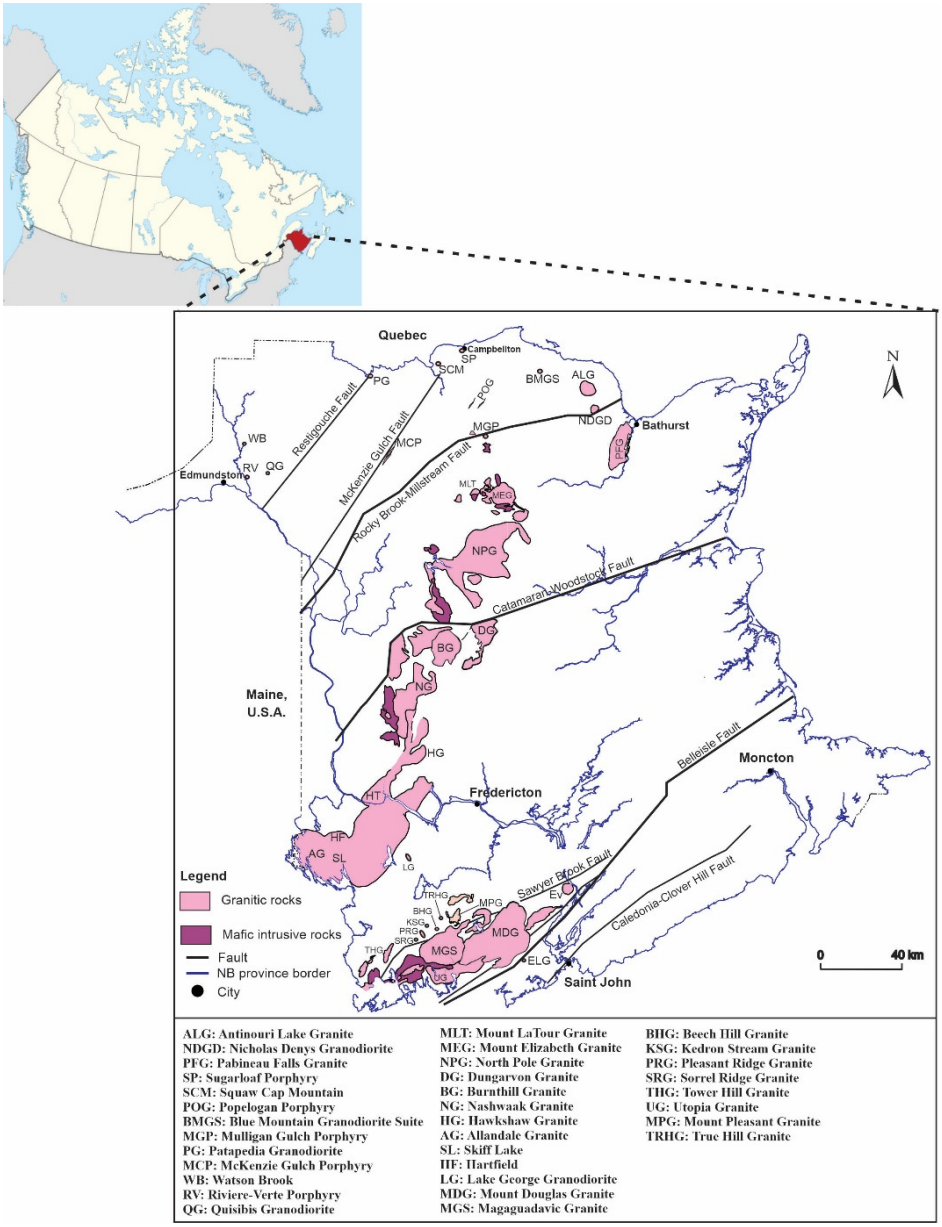


Figure 2. Regional map of the New Brunswick Appalachians, showing the location of Devonian mafic-to-felsic granitoids and major faults (modified from [28]).

2. Methods

Most of the geochemical and petrological data in this review are from Whalen [29], augmented with data from the Blue Mountain Granodiorite Suite [9] and McKenzie Gulch Porphyry dykes [20] with additional acquired data (Eagle Lake Granite, Riviere-Verte porphyry, and Watson Brook Granodiorite) collected as part of this study and analyzed at the ACTLABs laboratory. Whole-rock major and traceelement geochemical analyses were performed using a combination of X-ray fluorescence spectrometry (XRF technique developed by Norrish and Hutton [30]), lithium metaborate fusion inductively coupled plasma–mass spectrometry (ICP-MS; Thermo iCAP 6500 ICP), and instrumental neutron activation analysis (INAA) using the 4 Lithoresearch + 4B-INAA packages at ACTLABS. The INAA technique is detailed by Hoffman [31]. Certified reference materials SY4, GSP2, and RGM 2 were used as internal standards. In total, 99 samples were considered for lithogeochemical studies in this review of Devonian-aged adakitic intrusive rocks from New Brunswick.

3. Results

Geochemistry

Geochemical data from these Devonian NB adakitic rocks are presented in the Supplementary Files, with a total of 99 samples include both archived and new data. In the SiO_2 vs. $Na_2O + K_2O$ discrimination diagram of Cox et al. [32], these samples are plotted in the granite, granodiorite, quartz diorite, and diorite fields (Figure 3a), as well as in the calc-alkaline and high-K calc-alkaline fields in the K_2O vs. SiO_2 discrimination diagram ([33]; Figure 3b). The geochemical discrimination diagrams in Figure 3 show that the rocks from NB exhibit a broad range of major compositions. The NB adakitic rocks are plotted between peraluminous and metaluminous compositions using $Al_2O_3/(Na_2O + K_2O)$ (A/CNK) = 0.8–1.2. The elevated A/CNK values are attributed to subtle cryptic alterations in the samples, although biotite may also be responsible locally [2]. The calc-alkaline-to-shoshonitic affinity of these samples is confirmed by using selected major elements in Figure 3c. The investigated oxidized I-type granitoids are dominantly magnesian, but extend into the ferroan field (Figure 3d), and FeOt/(FeOt + MgO) increases with increasing SiO_2 (Figure 3d). By using geochemical discrimination techniques, the adakitic or adakite-like features of these oxidized I-type granitoids are recognized (Figure 4a–c). Most of these samples are plotted in the high-silica adakite field (HSA) and have a low MgO content (Figure 4). The adakitic samples are plotted in the transitional zone between adakite and rocks related to classic island arcs, suggesting that compositional gradation or alteration effects may be influencing their chemistry. This indicates a possible overlap in the geochemical characteristics due to these factors.

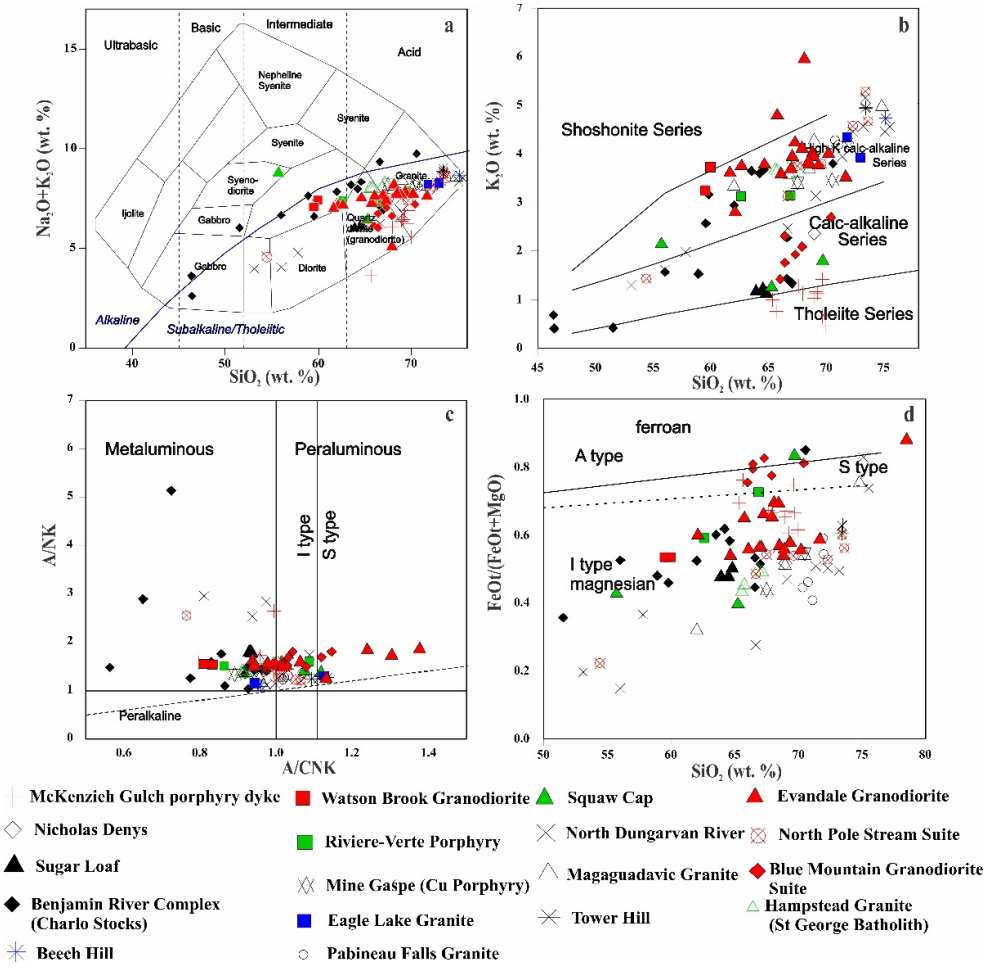


Figure 3. Geochemical discrimination diagrams for adakitic samples investigated: (**a**) SiO_2 vs. $Na_2O + K_2O$ discrimination diagram. Field boundaries from Cox et al. [32]; (**b**) SiO_2 vs. K_2O discrimination

diagram with field boundaries from [33]; (**c**) $Al_2O_3/(CaO + K_2O + Na_2O)$ (A/CNK) vs. $Al_2O_3/(Na_2O + K_2O)$ (A/NK) diagram modified from [34]. The line with an amount of A/CNK = 1.1 is a key parameter to discriminate S- from I-type granites [35]; (**d**) FeOt/(FeOt + MgO) vs. SiO_2 discrimination diagram with field boundaries from [36].

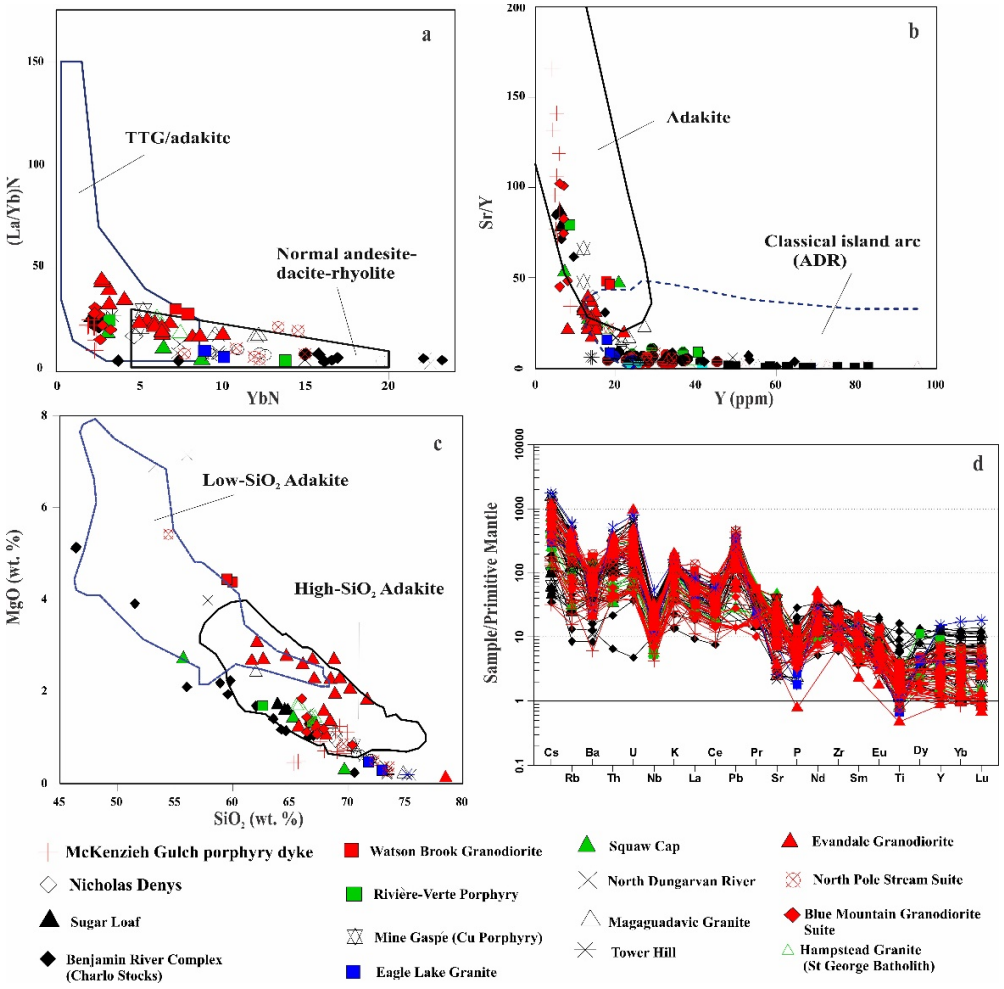


Figure 4. (**a**) $(La/Yb)_N$ vs. $(Yb)_N$ discrimination diagram with field boundaries from [37]; (**b**) Sr/Y vs. Y discrimination diagram with field boundaries from [37]; (**c**) SiO_2 vs. MgO discrimination diagram for high- and low-silica adakite; (**d**) primitive mantle-normalized extended element spider diagram. Symbols are the same as Figure 3. Normalized factors are from [38]. TTG = tonalite–trondhjemite–granodiorite, ADR = andesite–dacite–rhyolite.

Furthermore, the primitive mantle-normalized extended trace element spider diagram illustrates the enrichment of large ion lithophile elements (LILEs) (Figure 4d). Notably, there is a significant depletion in high field strength elements (HFSEs), which produce positive anomalies in Cs, Rb, Pb, U, Th, and K, and negative anomalies in Ti, Nb, P, Ba, and Sr (refer to Figure 4d). This distinct elemental pattern is arc-like, but more pronounced, and the enrichment of LILEs and the depletion of HFSEs is a key feature of adakites.

Partial melting coupled with selective crystal fractionation plays a pivotal role in the evolution of magmas that give rise to adakitic rock formed during slab break-off [39]. In the adakitic rocks considered, there is a discernible pattern where most major and trace elements correlate negatively or positively with SiO_2 depending on their compatibility. Notably, with increasing SiO_2 there is a decrease in MgO (Figure 4c), Al_2O_3, TiO_2, Ni, and Cr (Figure 5), and an increase in K_2O (Figure 3b), all of which are attributed to crystal differentiation during magma ascent. Based on the work in [39], the negative correlation of

the compatible elements Ni and Co with SiO_2 (Figure 5c,d) suggests the early fractionation of these elements into olivine and pyroxene during the magma differentiation process.

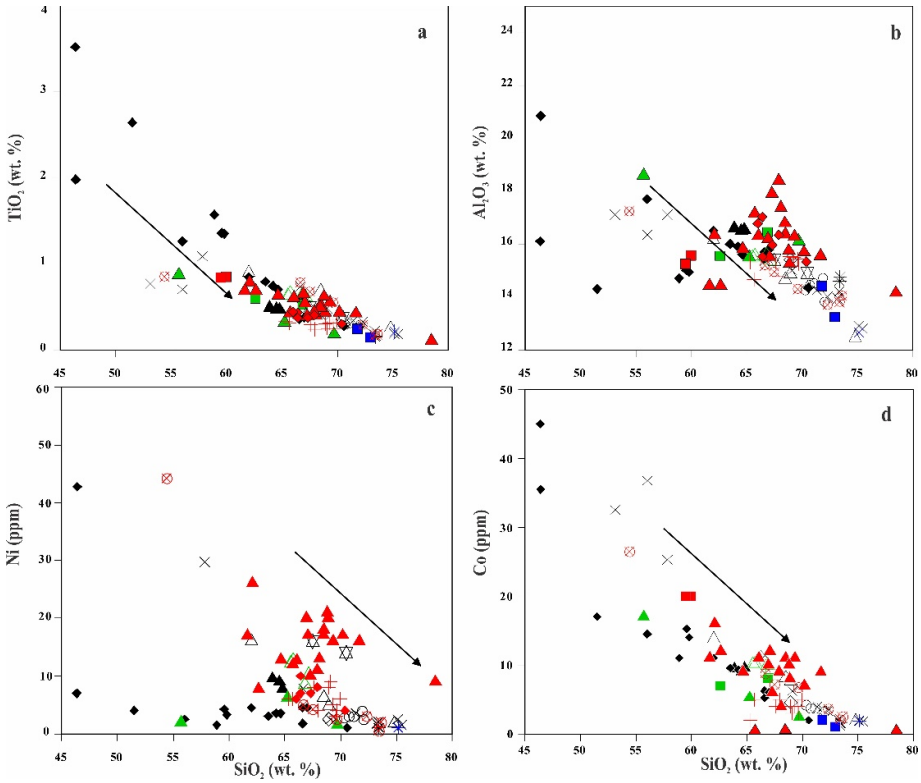


Figure 5. Harker diagrams of Devonian adakitic rocks of NB. SiO_2 vs. (**a**) TiO_2, (**b**) Al_2O_3, (**c**) Ni, and (**d**) Co. The same symbols as Figure 3 are used. The arrows indicate a general fractionation trend towards high silica.

According to the compositional discrimination diagrams in [40], these NB adakitic samples are mainly plotted in the field of unfractionated I-type granites (OTGs) (Figure 6).

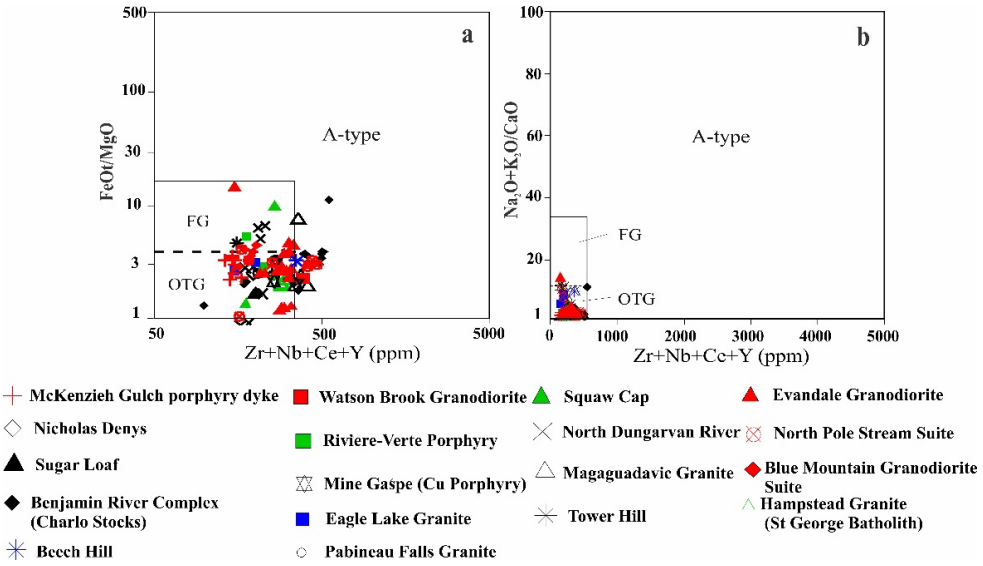


Figure 6. Geochemical discrimination diagrams. (**a**) FeOt/MgO vs. Zr + Nb + Ce + Y (ppm) and (**b**) Zr + Nb + Ce + Y (ppm) vs. $(Na_2O + K_2O)/CaO$. Field boundaries are from [40]. A-type: A-type granite, FG: fractionated granite rocks, OTG: unfractionated granite/other type of granite.

4. Discussion

4.1. Magmatic Sources of New Brunswick Adakites

Various hypotheses regarding the genesis of adakite rocks include (1) lower crustal melting or the melting of overlying rocks by rising basaltic magmas, (2) the high-pressure crystal fractionation of basaltic magma, and (3) the low-pressure crystal fractionation of water-enriched basaltic magma, coupled with magma mixing processes occurring in both arc and non-arc tectonic settings [41]. Several other hypotheses for the formation of adakite magma [37,42] include oceanic crustal melting, the high-pressure crystal fractionation of garnet and amphibole from hydrous basaltic magma, lower continental crustal melting triggered by basaltic magma underplating, eclogite or garnet amphibolite rock melting and crystal fractionation of mafic magma, or lower continental crustal melting in proximity to the mantle.

Zhang et al. [43] have also divided adakites into four groups and presented models outlining the petrogenetic processes of their formation. In the first group, adakites with $\geq$60 wt.% SiO_2 are classified as high silica (HSAs), whereas samples with <60 wt.% SiO_2 are classified as the low silica (LSAs) type, while HSAs exhibit lower MgO content (0.5–4.0 wt.%) compared to LSAs, which have MgO levels of 4–9 wt.%. HSAs are considered to result from the partial melting of subducted oceanic crust, followed by interaction with mantle wedge peridotites during their ascent. According to Martin et al. (2005), LSAs are formed through the partial melting of the peridotitic mantle wedge, coupled with interaction with silicic melts originating from subducted oceanic crust. A third type is high-Mg# adakite (HMA) with elevated MgO, Ni, and Cr, as well as Mg# in adakitic rocks, resulting from interactions between young hot basaltic melt in an arc setting and peridotite. Magmas from all three groups originate from melts generated in subducted slab, with compositional modification during ascent through the mantle [44]. In Zhang's theory, HMA is formed by mixing basic and acidic magmas in the lower crust. In another classification from Zhang et al. [43], the C-type/K-type adakitic group is formed through lower crustal partial melting driven by heat advection and crustal thickening. Although prevailing hypotheses attribute the origin of most modern subduction zone magmas to the partial melting of metasomatized mantle wedge peridotite, alternative mechanism have been proposed. Studies have demonstrated that subduction zone magmas can also be generated via the fusion of basalts from subducted oceanic crust [37]. Adakitic melts may originate from primitive 'normal' arc basalt melts that undergo fractional crystallization (involving garnet and amphibole) during ascent. Alternatively, these melts could supply the requisite heat to re-melt previously crystallized basic rock in the lowermost continental crust. In either scenario, the interaction between adakitic magma and mantle peridotite appears to be a viable process [45,46].

A review on oxidized I-type adakitic rocks selected from the GEOROC database was recently presented by the authors of this manuscript [39]; however, no information regarding the association of these rocks with mineralization was available. However, the relationship between adakitic rocks and mineralization, as well as slab failure, has been published [47,48] and many of the Devonian adakite rocks in NB have associated Cu-Au-Mo porphyry mineralization [49].

The application of trace element discrimination techniques allows for an in-depth examination of the mechanisms that generated the magmas responsible for New Brunswick's adakitic rocks, with a focus on slab subduction versus slab break-off/slab failure processes. Recent research has focused on the distinct trace element characteristics of arc, slab break-off/slab failure, and A-type granitoids [48,50]; this work has direct implications for the investigation of NB adakitic rocks (Figure 7). The majority of these Devonian adakitic samples fall within the slab failure field on the Ta/Yb, La/Yb, Gd/Yb, and Nb/Y versus Nb + Y, and Ta/Yb, Sm/Yb, Gd/Yb, and Nb/Yb versus Ta + Yb discrimination diagrams (Figure 7). In support of the slab break-off/slab failure interpretation for the origin of these adakite rocks, it is essential to consider additional geochemical indicators. Specifically, the New Brunswick rocks investigated have Nb/Y > 0.4, Ta/Yb > 0.3, La/Yb > 10,

Sm/Yb > 2.5, Gd/Yb > 2.0, Nb + Y < 60 ppm, and Ta + Yb < 6 ppm. The Nb/Y, Ta/Yb, La/Yb, and Sm/Yb values are all greater than those of typical arc magmas. Some samples have lower La/Yb values compared to others, which could be due to the mobilization of some of these elements by high-temperature aqueous fluids [47,48]. According to the Gd/Yb vs. La/Yb and Sm/Yb vs. La/Sm discrimination diagrams (Figure 8a,b), slab failure is the most likely origin for the magmas related to the adakitic rocks in NB.

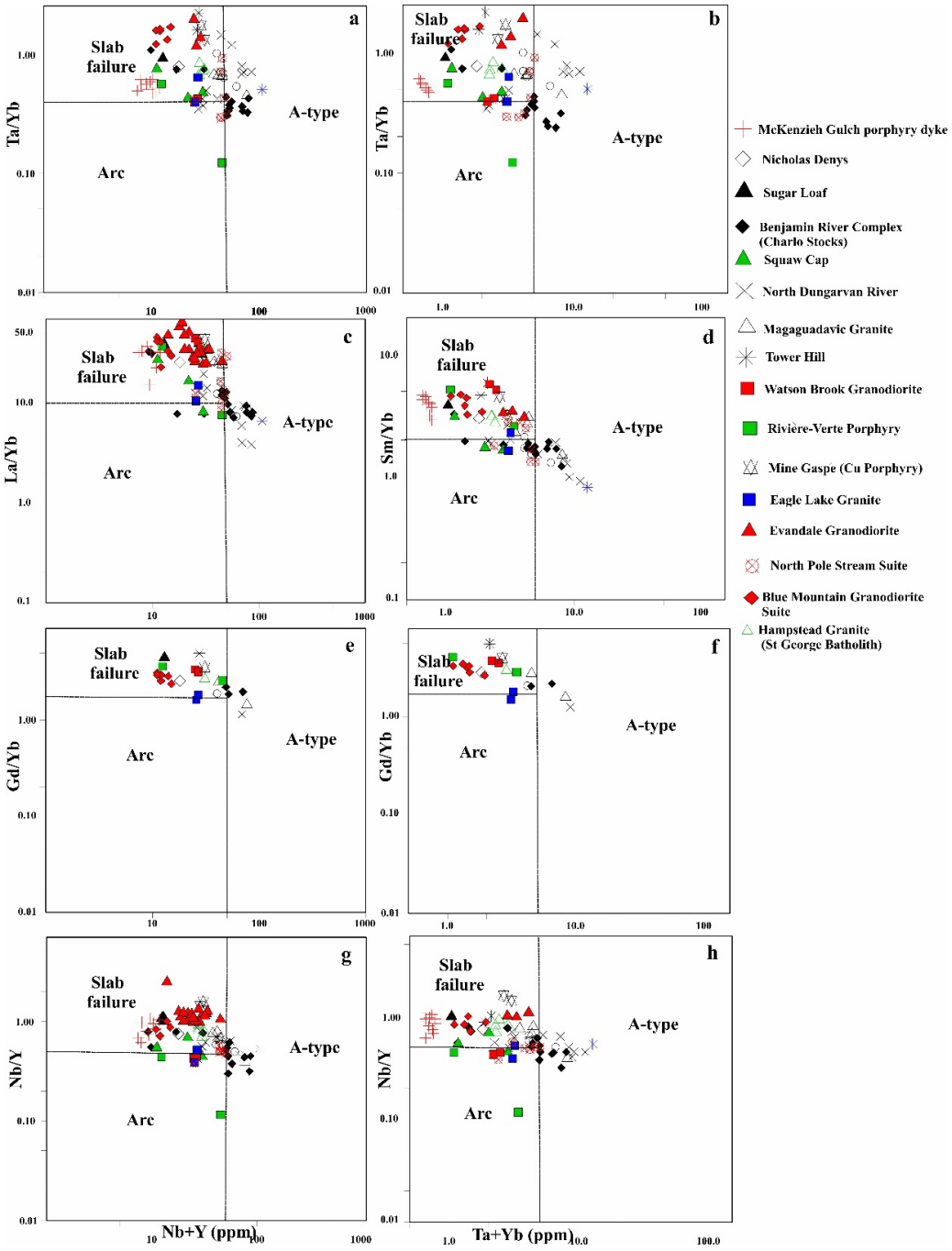


Figure 7. Tectonomagmatic discrimination diagrams for differentiating among slab failure, arc, and A-type granites applied to the New Brunswick granites investigated. (**a**) Nb + Y vs. Ta/Yb; (**b**) Ta + Yb vs. Ta/Yb; (**c**) Nb + Y vs. La/Yb; (**d**) Ta + Yb vs. Sm/Yb; (**e**) Nb + Y vs. Gd/Yb; (**f**) Ta + Yb vs. Gd/Yb; (**g**) Nb + Y vs. Nb/Y; (**h**) Ta + Yb vs. Nb/Y. All field boundaries are from [48,50,51], respectively.

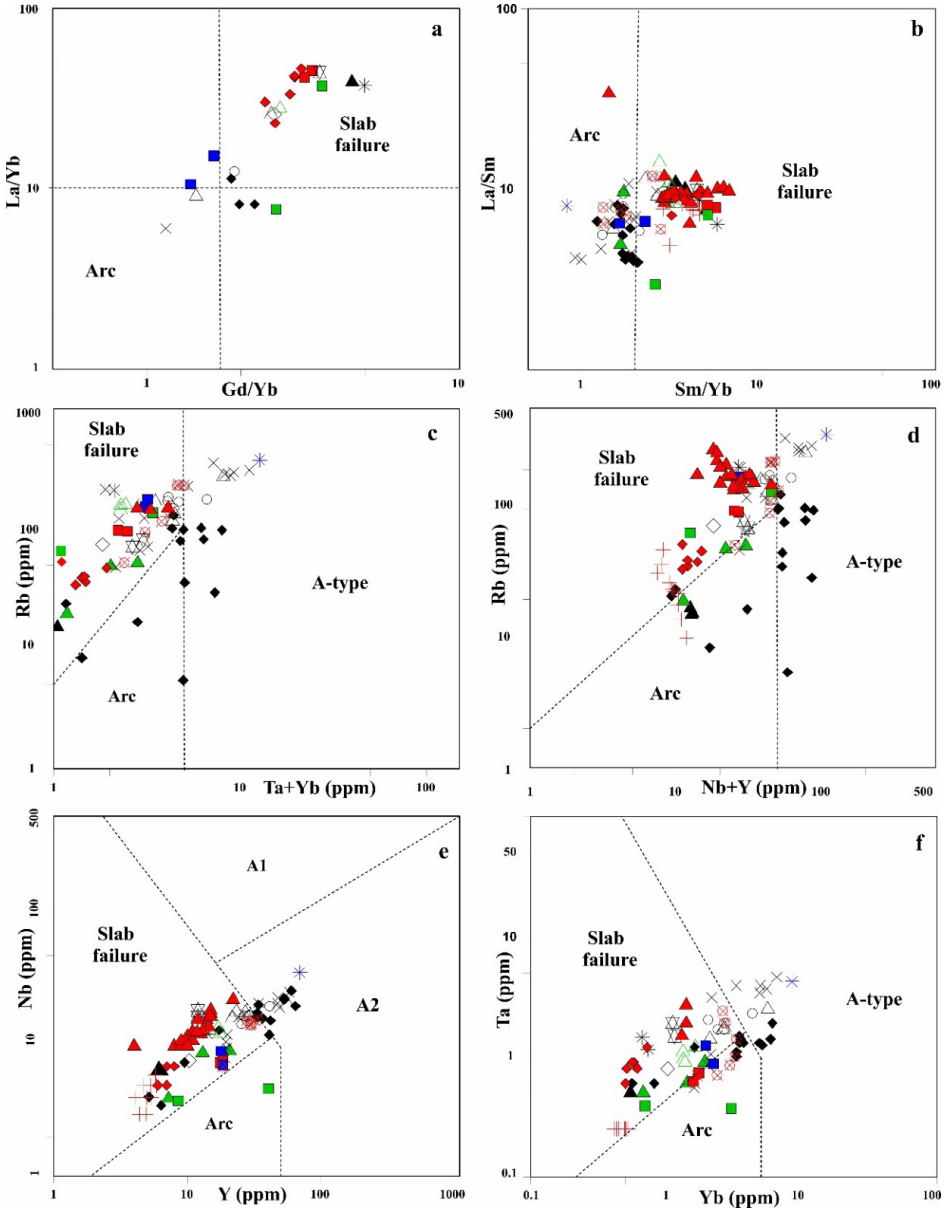


Figure 8. Continuation of tectonomagmatic discrimination diagrams. (**a**) Gd/Yb vs. La/Yb; (**b**) Sm/Yb vs. La/Sm; (**c**) Ta + Yb vs. Rb; (**d**) Nb + Y vs. Rb; (**e**) Y vs. Nb; (**f**) Yb vs. Ta. Symbols as in Figure 7.

Likewise, these samples fall mostly within the slab failure field on the Ta + Yb and Nb + Y vs. Rb; Y vs. Nb; and Yb vs. Ta discrimination diagrams (Figure 8c–f). Drawing insights from Figure 8c (Rb vs. Ta + Yb) and 6d (Nb + Y vs. Rb), some samples, i.e. those from North Dungarvan River and the Benjamin River Complex (Charlo Stock), deviate from the slab failure/break-off trend. This divergence is attributed to the alteration of Rb-bearing phases, such as microcline [47]. Alternatively, in some cases, they do not relate to slab failure. Looking at the ratio of Rb to Nb + Y (Figure 8d), some samples fall outside the slab failure field; this may be attributed to the fractionation of titanite or Ti-bearing phase that preferentially incorporate Nb-Ta and Y (cf. [52]). All presented field boundaries in Figure 8 are from [48,50,51].

Slab break-off or failure is viewed as a consequential effect of the terminal subduction process. The affiliation of these adakitic rocks with volcanic arcs in a subduction environment is supported by their elevated Th/Yb and lower Nb/Yb values, and their genesis is attributed to the incorporation of a thicker lithospheric cap and a hotter mantle compared

to normal mode, leading to the generation of melt (Figure 9a,b). The question is why are adakitic rocks linked to slabs that show higher concentrations of Nb and Ta compared to conventional arc-type rocks? The hypothesis, as presented, suggests the instability of rutile or other titanium (Ti) phases, which host Nb and Ta in the magmatic system, leads to the release of these elements into the magmatic system, resulting in elevated concentrations within the adakitic magmas. The instability of titanium-rich (rutile, titanomagnetite) phases is triggered by a greater heat in the environments that produce Nb-Ta-enriched adakite magmas.

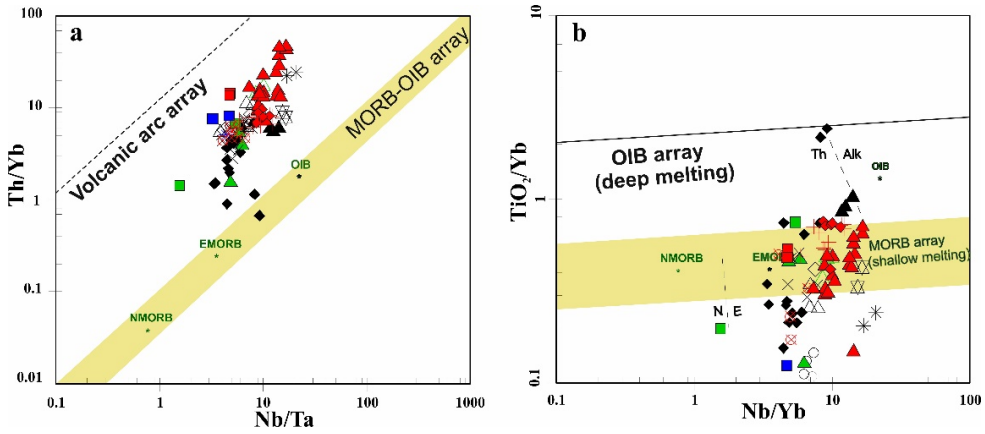


Figure 9. Tectonic discrimination diagrams for adakitic rocks investigated in this study. (**a**) Nb/Yb vs. Th/Yb, and (**b**) TiO_2/Yb vs. Nb/Yb. Field boundaries are from [53]. MORB: mid-ocean ridge basalt, OIB: ocean island basalt, Th: tholeiite, Alk: alkaline, EMORB: enriched mid-ocean ridge basalt, NMORB: normal mid-ocean ridge. Symbols as in Figure 7.

Drawing on the findings of Eyuboglu et al. [54], the majority of the adakitic samples considered in this study align closely with the fields exhibiting adakites originating from subducted oceanic crust, as well as those adakitic rocks derived from thickened lower crust (Figure 10). Although there is a degree of overlap with other fields, the geochemical attributes of the rocks considered strongly support the inference that the adakites in question originated primarily from subducted hydrothermally altered oceanic crust. Garnet fractionation not only impacts the trace element composition (Y, HREE, and Sc) of the resultant melts, but also elevates the Mg# and SiO_2 content of co-existing liquids [45].

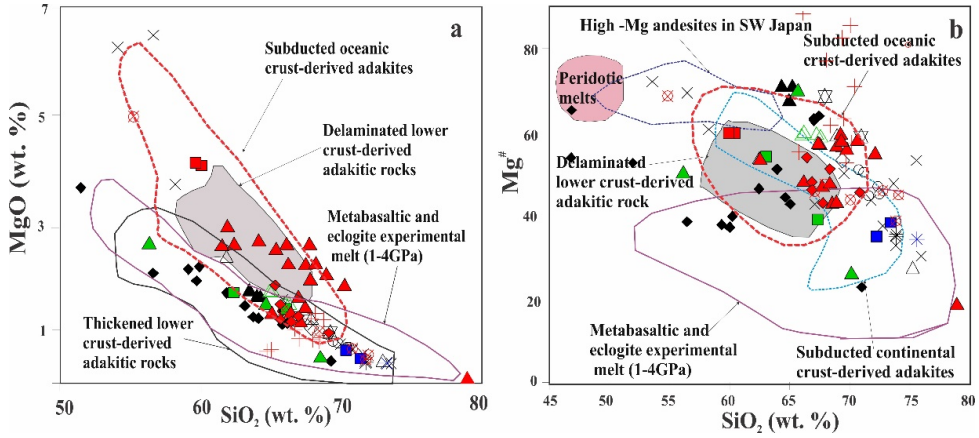


Figure 10. Discrimination diagrams for the determination of magmatic source rocks for adakites in New Brunswick. (**a**) MgO (wt.%) vs. SiO_2 (wt.%), and (**b**) $Mg^{\#}$ vs. SiO_2 (wt.%) diagrams for determining the effective factors in creating these adakitic magmas. Symbols as in Figure 7. Field boundaries are from [54].

Furthermore, the hypothesis of syn-collisional and post-collisional magmatism in this magmatic system is confirmed with the tectonic discrimination diagram from Figure 11 that compares R1 [4Si-11(Na + K)-2(Fe + Ti)] and R2 [6Ca + 2Mg + Al)]. Magmatism resulting from the slab failure/break-off is considered to be equivalent to the post-collisional field on this key figure.

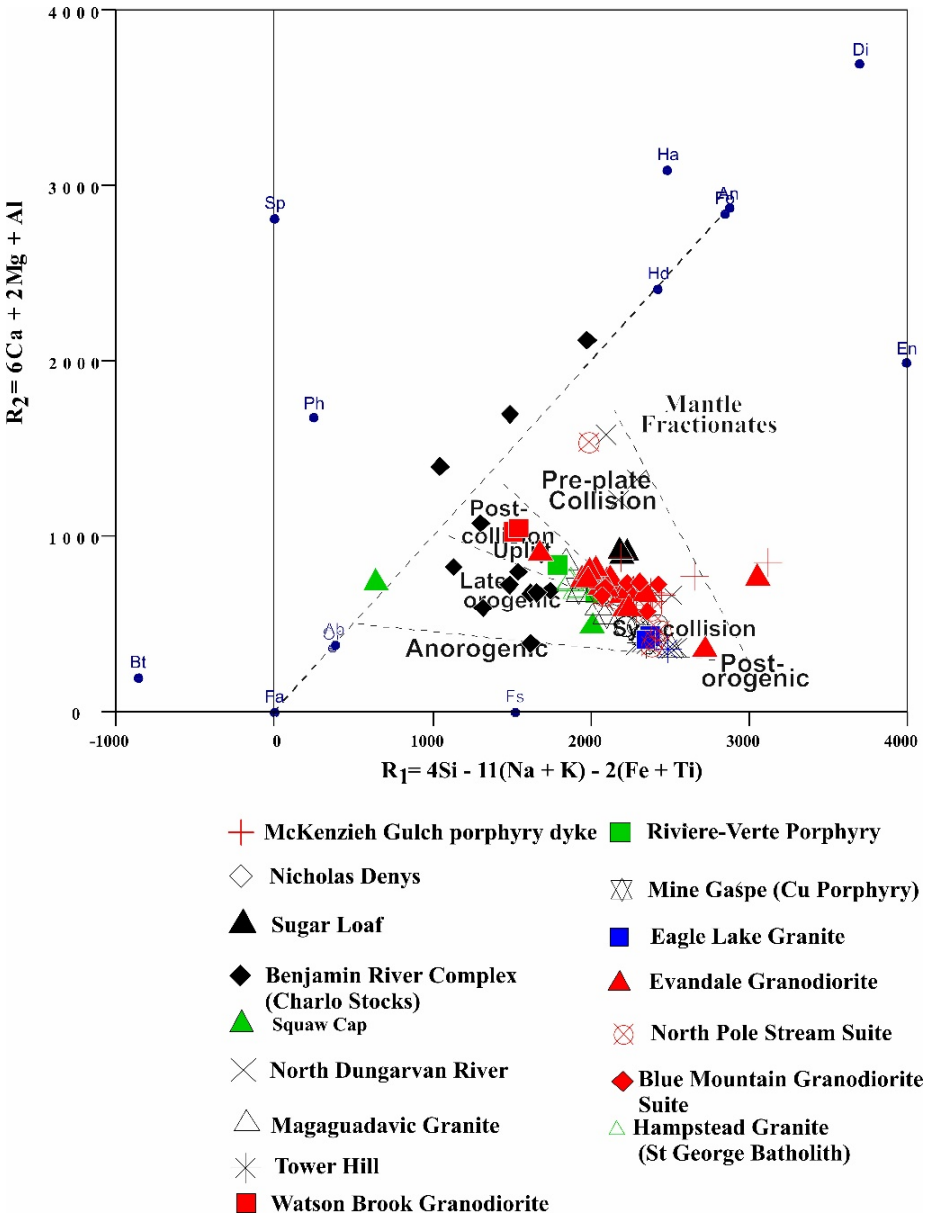


Figure 11. Tectonic discrimination diagram for New Brunswick adakites. Field boundaries are from [55]. Hb: hornblende, An: anorthite, Ab: albite, En: enstatite, Fa: fayalite, Fo: forsterite, Bt: biotite, Fs: feldspar, Sp: sphene (titanite), Hd: hedenbergite, Ha: haapalaite, and Di: diopside. Symbols as in Figure 7.

4.2. Tectonic Setting

The role of transpression and transtension is critical for the emplacement of significant volumes of adakitic and related mantle magmas in late-to-post-arc-collisional settings. Transpression and transtension are broadly characterized as deformation zones influenced by steep strike–slip geodynamics, deviating from simple shear through the presence of a component involving both shortening (transpression) and extension (transtension) across the respective zones (cf. [56]). The recognition of numerous pre- to post-emplacement shear

zones and faults in NB in the late Acadian orogeny supports the role of transpression and transtension in adakite emplacement. Piette-Lauzière et al. [57] referenced transpression and transtension, providing evidence to support these phenomena to some extent in Newfoundland, Nova Scotia, and New Brunswick.

According to Strong [58], at depths equivalent to 9, 7, and 6 kbar, melts are generated through the breakdown of hornblende, biotite, and muscovite resulting in dioritic, granodioritic, and granitic melts with water contents surpassing 2.7, 3.3, and 8.4 wt.%, respectively. These melts could ascend through the lithosphere to reach their solidus in an upper crustal setting; the more silicic magmas might evolve through differentiation from contaminated mafic magma with comparable water contents. The upwelling of the asthenosphere during oceanic slab rollback to break-off serves as the source of advective heat, contributing to the generation of syn- to post-collisional magmas from the hydrous oceanic slab. In this model, the role of transpression and transtension is significant for the ascent and emplacement of magma. According to Topuz et al. [45], the upwelling of adakitic magmas is attributed to a reduction in crustal thickness followed by regional extension. Based on the model we presented for the GEOROC data review [7], during subduction, in environments characterized by a high temperature and pressure, modified ocean crust undergoes a transition to basaltic eclogite [59]. This transformation initiates the release of residual H_2O, playing a pivotal role in the melting of the seawater-altered oceanic crust. Based on Spandler and Pirard [60], serpentinite is likely a component of the subducting slab, originating either from oceanic lithosphere that was hydrated at or near the seafloor, or from the fore-arc mantle wedge that absorbed water released by down-going crustal rocks. Slab coupling with the asthenospheric mantle at sub-arc depths causes the heating and devolatilization of deep slab serpentinite and/or hydrated mélange. When these fluids interact with coesite–phengite eclogite at the upper side of the slab, they produce hydrous slab melts. These melts then migrate out of the slab, ultimately contributing to the generation of magmatism within the evolving arc system. In this process, hydrous slab melts are the primary instrument for the transfer of elements from the slab to the arc magmatic system. However, serpentinites (and/or related hybrid mélange rocks) also contribute water and trace elements like base metals plus B, Cl, S, As, and Sb [60].

The correlation between magmas at convergent margins and the occurrence of Cu-Au mineralization has been recognized for some time [48,61–63], but the nature of this connection remains a subject of controversy—is it synsubduction to postsubduction magmatism? Further to this debate on the metallogenic connection, we focus on whether the association is attributed to melts and fluids with high oxygen fugacity (fO_2) released from subducted slabs and (or) to brine exsolution during the evolution of magmatic processes [25]. According to Gibert et al. [25,64], Au and Cu, being highly chalcophile elements, exhibit behaviors influenced by the abundance and oxidation state of sulfur and the formation Cl-complexing ligands in the fluids; Au and Cu have the capability to partition into chlorine-rich aqueous fluids where they complex with chlorine [65], as was cited by Sun et al. [25].

During the Late Silurian–Early Devonian (Figure 12a), the Acadian collision occurred via the accretion of Avalonia with composite Laurentia, marking the closure of the Acadian seaway [66]. This process trapped pockets of subduction-modified mantle above the leading edge of the subducted Avalonian plate, leading to localized arc-like magmatism (Figure 12a). The Middle Devonian through to Carboniferous convergence between the microcontinents of Avalonia and Meguma (Figure 12b) may have resulted from the flat-slab subduction of the Rheic Ocean, or the closure of an oceanic seaway between Meguma and Avalonia. In either case, the subsequent break-off of the ocean slab triggers melting beneath the collision zone between Ganderia and Avalonia.

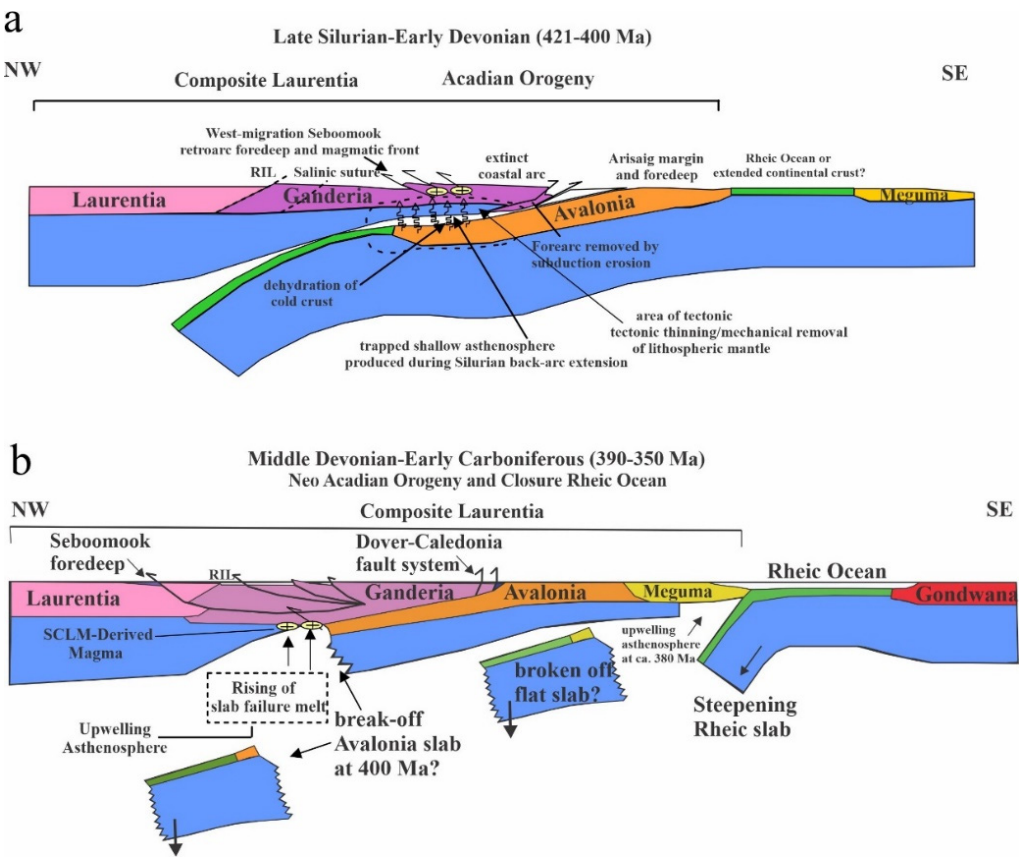


Figure 12. Schematic model showing the Silurian–Carboniferous tectonic evolution of the northern Appalachian orogen, and the generation of slab break-off-generated magmas; (**a**) late Silurian–Early Devonian, and (**b**) Middle Devonian–Early Carboniferous. Modified from [66].

The model presented by Yousefi et al. [2,15], which is derived from research by van Staal and Bar [66], indicates that Devonian adakitic rocks in the southern and northern parts of New Brunswick may have formed from magmas generated by slab failure/break-off processes. This is supported by Bustard et al. [8], who described intrusions and dykes in northeastern NB to be associated with the South Gold Zone occurrence, also attributing magma formation to oceanic slab break-off. Likewise, Pilote et al. [9] noted that the emplacement of the Landry Brook, Dickie Brook plutons, and the Blue Mountain Granodiorite Suite and Charlo Suite in northeastern NB are associated with the accretion of Ganderia to Laurentia and are related to the Avalonia composite Laurentia collision. The broad magmatic activity linked to this event is credited to 'flat-slab' subduction [67]. Wilson et al. [68] also proposed that the occurrence of bimodal volcanic rocks within the Silurian Bryant Point and Benjamin formations can be attributed to extensional tectonics and magmatism related to slab break-off. According to Whalen et al. [69], this sequence of events aligns with the interpretations of similar processes of slab rollback, and then slab break-off and subsequent uplift occurring along the strike in Newfoundland, following the Salinic collision.

In this model, the magmas generated result from the melting of the subducted oceanic slab and the mantle lithosphere following slab rollback and slab failure, in the absence of asthenosphere interaction. The space generated by the break-off and by the oceanic plate allows for asthenospheric ascent, thereby facilitating the transfer of heat to the subducted plate and providing sufficient conditions for melt formation and migration. Of particular importance in this model is the fact that the thickening of the mantle lithosphere occurs in response to the accelerated subduction rate of the cold oceanic slab; further details regarding this model can be found in [7]. According to Karsli et al. [70], when the subduction angle of the oceanic plate is shallow, the heat available for melting the oceanic plate is diminished.

Considering this factor, the role of heating by the asthenosphere must be considered. The sub-continental lithospheric mantle (SCLM) underwent metasomatic enrichment, likely due to H_2O-rich fluids released from the subducted oceanic crust [70]. The authors of this manuscript address the relationship between adakite magma, slab break-off/failure, and related tectonic evidence in a separate article in detail, where they review adakites associated with Au, Cu, and Mo porphyry mineralization worldwide [7].

We propose that Devonian intrusions in this part of the northern Appalachians record the transitions between multiple geodynamic regimes, including shifts from plate subduction to intra-arc extension resulting from slab rollback, as well as slab break-off due to terrane accretion and collision. Analysis of isotopic data (ε_{Nd} = −0.3 to −4.2 and $\delta^{18}O$ = +6.6 to +10.4 ‰) from Siluro–Devonian granitoid plutons in New Brunswick revealed that their magma originated from the mixing of crustal and mantle sources [14,15]. This origin has been confirmed for one of the intrusive units in southern NB, known as Eagle Lake Granite [15]. The whole rock $\delta^{18}O$ values for plutons in southern New Brunswick range from +7.1 to +10.3‰, confirming that they are normal granitoids derived from a combination of juvenile (mantle and lower crust) and supracrustal sources [71]. Ayuso and Bevier [72] used Pb isotope analysis to confirm that the source of these plutonic rocks in the northern Appalachians is a mixture of mantle-derived and crustal materials.

5. Conclusions

Devonian granitic intrusions in the NB portion of the northern Appalachians record a complicated geological history influenced by the Salinic then Acadian orogenies. The presence of oxidized I-type granitoids, particularly late tectonic adakitic varieties, is a significant factor in terms of both tectonic evolution and from the perspective of porphyry copper deposit prospectivity; Mines Gaspé in the Gaspé region of Québec is the most significant porphyry Cu-Mo and base metal skarn system in the northern Appalachians. Some geochemical features such SiO_2 > 56 wt.%, Na_2O content > 3 wt.%, Al_2O_3 content >16 wt.%, and a low amount of Y and Yb, as well as enrichment in large ion lithophile elements (LILEs) with positive Rb, Th, and Pb anomalies and negative Nb, Ta, and Ti anomalies, confirm the adakitic nature of these NB granitoids.

Like adakites elsewhere, those in NB are marked by elevated SiO_2, are enriched in large ion lithophile elements, and are depleted in high field strength elements, which together, point to a slab failure origin. Geochemical markers such as $Sr/Y \geq 33$ to 50, $Nb/Y > 0.4$, $Ta/Yb > 0.3$, $La/Yb > 10$, $Ta/Yb > 0.3$, $Sm/Yb > 2.5$, $Gd/Yb > 2.0$, $Nb + Y < 60$ ppm, and $Ta + Yb < 6$ ppm support the slab failure model and elucidate the tectonic evolution of the Appalachians during the concluding stages of the Acadian Orogeny. Slab failure is key in adakite genesis, which is supported by tectonic discrimination diagrams and distinct geological signatures.

The proposed model for adakitic magma formation during slab rollback and break-off involves the release of H_2O from subducted oceanic crust. The schematic model in Yousefi et al. [7] illustrates the dynamics of heat transfer, magma generation, and potential mineralization within the evolving geodynamic setting. The findings of this study strongly support slab break-off as a pivotal factor in the formation of adakitic rocks, highlighting the connection between these rocks and copper mineralization. This reinforces the link between specific intrusive formations in NB and porphyry Cu-Au deposits, paving the way for further exploration and understanding of porphyry Cu-Au mineralization in similar geological settings.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/geosciences14090241/s1. Table S1: Major and trace element contents of representative adakitic intrusions in New Brunswick.

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