Geochemical and Nd isotopic constraints on the origin of uppermost Silurian rhyolitic rocks in the northern Appalachians (northern New Brunswick): tectonic implications

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Voluminous bimodal volcanic rocks of the Silurian (~422 - 420 Ma) Dickie Cove Group in the Ganderia domain of northern New Brunswick, Canada, are subaerial units that were deposited in an extentional setting, with the mafic types corresponding to continental tholeiites. Felsic rocks are rhyolites with calc-alkaline affinities. They exhibit geochemical characteristics that are typical of A2-type felsic magmas, such as enrichments in the incompatible elements Zr, Nb and Y, as well as high FeO*/ (FeO*+MgO) and Ga/Al ratios. Their ƐNd(t) values are positive (+0.7 to 3.4), but lower than those of the associated basalts. Saturation thermometry has yielded average zircon crystallization temperature estimates for the rhyolites that are well above 900oC. The geochemical data indicate that the felsic melts were likely sourced from heterogeneous, Neoproterozoic lower crust, and generated by dehydration melting triggered by heat derived from underplated mafic magma. Parent melts of the rhyolites underwent fractional crystallization in a complex magma chamber prior to eruption. The Nd isotopic data suggest that the lower crust of Ganderia is similar to that of Avalonia in northern mainland Nova Scotia, and that the two microcontinents share a common Neoproterozoic history and origin as continental blocks rifted from neighboring parts of Gondwana. The tectono-magmatic setting of the Dickie Cove Group volcanic rocks is interpreted as being related to Pridolian, post-Salinic relaxation and slab breakoff, which generated volcanism initially constrained within the Chaleur Zone of the Chaleur Bay Synclinorium, a large domain of the northern Appalachians. This was followed later in the Pridolian by extensional collapse and widening of the area of magmatic activity, which then prograded into the Tobique Zone farther to the southwest.

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Abstract

Voluminous bimodal volcanic rocks of the Silurian (~422 - 420 Ma) Dickie Cove Group in the Ganderia domain of northern New Brunswick, Canada, are subaerial units that were deposited in an extentional setting, with the mafic types corresponding to continental tholeiites. Felsic rocks are rhyolites with calc-alkaline affinities. They exhibit geochemical characteristics that are typical of A2-type felsic magmas, such as enrichments in the incompatible elements Zr, Nb and Y, as well as high FeO*/(FeO*+MgO) and Ga/Al ratios. Their $\varepsilon_{Nd}(t)$ values are positive (+0.7 to 3.4), but lower than those of the associated basalts. Saturation thermometry has yielded average zircon crystallization temperature estimates for the rhyolites that are well above 900^{o}C. The geochemical data indicate that the felsic melts were likely sourced from heterogeneous, Neoproterozoic lower crust, and generated by dehydration melting triggered by heat derived from underplated mafic magma. Parent melts of the rhyolites underwent fractional crystallization in a complex magma chamber prior to eruption. The Nd isotopic data suggest that the lower crust of Ganderia is similar to that of Avalonia in northern mainland Nova Scotia, and that the two microcontinents share a common Neoproterozoic history and origin as continental blocks rifted from neighboring parts of Gondwana. The tectono-magmatic setting of the Dickie Cove Group volcanic rocks is interpreted as being related to Pridolian, post-Salinic relaxation and slab breakoff, which generated volcanism initially constrained within the Chaleur Zone of the Chaleur Bay Synclinorium, a large domain of the northern Appalachians. This was followed later in the Pridolian by

extensional collapse and widening of the area of magmatic activity, which then prograded into the Tobique Zone farther to the southwest.

Introduction

The Appalachian orogenic belt extends for more than 3,000 km along the eastern margin of North America from Alabama in the southern United States to Newfoundland in the north. The northern Appalachian Orogen underwent a protracted and complex tectonic evolution that led to a collage of accreted terranes sandwiched between the Laurentian and Gondwanan cratonic and peri-cratonic domains (Fig. 1). The orogen formed during the early Paleozoic closure of Iapetus (proto-Atlantic Ocean) and of several marginal seaways and basins. This led to the accretion of intra-oceanic and continental margin arcs and microcontinents that were located in the Iapetus Ocean (e.g., Pollock et al., 2012; van Staal and Barr, 2012; Wilson et al., 2017). Later stages of Iapetus closure are characterized by the accretion of two peri-Gondwanan microcontinents, Ganderia and Avalonia, which docked during the middle Paleozoic prior to the accretion of the Gondwanan continent (e.g., van Staal and Barr, 2012). However, the nature, timing and modes of accretion of these microcontinents are still debated. For example, there is even disagreement on whether or not Ganderia and Avalonia represent distinct terranes (e.g., van Staal and Hatcher, 2010; Keppie et al., 2012; Waldron et al., 2014).

Voluminous Silurian to Lower Devonian bimodal (mafic-felsic) volcanic rocks form part of an overstep sequence on the accreted vestiges of Iapetus at the margin of composite Laurentia. Study of these rocks can be critical for the understanding of accretionary/tectonic processes along the northern Appalachian Orogen and can also provide insights regarding the evolution of continental crust. This paper presents whole-rock major and trace element data as well as isotopic data from bimodal volcanic rocks of the Silurian Dickie Cove Group (formerly part of the Chaleur Group) in northern New Brunswick, with a focus on the felsic rocks, in order to (1) discuss their petrogenesis and (2) constrain their tectonic and geodynamic settings in the context of Iapetus Ocean closure.

Geological Setting

A prominent feature of the northern Appalachians, the Matapedia cover sequence (MCS) is a large Middle Paleozoic successor (overstep) basin-fill that was deposited across the accreted vestiges of Iapetus on composite Laurentia (Fig. 2). The MCS unconformably overlies Ordovician rocks of the Ganderian Popelogan arc and Tetagouche-Exploits back-arc basin (van Staal et al., 2009). It extends from the Gaspé Peninsula of eastern Quebec to central Maine, and underlies a large part of northern New Brunswick.

The MCS consists of three structural zones (Fig. 2), which are, from northwest to southeast, the Connecticut Valley-Gaspé Synclinorium, the Aroostook-Percé

Anticlinorium, and the Chaleur Bay Synclinorium (Rodgers, 1970; Wilson et al., 2004). The Chaleur Bay Synclinorium records extensive magmatic activity that immediately post-dates Silurian closure of the Tetagouche-Exploits back-arc basin and breakoff of the Tetagouche-Exploits lithosphere during the Salinic orogenic cycle. Closure of the back-arc basin is also responsible for the Upper Ordovician to Silurian formation of the Brunswick subduction complex, an accretionary wedge (van Staal et al., 2009; Wilson et al., 2017). The Chaleur Bay Synclinorium is divided into two parts by the WSW-ENE trending Rocky Brook-Millstream Fault (Fig. 2). The northern part (the Chaleur Zone) contains two prominent subaerial to subaqueous post-Salinic volcanic suites hosted by the Pridolian (Silurian) Dickie Cove Group and the Lochkovian to lowermost Emsian (Lower Devonian) Dalhousie Group (Fig. 2C).

The dominantly volcanic rocks of the Dickie Cove Group (DCG) (*sensu* Wilson and Kamo, 2012) were formerly assigned to the Chaleur Group by Irrinki (1990) and Walker and McCutcheon (1995). The DCG is composed of bimodal (mafic-felsic) volcanic rocks and minor associated volcanogenic sedimentary rocks. The upper part of the group (Benjamin Formation) predominantly consists of aphyric to feldspar-phyric rhyolites and felsic pyroclastic rocks (lithic tuff, lithic-crystal tuff and ignimbrite). Mafic volcanic and coarse-grained pyroclastic rocks are subordinate lithotypes. Facies of the felsic rocks are typical of volcanic rocks emplaced in subaerial environments. The DCG was dated by Wilson and Kamo (2008, 2012), who obtained a U-Pb zircon age of 422.3±0.3 Ma from the base of the group, and 419.7±0.3 Ma from the top. The DCG unconformably overlies Silurian sedimentary rocks (Quinn Point Group) and is disconformably overlain by the Lower Devonian Dalhousie Group (Fig. 2C), which comprises interbedded shallow marine sedimentary rocks as well as subaerial to shallow marine mafic and subordinate felsic effusive and pyroclastic rocks.

The southern part of the Chaleur Bay Synclinorium (the Tobique Zone) includes the Pridolian to Lochkovian Tobique Group (TG), which contains sedimentary rocks as well as abundant mafic and felsic volcanic rocks (Wilson et al., 2017; Dostal et al. 1989, 2016, 2020). Biostratigraphic and U-Pb zircon ages show that deposition of the TG overlaps that of both the Dickie Cove and Dalhousie groups (Wilson and Kamo, 2008), with the volcanic-dominated lower part of the Tobique Group correlating with the DCG, and the sedimentary-dominated upper part correlating with the Dalhousie Group. In the northern part of the Tobique Zone, near its faulted boundary with the Chaleur Zone, a continuous succession of Ludlovian to Lockhovian sedimentary rocks (Petit Rocher Group and Greys Gulch Formation; Fig. 2C) is conformably overlain by marine sedimentary rocks and subordinate subaqueous volcanic rocks of the upper part of the TG (Wilson, 2017), implying that the dominantly volcanic Pridolian successions of the DCG and basal TG belong to two distinct and geographically separated suites.

Petrography

Rhyolitic volcanic rocks of the DCG are massive to flow-banded, aphyric to porphyritic, and locally vesicular. The matrix of the volcanic rocks is fine-grained or glassy, and vitrification textures are common. Feldspar phenocrysts are euhedral to subhedral, whereas rare quartz phenocrysts are embayed. Biotite and Fe-Ti oxides are rare, and zircon, apatite and monazite are accessory minerals. The volcanic rocks underwent low-grade metamorphism of zeolite to lower greenschist facies, as indicated by mineral assemblages in the associated mafic rocks (Dostal et al., 1989; Mossman and Bachinski, 1972). Their primary mineral assemblages are variable, but extensively replaced by secondary minerals such as sericite and chlorite. Typically, their K-feldspar fraction is sericitized, and their plagioclase fraction is saussuritized.

Analytical Methods

The analyzed felsic volcanic rocks were selected from a collection of more than one hundred samples collected during regional mapping of the DCG (e.g., Wilson et al. 2005; Wilson, 2017). Whole-rock major and trace elements were analyzed at the Activation Laboratories Ltd. in Ancaster, Ontario, Canada. An inductively-coupled plasma-optical emission spectrometer was used for the analysis of major elements, whereas trace element contents were determined by inductively-coupled plasma mass spectrometry. Based on analytical results obtained from international standard rocks, the analytical precision and accuracy were typically better than 5% for major elements and better than 10% for trace elements.

Sm and Nd contents as well as Nd isotope ratios were determined at the Atlantic Universities Regional Isotope Facility of the Department of Earth Sciences at Memorial University of Newfoundland (St. John’s, Newfoundland, Canada) by a multicollector Finnigan MAT 262 thermal ionization mass spectrometer (Pollock et al., 2015). During the course of data acquisition, replicates of the JNdi-1 standard gave a mean value of $^{143}Nd/^{144}Nd = 0.512100 \pm 0.000007$ (2σ, n=21). All reported values for the samples were adjusted to the value of the JNdi-1 standard ($^{143}Nd/^{144}Nd_{certified} = 0.512115 \pm 7$). The 2 σ values for $^{143}Nd/^{144}Nd$ ratios are given in Table 1. Initial Nd isotope ratios and epsilon values (ε_{Nd}) were corrected using the age of 421 Ma (Table 1). T_{DM} model ages (Table 1) were calculated in accordance with DePaolo (1988).

Geochemistry

Alteration

As noted earlier, rocks of the DCG were modified by secondary processes that might have changed the concentration of mobile elements, including K_2O and Na_2O. Some samples were also hydrothermally altered. Several strongly altered samples were eliminated. The remaining samples show consistent variations of immobile- and mobile-element patterns on various diagrams, suggesting that most element variations are likely related to magmatic processes. Furthermore, to limit the problem of alteration, the interpretations in this paper are based mainly on elements that are generally considered to be little affected by secondary processes, such as rare-earth elements (REE) and high-field-strength elements (HFSE).

Major and Trace Elements

Volcanic rocks of the DCG range from basalts to rhyolites, with rare intermediate rock-types, implying that the suite is bimodal. Wilson (2017) estimated that rocks with < 52% silica constitute >30% of the suite, whereas rocks with >68% silica represent ~ 52% of the suite. The DCG mafic rocks are continental tholeiitic basalts and subordinate basaltic andesites (Dostal et al., 2016), but the felsic rocks are only poorly known. The DCG rhyolites have silica ranging from ~ 68% to 77% and plot mainly within the rhyolite field on the Zr/TiO_2 *versus* Nb/Y classification diagram (Fig. 3). The felsic rocks have high Fe* (FeO*/FeO*+MgO) values (Fig. 4) and are ferroan (Frost et al., 2001). Overall, the rocks have low contents of CaO, TiO_2, MgO and FeO*, but high contents of alkalis, which are characteristics of A-type felsic rocks. The rocks also show weak negative correlations of Al_2O_3, TiO_2, MgO, FeO* and CaO with increasing silica, which is broadly consistent with the fractionation of ferromagnesian minerals, Fe-Ti oxides and calcic plagioclase. Consistent with the rift-related signature of associated basalts in the group (Dostal et al., 2016), the DCG felsic rocks plot into the A-type granite fields (Fig. 5).

The chondrite-normalized REE patterns of the felsic rocks display slight enrichment in light REE (LREE), but flat heavy REE (HREE) accompanied by negative Eu anomalies (Fig. 6). The $(La/Yb)_n$ ratios vary between 3.5 and 8.5, whereas $(Tb/Yb)_n$ ratios are between 1 and 1.5. The patterns are generally parallel to subparallel. The variably pronounced negative Eu anomalies reflect feldspar fractionation and suggest low oxygen fugacity in the felsic melt. The relatively flat HREE patterns imply the absence of garnet at the source of these rhyolites, indicating an origin at relatively low pressures and at a depth that is shallower than the garnet stability field, which starts at a depth of ~60-80 km (McKenzie and O'Nions, 1991). Unlike those of the rhyolites, REE patterns in the associated basalts of the group are linear, negative Eu anomalies are absent, and HREE define a steeper slope [$(Tb/Yb)_n$ ~2] (Fig. 6B; Dostal et al., 2016).

According to their primitive mantle-normalized patterns, the felsic rocks are more enriched in both highly and moderately incompatible elements than the basalts (Fig. 7). The rhyolites display depletion in Ba, Sr, Ti and Eu, which suggests fractionation of feldspars and Fe-Ti oxides (Fig. 7), and which contrasts with the basalts. The felsic rocks also show negative Nb and Ta anomalies. The trace element patterns of some of these rocks resemble those of the continental crust (e.g., Rudnick and Gao, 2003).

Isotopes

$\varepsilon_{Nd}(t)$ values for the DCG rhyolites range from +0.73 to +3.37 (t=421 Ma). These values are notably higher that those of felsic volcanic rocks in the Tobique Zone (Dostal et al. 2020), but they are on average lower than those of the associated basalts (Table 1). They are also lower than values for the contemporaneous depleted mantle. The depleted mantle model age (T_{DM}; after De Paolo, 1988) of the DCG rhyolites vary between 0.7 and 1.0 Ga, and are slightly older than those of the basalts (0.65 - 0.8 Ga), but younger than those of felsic volcanic rocks in the Tobique Group (0.9 - 1.2 Ga). The DCG rhyolites also have lower $^{147}Sm/^{144}Nd$ ratios (0.1196 - 0.1337) compared to the basalts (0.1400 - 0.1475).

Discussion

Zircon saturation thermometry

The temperature of zircon saturation (T_{Zr}°C) in felsic magmas has been used to characterize various felsic rocks in terms of their origin and thermal history (Miller et al., 2003; Dostal et al. 2015; Xia et al., 2016; Murphy et al., 2018). For example, Miller et al. (2003) differentiate “hot” granites, which are assumed to be generated by anhydrous melting at high temperature (T_{Zr} >800°C), from “cold” granites (T_{Zr} < 800°C), which were derived from a crustal source in water-fluxed settings (Collins et al., 2016). The temperature at which zircon starts to crystallize is related to major element composition as well as Zr concentrations. The relationship was tested experimentally and is expressed by the M value of Watson and Harrison (1983). Within an experimental range of M values (i.e. M=1.3 -1.9), the temperature estimates may be useful for petrogenetic considerations (Hanchar and Watson, 2003; Collins et al., 2016). Values of M, as calculated in accordance with Boehnke et al. (2013), are within the experimental range of Watson and Harrison (1983) for most of the DCG felsic rocks, indicating that the rocks can provide meaningful temperature estimates (Table 2). The temperature estimates range from 845°C to 1047°C, with an average value of 929°C (± 64°C s.d.). This relatively wide temperature range could in part be related to magma evolution in shallow crust (fractionation, alteration, host rock assimilation). Hence, the average or maximum values are considered to be more diagnostic (Murphy et al., 2018).

Our results suggest that the initial magmatic temperature was well above 800^{o}C, and that the DCG rhyolites therefore issued from a "hot" felsic melt (*sensu* Miller et al., 2003). T_{Zr} (^{o}C) values were also calculated for felsic volcanic rocks of the TG in order to assess possible petrogenetic similarities or dissimilarities between the two suites. Rhyolite samples from the TG (Dostal et al., 2020) provide temperature estimates that range from 797^{o}C to 864^{o}C, with an average of 824^{o}C. Results from both suites are consistent with the relatively hot melting temperature of the anhydrous lower crust (Huppert and Sparks, 1988; Annen et al., 2006, 2015). Although there is an overlap in zircon saturation temperatures between the TG and DCG rhyolites, the latter have a higher average value, which is consistent with the conclusion that the TG basalts were generated at a shallower depth than those of the DCG (Dostal et al., 2016). The DCG rhyolites also bear higher ε_{Nd}(t) values than those of the TG suites (Dostal et al., 2020), which suggests that the DCG rhyolites had a larger proportion of mantle-derived material at their source.

Monazite saturation thermometry

To verify the relatively high crystallization temperature that is estimated for the DCG rhyolites, monazite saturation temperatures were calculated by relating the concentration of light REE to the bulk composition of the magma. The calculations (based on Montel, 1993) yielded an average temperature of 853^{o}C (± 40^{o}C) for the DCG rhyolites (Table 2), which is consistent with monazite crystallization occurring after that of zircon, but which still suggests a relatively high crystallization temperature. All these temperature estimates are similar to modeled temperatures of partial melting of the crust associated with basalt injection (Annen and Sparks, 2002).

Petrogenesis

Unlike Silurian (Llandovery to Ludlow) volcanic rocks of the Coastal volcanic belt in Maine and southern New Brunswick, which are typical continental arc calc-alkaline suites ranging from mafic to felsic types (Llamas and Hepburn, 2013), rocks of the Chaleur Bay Synclinorium farther inland are bimodal and include rift-related continental tholeiites inferred to be derived from the subcontinental lithospheric mantle (Dostal et al., 2016). However, the origin of the DCG rhyolitic rocks and of many other felsic rocks that are part of compositionally bimodal suites has been debated.

Various models for the origin of bimodal suites have been discussed for decades (e.g., Bowen, 1928; Barbarin, 1999; Riley et al., 2001). The two main models are based on either crystal fractionation or crustal melting. The first model (e.g., Lacasse et al. 2007; Waight et al., 2007) assumes a derivation of felsic magma by the extensive crystal fractionation of basaltic magma (up to 90%), or by a combined process of assimilation and fractional crystallization. The second model invokes partial melting of crustal rocks triggered by heating from underplated mantle-derived basaltic magmas (e.g., Huppert and Sparks, 1988). The latter model is frequently used (e.g., Annen and Sparks, 2002) to explain the formation of large felsic magma reservoirs, as fractional crystallization would require an unreasonably large volume of basaltic parental magma.

Variations in FeO*/MgO *versus* TiO_2 (Fig. 8) show that there is no obvious relationship between the DCG mafic rocks, which display a typical tholeiitic fractionation trend, and the DCG felsic rocks, which show a calc-alkaline trend. This and other geochemical characteristics of these rocks, such as contrasting Tb/Yb and Th/Nb ratios as well as significant differences in Nd isotopic values (Table 1), suggest that the felsic rocks were not derived from the mafic rocks by crystal fractionation. Thus, the paucity of intermediate rock types (Daly gap), large volume of felsic rocks relative to associated mafic rocks, and contrasting geochemical and Nd isotopic characteristics between the two rock-types are consistent with a derivation from different sources. This process can also account for some compositional variations within felsic magma bodies (Altherr et al., 2000; Shellnutt et al. 2011), as felsic magma heterogeneity may, in part, reflect heterogeneity of the crustal source.

As noted earlier, the DCG felsic rocks are similar in composition to A-type (i.e. within plate) granitic rocks. Eby (1992) noted that A-type granitic rocks can be subdivided into at least two types. The parental magma of granites in the A1 subgroup is mafic and derived from a mantle source. A1 granites have incompatible trace elemental ratios that are similar to those of ocean-island basalts. The compositionally diverse A2 subgroup is sourced from the lithosphere, and is characterized by elemental ratios that are similar to those of continental crust or island arc basalts. The DCG rhyolites have affinities with A2-type granites (Fig. 9). Many such granites are considered to represent magmas derived from the lower to middle crust (Eby 1992; King et al., 1997).

Some geochemical variation trends in the DCG rhyolitic rocks are likely related to differentiation processes, particularly fractional crystallization that occurred after the magma was formed. In addition to fractionation of major phases, mainly feldspars and minor ferromagnesian minerals and Fe-Ti oxides, accessory minerals also played a role during fractional crystallization as they control much of the REE variation. A graph of $(La/Yb)_n$ *versus* La (Fig. 10A) suggests that fractionation of REE, the bulk of which is hosted by accessory phases, was dominated by the crystallization of monazite. Although fractional crystallization involved the crystallization of feldspars, variations in Ba and Sr, which are elements that are preferentially hosted by feldspars, do not correlate with negative Eu anomalies (Eu/Eu*). This may indicate buffering from the activity of fluids. Two distinct trends on the Ba *versus* Eu/Eu* diagram (Fig. 11A) suggest the existence of a complex magma chamber, although all the DCG rhyolites have similar evolutions.

In addition to fractional crystallization, a variable degree of partial melting can also generate variations in rock composition. Schiano et al. (2010) suggested that partial melting and fractional crystallization processes can be identified from systematic changes in incompatible trace element concentrations and their ratios. The Ba/Zr *versus* Ba plot (Fig. 11B) shows that some samples were derived from different degrees of partial melting than the majority of the rhyolites. However, some significant compositional variations in the rhyolitic rocks cannot be attributed to fractional crystallization or to a variable degree of partial melting (e.g., variations in trace element ratios and Nd isotopic values), but rather point to a heterogeneous source. The Th/Nb *versus* Zr graph (Fig. 10B) is useful for an evaluation of source heterogeneity: Th/Nb, which is not significantly affected by fractional crystallization, is plotted against an incompatible trace element (Zr) that increases in concentration with fractionation. The variation in Th/Nb ratios (Fig. 10B) therefore likely reflect crustal source heterogeneity for the DCG rhyolites. The plot also implies that assimilation-fractional crystallization (AFC) processes, which lead to an enrichment trend that is intermediate between fractional crystallization and source heterogeneity vectors, do not appear to have played a significant role in the genesis of the rhyolites.

The DCG rhyolitic rocks likely represent melts that were derived from crustal material. This conclusion is also supported by their distribution patterns in primitive mantle normalized plots, which display depletions in Nb, Ta, Ti, Eu, Ba, and Sr (Fig. 7), altogether indicating that the DCG felsic rocks have been sourced from continental crust. Nd model ages for the DCG rhyolites are Neoproterozoic (Table 1), which is consistent with the age of Ganderian basement rocks (van Staal et al., 1996, 2012; Dostal et al., 2016, 2020; Fig. 12). Moreover, the $\varepsilon_{Nd}(t)$ values overlap the isotope envelope of Avalonian crustal values (Fig. 12), which suggests that Ganderia and Avalonia have a common Neoproterozoic history and a similar lower/middle crust (Dostal et al., 2020). The Nd isotopic data also shows that the crustal source of the DCG rhyolites was similar but distinct from that of the TG rhyolites.

Murphy et al. (2018) argued that partial melting of an anhydrous lower crustal source produced the A-type magmas of northern Nova Scotia, in West Avalonia. A similar process and source can be invoked for the DCG rhyolites. Partial melting of various crustal reservoirs has been invoked to explain the chemical characteristics of “A-type” felsic rocks, such as a charnockitic lower crust, an I-type granite precursor, calc-alkaline amphibole-bearing tonalite, mafic underplated rocks, and some others (e.g., Collins et al., 1982; Creaser et al., 1991; King et al., 1997; Bonin, 2007). Dostal et al. (2020) inferred that partial melts of granodioritic/tonalitic and charnockitic rocks or their sedimentary or metamorphic equivalents have a major element composition that is similar to that of the A2-type TG felsic volcanic rocks, and that either could represent the parent material. Similar crustal source possibilities can be suggested for the DCG felsic rocks. The continental crust is compositionally diverse and includes both juvenile and recycled material. The Neoproterozoic T_{DM} values for the DCG rhyolites suggest an ancient source that probably experienced episodic recycling, such as in a subduction zone or at the root of a continent-continent collision. Eby (1992) suggested that these processes may contribute to the "within-plate" signature of A2-type felsic rocks.

Continental crust can melt as a result of repeated injections of hot mafic magmas (Huppert and Sparks, 1988; Annen and Sparks, 2002; Annen et al. 2006). The temperature of the crust may exceed 800^{o}C during continuous basalt injection - hot enough to create partial melts (Annen and Sparks, 2002). Thus, rising mafic magma may have triggered melting of the crust from which the felsic rocks inherited their geochemical characteristics. This process is common during lithospheric extension and is a consequence of magmatic underplating (e.g. Huppert and Sparks, 1988). Hence, dry partial melting of the heterogeneous lower crust of Ganderia most likely produced the primary melt that sourced the DCG rhyolites. However, prior to its eruption, this primary melt may have resided in plutonic bodies such as the compositionally similar and almost coeval Landry Brook and Dickie Brook plutons, which intrude the DCG in the Chaleur Zone (Fig. 2) (Pilote et al., 2013; Wilson and Kamo, 2016).

Tectonic Setting

Following accretion of Ganderia's leading edge (the Popelogan arc) to Laurentia in the Upper Ordovician, the Tetagouche-Exploits back-arc basin that separated Ganderia's leading and trailing segments began to close, culminating with the ~425 Ma Salinic Orogeny (van Staal et al., 2009; Zagorevski et al., 2010; Wilson et al., 2017) (Fig. 13 A, B). At 422.3±0.3 Ma (Wilson and Kamo, 2008), the DCG provides some of the earliest record of extrusions related to post-Salinic extensional magmatism (*sensu* Dostal et al., 2020) in the northern Appalachians. A possible equivalent is the Stony Lake Rhyolite, which lies above the Salinic unconformity in Newfoundland, and which was roughly dated at 423+3/-2 Ma by Dunning et al. (1990). This volcanism has been associated with post-orogenic relaxation and breakoff of the Tetagouche-Exploits slab (van Staal et al., 2009; Wilson et al., 2017) (Fig. 13C). Mafic eruptions in the DCG may be linked to the ponding of asthenospheric melt in the rising root of the orogen, which resulted in high-degree partial melting of the subcontinental lithospheric mantle (Dostal et al., 2016) (Fig. 13C). Evidence for high heat flow during generation of the DCG felsic melts suggests that its lower crustal source was located in the focus zone of mafic upwelling and crustal underplating (Fig. 13C). Because it was associated with a post-orogenic rise of the lithosphere, initial post-Salinic magmatism was subaerial and limited in extent to a narrow, orogen-parallel belt.

In New Brunswick, volcanism in the early part of the Pridolian was constrained to the Chaleur Zone (Wilson et al., 2017). Later in the Pridolian, extensional collapse of the orogenic root (van Staal and de Roo, 1995) resulted in a widening of both the sub-lithospheric and sub-crustal areas of underplating. This led to an expansion of the area of volcanism into the Tobique Zone, thus triggering the onset of TG volcanism (418.6 - 420.8 Ma; Wilson et al, 2017) in a separate volcanic centre (Fig. 13D). Although these two zones are currently located roughly along-strike from each other, it is inferred that the Chaleur Zone lay farther west in relation to the Tobique Zone prior to post-Silurian dextral faulting along the Rocky Brook-Millstream fault system (Wilson, 2017). However, emplacement of both volcanic belts was originally parallel to the southwest-northeast-trending Salinic grain of the orogen (Fig. 13D).

Evidence for lower heat flow during generation of the TG felsic melts compared to the DCG melts suggests that the lower crustal source of the TG volcanic rocks was located farther away from the locus of mafic upwelling and crustal underplating (Fig. 13D). This is consistent with Nd isotopic data, which imply that felsic rocks of the DCG and TG issued from two slightly distinct crustal sources.

Conclusions

Following the Wenlock-Ludlow Salinic Orogeny (Fig. 13A, B), post-orogenic relaxation and breakoff of the Tetagouche-Exploits slab resulted in the development of extensional tectonics in Ganderian rocks of the northern Appalachian orogen, and eventually led to the emplacement of Pridolian to lowermost Emsian bimodal suites in a discontinuous, orogen-parallel belt stretching from Maine to eastern Quebec. The ~422 -

420 Ma Dickie Cove Group of northern New Brunswick provides the earliest record of this long period of extensional volcanism, which, in the early part of the Pridolian, was constrained to the Chaleur Zone in the northern part of the Chaleur Bay Synclinorium (Fig. 13C).

Rhyolites are the dominant felsic rock type in the voluminous bimodal volcanic suite of the Dickie Cove Group. Geochemical evidence suggests that these felsic rocks, which show a calc-alkaline trend, were not produced by fractional crystallization of associated mafic melts, which show a tholeiitic trend. The geochemical data indicate that the felsic melts, which plot as “within-plate”, A2-type melts on various discrimination diagrams, were likely sourced from heterogeneous, Neoproterozoic lower crust, and that they were generated by dehydration melting triggered by heat derived from the associated mafic magma. Saturation thermometry has yielded average zircon and monazite crystallization temperature estimates for the rhyolitic rocks that are well above 900^{o}C and 800^{o}C, respectively. Parent melts of the DCG rhyolites underwent fractional crystallization in a complex of magma chambers prior to erupting in sub-aerial conditions.

The $\varepsilon_{Nd}(t)$ values of the DCG rhyolites are positive (+0.73 to +3.37), but lower than those of the associated basalts. Nd model ages are Neoproterozoic (0.7 - 1.0 Ga), which is typical of Ganderian and Avalonian crust. The data also suggest that the lower crust of Ganderia is similar to that of Avalonia in northern mainland Nova Scotia. This is consistent with Nd isotopic data from some Silurian to Lower Devonian granitic and felsic rocks in other areas of Ganderia (e.g., Whalen et al., 1994, 1996), which also plot into the Avalonian envelope (Fig. 12; Dostal et al., 2020). The similarity of lower crust composition in both microcontinents suggests a common Neoproterozoic history and is consistent with their inferred origin as continental blocks rifted from neighboring parts of Gondwana (e.g., van Staal and Barr, 2012; van Staal et al., 2012; Waldron et al., 2014).

Acknowledgements

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Table captions

Table 1. Nd isotopic compositon of volcanic rocks of the Dickie Cove Group.

Table 2 Zircon and monazite saturation thermometry estimates of rhyolitic rocks of Dickie Cove Group.

Figure captions

Figure 1. Major lithotectonic domains of the northern Appalachians (modified after van Staal and Barr, 2012 and Dostal et al., 2016). NB: New Brunswick.

Figure 2. (A) Simplified geology of the Chaleur Bay Synclinorium and adjacent inliers in New Brunswick (modified from Wilson et al., 2017). U-Pb zircon dates from Silurian to Lower Devonian felsic volcanic rocks of the Tobique and Dickie Cove groups are indicated, as well as from the Silurian Landry Brook [LB] pluton and Silurian-Lower Devonian Dickie Brook [DB] pluton, both of which intrude the Dickie Cove Group. Data from (1) Wilson and Kamo (2008), (2) Wilson and Kamo (2012), (3) Pilote et al. (2013), and (4) Wilson et al. (2017). (B) Areal extent of the Chaleur and Tobique zones, which are respectively to the north and south of the Rocky Brook - Millstream Fault. (C) Stratigraphic columns showing the age of Silurian to Lower Devonian volcanic rocks of the Dickie Cove, Tobique and Dalhousie groups in the Chaleur Zone and in the northern part of the Tobique Zone.

Figure 3. Zr/TiO_2 versus Nb/Y classification diagram for the DCG bimodal suite (modified from Winchester and Floyd, 1977). Fields: TA - Trachyandesite; Alk-Bas - Alkali basalt.

Figure 4. Fe* [(FeO*/(FeO*+MgO)] versus SiO_2 (wt.%) for the DCG rhyolitic rocks showing the separation of ferroan and magnesian rocks (after Frost et al. 2001).

Figure 5. (A) 10,000xGa/Al versus Zr (ppm) diagram (after Whalen et al., 1987) for the DCG rhyolitic rocks classifying them as A-type rocks. Fields: I&S field is for I- and S-type granites while the A field is for the A-type granites. (B) Y+Nb (ppm) versus La/Yb

discrimination diagram of Whalen and Hildebrand (2019) showing the A-type characteristics of the DCG felsic volcanic rocks.

Figure 6. Chondrite-normalized rare-earth element diagrams for the DCG rocks (A) rhyolitic rocks: (B) basaltic rocks (after Dostal et al., 2016). Normalizing values are after Sun and McDonough (1989).

Figure 7. Primitive-mantle normalized incompatible element abundances for the DCG rocks: (A) rhyolitic rocks, (B) basaltic rocks (after Dostal et al., 2016). Elements are arranged in the order of decreasing incompatibility from left to right. Normalizing values are after Sun and McDonough (1989).

Figure 8. TiO_2 (wt.%) versus FeO*/MgO diagram for the DCG rocks. Vectors depict tholeiitic and calc-alkali fractionation trends (after Miyashiro, 1974). FeO* - total Fe as FeO.

Figure 9. Y-Nb-Ce diagram for the DCG rhyolitic rocks discriminating between A1 and A2-types of anorgenic granites (Eby, 1992). A1-type anorogenic granites related to ocean island-type sources; A2-type anorogenic granites derived from continental crust sources.

Figure 10. (A) Chondrite-normalized La/Yb ratio versus La (ppm) diagram for the DCG felsic rocks. Fractionation vectors for accessory minerals are after Wu et al. (2003). Mineral vectors are based on fractionation of monazite (Mon), allanite (Allan), apatite

(Ap), titanite (Tit) and zircon (Zr). (B) Variations of Th/Nb versus Zr (ppm) in the DCG rhyolitic rocks showing the vectors for increasing fractional crystallization (FC), combined assimilation-fractional crystallization (AFC) and source heterogeneity (modified after El-Bialy and Hassen, 2012).

Figure 11. (A) Variations of Ba (ppm) versus Eu/Eu* in the DCG rhyolitic rocks. Eu anomalies are calculated as (Eu/Eu*) where Eu denotes the chondrite-normalized value and Eu* represents the Eu value expected for a smooth chondrite-normalized REE pattern. (B). Variations of Ba/Zr versus Ba (ppm) in the DCG rhyolitic rocks showing the vectors for fractional crystallization and partial melting (after Schiano et al. 2010 and Wang et al. 2019).

Figure 12. $\varepsilon_{Nd}(t)$ versus time plot comparing Sm-Nd isotopic data of the DCG and TG rhyolitic rocks with basaltic rocks of Avalonia (Keppie et al., 1997; Murphy et al., 2011) and Ganderia (Dostal et al., 2016, 2020) of Nova Scotia and New Brunswick. Shaded area (envelope) is the Avalonian basement and SCLM (after Keppie et al., 2012; Murphy et al., 2011, 2018). The field for Mesoproterozoic rocks is from Murphy et al. (2008). CHUR- chondritic uniform reservoir.

Figure 13. Tectonic model for Silurian volcanism in the northern Appalachians. (A) Closure of the Tetagouche-Exploits back-arc basin and deposition of forearc rocks of the Matapedia cover sequence (MCS) following the Upper Ordovician accretion of Ganderia's leading edge (the Popelogan arc) to Laurentia. (B) Closure of the back-arc

basin culminating with the Wenlock-Ludlow Salinic Orogeny and initial deposition of the syn-orogenic Petit Rocher Group in northern New Brunswick. (C) Pridolian mafic magmatism triggered by detachment of the Tetagouche-Exploits slab (TES), post-orogenic root relaxation, and partial melting of the sub-continental lithospheric mantle (SCLM). Felsic melts were in turn produced at the base of the crust by heat derived from mafic underplating. The Dickie Cove Group (DCG) rhyolites of the Chaleur Zone were ultimately sourced from felsic diapirs issued from the base of the crust. (D) Extensional collapse of the Salinic root later in the Pridolian, and expansion of the volcanic belt to form a distinct volcanic suite in the Tobique Zone.

Figure 1

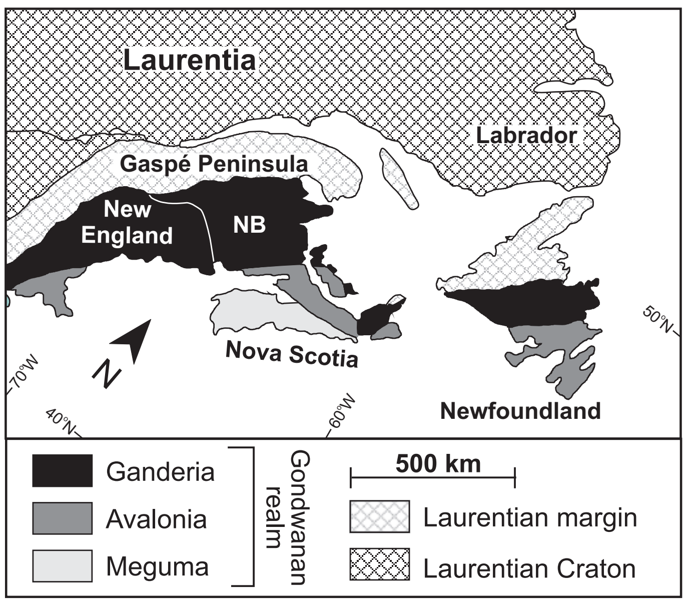


Fig. 1

Figure 2

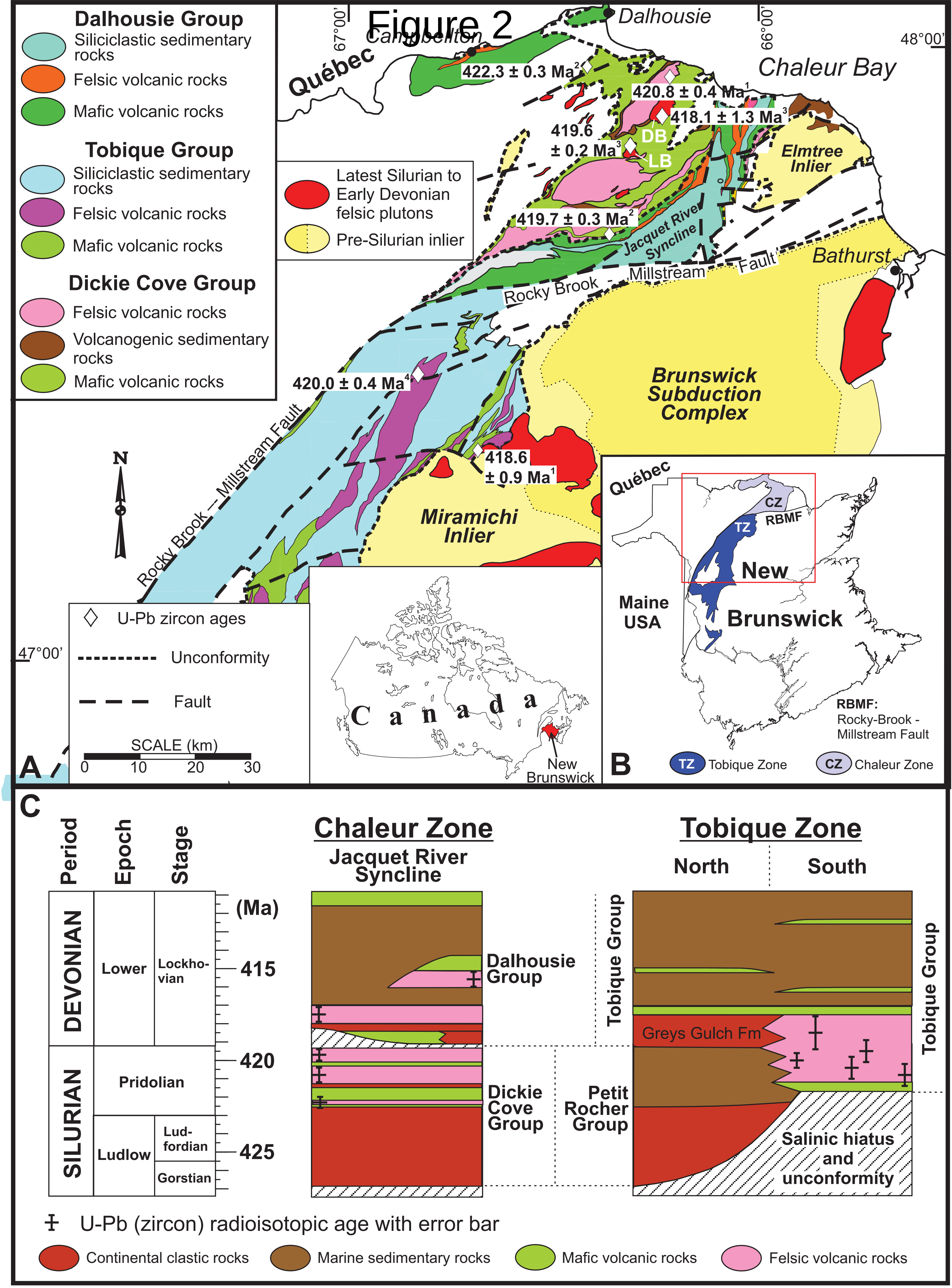
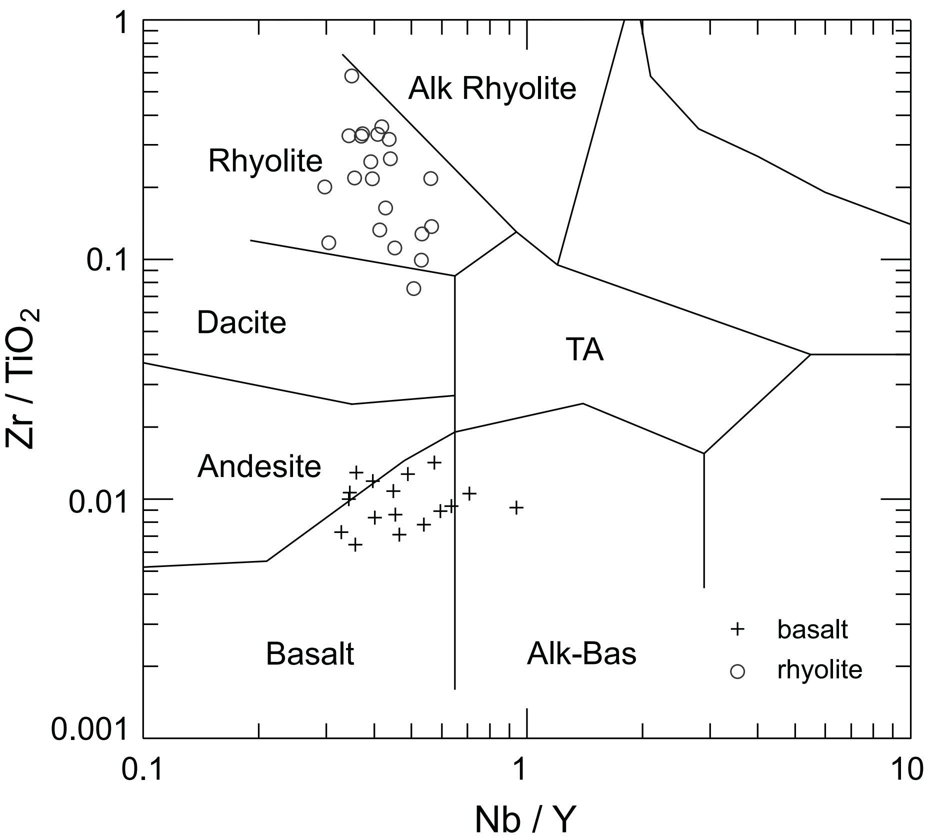


Fig. 2

Figure 3



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0.001
0.1
1
10
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Nb / Y
Alk Rhyolite
Rhyolite
Dacite
TA
Andesite
Basalt
Alk-Bas
basalt
rhyolite

Figure 4

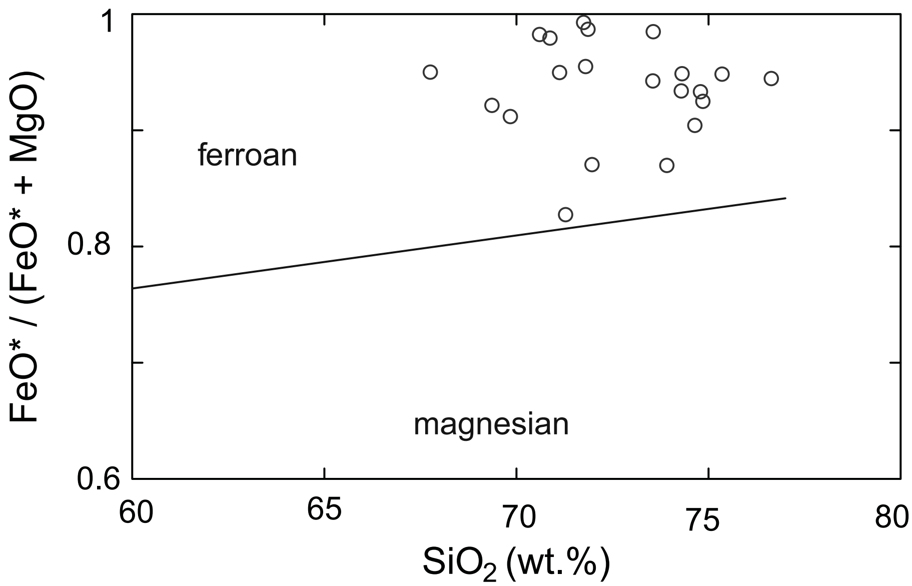


Figure 5A

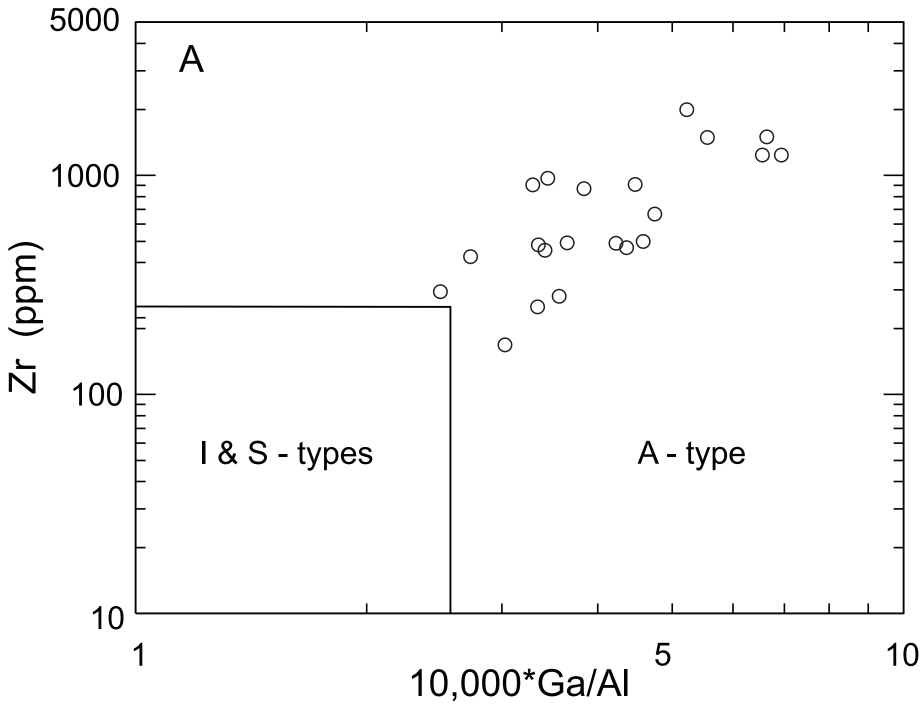


Figure 5B

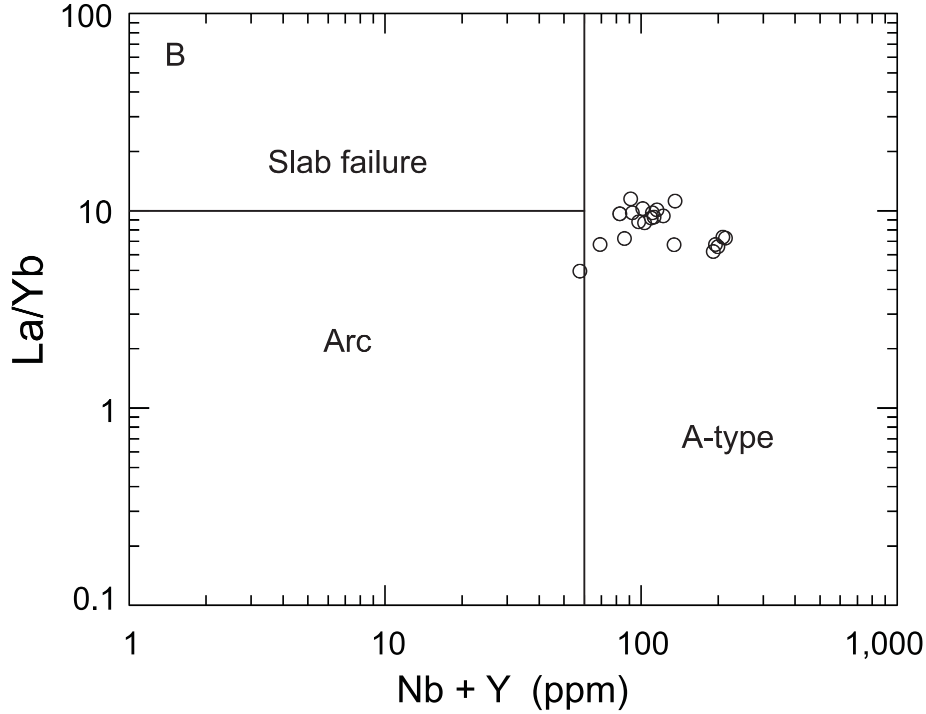


Figure 6A

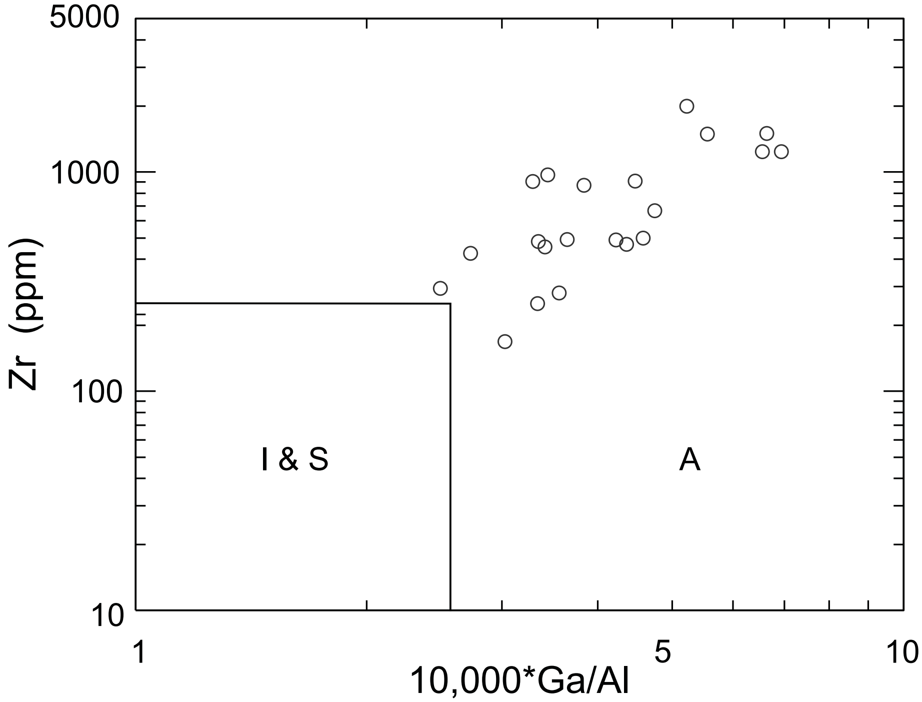


Figure 6B

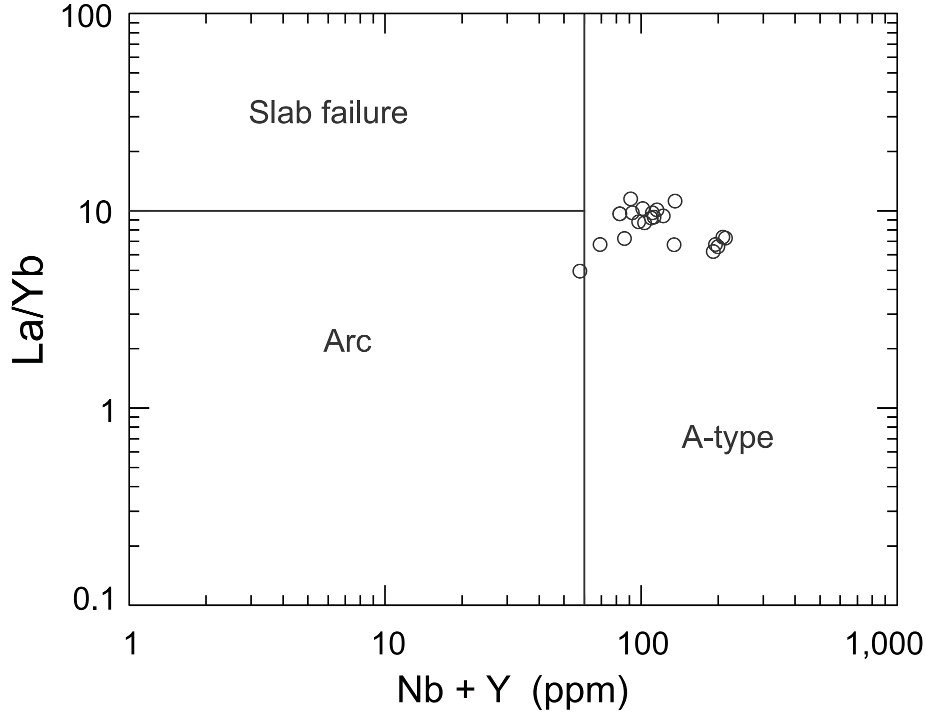
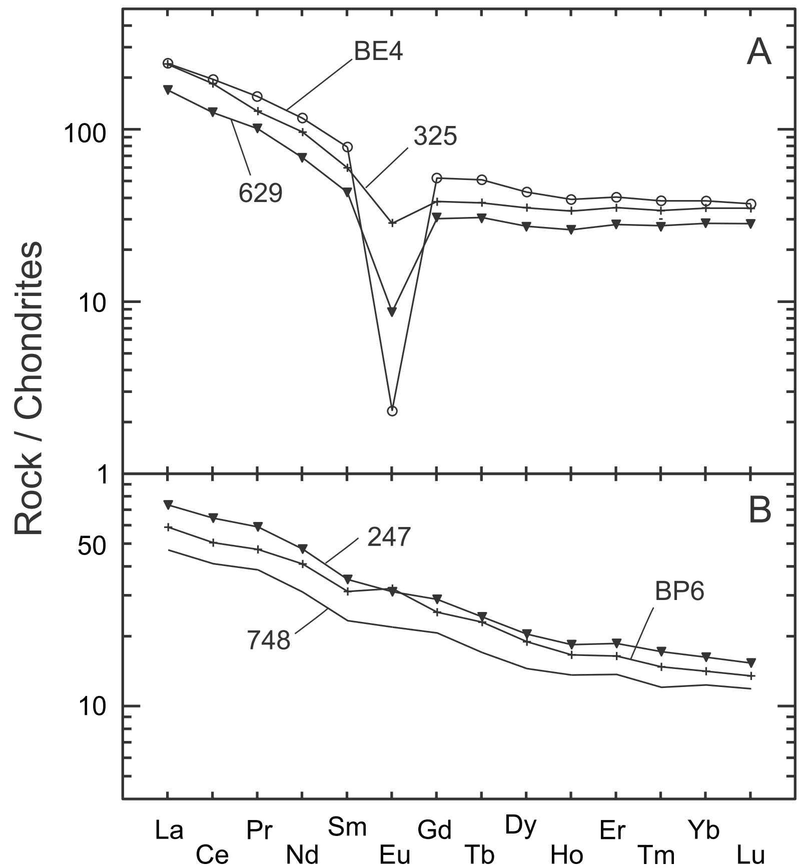
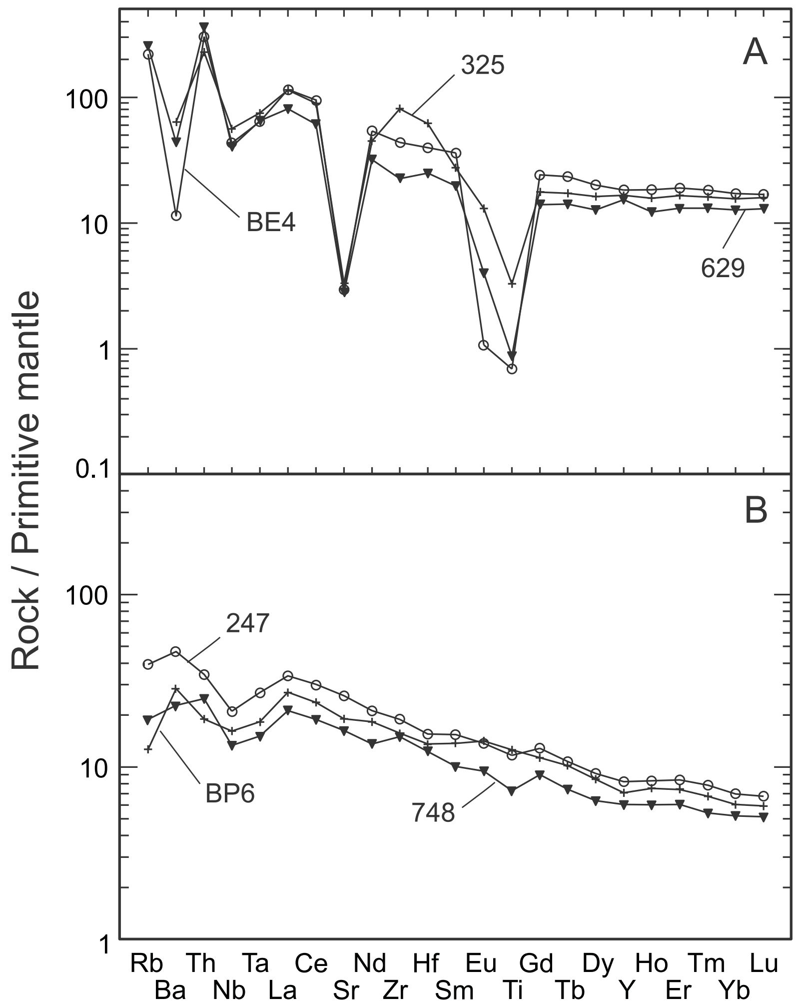


Figure 7



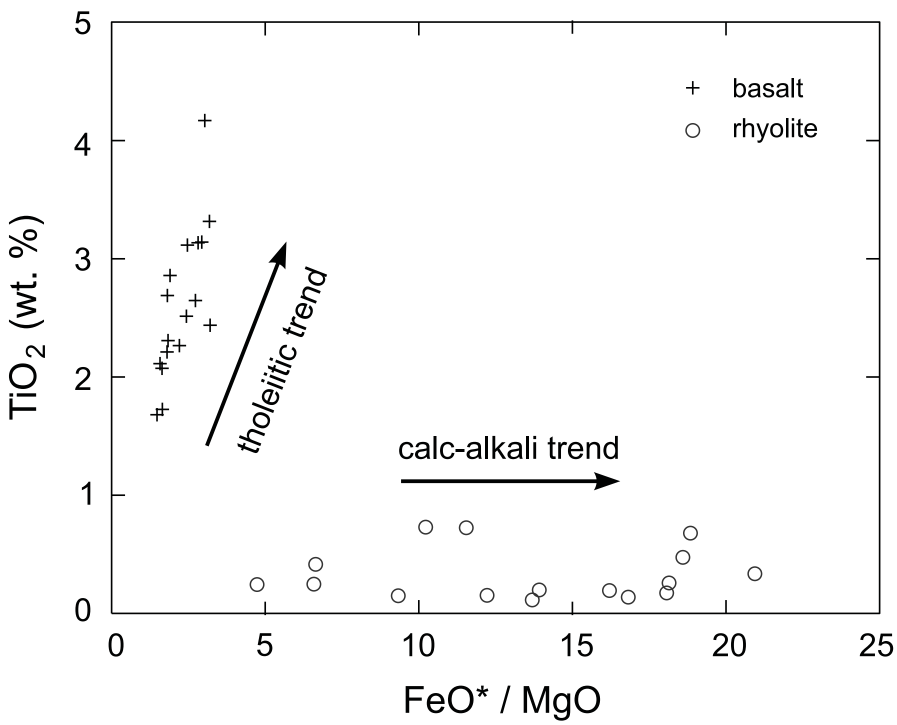
Rock / Chondrites
A
BE4
325
629
100
10
1
B
247
50
BP6
748
10
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Figure 8



A
325
BE4
629
B
247
BP6
748
Rock / Primitive mantle
100
10
1
0.1
Rb Th Ta Ce Nd Hf Eu Gd Dy Ho Tm Lu
Ba Nb La Sr Zr Sm Ti Tb Y Er Yb

Figure 9



5
4
3
2
1
0
0
5
10
15
20
25
TiO_2 (wt. %)
FeO* / MgO
basalt
rhyolite
tholeiitic trend
calc-alkali trend

Figure 10A

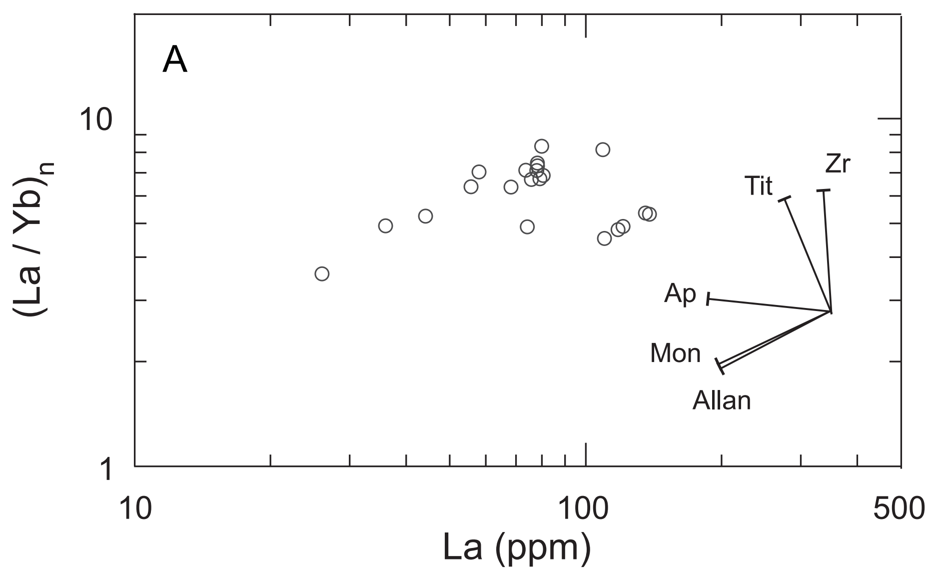
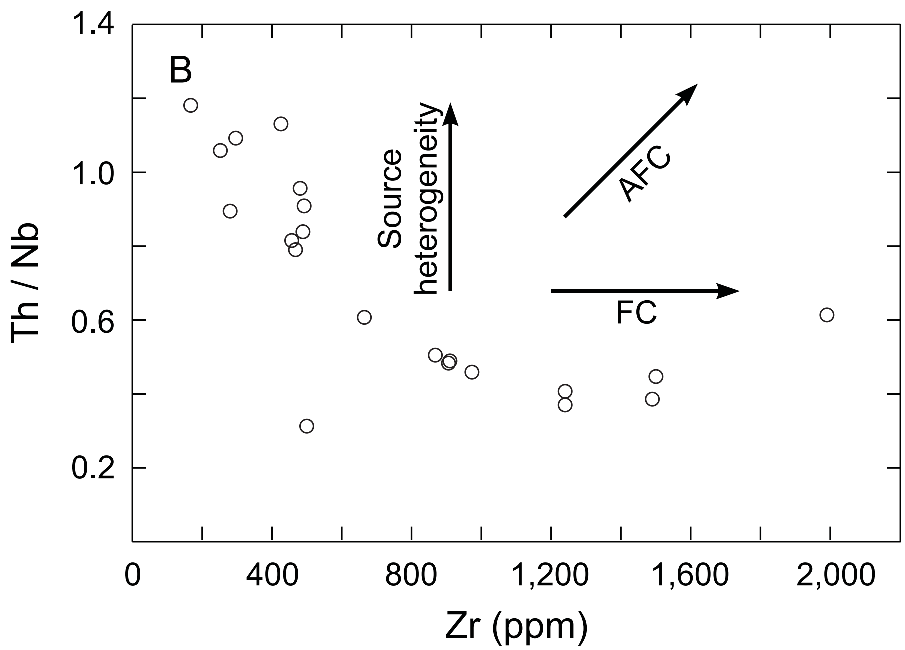


Figure 10B



B
Source heterogeneity
AFC
FC
Th / Nb
1.4
1.0
0.6
0.2
0
400
800
1,200
1,600
2,000
Zr (ppm)

Figure 11A

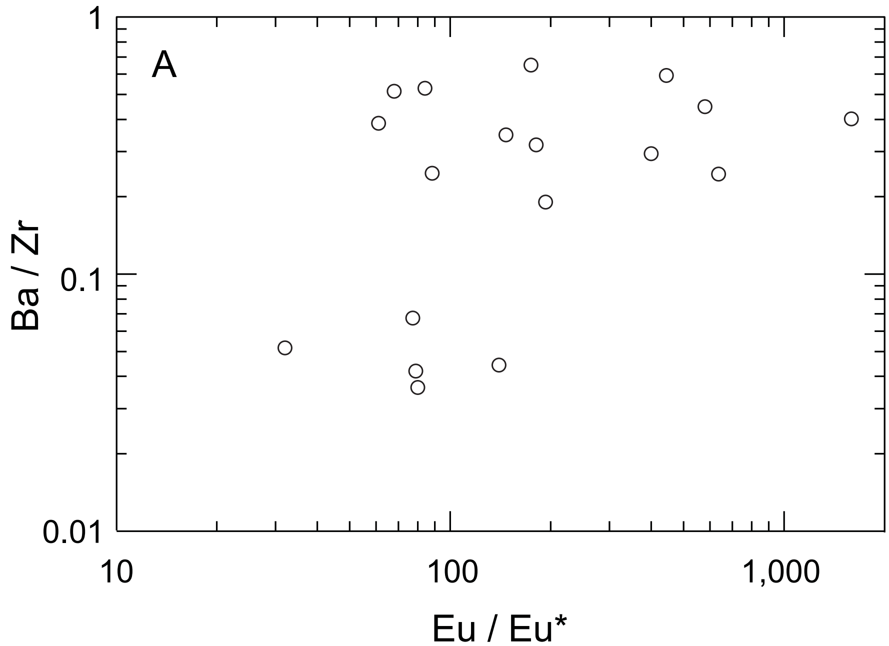
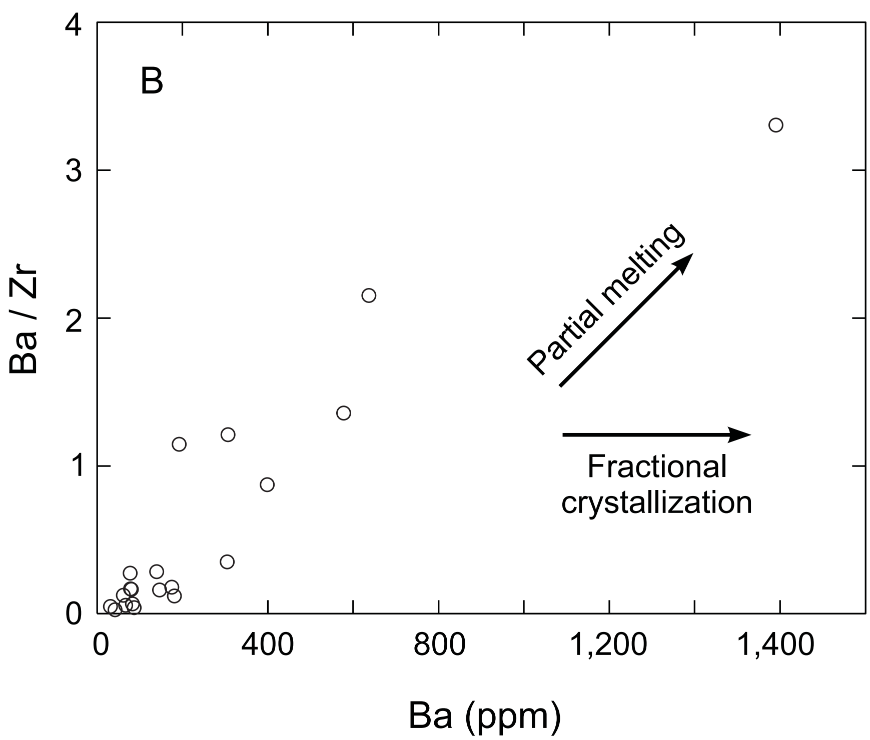


Figure 11B



B
Partial melting
Fractional crystallization
Ba / Zr
Ba (ppm)
0
1
2
3
4
0
400
800
1,200
1,400

Figure 12

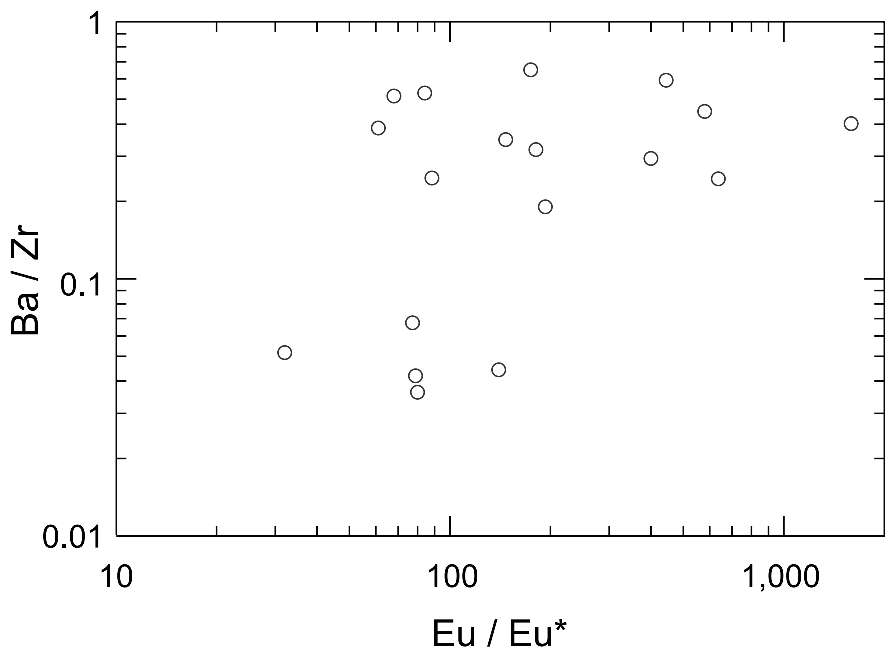


Figure 13

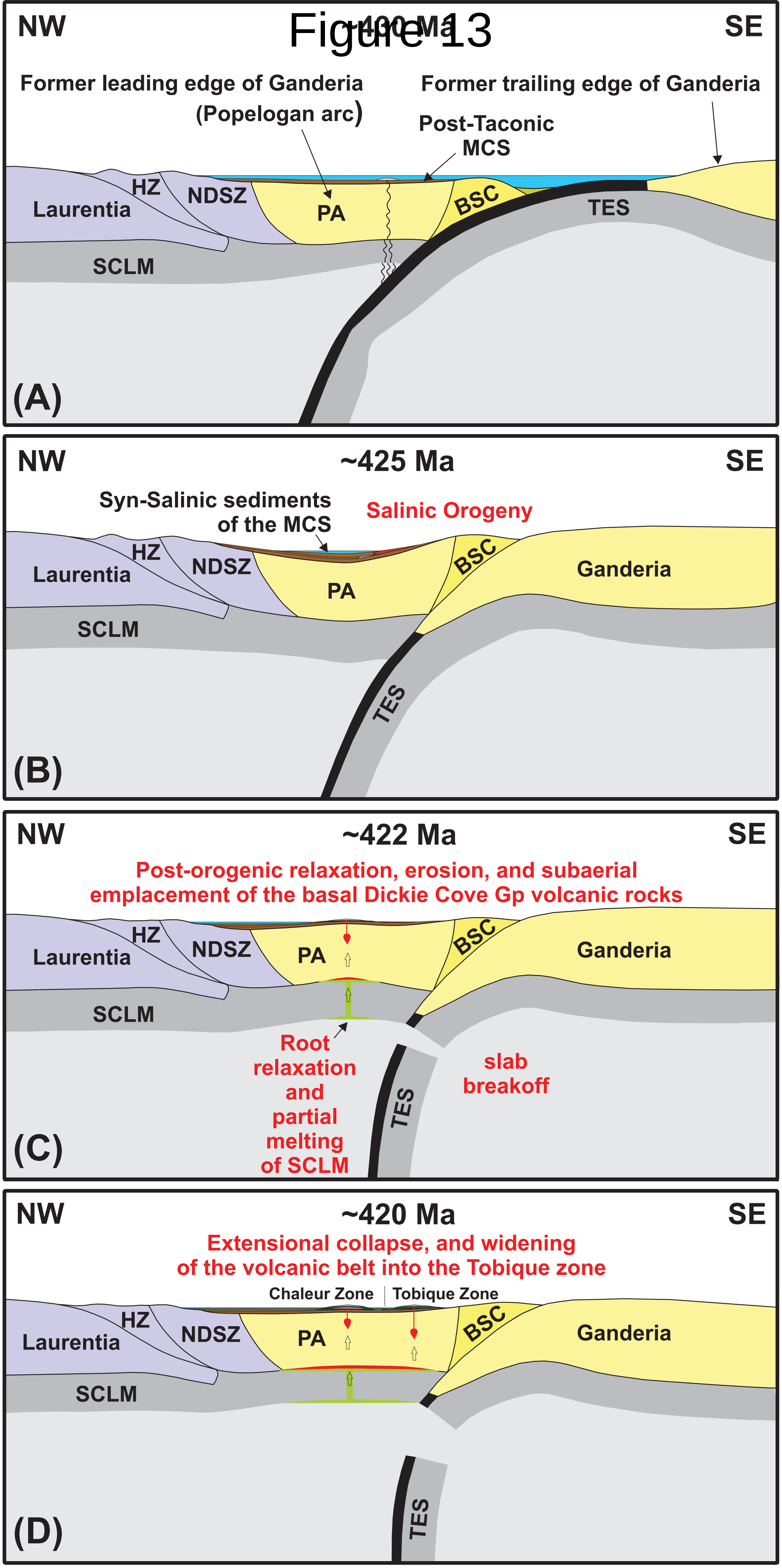


Fig. 13

Table 1. Nd isotopic compositon of volcanic rocks of the Dickie Cove Group

Sample	Age (Ma)	Nd(ppm)	Sm(ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd_{(m)}$	2σ	$^{143}Nd/^{144}Nd_{(i)}$	$\varepsilon_{Nd(t)}$	T_{DM} (Ma)
207	421	81.49	16.44	0.1219	0.512469	7	0.512133	0.73	958
402	421	36.57	8.09	0.1337	0.512556	7	0.512187	1.79	934
285	421	65.13	12.88	0.1196	0.512598	7	0.512268	3.37	733
629	421	45.21	9.36	0.1253	0.512524	6	0.512179	1.62	901
PB6*	421	23.87	5.82	0.1475	0.512769	6	0.512362	5.21	652
247*	421	28.01	6.48	0.1400	0.512653	7	0.512267	3.35	818
748*	421	18.35	4.25	0.1402	0.512694	6	0.512307	4.14	738

T_{DM}-depleted mantle model age calculated using the model of DePaolo (1988). $\varepsilon_{Nd(t)}$ - age-corrected values for the 421 Ma); crystallization age (t =143Nd/144Nd(m)- measured value; 143Nd/144Nd(i) - initial, calculated value;
*-after Dostal et al. (2016)

Table 2 Zircon and monazite saturation thermometry estimates of rhyolitic rocks of Dickie Cove Group

	177	629	BE3	BE4	BR5	207	266	285	325	402
M	1.28	1.28	1.32	1.4	1.36	1.26	1.59	1.25	0.06	1.33
$T_{Zr}{}^{o}C$			873	867	874		1006			869
$T_{Mz}{}^{o}C$	869	841	866	859	861	904	913	872	926	822

	482	204	278	C-1	C-3	C-6	C-7	19	23	17
M	1.28	1.17	1.39	1.87	1.86	1.74	1.57	1.27	1.54	1.57
$T_{Zr}{}^{o}C$			954	945	919	968	1047		975	845
$T_{Mz}{}^{o}C$	808	897	863	807	799	834	867	778	866	817

M = [Na+K+2Ca] / [Al*Si]; $T_{Zr}{}^{o}C$ = zircon saturation temparature calculated according to Boehnke et al. (2013);

TMzoC = monazite saturation temperature calculated according to Montel (1993).