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Title: Upper Paleozoic mafic and intermediate volcanic rocks associated with the Sn-W deposit of the Mount Pleasant caldera in southwestern New Brunswick (Canada): Petrogenesis and metallogenic implications

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Abstract: Upper Paleozoic (~365 Ma) mafic and intermediate volcanic rocks of the Piskahegan Group constitute a subordinate part of the Mount Pleasant caldera, which is associated with a significant polymetallic deposit (tungsten-molybdenum-bismuth zones ~ 33 Mt ore with 0.21% W, 0.1% Mo and 0.08% Bi and tin-indium zones ~ 4.8 Mt with 0.82% Sn and 129 g/t In) in southwestern New Brunswick (Canada). The epicontinental caldera complex formed during the opening of the late Paleozoic Maritimes Basin in the northern Appalachians. The mafic and intermediate rocks make up two compositionally distinct associations. The first association includes evolved rift-related continental tholeiitic basalts, and the second association comprises calc-alkaline andesites, although both associations were emplaced penecontemporaneously. The basalts have low Mg# ~ 0.34-0.40, smooth chondrite-normalized REE patterns with (La/Yb)n ~ 5-6, primitive mantle-normalized trace element patterns without noticeable negative Nb-Ta anomalies, and their εNd(T) ranges from +2.5 to +2.2. The basalts were generated by partial melting of a transition zone between spinel and garnet mantle peridotite at a depth of ~70-90 km. The calc-alkaline andesites of the second association have chondrite-normalized REE patterns that are more fractionated, with (La/Yb)n ~ 7-8.5, but without significant negative Eu anomalies. Compared to the basaltic rocks, they have lower εNd(T) values, ranging from +0.5 to +1.9, and their mantle-normalized trace element plots show negative Nb-Ta anomalies. The εNd(T) values display negative correlations with indicators of crustal contamination, such as Th/La, Th/Nb and SiO2. The andesitic rocks are interpreted to have formed by assimilation-fractional crystallization processes, which resulted in the contamination of a precursor basaltic magma with crustal material. The parent basaltic magma for both suites underwent a different evolution. The tholeiitic basalts experienced shallow-seated fractional crystallization and evolved along a tholeiitic trend of "early iron" enrichment (non-oxic conditions). The contaminated magma of the second association followed a calc-alkaline fractionation trend of "no iron" enrichment (oxidizing conditions) characterized by a high P(H2O) and P(O2) environment at the mid-crust levels. The Piskahegan Group, which is associated with an important polymetallic mineral deposit, differs from the numerous non-mineralized

rift-related volcanic suites of the regional Upper Devonian to Lower Carboniferous successions in the Maritimes Basin by the presence of a significant amount of coeval calc-alkaline andesite, which may be an indicator of potential mineralization.

Cover letter

Dear Editor:

Attached is a copy of our manuscript entitled “Upper Paleozoic mafic and intermediate volcanic rocks of the Mount Pleasant caldera associated with the Sn-W deposit in southwestern New Brunswick (Canada): Petrogenesis and metallogenic implications” by Dostal and Jutras for your consideration for publication in Lithos.

Major and trace elements, whole-rock Nd isotopes together with field work and petrography are used to characterize Upper Paleozoic basalts and andesites associated with the polymetallic deposit (Sn-W). The basalts are continental tholeiites while the andesites are calc-alkaline types, although both were emplaced penecontemporaneously. Compared to mantle-derived basalts, the calc-alkaline andesites are interpreted to have formed by assimilation-fractional crystallization processes, which resulted in the contamination of a precursor basaltic magma with crustal material. The volcanic package, which is related to an important polymetallic mineralization, differs from the numerous non-mineralized rift-related volcanic suites of the regional Upper Devonian to Lower Carboniferous successions by the presence of a significant amount of coeval calc-alkaline andesites. These rocks may be indicators of a fertile environment. The subcontinental lithospheric mantle of the Avalon and Gander terranes of the Northern Appalachians in Atlantic Canada had an isotopically similar composition during the Late Devonian and Early Carboniferous.

The research presented in this paper is new and not under consideration for publication anywhere else nor will be under consideration anywhere else unless the paper is rejected. If you have further questions regarding this manuscript, please do not hesitate to contact me.

Sincerely,

Jaroslav Dostal

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***Revision Notes**
Click here to download Revision Notes: Letter to Editor-revised.doc

Dear Dr. Eby:

We have revised the manuscript entitled "Upper Paleozoic mafic and intermediate volcanic rocks associated with Sn-W deposits of the Mount Pleasant caldera in southwestern New Brunswick (Canada): Petrogenesis and metallogenic implications (LITHOS5623)" according to the reviewers' comments. The reviewers' comments helped us to significantly improve the manuscript. In addition, we made some modifications in style and grammar. The marked original manuscript is attached.

I hope you will find the manuscript satisfactory.

Regards,

J. Dostal

email: jdostal@smu.ca

Revisions:

A.Comments of the reviewer #1:
We have modified the manuscript according to the comments of this reviewer marked on an annotated pdf. The changes were mainly of style and grammar so most of them are not enumerated below.
1.L. 60 references rearranged
2. L. 67 corrected
3. L. 89-90 references re-arranged
4. L. 98 corrected
5. L. 100 corrected
6. L. 302 corrected

B. Comments of the reviewer #2 (John Greenough)
Specific Comments:
1. L. 46 corrected
2. L. 46 added
3. p. 5 L. 121 corrected
4. p. 5 L. 126
5. p.9 L. 251 corrected; the same done on l. 221, 222, 251, 252, 269, 309.
6. p. 11 L. 300 corrected
7. p. 13, L. 355 modified
8. p. 13, L. 360 references added
9. p. 14, L. 378 reworded as suggested
10. p. 14-15 the problem clarified; we have added that the reason for a comparison is that the rocks are ~ 30 My younger.
11. Table 3. Info added

12. Caption to Figure 1B- references added
13. Noted in the text
14. Caption to Figure 14 – modified

C. Comments of the reviewer #3:

1. L. 22 the size of the deposit quantified
2. L. 29 “linear” replaced by “smooth” as suggested
3. L. 45 difficult to quantified in the abstract- done in the text
4. L. 46 corrected
5. L. 48 “fertile” replaced by “mineralization” as suggested
6. L. 100 text modified
7. L. 127 “volcanics” replaced by “volcanic rocks”
8. L. 129 the exact proportions of various rock-types are not known, however, we have added reference to Figure 2 from which they can be estimated
9. L. 139 dated moly samples by Thorne et al. described better
10. L. 145 all units have now acronyms
11. L. 179 the name of the analytical package added
12. L. 238 corrected
13. l. 251 “graph” replaced by “diagram”
14. L. 259 The sentence moved to discussion.
15. L. 278-280. We would like to keep this sentence here for sake of better understanding and following the text
16. L. 288 modified as suggested
17. L. 290 modified as suggested
18. L. 293-296 Moved to Discussion
19. L. 300 depleted model ages added to this section
20. L. 359-360 references added
21. L. 380+388. We added a section called “6.2. Contaminant and metallogenic province” to explain this.
22. L. 426 explanation is in the new section 6.2.
23. L. 438-442. Sentence modified
24. L. 442+462 explanation is in the new section 6.2.
25. Figure 2 and Caption to Figure 2 corrected and modified
26. Like in most papers in Lithos, we prefer to keep both chondrite- and primitive mantle normalized plots.
27. Caption to Figure 10 modified; gives an explanation for bars. Due to data overlaps, plotting of individual samples is not reader friendly
28. Table 1; average is defined in the footnote; raw data are given in Appendix 1
29. Table 2; note that the major element oxides are not recalculated given in the footnote; additional data are in Appendix 2.

***Abstract**

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Upper Paleozoic (~365 Ma) mafic and intermediate volcanic rocks of the Piskahegan Group constitute a subordinate part of the Mount Pleasant caldera, which is associated with a significant polymetallic deposit (tungsten-molybdenum-bismuth zones ~ 33 Mt ore with 0.21% W, 0.1% Mo and 0.08% Bi and tin-indium zones ~ 4.8 Mt with 0.82% Sn and 129 g/t In) in southwestern New Brunswick (Canada). The epicontinental caldera complex formed during the opening of the late Paleozoic Maritimes Basin in the northern Appalachians. The mafic and intermediate rocks make up two compositionally distinct associations. The first association includes evolved rift-related continental tholeiitic basalts, and the second association comprises calc-alkaline andesites, although both associations were emplaced penecontemporaneously. The basalts have low Mg# ~ 0.34-0.40, smooth chondrite-normalized REE patterns with $(La/Yb)_n$ ~ 5-6, primitive mantle-normalized trace element patterns without noticeable negative Nb-Ta anomalies, and their $\varepsilon_{Nd(T)}$ ranges from +2.5 to +2.2. The basalts were generated by partial melting of a transition zone between spinel and garnet mantle peridotite at a depth of ~70-90 km. The calc-alkaline andesites of the second association have chondrite-normalized REE patterns that are more fractionated, with $(La/Yb)_n$ ~ 7-8.5, but without significant negative Eu anomalies. Compared to the basaltic rocks, they have lower $\varepsilon_{Nd(T)}$ values, ranging from +0.5 to +1.9, and their mantle-normalized trace element plots show negative Nb-Ta anomalies. The $\varepsilon_{Nd(T)}$ values display negative correlations with indicators of crustal contamination, such as Th/La, Th/Nb and SiO_2. The andesitic rocks are interpreted to have formed by assimilation-fractional crystallization processes, which resulted in the contamination of a precursor basaltic magma with crustal material. The parent basaltic magma for both suites underwent a different evolution. The tholeiitic basalts experienced shallow-seated fractional crystallization and evolved along a tholeiitic trend of “early iron” enrichment (non-oxic conditions). The contaminated magma of the second association followed a calc-alkaline fractionation trend of “no iron” enrichment (oxidizing conditions) characterized by a high $P_{(H2O)}$ and $P_{(O2)}$ environment at the mid-crust levels. The Piskahegan Group, which is associated with an important polymetallic mineral deposit, differs from the numerous non-mineralized rift-related volcanic suites of the regional Upper Devonian to Lower Carboniferous successions in the Maritimes Basin by the presence of a significant amount of coeval calc-alkaline andesite, which may be an indicator of potential mineralization.

***Highlights (for review)**

- 365 Ma basalts and andesites are part of a bimodal suite of the Mount Pleasant caldera which hosts a polymetallic (Sn-W) deposit
- Rift-related continental tholeiites were formed by melting of a subcontinental lithospheric mantle at the spinel-garnet transition
- Calc-alkaline andesites were formed by crustal contamination of basaltic magma
- The suite differs from the non-mineralized rift-related volcanic sequences in the region by the presence of coeval calc-alkaline andesite

Upper Paleozoic mafic and intermediate volcanic rocks associated with the Sn-W deposit of the Mount Pleasant caldera in southwestern New Brunswick (Canada): Petrogenesis and metallogenic implications

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Abstract

Upper Paleozoic (~365 Ma) mafic and intermediate volcanic rocks of the Piskahegan Group constitute a subordinate part of the Mount Pleasant caldera, which is associated with a significant polymetallic deposit (tungsten-molybdenum-bismuth zones ~ 33 Mt ore with 0.21% W, 0.1% Mo and 0.08% Bi and tin-indium zones ~ 4.8 Mt with 0.82% Sn and 129 g/t In) in southwestern New Brunswick (Canada). The epicontinental caldera complex formed during the opening of the late Paleozoic Maritimes Basin in the northern Appalachians. The mafic and intermediate rocks make up two compositionally distinct associations. The first association includes evolved rift-related continental tholeiitic basalts, and the second association comprises calc-alkaline andesites, although both associations were emplaced penecontemporaneously. The basalts have low Mg# ~ 0.34-0.40, smooth chondrite-normalized REE patterns with $(La/Yb)_n$ ~ 5-6, primitive mantle-normalized trace element patterns without noticeable negative Nb-Ta anomalies, and their $\varepsilon_{Nd(T)}$ ranges from +2.5 to +2.2. The basalts were generated by partial melting of a transition zone between spinel and garnet mantle peridotite at a depth of ~70-90 km. The calc-alkaline andesites of the second association have chondrite-normalized REE patterns that are more fractionated, with $(La/Yb)_n$ ~ 7-8.5, but without significant negative Eu anomalies. Compared to the basaltic rocks, they have lower $\varepsilon_{Nd(T)}$ values, ranging from +0.5 to +1.9, and their mantle-normalized trace element plots show negative Nb-Ta anomalies. The $\varepsilon_{Nd(T)}$ values display negative correlations with indicators of crustal contamination, such as Th/La, Th/Nb and SiO_2. The andesitic rocks are interpreted to have formed by assimilation-fractional crystallization processes, which resulted in the contamination of a precursor basaltic magma with crustal material. The parent basaltic magma for both suites underwent a different evolution. The tholeiitic basalts experienced shallow-seated fractional crystallization and evolved along a tholeiitic trend of "early iron" enrichment (non-oxic conditions). The contaminated magma of the second association followed a calc-alkaline fractionation trend of "no iron" enrichment (oxidizing conditions) characterized by a high P_{H2O} and P_{O2} environment at the mid-crust levels. The Piskahegan Group, which is associated with an important polymetallic mineral deposit, differs from the numerous non-mineralized rift-related volcanic suites of the regional Upper Devonian to Lower Carboniferous successions in the Maritimes Basin by the presence of a

significant amount of coeval calc-alkaline andesite, which may be an indicator of potential mineralization.

1. Introduction

Felsic rocks of continental rift-related magmatic settings have been the focus of extensive investigation and numerous publications in part because they may host rare metal mineralization, which in some cases are of economic significance (e.g., Richardson and Birkett, 1996; Cerny et al. 2005; Linnen and Cuney, 2005). These rocks are commonly associated with a compositionally diverse variety of mafic and intermediate rocks (e.g., Nekvasil et al., 2000). Much is still unknown about the processes that lead to the diversity of magmas within such bimodal series and about the global diversity of intraplate magmatics. In mineralized bimodal complexes where felsic rocks are dominant, the subordinate mafic and intermediate rocks are commonly only poorly known, although they might provide important information on the tectonic environment of such bimodal associations, as well as on the origin of the felsic rocks and their mineralization, thus providing clues for the exploration for rare metal deposits. One such suite is the upper Paleozoic Piskahegan Group of southwestern New Brunswick (Canada). The latter group forms a volcanic caldera complex (e.g., McCutcheon, 1990; McCutcheon et al., 1997; Thorne et al., 2013) that is spatially and genetically associated with the Mount Pleasant polymetallic deposit (tungsten-molybdenum-bismuth zones containing ~ 33 Mt ore with 0.21% W, 0.1% Mo and 0.08% Bi and tin-indium zones ~ 4.8 Mt with 0.82% Sn and 129 g/t In). The deposit is recognized as the world's largest known undeveloped resource of indium (Sinclair et al., 2006; Thorne et al., 2013). To contribute to the debate on the origin of these bimodal suites, we have investigated mafic and intermediate volcanic rocks of the Mount Pleasant caldera (Figs. 1 and 2). Major and trace elements in these rocks, as well as neodymium isotopes, may provide information related not only to the origin of the bimodal suite and its mineralization, but also on the nature of the mantle source (e.g., DePaolo, 1988). Such data are also useful to evaluate the composition of the subcontinental lithospheric mantle (SCLM).

The purpose of this paper is: (1) to present geochemical data on the mafic and intermediate volcanic rocks of the Mount Pleasant caldera, including major and trace elements

and Nd isotopic ratios, (2) to constrain the origin of the rocks in the caldera, (3) to investigate the differences between mineralized and barren Devonian to Carboniferous bimodal volcanic suites in this part of the Northern Appalachians, (4) to evaluate the nature of the SCLM, and (5) to compare this information with data from time equivalent basaltic rocks of New Brunswick and Nova Scotia, which belong to the peri-Gondwanan Gander and Avalon terranes of the North American Appalachians. The comparison of SCLM properties in two neighboring exotic terranes could reveal whether or not both terranes were underlain by the same SCLM during the Paleozoic and thus contribute to the Ganderian controversy (i.e. whether or not the Gander and Avalon zones represent distinct terranes; e.g.,van Staal and Barr, 2012; Dostal et al., 2016a).

2. Geological setting

Volcanic rocks of the Piskahegan Group occur along the western margin of the Maritimes Basin in southwestern New Brunswick (Fig. 1). The Maritimes Basin is a major late Paleozoic successor basin (Gibling et al., 2008) that was initiated after the Early to Middle Devonian Acadian Orogeny (~400 Ma) in the Canadian Appalachians. This composite basin first developed as a series of pull-apart sub-basins along the Minas Fault Zone, a large east- trending dextral strike-slip system that juxtaposed the Meguma and Avalon terranes during the Late Devonian and the Carboniferous (Murphy et al., 2011a). Associated with these pull-apart structures are large bimodal plutons, as well as a series of NW-trending mafic dykes. Closely spaced U-Pb dates for peak Acadian metamorphism and for the emplacement and exhumation of post-Acadian plutons along the Minas Fault Zone suggest that the transition from orogenic compression to transtension along this fault system was very rapid (Dostal et al., 2006). Also associated with this transtensional magmatic event are widely distributed bimodal volcanic suites, one of which is the Piskahegan Group and its associated polymetallic deposit (Kooiman et al., 1986; McCutcheon et al., 1997; Thorne et al., 2013). The complex, referred to as the Mount Pleasant caldera, is a northeast-trending elliptical feature that is defined by geophysical data (regional gravimetric and magnetic studies) as about 13 km wide and 34 km long (McLeod and Smith, 2010). However, the northern part of the complex is overlain by middle Mississippian (Visean) and Pennsylvanian strata of the Maritimes Basin in such a way that the exposed length is restrained to about 17 km. This epicontinental caldera, which was emplaced in a transtensional

setting (Fyffe et al., 2011), is associated with high-level subvolcanic granitic intrusions and has been interpreted to have formed by roof collapse in an epizonal magma chamber. The Piskahegan Group (Figs. 1 and 2) disconformably overlies deformed Ordovician to Silurian turbiditic metasedimentary rocks of the Gander Terrane. These rocks bound the caldera to the east and west. The caldera is in turn paraconformably overlain by Visean clastic rocks formerly mapped as the Shin Redbeds by van de Poll (1967) and recently assigned the Shin Member of the Hopewell Cape Formation (Jutras et al., 2015), which confine the caldera to the north (Fig. 1). Late Silurian to Devonian granitic rocks of the Saint George Batholith represent the southern boundary of the complex (McLeod, 1990). Both the batholith and the caldera complex lie within the boundaries of the Gander Terrane.

The Piskahegan Group (Fig. 2) has been subdivided into three volcanic facies (in the sense of Fisher and Schmincke, 1984) in order to reflect their depositional setting in relation to the volcanic architecture: (1) exocaldera, (2) intracaldera and (3) late caldera-fill sequences (McCutcheon, 1990; McCutcheon et al., 1997; Thorne et al., 2013). The caldera is composed mainly of felsic volcanic and volcaniclastic rocks and associated sedimentary rocks, which are intruded by subvolcanic granitic bodies (McCutcheon et al., 1997). All three volcanic facies contain subordinate amounts of mafic and intermediate volcanic rocks (Fig. 2).

The Piskahegan Group was emplaced during the initial stages of basin development. Paleontological records and radiometric dating show that most of the caldera is Fammenian (Upper Devonian) in age and coincides with the emplacement of voluminous granitic intrusions. Anderson (1992) obtained a whole-rock Rb-Sr isochron age of 368 ±5 Ma for the Piskahegan Group. The Carrow Formation (CF) of the exocaldera sequence yielded a U-Pb zircon age of 363.8 ± 2.2 Ma (Tucker et al., 1998), whereas a spore assemblage recovered from drill core above the zircon sample yielded a late Famennian age (McGregor and McCutcheon, 1988). More recently, Thorne et al. (2013) reported Re-Os ages of 369.7 ± 1.6 Ma and 370.1 ± 1.7 Ma from molybdenite samples associated with W-Mo-Bi mineralization. There are also several $^{40}Ar/^{39}Ar$ ages of ca. 360 Ma on the granitic rocks (Sinclair et al., 1988), and the youngest phase of the neighbouring Saint George Batholith, which is probably related to them, gave a U-Pb zircon age of 367±1 Ma (Bevier 1988). Hence, all available data in the Piskahegan Group and associated plutonic rocks range within the Fammenian (*sensu* Richards, 2013).

The exocaldera sequence includes three units that also contain mafic or intermediate volcanic rocks. In ascending stratigraphic order, they are the Hoyt Station Basalt (HSB), the South Oromocto Andesite (SOA) and the Carrow Formation (CF). HSB is the basal unit of the exocaldera sequence (McCutcheon et al., 1997) and it consists mainly of a basalt flow unit that is about 20 m thick. The basalt is underlain by rhyolitic volcaniclastic rocks. The SOA unit is an up to 130 m thick succession of lava flows that is conformably overlain by the CF. The latter is composed mainly of clastic sediments, but also contains an aphyric basalt flow (< 20 m thick) near the top of the formation.

At the base, the intracaldera sequence includes the Scoullar Mountain Formation (SMF), which lies along the periphery of the caldera complex at the contact with pre-caldera rocks. This unit, the thickness of which ranges between 225 and 450 m, is composed predominantly of clastic sedimentary rocks and interbedded andesitic lava flows and felsic volcaniclastic rocks. The upper part of the late caldera-fill sequence contains the Kleef Formation (KF), which consists of conglomeratic redbeds (40-75 m thick), basalts (70-80 m), and volcaniclastic rocks (> 4 m).

The polymetallic deposit is located near the southwestern margin of the caldera complex (McCutcheon et al., 1997). It consists of mineralized stockworks and quartz veinlets, breccia infill and lode mineralization. Its formation is associated with the emplacement of the subvolcanic granitic rocks that host it. Thorne et al. (2013) inferred that the mineralization was associated with caldera collapse, which was marked by the emplacement of a series of subvolcanic granitic intrusions (Fig. 2).

3. Analytical methods

Mineral compositions (Table 1; Appendix 1) were determined using a JEOL Superprobe 733 equipped with four wave-length-dispersive spectrometers and one energy-dispersive spectrometer, and operated with a beam current of 15 kV at 5 nA at the Department of Earth Sciences of Dalhousie University, Halifax, Nova Scotia (Canada).

Major and several trace element analyses of whole rocks (Table 2; Appendix 2) were performed on fused glass disks using a Philips PW2400 X-ray fluorescence spectrometer at the University of Ottawa, Ontario (Canada). Duplicate analyses of the samples yielded total errors of

± 3% (1σ). Trace element analysis was done using lithium metaborate-tetraborate fusion and a Perkin Elmer Optima 3000 ICP mass spectrometer at Activation Laboratories, Ancaster, Ontario (Canada). Replicate analyses of the reference standard rocks indicate that the errors were between 2 and 8 % of the values cited. The detection limits and other information on the trace element analyses (analytical package 4B2) are available at the Activation Laboratories web site (www.actlabs.com).

Nd isotope ratios (Table 3) were determined by isotope dilution mass spectrometry at the Department of Earth Sciences of the Memorial University of Newfoundland (St. John's, Newfoundland, Canada). Concentration data are standard ICP-MS analyses and are precise to ±5% (2σ). Ratios of $^{147}Sm/^{144}Nd$ (except samples 38A and 69) were measured directly by high-precision ICP-MS with an estimated precision of ± 0.5 % (2σ). The isotopic ratios of $^{143}Nd/^{144}Nd$ were determined using a multicollector Finnigan MAT 262V thermal ionization mass spectrometer operated in a static mode. Measured $^{143}Nd/^{144}Nd$ values were normalized to a $^{146}Nd/^{144}Nd$ ratio of 0.7219. Replicate analyses of the LaJolla standard, which was analyzed repeatedly throughout, gave an average value for $^{143}Nd/^{144}Nd=0.511849 \pm 9$. The 2σ values for all samples are less than or equal to 0.000008 for $^{143}Nd/^{144}Nd$ and are given in Table 3. Values for $\varepsilon_{Nd\,(T)}$ were calculated with respect to CHUR using present-day $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios of respectively 0.512638 and 0.196593, and subsequently age-corrected. A T_{DM1} model age was calculated using a linear evolution for a mantle that separated from CHUR at 4.55 Ga, and that has a present day ε value of +10. The T_{DM2} model age was calculated according to the model of DePaolo (1988).

4. Petrography and mineral chemistry

Basalts and andesites of the Piskahegan Group vary from massive to amygdaloidal. Amygdales occur particularly in the upper part of the flows and are commonly filled by carbonates or silica. Although rocks of the caldera are not significantly deformed and contain unstrained quartz with primary glass inclusions (Gray et al., 2011), the amygdaloidal rocks are altered. Igneous textures are mostly preserved, but the primary magmatic minerals are frequently replaced by secondary phases. The rocks exhibit greenschist grade metamorphism that produced chlorite, epidote and actinolite. Textures range from aphyric to coarse subophitic and ophitic, as

well as porphyritic and glomeroporphyritic. The basalts are composed predominantly of plagioclase and clinopyroxene, which are variably altered and occur both as phenocrysts and as the main components of the groundmass. The rocks also contain minor Fe-Ti oxides and accessory apatite. No orthopyroxene was observed. When fresh, the plagioclase phenocrysts show zoning with labradorite-bytownite cores and andesine rims. However, plagioclase is mostly albitized or altered to sericite and calcite. Some plagioclase phenocrysts contain zones of sieve texture. The intermediate rocks contain relics of dark brownish-green amphibole replaced mainly by chlorite and epidote. In these rocks, subhedral amphibole crystallized together with plagioclase, Fe-Ti oxide, and apatite after the crystallization of clinopyroxene (Anderson, 1992). Amphibole may contain a core of clinopyroxene. The clinopyroxene phenocrysts show zoning, but are partially replaced by chlorite and epidote. Clinopyroxenes typically form subhedral phenocrysts and microphenocrysts or occur in a subophitic to ophitic groundmass of the mafic rocks. Relics of fresh clinopyroxene in the mafic and intermediate rocks are typically augite (Anderson, 1992; Table 1; Appendix 1). On tectonic discrimination diagrams for pyroxene (Leterrier et al., 1982), clinopyroxenes of the basalts plot in the "non-orogenic" field (Anderson, 1992; McCutcheon et al., 1997). Clinopyroxenes from the intermediate rocks (Table 1) also plot in the "non-orogenic" field (Fig. 3) of Leterrier et al. (1982). The rarity of phenocrysts in some samples of evolved rocks may be caused by the separation of early fractionated phases from the melt on the way to the surface.

5. Whole-rock geochemistry

5.1. Alteration

Alteration and metamorphic processes have affected the rocks. Petrographic evidence includes the saussuritization, sericitization, and albitization of feldspar, the chloritization of clinopyroxene as well as the accumulation of silica and calcite in amygdales. Although the original abundances of mobile elements such as Ca, Na and K might have been modified, the concentrations and ratios of high-field strength elements (HFSE) and rare earth elements (REE) show well-defined trends indicating that these elements were immobile during alteration. This is also supported by many other studies (e.g., Winchester and Floyd, 1977) indicating that HFSE and REE retain their distribution during alteration. Furthermore, an investigation of melt

inclusions in quartz of associated rhyolitic rocks (Gray et al., 2011) showed that post-magmatic processes did not modify the whole-rock composition. Similarly, it is typically inferred that the Sm and Nd isotope characteristics of a rock are resistant to geological disturbances (e.g., DePaolo, 1988).

5.2. Major and trace elements

All the major oxide compositions were recalculated to 100% on a volatile free basis for plotting on geochemical diagrams. According to their major element compositions (Fig. 4), the mafic and intermediate volcanic rocks of the Piskahegan Group can be subdivided into two associations: Association 1 includes basalts of the KF and CF formations, which are characterized by low SiO_2 (48-52 wt.%), and high TiO_2 (> 2.5 wt.%) and $FeO_{(t)}$ (~ 13-15 wt.%), whereas Association 2 comprises intermediate rocks of the SOA and SMF, with SiO_2 > 54 wt.%, TiO_2 < 2 wt.%, and $FeO_{(t)}$ < 9 wt.% . The division is also shown in the Zr/TiO_2 versus Nb/Y diagram (Fig. 5), in which Association 1 rocks plot in the basaltic field, whereas rocks of Association 2 plot mainly in the andesitic field.

According to the conventional AFM [(K_2O+Na_2O)-$FeO_{(t)}$-MgO] diagram (Fig. 6), Association 1 rocks are tholeiites. They have characteristics of differentiated tholeiitic basalts with low MgO, Ni and Cr, as well as high Fe, Ti and P. Their chondrite-normalized REE patterns show a negative slope, resulting from an enrichment of light REE (LREE) with $(La/Yb)_n$ ~5-6, but without Eu anomalies (Fig.7). The primitive mantle-normalized incompatible element plots of Association 1 rocks do not display noticeably negative Nb-Ta anomalies (Fig. 8). The patterns show distinct negative anomalies for Ti and Sr, which together with low Ni and Cr indicate that the rocks underwent fractional crystallization dominated by plagioclase and clinopyroxene. Both patterns (Figs. 7 and 8) resemble those of rift-related continental tholeiites or transitional basalts (e.g., Dostal and Dupuy, 1984; Pegram, 1990; Dostal et al., 1992; Peate and Hawkesworth, 1996). In comparison with arc mafic rocks, the basalts have high Ti/V (70-100) and Zr/Y (6-8), and their primitive mantle-normalized trace element patterns do not exhibit pronounced negative Nb-Ta anomalies (Fig. 8). In addition, on geochemical discrimination diagrams, they plot in the field of rift-related basalts (Fig. 9).

Compared to those of Association 1, rocks of Association 2 have calc-alkaline characteristics (e.g., Fig. 6), although they were emplaced penecontemporaneously and in the same tectonic and geographic settings. With increasing SiO_2, the andesites show a decrease in Fe, Ti, Mg# ($MgO/[MgO+FeO_{(t)}]$) and Ni, but also an increase in alkalis and in the Al_2O_3/CaO and La/Yb ratios (Fig. 4), indicating the crystallization of clinopyroxene, plagioclase and Fe-Ti oxide. The fractionation of Fe-Ti oxides, which is implied by a decrease of $FeO_{(t)}$, TiO_2, and V with increasing SiO_2 in the calc-alkaline suite, suggests high P_{H2O} and P_{O2} conditions. The difference between tholeiitic and calc-alkaline suites can be partially due to the depth of fractional crystallization (e.g., Grove and Kinzler, 1986). Crystallization of the calc-alkaline magmas at mid-crustal depth may have differed from that of tholeiitic magma, which could have taken place at lower P_{tot} and lower P_{O2} conditions (i.e., within a shallow upper crustal magma chamber).

There are subtle differences between the SOA and SMF rocks. The SOA have SiO_2 ~55-58 wt.%, $TiO_2 < 2$ wt.% and $FeO_{(t)} \sim 8$ wt.%. The SMF rocks are more fractionated, although there is some overlap in composition. They have typically higher SiO_2 (59-66 wt.%), lower $TiO_2 < 1.5$ wt.% and lower $FeO_{(t)} < 8$ wt.% (Table 2).

In addition to the differences in major element compositions between associations 1 and 2, the andesites have more fractionated REE patterns, with $(La/Yb)_n \sim 7\text{-}8.5$, but also without significant Eu anomalies. Their light REE (LREE) abundances are similar to those of the first association, but they have lower heavy REE (HREE) contents. The primitive mantle-normalized incompatible element plots of Association 2 show distinct negative Nb-Ta anomalies, which are indicative of either subduction or crustal assimilation.

5.3. Nd isotopic ratios

The Sm-Nd isotopic signatures of the basaltic and andesitic rocks are given in Table 3, in which they are all age-corrected to 365 Ma. The $\varepsilon_{Nd(T)}$ values of the basalts range from +2.5 to +2.2, and $^{147}Sm/^{144}Nd$ ratios vary from 0.13 to 0.14 (Table 3). The values are in good agreement with the data of Anderson (1992) for mafic rocks of the caldera. The data plot within the range reported for the Devonian to Carboniferous basaltic rocks of the Maritimes Basin in New Brunswick and Nova Scotia (Fig. 10). They are also similar to those from rift-related basalts, continental flood basalts and xenoliths from the subcontinental lithosphere (Faure and Mensing,

2005). These $\varepsilon_{Nd(T)}$ values are considerably lower than values expected for juvenile magmas from a depleted mantle source (Fig. 10), although the positive $\varepsilon_{Nd(T)}$ values preclude a significant contribution from substantially older continental crust or sedimentary rocks derived from it. The Piskahegan basaltic rocks plot in the field of Avalonian and peri-Rodinian lithosphere (Fig. 10), and their $\varepsilon_{Nd(T)}$ values are consistent with derivation from a SCLM.

Neodymium depleted-mantle model ages of DePaolo (1988) for these rocks range between 800 and 900 Ma (Table 3) and are similar to those determined for the Devonian to Carboniferous basaltic rocks above the Avalon and Gander terranes in the Maritimes Basin (Keppie et al., 1997; Pe-Piper and Piper, 1998). These similarities suggest that the model ages represent a bulk weighted average of the source composition.

The andesites have lower $\varepsilon_{Nd(T)}$ than the basalts (Table 3), but they still plot in the field of Avalonian and Ganderian lithosphere (Fig. 10). The negative Nb-Ta anomalies and the lower $\varepsilon_{Nd(T)}$ values (+0.5 to +1.9) of these rocks are consistent with an inferred involvement of continental lithosphere in their evolution, most probably through crustal contamination.

6. Discussion

6. 1. Petrogenesis

Although all volcanic rocks of the Piskahegan Group are spatially and temporarily associated, the Association 1 basalts are not related to the Association 2 andesites through simple crystal-liquid equilibria processes. The absence of smooth variation trends when various elements and element ratios are plotted against a differentiation index, such as SiO_2 (Fig. 4), suggests that the Association 2 andesites did not simply result from the fractional crystallization of Association 1 basalts.

The Association 1 rocks are evolved tholeiites that were emplaced in an epicontinental rift-related setting. Compared to primitive basalts that have Mg# values of ~ 0.70 (Hanson and Langmuir, 1978), the Piskahegan basalts (Table 2) have significantly lower values (0.34-0.40), suggesting that they have undergone high degrees of fractional crystallization. The fractional crystallization was dominated by crystallization of clinopyroxene and plagioclase. On the Th/Yb versus Nb/Yb diagram (Fig. 11), which has been used for the evaluation of lithospheric inputs in basalts (Pearce, 2008), the averages of N-type MORB, E-type MORB and OIB form a diagonal

mantle array (Fig. 11). Magmas that were modified by an interaction with continental crust or that involved material with a subduction history are displaced to higher Th/Yb values. The basaltic rocks of the Piskahegan Group straddle the boundary of the mantle array, implying that crustal contamination and subduction imprints were insignificant. This is also consistent with the lack of a discernible negative Nb-Ta anomaly on the spider plots (Fig. 8). Thus, the composition of the basalts mostly reflects the original characteristics of the mantle source and, together with positive $\varepsilon_{Nd(T)}$ values, indicate that they were derived from a relatively uncontaminated and moderately enriched mantle, similar to an ocean island basalt (OIB)-type source (Faure and Mensing, 2005).

On the Tb/Yb versus La/Sm graph (Fig.12), the basaltic samples straddle the spinel peridotite-garnet peridotite boundary, suggesting that they were formed in a spinel-garnet transition zone, at a depth of ~70-90 km (Wang et al., 2002). Whereas Tb/Yb ratios are related to the pressure conditions and depth at which melting occurred, La/Sm ratios correlate with the degree of partial melting and tend to decrease with an increase of mantle peridotite melting. Ratios for the CF and KF basalts are overlapping, which indicates that they were generated at the same depth by similar degrees of partial melting from a similar mantle source.

The andesites of the Piskahegan Group underwent fractional crystallization dominated by plagioclase, clinopyroxene and Fe-Ti oxide, as indicated by the variation trends of several elements and element ratios when plotted against SiO_2 (Fig. 4). The compositional characteristics of the Association 2 rocks, including negative Nb-Ta anomalies and their position on the Th/Yb versus Nb/Yb diagram (Fig. 11), suggest that the rocks record an additional process to fractional crystallization. The SOA and SMF andesites are displaced toward higher Th/Yb ratios relative to the mantle array, implying crustal contamination or inputs from a subcontinental mantle that had previously been affected by subduction fluids.

Correlation of element and isotopic ratios suggests that the andesites were significantly changed by crustal contamination as discussed below. Trace element ratios, which are not modified by the fractional crystallization of major rock forming minerals and which have significantly different values for oceanic basalts (OIB, MORB) and continental crust (e.g., Th/La, Th/Nb, Th/Ta, Nb/U), are typically used as indicators for crustal contamination (e.g., Jochum et al., 1991; D'Antonio et al., 2007). The SOA andesites have higher Th/La (~0.15-

0.16), Th/Nb (0.3-0.45) and Th/Ta (5-7) ratios than the basalts (Th/La~0.08-0.1, Th/Nb ~0.11-0.19, and Th/Ta~1-3), indicating crustal input. The same applies for the SMF andesites, which have even higher Th/La (~0.20-0.25), Th/Nb (>0.5) and Th/Ta (8-11) ratios. These ratios, which are sensitive indicators of crustal contamination, correlate with SiO_2 (Fig. 4) and are consistent with an origin of the intermediate rocks by the crustal contamination of basalts accompanied by fractional crystallization. Such a process is also supported by mixing trends on the Nb/Th versus Th/Yb diagram (Fig. 13), in which the andesitic rocks plot along the mixing line between typical mantle-derived tholeiites and crustal material. A similar trend is also shown on Figure 9. Due to the absence of geochemical analyses from the underlying basement/continental crust, we have used the average continental crust composition of Taylor and McLennan (1985) as a reference contaminant for these graphs. Likewise, the plots involving Nd isotopes and contamination-sensitive trace element ratios or SiO_2 suggest a mixing between the basaltic melts derived from the SCLM and crustal material. The rocks show a general trend of lower $\varepsilon_{Nd(T)}$ with higher Th on the $\varepsilon_{Nd(T)}$ versus Th/La graph (Fig. 14), confirming the involvement of continental crust in the rocks with lower $\varepsilon_{Nd(T)}$.

The highly fractionated nature of the basalts as well as the observed gap between basalts and intermediate rocks indicate that the original magmas of each association had to undergo a separate evolution, although they may have had comparable parent magma. The Association 1 basalts underwent fractional crystallization during their rise to the surface, whereas the Association 2 andesites were modified by crustal contamination through assimilation-fractional crystallization (AFC) processes, probably at mid-crust levels. As the andesitic rocks contain hornblende indicative of mid-crust crystallization and show a calc-alkaline fractionation trend that is typical of high $P_{(tot)}$ and P_{H2O} conditions, the contamination had to take place at a deeper crustal level (e.g., Osborn, 1959; Zimmer et al., 2010). In addition to amphibole, the calc-alkaline rocks also contain clinopyroxene phenocrysts, which, like those of the basalts, are typical of within plate, "non-orogenic" rocks (Fig. 3). The wet and/or oxidizing environment is also consistent with the lack of distinct negative Eu anomalies in most of the andesitic rocks (Fig. 7) which could be because the magmatic water content was high (Moore and Carmichael, 1998) and/or because the magmatic oxidation state was high, in which case most of the Eu would

have been present as Eu^{3+} and would not have been incorporated into the crystallizing plagioclase (e.g., Sisson and Grove, 1993).

Crustal contamination led to a change from a non-oxic environment, typical of tholeiitic rocks, to the oxidizing environment that is typical of calc-alkaline rocks (e.g., Osborn, 1959; Zimmer et al., 2010). In the case of the tholeiitic basalts, the original magma fractionated along a tholeiitic trend of "early iron" enrichment (non-oxic conditions). The magma which mixed with continental crust material followed a calc-alkaline fractionation trend of "no iron" enrichment (oxidizing conditions).

6.2. Crustal contamination in a metallogenic province

In the near vicinity of the Mount Pleasant caldera, there are several small Late Devonian plutons composed of Li-F-rich granites (e.g., Taylor, 1992; Whalen et al., 1996). These plutons as well as the Mount Pleasant complex are a part of a large tin belt described by Schuiling (1967) and Strong (1980), among others, which extends from North America to Europe. This belt, characterised by the occurrences of the mineralized Devono-Carboniferous Li-F- rich peraluminous leucogranites with broadly contemporaneous S-W-(U) mineralization, can be followed along the late Paleozoic fold belts of the Canadian Appalachians and the Hercynian Orogen of western and central Europe, from New Brunswick (Mount Pleasant complex) and Nova Scotia (South Mountain Batholith at East Kemptville), to Newfoundland (Ackley Pluton), and across the Atlantic Ocean to southwestern England (Cornwall), France (Armorican Massif and Massif Central), Germany (Altenberg, Erzgebirge) and the Czech Republic (Zinnwald, Erzgebirge). The belt has a long mining history of Sn, W and U dating back to the Romans. Numerous studies (e.g., Dostal and Chatterjee, 1995; Haapala, 1997; Cuney et al., 2002; Dostal et al., 2004; Cerny et al., 2005) inferred that the magmatic and hydrothermal mineralizing events were essentially synchronous and that the uncommon chemical characteristics of the Li-F-rich leucogranites require an uncommon source material. It has been inferred that the parental magmas of the leucogranites, including those around the Mount Pleasant caldera, were derived from similar source reservoirs (Romer and Kroner, 2014), probably phlogopite/biotite-rich mid-crustal metasedimentary rocks (e.g., Dostal et al., 2004). Similar fluid-rich rocks could have acted as a crustal contaminant.

6. 3. Comparable rock suites and possible mantle sources

Comparable Upper Devonian to Lower Carboniferous bimodal volcanic suites occur within the Maritimes Basin in Nova Scotia (western Cape Breton Island, Antigonish Highlands and Cobequid Highlands) and southern New Brunswick (e.g., Dostal et al., 1983; Keppie and Dostal, 1980; Keppie et al., 1997; Pe-Piper and Piper, 1998). The basaltic rocks are rift-related, mainly fractionated continental tholeiites. In these basaltic rocks, $\varepsilon_{Nd(T)}$ values are variable, ranging from +2.2 to +5.2 (Keppie et al., 1997; Pe-Piper and Piper, 1998). The basalts are considered to be derived from the SCLM (Pe-Piper and Piper, 1998).

To evaluate lithospheric mantle sources in the area, as well as the changes that they underwent during the Carboniferous, we have also determined the Nd isotopic ratios of the Carboniferous trachytes (~335 Ma old) from the Cumberland Hill Formation (Gander Terrane) of southern New Brunswick as these rocks are younger by about 30 M.y. than the bulk of the Devono-Carboniferous magmatism. These rocks were interpreted to be derived from an alkali basaltic magma by extensive fractional crystallization without being affected by crustal contamination (Gray et al., 2010). Such an origin is also in an agreement with their primitive mantle-normalized plots, in which the rocks do not show any negative Nb-Ta anomalies (Gray et al., 2010). These rocks have higher $\varepsilon_{Nd(T)}$ values (+4.3 to + 3.3) than the basaltic rocks of the Piskahegan Group, but have younger model ages (~0.6 Ga; Table 3).

Model ages, variation ranges of $\varepsilon_{Nd(T),}$ and chemical compositions of the basaltic rocks of the Piskahegan Group, which are similar to those recorded in penecontemporaneous mafic lavas in both Avalonia and Ganderia, can be accounted for by derivation from a subcontinental lithospheric mantle that was locally modified by the upward invasion of enriched (OIB) asthenospheric magma (e.g., Pe-Piper and Piper, 1998). The basaltic magmas extruded due to rapid lithospheric thinning and an associated steepening of the geothermal gradient (e.g., Lynch and Tremblay, 1994; Pe-Piper and Piper, 1998). There does not appear to be a systematic difference between the Avalon and Gander terranes in the isotopic composition of the SCLM during the Late Devonian and the Early Carboniferous, and composition of the SCLM could therefore have been similar beneath both terranes in this part of the Appalachians.

6. 4. Possible link between mineralization and the development of a subordinate calc-alkaline suite

The Upper Devonian to Lower Carboniferous rift-related volcanic suites that onlap the Avalon and Gander terranes along the margin of the Maritimes Basin are mostly bimodal continental tholeiite - rhyolite associations. The Piskahegan Group, which is associated with a significant polymetallic mineralization, differs from the rest of them by the presence of a significant amount of coeval calc-alkaline intermediate rocks. This calc-alkaline suite is interpreted to be the result of AFC processes involving the crustal contamination of a basaltic magma precursor, and of a change from non-oxic to oxidizing conditions accompanied by a relatively high content of magmatic water. The basalts also display an iron enrichment trend that is typical of low P shallow-seated fractionation that occurs in a non-oxic environment (Osborn, 1959; Zimmer et al., 2010). The calc-alkaline suite had a relatively high magmatic water content and/or high oxidation state, which are considered to be an indication of fertility for many polymetallic ore-bearing felsic and intermediate units (Candela, 1992; Richards, 2011). As rhyolites of the Piskahegan Group are also related to the andesitic rocks (Anderson, 1992; McCutcheon et al., 1997; Dostal et al., 2016b), it can be suggested that the evolution of these felsic rocks differed from those of other Upper Devonian to Lower Carboniferous bimodal volcanic suites. The presence of a significant amount of calc-alkaline volcanic rocks in such bimodal suites could be an indicator of potential mineralization.

7. Conclusions

Mafic and intermediate rocks of the Piskahegan Group constitute two distinct associations that are spatially and temporarily related within a Late Paleozoic caldera complex that hosts a significant polymetallic deposit of tin, tungsten, molybdenum, indium and bismuth. The first association includes basalts of the Kleef and Carrow formations, whereas the second association encompasses andesites of the South Oromocto Andesite and Scoullar Mountain formations. The basalts of the first association are fractionated, rift-related continental tholeiites with high contents of Fe, Ti, P and V, but low Mg, Mg#, Ni and Cr. They display tholeiitic fractionation trends of Fe and Ti enrichment that are characteristic of dry and non-oxic environments. They underwent the main pulse of fractional crystallization at a relatively shallow

depth, although the parent magma was generated in the transition zone between spinel and garnet peridotite at a depth of ~70-90 km. The mantle- normalized patterns of the basalts do not show distinct negative Nb-Ta anomalies, and their geochemical characteristics mainly reflect a mantle source without noticeable signs of significant crustal contamination. Rocks of the second association display a typical calc-alkaline fractionation trend that is characterized by a gradual depletion of Fe and Ti with increasing differentiation, which is indicative of a wet and oxidizing environment. This is also consistent with the absence of a negative Eu anomaly in the REE patterns of these rocks, and with the presence of hornblende in their modal composition. The rocks resulted from the mixing of continental crust material (probably phlogopite/biotite-rich metasedimentary rocks) with primitive basaltic melt, probably at mid-crust level. Although the parent basaltic magmas of both suites could have been derived from the same SCLM source, they underwent separate and different evolution pathways. The Piskahegan Group, which is associated with the Mount Pleasant polymetallic deposit, differs from penecontemporaneous, non-mineralized bimodal suites that occur along the margins of the Maritimes Basin through New Brunswick and Nova Scotia by the presence of a significant amount of coeval calc-alkaline intermediate rocks. As such rocks evolve in water- and oxygen-rich magmatic environments, their presence may be considered to be an indicator of potential mineralization.

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707 **Captions to Figures**

708 Figure 1. A - Map of a part of Atlantic Canada that shows the western boundary of the Maritimes
709 Basin and the location of the Harvey and Piskahegan groups (black fields). B - Simplified
710 geological map of the southwestern part of the Marysville sub-basin and its surroundings
711 (modified from Smith, 2006, and Smith and Fyffe, 2006) showing the location of Figure 2.
712 The insert (map of Canada) shows the location of Figure 1A.

713 Figure 2. Geology of the Mount Pleasant Caldera Complex and its surroundings (modified from
714 McCutcheon et al. 2010, and Thorne et al., 2013). Late Devonian caldera complex includes
715 Late caldera-fill sequence, Subvolcanic intrusive rocks, Intracaldera and Exocaldera
716 sequences while the Piskahegan Group encompasses Late caldera-fill, Intracaldera and
717 Exocaldera sequences.

718 Figure 3. (Ti + Cr) versus Ca (number of cations per six oxygens) discrimination diagram of
719 Leterrier et al. (1982) comparing the composition of clinopyroxenes from the intermediate
720 rocks of the Piskahegan Group with compositional fields for clinopyroxenes from
721 nonorogenic and orogenic rocks. Each value (Table 1) is an average composition of a
722 number of analyzed crystals, and composition of each crystal is an average of 4 analyses
723 (Table 1).

724 Figure 4. Variations of $FeO_{(tot)}$, TiO_2 (wt.%) and various element ratios versus SiO_2 (wt.%) in the
725 basaltic and andesitic rocks of the Piskahegan Group. Association 1 - basalt: Carrow
726 Formation (CF), Kleef Formation (KF); Association 2 - andesite: South Oromocto Andesite
727 Formation (SOA); Scoullar Mountain Formation (SMF). In A and B, the vectors show calc-
728 alkaline and tholeiitic trends whereas E and F show vectors for crustal contamination (cc)
729 and fractional crystallization (fc).

730 Figure 5. Zr/TiO_2 versus Nb/Y discrimination diagram of Winchester and Floyd (1977) for mafic
731 and intermediate rocks of the Piskahegan Group. Alk-Bas - alkali basalt; TrachAnd -
732 trachyandesite. Association 1 - basalt: Carrow Formation (CF), Kleef Formation (KF);
733 Association 2 - andesite: South Oromocto Andesite (SOA); Scoullar Mountain Formation
734 (SMF).

735 Figure 6. AFM diagram ($A = Na_2O + K_2O$, F = total Fe as FeO, M = MgO) for analyzed

mafic and intermediate volcanic rocks from the Piskahegan Group. The solid line is the boundary between tholeiitic and calc-alkaline fields after Irvine and Baragar (1971); Association 1 (basalts): Carrow Formation (CF), Kleef Formation (KF); Association 2 (andesites): South Oromocto Andesites (SOA), Scoullar Mountain Formation (SMF).

Figure 7. Chondrite-normalized REE patterns for basaltic and andesitic rocks of the Piskahegan Group. A- Range of basalts from the Carrow Formation; B - Range of basalts from the Kleef Formation; C - Range of andesites from the South Oromocto Andesite Formation; D - range of andesites from the Scoullar Mountain Formation. Normalizing values are after Sun and McDonough (1989).

Figure 8. Primitive mantle-normalized multielement patterns in basaltic and andesitic rocks of the Piskahegan Group. A - Basalts of the Carrow Formation; B - basalts of the Kleef Formation; C- andesites of the South Oromocto Andesite Formation; D- andesites of the Scoullar Mountain Formation. Normalizing values are after Sun and McDonough (1989).

Figure 9. Th-Hf-Ta tectonic discrimination diagram of Wood (1980) for mafic and intermediate volcanic rocks of the Piskahegan Group. Fields: N-MORB - normal, depleted mid-ocean ridge basalt; E-MORB/WPT - enriched mid-ocean ridge basalt and within-plate tholeiite; Alk WPB - alkaline within-plate basalt; CAB - calc-alkaline volcanic arc basalts; ATB - volcanic arc tholeiites; CC (star) - average continental crust composition of Taylor and McLennan (1985). Note that the trend of the Piskahegan rocks is suggestive of a mixing between basaltic magma and crustal material.

Figure 10. $\varepsilon_{Nd(t)}$ versus time plot comparing Sm-Nd isotopic data of the Piskahegan basalts and andesites and the Carboniferous Cumberland Hill trachytes with a compilation of Sm-Nd isotopic data for the Upper Devonian-Lower Carboniferous volcanic rocks of the Maritimes Basin and the Avalon Terrane (Keppie et al., 1997, Pe-Piper and Piper, 1998). The shaded area is the Avalonian basement and the SCLM (after Murphy et al., 2011b, Dostal et al., 2016a). The field for Mesoproterozoic rocks is from Murphy et al. (2008). Bars show a range of samples.

Figure 11. Th/Yb versus Nb/Yb diagram of Pearce (2008) for Piskahegan basalts and andesites. Vectors indicate the influence of a subduction component (S), within-plate enrichment (W), crustal contamination (C), and fractional crystallization (FC); N-MORB- N-type mid-ocean

ridge basalt; E-MORB- enriched mid-ocean ridge basalt; OIB-ocean island basalt (after Sun and McDonough, 1989). The star (CC) is the average of continental crust (Taylor and McLennan, 1985).

Figure 12. $(Tb/Yb)_n$ versus $(La/Sm)_n$ diagram for the Piskahegan basalts and andesites. The values are normalized to the primitive mantle after Sun and McDonough (1989). The solid line separating the range of magmas formed by the melting of spinel peridotite mantle from that of magmas formed by the melting of garnet peridotite mantle is after Wang et al. (2002). Vector D indicates an increase of melting depth whereas the vector M depicts an increase in the degree of partial melting. The limited range of $(Tb/Yb)_n$ values for the basalts indicates a similar mantle source. The higher $(La/Sm)_n$ ratios of the calc-alkaline rocks is more suggestive of crustal contamination than of changes in the magma source region. The E-MORB (enriched mid-ocean ridge basalt) and OIB (ocean island basalt) are after Sun and McDonough (1989).

Figure 13. $(Nb/Th)_n$ versus $(Th/Yb)_n$ diagram for the Piskahegan basalts and andesites. The ratios are normalized to the primitive mantle values of Sun and McDonough (1989). N-MORB and E-MORB compositions are from Sun and McDonough (1989). CC (star) - average continental crust (Taylor and McLennan, 1985). Note that the very distinct trend (the solid curve is a mixing curve) of the Piskahegan rocks is suggestive of a mixing between parental basaltic magmas and crustal material, indicating that the andesitic magma assimilated significant amounts of crustal material prior to its emplacement.

Figure 14. Th/La versus $\varepsilon_{Nd(T)}$ plot for the Piskahegan basalts and andesites. An increase of the Th/La ratio accompanied by a decrease of $\varepsilon_{Nd(T)}$ is indicative of a crustal contamination of the basaltic magmas. CC (star) - average continental crust composition (Taylor and McLennan, 1985). The solid triangles are data from Anderson (1992) for the Piskahegan basaltic and andesitic rocks.

Tables

Upper Paleozoic mafic and intermediate volcanic rocks associated with the Sn-W deposit of the Mount Pleasant caldera ~~associated with the Sn-W deposit~~ in southwestern New Brunswick (Canada): Petrogenesis and metallogenic implications

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Abstract

Upper Paleozoic (~365 Ma) mafic and intermediate volcanic rocks of the Piskahegan Group constitute a subordinate part of the Mount Pleasant caldera, which is associated with~~related to~~ a~~a~~ significant polymetallic deposit (~~tin,~~ tungsten~~,~~ molybdenum-bismuth zones ~ 33 Mt ore with 0.21% W, 0.1% Mo and 0.08% Bi and tin-indium zones ~ 4.8 Mt with 0.82% Sn and 129 g/t In~~,~~ ~~zinc, indium and bismuth~~) in southwestern New Brunswick (Canada). The epicontinental caldera complex formed during the opening of the late Paleozoic Maritimes Basin ~~of~~ in the ~~Northern~~ northern Appalachians. The mafic and intermediate rocks make up two compositionally distinct associations. The first association includes evolved rift-related continental tholeiitic basalts, and the second association comprises~~encompasses~~ calc-alkaline andesites, although both associations were emplaced penecontemporaneously. The basalts have low Mg# ~ 0.34-0.40, smooth~~linear~~ chondrite-normalized REE patterns with $(La/Yb)_n$ ~ 5-6, primitive mantle-normalized trace element patterns without noticeable negative Nb-Ta anomalies, and their $\varepsilon_{Nd(T)}$ ranges from +2.5 to +2.2. The basalts were generated by partial melting of a transition zone between spinel and garnet mantle peridotite at a depth of ~~(~~~70-90 km ~~depth)~~. The calc-alkaline andesites of the second association have chondrite-normalized REE patterns that are more fractionated, with $(La/Yb)_n$ ~ 7-8.5, but without significant negative Eu anomalies. Compared to the basaltic rocks, they have lower $\varepsilon_{Nd(T)}$ values, ranging from +0.5 to + 1.9, and their mantle-normalized trace element plots show negative Nb-Ta anomalies. The $\varepsilon_{Nd(T)}$ values display negative correlations with indicators of crustal contamination, such as Th/La, Th/Nb~~,~~ and SiO_2. The andesitic rocks are interpreted to have formed by assimilation-fractional crystallization processes, which resulted in the contamination of a precursor basaltic magma with crustal material. The parent basaltic magma for both suites underwent a different evolution. The tholeiitic basalts experienced shallow-seated fractional crystallization and evolved along a tholeiitic trend of "early iron" enrichment (non-oxic conditions). The contaminated magma of the second association followed a calc-alkaline fractionation trend of "no iron" enrichment (oxidizing conditions) characterized by a high P_{H2O} and P_{O2} environment at the mid-crust levels. The Piskahegan Group, which is associated with~~to~~ an ~~an~~ important polymetallic mineral deposit ~~ization~~, differs from the numerous non-mineralized rift-related volcanic suites of the regional Upper Devonian to Lower Carboniferous successions ~~of~~ in the Maritimes Basin by the presence of a significant amount of

coeval calc-alkaline andesite, which may be an indicator of potential mineralization. These rocks may be indicators of a mineralizationfertile environment. The subcontinental lithospheric mantle of the Avalon and Gander terranes of the Northern Appalachians in Atlantic Canada had an isotopically similar composition during the Late Devonian and Early Carboniferous.

1. Introduction

Felsic rocks of continental rift-related magmatic settingsregimes have been the focus of extensive investigation and numerous publications in part because they may host rare metal mineralizations, which in some cases is are of economic significance (e.g., Richardson and Birkett, 1996; Cerny et al. 2005; Linnen and Cuney, 2005; Richardson and Birkett, 1996). These rocks granites and rhyolites are commonly associated with a compositionally diverse variety of mafic and intermediate rocks (e.g., Nekvasil et al., 2000). Much is still unknown about the processes that lead to the diversity of magmas within such bimodal series bimodal suites or and aboutto the global diversity of intraplate magmatic suitessuite types. In mineralized bimodal complexes where felsic rocks are dominant, the subordinate mafic and intermediate rocks are commonly only poorly known, although they might provide important information on the tectonic environment of such bimodal complex the bimodal associations, as well as on the origin of the felsic rocks and their mineralization, thus providing clues for the exploration for rare metal deposits. One of such bimodal suitessuite is the upper Paleozoic Piskahegan Group in of southwestern New Brunswick (Canada). The latter group forms a volcanic caldera complex (e.g., McCutcheon, 1990; McCutcheon et al., 1997; Thorne et al., 2013) that is spatially and genetically associated with the Mount Pleasant polymetallic deposit (tin, tungsten-molybdenum-bismuth zones containing ~ 33 Mt ore with 0.21% W, 0.1% Mo and 0.08% Bi and tin-indium zones ~ 4.8 Mt with 0.82% Sn and 129 g/t In), molybdenum, zinc, indium, and bismuth). The deposit is recognized as the world's largest known undeveloped resource of indium (Sinclair et al., 2006; Thorne et al., 2013). To contribute to the debate on the origin of these bimodal suites, we have investigated mafic and intermediate volcanic rocks of the Mount Pleasant caldera (Figs.

1 and 2). ~~Whole-rock major~~ Major and trace elements in these rocks, as well as neodymium ~~isotopic~~ isotopes~~ratios of these rocks~~, may provide information related not only to the origin of the bimodal suite and its mineralization, but also on the nature of the mantle source (e.g., DePaolo, 1988). Such data are also useful to evaluate the composition of the subcontinental lithospheric mantle (SCLM).

The purpose of this paper is: (1) to present geochemical data on the mafic and intermediate volcanic rocks of the Mount Pleasant caldera, including major and trace elements and Nd isotopic ratios, (2) to constrain the origin of the rocks in the caldera, (3) to investigate the differences between mineralized and barren Devonian to Carboniferous bimodal volcanic suites in this part of the Northern Appalachians, (4) to evaluate the nature of the SCLM, and (5) to compare this information with data from time equivalent basaltic rocks of New Brunswick and Nova Scotia, which belong to the peri-Gondwanan Gander and Avalon terranes of the North American Appalachians~~ of eastern North America~~. The comparison of SCLM properties in two neighboring exotic terranes could reveal whether or not both terranes were underlain by the same SCLM during the Paleozoic and thus contribute to the Ganderian controversy (i.e. whether or not the Gander and Avalon zones represent distinct terranes; e.g.,~~-~~van Staal and Barr, 2012~~; van Staal et al., 2009~~; Dostal et al., 2016a~~5~~).

2. Geological setting

Volcanic rocks of the Piskahegan Group occur along the western margin of the Maritimes Basin in southwestern New Brunswick (Fig. 1). The Maritimes Basin ~~of the Northern Appalachians~~ is a major ~~Late~~ late Paleozoic successor basin (Gibling et al., 2008) that was initiated after the Early to Middle Devonian Acadian Orogeny (~400 Ma) in the Canadian Appalachians. ~~The~~ This composite ~~Maritimes Basin~~ basin first developed as a series of pull-apart sub-basins along the Minas Fault Zone, a large east-~~west~~ trending dextral strike-slip system that juxtaposed the Meguma and Avalon terranes during the Late Devonian and the Carboniferous (Murphy et al., 2011a~~b~~). Associated with these pull-apart structures are large ~~felsic, intermediate and mafic plutons~~ bimodal plutons, as well as ~~is~~ a series of NW-~~SE~~ trending mafic dykes~~, as well as large felsic, intermediate, and mafic plutons~~. Closely spaced U-Pb dates for peak Acadian metamorphism and for the emplacement and exhumation of post-Acadian plutons along the

Minas Fault Zone suggest that the transition from orogenic compression to transtension along this fault system was very rapid (Dostal et al., 2006). Also associated with this transtensional magmatic event are widely distributed bimodal volcanic suites, one of which is the Piskahegan Group~~. This group forms a volcanic caldera complex that is spatially, temporarily, and genetically~~ and its associated ~~with the Mount Pleasant~~ polymetallic deposit (Kooiman et al., 1986; McCutcheon et al., 1997; Thorne et al., 2013). The complex, referred to as~~called~~ the Mount Pleasant caldera, is a northeast-trending elliptical feature that is defined by geophysical data (regional gravimetric and magnetic studies) as about 13 km wide and 34 km long (McLeod and Smith, 2010).~~–~~ However, the northern part of the complex is overlain by middle Mississippian (Visean) and Pennsylvanian strata of the Maritimes Basin in such a way that the exposed length is restrained to about 17 km. This epicontinental caldera, which was emplaced in a trans~~-~~tensional setting (Fyffe et al., 2011), is associated with high-level subvolcanic granitic intrusions and has been interpreted to have formed by roof collapse in an epizonal magma chamber. The Piskahegan Group (Figs. 1 and 2) disconformably overlies ~~poly~~deformed Ordovician to Silurian turbiditic metasedimentary rocks of the Gander Terrane. These rocks bound the caldera to the east and west. The caldera is in turn paraconformably overlain by Visean ~~(mid-Mississippian)~~ clastic rocks formerly mapped as the Shin Redbeds by van de Poll (1967)~~, which were~~ and recently assigned the Shin Member of the Hopewell Cape Formation (Jutras et al., 2015), ~~and~~ which confine the caldera to the north (Fig. 1). Late Silurian to Devonian granitic rocks of the Saint George Batholith represent~~s~~ the southern boundary of the complex (McLeod, 1990). Both the batholith and the caldera complex lie within the boundaries of the Gander Terrane.

The Piskahegan Group (Fig. 2) has been subdivided into three volcanic facies (in the sense of Fisher and Schmincke, 1984) in order to reflect their depositional setting in relation to the volcanic architecture: (1) exocaldera, (2) intracaldera and (3) late caldera-fill sequences (McCutcheon, 1990; McCutcheon et al., 1997; Thorne et al., 2013).~~–~~ The caldera is composed mainly of felsic volcanic and~~s,~~ volcaniclastic rocks and associated sedimentary rocks, which are ~~and it is~~ intruded by subvolcanic granitic bodies (McCutcheon et al., 1997). All three volcanic facies contain subordinate amounts of mafic and intermediate volcanic rocks (Fig. 2).

The Piskahegan Group was emplaced during the initial stages of basin development. ~~The~~ ~~p~~Paleontological records~~, as well as~~ and radiometric dating~~.~~ show that most of the caldera is Fammenian (Upper Devonian) in age and coincides with the emplacement of voluminous granitic intrusions. Anderson (1992) obtained a whole-rock Rb-Sr isochron age of 368 ±5 Ma for the Piskahegan Group. The Carrow Formation (CF) of the exocaldera sequence yielded a U-Pb zircon age of 363.8 ± 2.2 Ma (Tucker et al., 1998), whereas a spore assemblage recovered from drill core above the zircon sample yielded a late Famennian age (McGregor and McCutcheon, 1988). More recently, Thorne et al. (2013) reported Re-Os ages of 369.7 ± 1.6 Ma and 370.1 ± 1.7 Ma from molybdenite samples associated with W-Mo-Bi mineralization. There are also several $^{40}Ar/^{39}Ar$ ages of ca. 360 Ma on the granitic rocks (Sinclair et al., 1988), and~~–~~ the youngest phase of the neighbouring Saint George Batholith, which is probably related to them, gave a U-Pb zircon age of 367±1 Ma (Bevier 1988). Hence, all available data in the Piskahegan Group and associated plutonic rocks range within the Fammenian (*sensu* Richards, 2013).

The exocaldera sequence includes three units that also contain mafic or intermediate volcanic rocks. In ascending stratigraphic order, they are the Hoyt Station Basalt (HSB), the South Oromocto Andesite (SOA) and the Carrow Formation (CF). HSB~~The Hoyt Station Basalt~~ is the basal unit of the exocaldera sequence (McCutcheon et al., 1997) and it consists mainly of a basalt flow unit that is about 20 m thick. The basalt is underlain by rhyolitic volcaniclastic rocks. The SOA unit is an up to 130 m thick succession of lava flows that is conformably overlain by the CF. The latter is composed mainly of clastic sediments, but also contains an aphyric basalt flow (< 20 m thick) near the top of the formation.

At the base, the intracaldera sequence includes the Scoullar Mountain Formation (SMF), which lies along the periphery of the caldera complex at the contact with pre-caldera rocks. This unit, the thickness of which ranges between 225 and 450 m, is composed predominantly of clastic sedimentary rocks and interbedded andesitic lava flows and felsic volcaniclastic rocks. The upper part of the late caldera-fill sequence contains the Kleef Formation (KF), which consists of conglomeratic redbeds (40-75 m thick), basalts (70-80 m), and volcaniclastic rocks (> 4 m).

The polymetallic deposit is~~is~~ located near the southwestern margin of the caldera complex (McCutcheon et al., 1997). It~~It~~ consist~~s~~s of mineralized stockworks and quartz veinlets,

breccia infill and lode mineralization~~, and its~~. ~~i~~Its formation is associated with the emplacement of the subvolcanic granitic rocks that host it. Thorne et al. (2013) inferred that the mineralization was associated with caldera collapse, which was marked by the emplacement of a series of subvolcanic granitic intrusions (Fig. 2 ~~McDougall Brook and Mount Pleasant granitic suites; e.g., Yang et al., 2003~~).

3. Analytical methods

Mineral compositions (Table 1; Appendix 1) were determined using a JEOL Superprobe 733 equipped with four wave-length-dispersive spectrometers and one energy-dispersive spectrometer, and operated with a beam current of 15 kV at 5 nA at the Department of Earth Sciences of Dalhousie University, Halifax, Nova Scotia (Canada).

Major and several trace element analyses of whole rocks (Table 2; Appendix 2~~1~~) were performed on fused glass disks using a Philips PW2400 X-ray fluorescence spectrometer at the University of Ottawa, Ontario (Canada). Duplicate analyses of the samples yielded total errors of ± 3% (1σ).~~–~~ Trace element analysis was done using lithium metaborate-tetraborate fusion and a Perkin Elmer Optima 3000 ICP mass spectrometer at Activation Laboratories, Ancaster, Ontario (Canada). Replicate analyses of the reference standard rocks indicate that the errors were between 2 and 8 % of the values cited. The detection limits and other information on the trace element analyses (analytical package 4B2) are available at the Activation Laboratories web site (www.actlabs.com).

Nd isotope ratios (Table 3) were determined by isotope dilution mass spectrometry at the Department of Earth Sciences of the Memorial University of Newfoundland (St. John's, Newfoundland, Canada). Concentration data are standard ICP-MS analyses and are precise to ±5% (2σ). Ratios of $^{147}Sm/^{144}Nd$ (except samples 38A and 69) were measured directly by high-precision ICP-MS with an estimated precision of ± 0.5 % (2σ). The isotopic ratios of $^{143}Nd/^{144}Nd$ were determined using a multicollector Finnigan MAT 262V thermal ionization mass spectrometer operated in a static mode. Measured $^{143}Nd/^{144}Nd$ values were normalized to a $^{146}Nd/^{144}Nd$ ratio of 0.7219. Replicate analyses of the LaJolla standard, which was analyzed

repeatedly throughout, gave an average value for $^{143}Nd/^{144}Nd=0.511849 \pm 9$. The 2σ values for all samples are less than or equal to 0.000008 for $^{143}Nd/^{144}Nd$ and are given in Table 3. Values for $\varepsilon_{Nd\,(T)}$ were calculated with respect to CHUR using present-day $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ ratios of respectively 0.512638 and 0.196593, and subsequently age-corrected. A T_{DM1} model age was calculated using a linear evolution for a mantle that separated from CHUR at 4.55 Ga, and that hashaving a present day ε value of +10. The T_{DM2} model age was calculated according to the model of DePaolo (1988).

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4. Petrography and mineral chemistry

Basalts and andesites The mafic and intermediate rocks of the Piskahegan Group include basalts and andesites. The rocks vary from massive to amygdaloidal. Amygdales occur particularly in the upper part of the flows and are commonly filled by carbonates or silica. Although rocks of the caldera are not significantly deformed and contain unstrained quartz with primary glass inclusions (Gray et al., 2011), the amygdaloidalAmygdaloidal rocks are extensively altered, although the rocks of the caldera are not significantly deformed, and felsic rocks contain unstrained quartz with primary glass inclusions (Gray et al., 2011).. Igneous textures are mostly preserved, but the primary magmatic minerals are frequently replaced by secondary phases. The rocks exhibit greenschist grade metamorphism that produced chlorite, epidote and actinolite. Textures range from aphyric to coarse subophitic and ophitic, as well as porphyritic and glomeroporphyritic. The basalts are composed predominantly of plagioclase and clinopyroxene, which are variably altered and occur both as phenocrysts and as the main components of the groundmass. The rocks also contain minor Fe-Ti oxides and accessory apatite. No orthopyroxene was observed. When fresh, the plagioclase phenocrysts show zoning with labradorite-bytownite cores and andesine rims. However, plagioclase is mostly albitized or altered to sericite and calcite. Some plagioclase phenocrysts contain zones of sieve texture. The intermediate rocks contain relics of dark brownish-green amphibole replaced mainly by chlorite and epidote. In these rocks, subhedral amphibole crystallized together with plagioclase, Fe-Ti oxide, and apatite after the crystallization of clinopyroxene (Anderson, 1992). Amphibole may contain a core of clinopyroxene. The clinopyroxene phenocrysts show zoning, but are partially

replaced by chlorite and epidote. Clinopyroxenes typically forms subhedral phenocrysts and microphenocrysts or occurs in a subophitic to ophitic groundmass of the mafic rocks. The rRelics of fresh clinopyroxene in the mafic and intermediate rocks are typically augite (Anderson, 19982; Table 1; Appendix 1). On tectonic discrimination diagrams for pyroxene (Leterrier et al., 1982), the clinopyroxenes of the basalts plots into the "non-orogenic" field (Anderson, 1992; McCutcheon et al., 1997). We have analyzed cClinopyroxenes from the intermediate rockunits (Table 1), which also plot into the "non-orogenic" field (Fig. 3) of Leterrier et al. (1982). The rarity of phenocrysts in some samples of evolved rocks may be caused by the separation of early fractionated phases from the melt on the way to the surface.

5. Whole-rock geochemistry

5.1. Alteration

Alteration and metamorphic processes have affected the rocks. Petrographic evidence includes the saussuritization, sericitization, and albitization of feldspar, the chloritization of clinopyroxene as well as the accumulation of silica and calcite in amygdales. Although the original abundances of mobile elements such as Ca, Na, and K might have been modified, the concentrations and ratios of high-field strength elements (HFSE) and rare earth elements (REE) show well-defined trends indicating that these elements were immobile during alteration. This is also supported by many other studies (e.g., Winchester and Floyd, 1977) indicating that HFSE and REE retain their distribution during alteration. Furthermore, an investigation of melt inclusions in quartz of associated rhyolitic rocks (Gray et al., 2011) showeds that post-magmatic processes did not modify the whole-rock composition. Similarly, it is typically inferred that the Sm and Nd isotope characteristics of a rock for the Nd isotopic ratios, the Sm-Nd isotopic pair is are resistant to geological disturbances (e.g., DePaolo, 1988) and it is typically inferred that the Nd isotope characteristics of rocks were not modified.

5.2. Major and trace elements

All the major oxide compositions were recalculated to 100% on a volatile free basis for plotting on geochemical diagrams. According to their major element compositions (Fig. 4), the

mafic and intermediate volcanic rocks of the Piskahegan Group can be subdivided into two associations: Association 1 includes basalts of the KF and CF formations, which are characterized by low SiO_2 ~50 wt.% (48-52 wt.%), and high TiO_2 (> 2.5 wt.%) and $FeO_{(t)}$ (~ 13-15 wt.%), whereas Association 2 comprises intermediate rocks of the SOA and SMF, with SiO_2 > 54 wt.%, TiO_2 < 2 wt.%, and $FeO_{(t)}$ < 9 wt.% . The division is also shown in a the Zr/TiO_2 versus Nb/Y diagramgraph (Fig. 5), in which Association 1 rocks plot into the basaltic field, whereas rocks of Association 2 plot mainly into the andesitic field.

According to the conventional AFM [(K_2O+Na_2O)-$FeO_{(t)}$-MgO] diagram (Fig. 6), Association 1 rocks are tholeiites. They have characteristics of differentiated tholeiitic basalts with low MgO, Ni, and Cr, as well as high Fe, Ti, and P. Compared to primitive basalts that have Mg# ($MgO/[MgO+FeO_{(t)}]$) values of ~ 0.70 (Hanson and Langmuir, 1978), the Piskahegan basalts (Table 2) have significantly lower values (0.34-0.40), suggesting that they have undergone high degrees of fractional crystallization. Their chondrite-normalized REE patterns show a negative slope, resulting from an enrichment of light REE (LREE) with $(La/Yb)_n$ ~5-6, but without Eu anomalies (Fig.7). The primitive mantle-normalized incompatible element plots of Association 1 rocks do not display noticeable show distinctsignificant negative Nb-Ta anomalies (Fig. 8). The patterns show distinct negative anomalies for Ti and Sr, which together with low Ni and Cr indicate that the rocks underwent fractional crystallization dominated by that of plagioclase and clinopyroxene. Both patterns (Figs. 7 and 8) resemble those of rift-related continental tholeiites or transitional basalts (e.g., Dostal and Dupuy, 1984; Pegram, 1990; Dostal et al., 1992; Peate and Hawkesworth, 1996). In comparison with arc mafic rocks, the basalts have high Ti/V (70-100) and Zr/Y (6-8), and their primitive mantle-normalized trace element patterns do not exhibit pronounceddistinctsignificant negative Nb-Ta anomalies (Fig. 8). In addition, on geochemical discrimination diagrams, they also plot into the field of rift-related basalts (Fig. 9).

Compared to those of Association 1, rocks of Association 2 have calc-alkaline characteristics (e.g., Fig. 6), although they were emplaced penecontemporaneously and in the same tectonic and geographic settings. With increasing SiO_2, the andesites show a decrease in Fe, Ti, Mg# ($MgO/[MgO+FeO_{(t)}]$), and Ni, but also an increase of in alkalis and of in the Al_2O_3/CaO and La/Yb ratios (Fig. 4), indicating the crystallization of clinopyroxene, plagioclase and Fe-Ti oxide. The fractionation of Fe-Ti oxides, which is implied by a decrease of $FeO_{(t)}$,

TiO_2, and V with increasing SiO_2 in the calc-alkaline suite, suggests high P_{H2O} and P_{O2} conditions. The difference between tholeiitic and calc-alkaline suites can be partially due to the depth of fractional crystallization (e.g., Grove and Kinzler, 1986). Crystallization of the calc-alkaline magmas at mid-crustal depth may have differed from that of tholeiitic magma, which could have taken place at lower P_{tot} and lower P_{O2} conditions (i.e., within a shallow upper crustal magma chamber).

There are subtle differences between the SOA and SMF rocks. The SOA have SiO_2 ~55-58 wt.%, TiO_2 < 2 wt.% and $FeO_{(t)}$ ~ 8 wt.%. The SMF rocks are more fractionated, although there is some overlap in composition. They have typically higher SiO_2 (59-66 wt.%), lower TiO_2 < 1.5 wt.% and lower $FeO_{(t)}$ < 8 wt.% (Table 2).

In addition to the differences in major element compositions between associations 1 and 2, the andesites have more fractionated REE patterns, with $(La/Yb)_n$ ~ 7-8.5, but also without significant Eu anomalies. Their light REE (LREE) abundances are similar to those of the first association, but they have lower heavy REE (HREE) contents. The primitive mantle-normalized incompatible element plots of Association 2 show distinct negative Nb-Ta anomalies, which are indicative of either subduction or crustal assimilation.

5. Nd isotopic ratios

The Sm-Nd isotopic signatures of the basaltic and andesitic rocks are given in Table 3, in which they are all aged-corrected to 365 Ma. The $\varepsilon_{Nd(T)}$ values of the basalts range from +2.5 to + 2.2, and $^{147}Sm/^{144}Nd$ ratios vary from 0.13 to 0.14 (Table 3). The values are in good agreement with the data of Anderson (1982) for mafic rocks of the caldera. The data plot within the range reported for the Devonian to Carboniferous basaltic rocks of the Maritimes Basin in New Brunswick and Nova Scotia (Fig. 10). They are also similar to those from rift-related

basalts, continental flood basalts and xenoliths from the subcontinental lithosphere (Faure and Mensing, 2005). These $\varepsilon_{Nd(T)}$ values are considerably lower than values expected for juvenile magmas from a depleted mantle source (Fig. 10), although the positive $\varepsilon_{Nd(T)}$ values precludenegate a significant contribution from substantially older continental crust or sedimentary rocks derived from it. The Piskahegan basaltic rocks plot into the field of Avalonian and peri-Rodinian lithosphere (Fig. 10), and their $\varepsilon_{Nd(T)}$ values are consistent with derivation from a SCLM.

Based on DePaolo (1988), depleted mantle Nneodymium depleted-mantle model ages of DePaolo (1988) for these rocks range between 800 and 900 Ma (Table 3) and are similar to those determined for the Devonian to Carboniferous basaltic rocks above the Avalon and Gander terranes in the Maritimes Basin (Keppie et al., 1997; Pe-Piper and Piper, 1998). The similarities of the model ages for the Devonian to Carboniferous basaltic rocks above the Avalon and Gander terranes in the Maritimes Basin (Keppie et al., 1997; Pe-Piper and Piper, 1998). These similarities suggest that the model ages represent a bulk weighted average of the source composition.

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The andesites have lower $\varepsilon_{Nd(T)}$ (Table 3) than the basalts (Table 3), but they still plot in the field of Avalonian and Ganderian lithosphere (Fig. 10). The negative Nb-Ta anomalies along with and the lower $\varepsilon_{Nd(T)}$ values (+0.5 to +1.9) of these rocks are consistent with an inferred involvement of continental lithosphere in their evolution, most probably through crustal contamination.

6. Discussion

6. 1. Petrogenesis

Although all volcanic rocks of the Piskahegan Group are spatially and temporarily associated, the Association 1 basaltic rocks are not related to the Association 2 andesitic rocks through simple crystal-liquid equilibria processes. The absence of smooth variation trends when various elements and element ratios are plotted against a differentiation index, such as SiO_2 (Fig. 4), suggests that the Association 2 andesites did not simply result from the fractional crystallization of Association 1 basalts.

The Association 1 rocks are evolved tholeiites that were emplaced in an epicontinental rift-related setting. Compared to primitive basalts that have Mg# values of ~ 0.70 (Hanson and Langmuir, 1978), the Piskahegan basalts (Table 2) have significantly lower values (0.34-0.40), suggesting that they have undergone high degrees of fractional crystallization. The ~~y underwent extensive~~ fractional crystallization was dominated by crystallization ~~that~~ of clinopyroxene and plagioclase. On the Th/Yb versus Nb/Yb diagram (Fig. 11), which has been used for the evaluation of lithospheric inputs in basalts (Pearce, 2008), the averages of N-type MORB, E-type MORB~~,~~ and OIB form a diagonal mantle array (Fig. 11). Magmas that were modified by an interaction with continental crust or that involved material with a subduction history are displaced to higher Th/Yb values. The basaltic rocks of the Piskahegan Group straddle the boundary of the mantle array, implying that crustal contamination and subduction imprints were insignificant. This is also consistent with the lack of a discernible negative Nb-Ta anomaly on the spider plots (Fig. 8). Thus, the composition of the basalts mostly reflects the original characteristics of the mantle source~~,~~ and, together with positive $\varepsilon_{Nd(T)}$ ~~–~~ values, indicate that they were derived from a relatively uncontaminated and moderately enriched mantle, similar to an ocean island basalt (OIB)-type source (Faure and Mensing, 2005).

On the Tb/Yb versus La/Sm graph (Fig.12), the basaltic samples straddle the spinel peridotite-garnet peridotite boundary, suggesting that they were formed in a spinel-garnet transition zone, at a depth of ~70-90 km (Wang et al., 2002). Whereas ~~the~~ Tb/Yb ratios ~~is~~ are related to the pressure conditions and depth at which melting occurred, ~~the~~ La/Sm ratios correlate~~s~~ with the degree of partial melting~~,~~ and ~~it~~ tend~~s~~ to decrease with an increase of mantle peridotite melting. ~~-~~Ratios for the CF and KF basalts are overlapping, which indicates that they were generated at the same depth by similar degrees of partial melting from a similar mantle source.

The andesites of the Piskahegan Group underwent fractional crystallization dominated by ~~that of~~ plagioclase, clinopyroxene and ~~–~~ Fe-Ti oxide, as indicated by the variation trends of several elements and element ratios when plotted against SiO_2 (Fig. 4). The compositional characteristics of the Association 2 rocks, including negative Nb-Ta anomalies and their position on the Th/Yb versus Nb/Yb diagram (Fig. 11), suggest that the rocks record an additional process ~~in addition~~ to fractional crystallization~~, the rocks record an additional process~~. The SOA

and SMF andesites are displaced toward higher Th/Yb ratios relative to the mantle array, implying crustal contamination or inputs from a subcontinental mantle that had previously been affected by subduction fluids.

Correlation of element and isotopic ratios suggests that the andesites were significantly changed by crustal contamination as discussed below. Trace element ratios, which are not modified by the fractional crystallization of major rock forming minerals~~,~~ and which have significantly different values for oceanic basalts (OIB, MORB) and continental crust (e.g., Th/La, Th/Nb, Th/Ta, Nb/U), are typically used as indicators for crustal contamination (e.g., Jochum et al., 1991; D'Antonio et al., 2007). The SOA andesites have higher Th/La (~0.15-0.16), Th/Nb (0.3-0.45)~~;~~ and Th/Ta (5-7) ratios than the basalts (Th/La~0.08-0.1~~,;~~ Th/Nb ~0.11-0.19~~;~~ , and Th/Ta~1-3), indicating crustal input. The same applies ~~to~~ for the SMF andesites, which have even higher Th/La (~0.20-0.25), Th/Nb (>0.5) and Th/Ta (8-11) ratios. These ratios, which are sensitive indicators of crustal contamination, correlate with SiO_2 (Fig. 4) and are consistent with an origin of the intermediate rocks by the crustal contamination of basalts accompanied by fractional crystallization.~~–~~ Such a process is also supported by mixing trends on the Nb/Th versus Th/Yb diagram (Fig. 13), in which the andesitic rocks plot along the mixing line between typical mantle-derived tholeiites and crustal material.~~–~~ A similar trend is also shown on Figure 9. Due to the absence of geochemical analyses from the underlying basement/continental crust, we have used ~~in these graphs~~ the average continental crust composition of Taylor and McLennan (1985) as a reference contaminant for these graphs. Likewise, the plots involving Nd isotopes and contamination-sensitive trace element ratios or SiO_2 suggest a mixing between the basaltic melts derived from the SCLM and crustal material. The rocks show a general trend of lower $\varepsilon_{Nd(T)}$ with higher Th on the $\varepsilon_{Nd(T)}$~~–~~ versus Th/La graph (Fig. 14),~~–~~ confirming the involvement~~–~~ of continental crust in the rocks with lower $\varepsilon_{Nd(T)}$.

The highly fractionated nature of the basalts as well as the observed gap between basalts and intermediate rocks indicate that the original magmas of each association had to undergo a separate evolution, although they may have~~probably~~ had a comparable parent magma.~~–~~ The Association 1 basalts underwent fractional crystallization during their rise to the surface, whereas the Association 2 andesites were modified by crustal contamination through assimilation-fractional crystallization (AFC) processes, probably at mid-crust levels. As the andesitic rocks

contain hornblende indicative of mid-crust crystallization and show a calc-alkaline fractionation trend that is typical of high $P_{(tot)}$ and P_{H2O} conditions, the contamination had to take place at a deeper crustal level (e.g., Osborn, 1959; Zimmer et al., 2010). In addition to amphibole, the calc-alkaline rocks also contain clinopyroxene phenocrysts, which, like those of the basalts, are typical of within plate, ~~(~~"non-orogenic"~~)~~ rocks (Fig. 3). ~~-~~The wet and/or oxidizing environment is also consistent with the lack of distinct negative Eu anomalies in most of the andesitic rocks (Fig. 7) which could be because the magmatic water content was high (Moore and Carmichael, 1998) and/or because the magmatic oxidation state was high, in which case most of the Eu would have been present as Eu^{3+} and would not have been incorporated into the crystallizing plagioclase (e.g., Sisson and Grove, 1993).

Crustal contamination le~~a~~d to a change from a non-oxic environment, typical of tholeiitic rocks, to the oxidizing environment that is ~~of~~ typical of calc-alkaline rocks (e.g., Osborn, 1959; Zimmer et al., 2010). In the case of the tholeiitic basalts, the original magma fractionated along a tholeiitic trend of "early iron" enrichment (non-oxic conditions).~~–~~ The magma which mixed with continental crust material followed a calc-alkaline fractionation trend of "no iron" enrichment (oxidizing conditions).

6.2 Crustal contamination in a ~~Contaminant and~~ metallogenic province

In the near vicinity of the Mount Pleasant caldera, there are several small Late Devonian plutons composed of Li-F-rich granites (e.g., Taylor, 1992; Whalen et al., 1996). These plutons as well as the Mount Pleasant complex are a part of a large tin belt described by ~~the tin belt of~~ Schuiling (1967) and Strong (1980), among others, which extends ~~from one continent to another,~~ from North America to Europe. This belt, characterised by the occurrences of the mineralized Devono-Carboniferous Li-F- rich peraluminous leucogranites with broadly contemporaneous S-W-(U) mineralization, can be followed along the ~~L~~late Paleozoic fold belts ~~in~~of the Canadian~~s~~ Appalachians and the Hercynian Orogen of western and central Europe, from ~~-~~New Brunswick (Mount Pleasant complex) to Nova Scotia (~~East Kemptville,~~ South Mountain ~~b~~Batholith at East Kemptville), ~~New Brunswick (Mount Pleasant complex)~~ and Newfoundland (Ackley ~~p~~Pluton), and across the Atlantic Ocean ~~–~~to southwestern England (Cornwall), France (Armorican Massif and ~~French~~ Massif Central), ~~-~~Germany (Altenberg, Erzgebirge) and the Czech Republic

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(Zinnwald) ~~Armorican Massif to ()(Czech Republic and Germany)~~. The belt has a long mining history ~~of mining~~ of Sn, W and U ~~(mined already by~~dating back to the Romans~~)~~. Numerous studies (e.g., Dostal and Chatterjee, 1995; Haapala, 1997; Cuney et al., 2002; Dostal et al., 2004; Cerny et al., 2005) inferred that the magmatic and hydrothermal mineralizing events were essentially synchronous and that the uncommon chemical characteristics of the Li-F-rich leucogranites require an uncommon ~~a distinct~~ source material. It has been inferred that the parental magmas of the leucogranites, including those around the Mount Pleasant caldera, were derived from similar ~~but uncommon~~ source reservoirs (Romer and Kroner, 2014), probably phlogopite/biotite-rich mid-crustal metasedimentary rocks (e.g., Dostal et al., 2004). Similar fluid-rich rocks could have acted as~~been~~ a crustal contaminant.

~~In the near vicinity of the Mount Pleasant caldera, there are several small Late Devonian plutons composed of Li-F-rich granites (e.g., Taylor, 1992; Whalen et al., 1996). These plutons were probably derived from phlogopite/biotite-bearing mid-crustal metasediments. Similar fluid-rich rocks could have been a crustal contaminant.~~

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6. 3~~2~~. Comparable rock suites and possible mantle sources

Comparable Upper Devonian to Lower Carboniferous bimodal volcanic suites occur within the Maritimes Basin in Nova Scotia (western Cape Breton Island~~,~~; Antigonish Highlands~~,~~ and Cobequid Highlands) and~~,~~ southern New Brunswick ~~and Magdalen Islands~~ (e.g., Dostal et al., 1983~~; Barr et al., 1985; Fyffe and Barr, 1986~~; Keppie and Dostal, 1980; Keppie et al., 1997; ~~LaFlèche et al., 1998;~~ Pe-Piper and Piper, 1998). The basaltic rocks are rift-related, mainly fractionated continental tholeiites. In these basaltic rocks, $\varepsilon_{Nd(T)}$ values are variable, ranging from +2.2 to +5.2 (Keppie et al., 1997; Pe-Piper and Piper, 1998). The basalts are considered to be derived from the SCLM (Pe-Piper and Piper, 1998).

To evaluate lithospheric mantle sources in the area, as well as the changes that they underwent during the Carboniferous, we have also determined the Nd isotopic ratios of the Carboniferous trachytes (~335 Ma old) from the Cumberland Hill Formation (Gander Terrane) of southern New Brunswick as these rocks are younger ~~(~~by about 30 M.y.~~)~~ than the bulk of the

Devono-Carboniferous magmatism. These rocks were interpreted to be derived from an alkali basaltic magma by extensive fractional crystallization without being affected by crustal contamination (Gray et al., 2010). Such an origin is also in an agreement with their primitive mantle-normalized plots, in which the rocks do not show any negative Nb-Ta anomalies (Gray et al., 2010). These rocks have higher $\varepsilon_{Nd(T)}$ values (+4.3 to + 3.3) than the basaltic rocks of the Piskahegan Group, but have younger model ages (~0.6 Ga; Table 3).

Model ages, variation ranges of $\varepsilon_{Nd(T),}$ and chemical compositions of the basaltic rocks of the Piskahegan Group, which are similar to those recorded in penecontemporaneous mafic lavas in both Avalonia and Ganderia, can be accounted for by derivation from a subcontinental lithospheric mantle that was locally modified by the upward invasion of enriched (OIB) asthenospheric magma (e.g., Pe-Piper and Piper, 1998). The basaltic magmas extruded due to rapid lithospheric thinning and an associated steepening of the geothermal gradient (e.g., Lynch and Tremblay, 1994; Pe-Piper and Piper, 1998). There does not appear to be a systematic difference between the Avalon and Gander terranes in the isotopic composition of the SCLM during the Late Devonian and the Early Carboniferous, and composition of the SCLM could therefore have been similar beneath both terranes ~~Avalonia and Ganderia~~ in this part of the Appalachians.

6. ~~4~~3. Possible link between mineralization and the development of a subordinate calc-alkaline suite~~Relationship between mineralization and the mafic and intermediate rocks~~

The Upper Devonian to Lower Carboniferous rift-related volcanic suites that onlap the Avalon and Gander terranes along the margin of the Maritimes Basin are mostly bimodal continental tholeiite - rhyolite associations.~~–~~ The Piskahegan Group, which is associated with a significant polymetallic mineralization, differs from the rest of them by the presence of a significant amount of coeval calc-alkaline intermediate rocks.~~–~~ This calc-alkaline suite is interpreted to be the result of AFC processes involving the crustal contamination of a basaltic magma precursor, and of a change from non-oxic to oxidizing conditions accompanied by a relatively high content of magmatic water.~~– As the andesitic rocks contain hornblende indicative of mid-crust crystallization and show a calc-alkaline fractionation trend that is typical of high $P_{(tot)}$ and P_{H2O} conditions, the contamination had to take place at a deeper crustal level (e.g.,~~

~~Osborn, 1959; Zimmer et al., 2010). In addition to amphibole, the calc-alkaline rocks also contain clinopyroxene phenocrysts, which, like those of the basalts, are typical of within plate ("non-orogenic") rocks (Fig. 3).~~

The basalts also display an iron enrichment trend that is typical of low P shallow-seated fractionation that occurs in a non-oxic environment (Osborn, 1959; Zimmer et al., 2010). The calc-alkaline suite had a relatively high magmatic water content and/or high oxidation state, which are considered to be an indication of fertility for many polymetallic ore-bearing felsic and intermediate units (Candela, 1992; Richards, 2011). As rhyolites of the Piskahegan Group are also related to the andesitic rocks (Anderson, 1992; McCutcheon et al., 1997; Dostal et al., 2016b), it can be suggested that the evolution of ~~these~~ these felsic rocks differed from those of other Upper Devonian to Lower Carboniferous bimodal volcanic suites~~, although the isotopic composition of the underlying SCLM was similar~~. The presence of a significant amount of ~~the~~ calc-alkaline volcanic rocks in such bimodal suites could be an indicator of ~~fertility~~potential mineralization.

7. Conclusions

Mafic and intermediate rocks of the Piskahegan Group constitute two distinct associations that are spatially and temporarily related within a Late Paleozoic caldera complex that~~, which~~ hosts a significant polymetallic deposit of tin, tungsten, molybdenum~~, zinc~~, indium and bismuth. The first association includes basalts of the Kleef and Carrow ~~KF and CF~~ formations, whereas the second association encompasses andesites of the South Oromocto Andesite and Scoullar Mountain formations~~SOA and SMF~~. The basalts of the first association are fractionated, rift-related continental tholeiites with high contents of Fe, Ti, P~~,~~ and V, but low Mg, Mg#, Ni and Cr. They display tholeiitic fractionation trends of Fe and Ti enrichment that are characteristic of dry and non-oxic environments. They underwent the main pulse of fractional crystallization at a relatively shallow depth, although the parent magma was generated in the transition zone between spinel and garnet peridotite at a depth of ~70-90 km. The mantle-normalized patterns of the basalts do not show distinct negative Nb-Ta anomalies, and their geochemical characteristics mainly reflect a mantle source without noticeable signs of significant crustal contamination. Rocks of the second association display a typical calc-alkaline

fractionation trend that is characterized by a gradual depletion of Fe and Ti with increasing differentiation, which is indicative of a wet and oxidizing environment. This is also consistent with the absence of a negative Eu anomaly in the REE patterns of these rocks, and with the presence of hornblende in their modal composition. The rocks resulted from the mixing of continental crust material (probably phlogopite/biotite-rich~~water-bearing~~ metasedimentary rocks~~s~~) with primitive basaltic melt, probably at mid-crust level.~~–~~ Although the parent basaltic magmas of both suites could have been derived from the same SCLM source, they underwent separate and different evolution pathways. The Piskahegan Group, which is associated with the Mount Pleasant polymetallic deposit, differs from ~~other~~ penecontemporaneous, non-mineralized bimodal suites that occur along the margins of the Maritimes Basin through New Brunswick and Nova Scotia by the presence of a significant amount of coeval calc-alkaline intermediate rocks. As such rocks evolve in water- and oxygen-rich magmatic environments, their ~~Their~~ presence may be considered to be an indicator of potential mineralization~~fertility~~. ~~The isotopic composition of the SCLM beneath the Avalon and Gander terranes of the Northern Appalachians in Atlantic Canada did not show significant differences during the Late Devonian and the Early Carboniferous.~~

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Captions to Figures

Figure 1. A - Map of a part of Atlantic Canada that shows the western boundary of the Maritimes Basin and the location of the Harvey and Piskahegan groups (black fields). B - Simplified geological map of the southwestern part of the MarysvilleFredericton sub-basin and its surroundings (modified from Smith, 2006, and Smith and Fyffe, 2006) showing the location of Figure 2. The insert (map of Canada) shows the location of Figure 1A.

Figure 2. Geology of the Mount Pleasant Caldera Complex and its surroundings (modified from McCutcheon et al. 2010, and and Thorne et al., 2013). Late Devonian caldera complex includes Late caldera-fill sequence, Subvolcanic intrusive rocks, Intracaldera and Exocaldera sequences while the Piskahegan Group encompasses Late caldera-fill, Intracaldera and Exocaldera sequences.

Figure 3. The (Ti + Cr) versus Ca (number of cations per six oxygens) discrimination diagram of Leterrier et al. (1982) comparing the composition of clinopyroxenes from the intermediate rocks of the Piskahegan Group with compositional fields for clinopyroxenes from nonorogenic and orogenic rocks. Each value (Table 1) is an average composition of a number of analyzed crystals, and composition of each crystal is an average of 4 analyses (Table 1).

Figure 4. Variations of $FeO_{(tot)}$, and TiO_2 (wt.%) and various element ratios versus SiO_2 (wt.%) in the basaltic and andesitic rocks of the Piskahegan Group. Association 1 - basalt: Carrow Formation (CF), Kleef Formation (KF); Association 2 - andesite: South Oromocto Andesite Formation (SOA); Scoullar Mountain Formation (SMF). In A and B, the vectors show calc-alkaline and tholeiitic trends whereas E and F show vectors for crustal contamination (cc) and fractional crystallization (fc).

Figure 5. The Zr/TiO_2 versus Nb/Y discrimination diagram of Winchester and Floyd (1977) for mafic and intermediate rocks of the Piskahegan Group. Alk-Bas - alkali basalt; TrachAnd - trachyandesite. Association 1 - basalt: Carrow Formation (CF), Kleef Formation (KF);

Association 2 - andesite: South Oromocto Andesite (SOA); Scoullar Mountain Formation (SMF).

Figure 6. AFM diagram (A = $Na_2O + K_2O$, F = total Fe as FeO, M = MgO) for analyzed mafic and intermediate volcanic rocks from the Piskahegan Group. The solid line is the boundary between tholeiitic and calc-alkaline fields after Irvine and Baragar (1971); Association 1 (basalts): Carrow Formation (CF), Kleef Formation (KF); Association 2 (andesites): South Oromocto Andesites (SOA), Scoullar Mountain Formation (SMF).

Figure 7. Chondrite-normalized REE patterns for basaltic and andesitic rocks of the Piskahegan Group. A- Range of basalts from the Carrow Formation; B - Range of basalts from the Kleef Formation; C - Range of andesites from the South Oromocto Andesite Formation; D - range of andesites from the Scoullar Mountain Formation. Normalizing values are after Sun and McDonough (1989).

Figure 8. Primitive mantle-normalized multielement patterns ~~of~~ in basaltic and andesitic rocks of the Piskahegan Group. A - Basalts of the Carrow Formation; B - basalts of the Kleef Formation; C- andesites of the South Oromocto Andesite Formation; D- andesites of the Scoullar Mountain Formation. Normalizing values are after Sun and McDonough (1989).

Figure 9. ~~The~~ Th-Hf-Ta tectonic discrimination diagram of Wood (1980) for mafic and intermediate volcanic rocks of the Piskahegan Group. Fields: N-MORB - normal, depleted mid-ocean ridge basalt; E-MORB/WPT - enriched mid-ocean ridge basalt and within-plate tholeiite; Alk WPB - alkaline within-plate basalt; CAB - calc-alkaline volcanic arc basalts; ATB - volcanic arc tholeiites; CC (star) - average continental crust composition of Taylor and McLennan (1985). Note that the trend of the Piskahegan rocks is suggestive of a mixing between basaltic magma and crustal material.

Figure 10. $\varepsilon_{Nd(t)}$ versus time plot comparing Sm-Nd isotopic data of the Piskahegan basalts and andesites and the Carboniferous Cumberland Hill trachytes with a compilation of Sm-Nd isotopic data for the Upper Devonian-Lower Carboniferous volcanic rocks of the Maritimes Basin and the Avalon Terrane (Keppie et al., 1997, ~~and~~ Pe-Piper and Piper, 1998). ~~–~~ The shaded area is the Avalonian basement and the SCLM (after Murphy et al., 2011b, Dostal et al., 2016a~~5; Murphy et al., 2011a~~). ~~–~~ The field for Mesoproterozoic rocks is from Murphy et al. (2008). Bars show a range of samples.

Figure 11. ~~The~~ Th/Yb versus Nb/Yb diagram of Pearce (2008) for Piskahegan basalts and andesites. Vectors indicate the influence of a subduction component (S), within-plate enrichment (W), crustal contamination (C), and fractional crystallization (FC); N-MORB- N-type mid-ocean ridge basalt; E-MORB- enriched mid-ocean ridge basalt; OIB-ocean island basalt (after Sun and McDonough, 1989). The star (CC) is the average of continental crust (Taylor and McLennan, 1985).

Figure 12.~~–~~ $(Tb/Yb)_n$ versus $(La/Sm)_n$ diagram for the Piskahegan basalts and andesites. The values are normalized to the primitive mantle after Sun and McDonough (1989). The solid line separating the range of magmas formed by the melting of spinel peridotite mantle from that of magmas formed by the melting of garnet peridotite mantle is after Wang et al. (2002). Vector D indicates an increase of melting depth whereas the vector M depicts an increase in the~~of~~ degree of partial melting. The limited range of ~~the~~ $(Tb/Yb)_n$ values for the basalts indicates a similar mantle source. The higher $(La/Sm)_n$ ratios of the calc-alkaline rocks is more suggestive of crustal contamination than of changes in the magma source region. The E-MORB (enriched mid-ocean ridge basalt) and OIB (ocean island basalt) are after Sun and McDonough (1989).

Figure 13. $(Nb/Th)_n$ versus $(Th/Yb)_n$ diagram for the Piskahegan basalts and andesites. The ratios are normalized to the primitive mantle values of Sun and McDonough (1989). N-MORB and E-MORB compositions are from Sun and McDonough (1989). CC (star) - average continental crust (Taylor and McLennan, 1985). Note that the very distinct trend (the solid curve is a mixing curve) of the Piskahegan rocks is suggestive of a mixing between parental basaltic magmas and crustal material, indicating that the andesitic magma assimilated significant amounts of crustal material prior to its emplacement.

Figure 14. Th/La versus $\varepsilon_{Nd(T)}$~~–~~ plot for the Piskahegan basalts and andesites. An increase of the Th/La ratio accompanied by a decrease of $\varepsilon_{Nd(T)}$ is indicative of a crustal contamination of the basaltic magmas. CC (star) - average continental crust composition (Taylor and McLennan, 1985). The solid triangles are ~~the~~ data from~~of the~~ Anderson (1992) for the Piskahegan basaltic and andesitic rocks.

Tables

Table 1. Chemical composition and structural formulas of clinopyroxene in andesites of the Piskahegan Group

Table 2. Major and trace element compositions ~~of~~ in the mafic and intermediate rocks of the Piskahegan Group

Table 3. Sm-Nd isotopic data for volcanic rocks of the Piskahegan Group and Cumberland Hill Formation

Figure 1

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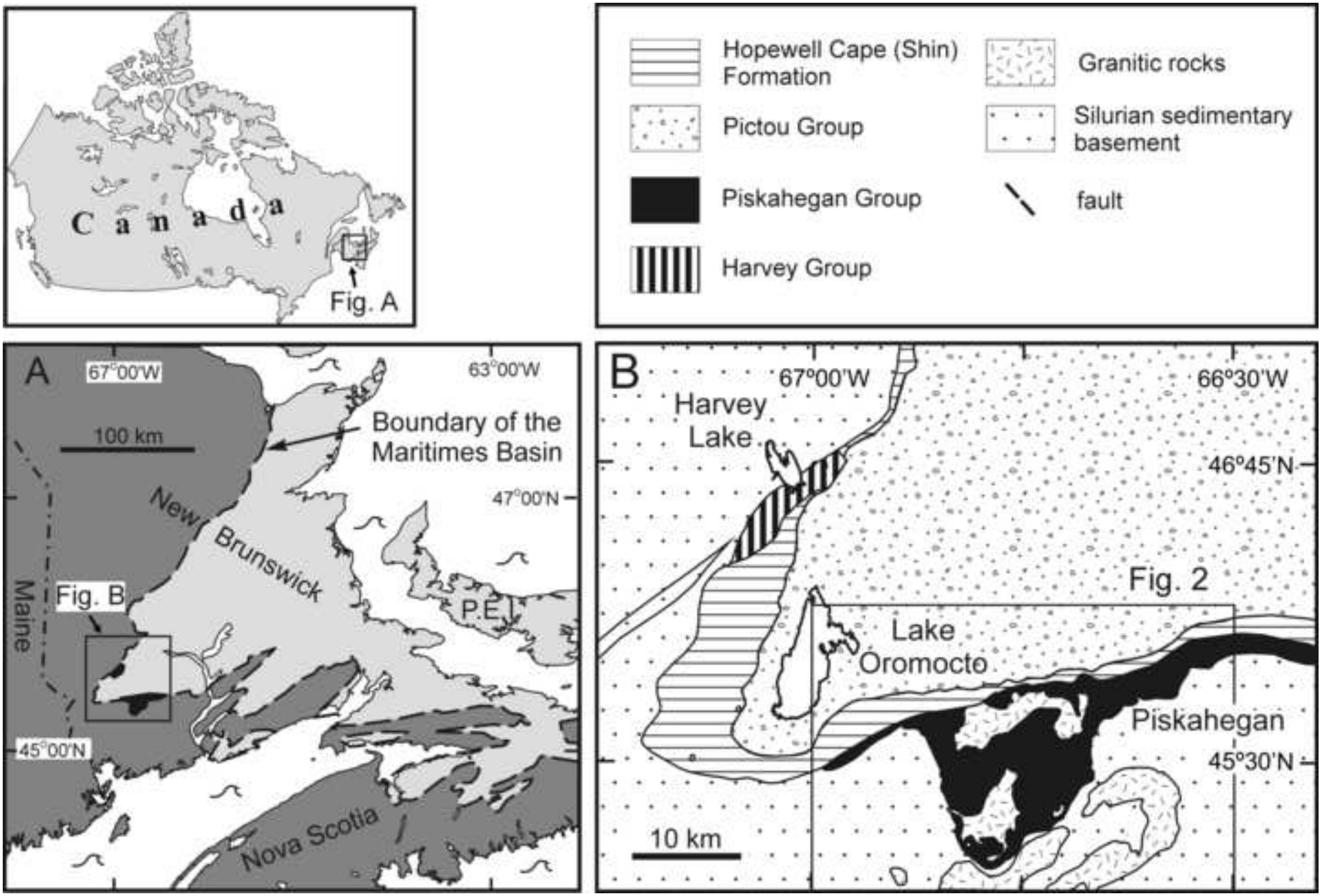

Figure 2

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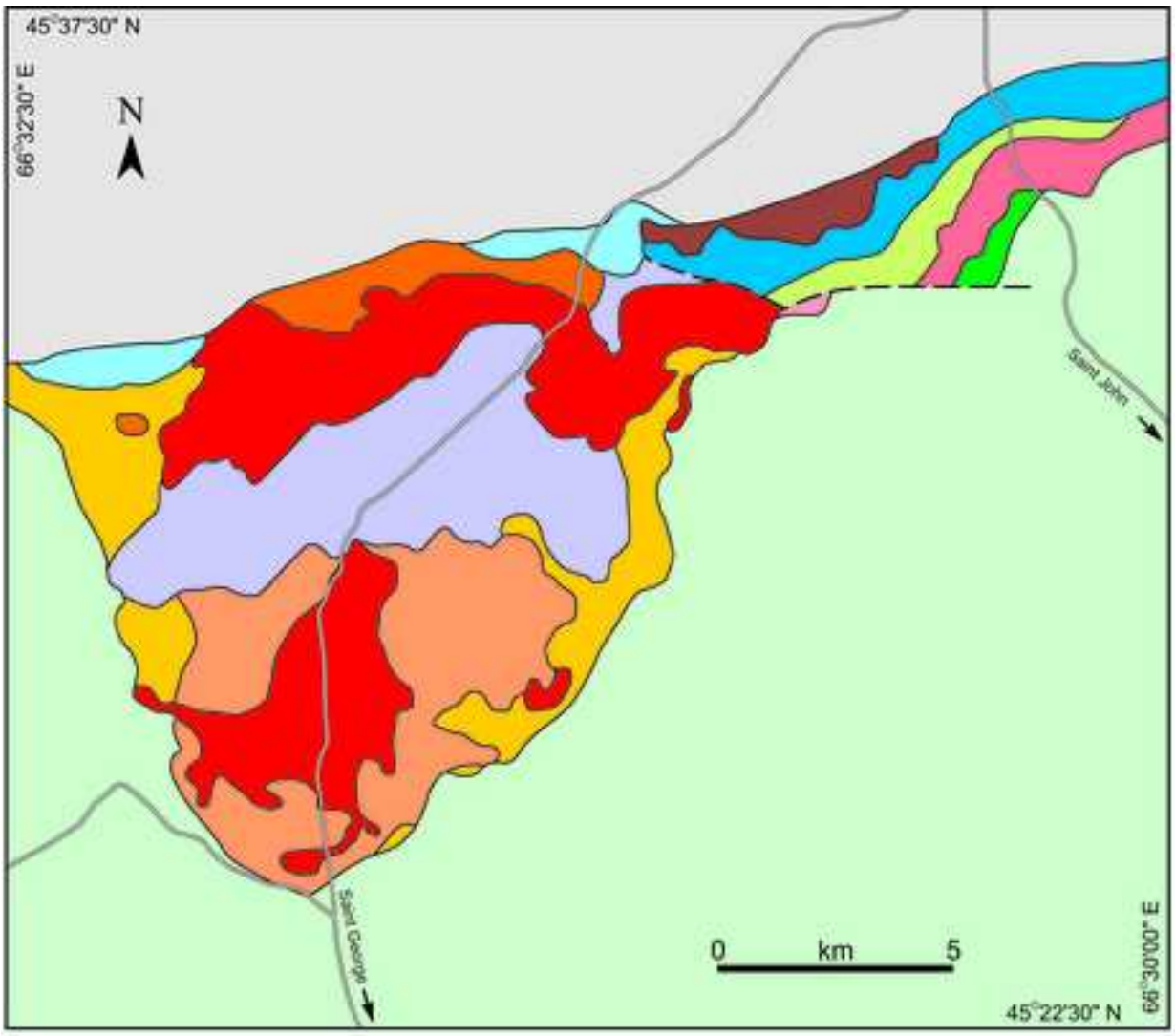

CARBONIFEROUS

sedimentary rocks

LATE DEVONIAN

Late Caldera - Fill Sequence

Kleef Formation

Big Scott Mountain Formation

Subvolcanic Intrusive Rocks

McDougall Brook Granite Suite

Intracaldera Sequence

Seelys Formation

Little Mount Pleasant Formation

Scoullar Mountain Formation

Exocaldera Sequence

Bailey Rock Rhyolite

Carrow Formation

South Oromocto Andesite

Rothea Formation

Hoyt Station Basalt

ORDOVICIAN - LATE SILURIAN

Pre-caldera rocks

Figure 3
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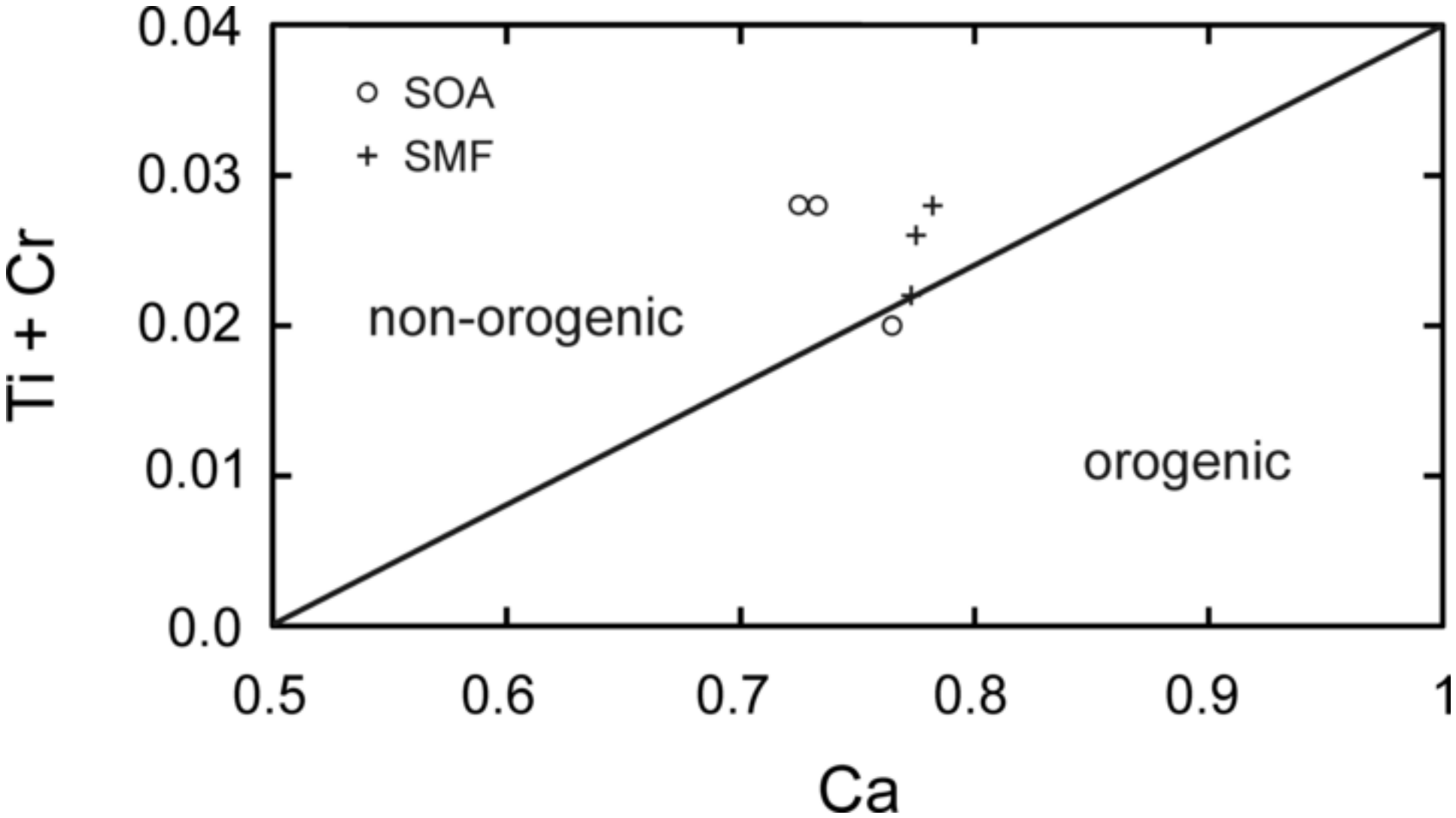

Figure 4

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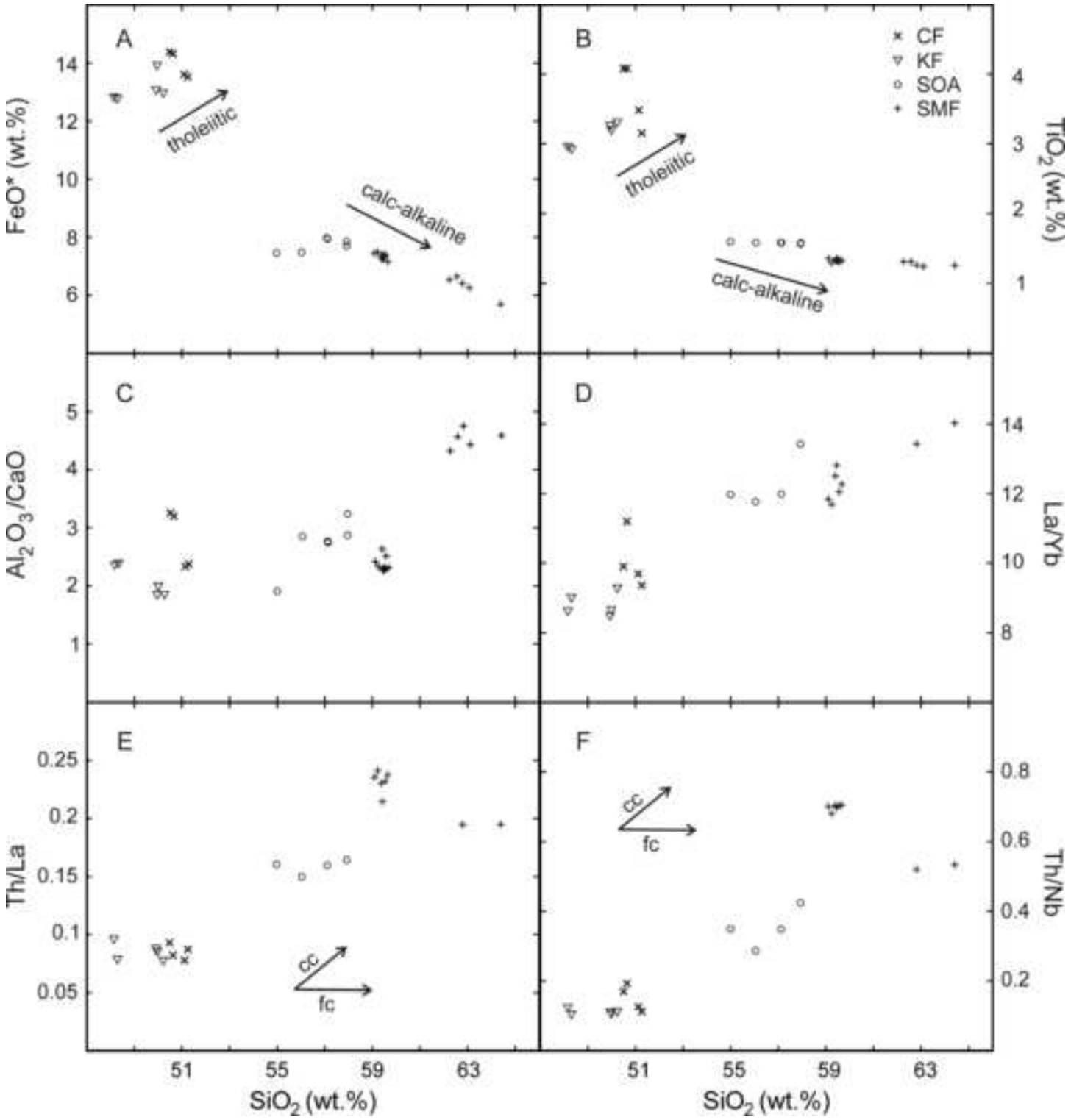

Figure 5

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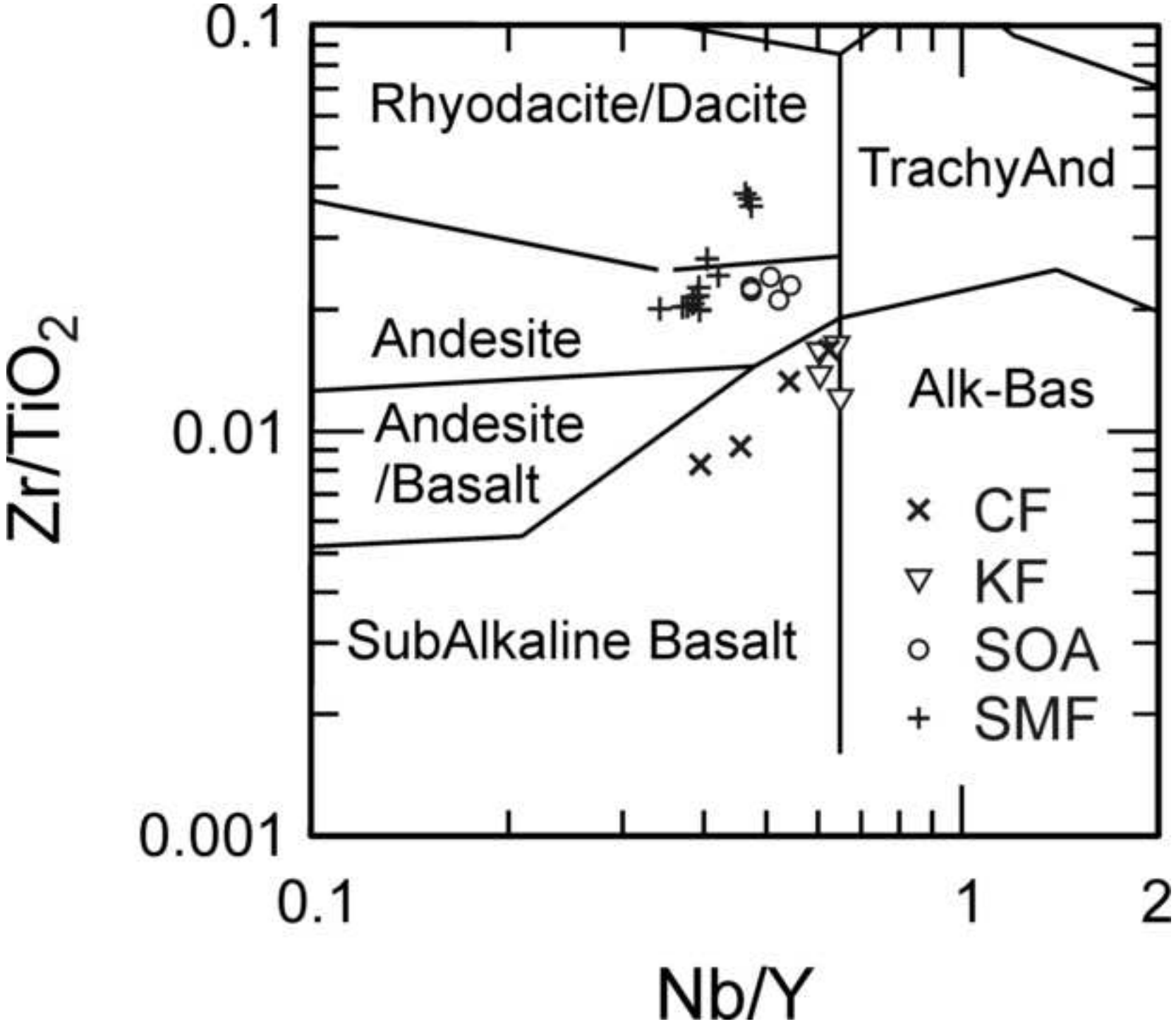

Figure 6

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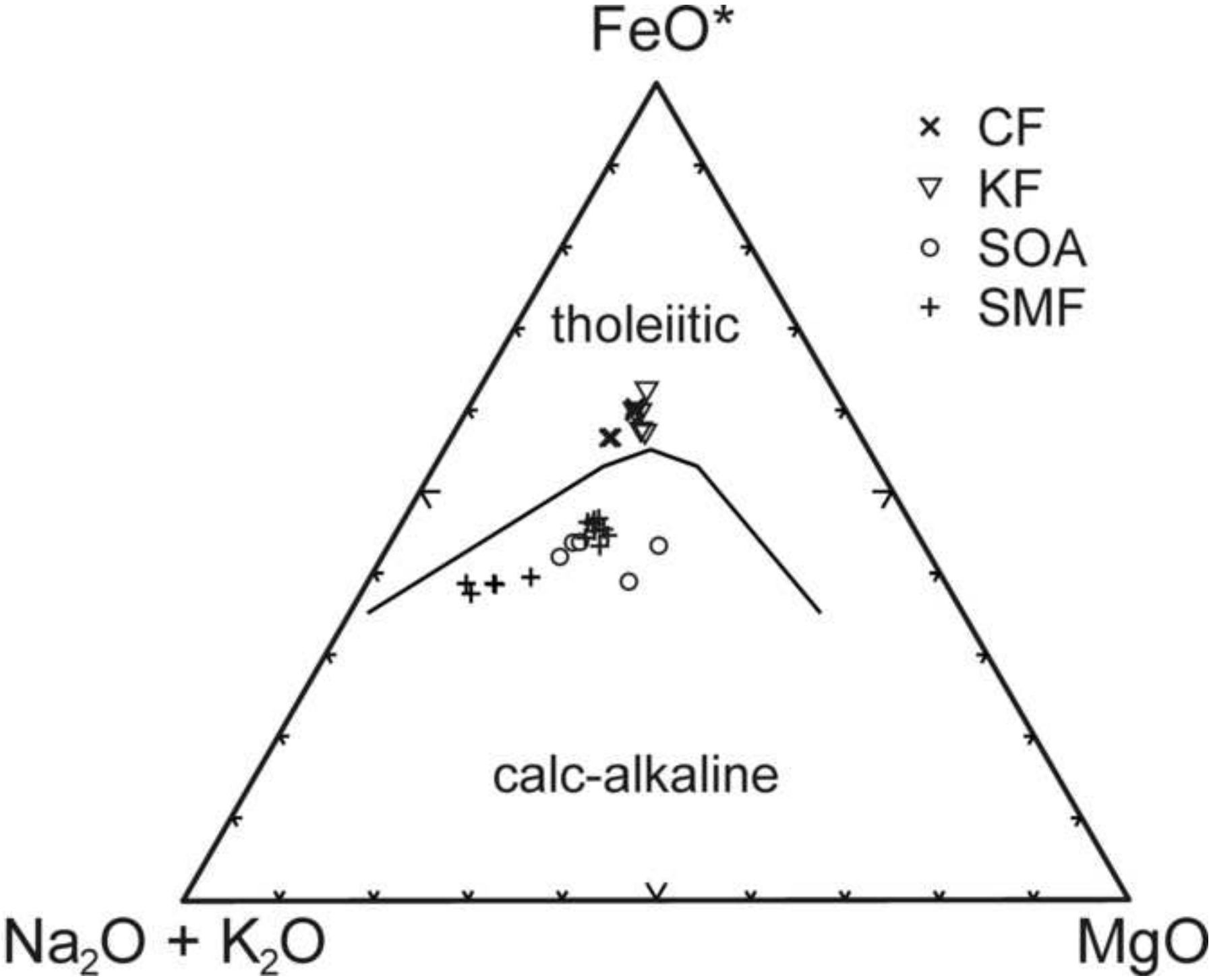

Figure 7

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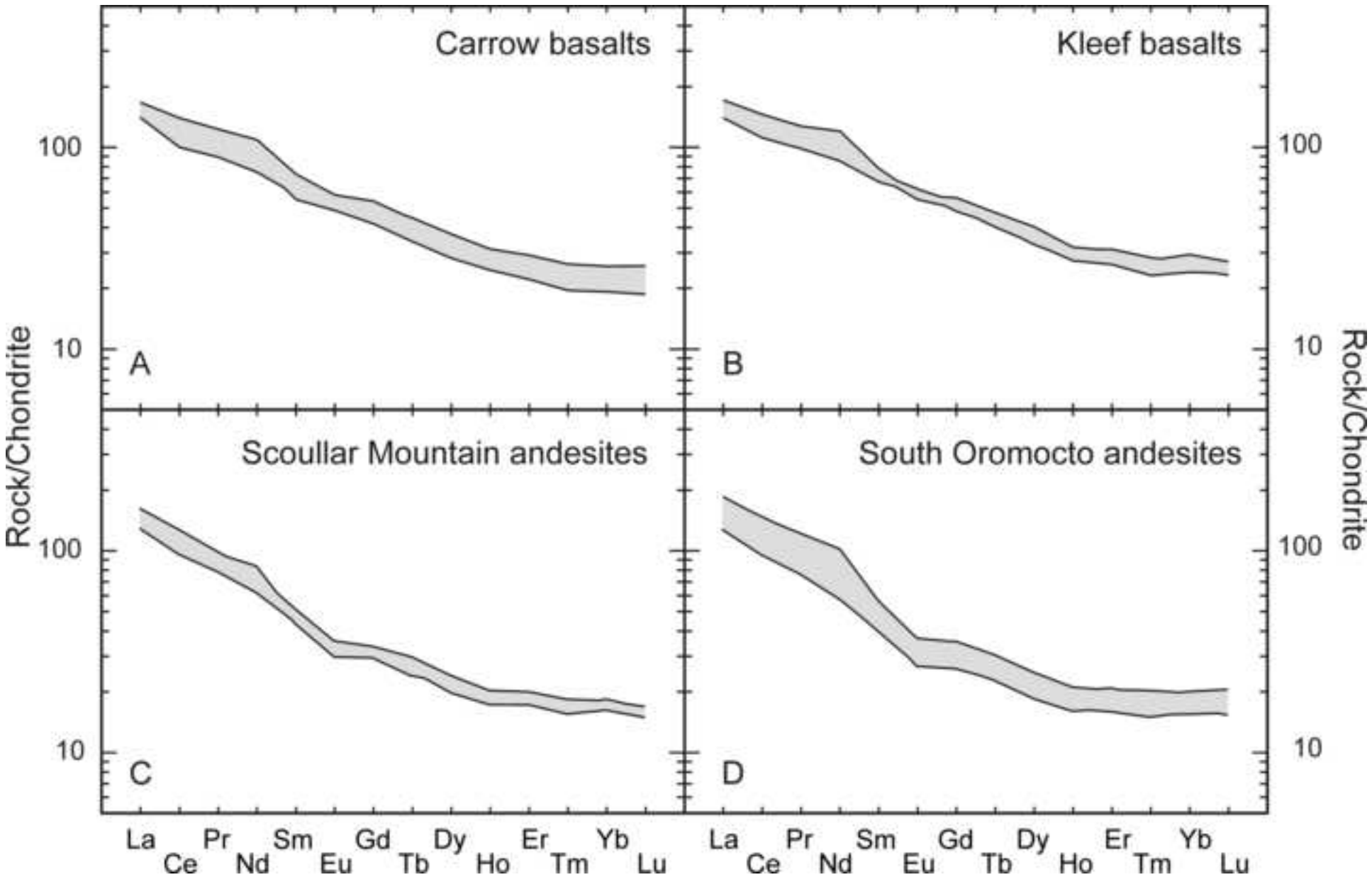

Figure 8

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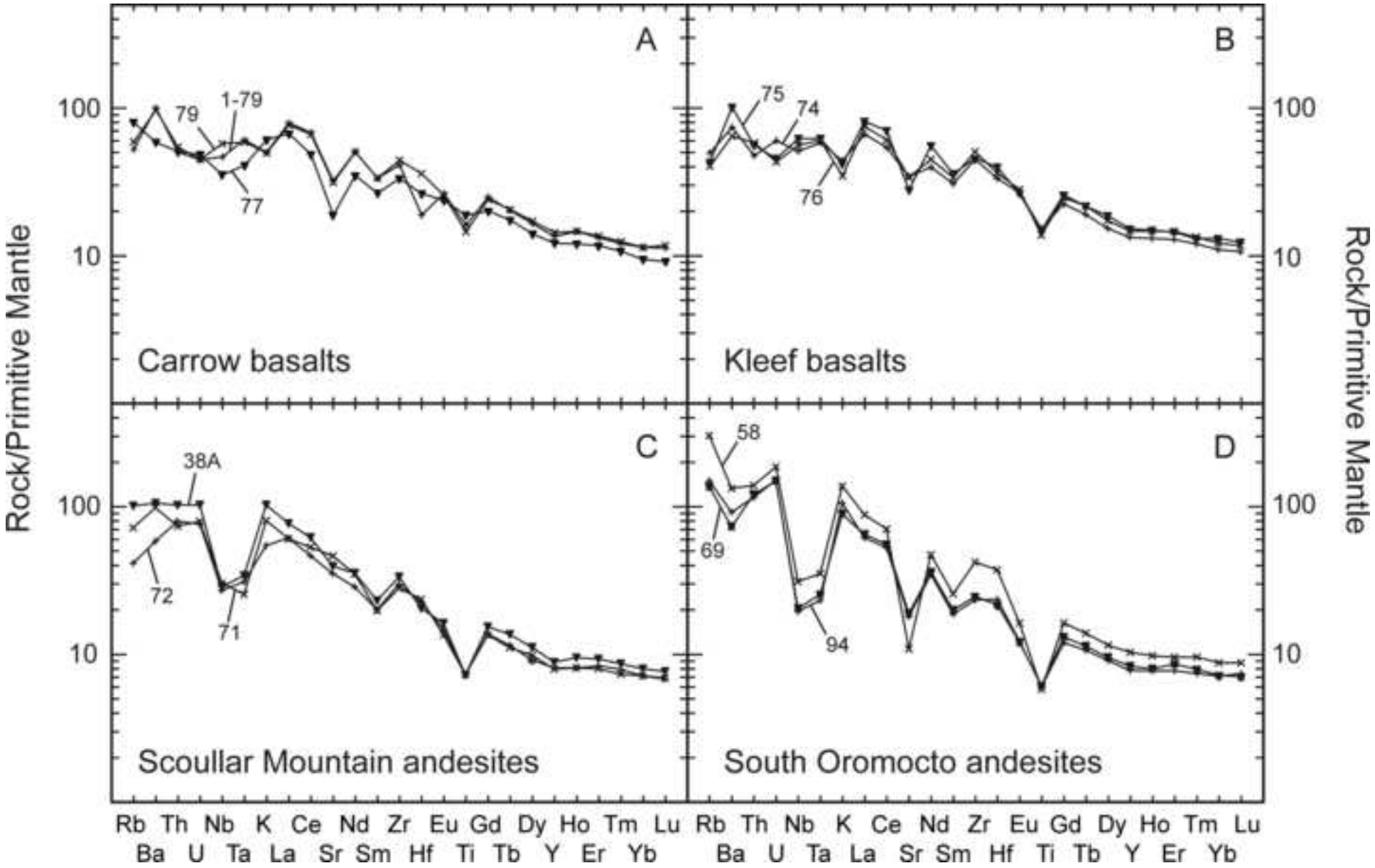

Figure 9

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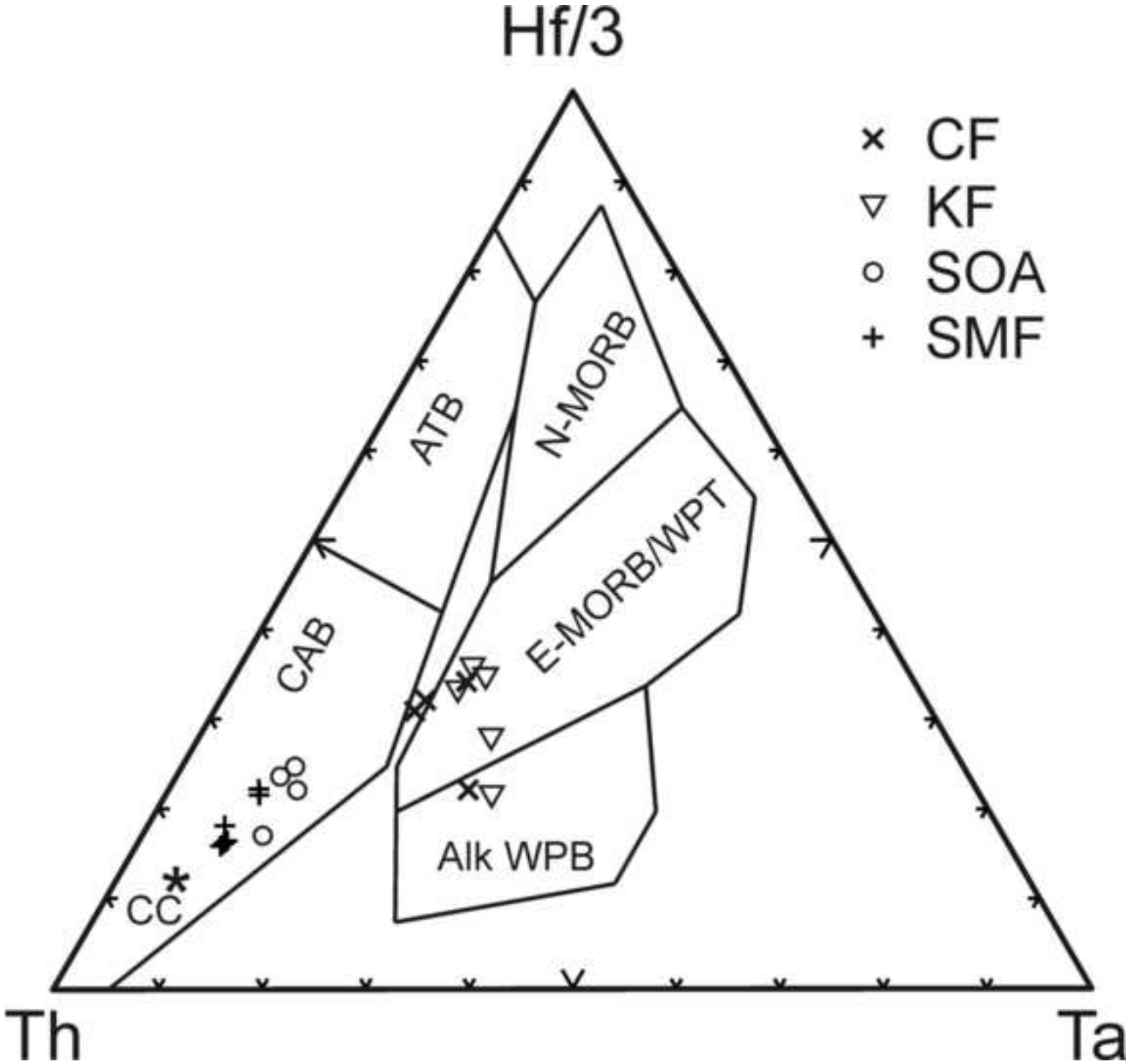

Figure 10

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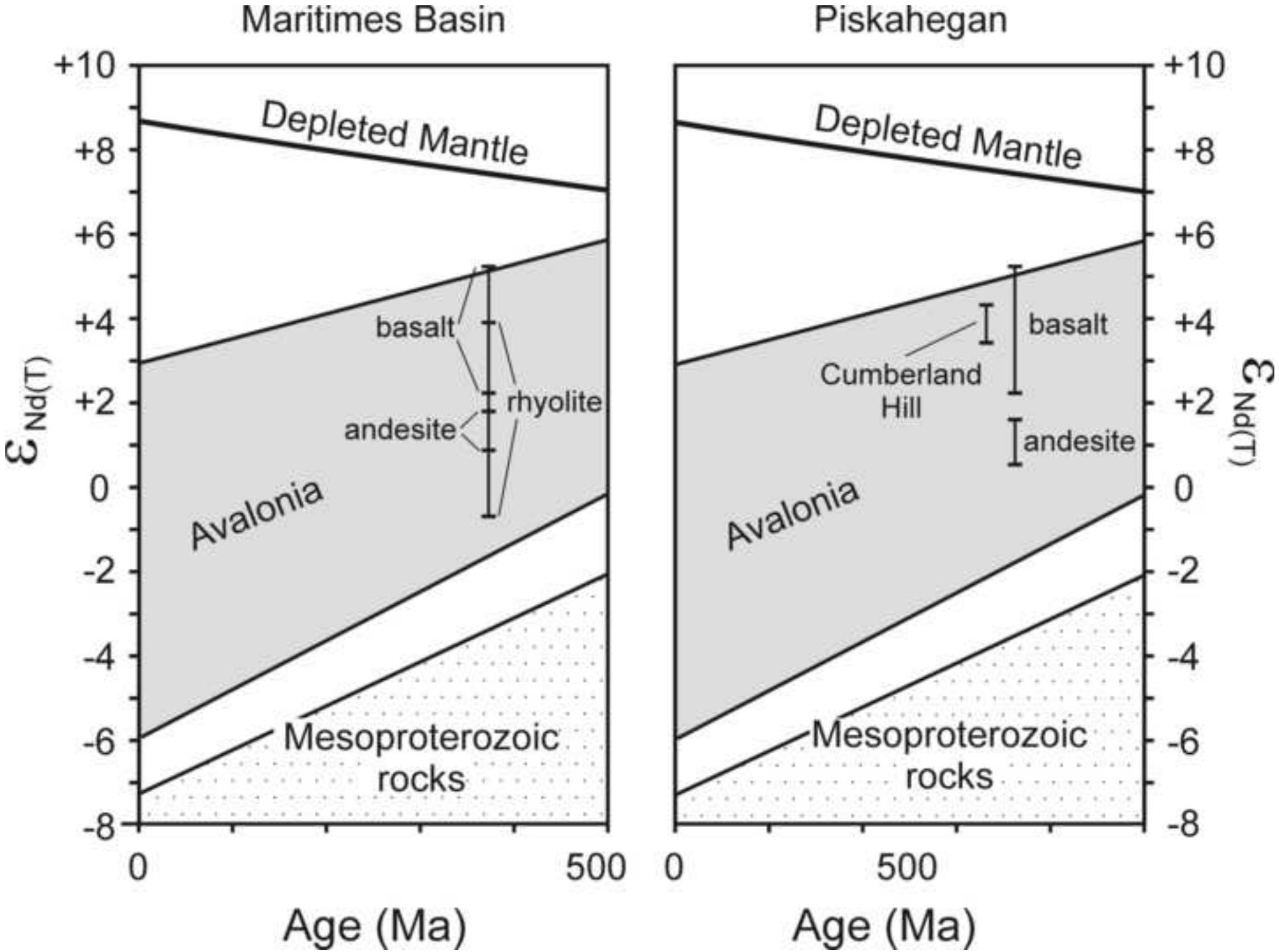

Figure 11

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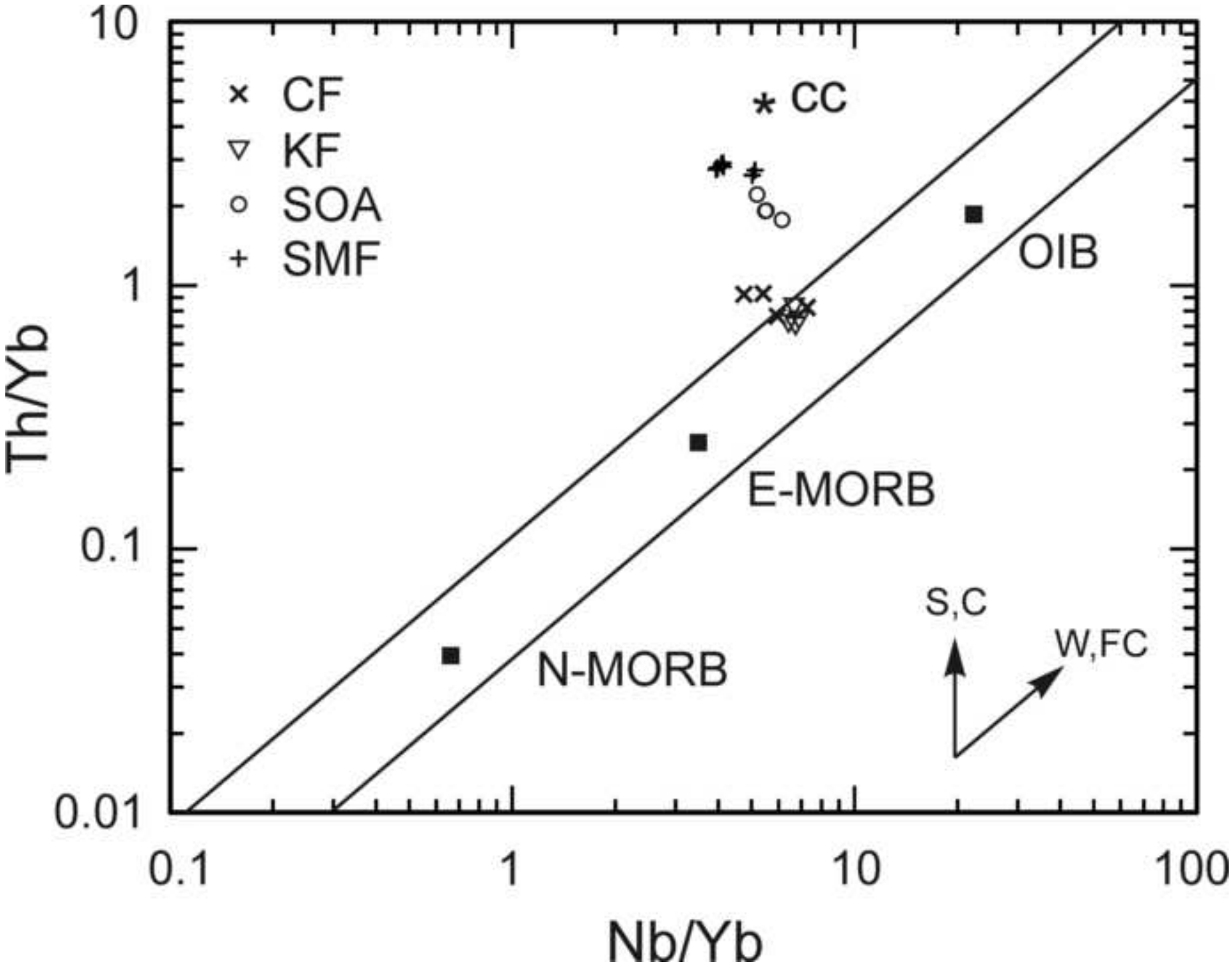

Figure 12

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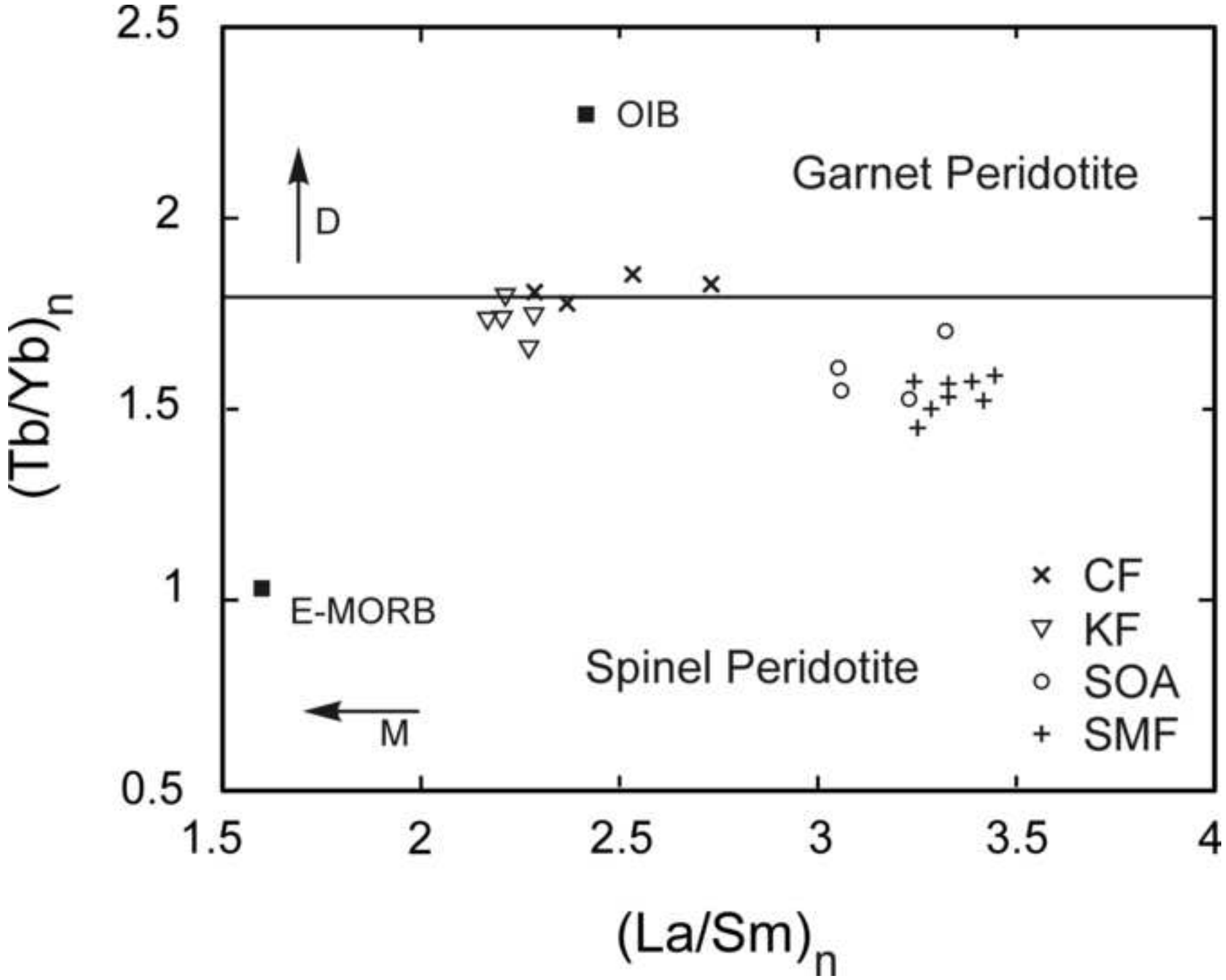

Figure 13

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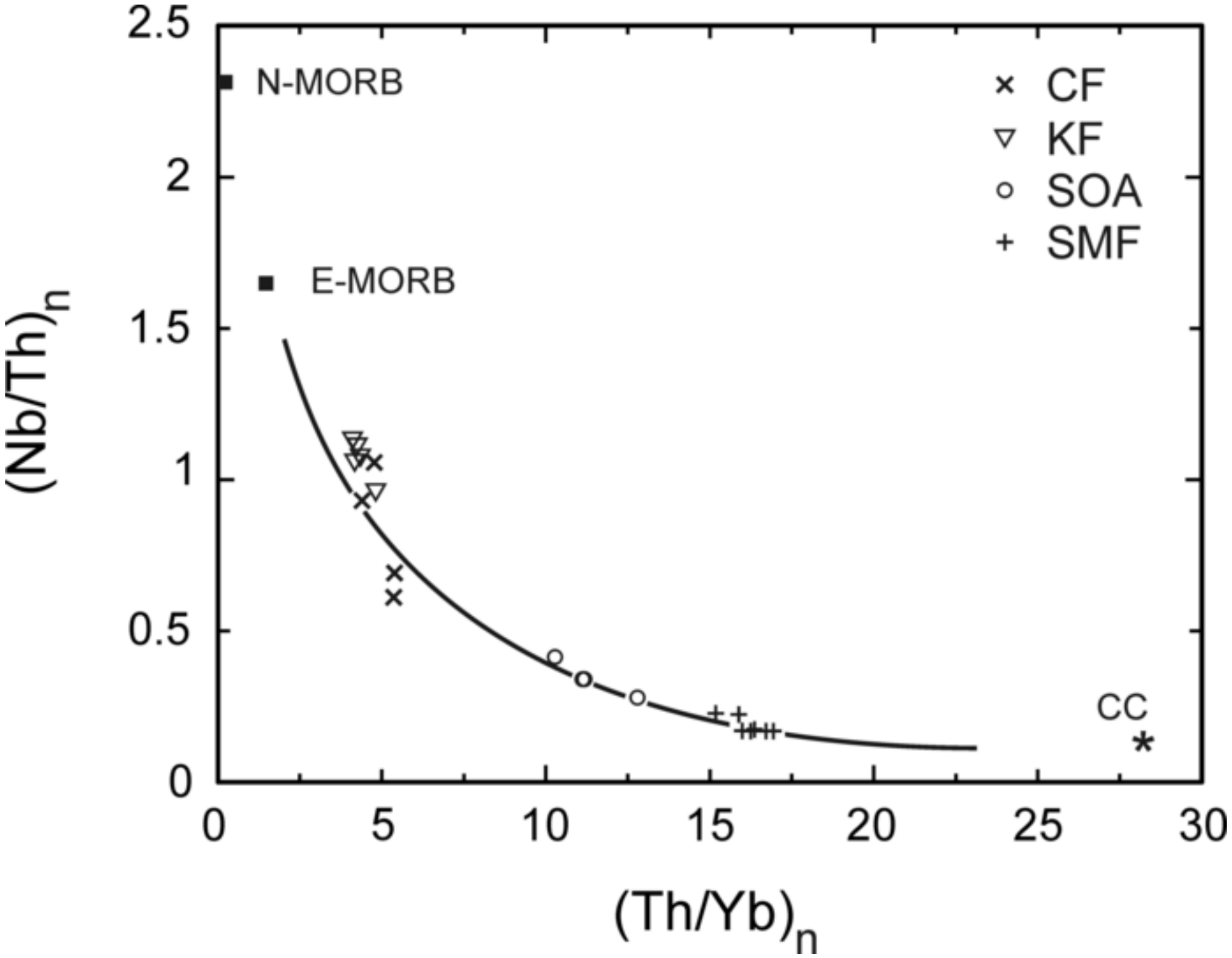

Figure 14

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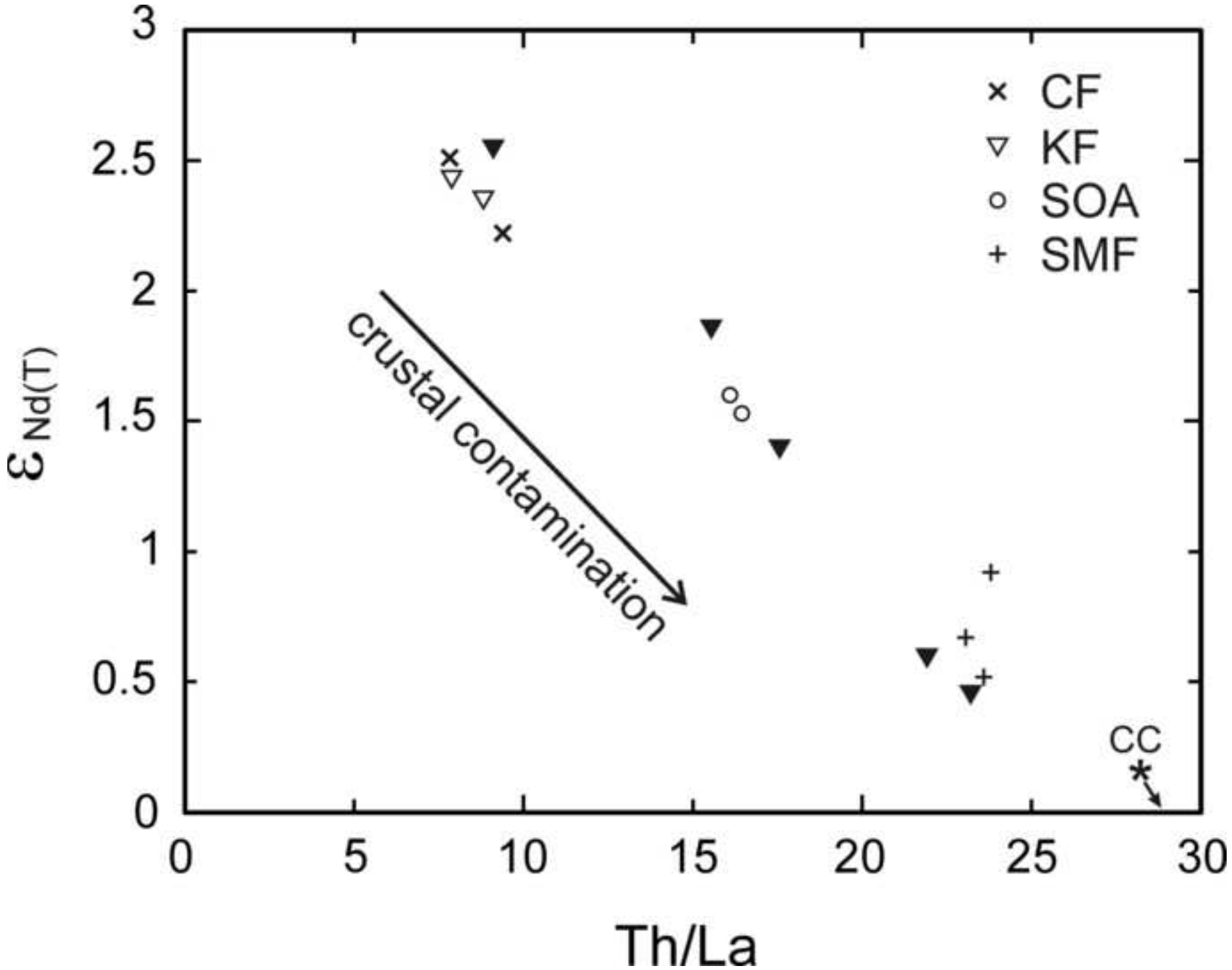

Table 1

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Table 1. Composition and structural formulas of clinopyroxene from andesites of the Piskahegan Group

	South Oromocto Andesite						Scoullar Mountain Formation					
	38A		38B		38C		68		69		92	
(wt.%)	average	sd	average	s.d.	average	s.d.	average	s.d.	average	s.d.	average	s.d.
SiO_2	50.40	0.49	50.54	0.50	50.89	1.02	51.02	0.39	51.00	0.32	51.09	0.31
TiO_2	0.87	0.10	0.65	0.15	0.64	0.22	0.71	0.11	0.70	0.10	0.70	0.15
Al_2O_3	2.79	1.79	3.51	0.26	2.20	1.16	2.04	0.34	2.31	0.42	1.84	0.44
Cr_2O_3	0.09	0.07	0.35	0.24	0.08	0.07	0.21	0.20	0.26	0.15	0.08	0.15
FeO^t	10.75	1.00	8.08	2.20	9.65	1.32	9.50	1.90	8.62	0.78	10.75	1.69
MnO	0.31	0.02	0.20	0.09	0.30	0.07	0.26	0.06	0.25	0.04	0.29	0.07
MgO	15.05	1.29	15.84	1.02	15.76	0.75	15.87	0.80	16.07	0.51	15.03	1.03
NiO	0.02	0.02	0.03	0.01			0.01	0.01	0.01	0.01	0.03	0.02
CaO	18.01	1.30	19.43	0.91	19.13	0.74	19.40	0.57	19.59	0.22	19.22	0.51
Na_2O	0.53	0.52	0.46	0.09	0.39	0.11	0.27	0.02	0.26	0.02	0.27	0.02
K_2O	0.05	0.05	0.02	0.01	0.02	0.00	0.02	0.01	0.02	0.01	0.02	0.02
∑	98.86		99.11		99.06		99.31		99.08		99.32	
n	7		10		11		16		16		21	
Si	1.893		1.877		1.900		1.902		1.901		1.917	
Ti	0.025		0.018		0.018		0.020		0.020		0.020	
Al	0.124		0.154		0.097		0.089		0.101		0.081	
Fe^{3+}	0.079		0.080		0.094		0.081		0.070		0.064	
Cr^{3+}	0.003		0.010		0.002		0.006		0.008		0.002	
Fe^{2+}	0.259		0.172		0.208		0.215		0.199		0.273	
Mn	0.010		0.006		0.010		0.008		0.008		0.009	
Mg	0.843		0.877		0.877		0.882		0.893		0.840	
Ca	0.725		0.773		0.765		0.775		0.782		0.773	
Na	0.039		0.033		0.028		0.020		0.018		0.020	
K	0.002		0.001		0.001		0.001		0.010		0.001	
∑	4.00		4.00		4.00		4.00		4.01		4.00	
Wo	39.69		42.44		41.37		41.39		41.74		40.97	
En	46.14		48.15		47.40		47.13		47.65		44.55	
Fs	14.17		9.42		11.22		11.48		10.61		14.48	

n = number of crystals; each crystal had four analyses; average is the arithmatic mean; s.d. = standard deviation; formulas based upon 6 oxygens; End-member components: Wo - wollastonite; En - enstatite; Fs - ferrosilite; FeO^t - total Fe as FeO

Table 2 a

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Table 2. Major and trace element compostions of mafic and intermediate rocks of the Piskahegan Group

	Carrow Formation				Kleef Formation				
Sample #	77	79	1-77	1-79	74	75	76	1-74	1-76
SiO_2 (wt.%)	47.64	48.87	47.93	49.08	47.87	47.57	45.45	48.09	45.60
TiO_2	3.85	3.00	3.86	3.34	3.12	3.04	2.79	3.16	2.76
Al_2O_3	13.77	14.41	13.76	14.36	14.65	14.53	16.49	14.58	16.65
FeO*	13.55	12.88	13.54	13.06	12.51	13.23	12.07	12.39	12.03
MnO	0.16	0.24	0.17	0.24	0.18	0.28	0.26	0.17	0.26
MgO	4.12	3.88	4.01	3.85	3.92	3.82	4.33	3.75	4.17
CaO	4.24	6.08	4.31	6.18	7.99	7.35	7.03	7.95	7.02
Na_2O	4.59	3.40	4.62	3.35	3.33	3.03	3.81	3.33	3.81
K_2O	1.74	1.43	1.80	1.45	1.26	1.18	0.98	1.31	1.00
P_2O_5	0.68	1.13	0.65	1.09	1.01	1.13	1.14	0.98	1.07
LOI	4.00	3.40	3.50	2.61	2.40	3.50	4.20	2.14	3.79
∑	98.34	98.72	98.15	98.61	98.24	98.66	98.55	97.86	98.16
Mg #	0.35	0.35	0.35	0.34	0.36	0.34	0.39	0.35	0.38
Cr (ppm)	0	8	30	30	19	6	6	40	30
Ni	16	16	60	60	21	17	18	60	30
Co	50	31	40	27	30	32	29	29	29
V	393	204	421	208	247	205	196	247	192
Pb	34	3	31	12	13	12	30	9	36
Zn	417	160	420	170	146	162	153	160	160
Rb	48	36	42	32	30	26	24	28	23
Ba	386	645	447	670	493	672	422	529	472
Sr	374	630	387	649	691	555	672	714	701
Ga	23	22	24	23	21	21	22	23	26
Ta	1.58	2.30	1.50	2.40	2.27	2.40	2.32	2.30	2.60
Nb	23.7	39.0	19.0	32.0	34.7	42.0	37.4	32.0	37.0
Hf	7.7	10.6	7.5	5.6	9.8	11.6	10.5	6.9	5.4
Zr	352	474	319	443	478	484	531	426	325
Y	52	62	48	59	57	66	63	53	57
Th	4.08	4.40	3.70	4.10	3.85	4.50	4.65	3.60	3.90
U	0.96	0.90	0.90	0.90	1.20	0.90	0.85	1.20	0.90
La	43.5	50.2	44.8	52.4	43.6	52.7	48.3	46.4	49.5
Ce	81.6	112	90.5	116	91.6	118	101	105	112
Pr	11.0	14.7	12.1	15.3	12.1	15.6	13.4	13.8	14.3
Nd	44.7	64.8	50.4	65.5	51.2	71.2	56.9	58.3	60.8
Sm	11.1	14.2	10.6	14.3	13.0	15.0	14.1	13.6	14.0
Eu	3.77	4.11	3.54	4.26	4.29	4.19	4.42	4.03	4.01
Gd	11.3	13.6	10.9	14.3	12.7	14.5	13.8	13.0	13.9
Tb	1.78	2.12	1.60	2.10	1.95	2.21	2.20	1.90	2.10
Dy	9.77	12.1	9.10	11.7	10.7	12.9	11.9	10.8	11.9
Ho	1.86	2.29	1.80	2.30	2.04	2.30	2.25	2.00	2.20
Er	5.31	6.24	4.70	6.10	5.87	6.53	6.54	5.60	6.10
Tm	0.75	0.88	0.65	0.86	0.84	0.91	0.93	0.77	0.87
Yb	4.39	5.36	4.00	5.40	5.14	6.09	5.60	5.00	5.50
Lu	0.64	0.83	0.60	0.80	0.75	0.86	0.81	0.76	0.80

FeO* - total Fe as FeO; LOI - loss on ignition; Mg# = MgO/(MgO+FeO*) mol%; major element oxides are not recalculated to 100%

Table 2 b

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Table 2 cont. Major and trace element compostions of mafic and intermediate rocks of the Piskahegan Group

	South Oromocto andesite				Scoullar Mountain Formation							
Sample #	71	72	38-C	38A	56	58	1-60	61	68	69	94	96
SiO_2 (wt.%)	53.73	52.37	55.15	55.91	56.65	56.33	56.54	55.60	57.12	56.74	62.51	60.21
TiO_2	1.52	1.52	1.53	1.51	1.26	1.24	1.28	1.28	1.25	1.27	1.22	1.21
Al_2O_3	15.91	15.94	15.85	15.70	15.02	14.91	15.30	15.06	14.88	15.16	14.76	14.85
FeO*	7.16	7.10	7.67	7.57	6.80	6.99	6.87	7.00	7.22	6.98	5.51	6.15
MnO	0.16	0.17	0.14	0.14	0.13	0.12	0.13	0.12	0.14	0.12	0.11	0.13
MgO	5.12	4.70	3.43	3.46	3.17	3.57	2.95	3.38	3.34	3.64	1.74	2.16
CaO	5.60	8.36	5.78	5.48	6.51	5.95	6.67	6.25	6.40	5.77	3.22	3.13
Na_2O	3.84	3.03	3.48	3.24	2.17	2.15	2.06	1.92	3.20	2.98	3.47	3.86
K_2O	2.33	1.57	3.01	2.99	2.94	3.00	3.02	3.15	2.57	2.56	4.03	3.73
P_2O_5	0.49	0.49	0.50	0.50	0.30	0.30	0.28	0.31	0.30	0.31	0.47	0.44
LOI	3.20	3.80	3.00	2.70	4.80	4.80	4.51	5.40	2.10	2.80	1.00	2.70
∑	99.06	99.04	99.54	99.20	99.74	99.37	99.62	99.47	98.51	98.33	98.05	98.56
Mg #	0.56	0.54	0.44	0.45	0.45	0.48	0.43	0.46	0.45	0.48	0.36	0.39
Cr (ppm)	58	61	24	21	75	81	90	70	88	64	19	26
Ni	42	38	20	24	15	15	30	22	28	15	7	8
Co	24	24	26	20	27	24	21	26	25	22	15	13
V	162	163	145	140	163	147	166	161	155	154	91	98
Pb	0	8	4	13	12	17	18	12	12	12	18	17
Zn	95	92	95	95	78	79	80	78	81	79	88	91
Rb	44	25	65	62	79	90	74	100	82	83	187	151
Ba	659	388	751	713	556	606	606	599	476	489	901	899
Sr	936	707	835	805	346	359	356	322	409	381	223	360
Ga	17	19	20	17	17	18	18	20	19	17	17	18
Ta	1.00	1.21	1.10	1.35	0.99	0.90	1.00	1.02	1.01	1.00	1.40	1.40
Nb	20.8	18.4	21.2	19.7	13.3	13.2	13.0	13.4	14.2	13.9	21.5	21.1
Hf	7.0	6.6	8.0	6.1	6.1	6.9	6.1	6.1	6.2	6.4	11.2	10.4
Zr	300	319	348	362	272	248	255	272	282	263	458	434
Y	35	35	39	39	34	34	33	35	36	36	46	45
Th	6.00	6.45	7.40	8.39	9.40	9.30	9.10	9.41	9.68	9.80	11.50	11.00
U	1.60	1.53	1.90	2.08	2.91	3.00	2.80	2.80	2.74	3.00	3.80	3.60
La	39.9	40.1	46.3	51.0	39.5	40.0	42.3	39.9	40.1	42.5	58.9	56.4
Ce	90.4	78.7	101	106	78.2	88.3	90.4	79.1	79.4	94.3	122	122
Pr	10.8	9.65	12.0	12.3	9.42	10.5	10.7	9.36	9.53	11.2	15.3	14.8
Nd	45.4	36.8	50.5	46.5	35.7	44.6	40.4	34.7	35.2	46.8	62.1	60.6
Sm	8.43	8.49	9.26	9.92	7.67	7.87	8.00	7.61	7.97	8.47	11.05	10.95
Eu	2.18	2.36	2.34	2.64	1.97	1.95	2.01	2.11	2.07	1.94	2.66	2.70
Gd	7.74	7.80	8.16	8.84	7.05	6.76	7.00	7.25	7.13	7.48	9.46	9.29
Tb	1.15	1.18	1.29	1.42	1.08	1.09	1.10	1.16	1.09	1.17	1.46	1.44
Dy	6.97	6.42	7.43	7.93	6.15	6.33	6.10	6.82	6.10	6.71	8.26	8.16
Ho	1.27	1.26	1.32	1.50	1.18	1.20	1.20	1.27	1.19	1.25	1.56	1.51
Er	3.68	3.81	3.97	4.31	3.53	3.52	3.40	3.74	3.54	3.94	4.46	4.45
Tm	0.52	0.56	0.56	0.62	0.51	0.52	0.50	0.54	0.53	0.56	0.69	0.65
Yb	3.39	3.35	3.86	3.80	3.22	3.32	3.30	3.37	3.43	3.40	4.20	4.20
Lu	0.49	0.48	0.54	0.55	0.50	0.52	0.51	0.49	0.51	0.50	0.63	0.66

FeO* - total Fe as FeO; LOI - loss on ignition; Mg# = MgO/(MgO+FeO*) mol%; major element oxides are not recalculated to 100%

Table 3

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Table 3. Sm-Nd isotopic data for volcanic rocks of the Piskahegan Group and Cumberland Hill Formation

Sample	Nd (ppm)	Sm (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd_m$	2σ	$^{143}Nd/^{144}Nd_i$	$\varepsilon_{Nd(T)}$	T_{DM1} (Ma)	T_{DM2} (Ma)
Carrow Fm (basalts)									
77	48.3	10.4	0.1302	0.512593	6	0.512282	2.22	1016	831
1-79	62.1	13.7	0.1337	0.512616	6	0.512296	2.51	1017	824
Kleef Fm (basalts)									
74	58.5	13.2	0.1368	0.512615	8	0.512288	2.35	1059	857
1-76	60.7	13.4	0.1338	0.512612	7	0.512292	2.43	1025	832
South Oromocto Andesite Fm (andesites)									
72	40.8	8.02	0.1189	0.512534	6	0.512250	1.60	990	827
38A	46.5	9.92	0.1291	0.512556	8	0.512247	1.55	1069	885
Scoullar Mt. Fm (andesites)									
61	39.6	7.63	0.1165	0.512473	6	0.512195	0.52	1061	900
69	46.8	8.47	0.1095	0.512464	8	0.512202	0.67	1004	854
56	39.0	7.48	0.1160	0.512492	6	0.512215	0.92	1026	867
Cumberland Hill Fm (trachytes)									
1-203	104	20.9	0.1210	0.512690	7	0.512425	4.26	757	598
1-208	84.8	16.0	0.1137	0.512630	7	0.512381	3.40	793	644

T_{DM1}-depleted mantle model age calculated using a linear evolution for a mantle separated from the CHUR at 4.55 Ga and having a present day ε_{Nd} value of +10; T_{DM2}- depleted mantle model age calculated using the model of DePaolo (1988); $^{143}Nd/^{144}Nd_i$ and $\varepsilon_{Nd(T)}$ values were calculated for the respective crystallization ages (T=365 Ma, Piskahegan Group; T=335 Ma, Cumberland Hill Formation); $^{143}Nd/^{144}Nd_m$ – measured values; $^{143}Nd/^{144}Nd_i$ – initial, calculated; 2σ – uncertainty in measured $^{143}Nd/^{144}Nd$ – the value is the sixth decimal place; estimated precision of $^{147}Sm/^{144}Nd$ data is +/- 0.5% (2σ)

Appendix 1

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Appendix 2

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