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Geochemistry of mantle-related intermediate rocks from the Tibbit Hill volcanic suite, Quebec Appalachians

ABDEL-FATTAH M. ABDEL-RAHMAN

Department of Geology, American University of Beirut, Beirut, Lebanon

AND

P. STEPHEN KUMARAPELI

Department of Geology, Concordia University, 7141 Sherbrooke Street West, Montreal, QC, Canada, H4B 1R6

ABSTRACT

We present a study on major and trace element geochemistry of some intermediate lithologies from the predominantly basaltic Tibbit Hill volcanic suite in the Humber Zone of the Quebec Appalachians. The intermediate rocks probably formed as lava flows in the volcanic sequence. Their presence shows that this rift-related, *c.* 554 Ma volcanic sequence is not bimodal (basaltic-comenditic) as previously thought, but consists of a spectrum of compositions ranging from mafic through intermediate to felsic lithologies. The entire volcanic sequence is poly-deformed and generally metamorphosed to greenschist facies conditions.

The intermediate rocks of the Tibbit Hill Formation are trachyandesitic, trachytic and comenditic in composition, and exhibit a wide range of SiO_2 content (52 to 68 wt.%). Mg is highly depleted in most samples. Variations of silica versus the alkalis show that most of the samples are alkaline in nature. The rocks display a tholeiitic trend on a standard AFM diagram.

In general, the examined rocks also exhibit a wide range of Sr (15 to 174 ppm), Rb (0 to 156 ppm), Zr (155 to 899 ppm), Nb (18 to 123 ppm), and Y (18 to 94 ppm). The concentration of Hf and Ta are generally low (6.6–14.8 ppm, and 3.3–6.6 ppm, respectively), compared to those of Zr and Nb. Nevertheless, these rocks contain relatively high concentrations of the HFS elements, thus reflecting an enriched source. The suite is also relatively enriched in the rare earth elements (*REE*), and exhibits fractionated, subparallel *REE* patterns; the latter are generally uniform and conformable.

Chemical features of these volcanic rocks are typical of those of anorogenic A_1 type suites, related to hotspots, mantle plumes, or continental rift zones. This is consistent with earlier interpretation of volcanism associated with an Iapetan RRR triple junction, occurring shortly before the onset of seafloor spreading. At that stage of crustal evolution, alkaline to transitional basaltic magma pierced into the crust, and experienced fractionation to produce the liquids of intermediate composition. Rare earth element geochemical modelling supports the hypothesis that the most evolved composition for which *REE* data are available (comendite; 67.9 wt.% SiO_2) was produced by 20% fractional crystallization of the least evolved trachyandesite (56.7 wt.% SiO_2) of this intermediate volcanic assemblage.

KEYWORDS: Quebec, trachyte, geochemistry, mantle plumes, fractionation, rare earth elements, rift.

Introduction

REMNANTS of several Late Neoproterozoic (*c.* 570 to 555 Ma) volcanic assemblages that occur along the western flank of the Appalachian foldbelt are thought to be related to continental rifting as a prelude to the formation of the Iapetus Ocean (Aleinikoff *et al.*, 1995). Of these, the 554^{+4}_{-2} Ma (U-Pb zircon; Kumarapeli *et al.*, 1989) volcanic suite that makes up the Tibbit Hill Formation (THF), exposed along a belt about 250 km long in the Appalachian Humber Zone of southern

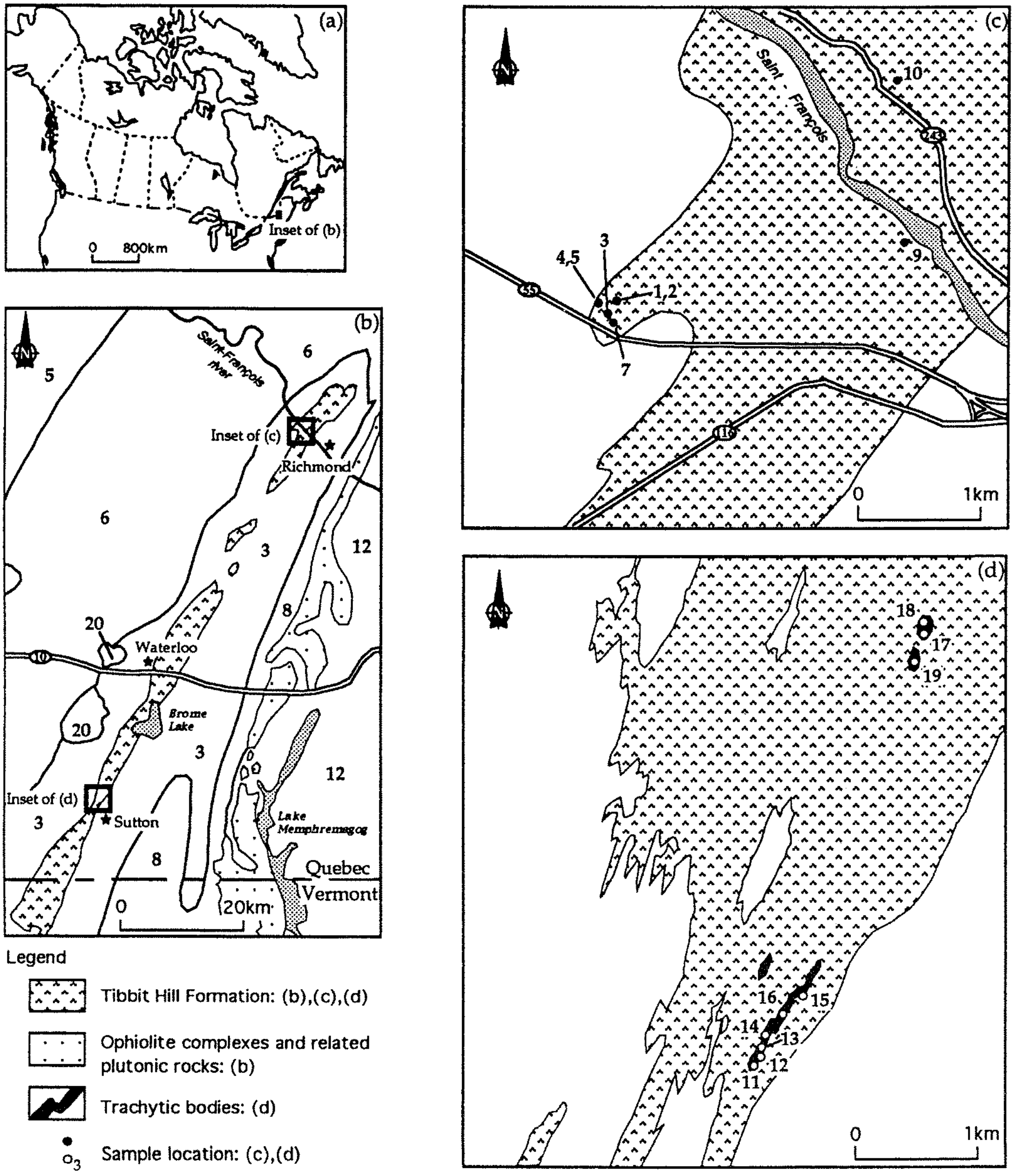

FIG. 1. (*a*) Location map. (*b*) Tectonic-lithofacies maps of parts of southeastern Quebec and northern Vermont (after Williams 1978) to include the Tibbit Hill Formation. The numbers on the various units corresponds to those in Williams (1978). (*c*) Sample locations of intermediate rocks from the Richmond area. (*d*) sample locations of intermediate rocks from the Sutton area.

Quebec and northern Vermont (Fig. 1), represents the one clear example of a volcanic shield that formed at an RRR (rift–rift–rift) triple junction (Kumarapeli *et al.*, 1981). Such rift-related volcanic suites are commonly bimodal and the Tibbit Hill volcanics were thought to be no exception. Within-plate, mildly alkaline to transitional basalts constitute the bulk of the THF (Pintson *et al.*, 1985). Comenditic rocks occur locally in the Waterloo area, Quebec (Kumarapeli *et al.*, 1989). However, there has been a growing body of information to suggest that the THF also contains a minor component of intermediate rocks. The aim of this study is to contribute data on this intermediate member (which has not been previously investigated), to delineate its petrological/geochemical characteristics, and to examine its origin in the context of the overall evolution of the Tibbit Hill volcanic sequence.

The intermediate rocks

Field relations

The batch of felsic volcanic rocks analysed by Kumarapeli *et al.* (1989) from the Waterloo area contained two samples of intermediate composition. However, it is virtually impossible to distinguish these intermediate rocks from the associated comenditic rocks based solely on their field characteristics. The intermediate rocks described here occur within metabasaltic rocks as deformed, weakly metamorphosed (greenschist facies) remnants of thin (commonly <1 m thick) igneous bodies. They are known from two sectors of the THF: one in the Richmond area and the other in the Sutton area (Fig. 1). In the field, they are distinguishable by their colours which are light to medium grey, light pinkish or purplish. In contrast, the metabasaltic rocks are green, dark green or greenish grey. Weathered surfaces of both types, however, are light grey. Field relations suggest that the intermediate bodies were initially tabular. The fact that some of them contain large proportions of amygdules may suggest that those may have been lava flows. The thinner (<0.5 m) bodies are often boudinaged; they appear as sequences of lenses in road cuts. The foliation of the metabasalts wrap around these lenses; the latter show no obvious foliation. Instead, the lenses show extension fractures filled with quartz veins. The largest intermediate body occurs about 5 km north of Sutton (Fig. 1*d*) and is mapped as a sinuous band about 50 m wide and 1 km long (unpublished manuscript map, Cowansville area, Quebec, M. Colpron, 1991). Parts of this body contain features that resemble deformed pillows. Thus, the balance of evidence, although meagre, suggests that the intermediate rocks are parts of the volcanic sequence and probably formed as minor lava flows.

The intermediate rocks in the Richmond area show differences from those in the Sutton area. These differences are clearly visible in outcrop as well as in hand specimen scales. The former include purplish and pinkish rocks and are aphanitic. They commonly contain amygdules, sometimes with cylindrical shapes elongated parallel to the dominant foliation of the THF, that are filled mostly with alkali feldspar and subordinate quartz. They are also laced with numerous mm- to cm-thick quartz veins and stringers containing minor alkali feldspar and traces of specular hematite. In some rocks the vein material makes up more than 50% by volume. In contrast, rocks in the Sutton area contain neither amygdules nor quartz veins. They are aphanitic to very fine-grained, pale to medium grey, and show faint traces of foliation. Locally, they contain cm- to mm-thick, moderately magnetic, opaque-rich layers which are dismembered and thrown into intricately convolute fold-like patterns.

Petrography

Under the microscope, rocks from the Richmond area show characteristics distinct from those in the Sutton area. The principal difference is the higher degree of alteration shown by the rocks in the Richmond area. Mafic minerals have been altered to aggregates of opaque iron oxides and minor chlorite. Feldspars have undergone varying degrees of albitization, but still preserve a preferred orientation of laths, indicating their original trachytic flow texture. Some samples show pervasive silicification. Silica blebs in these rocks are rimmed by specks of jasper which give the rocks their pinkish and purplish colorations. Zircon is a common accessory mineral. Epidote is also present in minor amounts as a secondary mineral.

In general, rocks in the Sutton area contain some phenocrysts (typically less than 25% of the rock), set in an inequigranular matrix, consisting of feldspar laths showing distinct, preferred orientation of their long axes, and is enclosed in a microcrystalline groundmass. The feldspar laths in the matrix make up about 25% of the rock and are on the average about 0.25 mm by 0.03 mm. The phenocrysts occur as discrete grains or clusters. The largest grain observed is 5 mm long. They are highly sodic alkali feldspars that have reacted to varying degrees with the magma. The microcrystalline groundmass, comprising nearly 75% of the rock, appears to be composed largely of alkali feldspar (~60%), minor epidote (~5%) and opaque iron oxides (10%).

Analytical techniques

Major elements

Concentrations of the major elements were determined for 19 samples. Sample locations are shown in Fig. 1. The analyses were obtained on fused lithium-metaborate discs using the X-ray fluorescence spectrometry (Philips PW2400 Spectrometer); operating conditions: Rh radiation, 40 kV, 70 mA. Loss on ignition (LOI) was determined by heating powdered samples for 50 minutes at 1000°C.

Trace elements

Concentrations of Rb, Sr, Zr, Y, Nb, U, Th and other trace elements (Table 1) were determined on pressed pellets by X-ray fluorescence (operating conditions: Rh radiation, 70 kV, 40 mA). The analytical precision, as calculated from 20 replicate analyses of one sample, is better than 1% for most major elements and better than 5% for most trace elements.

Rare earths and other trace elements

Concentrations of fourteen rare earth elements (*REE*; La to Lu, all except Pm) as well as Hf and Ta were determined for 5 samples (Table 2) using the ICP-MS techniques. The analytical procedure was as follows: (1) sintering of a 0.2 g sample aliquot with sodium peroxide; (2) dissolution of the sinter cake, separation and dissolution of *REE* hydroxide-bearing precipitate; and (3) analysis by ICP-MS using the method of internal standardisation to correct for matrix and drift effects. The advantage of the sintering technique is that it practically ensures complete digestion of resistant *REE*-bearing accessory phases (e.g. zircon, fluorite) which may not dissolve during an acid digestion. Full details of the procedure are given in Longerich *et al.* (1990). A pure quartz reagent blank, and several certified geological reference standards as well as internal lab standards were analysed with these samples. Detection limits and reagent blanks are generally about 10% of chondrite values. The chondrite values used for normalization are those of Taylor and McLennan (1985), compiled from Anders and Ebihara (1982) and Evensen *et al.* (1978).

Geochemistry

Major and trace element geochemistry

Major and trace element abundances are given in Table 1. The Tibbit Hill intermediate volcanic rocks of Sutton and Richmond areas span a wide range (52 to 68 wt.%) of SiO_2 contents. The volatile contents, shown as LOI values, are generally low and vary from 0 to 1.2 wt.%. This may reflect the low abundance of primary hydrous phases such as amphibole and mica (possibly due to their oxidation upon eruption), and the scarcity of secondary chlorite. These features are consistant with the petrographic characteristics described above.

A plot of both major and trace elements versus silica (Fig. 2) indicates that the examined rocks show relatively smooth variations with gradual decreases in Ca, FeO_t, and TiO_2 and a gradual increase in Zr with increasing silica. Mg is highly depleted in most samples, and Sr displays a somewhat constant distribution with respect to silica (Fig. 2). Variations of silica versus the alkalis (Fig. 3) show that most of the samples are alkaline in nature, with only four samples plotting in the subalkaline field of Miyashiro (1978). The tholeiitic nature of this volcanic assemblage is clearly indicated in the standard AFM diagram (Fig. 4). In Nb/Y–Zr/Ti space (Fig. 5), most data points occupy the fields of alkali basalt, trachyandesite, trachyte and comendite.

The relatively high Na content (4.5 to 10 wt.% Na_2O) of most of these rocks reflects the common presence of albite, as observed microscopically. K_2O values are highly variable, ranging from 0.01 to 5.44 wt.%. The wide variability of the contents of the alkalis in these rocks reflects the mobility of the two elements in volcanic systems. It should be noted that alkali metasomatism is generally common in volcanic rocks due to their nature, texture and the relatively high porosity in the case of intermediate volcanic rocks, combined with the mobility of K and Na, as documented for several volcanic complexes such as the Deloro A-type complex, Madoc, Ontario (Abdel-Rahman and Martin, 1990*a*).

In general, the examined rocks also exhibit a wide range of Sr (15 to 174 ppm), Rb (0 to 156 ppm), Zr (155 to 899 ppm), Nb (18 to 123 ppm), and Y (18 to 94 ppm; Table 1). Although the pairs Zr-Hf and Nb-Ta are known to be geochemically strongly coherent (Černý *et al.*, 1985), the concentration of Hf and Ta are generally low (6.6 to 14.8 ppm, and 3.3 to 6.6 ppm,

TABLE 1. Major and trace element analyses of intermediate rocks from the Tibbit Hill Formation

Sample	DTH1	DTH2	DTH3	DTH4	DTH5A	DTH5C	DTH7	DTH9	DTH10	DTH11	DTH12	DTH13	DTH14	DTH15	DTH16	DTH17	DTH18	DTH18A	DTH19
SiO_2	54.61	59.97	53.15	58.28	62.26	56.22	55.52	56.51	51.98	63.81	65.91	64.22	64.7	63.58	64.51	64.54	67.9	63.79	56.72
TiO_2	3.23	2.01	3.01	2.91	1.47	2.79	2.59	3.61	3.55	0.5	0.47	0.51	0.46	0.45	0.46	0.93	0.77	0.74	1.72
Al_2O_3	14.6	16.75	14.84	14.08	17.36	15.32	15.08	14.59	13.48	17.88	16.77	17.24	15.97	15.41	15.74	16.93	16.78	16.82	16.74
Fe_2O_3	13.73	9.69	17.07	13.89	7.26	14.15	14.74	13.01	19.24	5.73	5.61	7.37	7.74	8.06	6.67	6.17	3.21	7.43	12.99
MnO	0.1	0.02	0.05	0.01	0.01	0.01	0.03	0.01	0.02	0.08	0.06	0.02	0.16	0.14	0.29	0.05	0.04	0.05	0.12
MgO	2.03	0.29	0.69	0.01	0	0	0.08	0.08	0	0.55	0.42	0	0.28	0.02	0.15	1.76	0.01	0.06	0.93
CaO	3.09	1.66	2.64	2.59	1.21	2.56	2.2	3.41	3.51	0.48	0.5	0.41	1.56	0.89	1.42	0.77	0.81	0.72	0.86
Na_2O	6.97	9.52	8.15	7.76	9.66	8.73	8.42	7.88	7.43	9.69	9.01	9.83	7.97	5.21	6.22	1.96	8.94	8.63	8.77
K_2O	0.02	0.03	0.04	0.06	0.02	0.04	0.09	0.21	0.08	0.05	0.04	0.04	0.27	5.44	4.54	5.37	0.69	0.82	0.12
P_2O_5	0.39	0.09	0.47	0.39	0.1	0.41	0.39	0.55	0.96	0.05	0.05	0.05	0.04	0.05	0.04	0.08	0.15	0.15	0.61
LOI	1.19	0.4	0.62	0.27	0.12	0.22	0.9	0.24	0.2	0.43	0.36	0.11	0.22	0	0	1.15	0.16	0.22	0.68
Total	100.04	100.49	100.81	100.34	99.52	100.54	100.3	100.17	100.5	99.3	99.25	99.85	99.44	99.32	100.1	99.88	99.54	99.53	100.33
V	236	165	249	243	120	244	240	258	175	16	21	46	7	6	8	80	6	14	32
Sc	13	9	19	13	13	12	16	26	18	3	3	3	2	4	3	8	11	9	12
Co	23	16	25	29	17	13	16	22	13	11	2	9	10	12	21	22	19	4	5
Cr	163	118	125	140	107	273	217	40	11	1	11	5	8	8	0	97	7	0	7
Ni	46	11	26	7	2	9	2	0	4	0	0	0	0	0	0	31	0	0	0
Ga	14.5	12.5	11.9	9.6	8.7	10.4	11.3	13.4	17.3	37.6	31.5	25.7	33.7	29.5	34.7	21.4	23.9	25.4	28.5
Pb	13.2	6.3	11.6	9.1	0.6	9.3	10.6	10.1	15.8	4.7	4.7	4.7	12.3	15	10.4	10.7	1.6	5.1	7.9
Ba	215	179	216	217	181	233	206	260	291	155	158	163	187	496	373	1289	537	688	257
Rb	9	5	12.1	10.2	3.3	9	11.6	10.9	14.6	0	0	1	7.8	95.9	104	156.1	5.5	11.5	9.1
Sr	154.9	123	99.7	105.4	104.8	125.3	111.2	85.9	84.8	58.1	52.6	29.7	174.2	48.2	33.5	129.5	77.1	80.6	45.2
Nb	31.4	42.8	29.5	28.3	21.4	28.1	26.4	32.8	46.5	123.2	117.8	118.7	117.7	107.3	113.5	18	100.9	95.4	65.9
Y	34.9	35.9	30.9	33.6	17.6	34.1	29.2	54	65.2	89.5	93.7	69.7	79.7	81.7	90.7	37.1	70.9	67.3	45.4
Zr	243.4	394.1	227.9	219.6	155	216.5	204	249.6	386.9	898.8	841.6	852	837.1	765.1	810	338.3	614.4	227.9	378.4
Hf										13.13	12.45		14.81				7.74		6.6
Ta										6.22	6.35		6.64				5.13		3.32
Th	1.8	4.7	3	2.3	0	1.8	0.6	2	5	7.8	7	8	8.9	8.5	8.2	9.4	3	5	4.3
U	1.8	2.4	0	2.1	0	1.5	0.9	1.8	2.6	5.7	4.6	4.6	3	5.8	3.2	3.6	3.8	3.6	3.1

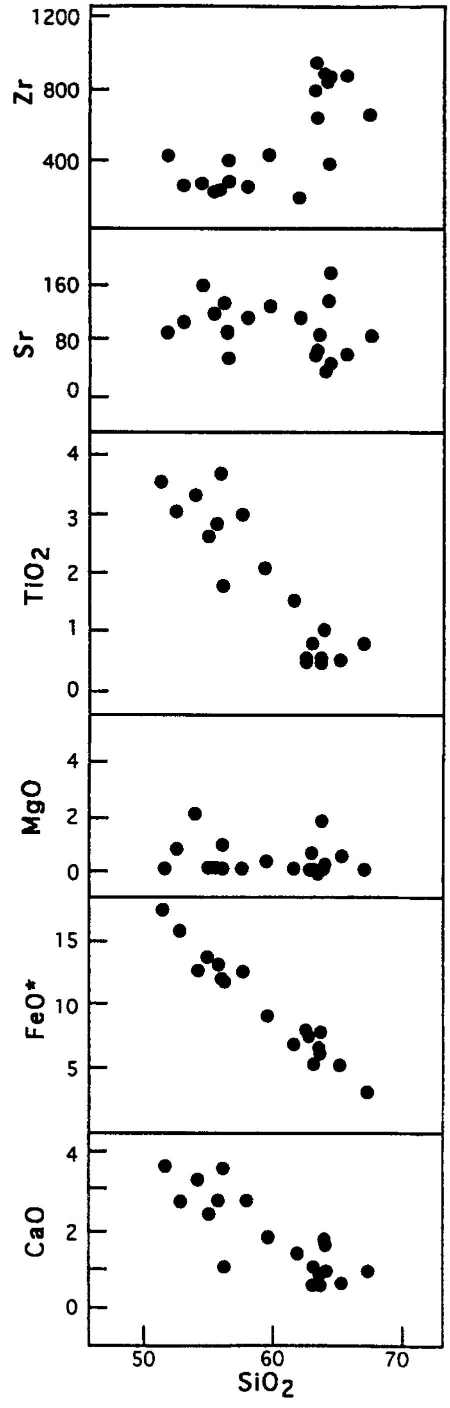

FIG. 2. Variations of selected major elements (in wt.%), and trace elements (in ppm) *vs* SiO_2 for whole-rock samples of the Tibbit Hill intermediate volcanic rocks.

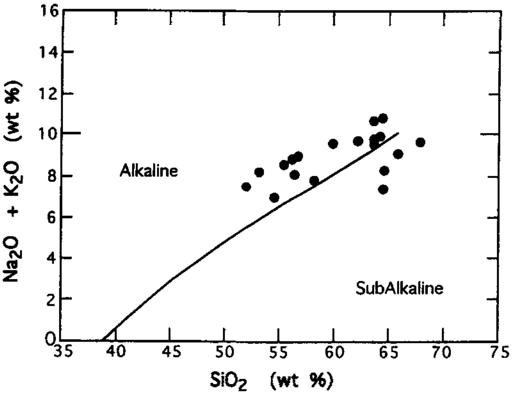

FIG. 3. SiO_2 *vs* Na_2O+K_2O variation diagram (in wt.%), showing the alkaline nature of the examined volcanic rocks; the alkaline and subalkaline fields are after Miyashiro (1978).

respectively), compared to those of Zr and Nb. Nevertheless, these rocks contain relatively high concentrations of the high field strength elements, thus reflecting an enriched source (see below). Inter-element relationships (e.g. Zr *vs* Y; Fig. 6) reflect a general gradual increase in both incompatible elements from the less evolved to the more evolved compositions of this volcanic suite. Values of both U and Th are low for such an alkaline suite, as they range from 0 to 5.8 ppm, and 0 to 9.4 ppm, respectively.

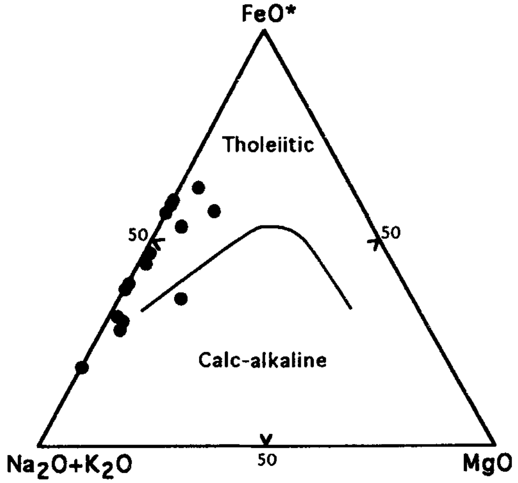

FIG. 4. A–F–M diagram (after Irvine and Baragar, 1971), showing the tholeiitic trend displayed by the volcanic rocks.

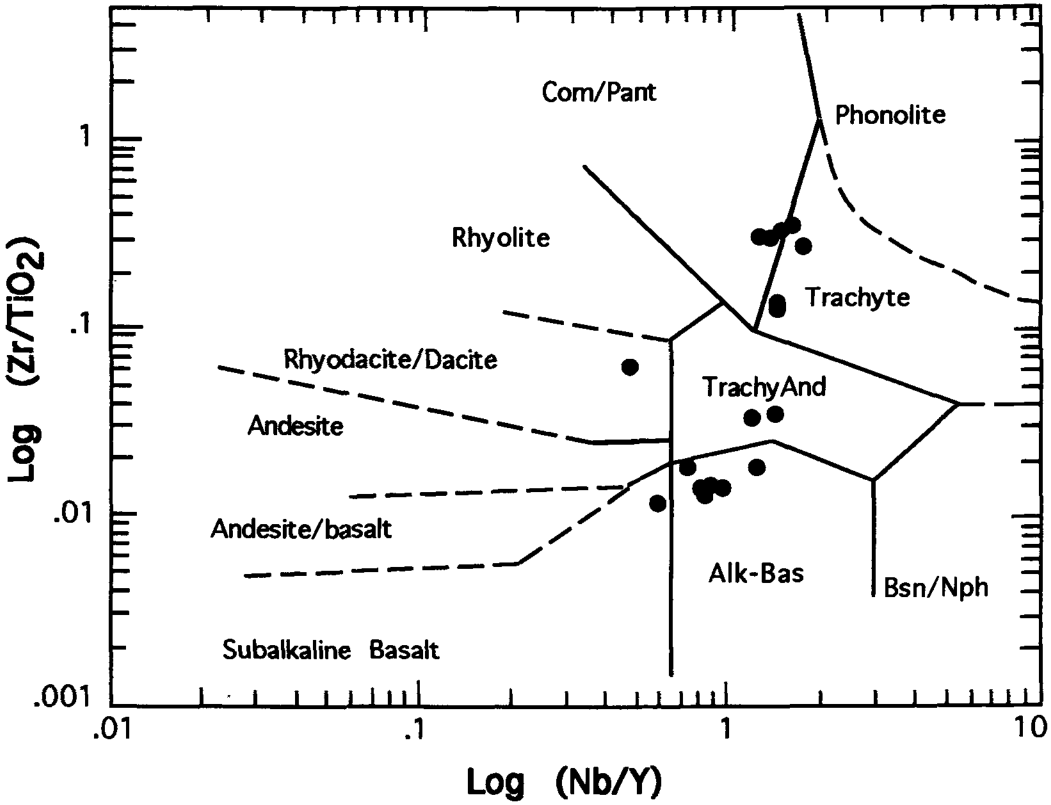

FIG. 5. Plot of Nb/Y *vs* Zr/TiO_2 (after Winchester and Floyd, 1977), showing the classification of the Tibbit Hill intermediate volcanic suite.

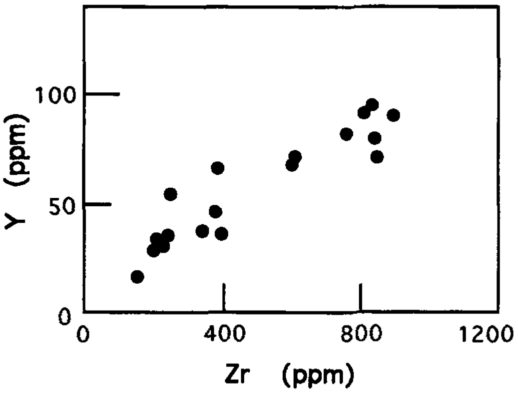

FIG. 6. Variations of Zr *vs* Y (in ppm). Note the gradual increase of both elements from mafic to felsic compositions.

Rare-earth element geochemistry

The concentration of the rare earth element (*REE*) is given in Table 2, and the chondrite-normalized *REE* patterns, are shown in Fig. 7. The *REE* patterns are generally parallel to subparallel, uniform and conformable. All samples are light rare earth element (*LREE*) enriched over heavy rare earth elements (*HREE*); the *LREE* show a pronounced fractionation compared to the *HREE*. Three of the five samples analysed exhibit negative Eu-anomalies, whereas the other two samples show small, positive Eu-anomalies. Fluctuations in the oxidation state of the melt, possibly related to localized volatile saturation may have locally produced higher oxidation state in some patches of the liquid, which crystallized to give negative Eu-anomalies.

TABLE 2. Concentrations of the rare earth elements in the Tibbit Hill intermediate rocks

Sample	DTH11	DTH12	DTH14	DTH18	DTH19
La	49.9	50.88	62.44	41.26	36.1
Ce	116.52	116.9	150.31	91.43	99.08
Pr	14.99	15.61	17.77	11.88	9.74
Nd	61.54	65.84	71.03	47.54	41.0
Sm	12.39	14.87	15.18	10.84	8.27
Eu	1.74	1.98	2.28	4.23	3.49
Gd	11.07	13.33	14.56	10.2	7.63
Tb	1.9	2.27	2.33	1.66	1.19
Dy	12.12	14.07	14.07	10.45	7.48
Ho	2.83	3	2.85	2.2	1.5
Er	9.1	8.79	8.49	6.29	4.69
Tm	1.39	1.28	1.28	0.95	0.69
Yb	9.06	8.65	8.95	5.61	4.25
Lu	1.36	1.29	1.38	0.78	0.67

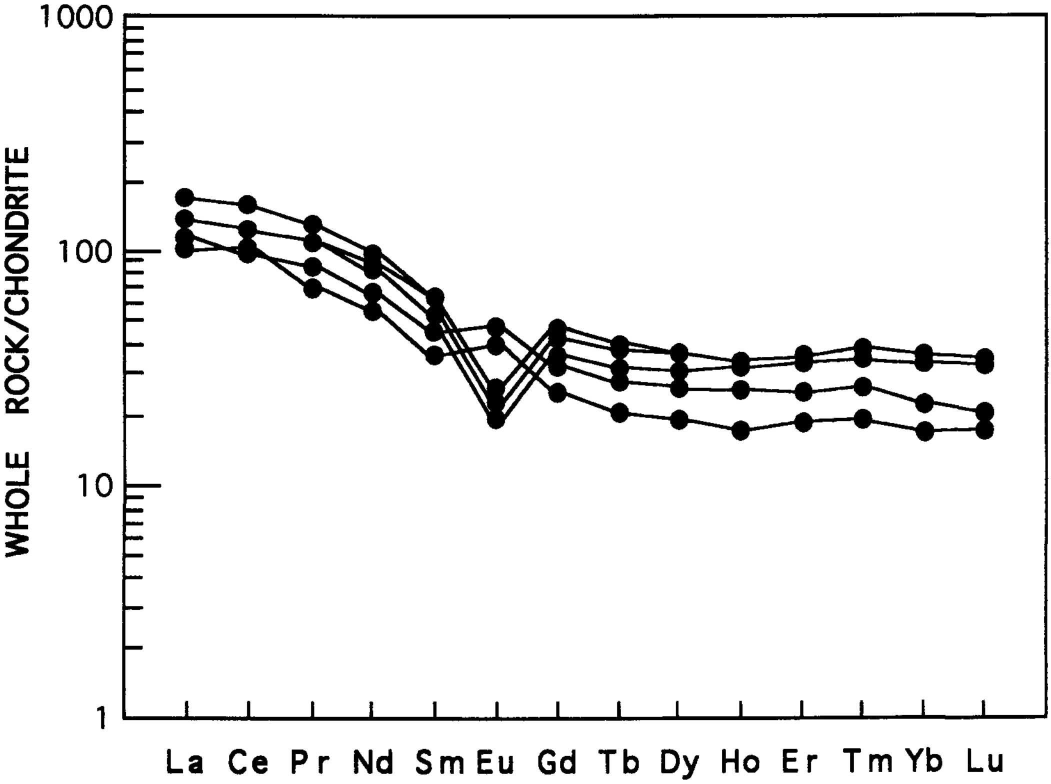

FIG. 7. Chondrite-normalized plots for the Tibbit Hill intermediate rocks. Normalization values used are taken from Taylor and McLennan (1985).

Discussion

Tectonic setting

Nb and Y, among other trace element tracers, have been used to discriminate the different tectonic settings of felsic and intermediate magmas (Pearce *et al.*, 1984). All except one of the samples under investigation plot in the field of within-plate complexes (Fig. 8*a*), as is typical of A-type suites from other regions worldwide (e.g. Collins *et al.*, 1982; Whalen *et al.*, 1987; Abdel-Rahman and Martin, 1990*b*; Eby, 1992). Batchelor and Bowden (1985) proposed a discrimination diagram based on the multicationic parameters R1 and R2 of de la Roche *et al.* (1980); most data points line up along a trend, occupying the field of anorogenic suites (Fig. 8*b*). Thus, these rocks exhibit chemical characteristics of within-plate complexes, and conform with the interpretation given in Kumarapeli *et al.* (1981) that the Tibbit Hill volcanism occurred at an RRR triple junction in a setting similar to that of the Afar triangle. Continued igneous activity (*c.* 590 to 555 Ma) at the triple junction and the associated rifts accompanied the continental breakup that led to the formation of the Iapetus ocean (Kamo *et al.*, 1995).

Petrogenetic indicators

Bonin (1990) recognized the distinctive nature of A-type magmas, and subdivided them into two groups: post-orogenic and early anorogenic. Also, Eby (1990, 1992) subdivided the A-type intermediate and felsic magmas into two groups: A_1 which represents differentiates of mantle-derived oceanic-island basalt (anorogenic or rift zone magmas), and A_2 which represents crustal-derived magmas of a post-orogenic setting. The Y/Nb–Yb/Ta systematics of the Tibbit Hill intermediate rocks (Fig. 9*a*; Eby, 1990; 1992) suggest that they have fractionated from a mantle-derived source similar to that of ocean island basalts (OIB). It should be noted that the trace element characteristics of OIBs are generally similar to those of continental anorogenic basalts, and together they constitute within plate basalts (e.g. Pearce and Cann, 1973). Since the Tibbit Hill basalts are within-plate anorogenic basalts (Coish *et al.*, 1985; Pintson, 1986), they constitute the most obvious source from which the intermediate rocks fractionated. A mantle derivation for these rocks is also suggested by the fact that crustal-derived magmas would not produce large volumes of basalts in association with only minor intermediate and felsic compositions.

Diagrams designed to discriminate between the A_1 and A_2 groups of anorogenic magmas indicate that the Tibbit Hill intermediate rocks belong mostly to the A_1 group (Fig. 9*b*), representing differentiates of within-plate basalts, typically related to hot spots, plumes, or continental rift-zones (Eby, 1992). The RRR triple junction that localized the Tibbit Hill volcanism is, in fact, thought to have been plume generated (Kumarapeli, 1993). Thus, a mantle derived, rift-related, basaltic magma most likely represents the parent liquid which fractionated to produce the examined intermediate rocks (see below).

The Tibbit Hill basalts are geochemically similar to the basaltic dykes of the Adirondack dyke swarm (Coish and Sinton, 1992). Furthermore, the space relations of the volcanic shield and the dyke swarm (Kumarapeli and Isachsen, 1991) and the available isotopic age data suggest that the THF and the Adirondack dyke swarm are comagmatic and coeval. Additional support to this idea comes from the fact that the intermediate rocks of the THF have their counterpart in the Adirondack dyke swarm, in the form of a minor subset of trachytic dykes.

Fractionation of the intermediate compositions

Field relations, combined with volume considerations, along with the chemical characteristics described above (cf. Fig. 9), indicate that the Tibbit Hill intermediate rocks are not crust-derived. On the contrary, these rocks represent differentiates of mantle derived basaltic magma, as they belong to the A1 group of anorogenic suites. No evidence was found to suggest that processes such as assimilation or magma mixing were responsible for the evolution of this volcanic assemblage. The linear geochemical trends observed and the parallel nature of the normalized patterns with increasing total abundance of the *REE* of the intermediate assemblage suggest that it was produced by fractional crystallization. In a diagram such as La/Sm *vs* La (Fig. 10), data points plot along a horizontal line, a feature restricted solely to the process of fractional crystallization (e.g. Allègre and Minster, 1978).

To further constrain this fractional crystallization hypothesis, trace element modelling using the equation of Arth (1976) was applied.

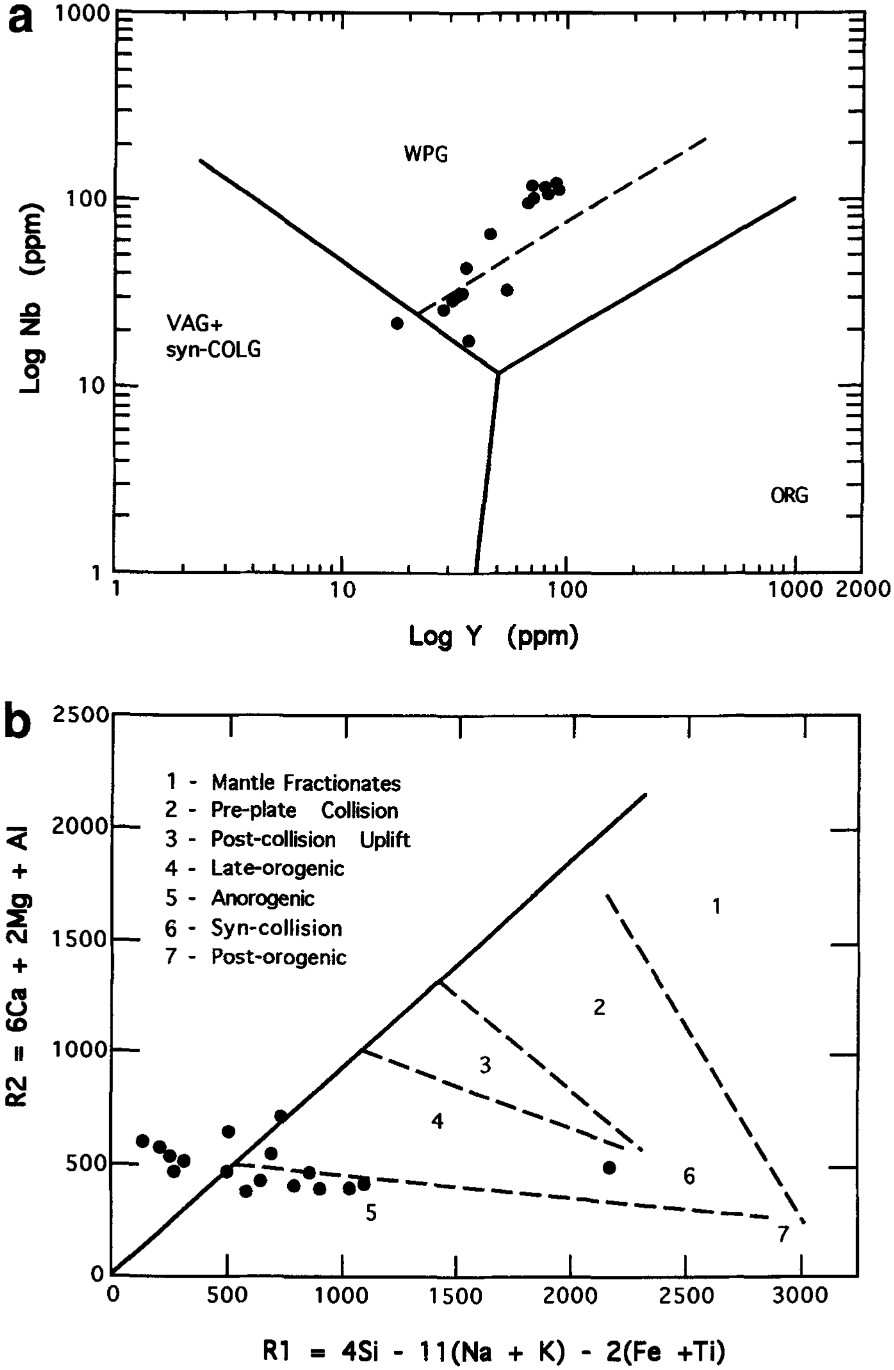

FIG. 8. (*a*) Plot of Nb *vs* Y; fields: VAG, volcanic arc granite; Syn-COLG, syncollision granite; WPG, within-plate granite; and ORG oceanic ridge granite. After Pearce *et al.* (1984). (*b*) Plot of R1 = 4Si − 11(Na+K) − 2(Fe+Ti) *vs* R2 = 6Ca + 2Mg + Al showing that the examined rocks are anorogenic. Fields are after Batchelor and Bowden (1985).

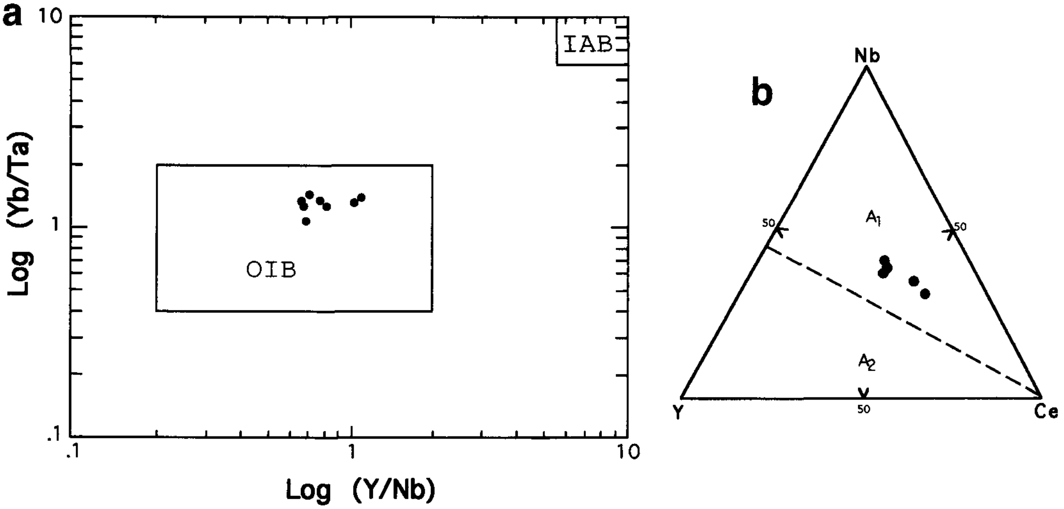

FIG. 9. (*a*) Y/Nb *vs* Yb/Ta diagram (after Eby, 1990, 1992); OIB = field for Oceanic Island Basalts and IAB = field for relatively Nb and Ta enriched Island Arc Basalts (see text for details). (*b*) Nb–Y–Ce triangular diagram. Field A_1 represents anorogenic settings with an OIB-type source, and field A_2 represents crustal-derived magmas of post-orogenic settings (after Eby, 1990, 1992). Note that all data points of the Tibbit Hill trachytic rocks belong to the A_1 group of anorogenic magmatism.

This equation was solved for C_L (the concentration of the trace element in the differentiated liquid):

$$C_L/C_i = F^{(Ds-1)}$$

where C_i is the initial concentration of the trace element in the source, F is the fraction of liquid remaining, and Ds is the bulk distribution coefficients of the fractionating minerals. The calculations were done using trace element values (C_i) of the least fractionated sample for which rare earth data are available (DTH19, trachyandesite; 56.7 wt.% SiO_2). The percentage of fractionating phases used was based upon the general petrographic characteristics of the rocks, and was normalized to 100: plagioclase 70%, pyroxene 15%, and amphibole 15%. The distribution coefficients (K_Ds) used are taken from Arth (1976) and Gill (1981), and are listed in Table 3.

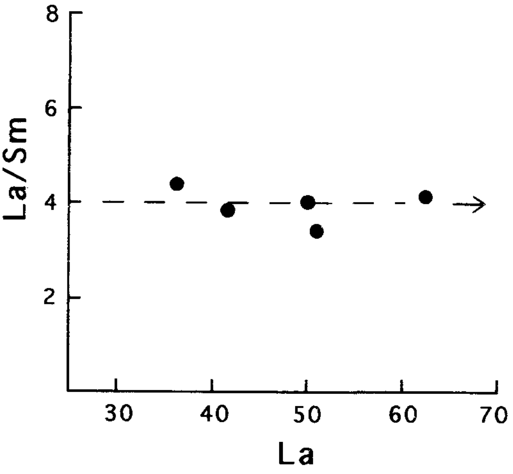

FIG. 10. La/Sm *vs* La diagram showing that the data points plot along a horizontal trend (see text for details).

The results (Table 4), indicate a close match between calculated *REE* values in the differentiated liquid at 20% fractional crystallization and those in the most fractionated sample (DTH18, trachyte; 67.9 wt.% SiO_2). It should be noted that calculated trace element abundances are considered acceptable if model values are within 20% of measured values (Graham and Hackett 1987). However, the calculated Ce values differ significantly from those measured. This is due, in part, to the wide range of K_Ds of some elements (some may differ from actual K_D).

Major element modelling by least-squares methods was also carried out, but the results are inconclusive. This was expected since the rocks have been subjected to low grade metamorphism and alkali metasomatism as described above (see petrography and geochemistry sections). These

TABLE 3. Partition coefficients used in the trace-element fractional crystallization modelling

	Augite	Amphibole	Plagioclase
La	0.2500	0.4000	0.3500
Ce	0.3000	0.5100	0.2400
Pr	0.3800	0.8000	0.2000
Nd	0.4900	1.2000	0.1700
Sm	0.7000	2.0000	0.1300
Eu	0.8700	1.7000	2.1100
Gd	0.9600	2.5000	0.0900
Dy	1.2000	3.5000	0.0860
Er	1.2000	2.7500	0.0840
Yb	0.9000	2.0000	0.0770
Lu	0.8000	1.7000	0.0620

TABLE 4. Results of rare earth element fractional crystallization modelling

	Source (DTH19)	Fractionated (DTH18)	Fractionated liquid caculated
La	36.10	41.26	41.57
Ce	99.08	91.43	115.49
Pr	9.74	11.88	11.28
Nd	41.0	47.54	46.88
Sm	8.27	10.84	9.20
Eu	3.49	4.23	2.98
Gd	7.63	10.20	8.33
Dy	7.48	10.45	7.85
Er	4.69	5.29	5.04
Yb	4.25	5.61	4.73
Lu	0.67	0.78	0.76

post magmatic processes have disturbed the concentration of many of the major elements (e.g. Na, K, Fe, and Mg) and some of the trace elements (e.g. Rb, Sr, Ba), thus rendering major element- (and some trace element-) modelling of little use. The rare earth elements were least affected by these post magmatic processes as they are found to be relatively immobile.

The question of bimodality

In general, rift-related volcanism typically produces basalt-rhyolite bimodal suites. The absence of intermediate compositions in such typically transitional to alkaline bimodal suites has been termed the 'Daly gap', after Daly (1925). Earlier studies questioned the statistical validity of the inference that intermediate lavas are absent, suggesting instead that sampling bias might cause under-representation of poorly recognized intermediate compositions. Claugue (1978) suggested that the use of an incompatible trace element as a differentiation index would make the gap disappear. He argued that the gap is an artifact of using normative mineralogy to distinguish among rock types.

Most, however, have accepted the existence of such a compositional gap. The latter has been explained by a variety of means. For example, Chayes (1977) related the presence of the Daly gap to the formation of the felsic lavas by partial melting of the base of the volcanic pile. Bonin and Giret (1990) demonstrated that intermediate liquids are produced directly by partial melting of mantle material; the magmas rise and pond within the crust to form magma chambers which evolve by fractional crystallization, until such time as a brittle fracture in the overlying crust permits ascent and eruption of the more buoyant felsic differentiates (e.g. Mungall, 1993).

As documented above, the intermediate volcanic rocks of the THF did not originate by partial melting of older crustal rocks, nor were they produced directly by partial melting of mantle material. Thus, the main competing explanations for the presence of the Daly gap as those introduced by Chayes (1977) and Bonin and Giret (1990) do not apply to the Tibbit Hill volcanic assemblage. This is consistent with our findings that the Daly gap does not exist within the THF. The latter forms a continuum in composition from alkali basalt, trachyandesite, to trachyte and comendite, a suite produced by fractional crystallization from an initially mantle-derived basaltic magma. Although volumetrically insignificant, the presence of intermediate volcanic rocks within the Tibbit Hill anorogenic alkaline suite, suggests that the Daly gap is not necessarily a characteristic feature of all rift-related volcanic assemblages.

Conclusions

1. The predominantly basaltic Tibbit Hill Formation contains a minor component of intermediate rocks. Therefore, it is not strictly bimodal (basaltic-comenditic) as was previously thought, but contains a spectrum of compositions ranging from mafic through intermediate to felsic

lithologies. Thus, the Daly gap is not necessarily a characteristic feature of all rift-related volcanic assemblages.

2. Geochemically the examined rocks are trachyandesites, trachytes and comendites. The rocks are mildly alkaline to subalkaline in nature, form a tholeiitic trend, and are relatively enriched in incompatible elements. Rare earth elements (*REE*) chondrite normalized patterns are generally uniform and conformable.

3. On tectonic discriminant diagrams, these rocks exhibit the geochemical characteristics of within-plate lavas. This is consistent with the regional geological context with the volcanism associated with an Iapetan RRR triple junction, occurring shortly before the onset of sea floor spreading.

4. Chemical characteristics of the intermediate rocks examined suggest that they are not crust-derived, but belong to the A_1 group of anorogenic magmas, representing differentiates of within plate basalts, which are related to hotspots, plumes, or continental rift zones.

5. Rare earth element geochemical modelling supports the hypothesis that the most evolved composition (comendite; 67.9 wt.% SiO_2) was produced by 20% fractional crystallization of the least evolved trachyandesite (56.7 wt.% SiO_2) of this intermediate volcanic assemblage.

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