## GEOLOGY, PETROLOGY AND GEOCHEMISTRY OF TRAVELER RHYOLITE

## AND KATAHDIN PLUTON (NORTHCENTRAL MAINE)

by

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#### ABSTRACT

The Traveler Rhyolite-Katahdin Pluton Igneous Complex of of the Lower Devonian age in Northcentral Maine consists of two penecontemporaneous but genetically independent magmatic episodes. The earlier, voluminous episode includes the Traveler Rhyolite and the Katahdin Granite, whereas the slightly younger episode is comprised of minor intrusions of Horserace Quartz Diorite, Harrington Lake Porphyry and Debsconeag Granodiorite. Electron microprobe analyses of mineral assemblages, as well as major element geochemistry, provide data that show the earlier episode being derived by partial melting of graphite bearing sediments at a depth af 25-30 km and at a temperature of 810°C. The pre-eruption temperature and  $P(H_2O)$  for the Traveler Rhyolite is estimated at 800°C and 1100 bars respectively. Similar estimates for Katahdin Granite yield 710°C and 1200 bars. Both units were buffered at oxygen fugacities slightly below the QFM buffer  $(10^{-15.00} \text{ for rhyolites}; \text{ and } 10^{-17.25} \text{ for granites})$  as a consequence of the presence of graphite in the parental sediments. The younger episode, as evidenced by the trend on an AFM diagram, crystallized under oxidizing conditions.

Trace element abundances are consistent with the derivation of the earlier episode from the Appalachian eugeosynclinal sediments. In particular, the unusually high Sc abundances (25-35 ppm) in the acidic rocks preclude a derivation by extensive fractional crystallization of a basaltic magma. Variations of trace element abundances in the Traveler Rhyolite and Katahdin Granite are best explained if the granites represent fractionated rhyolitic magma after removal ABSTRACT (continued)

of 25% crystals of alkali feldspar (35 wt%),plagioclase (25 wt%), quartz (31 wt%), biotite (8 wt%), and magnetite (1 wt%). Aplitic magmas require approximately 80-90% crystal removal of the same mineral proportions as granites. The calculated mean partition csefficients required by this model for Co, Rb, Hf, Sr, and Eu are 3.18, 0.49, 2.42, 2.08, and 2.41. The mean partition coefficient for Hf is largely due to a removal of accessory zircon. The similar values of partition coefficients for Eu and Sr are consistent with the estimated very low oxygen fugacities. The trace element data further show that the Horserace Quartz Diorite and Harrington Lake Porphyry are genetically independent from the earlier episode and that the Debsconeag Granodiorite is a result of mixing of 40% Traveler Rhyolite magma and 60% Harrington Lake Porphyry. Higher abundances of heavy rare earth elements (Gd-Lu) and Hf in aplites, relative to granites, suggest that zircon ceased to crystallize during the late stages of differentitation due to the gradual loss of zirconium via an exsolving vapor phase.

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#### OBJECTIVE AND STUDY PLAN

The goal of this study is to gain an understanding of the tectonic significance of the two igneous belts in northcentral Maine, the Piscataquis Volcanic Belt and the Greenville Plutonic Belt. As a first step in achieving this goal, this study is focused on the origin, evolution, and mode of emplacement of the Traveler Rhyolite - Katahdin Granite Igneous Complex.

Noting the geological proximity of the Traveler Rhyolite and Katahdin Granite, Rankin (1968) tentatively suggested their origin to be from the same parental magma. In order to test this hypothesis, a detailed geological, petrological and geochemical study of the Traveler Rhyolite and Katahdin Granite is hereby undertaken. Furthermore this study can provide additional insights into the geological processes that lead to the formation of a volcano-plutonic association.

This work is divided into three parts. The first part is devoted to the geology, mineralogy and major element geochemistry of the Traveler Rhyolite, emphasizing the equilibria among mineral phases as a tool to estimate intensive parameters. In the second part, a similar approach is used to study plutonic rocks of the Katahdin Pluton. The third section studies the trace element geochemistry of the Traveler Rhyolite - Katahdin Pluton Igneous Complex.

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## I. INTRODUCTION

A linear distribution of Lower Devonian extrusive acidic rocks in northwestern and northcentral Maine, and another subparallel belt of intrusive granitic and gabbroic bodies to the southeast (Fig. 2) has led some geologists to interpret these linear features, in terms of plate tectonic models, as an island arc structure (D. W. Rankin, 1968), or as a plate suture (G. M. Boone, 1974), resulting from a closure of Iapetus Ocean between the Avalon Prong and the North American continent (McKerrow, Ziegler, 1972; Dewey, Kidd, 1974). Both belts, the extrusive Piscataquis Volcanic Belt of Rankin (1968) and the intrusive Greenville Plutonic Belt (after the town of Greenville, situated approximately in the center of the belt--this study), are about 10 to 50 km wide and about 160 to 200 km long. They are approximately 25 km apart at their southwestern extension and converge slightly to the northeast where Traveler Rhyolite is intruded by granites of the Katahdin Pluton (D. W. Rankin, These granites are in turn intruded by a few stocks 1968). of Debsconeag Granodiorite and by a stock of Horserace Diorite (A. Griscom-in preparation). The close spatial association and good exposures of extrusive and intrusive rocks, as well as their well defined intrusive contacts, make this volcano-plutonic complex most suitable for detailed geological, petrological, and geochemical studies.

Fig. 1. Index Map With Metamorphic Zones in Maine.

Legend: TR - Traveler Rhyolite KP - Katahdin Pluton la - Subchlorite Zone 1 - Chlorite Zone 2 - Biotite Zone 3 - Garnet Zone 4 - Staurolite Zone 5 - Sillimanite Zone 6 - Sillimanite & Orthoclase Zone <u>Note:</u> Metamorphic zones in the extreme SW Maine are omitted.



INDEX MAP AND METAMORPHIC ZONES (GEOLOGIC MAP OF MAINE, 1967)

- Fig. 2. Generalized Geological Map of Western Maine.
  - Legend: 1 Rhyolitic Volcanics of Piscataquis Volcanic Belt
    - 2 Mafic Plutonics of Greenville Plutonic Belt
    - 3 Silicic Plutonics of Greenville Plutonic Belt
    - 4 Silurian and Older Rock Formations
    - 5 Other Granitoids (Not Part of Greenville Plutonic Belt)
    - 6 Devonian Rock Formations



GENERALIZED GEOLOGIC MAP OF WESTERN MAINE

Fifty-five major element analyses and fifty-two trace element abundance data for 18 elements (9REE, Sc, Co, Rb, Cs, Hf, Ta, Th, U, Sr) were determined by electron microprobe, XRF and instrumental neutron activation techniques. The samples include the Traveler Rhyolite (11), Kineo Rhyolite (1), Katahdin Granite (22), aplites and pegmatites (9), Horserace Diorite (3), Debsconeag Granodiorite (2), Harrington Lake Granite Porphyry (2), mafic dike rock (1), Granite of the Moxie Pluton (1), Lexington Granite (1), Echo Pond Granite (1), and Pierce Pond Gabbro (3) (See Fig. 3). Additional microprobe data were obtained on coexisting minerals in two very fresh samples of Traveler Rhyolite (biotite, olivine, clinopyroxene, plagioclase, groundmass, opaques, and "chlorite") and on four samples of Katahdin Granite (alkali feldspar, plagioclase, opaques, biotite and, in one case, also olivine). Biotite and opaque minerals were also analyzed by microprobe in four other samples of Katahdin Granite.

These data, as well as the geologic setting and the rock petrography, are discussed with the objective of understanding the relationships within the intrusive and volcanic belts.

# II. <u>GEOLOGY</u>, <u>MINERALOGY</u>, <u>AND</u> <u>PETROLOGY</u> OF TRAVELER <u>RHYOLITE</u>

A. General Statement

The Traveler Rhyolite is a large, almost rectang-

Fig. 3. Location of Igneous Bodies Included in This Study. Legend: Light Stipple - Granites Medium Stipple - Rhyolites Heavy Stipple - Mafic Plutonics



ular (20 X 12 km, 215 km<sup>2</sup>), tectonically sunken block of topographically prominent Lower Devonian volcanic rocks, occurring on the northern side of the Katahdin Pluton (Rankin, 1968). The estimated present day stratigraphic thickness of the volcanic sequence is approximately 3.5 km.

On a regional scale, the Traveler Rhyolite, and a few outlying rhyolitic and granophyric occurrences between Snowshoe Mountain and Soubunge Mountain (all considered to be part of the same magmatic sequence), are situated within a broader synclinorial structure on strike with the Roach River and Moose River synclinoria to the southwest (Boucot, 1969) (Fig. 2). All three regional depressions are doubly plunging synclinoria with weakly metamorphosed (chlorite zone) axial Lower Devonian sedimentary strata, containing large masses of Lower Devonian acidic volcanic rocks of identical stratigraphic correlation (Table 1).

From fossil records of the respective underlying and overlying sedimentary formations, the best stratigraphic age for the Traveler Rhyolite is Middle to Upper Lower Devonian: Oriskany to Schoharile (Boucot, 1969; Andrews, Kasper, 1970).

The Traveler Rhyolite unconformably overlies the Matagamon Sandstone (type locality at Horserace Mountain) and is in turn overlain with angular unconformity by continental deposits of the Trout Valley Formation within and along the northern edge of the block (Table 1). The contact with the granites of the Katahdin Pluton clearly show



Stratigraphic correlation of Traveler Rhyolite with Spencer and Kineo Rhyolites in Roach River and Moose River Synclinoria. Modified from Boucot (1969); Rankin (1965, 1968); Andrews, Kasper (1970). the granite intruding the rhyolites: at several places, numerous aplogranitic, apophysical injections of the Katahdin Granite are observed to intrude for a short distance into the rhyolites. This contact is also marked by a narrow, 50-100 m wide, hornfelsitic zone of recrystallized metarhyolites which retained the original porphyritic texture, but the groundmass consists of a fine-grained mosaic of newly formed feldspars, quartz, biotite, and hornblende. A system of steep faults, believed to be partly the result of cauldron subsidence, terminates the volcanics on their western and northern sides.

From the character of the lower contact of Traveler Rhyolite, Rankin (1968) deduced that the early volcanics were deposited into a shallow marine environment which changed rapidly into a land area. The dominant volcanic type throughout the volcanic sequence is an ignimbritic welded ash flow tuff, with varying degrees of compaction and variable phenocrystic contents. Based on the latter, the volcanics were subdivided by Rankin (1961, 1968) into the basal Pogy Member and the overlying Black Cat Member (Table 2).

## B. Geology of the Traveler Rhyolite

## 1. Pogy Member

The basal Pogy Member, named after type exposures on North Pogy Mountain, occurs as a unit about 1000 m thick, between underlying Matagamon Sandstone and overlying Black Cat Member. A number of features indicate that

- Geologic Map of Traveler Rhyolite and Sample Locations. Geology Modified After Rankin (1968). Fig. 4.
  - Legend: 1 Black Cat Member of Traveler Rhyolite 2 Pogy Member of Traveler Rhyolite 3 Trout Valley Formation

    - 4 Matagamon Sandstone
  - Sample Locations: Diamonds Samples Analyzed Circles Samples Not Analyzed



the early volcanic deposits were emplaced on unconsolidated sediments and in a shallow marine environment (tuffaceous character of the sediments directly below the contact, scouring, clastic dikes, etc.--Rankin, 1968). The contact with the upper Black Cat Member is gradational, marked by: (1) quartz, the major phenocrystic component of the Pogy unit, becomes rare or absent; (2) mafic silicates are more abundant and less altered in the Black Cat unit; and (3) the total amount of phenocrysts is lower in the Black Cat unit. The prominent rock types are welded ash flow tuffs, deposited as loosely packed, ignimbritic pyroclastics, which were subsequently compacted while still retaining their own heat and "welded" into a banded solid rock.

The welded tuff in fresh hand-speciments is a dark, almost black, flint-like, dense rock with conchoidal fracture surfaces and large, glassy phenocrysts of quartz and plagioclase up to 3 mm in size. Upon hydrothermal alteration, the rock is gradually bluish, greyish, greenish and light greenish-grey, with plagioclase phenocrysts becoming opaque-white or greenish-white. Banding, produced by numerous subparallel flattened shards and lithic fragments, is not commonly visible in fresh hand-specimens; however, it is strongly enhanced on whitish, weathered surfaces by a selective erosion of the softer groundmass. Frequently, crude columnar jointing is well developed.

## 2. Black Cat Member

The upper Black Cat Member, named after type exposures on Black Cat Mountain, has a stratigraphic thickness of about 2.5 km. It is composed mainly of well compacted, welded ash flow tuffs with a compaction ratio of up to 1:20. The ash flow sheets have well developed planar features and columnar jointing. Compared to the Pogy Member, it has less extensive deuteric alteration, a lower phenocryst content, and a much lower abundance of quartz phenocrysts (Table 2).

# C. Mineralogy of the Traveler Rhyolite

The lower Pogy unit contains between 10 and 25% phenocrysts, typically about 15%, made up of 60% plagioclase, 30% quartz, 8% mafic silicates (clinopyroxene, biotite), and 2% opaques, plus accessory zircon, monazite(?), apatite, and occasionally alkali feldspar, garnet and hornblende (Table 2). The Black Cat Member has on average a smaller proportion of phenocrysts (10%), ranging from about 5 to 15%, and a significantly different proportion of phenocrysts: 75% plagioclase, 20% mafic silicates, 4% opaques plus accessory zircon, apatite, monazite(?), 0 to 5% quartz, no alkali feldspar, no garnet and frequently fayalitic olivine. These mineral differences, particularly the virtual absence of quartz in the Black Cat Member, are fundamental and serve as the criteria for distinguishing these two units (Rankin, 1968). Noticeable differences also include the

# Table 2

	POGY MEMBER	BLACK CAT MEMBER
Stratigraphic Position	Lower	Upper
Estimated Thickness	1000 m	2500 m
Average Content Of Phenocrysts	15%	10%
Percentage Range Of Phenocrysts	10-25%	5-15%
Extent Of Alteration	Extensive	Moderate
Aggregation Of Phenocrysts	Single Crystals	Common Mineral Aggregates

Plagioclase	60	75
Quartz	30	<u>+</u>
Alkali Feldspar	±	-
Clinopyroxene & Biotite	8	20
Hornblende	±	±
Garnet	±	-
Olivine	-	+
Opaques	2	4
Microphenocrysts Of Apatite, Zircon, Monazite	+	+

freshness of phenocrysts and their mode of aggregation. Rocks within the Pogy unit display phenocrysts freely suspended in the groundmass, whereas the phenocrysts in the Black Cat unit frequently form mineral aggregates. The phenocrysts of the Pogy Member show a more advanced degree of alteration. The mafics are commonly fully altered and the plagioclase is often completely obliterated by secondary minerals. Occasionally, the mafic phenocrysts of the Black Cat unit are also altered, but more frequently they are fresh or have at least unaltered remnants in their centers. Plagioclase is usually fresh.

Two rhyolitic samples from the Black Cat unit (Sample #217 taken near the contact with the Pogy unit, and Sample #219 taken from the interior of the Black Cat member) were selected for a detailed electron microprobe study. All the samples collected along the Pogy Notch (N-S) profile, how-ever, were examined optically. The sample localities are given on Fig. 4.

## Plagioclase:

Plagioclase forms up to 4 mm large, thick tabular euhedral or subhedral phenocrysts. They are typically oscillatory zoned, with continuous or stepwise normal zoning in each oscillatory section. Occasionally, one of the inner oscillatory sections is resorped or corroded. Plagioclase composition in Sample #219 ranges from An54 Ab44 Or2 to An33 Ab63 Or4, and in Sample #217 from An53 Ab45 Or2 to An31 Ab65 Or4 (Fig. 5). Optical examination indicates a similar compositional range for all samples. There is a slightly lower anorthite content (by 2 to 5 mol.% An) in plagioclases from the Pogy unit. When mildly altered, plagioclase is either sericitized or saussuritized, or in a more advanced alteration stage, it is completely replaced by a mixture of secondary minerals: sericite, calcite, kaolinite, epidote group, and chlorite, with calcite being the dominant phase. Many plagioclase phenocrysts contain accessory apatite or, less commonly, zircon and opaques. Polysynthetic albite twinning is pronounced; Carlsbad twinning is frequent.

#### Alkali Feldspar:

No alkali feldspar has been observed in any of the samples examined in this study, but Rankin (1968) reported its infrequent trace occurrence in a few samples of the Pogy Member. In one sample, where he reports the presence of alkali feldspar in large amounts, the alkali feldspar is slightly perthitic, low sanidine, with an estimated composition of Or67. Alkali feldspars have never been found in the Black Cat unit.

#### Quartz:

Quartz is present in significant amounts in the Pogy unit only. Euhedral, subhedral or fragmental quartz phenocrysts have an hexagonal outline (high quartz); they are up to 2 mm large and contain frequent, open or closed, embayments of groundmass. Quartz also contains numerous fluid

Fig. 5. Plagioclase and Alkali Feldspar Compositions Determined by Electron Microprobe Analysis. Plotted on Molecular An-Ab-Or Diagram.

Legend:	TRBC	-	Traveler	Rhyolite:	Black	Cat	Member
	KGD		Katahdin	Granite:	Doublet	cop	Facies
	KGCT	-	Katahdin	Granite:	Cathedi	ral	Facies
	HQD	-	Horserace	e Quartz I	Diorite		



inclusions (in tens of microns or less) and occasionally small inclusions of apatite and opaques.

The volcanics of the Black Cat Member contain quartz only occasionally and only in trace amounts. There is, however, no proof that the quartz in the Black Cat samples is of a primary magmatic nature. Most of the quartz is believed to be of a secondary origin; that is, it crystallized into open voids upon cooling of the stil hot layers of tuffaceous deposits.

#### Clinopyroxene:

Clinopyroxene was positively identified only in samples from the Black Cat Member. Its presence in the Pogy Member is implied on the basis of abundant pseudomorphs now filled by chlorite, calcite, epidote minerals, opaques, and possibly prehnite. Short prismatic, up to 2 mm large, euhedral or subhedral crystals of clinopyroxene are frequently twinned with infrequent inclusions of accessory apatite, zircon, monazite(?), and opaques. Microprobe data on clinopyroxene from Samples #217 and #219 show a tight clustering of individual analyses around Wo39 En20 Fs21--ferroaugite (Fig. 6). These phenocrysts are very homogeneous except for the cores which show slight enrichment in the Tschermark's molecule. Based on identical optical properties, it is concluded that the composition of clinopyroxene was essentially constant throughout the Black Cat Member and possibly throughout the entire section of the Traveler Rhyolite.

Fig. 6. Chemical Compositions of Coexisting Olivine And Clinopyroxene in Black Cat Member of Traveler Rhyolite: Sample # 219. Compositions Determined by Electron Microprobe Analysis. Olivine Compositions Are Plotted on Molecular Forsterite-Fayalite-Tefroite Diagram And Clinopyroxene Compositions Are Plotted on Wollastonite-Enstatite-Ferrosilite Molecular Diagram. Heavy Contoured Lines And Tie-Lines Are For Coexisting Olivines, Orthopyroxenes And Clinopyroxenes in Tertiary Acid Glasses as Determined by Carmichael (1960).



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# Olivine:

Fayalitic olivine (Fol4 Fa84 Tf2), representing about 10% of phenocrysts, was found in only one fresh sample (Sample #219) from the Black Cat unit (Fig. 6). Here, the olivine is unaltered and forms equidimensional subhedral, fractured grains (up to 1.5 mm in size), with frequently attached or enclosed opaques. Microprobe data of the opaques show that they are mostly magnetites and only rarely ilmenites. The textural relationships within the fayaliteopaque aggregation suggest that at least some of the magnetite may be the product of oxidation of fayalites (QFM reaction).

Since it is difficult to relate the chlorite-epidotecalcite-opaque pseudomorphs to their original minerals, it is probable that the fayalitic olivine was originally far more widespread, not only within the Black Cat Member, but possibly even within some parts of the Pogy Member. This conclusion is supported by the occurrence of fayalitic olivine in the Katahdin Granite, which is, as will be shown later, comagmatic with the rhyolites.

#### Biotite:

Next to clinopyroxene, biotite is the most frequently preserved mafic mineral commonly found in both the Pogy and the Black Cat Members. Biotite forms up to 1 mm in diameter, euhedral to subhedral, flaky phenocrysts, which contain abundant inclusions of apatite and zircon. The intense pleochroism of biotite from straw-yellow to dark-reddish brown is in accordance with the microprobe-determined, chemical composition: Fe/(total octahedral ions) = 0.52 and 4.05 wt.%  $\text{TiO}_2$ . Upon alteration, biotite is replaced by chlorite with numerous sagenitic needles.

# Chlorite(?):

A number of conspicuous grains in Sample #219 display pronounced, hornblende-like, pleochroism, from yellow-tan to deep green. Upon detailed microscope examination, this mineral shows parallel extinction, one direction of excellent cleavage, birds-eye texture typical of sheet silicates, uniaxial or nearly uniaxial negative character, and a moderate birefrigence.

Up to 1.5 mm large, thick tabular, subhedral grains, representing about 5% of phenocrysts, are alteration-free and the overall appearance suggests a primary origin. The microprobe-determined chemical composition shows very low oxide total (87.5%) and the absence of alkali metals, alkali earth, and titanium. The cation proportions are best matched by the general formula for chlorites:

<sup>(Mg</sup>1.63<sup>Mn</sup>0.12<sup>Ca</sup>0.08<sup>Fe</sup>8.39<sup>A1</sup>1.69<sup>)</sup> <sup>(A1</sup>1.51<sup>Si</sup>6.59<sup>O</sup>20<sup>)(OH)</sup>16

In the chlorite quadrilaterial (Fig. 7), this composition lies near the extreme limit of naturally occurring chlorites; therefore, it is believed that this mineral belongs to the Fig. 7. Plot of Electron Microprobe Determined Composition of Primary Chlorite(?) Phenocrysts in Sample #219 From the Black Cat Member of Traveler Rhyolite. Chlorite Quadrilateral After Deer, Hovie, Zussman, 1963.


chlorite group, the dominant end-member being the iron analogue of pennin (brunswigite).

### Other Mafic Silicates:

Garnet is a rare, medium-size, euhedral, equidimensional mineral not observed in any of the samples studied here, but reported by Rankin (1968) as an occasional accessory. Also reported by Rankin (1968) is the rare occurrence of hornblende.

### Iron-Titanium Oxides:

In all the fresh samples studied, the titanomagnetites and ilmenites are ubiquitous microphenocrysts. The microphenocrysts, usually 0.05-0.1 mm in size, constitute approximately 2% and 4% of the total phenocryst content within the Pogy and Black Cat units, respectively. In Sample #219 (Black Cat Member) ilmenites are frequently associated with clinopyroxene and plagioclase, whereas titanomagnetites are always attached to fayalites. Microprobe analyses of coexisting titanomagnetites and ilmenites from Sample #219 were recalculated according to the method described by Carmichael (1967): the ulvospinel content (mole percent of the titanomagnetites) ranges from 44.3% to 54.2% (average 50.4%). The ilmenites contain between 2.8% and 4.6% of  $Fe_2O_3$  in solid solution (average 4.0%). The average ilmenitetitanomagnetite tie-line is shown on Fig. 8. The analysis of Co, Ni, V and Zn was attempted, but none of these elements were found. Low oxide totals of titanomagnetites are attributed to deuteric oxidation.

- Fig. 8. Chemical Compositions of Coexisting Ilmenite And Magnetite in Black Cat Member of Traveler Rhyolite: Sample # 219. Compositions Determined by Electron Microprobe Analysis Are Plotted on Molecular TiO<sub>2</sub> -FeO - Fe<sub>2</sub>O<sub>3</sub> Diagram.
  - Legend: 1 Magnetite s.s. of Sample # 219
    - 2 Ilmenite of Sample # 219
      - 3 Range And Limits of Naturally Occurring Coexisting Fe-Ti Oxides And Their Tie-lines (Carmichael, 1967)



# D. Petrology of the Traveler Rhyolite

# 1. Estimates of Temperature, Oxygen Fugacity, and Water Fugacity

A preliminary optical examination of 11 samples showed that only one specimen, Sample #219, was fresh enough to ensure accurate estimates of intensive parameters from coexisting mineral phases. The essentially identical mineralogy of other samples, even if not as fresh, warrants a cautious but reasonable extrapolation to the entire volcanic sequence, or, at least, to a major part of it.

# Oxygen Fugacity Estimates

Estimated values of oxygen fugacity and temperature from ilmenite-magnetite pairs have resulted in considerably uncertainties, largely due to a compositional variation of the magnetite solid solution (Mt45 Usp55 -Mt55 Usp45) and due to a decreased sensitivity of the ilmenite-hematite solid solution in the range of low oxygen fugacities. Since both opaques coexist with fayalitic olivine, the temperature and  $f(O_2)$  can be estimated, instead, from an oxidation reaction of fayalitic olivine, as determined by Wones and Gilbert (1969):

 $3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2$ Fayalite + Oxygen = Magnetite + Quartz Log f(O<sub>2</sub>) = -25738/T(<sup>O</sup>K) + 9.00 + 2 log a(Mt) + 3 log a(Q) - 3 log a(Fa) Fig. 9. Plot of Log f(O<sub>2</sub>) - T(<sup>O</sup>C) for Coexisting Ilmenite s.s. And Magnetite s.s. in Black Cat Member of Traveler Rhyolite: Sample # 219.(Buddington, Lindsley,1964). Compositions Determined by Electron Microprobe Analysis. Lines Designated as QFM-1, QFM-2, QFM-3 Are Quartz + Magnetite + Fayalite Univariant Lines Calculated For a(Q)=0.95, a(Fa)=0.72, a(Mt)=0.45; 0.50; 0.55, Resp. Equilibrium Constant For QFM Reaction From Wones, Gilbert, 1969.



Assuming ideal solution models for magnetite and olivine solid solutions, and assuming the activity of quartz to be about 0.95, the oxygen fugacity can be readily expressed in terms of temperature. The activity of quartz, equal to 0.95, is based on equilibrium constant for reaction  $SiO_2$ (glass) and quartz (Nicholls, 1972). The quartz is assumed to be a stable phase at temperatures 50 degrees lower than the liquidus. Three curves, relating temperature and  $f(O_2)$ , were calculated for a compositional range determined by microprobe analysis: olivine x(Fa) = 0.85 and X(Mt) = 0.45; 0.50; 0.55. These curves, including relevant curves for coexisting ilmenite-magnetite pairs from Buddington, Lindsley (1964), are shown in Fig. 9.

 $a(Fa) = (x(Fe))^2 = 0.72$ a(Mt) = x(Mt) = 0.45; 0.50; 0.55

The intersection of the calculated QFM curve, with the corresponding curve for magnetite solid solution, indicates the temperature and  $f(O_2)$  at which olivine, magnetite, and ilmenite are in equilibrium. The intercepts are (Fig. 9):

	x(Mt)	x(Hm) 7	C C	$\log f(0_2)$
1.	0.55	0.045	787	-15.42
2.	0.50	0.043	810	-15.00
3.	0.45	0.039	837	-14.51
Fe-Ti Oxides	:0.50	0.040	803	-15.22

The estimates based on the coexisting titanomagnetite and ilmenite pair are given for comparison.

Note that the equilibrium ilmenite composition should lie between Ilm96.1 Hm3.9 and Ilm95.5 Hm4.5, which agrees well with the compositions determined via microprobe (Ilm96 Hm4). The uncertainty due to the estimated activity of quartz is very small and can for all practical purposes be ignored. However, there is a possibility that the magnetite solid solution is not in equilibrium with ilmenite and, in such a case, these temperature estimates would represent minimum values.

#### Temperature Estimates:

Kudo, Weill (1970), Roeder, Emslie (1970), and Roeder (1974) give empirical sets of equations which enable temperature estimates to be made based on equilibrium of plagioclase or olivine with their respective groundmasses. The rim of plagioclase phenocrysts (Sample #219) has a composition of An34.5 and coexists with a groundmass of normalized molar proportions equal to:

- x  $(SiO_2) = 0.7890$ ,  $x(Al_2O_3) = 0.1485$ , x(CaO) = 0.0120and
- $x (Na_2 0) = 0.0505.$

Temperature estimates calculated for several assumed values of  $P(H_2O)$  yield the following results (Kudo, Weill, 1970):

P(H <sub>2</sub> O) (Kb)	т
Dry	927
0.5	877
1.0	805
1.5	709
1.8	605

The equation coefficients for 1.5 Kb and 1.8 Kb were obtained by interpolation. The equation at pressures above 1.8 Kb becomes unsolvable; this pressure places a minimum limit on temperature and a maximum limit on  $P(H_2O)$ .

The olivine-groundmass equilibrium equation gives the following set of temperature estimates:

		Roeder, Emslie (1970)	Roeder (1974)	Avg.
MgO	distribution	795 <sup>0</sup> C	758 <sup>0</sup> C	776 <sup>0</sup> C
Fe0	distribution	685 <sup>0</sup> C	661 <sup>0</sup> C	673 <sup>0</sup> C

The temperature estimates, based on FeO distribution, are clearly too low. This can be partly attributed to the large scatter of data on which the equation is based, especially since the experiments were done at temperatures above  $1150^{\circ}$ C. The above calculations assume the total absence of Fe<sup>+3</sup> in the melt; if Fe<sup>+3</sup> were present, the temperature estimates would yield even lower values.

#### Water Fugacity Estimates:

A semi-quantitative method for estimating the preeruption water pressure for the Black Cat rhyolite is provided by the plagioclase geothermometer of Kudo, Weill (1970). The thermometer allows calculations of equilibration temperatures between plagioclase and groundmass for several assumed water pressures (dry, 0.5, 1.0, and 5 Kb). By interpolation, it can be solved for other values of water pressures to obtain an agreement with the temperature calculated from coexisting iron-titanium oxides and/or from coexisting olivine and groundmass. Such an agreement is obtained at water pressures in the range of 1050 to 1200 bars.

A direct calculation of  $P(H_2O)$  utilizes the stability of biotite, as expressed by the following reaction:

(1)  $2KFe_3A1Si_3O_{10}(OH)_2 + 3SiO_2 = 2KA1Si_3O_8 + 3Fe_2SiO_4 + 2H_2O$ 

Annite + Quartz = Sanidine + Fayalite + Water

An oxidation-dehydration reaction suggested earlier by Wones, Eugster (1965) and Wones (1972) is expressed as follows:

(2)  $\text{KFe}_3\text{AlSi}_3\text{O}_{10}(\text{OH}_2) + \frac{1}{2}\text{O}_2 = \text{KAlSi}_3\text{O}_8 + \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$ Annite + Oxygen = Sanidine + Magnetite + Water The equation based on the above reaction requires as input data from the ilmenite-magnetite oxygen barometer-thermometer. Since there is a considerable compositional uncertainty associated with this pair, particularly in the composition of magnetite, reaction (1) is, therefore, preferred.

The equilibrium constant for the annite-fayalite reaction is readily obtained by arithmetical manipulation of the equilibrium constants of the annite oxidationdehydration reaction (2) and the QFM buffer reaction (3):

(3) 
$$3 \operatorname{Fe}_2 \operatorname{SiO}_4 + \operatorname{O}_2 = 2 \operatorname{Fe}_3 \operatorname{O}_4 + 3 \operatorname{SiO}_2$$

- - - - -

When expressed as functions of  $f(\rm O_2)$  and  $f(\rm H_2O),$  the equilibrium constants are:

ad(2)	$\log f(H_2 0) = \frac{7409}{T} + 4.25$	Wones (1972)
ad(3)	$\log f(0_2) = \frac{-25738}{T} + 9.00$	Wones, Gilbert (1969)
ad(1)	$\log f(H_2 0) = \frac{-5460}{T} + 8.75 + 3$	3log x (Ann) +
	$\frac{3}{2} \log a$	(Q) - log a(San)
		$-\frac{3}{2}\log a(Fa)$

The annite mole fraction taken from microprobe analysis as Fe\*/(sum octahedral ions) would be equal to x(Ann) = 0.52. Wones, Eugster (1965) have shown that x(Ann) at QFM buffer is actually 5 mol.% lower than the Fe\*/(sum octahedral ions) value. (Note: Fe\* is total atomic iron). After applying this correction, x(Ann) is 0.47. Assuming ideal solution model for olivines, the a(Fa) taken as  $x^2(Fa)$  is equal to 0.72, and the activity of quartz is assumed to be 0.95 (see discussion on Oxygen Fugacity). The activity of sanidine is estimated from x(Or) in plagioclase, i.e., x(Or) = 0.046. According to Seck (1972), the Or level of saturated plagioclase at a temperature of  $800^{\circ}C$ and 1 Kb pressure is x(Or) = 0.063. On the assumption that the Or component in plagioclase obeys Henry's law, the sanidine activity in the TRBC magma is equal to a fractional value (0.046/0.063) of a(Or) in the plagioclase-alkali feldspar pair. From the coexisting alkali feldspar and the numerical model of Waldbaum and Thompson (1969), the calculated a(Or) for the olivine-biotite reaction is equal to 0.55.

Table 3 tabulates  $f(H_2O)$ 's calculated for several assumed values of sanidine and quartz activities. For reasons that biotite may contain an appreciable amount of fluorine, the  $f(H_2O)$ 's represent maximum values.

As shown on the diagram in Fig. 10, all temperature and  $P(H_2O)$  estimates, including the estimates derived from the fayalite-annite reaction (a(Q) = 0.93, a(San) = 0.55), are graphically illustrated.  $P(H_2O)$ 's were obtained from  $f(H_2O)$ 's, using the tables of Burnham et. al. (1973). Since the olivine-biotite pair indicates maximum  $P(H_2O)$ 's, the best temperature and  $P(H_2O)$  estimate is  $800^{O}C$  and 1100 bars.

Table 3

			Te	mperature	°c	
a(Q)	a(San)	760	780	800	820	840
0.90	0.45	936	1180	1474	1826	2245
	0.50	843	1062	1326	1643	2020
	0.55	766	965	1206	1494	1837
	0.60	702	885	1105	1369	1684
	0.65	648	817	1020	1264	1554
0.95	0.45	1015	1279	1518	1980	2435
	0.50	914	1151	1438	1782	2191
	0.55	831	1047	1307	1620	1992
	0.60	761	959	1199	1485	1826
	0.65	703	886	1106	1371	1685
1.00	0.45	1097	1382	1726	2138	2629
	0.50	987	1243	1553	1925	2366
	0.55	897	1130	1412	1750	2151
	0.60	822	1036	1294	1604	1972
	0.65	759	956	1195	1480	1820
	]					

Water fugacities calculated from equation (3):

a(Fa) = 0.72, x(Ann) = 0.47.

Fig. 10. Plot of Various Geothermometers And Geobarometers For the Black Cat Member of Traveler Rhyolite: Sample # 219. See Text For More Details on Calculations And Selected Reactions. Various Geothermometers And Geobarometers Obtain From Mineral Assemblages of Sample # 219 of Black Cat Member, Traveler Rhyolite.





# 2. <u>Major Element Geochemistry and Origin of the</u> <u>Traveler Magma</u>

The equilibrium composition of granitic melts coexisting with one or two feldspars and quarts has been shown by several investigators to be sensitive to changing water pressure, temperature, total pressure, and other volatile components. Experimental studies presenting data on these equilibria are listed below:

- (1) Tuttle, Bowen (1958), and Luth, Jahns, Tuttle (1964) studied the water saturated portion of Q-AB-OR-H<sub>2</sub>O systems at pressures up to 10 Kb  $P(H_2O)$ ;
- (2) v. Platten (1965), James, Hamilton (1969), Winkler,
  Lindemann (1972) and Winkler, Ghose (1973) investigat ed similar systems but included an AN component;
- (3) Luth (1969), Whitney (1972), and Steiner, Jahns, Luth (1975) studied the effect of water undersaturation in the granitic system;
- (4) Goranson 1931), Burnham, Jahns (1962), Burnham (1967), Brown (1970), and Cann (1970) determined water solubility and the role of water during partial melting in granitic systems;
- (5) Wyllie, Tuttle (1961, 1964), v. Platten (1965), and Glyuk, Anfilogov (1973) presented data on water saturated granitic systems containing halogens (HF, HCl) as additional volatile components.

Fig. 11 illustrates pertinent experimental data within the Q-OR-AB-AN tetrahedron. The lower part of the diagram shows projections of the alkali feldspar-plagioclase-quartz melt cotectics onto the front AN-AB-OR plane, whereas the center part is a projection on the Q-OR-AB base.

This combined diagram allows a reconstruction in space of each of the cotectic curves within the tetrahedron. The important characteristic of each cotectic line is a nearly constant AN content, decreasing sharply as it approaches its corresponding minimum melting point in the Q-OR-AB plane. The Ab/Or ratio of the cotectic "elbows" is a very sensitive function of  $P(H_2O)$ . The ratio increases with increasing  $P(H_2O)$ . This effect is counteracted by even a very small concentration of halogens (v. Platten, 1965). There are also indications of the possibility of a quarternary minimum near the vicinity of the cotectic "elbow". Strongly differentiated granitic melts, e.g., aplitic dikes, still contain significant amounts of CaO. Noble et. al. (1970) documented a quarternary minimum in natural, slightly paralkaline melts. Any set of granitic melts that clusters near one of these "elbows" can be considered as being in equilibrium with two feldspars and quartz at  $\mathrm{P(H}_2\mathrm{O})$  indicated by the particular cotectic line.

Thirteen fresh samples of whole rocks and groundmass from the Traveler and Kineo Rhyolites were analyzed for major elements by electron microprobe. The techniques

- Fig. 11. Experimentally Determined Crystal-Liquid Equilibria Within Q-Or-Ab-An Tetrahedron For P(H<sub>2</sub>O) Up to 4 Kb.
  - Legend: 1 Shift And Range of Change of Q-Or-Ab Eutectics With Increasing Water Undersaturation at P(T)= 4 Kb (Steiner and Others, 1975)
    - 2 Two Feldspar, Quartz And Melt 4 Kb P(H2O) Cotectic; (From Winkler And Lindeman, 1972, And From Luth and Others, 1964)
    - 3 Data Points And Quaternary Cotectic For P(H<sub>2</sub>O)= 2 Kb (v.Platten, 1965; Winkler And Lindeman, 1972; Tuttle And Bowen, 1958)
    - 4 Data Points And Quaternary Cotectic For P(H<sub>2</sub>O)= 1 Kb (James and Hamilton, 1969)
    - 5 Data Points For  $P(H_2O)= 2$  Kb With 0.05 M Added HCl (v.Platten, 1956)
    - 6 Q-Or-Ab Ternary Minima And Eutectics For  $P(H_2O)=$  0.5; 1; 2; 3; 4; 5; 10 Kb.(Tuttle And Bowen, 1958; Luth And Others, 1964)



used employed a defocused beam (groundmass) and analysis of fluxed glasses (whole rock); included are also three analyses from Rankin's Ph.D. thesis and one from Smith (1933). The analyses given in Smith's (1930) and Boucot's (1969) works were excluded on the grounds of high  $Fe_2O_3$ or  $H_2O^+$  contents. The plots of normative (wt.%-CIPW) Q-AB-OR and OR-AB-AN ratios are illustrated in Fig. 12.

The whole rock data cluster near two lines defined by Black Cat and Pogy samples. These lines can be interpreted as halogen-bearing cotectics at 4 Kb and 3.5 Kb  $P(H_2O)$ , respectively. The presence of halogens in the Traveler magma is consistent with the occurrence of fluorite in the groundmass of the Traveler rhyolites.

From water solubility data of Burnham and Jahns (1962), the water content in granitic magma at  $P(H_2O) = 1100$  bars is 4.4 wt.%, which represents the average solubility for temperatures between 750 and 850°C. However, if the anhydrous phenocrysts are included as part of the molten magma, the whole rock water content is somewhat lower (3.9 wt. %). Assuming that there was no significant change of water content after the magma was formed, and that the original magma temperature was slightly higher (e.g., 810°C), Fig. 13 then demonstrates that the maximum total pressure at which an undersaturated granitic magma, with 3.9 wt.% of  $H_2O$ at 810°C can still form, is approximately 8 Kb.

It is evident that the Traveler magma was formed by partial fusion at a depth of 25-30 km and at a temperature

Sample Symbol :	4	8	13	21	29	41	43	46	64	69	74
Rock Unit	HLP	HLP	DGD	Mafic <u>Dike</u>	KGD	KGD	KGW	TRP	KGS	КССН	KGD
SiO <sub>2</sub>	70.60	70.85	72.42	55,88	72.90	75 89	74.38	74 18	75 65	75.18	76.36
TiO2	0.35	0.36	0.33	0.71	0.26	0.23	0.30	0.26	0.23	0.23	0.21
A1203	15.78	16.13	14.70	14.29	13.21	12.54	12.76	13.12	12.64	12.86	12.07
Fe0	2.40	2.30	2.43	7.05	2.48	2.01	2.32	2,28	2.32	2.41	1.53
MnO	0.02	0.07	0.05	0.16	0.03	0.09	0.02	0.07	0.13	0.04	0.03
MgO	1.03	0.95	0.72	9.97	0.24	0.14	0.26	0.18	0.13	0.11	0.08
Ca0	2.55	1.81	2.06	6.69	1.35	0.50	0.43	1,15	0.86	1.15	0.63
Na <sub>2</sub> 0	4.66	5.83	3.91	2.59	3.60	4.27	3.90	3.48	3.37	3.01	3.18
K20	2.35	1.68	3.90	1.48	4.64	4.20	5.05	4.83	4.79	4.77	4.94
P <u>2</u> 05	0.09	0.17	0.02	0.41	0.07	0.07	0.23	0.11	0.02	0.03	0.14
Total	99.83	100.17	100.54	99.23	98.78	99.96	99.65	99.66	100.14	99.79	99.17
Loss on Ignition	1.81	1.71	0.52	5.44	0.60	0.35	0.38	0.68	0.64	0.69	0.49
CIPW Norm:											
Or	13.89	9,93	23.05	8 75	27 42	24 82	29 84	28 54	28 31	28 19	29 19
Ab	39.43	49.33	33.09	21.92	30 46	36.13	33.00	20.04	28 52	25.47	26 91
An	12.07	7.88	10.09	23.00	6 18	1,90	0.65	/ 99	4 14	5.51	2.22
Q	25.99	23.98	27.49	3.23	29 25	32 36	29.97	31 26	33 86	34 99	36.73
C	1.15	1.83	0.35			0.27	0.64	0 34	0 40	0.73	0.68
Di				6.10	0.05						
Wo				3.15	0.03						
En				1,99	0.00						
Fs				0.97	0.02						
Hy	6.43	6.13	5.80	33.95	4.75	3.83	4 45	4 34	4 45	4.39	2.72
En	2.57	2.37	1.79	22.84	0.59	0.35	0.65	0 45	0 32	0.27	0.20
Fs	3.87	3.76	4.01	11.11	4.16	3.48	3.80	3 89	4 12	4.12	2.52
Ар	0.21	0.40	0.05	0.95	0.16	0.21	0.53	0.26	0.05	0.07	0.33
IÌ	0.66	0.68	0.63	1.35	0.49	0.44	0.57	0.49	0.44	0.44	0.40 v

Table 4. Major Element Geochemistry. Samples Arranged in Ascending Numeric Order and Alphabetically.

	0		b (	,							
Sample : Symbol :	81	115	121	127A	134-1	134-2	134-3	134-4	134-5	134-6	 134 <b>-</b> 7
Rock : Unit :	KGD	KGD	KGCT	HQD	KGD	KGD	AP3	PEG3	PEG3	AP3	AP3
Si02	73.92	73.99	74.08	62.67	74.91	75.14	76.89	75.90	76.42	77.32	77.35
$TiO_2^-$	0.20	0.29	0.25	0.67	0.26	0.27	0.04	0.05	0.08	0.06	0.08
$A1_2\overline{0}_3$	13.43	13.09	13.44	15.69	13.06	13.29	13.17	13.06	13.19	12.23	12.21
FeÕ	3.07	2.28	2.02	4.30	2.57	2.56	0.63	0.56	0.56	0.99	0.90
MnO	0.05	0.07	0.06	0.08	0.02	0.04	0.00	0.02	0.03	0.03	0.03
MgO	0.26	0.20	0.28	4.60	0.24	0.20	0.05	0.08	0.12	0.09	0.08
Ca0	1.29	1.07	1.36	4.55	1.08	0.84	0.40	0.28	0.28	0.53	0.60
Na2O	4.82	3.37	3.48	4.25	3.38	3.80	4.21	3.52	3.22	3.85	3.90
K20	3.29	4.79	4.49	2.57	4.70	4.50	5.04	6.51	6.96	4.75	4.88
P <sub>2</sub> O <sub>5</sub>	0.20	0.13	0.02	0.28	0.02	0.04	0.02	0.03	0.05	0.00	0.00
Total	100.53	99.28	99.48	99.66	100.24	100.68	100.45	100.01	100.91	99.85	100.03
Loss on Ignition	1.39	0.92	0.53	1.14	0.50	0.62	0.24	0.43	0.33	0.82	0.40
CIPW Norm:											
Or	19.44	28.31	26.53	15.19	27.78	26.59	29.79	38.47	41.13	28.07	28.84
Ab	40.79	28.52	29.45	35.96	28.60	32.16	35.62	29.79	27.25	32.58	33.00
An	5.11	4.47	6.62	16.15	5.23	3.91	1.86	0.61	0.98	2.06	1.40
Q	28.24	32.08	31.82	10.12	32.67	31.85	31.74	29.55	30.00	34.79	34.20
С	0.07	0.72	0.43		0.50	0.74	0.11				
Di				3.76				0.51	0.07	0.50	1.38
Wo				1.93				0.24	0.04	0.24	0.66
En				1.14				0.04	0.01	0.03	0.08
Fs				0.69				0.22	0.03	0.23	0.64
Ну	6.05	4.34	4.11	16.56	4.92	4.83	1.22	0.92	1.21	1.74	1.05
En	0.65	0.50	0.70	10.32	0.60	0.50	0.12	0.15	0.29	0.19	0.12
Fs	5.40	3.84	3.41	6.25	4.33	4.33	1.09	0.76	0.92	1.54	0.93
Ap	0.46	0.30	0.05	0.65	0.05	0.09	0.05	0.07	0.12	0.00	0.00
I1	0.38	0.55	0.47	1.27	0.49	0.51	0.08	0.09	0.15	0.11	0.15

Table 4. Major Element Geochemistry (cont.).

Sample Symbol :	134-8	145	150	166	188	190F	190W	198	209	214	215
Rock Unit :	AP3	AP 2	KGD	DGD	AP4	KGD	KGD	КССТ	KGD	TRP	TRP
Si02	78.25	76.79	74.67	73.00	77.31	75.20	75.05	72.86	74.34	73.47	75.78
Ti02	0.09	0.11	0.19	0.36	0.08	0.14	0.27	0.34	0.26	0.36	0.30
$A1_2 \tilde{O}_3$	12.19	12.28	12.86	13.82	13.11	13.60	13.09	13.80	13.30	13.09	12.50
FeÕ	0.93	1.06	2.38	2.68	0.99	1.41	2.47	2.95	2.55	2,60	2,43
MnO	0.03	0.03	0.07	0.02	0.04	0.08	0.09	0.05	0.05	0.02	0.01
MgO	0.10	0.04	0.19	0.54	0.08	0.35	0.24	0.27	0.16	0.19	0.23
CaO	0.59	0.31	1.08	2.34	0.46	1.38	0.79	1.43	1.23	1.71	1.45
$Na_{2}O$	3.71	3.65	3.30	3.70	4.21	4.21	3.65	3.32	3.26	2.79	1.85
К <sub>2</sub> б	4.73	4.80	4.55	3.38	4.90	3.86	4.55	4.42	4.62	5.04	4.73
P <sub>2</sub> 0 <sub>5</sub>	0.01	0.00	0.08	0.13	0.00	0.13	0.14	0.04	0.14	0.00	0.00
- <b></b> Total	100.63	99.07	99.37	99.97	101.18	100.36	100.34	99.48	99.91	99.27	99.28
Loss on Ignition	0.40	0.47	0.48	0.68	0.44	0.40	0.77	0.75	0.79	2.22	2.07
CIPW Norm:											
Or	27.95	28.37	26.89	19,98	28,96	22.81	26.89	26.12	27 30	29 79	27 95
Ab	31.39	30.89	27.92	31.31	35.62	35.62	30.89	28.09	27 59	23.61	15 65
An	2.64	1.54	4.84	10.77	2.28	6.01	3.01	6.84	5 20	8 31	7 19
Q	36.49	35.63	33.78	31.10	32.16	31.68	32.81	31.02	33.23	32.12	41.65
ċ		0.52	0.73	0.13	0.04	0.30	1.06	1.05	1.03		1 70
Di	0.19									0.15	
Wo	0.09									0.07	
En	0.01									0.01	
$\mathbf{Fs}$	0.09									0.07	
Hy	1.76	1.92	4.66	5.71	1.96	3.38	4.85	5.62	4.74	4.61	4.56
En	0.24	0.10	0.47	1.34	0.20	0.87	0.60	0.67	0.40	0.47	0.57
Fs	1.53	1.82	4.19	4.36	1.76	2.51	4.26	4.95	4.35	4.15	3.99
Ap	0.02	0.00	0.19	0.30	0.00	0.30	0.33	0.09	0.33	0.00	0.00
11	0.17	0.21	0.36	0.68	0.15	0.27	0.51	0.65	0.49	0.68	0.57

Table 4. Major Element Geochemistry (cont.).

Sample :	216	217	219	220	235	238	240	244	247	6291	KM1
Rock Unit	TRP	TRBC	TRBC	TRBC	HQD	HỌD	KGD	Moxie Granite	Kineo Rhyol.	Echo Pond Gr.	KGS
SiO <sub>2</sub>	69.58	71.48	71.06	73.00	62.46	63.71	76.61	74.03	73.79	72.09	74.28
TiO <sub>2</sub>	0.56	0.40	0.50	0.39	0.63	0.55	0.50	0.27	0.27	0.40	0.21
$A1_20_2$	13.95	13.20	13.65	13.27	16.42	16.43	12.55	12.88	13.37	12.77	13.00
FeŐ	5.33	4.34	4.13	3.93	4.35	4.05	1.40	2.43	2.45	3.99	2.97
MnO	0.07	0.08	0.04	0.04	0.10	0.00	0.02	0.05	0.06	0.09	0.04
MgO	0.52	0.30	0.36	0.20	3.62	3.48	0.12	0.21	0.21	0.29	0.13
Ca0	2.13	1.94	2.04	1.44	4.92	4.61	0.50	1.06	1.18	1.86	0.86
Na <sub>2</sub> 0	3.68	2.99	3.02	3.11	4.47	4.47	3.22	3.38	3.74	3.24	3.50
K2Ó	3.93	4.74	4.58	4.31	1.99	2.03	5.11	4.71	5.00	4.36	5.02
P205	0.21	0.06	0.09	0.09	0.20	0.24	0.08	0.12	0.18	0.28	0.00
Total	99.96	99 <b>.</b> 53	99.47	99.78	99.16	99.57	100.11	99.14	100.25	99.37	100.01
Loss on Ignition	1.22	0.57	0.42	1.13	0.83	0.79	0.58	0.41	0.48	0.52	0.48
CIPW Norm:											
Or	23.23	28.01	27.07	25.47	11.76	12.00	30.20	27.83	29.55	25.77	29.67
Ab	31.14	25.30	25.55	26.32	37.82	37.82	27.25	28.60	31.65	27.42	29.62
An	9.21	8.60	9.54	6.56	18.86	18.77	1.96	4.48	4.69	7.42	4.27
Q	24.28	28.24	28.19	32.25	11.13	13.12	36.48	32.22	28.66	29.81	30.31
Ċ	0.27		0.23	1.08			1.00	0.58	0.09	0.00	0.25
Di		0.56			3.49	2.09					
Wo		0.27			1.78	1.06					
En		0.03			0.96	0.58					
Fs		0.27			0.76	0.44					
Hy	10.29	7.91	7.73	7.15	14.43	14.17	2.08	4.63	4.69	7.56	5.51
Ēn	1.29	0.72	0.90	0.50	8.06	8.08	0.30	0.52	0.52	0.72	0.32
Fs	8.99	7.19	6.83	6.65	6.38	6.09	1.78	4.11	4.16	6.83	5.18
Ар	0.49	0.14	0.21	0.21	0.46	0.56	0.19	0.28	0.42	0.65	0.00
II	1.06	0.76	0.95	0.74	1.20	1.04	0.95	0.51	0.51	0.76	0.40

Table 4.	Major	Element	Geochemistry	(cont.)	).
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Sample : Symbol :	КМ2	KM6	км6	км8	КМ9	NNP2	TR3	TR8	TR10	217GR(*)	219GR(*)
Rock Unit	KGCT	KGS	AP1	KGS	КССН	Lexington Granite	TRBC	TRBC	TRBC	TRBC	TRBC
Si02	72.58	74.40	77.87	74.26	74.63	73.67	72,94	72.79	73.57	77.46	76.37
$Ti0^{2}$	0.35	0.24	0.09	0.24	0.28	0.17	0.35	0.42	0.43	0.02	0.13
$A1_20_2$	14.24	12.37	12.68	13.09	13.08	14.59	13.15	13.30	13.35	12.36	12.19
FeŐ	3.03	2.68	1.33	2.63	2.80	1.37	3.57	4,56	3.86	0.54	1.49
MnO	0.05	0.06	0.03	0.04	0.04	0.05	0.05	0.06	0.06	0.03	0.00
MgO	0.31	0.15	0.08	0.13	0.16	0.37	0.32	0.38	0.15	0.01	0.12
CaO	1.24	0.96	0.26	0,91	1.08	0.93	1.53	0.67	1.47	0.64	1.08
Na <sub>2</sub> 0	3.83	3.18	3.48	3.55	3.36	2,91	3.31	3.74	3.13	2,58	2.52
K20	4.39	4,95	4.64	4.97	4.47	5.10	4.49	4.25	4.04	6.69	5.63
P <sub>2</sub> <sup>2</sup> 0 <sub>5</sub>	0.15	0.12	0.00	0.06	0.02	0.25	0.08	0.08	0.07	0.00	0.00
Total	100.17	99.11	100.46	99.88	99.91	99.41	99.79	100.25	100.13	100.34	99.53
Loss on Ignition	0.81	0.64	0.60	0.65	0.38	0.80	1.10	1.78	2.14		
CIPW Norm:											
Or	25,94	29.25	27.42	29.37	26.37	30.14	26.53	25.12	23.88	39.54	33,27
Ab	32.41	26,91	29.45	30.04	28,43	24.62	28,01	31.65	26.49	21.83	21.32
An	5.18	3,99	1,29	4.13	5.23	3.00	7.07	2.81	6.84	2.39	5.32
0	28.49	32,90	38,12	30,56	33.35	34.32	30,20	29.44	33.77	35.18	36.53
č	1.29	0.32	1.46	0.36	0.81	3.18	0.25	1.52	1.32		
Di						~~~				0.70	0.03
Wo										0.33	0.01
En										0.01	0.00
Fs										0.36	0.01
Hv	5.85	5.01	2,55	4.83	5,15	3.25	6.87	8.74	6.86	0.67	2 80
En	0.77	0.37	0.20	0.32	0.40	0.92	0.80	0.95	0.37	0.02	0.30
Fs	5.08	4.64	2.35	4.51	4.75	2.33	6.07	7,79	6.49	0.65	2.51
Ар	0.35	0.28	0.00	0.14	0.05	0.58	0.19	0.19	0.16	0.00	0.00
II	0.66	0.46	0.17	0.46	0.53	0.32	0.66	0.80	0.82	0.04	0.25 o

Table 4. Major Element Geochemistry (cont.).

(\*) Data for the groundmass ONLY.

Fig. 12. Q-Or-Ab-An Normative (CIPW) Plot of Chemically Analyzed Samples of Traveler Rhyolite.

> Legend: Traveler Rhyolite: Black Cat Member

- 1 This Study
- 2 Rankin, 1961
- 3 Composition of Coexisting Groundmass
- Traveler Rhyolite: Pogy Member
  - 4 This Study--Fresh Samples

  - 5 This Study--Hydrothermally Altered 6 This Study--Specimen With Abundant
  - Plagioclase Crystals (Xenocrysts ?)
  - 7 Rankin, 1961
- Kineo Rhyolite
  - 8 This Study 9 Smith, 1935



Fig. 13. Minimum Melting Temperatures for Granitic Liquids For Various P(T) in Kb, P(H<sub>2</sub>O) in Kb, And T in <sup>O</sup>C. Corresponding Water Content of The Granitic Melts in Wt% H<sub>2</sub>O. Open Circle And Dashed Lines Are For Sample # 219 From Traveler Rhyolite. See Text For Further Discussion. (Based on Data of Burnham And Jahns, 1962; and Steiner And Others, 1975. Muscovite Plus Quartz Reaction is After Althaus And Others, 1970).



of 800-820<sup>0</sup>C. The melting process was apparently initiated by a breakdown of micas. On Fig. 13 the muscovite-quartz reaction occurs at temperatures about 60°C lower than the temperature indicated for the formation of the Traveler magma. Either muscovite was not present (only biotite mica) or the stability of muscovite was increased by the presence of fluoromuscovite in the solid solution. The oxygen fugacity was presumably maintained through an equilibrium with graphite between the QFM and MW buffers (French, 1966). The estimated partial pressure of  $H_2O$  (Fig. 13) was 4 Kb and the composition of the melt was controlled by an equilibrium with quartz, alkali feldspar, and plagioclase. Partial pressure of  $H_2O$  is also implied by projections of the Black Cat Member analyses near a 4 Kb P(H<sub>2</sub>O) cotectic (Fig. 12). Since the geometry of the cotectics is essentially independent of the confining pressure, the 4 Kb  $P(H_2O)$  estimate from Fig. 12 provides additional support in favor of the above model.

Forces resulting from a gravitational instability forced the newly formed magma to move upward. At a shallower depth of approximately 3 km, the magma reached a stagnation point during which time the  $P(H_2O)$  became equal to lithostatic pressure. At occasional intervals, violent eruptions transported the rhyolitic melt to the earth's surface where a sudden release of confining pressure brought about the formation of dense and thick ash flows. These ignimbritic deposits were, while still hot, compressed and compacted under their own lithostatic pressure and were "welded" into a dense rock known as welded ash flow tuffs (Smith, 1960).

At the time of eruption, the magma of the Pogy Member was undoubtedly colder and possibly slightly more fractionated, presumably because it had to migrate through a colder overlying sedimentary section which was already "preheated" during the ascent of the later Black Cat magma.

Thornton's differentiation index and an AFM diagram show that the whole rock Pogy samples are more fractionated than the Black Cat samples, and that they are in line with the groundmass of the Black Cat Rhyolite. A higher percentage of phenocrysts, ubiquitous quartz, and the occasional presence of alkali feldspar in the Pogy unit, are all consistent with the above model.

The homogeneous major element composition and relatively constant petrology throughout the Traveler Rhyolite imply a steady state of a continuous melting process and concurrent continuous removal of the magma as the only possible mechanism that was able to generate such large quantities of chemically very homogeneous magma. This magma, which at its origin was in equilibrium with two feldspars and quartz, was most likely formed by a partial melting of eugeosynclinal sedimentary rocks from which the magma was separated by filter-pressing mechanism.

The fraction of partial fusion can be indirectly estimated from the typical content of micas in metamorphosed sediments. Since micas and TRBC magma have about the same water content, e.g., 4 wt.%, the maximum partial melt fraction should therefore be equivalent to the fraction of micas in parental rocks, typically between 20 and 40%. This estimate is in accord with the experimental results of Brown (1970).

# III. <u>GEOLOGY, MINERALOGY, AND PETROLOGY OF THE</u> KATAHDIN PLUTON

# A. Katahdin Pluton

The Katahdin Pluton (KP) marks the northeastern limit of a linear belt of plutonic rocks, extending across north-central and northwestern Maine. With an exposed area of 1330 square kilometers it ranks among the most prominent intrusive bodies of the Northern Appalachians.

The pluton is a shallow, composite, predominantly granitic body, with a pear-like shape, having a longer axis in the NE-SW direction, which parallels the prevalent tectonic trend (Preliminary Geologic Map of Maine, 1967). The name of the pluton is borrowed from the highest mountain in Maine--Mount Katahdin (1580 m), which is situated approximately in the center of the intrusion (Jackson, 1838; Hitchcock, 1861; Griscom, in prep.).

Topographically, the pluton consists of two unequal areas of strikingly contrasting morphologies with approximate divisions running along the West Branch Penobscot River and following a line between Katahdin Lake and Togue Pond. The northern, mountainous part is formed by an elevated plateau, gently dipping northward and sharply edged by steep ridges along the southern side and by deep valleys and glacial cirques in the remaining part of the plateau (Caldwell, 1969). The plateau, with a mean slope of 6.2%, extends from Thoreau's Springs (1380 m) in the south and near the summit of Mount Katahdin to the 8.8 km distant Russell Mountain (840 m) in the north (Fig. 15). This inclination is caused by a later differential regional uplift in northwestern Maine and it is not intrinsic to the pluton. The gradient of this regional uplift, as estimated from the metamorphic isograds (progressively deeper toward the southwest), is identical with the earlier stated mean slope of the plateau.

In contrast, the much larger, southern area of the pluton is a hilly lowland covered mostly by thick, glacial deposits with elevations generally less than 450 m. The area investigated in this study is principally restricted to the northern mountainous part, where excellent outcrops are abundant.

As suggested by several lines of evidence to be discussed, the pluton is a slightly flattened, funnel-shape intrusion, not yet fully unroofed along the northern border (Fig. 14). The contact on the northwestern side of the Harrington Lake quadrangle dips under the pluton. This observation is evident from the exposures near the power house in Ripogenus Gorge and by the inward inflection of the contacts into the valleys north of Harrington Lake. On the northeast side, the continuation into the pluton of strong magnetic anomalies associated with Ordovician volcanics suggests the presence of these volcanics at a shallow depth beneath the granites (A. Griscom, 1964). The lack of a negative gravity anomaly near the pluton margin implies that the granitic rocks near the contacts cannot extend to greater

Fig. 14. Geologic Map of Katahdin Pluton and Stock of Harrington Lake Porphyry.

(Note: For Geologic Map of Traveler Rhyolite see Fig. 4.)

Legend:	HLP	-	Harringto	on Lake Po	orphyry
-	DGD	-	Debsconea	ag Granod:	iorite
	HQD	-	Horserace	e Quartz I	Diorite
	KGW	-	Katahdin	Granite:	Wassataqoik Facies
	KGD		Katahdin	Granite:	Doubletop Facies
	KGCH	_	Katahdin	Granite:	Chimney Facies
	KGS	_	Katahdin	Granite:	Summit Facies
	KGSB	_	Katahdin	Granite:	South Brother Facies


Fig. 15. Localities of Chemically Analyzed Samples from Katahdin Pluton and from Harrington Lake Porphyry.



depths (M. Kane, 1974). Another indication of the funnelshape of the pluton stems from the outline of the pluton. The structurally deeper southern part is conspicuously narrower than the shallower northern part. The contacts with the Traveler Rhyolite volcanics on the northern side undoubtedly dip under the volcanics.

The character of the contacts implies a rather permissive intrusion of granitic magma. The contacts are generally sharp, with only a few incidental blocks of country rock enclosed in the granite, crosscut by short, thin apophyses typically 20 cm wide and up to 10 m long. However, where the country rocks are ductile (pre-Silurian metamorphosed, sedimentary and igneous rocks), the intrusion takes on a more pervasive character. These contacts are formed by a brecciated zone, up to 100 m wide, of closely packed inclusions of country rock cemented by granitic matrix. The proportion of granitic matrix lessens with the distance from the pluton. The relatively narrow (approximately 100 m wide) metamorphic aureole of the pluton consists almost exclusively of biotite hornfels.

About 95% of the KP area is underlain by one of the six textural types (facies) of the Katahdin Granite. All the facies are massive, medium-to-fine grained biotite granites of identical mineralogy. Except for the porphyritic dikes, the facies have mutually gradational contacts and possess definite spatial positions within the pluton, undoubtedly as a response to local differences in cooling rates.

Fig. 16. Generalized N-S Cross-section through Traveler Rhyolite - Katahdin Pluton Complex.

# Legend: 1 - Seboomook Formation 2 - Traveler Rhyolite

- 3 Katahdin Granite: Chimney Facies4 Katahdin Granite: Summit Facies
- 5 Trout Valley Formation
- 6 Katahdin Granite: Wassataqoik Facies
- 7 Matagamon Sandstone
- 8 Katahdin Granite: Doubletop Facies
- 9 Debsconeag Granodiorite



# TRAVELER RHYOLITE-KATAHDIN GRANITE

The composite character of the Katahdin Pluton results from the presence of two younger rocks of medium grained, amphibole-bearing, biotitic Debsconeag Granodiorite and by a stock of the youngest intrusion--the Horserace Quartz Diorite (Fig. 14). The Harrington Lake porphyry, still another igneous body nearly colinear with the Debsconeag and Horserace intrusion, is outside of the NW limit of the Katahdin Pluton south of Harrington Lake. It seems almost certain that the location of these small, younger intrusions results from tectonic control by the Chesuncook Lake-West Branch Penobscot River fault system, which shows evidence of activity during the ascent of the Horserace intrusion.

#### B. Katahdin Granite

#### 1. Geology

The rocks of the Katahdin Granite (KG) are massive, structureless, mineralogically and chemically homogeneous granites, underlying over 95% of the Katahdin Pluton (KP). This description purposely omits any reference to the rock textures solely to emphasize, that all textural types of the KG have crystallized from the same original magma. Six textural types of KG are identified below: Table 5A. Textural Facies of Katahdin Granite.

===:			
Kata	ahdin Granite Facies	Characteristic Texture	Occurrence Within The Pluton
1.	Doubletop	Granitic	Core of the Pluton
2.	Chimney	Granophyric	
3.	Summit	Granophyric With Miarolitic Cavities	Outer Zone Near The Roof Of The
4.	South Brother	Subporphyritic With Rapakivi Overgrowths	Pluton
5.	Wassataqoik	Aplogranitic	
6.	Cathedral	Porphyritic With Aplitic Groundmass	Porphyritic Dikes

An idealized distribution of these facies is schematically illustrated in Fig. 17. The predominant Doubletop facies forms the core of the pluton, whereas the other nondike facies are found near the actual and presumed upper contacts. Excluding the porphyritic dikes of the Cathedral facies, all other contacts within the pluton are of a gradational nature, having a width of up to several hundred meters.

Toward higher elevations, the first appearance of a granophyric texture in the center of the pluton marks the transition point from the Doubletop to the Chimney facies. With increasing elevations, the granophyric texture becomes even more prominent. The first appearance of filled, miarolitic cavities indicates the transition from Chimney facies to Summit facies. At the highest structural levels, the filled miarolitic cavities change into open cavities. Identified minerals contained in the miarolitic cavities are: epidote, tourmaline, and, infrequently, fluorite.

Toward the side contacts, the vertical cross-section is markedly different from the analogous cross-section in the center of the pluton. The landslide exposures on the western face of South Brother Mountain show a transitional change from Doubletop into South Brother facies by the gradual increase of fine-grained groundmass. Near the contact with Traveler Rhyolite, the Wassataquoik facies of KG is aplogranitic with abundant "nests" containing black to dark-blue tourmaline. The Summit, Chimney, Wassataquoik, and South Brother form an 'outer shell' around the Doubletop facies

core of the Katahdin Pluton. The stratigraphic thickness of this 'outer shell' varies from zero to a minimum of 450 m in the center of the pluton, which may be best explained by differential cooling rates. The 'outer shell' granites, when compared with the Doubletop facies, are often more hydrothermally altered, less texturally uniform, and more resistant to erosion. The extensive hydrothermal alteration of the 'outer shell' correlates with the joint pattern. The common, vertical sheeting observed at the highest elevations may have provided pathways for the escaping pneumatolytic and hydrothermal solutions of the late magmatic stages. The frequency of hydrothermal and pneumatolytic alterations is inversely proportional to the frequency of pegmatitic dikes. The pegmatitic dikes are absent at the highest elevations but become more frequent toward the core of the pluton. At intermediate levels, the pegmatites are restricted to thin linings along selected fractures. At intermediate and lower elevations, the pegmatites and aplites occasionally form layered dikes of either single or multiple intrusions. Aplitic dikes occur throughout the pluton and their frequency seems to be independent of elevation. The 'outer shell' facies have structural features suggesting a complex and dynamic crystallization environment. For example, biotite is concentrated into schlieren, but most often it is merely lineated. Also. north of Mt. Katahdin (Baxter Peak), near the headwalls around North and Great Basins, there are rare, sharp internal contacts with chilled margins. However, the rocks are identical

Fig. 17. Idealized Distribution of Textural Facies of Katahdin Granite Within the Katahdin Pluton.

Legend:	KGS -	Katahdin	Granite:	Summit Facies
-	KGCH-	Katahdin	Granite:	Chimney Facies
	KGW -	Katahdin	Granite:	Wassataqoik Facies
	KGSB-	Katahdin	Granite:	South Brother Facies
	KGD -	Katahdin	Granite:	Doubletop Facies
	KGCT-	Katahdin	Granite:	Cathedral Facies



in appearance only half a meter on either side of the contacts.

The erosional resistance of the 'outer shell' granites provides an explanation for the contrasting morphology of the pluton. The areas underlain by the Doubletop facies are often deeply weathered (up to 10 m) into decayed and crumbling granites, as evidenced in the lower parts of landslides on the south side of Mt. OJI and the west side of South Brother Mtn. In contrast, the Summit facies is extremely resistant to weathering and erosion and provides an effective shield against erosion. Wherever this shield eroded away, the granite of Doubletop facies was in turn eroded relatively quickly because of its poor resistance. This explains the existence of steep ridges around the exposures of the Summit facies and the topographic lows in the remaining part of the pluton. Except for two occurrences, mafic dikes are conspicuously absent throughout the pluton. One sub-horizontal dike, about 0.75 m thick, crops out along the mid-elevation of the entire eastern side of Doubletop Mtn. The second dike, as reported by Rankin (personal communication) occurs near the Chimneys underneath Pamola in the South Basin.

#### 2. Mineralogy

The principal minerals of all six facies of the Katahdin Granite are (in decreasing abundance): alkali feldspar, quartz, plagioclase, biotite, opaques, and minor or

trace occurrences of amphibole, fayalite, tourmaline, epidote and fluorite. Accessories are apatite, zircon, allanite, and possibly monazite. The noted absence of primary magmatic muscovite and sphene places an upper limit for  $P(H_2O)$  at 3.7 Kb and an upper limit for  $f(O_2)$  at approximately the nickel-nickel oxide buffer curve (Czamanske and Wones, 1973). As muscovite occurs only extremely rarely in the pegmatitic dikes and pegmatitic linings of joints, the water pressure may have been as low as 1 Kb if the temperature is assumed to be  $550^{\circ}$  to  $600^{\circ}$  (Althaus, et. al., 1970; Kerrick, 1972).

A scanning electron microscope study of feldspars from the Chimney facies (Sprunt, 1973) revealed an extensive abundance of submicroscopic open cavities, frequently showing a negative crystallographic outline. In this same study, albite from Amelia pegmatites had an identical texture. These 'holes', thought to represent trapped vapor bubbles, suggest a water-saturated, magmatic environment.

#### Alkali feldspar:

In equigranular granites, the perthitic alkali feldspar is generally subhedral to anhedral, and occurs as euhedral phenocrysts in the Summit and Cathedral facies. The average grain size is about 3 mm with a maximum grain size of 5 mm. The composition of four perthitic alkali feldspars was determined by microprobe analysis of fluxed glasses to ensure exact bulk composition (Or70 Ab28.5 An1.5); one sample was slightly more albitic (see Fig. 5). The above compositions fall within the range Or66-Or75, as determined by the sanidization and x-ray techniques used by A. Griscom (in prep.). The composition of the perthite host and the exsolved albite lamellae from Sample #74 yield Or90 Ab10 and Or40 Ab88 An8, respectively. The bulk composition of this alkali feldspar, as determined from fused glasses, can be reconstituted by mixing 86% of the host and 24% of the lamellae, which is in accord with the microscopic estimate.

The structural states of alkali feldspars in unhomogenized samples (A. Griscom - in prep.) vary from orthoclase to maximum microcline, with intermediate microcline being the most frequent state. A. Griscom identified orthoclase in samples from near the contacts and maximum microcline in a sample from the Summit facies. However, there is no systematic correlation between structural state or composition of the alkali feldspar and sample location (notably its elevation).

In the Doubletop facies, the ubiquitous Carlsbad twinning is occasionally combined with fine microcline grid twinning. In the Summit facies, alkali feldspar, as well as plagioclase phenocrysts, are surrounded by a fan-like, graphic matrix of very fine intergrowth of alkali feldspar and quartz. The crystal size of the intergrowth increases toward the miarolitic cavities. The alkali feldspar phenocrysts of South Brother and Cathedral facies often show rapakivi overgrowth of albite or sodic oligoclase. The

average composition of alkali feldspars in the groundmass of the Cathedral facies is Or94 Ab6. In some fresh samples, alkali feldspar is slightly sericitized and in the redcolored, hydrothermally altered samples, alkali feldspar is densely clouded and impregnated by submicroscopic hematite specks.

#### Quartz:

Equidimensional quartz is usually anhedral and commonly agglomerated into groups of several grains of an average grain size of 1.5 mm. The quartz contains numerous fluid inclusions and sometimes inclusions of accessories or opaques. Porphyritic quartz of the Summit and Cathedral facies is euhedral with occasional embayments.

#### Plagioglase:

The thick, tubular grains of plagioclase are subhedral in the equigranular facies of KG, or euhedral as phenocrysts in the porphyritic facies; the average grain size is about 2 mm. Albite polysynthetic twinning is common and is often combined with less frequent Carlsbad twinning. Compositional zoning is normal and continuous; sudden steppings are rare. The plagioclase composition. determined by electron microproble, varies from An34 to An4 with an average of An25 to An30. The calcic cores of the interior of Katahdin Pluton are commonly saussuritized and sericitized while the more acidic rims remain clear. This deuteric re-equilibration is believed to have caused a partial resetting of the feldspar geothermometer (about 60°C in sample #74 located near the center of the Katahdin Pluton). These plagioclases also contain approximately half of the 'normal'  $K_2O$  content: approximately 0.25 wt.% instead of the usual 0.50 wt.%.

Groundmass plagioclase in the Cathedral facies has an anomalous composition (AnO to An15). The presence of sodic plagioclase and Or-rich alkali felspar, in combination with the aplitic texture, suggests that the intruding magma was supercooled and that the groundmass feldspars crystallized by devitrification from the glass-like matrix at much lower temperatures.

#### Biotite:

Biotite constitutes approximately 6% of all samples. It is frequently partially chloritized and it occurs as subhedral tablets up to 2.5 mm large and 1 mm wide; its size decreases slightly toward the contacts. Intense pleochroism, deep brown to straw yellow in color is further accentuated within the halos mantling common zircon inclusions. The composition of biotite throughout the KG is almost constant. except for noticeable differences in the rapidly cooled or quenched Summit and Cathedral facies, as well as in the aplites. Biotites of the Summit facies are lower in Fe and Ti and higher in Mn; Cathedral facies shows lower Fe content. whereas aplitic biotite is enriched in Fe and is poorer in Ti.

#### Olivine:

A single grain of equidimensional and subhedral olivine was identified in Sample #29 of Doubletop facies. From microprobe analysis, the composition corresponds to mangano-ferrous fayalite: Fo2.0 Fa90.5 Tf7.5. Although the grain is almost entirely enclosed in plagioclase, it is believed that during crystallization, the olivine was in equilibrium with magnetite and quartz. This indicates that the granitic magma crystallized under oxygen fugacites near the QFM buffer. Identical mineralogical and chemical composition of Sample #29 with other Doubletop samples suggests that fayalite may be more widespread though it is rarely found in thin sections.

#### Amphibole:

Two rare amphibole occurrences are reported from outcrops along the West Branch Penobscot River (A. Griscomin preparation).

#### Tourmaline, Epidote, and Fluorite:

Tourmaline, epidote, and fluorite are mainly found in the Summit facies. Tourmaline, which is a deep-blue variety of indicolite, is present in both matrix and in miarolitic cavities; epidote occurs in cavities and along microcracks, and fluorite mainly along microcracks. Tourmaline and fluorite are seldom observed in the Doubletop facies, where epidote and clinozoisite are common alteration products. Tourmalines of the Wassataquoik facies are noted not only for their presence within the rock matrix but mainly for their conspicuous tourmaline nests and linings along the joints.

#### Opaques:

Optical examination and microprobe study revealed that ilmenites are essentially absent and, when present, they occur only as cores of magnetite grains. Magnetite is always oxidized, displaying common exsolution textures which inhibit the use of the magnetite-ilmenite geothermometer and the geobarometer. The pre-exsolution composition was estimated by two different averaging techniques, both yielding identical results: Mt75 Usp25. The first method averaged 10 to 15 random microprobe point analyses, and the second method utilized a defocused electron beam with a diameter equivalent to the approximate width of the magnetite grains (50 to 60 microns).

#### 3. Facies of the Katahdin Granite

#### a. Doubletop Facies

The Doubletop facies is a medium grained biotite granite. The type exposures are on the lower east side of Doubletop Mtn. Recent landslides in that region unearthed excellent bedrock ledges. The granite is a massive, structureless rock with a typical granitic, hypidiomorphic granular texture. The color in fresh specimens is bluishgray turning into whitish-gray, pinkish or red near the joints, faults, and/or pegmatitic and aplitic dikes. The Fig. 18. Plot of Normative (CIPW) Q-OR-AB-AN Components for Doubletop Facies of Katahdin Granite.

<u>Upper Diagram:</u> Projections onto Q-AB-OR Plane. <u>Lower Diagram:</u> Projections onto AN-AB-OR Plane.

Legend: 1 - Fresh Samples - No Alteration Observed

- 2 Sample Next to Aplitic Dike (#134-2)
- 3 Hydrothermaly Altered Granite (#240)
- 4 Slightly Weathered Granite (#41 & #190W)
- 5 Mylonitized Granite (#81)
- 6 From Griscom (in prep.)

Note: Cotectic Lines, Minima and Eutectic Points are From Fig. 11.



mineral components are perthitic alkali feldspar (34%), plagioclase (26%), quartz (34%), biotite (6%); the remaining components are accessory apatite, zircon, allanite, tourmaline, and opaques. Representative modal analyses are given in Table 5B, and all available modal analyses from Griscom and Rankin (Griscom-in prep.; Rankin, 1961) are plotted on Fig. 22. Rare minerals, which include fayalitic olivine and amphibole, are found in only a few of the specimens; sphene and magmatic muscovite were never observed.

Twelve selected samples from the northern section of the pluton were analyzed chemically. The AN-OR-AB and Q-OR-AB normative compositions (including one chemical analysis of A. Griscom (in preparation) are given on Fig. 18. The comparison of these diagrams with experimentally determined cotectic lines is complicated by the presence of biotite (which contributes to the OR component), and by the rock's "chemical memory". Nevertheless, an inspection of this diagram places an upper limit of 2 Kb  $P(H_2O)$  for the granites of this facies.

#### b. Chimney Facies

The Chimney facies is sandwiched between the Doubletop facies on the bottom and the Summit facies on the top. This facies differs from the Doubletop facies by the presence of granophyric texture, and from the Summit facies by the absence of miarolitic cavities. The contact between the Doubletop and Chimney facies dips toward the north.

Table 5B

### Modal Analysis of Doubletop Facies of

			the second s						
Sample #	29	41	74	115	150	190	209	134-1	Avg.
Ally Foldener		21 /		35 7		 99 7	 33 8	34 0	33.9
Alk.Feldspar	34.4	51.4	30.5	04.0	04.7	20.1		04.0	05.0
Plagioclase	26.6	28.1	20.4	24.2	24.1	32.4	26.2	24.0	20.0
Quartz	20.9	34.7	36.2	33.1	35.5	32.8	32.7	34.3	33.8
Biotite	6.8	5.4	4.5	6.7	6.5	4.8	6.9	6.9	6.1
Others	0.3	0.4	0.4	0.3	0.4	0.3	0.4	0.3	0.4
Average An	22	18	17	28	26	22	26	23	

Katahdin Granite.

Fig. 19A. Plot of Normative (CIPW) Q-OR-AB-AN Components For Other Than Doubletop Facies of Katahdin Granite.

Upper Diagram: Projections onto Q-AB-OR Plane.

Lower Diagram: Projections onto AN-AB-OR Plane.

- Legend: KGS Katahdin Granite: Summit Facies AP1 - Aplite (Sample #KM-7) KGCH- Katahdin Granite: Chimney Facies KGW - Katahdin Granite: Wassataqoik Facies KGCT- Katahdin Granite: Cathedral Facies
- Note: Cotectic Lines, Minima and Eutectic Points are From Fig. 11.



Fig. 19B. Plot of Normative (CIPW) Q-OR-AB-AN Components for Aplites and Pegmatites from Katahdin Pluton. <u>Upper Diagram:</u> Projections onto Q-AB-AN Plane. <u>Lower Diagram:</u> Projections onto AN-AB-OR Plane. Note: Cotectic Lines, Minima and Eutectic Points are From Fig. 11.



Fig. 20. Plot of Normative (CIPW) Q-OR-AB-AN Components for All Chemicaly Analyzed Samples From the Entire Traveler Rhyolite - Katahdin Granite Magmatic Complex.

> <u>Upper Diagram:</u> Projections onto Q-AB-OR Plane. <u>Lower Diagram:</u> Projections onto AN-AB-OR Plane. Legend: TRBC - Traveler Rhyolite: Black Cat Member TRP - Traveler Rhyolite: Pogy Member KGD - Katahdin Granite: Doubletop Facies KGCH - Katahdin Granite: Chimney Facies

KGS - Katahdin Granite: Summit Facies KGCT - Katahdin Granite: Cathedral Facies Note: Cotectic Lines, Minima and Eutectic Points are From Fig. 11.



The altitude of the contact on the southern side is approximately 900 m and on the northern side of the plateau 600 m. The type locality for the Chimney facies is at the base of the cliffs below the Chimneys. This facies mainly occurs around the main mountain chain, on both Turner Mountains, and around North Brother Mtn. The texture of this facies is characterized by a granophyric intergrowth and, toward the higher elevations, by the presence of quartz, plagioclase, and alkali feldspar phenocrysts. Its color is grey at lower elevations, but frequently pink or red at higher elevations. Two analyzed samples of the Chimney facies show strong chemical similarities to the Doubletop facies (Figs. 18 and 19); the mineral composition of both facies is identical.

#### c. Summit Facies

The Summit facies of Katahdin Granite (KGS) is recognized only at higher elevations in two out of the three high elevation plateaus. These are (1) North Turner and (2) Mt. Katahdin-Russel Mtn. The type exposures are on Tableland (between Baxter Park and Hamlin Peak), where the facies crops out as the more characteristic pinkish-white variety. Near the vicinity of Mt. Katahdin and Hamlin Peak, KGS is distinctly red colored as a result of extensive hydrothermal alteration.

The granite of the Summit facies has a massive, subporphyritic texture, composed of fine grained granophyric

intergrowths of alkali feldspar and quartz, radiating away from the 1-4 mm tablets of alkali feldspar and plagioclase phenocrysts. The groundmass becomes coarser and pinkish toward the abundant miarolitic cavities. The vugs are lined with euhedral projections of alkali feldspar and quartz and are partly or fully filled with epidote, tourmaline, and occasional fluorite. The size of these cavities ranges in diameter from 0.5-5.0 cm, rarely exceeding 2 cm. The frequency of cavities increases with higher elevations.

Major element data, plotted on granitic diagrams, show that KGS (Fig. 19) is similar to KGD (Fig. 18), except for lower An normative content in KGS. This difference may have been caused by hydrothermal alteration or by fractionation.

## d. <u>Other Facies of Katahdin Granite</u> Wassataquoik Facies:

The type exposures of Wassataquoik facies (KGW) are along the southern shore of Wassataquoik Lake. KGW is restricted to a zone, up to 0.5 km wide, between the Traveler Rhyolite and Debsconeag facies of Katahdin Granite. Near the contacts the facies have a panxenomorphic texture with occasional granophyric developments. As the distance from the contacts increases, the texture changes into subaplitic and subporphyritic.

#### South Brother Facies

The South Brother facies (KGSB) is a transitional

facies between KGD and KGCH, extending from South Brother Mtn. to Wassataquoik Mtn. The type locality is on the upper part of a ledge unearthed by a recent landslide on the western face of South Brother Mtn. The texture is porphyritic to subporphyritic with rapakivi overgrowth around alkali feldspar phenocrysts. As the elevation increases, the groundmass becomes finer.

#### Cathedral Facies

Cathedral facies (KGCT) occurs only as thick, porphyritic dikes (30-200 m wide), usually at higher elevations. The type locality is on the southern face of OJI Mtn. at an elevation of 695 m. KGCT is a porphyritic granite with approximately 20-25% of alkali feldspar, plagioclase, quartz, and biotite phenocrysts. The matrix consists of identical mineral composition. The dike contacts are sharp, with fine grained, chilled margins; occasional aplitic and pegmatitic dikes cross-cut or intrude along the contacts. Therefore, KGCT is essentially of the same age as KGD.

The tie-line between coexisting feldspars in the goundmass (Fig. 5) indicates that the matrix crystallized from a supercooled magma.

#### 4. Estimates of Temperature, Total Pressure, Water Pressure and Oxygen Fugacity

The deuteric oxidation of magnetite-ulvospinel solid solution, and the rarity of ilmenite prevented the

use of the ilmenite-magnetite geothermometer and geobarometer. Temperatures may be estimated from coexisting alkali feldspar and plagioclase; oxygen fugacity and water pressure can be obtained from the stability of the biotite mica. Total pressure can be independently estimated from the geologic evidence; that is, the lithostatic pressure applied by the now eroded sequence of overlying rocks.

#### a. Alkali Feldspar - Plagioclase Pair

Hon (1973) and Stormer (1974, 1975) independently suggested a modification of Barth's geothermometer as a means of estimating an equilibration temperature from coexisting alkali feldspar and plagioclase. The thermometer is based on the equilibrium requirement that the activity of albite in alkali and plagioclase feldspars must be equal. The activity of albite in alkali feldspar solid solution is obtained from the numerical model of the excess-free energy of mixing, as given by Waldbaum and Thompson (1969). Α similar model is not available for the plagioclase solid solution. Although plagioclases are distinctly non-ideal at lower temperatures (J. C. Smith, 1972; Crawford, 1966) and at compositions above An50, Orville's (1972) ion exchange experiments indicate that, at magmatic temperatures, the ideal solution model is applicable for plagioclase compositions between AnO and An50. A similar conclusion for a more restricted range of compositions (An20 to An45) was deduced from a thermodynamic analysis of experimentally determined tie-lines between alkali feldspars and plagioclases (Saxena,

1971; Hon, 1972). We believe, therefore, that the ideal solution model is a sound assumption for a composition between An2O and An5O at or near magmatic temperatures. With this assumption and knowing the compositions of both feld-spars (in terms of their albite mole fractions), the feld-spar equilibration temperature may be estimated from the following expression (Hon, 1973):

$$T (^{O}K) = \frac{1970.61 + 0.02878*P - (587.93 + 0.0085*P)*(1.0-X)}{(\log(Y/X))/(1-X)^2 + 0.67332 + 0.33901 * (1.0-X)}$$

X = mole fraction of albite in alkali feldspar

Y = mole fraction of albite in plagioclase

P = assumed total pressure in bars

Coexisting feldspars of three selected samples of the Doubletop facies (Samples #29, 74, 150) and hand-picked phenocrystic feldspars from one sample of the Cathedral facies (Sample #121) were analyzed by electron microprobe (Fig. 5). To determine their exact bulk compositions, the perthitic alkali feldspars were analyzed as fused glasses. The compositions of these four feldspar pairs, and the computed equilibration temperature at three different pressures, are listed below.

			remperature c			
Sample #	X(Ab in AF)	Y(Ab in PL)	1.0 Kb	1.5 Kb	2.0 Kb	
29	0.347	0.724	706	713	720	
74	0.285	0.743	636	642	648	
121	0.291	0.658	701	708	715	
150	0.288	0.682	679	686	693	

Temperature <sup>O</sup>C

The calculated temperatures (except for Sample #74) are acceptable magmatic temperatures intersecting the granite minimum melting curve between 1200 and 1500 bars of  $\mathrm{P(H_{2}O)}$ (Fig. 21). The plagioclase of Sample #74 is noticeably lower in Ca and K, apparently as a result of deuteric reequilibrium demonstrated by saussuritization and sericitization of its plagioclase cores. The temperature estimate is consequently lowered by 60 degrees. The average temperature (excluding Sample #74) is  $695^{\circ}$ C at 1 Kb and  $709^{\circ}$ C at 2 Kb; the preferred estimate is 703°C at 1 Kb and 717°C at 2 Kb. As a consequence of water undersaturation, an increase in total pressure would tend to increase the temperature estimate by 1.4°C per 100 bars. The granitic minimum melting curve is intercepted at a temperature of 700°C and P(H<sub>2</sub>0) of 1300 bars (Fig. 21).

#### b. Biotite as an Indicator of Magmatic Environment

Wones and Eugster (1965) suggested a dehydrationoxidation reaction of biotite as a potential means of relating magmatic temperature, water fugacity, and oxygen fugacity. However, Wones (1972) modified the earlier numerical expression to the following:

$$\log f(H_2O) = 7409/T + 4.25 + 0.5 \log f(O_2) + 3 \log x (Ann) - \log a(San) - \log a(Mt)$$

The above expression, given the compositions of all mineral phases, defines a unique surface in three-dimensional space with the temperature,  $f(O_2)$  and  $f(H_2O)$  as principal axes.

This surface can be projected on the  $f(O_2)$ -T plane as a series of isobaric lines, each relating oxygen fugacity and temperature at constant water fugacities. Such a diagram, constructed for the mineral assemblage of the Katahdin Granite, is shown in Fig. 21 using the following input data:

1. The mole fraction of annite in the biotite solid solution was determined from the structural formula as follows:

x(Ann)=(tot.Fe/sum of octahedral ions) - 0.05

The correction of five mole percent appears to be a difference between tot.Fe and Fe<sup>+2</sup> at QFM buffer (Wones, Eugster, 1965, p. 1245). For the KGD biotite the corrected x(Ann)is equal to 0.72.

2. The composition of partially exsolved magnetiteulvospinel solid solution was determined by electron microprobe using two different averaging techniques, both yielding an essentially identical result: Mt75 Usp25. In the first case, the composition was obtained by averaging 10 to 15 randomly analyzed points, and in the second case, by defocusing the beam to about 50 microns which is the approximate width of the grain. The activity of magnetite in the above solid solution is considered to be equal to its mole fraction a(mt) = 0.75.
3. The activity of sanidine is estimated from the analyzed alkali feldspars. For x(Or) = 0.70,  $T = 700^{\circ}C$  and P = 1 Kb, a(San) = 0.74 (Waldbaum, Thompson, 1969). Variations due to pressure uncertainties are negligible and are, therefore, ignored.

4. Water fugacities are taken from tables of Burnham et. al. (1969).

Figure 21 is a plot of log  $f(0_2)$  versus T at constant  $p(H_2O)$ 's for six assumed water pressures between 600 and 2600 bars. Also plotted on this diagram are the temperatures estimated from the coexisting feldspar pairs (three double lines) and two curves: one for the granitic minimum melting temperatures (as indicated by the isobaric lines) and another curve for minimum melting under constant total pressure  $(P_t = 2 \text{ Kb})$  but at a variable effective water pressure  $P(H_2O)$  less than P(T). Total pressure of 2 Kb was chosen as the maximum possible pressure under which the magma of the Katahdin Granite could have crystallized. This limit, probably grossly exaggerated, is estimated from both the grade of the regional metamorphism (chlorite zone to subchlorite zone) and from the thickness of the overlying volcanic sequence of the Traveler Rhyolite, presently assumed to be only one-half of the original thickness.

Fig. 21. Plot of Doubletop Facies Biotite Equilibrium Surface  $(T^{O}C-\log f(O_2)-P(H_2O))$  Projected onto  $\log f(O_2)-T^{O}C$  Plane. Calculations Are Based on Numerical Values of the Biotite Equilibrium Constant of Wones(1972): X(Ann)=0.72, a(Mt)=0.75, a(San)=0.74. See Text For Further Discussion and Significance of Other Equilibria Curves.



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It is thus expected that the  $f(0_2)$ , T and  $P(H_2O)$ for the Katahdin Granite (KG), as shown on Fig. 21, will be anywhere between the granitic minimum and  $P_t = 2$  Kb lines. We can further narrow the possible range by constraining  $f(O_2)$  variations by information obtained from the coexisting olivine and iron-titanium oxide. From the experimental data on coexisting iron-titanium oxides by Buddington and Lindsley (1962), it appears that a spinel phase of the composition Mt75 Usp25, not coexisting with ilmenites, can be a stable phase at higher T's or lower  $f(O_2)$  away from the curve where it would coexist with the ilmenites (see Fig. 21). Furthermore, in one sample (Sample #29), ilmenites are virtually absent, but a grain of a fayalitic olivine has been identified nearly entirely enclosed within a larger grain of plagioclase. Provided that the olivine was in equilibrium at the time of its crystallization with quartz and magnetite, and assuming that the melt could only be oxidized after the olivine is formed, the possible range for the intensive parameters of Fig. 21 is further limited (see Fig. 21) between the QFM\* curve and the line bearing numerals 25 (Usp25)<sup>(\*)</sup>. The uncertainty range for temperatures is between 697°C and 735°C for total pressure between 1200 and 2000 bars, water pressure between 1200 and 1800 bars, and for log f(0 $_2$ ) between -16.65 and -17.35. It is quite

<sup>(\*)</sup> The QFM\* curve is calculated for a(Fa)=0.81, a(Q)=1.0 and a(Mt)=0.75.

reassuring that the temperature estimated from the coexisting feldspars is in excellent agreement with this range. The best estimate is taken at the intersection of the QFM\* line with the granitic minima and the coexisting feldspar estimates. These are:

T = 710°C, log 
$$f(O_2)$$
 = -17.25 and  $P_t = P(H_2O) = 1200$  bars.

The pressure estimate compares very well with the 1100 bars estimated earlier for the Traveler Rhyolite, suggesting that the KG represents essentially a solidifed magma chamber underneath the volcano. Additional evidence for this conclusion is that both rhyolitic and granitic rocks registered oxygen fugacities on the same  $f(0_2)$  buffer curve, notably An apparent discrepancy between the above estimated QFM. pressure and pressure implied by the whole-rock chemical composition (P( $H_2O$ )=2 Kb; Fig. 18) is best explained by the chemical memory of the granitic rocks; that is, the wholerock chemistry is a weighed average of several crystallization stages. The biotites of the Doubletop and Wassataquoik facies have the same composition. However, the biotites of the Summit facies are significantly lower in Ti and Fe and noticeably higher in Mn. Petrographic study of the Summit facies reveals that these biotites are phenocrysts within a very fine graphic and granophyrically intergrown groundmass of quartz and feldspars. These biotites may have crystallized at higher temperatures, which were subsequently quenched as the magma was intruded into a colder environment.

Using the biotite reaction and assuming that the granitic melt was internally buffered with respect to  $f(O_2)$  (on QFM buffer curve), the crystallization temperatures for these biotites may then be estimated as follows: 740°C for Sample #183, and 727°C for Sample KM6. The alternative explanation of constant T would invariably result in higher oxygen fugacity estimates. Biotite from the aplitic dike (Sample #145) also indicates an internally buffered  $f(0_2)$ granitic melt with an estimated  $f(O_2)$  just slightly below the QFM line. A temperature of 725°C and a pressure of 1 Kb for the aplite were derived from the Q-OR-AB and AN-OR-AB diagrams.

The proposed existence of an internally  $f(0_2)$  buffered natural melt is not without foundation. From  $f(0_2)-T$ plots of coexisting iron-titanium oxides for different suites of cogenetic rocks, it is apparent that there are definite  $f(O_2)$ -T trends parallel or subparallel with the QFM or the Ni-NiO buffer curves (Carmichael, 1967; Lipman, 1971; Hemming, Carmichael, 1972; Frisch, 1971). The results of these studies also suggest that internally  $f(0_2)$  buffered magmatic environments are a rather common occurrence.

The internal buffer may be maintained by one or both of the following reactions:

	T0 T0		
1)	through the $Fe^{-2}/Fe^{-3}$	equilibria and	precipitation
	of magnetite (Mueller	1971): and	procipionoton

2) through the  $\rm H_2/\rm H_2O$  equilibria within the melt attributable to the ability of hydrogen to enter the silicate melts (Nakamura, 1974).

## C. Horserace Quartz Diorite

#### 1. Geology and Petrology

The Horserace Quartz Diorite (HQD) forms a small elongated stock intruding the Doubletop facies of Katahdin Granite (KG) in the western part of the Katahdin Pluton (Fig. 14). This body, first described by A. Griscomin prep.), was named after the Horserace, a series of rapids in the West Branch Penobscot River. The HQD is about 5.5 km long, and at its maximum 2.0 km wide. It forms a pronounced topographic low on both sides of the Penobscot River between Big Ambejackmockamus Falls and Nesowadnehunk Deadwater.

The Horserace intrusion parallels a prominent fault system of the West Branch Penobscot River. This same fault system intersects the HQD and extends for a minimum of 30 km from Chesuncook Lake along the West Branch River to the center of the Katahdin Pluton, where its possible continuation is obscured by thick glacial deposits. A swarm of lamprophyre-like dikes, which seem to parallel the fault along its entire length, are considered part of the Horserace intrusion on the basis of geological, major and trace element similarities. Thus, it is evident that the ascent of the quartz dioritic magma was tectonically controlled, and that the fault remained active after the solidification of the intrusion.

The shape of the Horserace stock on the vertical plane was deduced from aeromagnetic data (Allingham, 1960).

The intrusion is symmetric; both, north and south contacts dip outward at angles of about  $55^{\circ}$  to a depth of at least 3 km. The character of the contacts with the surrounding Katahdin Granite is consistent with the model of a forceful, tectonically controlled intrusion. Brecciation of the granite and granitic inclusions within the quartz diorite are commonly observed near the contacts.

In fresh hand-specimens the quartz diorite is a bluish-grey rock; the varying intensities of grey depend on the modal content of mafic minerals. On the weathered surfaces, however, the HQD turns light-grey and/or pinkish near the joints or faults. The grain size varies from fine grain near the contacts to medium grain in the interior. The Horserace intrusion is concentrically zoned, with a composition of biotite-amphibole quartz diorite at the margins and a composition of amphibole-bearing biotite granodiorite in the interior. The content of the mafic minerals varies accordingly from about 25 modal percent to about 7 modal per-The principal mineral components of the stock are cent. plagioclase, quartz, alkali feldspar, amphibole and biotite: the last two are often fully or partially chloritized. Common accessories are apatite, zircon, sphene, opaques, and sulphides.

Modal analyses of two very fresh specimens collected from the marginal zones are given in Table 6. These two (and additional modal analyses by A. Griscom) were plotted on the IUGS recommended classification diagram (Fig. 22)

along with other plutonics of the Katahdin Pluton. From this diagram there is no indication that the Horserace rocks and the Katahdin granites may be related by either fractional crystallization or fractional melting (see also discussion on "Trace Element Geochemistry of the Traveler Rhyolite-Katahdin Pluton Igneous Complex"). On the same diagram, several hundred modal analyses from the Sierra Nevada Batholith (Bateman, 1963) are shown for comparison.

A strong correlation between Horserace Quartz Diorite and Debsconeag Granodiorite is suggested by the AFM diagram (Fig. 23). Here, a unique and distinct trend is defined by nearly colinear points of the Debsconeag, Harrington Lake, and Horserace intrusions and by samples from the West Branch dike swarm and the mafic dike on the east side of Doubletop Mtn. This trend is not similar to that of the Traveler Rhyolite-Katahdin Granite association. The HQD trend requires removal of mafic silicates and substantial amounts of magnetite. This implies a differentiation via fractional crystallization under strongly oxidizing conditions (Mueller, 1971).

Numerous aplitic and pegmatitic dikes, found mainly in the marginal zones, commonly contain albitic oligoclase, alkali feldspar, quartz, and minor amounts of biotite along with secondary chlorite and epidote. The marginal zone is also noticeable because of a narrowly spaced network of thin veinlets thought to be healed joints and fractures.

# Table 6

# Modal Analysis of Horserace Quartz Diorite

and

# Debsconeag Granodiorite.

Horse Quartz I	erace Diorite	Debsco Granodi	oneag .orite
235	238	13	166
4.7	5.1	23.4	19.4
58.3	54.9	37.9	36.4
8.8	13.0	29.3	33.8
10.8	10.5	8.3	8.9
16.2	15.1	0.5	0.7
1.2	1.4	0.6	0.8
0.93	0.92	0.62	0.65
0.60	0.59	0.06	0.07
	Horse Quartz I 235 4.7 58.3 8.8 10.8 16.2 1.2 0.93 0.60	Horserace Quartz Diorite $235$ $238$ $4.7$ $5.1$ $58.3$ $54.9$ $8.8$ $13.0$ $10.8$ $10.5$ $16.2$ $15.1$ $1.2$ $1.4$ $0.93$ $0.92$ $0.60$ $0.59$	Horserace Quartz DioriteDebsco Granodi23523813 $4.7$ $5.1$ $23.4$ $58.3$ $54.9$ $37.9$ $8.8$ $13.0$ $29.3$ $10.8$ $10.5$ $8.3$ $16.2$ $15.1$ $0.5$ $1.2$ $1.4$ $0.6$ $0.93$ $0.92$ $0.62$ $0.60$ $0.59$ $0.06$

- Modal Abundances of the Katahdin Pluton Granitoids Fig. 22. Plotted on the IUGS APQ Diagram (After Streckeisen, 1973).
  - Legend: KGD Katahdin Granite: Doubletop Facies DGD - Debsconeag Granodiorite HQD - Horserace Quartz Diorite
  - Labeled Fields: 1 Granite
    - 2 Granodiorite
    - 3 Tonalite
    - 4 Quartz Syenite
    - 5 Quartz Monzonite
    - 6 Quartz Monzodiorite 7 Quartz Diorite



Fig. 23A. AFM Plot of the Katahdin Pluton Granitoids and Harrington Lake Porphyry. The Lower California Batholith Trend is After Larsen, 1948, and the Skaergaard Trend After Chayes, 1970.

Legend:	TR-KG	-	Traveler Rhyolite-Katahdin nite Magmatic Sequence	Gra-
	DGD	-	Debsconeag Granodiorite	
	HLP		Harrington Lake Porphyry	

HQD - Horserace Quartz Diorite



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Fig. 23B. Plot of Normative (CIPW) Q-OR-AB Components of the Katahdin Pluton Granitoids and Other Analyzed Granites of Northern New England. For Locations See Fig. 3.

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Legend:	Small Dots	-	Katahdin Granite
-	DGD	-	Debsconeag Granodiorite
	HLP	-	Harrington Lake Porphyry
	HQD	-	Horserace Quartz Diorite



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Fig. 23C. Plot of Normative (CIPW) AN-AB-OR Components of the Katahdin Pluton Granitoids and Other Analyzed Granites of Northerh New England. For Locations See Fig.3.

Legend:	Small	Dots	-	Katahdin Granite
U	DGD		-	Debsconeag Granodiorite
	HQD			Horserace Quartz Diorite
	HLP		_	Harrington Lake Porphyry



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#### 2. Mineralogy

The modal proportions in Horserace rocks varies appreciably from a rather mafic amphibole-rich quartz diorite to a relatively felsic biotite granodiorite. The modal variations of optically analyzed samples are graphically illustrated on Fig. 24. The diagram shows a convincing correlation between the abundances of amphibole, biotite and alkali feldspar, but shows a considerable scatter for the plagioclase and quartz contents. A similar variation diagram plotting the modal amphibole as a fraction of the total mafics against the modal plagioclase as a fraction of the total feldspars, suggests that the principal cause of differentiation was a simultaneous removal of plagioclase and amphibole (lower part of Fig. 24).

#### Plagioclase:

Euhedral to subhedral oscillatory-zoned, elongated crystals of plagioclase feldspars form a framework giving the rock a subophitic or subgabbroic textural character. The crystals are on average about 2 mm large, somewhat coarser in the center and finer at the margins of the intrusion . The composition varies from andesine to oligoclase with the mean composition around An25. alteration of plagioclase is scarce and limited to saussuritization of a basic core within the interior of the stock. Microprobe analysis of three different grains from Sample #235 yields an average composition of An24. Fig. 24. Mineral Variation Diagrams in the Horserace Quartz Diorite. Data From Griscom (in prep.) and This Work.

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Upper Diagram: Modal Variation of Biotite, Plagioclase, Alkali Feldspar and Quartz Plotted Against Modal Content of Amphibole.

Lower Diagram: Variation of Modal Plagioclase as Fraction of Total Feldspars Against Modal Amphibole as Fraction of Total Mafics.



#### Alkali Feldspar:

Alkali feldspar is always present in the form of interstitial grains, filling residual voids between euhedral and subhedral plagioclases, amphiboles, and biotites. The grains are fresh and homogeneous. An average of four microprobe analyses from two different grains corresponds to a composition of Or87 Ab13.

#### Amphibole:

Amphibole is euhedral to subhedral within the marginal zone of the intrusion but is more irregular toward the center. The grains are up to 4 mm large with occasional resorption remnants of clinopyroxenes in samples from near the contacts. The pleochroism is strong from intense green to straw-yellow. From indices of refraction, A. Griscom (in prep.) has shown that the amphibole composition is constant throughout the intrusion. The textural relationship with biotite indicates that amphibole crystallization preceded biotite crystallization. Amphiboles are conspicuous because of common, fine sulphide grains in the interior of larger amphiboles. Chloritization is commonly observed in the center of the stock.

#### Biotite:

Euhedral or subhedral grains, up to 2 mm in size, are intensely pleochroic from dark brown to yellowish-tan. Biotite occasionally encloses irregular grains of green amphibole. Small grains of accessory zircon and apatites are frequent. The biotite composition in the marginal zone, as determined by electron microprobe, is distinctly different from the biotite of the Katahdin Granite.

Fe\*/sum (octahedral ions) = 0.38. This compares with 0.77 of the Katahdin Granite. Assuming the same total pressure for the Katahdin Granite and a water pressure of at least one-half of P(tot), approximate calculations indicate that the logarithm of oxygen fugacity for the Horserace intrusion was 1.7 to 2.3 units higher than for the Katahdin Granite; i.e., near or above the Ni-NiO buffer. Biotites from the interior are less ferrous, possibly by as much as 10 mole%, indicating therefore an oxidizing, magmatic environment.

#### Minor Minerals:

Other common minerals are sulphides and iron-titanium oxides. Sulphides occur as fine "droplets" almost exclusively in the cores of amphiboles. They are probably pyrrhotites with minor chalcopyrites. A typical accessory mineral is sphene; apatite and zircon are less frequent.

In conclusion, the chemistry and mineralogy of the Horserace intrusion suggest that the quartz dioritic magma, in contrast to the Katahdin Granite, crystallized under a more oxidizing environment. The calculation based on biotite composition shows that for the temperature range between 700<sup>°</sup> and 800<sup>°</sup>C, the oxygen fugacity was above the Ni-NiO buffer curve. This conclusion is supported by the presence of sphene (Czamanske and Wones, 1973, p. 374) and by the trend in the AFM diagram.

# D. Harrington Lake Porphyry

The porphyry is a light-grey, porphyritic rock, consisting of a fine-grained, subcrystalline matrix, with up to 15 modal% plagioclase phenocrysts, and fully chloritized mafic silicates--probably amphiboles.

All the samples studied are extensively hydrothermally altered to a mixture of sericite, chlorite, epidote, calcite, and other secondary minerals.

The Harrington Lake Porphyry is a semi-arcuate, silllike intrusion, approximately 4.5 km long and 650 m wide, which crops out along the southern shore of Harrington Lake. A fault terminates the intrusion on the northwestern side; on the southeastern side it is ended by the Katahdin Pluton. The contact relationship with the Katahdin Pluton is uncertain due to the scarcity of exposures. A few crystalline inclusions, found within the interior of the intrusion, are mineralogically and texturally similar to the rocks of the Horserace Quartz Diorite stock. As a consequence, the Harrington Lake intrusion appears to be younger, possibly a differentiation product of the original Horserace magma. This possibility is further supported by the major elemental abundances; that is, low K/Na, intermediate Fe/(Fe+Mg), and by trends on the AFM, Q-OR-AB and OR-AB-AN diagrams (Figs. 22 and 23).

In 1968, Rankin considered this intrusion as part of a broader belt of granophyric bodies scattered between

Harrington Lake and Grand Lake Matagamon, describing them as shallow igneous bodies, analogous to the Traveler Rhyolite. However, a comparison of chemical compositions of Grand Lake Matagamon granophyric sill with the analyses of the Harrington Lake Porphyry and Traveler Rhyolites indicates, that Rankin's interpretation may hold true only for some of these bodies. The Harrington Lake Porphyry correlates with the Horserace magmatic episode emplaced after the Katahdin Granite. The magmatic association of the other "granophyric" bodies is uncertain.

# E. Debsconeag Granodiorite

Debsconeag Granodiorite (DGD) is a medium-grained biotite-granodiorite, principally found in an  $80\text{-km}^2$  large, V-shaped stock in the southeastern portion of the Katahdin Pluton (KP). Another occurrence of DGD is mapped as a separate, (1.5 km<sup>2</sup>) small stock in the southern part of KP. The type exposures are along the rapids in the West Branch Penobscot River, namely at Abol Falls, Pockwockamus Falls, and Debsconeag Falls.

DGD, the larger of the two stocks, is intruded by the West Branch Penosbscot River dike swarm. Both stocks, which are for the most part covered by extensive glacial deposits, are entirely surrounded by Doubletop facies of Katahdin Granite. Their contacts, however, were never observed due to the absence of critical exposures. A study of DGD float boulders near the vicinity of the contacts indicates that DGD is finer-grained with increasing concentration of as much as 15% biotite and increasing abundances of aplites and pegmatites.

Mineralogically and texturally, DGD shows considerable similarity to KGD. The noticeable differences include a finer grain size of biotite and quartz, a lower modal content of alkali feldspar, higher proportions of biotite and plagioclase, along with subordinate amounts of hornblende which are present in all samples (Fig. 22). DGD alkali feldspar tends to be more euhedral giving the DGD rock a subporphyritic appearance. From a comparison of KGD and DGD biotites, the latter are frequently euhedral with distinctly lower Fe/sum (octahedral ions) = 0.59 vs. 0.77 for KGD. Plagioclase is continuously and cyclically zoned, varying from An35 to An18 with occasional albitic rims. Apatite, zircon, and allanite are frequent accessory minerals.

The deuteric alteration of DGD is much less extensive than that of KGD. DGD specimens are light-grey and never pink, even near joints. The only evidence of deuteric changes is documented by partly chloritized biotites and by infrequently saussuritized and sericitized plagioclase cores.

Two DGD analyses are plotted on Q-AB-OR (Fig.23B), AN-AB-OR (Fig.23C), and on AFM (Fig.23A) diagrams. The major element abundances are in support of the genetic relationship of DGD with the younger HQD-HLP sequence. Based on field relationships, the time of DGD emplacement is bracketed by earlier KGD and younger HQD intrusions.

## IV. TRACE ELEMENT GEOCHEMISTRY OF THE TRAVELER RHYOLITE-KATAHDIN PLUTON IGNEOUS COMPLEX

#### A. Introduction

Trace element abundances are a more sensitive indicator of igneous rock petrogenesis than are abundances of major elements. This is particularly true for acidic rocks where the bulk composition of the fractionating crystals is often very similar to the parent magma. For this reason, trace element (TE) abundances were determined in selected samples of the Traveler Rhyolite-Katahdin Pluton Igneous Complex.

As discussed in the preceding chapters, petrological and geological studies of igneous rocks from the Traveler Rhyolite-Katahdin Pluton Igneous Complex suggest two genetically independent magmatic episodes, each of a different igneous style. The earlier episode includes voluminous ignimbritic depositions of the Traveler Rhyolite (TR) and crystallization of six facies of the Katahdin Granite (KG) which underlies more than 95% of the 1330 km<sup>2</sup> large Katahdin Pluton. The younger igneous episode is comprised of three small intrusions of Horserace Quartz Diorite (HQD), Harrington Lake Porphyry (HLP), and Debsconeag Granodiorite (DGD), all of which intrude along the NW-SE West Branch Penobscot River fault system (Fig. 14). Fifty-two (52) samples included in this study are representative of both episodes:

	Number
	of Samples
	ballpies
Traveler Rhyolite	
Pogy Member - Sample codes: 46, 51, 214, 215 and 216	5
Black Cat Member - Sample codes: 217, 219, 220, TR3, TR8, and TR10	6
Katahdin Granite	
Doubletop Facies - Sample codes: 29, 41, 74, 81, 134-1, 134-2, 150, 190F, 190W, 209 and	
240	12
Chimney Facies - Sample codes: 69 and KM9	2
Summit Facies - Sample codes: 64, KM1 and KM6	3
Wassataquoik Facies – Sample code: 43	1
Cathedral Facies - Sample codes: 121, 198, and KM2	3
Horserace Quartz Diorite - Sample codes: 127A, 235 and 238	3
<u>Debsconeag Granodiorite</u> – Sample code: 166	1
Harrington Lake Porphyry - Sample code: 4	1
<u>Aplites</u> - Sample codes: 134-3, 134-6, 134-7, 134-8, 145 and KM7	6
Pegmatites - Sample codes: 134-4 and 134-5	2
Total number of analyzed samples for TE from the TR-KP igneous complex	45 ==

In addition, samples from similar magmatic complexes of Northcentral Maine and Northern Vermont were also analyzed (Fig. 3). The additional samples include:

Rhyolite of the Kineo Rhyolite (Piscataquis Volcanic Belt - Rankin, 1968): Sample code: 247 1 sample Granite of the Lxington Pluton (Greenville Plutonic Sample code: NNP-2<sup>(\*)</sup> Belt): 1 sample Granite of the Moxie Pluton (Greenville Plutonic Sample code: 244 1 sample Belt): Gabbros of the Pierce Pond Pluton (Greenville Sample codes: PP1, PP235 and PP379(\*\*) Plutonic Belt): 3 samples Granite of Echo Pond Pluton (Northern Vermont): Sample Code: 6291<sup>(\*)</sup> 1 sample

Postmagmatic changes, such as weathering, tectonic shearing, hydrothermal and pneumatolytic alterations, may significantly alter primary (magmatic) TE abundances (Rice, 1973); Blaxland, 1974; Neiva, 1974) and, as such, could lead do erroneous petrogenetic interpretations. In order to evaluate the effects of postmagmatic alterations, several altered granitic and rhyolitic samples were purposely analyzed to study the possible extent of such changes. Also, the possible loss of TE due to vapor transport was studied by analyzing aplites and pegmatites from a layered aplitepegmatite dike.

(\*) Courtesy of R. S. Naylor (\*\*) Courtesy of P. Lyttle

#### B. Analytical Methods

TE abundances were determined by instrumental neutron activation (INNA) analysis (Gordon et al., 1968) and by X-ray fluorescence (XRF). The precision of the INNA technique, expressed as % fractional standard deviation (also known as variation coefficient - VC), was obtained by multiple analyses of USGS Standard G-2. The precision (at +1 sigma level) is less than 5% for Cr, Co, Cs, Ce, Nd, Sm, Ho, Hf, and Th; less than 10% for Sc, Rb, La, Eu, Gd and U; and 10-12% for Yb, Lu and Ta. The lower precision for Yb and Lu is attributed to low concentration of these elements in the USGS G-2 standard. Cr abundances in the majority of the analyzed rocks are below the detection limit. The Cr detection limit, calculated at 3 sigma significance level, is between 4 and 5 ppm. The XRF precision is probably better than 20% (H. W. Fairbairn - personal communication). The accuracy level of both techniques is comparable with precision. In the XRF analyses, G-2 is used as a primary standard.

## C. Postmagmatic Changes of TE Abundances in Rhyolites and Granites

In order to evaluate the extent of deuteric changes on TE abundances in rhyolitic and granitic rocks, the following two tests were carried out:

(1) The variation coefficients for individual elements of seven, both fresh and altered, rhyolitic rocks were compared

with the variations caused by analytical imprecision (samples analyzed by L. Lopez, 1972). These samples, collected from a narrow stratigraphic zone of the Black Cat Unit of the Traveler Rhyolite, were thought to represent an originally homogeneous section of rhyolitic rocks with idential TE abundances. For this reason, the variation beyond the limit of analytical imprecision is possibly due to postdepositional changes (Figs. 25A, 25B). Both figures also show variation coefficients (% standard deviation) calculated for eleven (11) different samples from different localities of Doubletop Facies of Katahdin Granite. These variations represent a combination of analytical errors and actual differences among the analyzed samples. The significance of these variations and their interpretation will be discussed later in this study.

(2) Another evaluation of postmagmatic changes was obtained by comparing trace element data of five (5) altered samples at the KG Doubletop facies with the average trace element abundances of unaltered Doubletop facies of the Katahdin Granite (see Fig. 26). These altered samples are:

(a) Sample #81 - Tectonic mylonite: silicified fault gouge;
(b) Sample #190-W - Weathered crust around sample #190-F;
(c) Sample #240 - Hydrothermally altered zone near fault: deeply reddened Doubletop Facies granite;
(d) Samples #134-1 and 134-2 - From the contact with layered pegmatite-aplite. Sample #134-2 is directly from the contact; Sample #134-1 is 4 cm away from the contact and is unaffect-

ed by the presence of the dike.

Fig. 25A, B. Comparison of Analytical Precisions With Variation Coefficients Obtained on 6 Different Samples of Black Cat Member of Traveler Rhyolite And on 8 Different Samples of Doubletop Facies of Katahdin Granite. Fig. 25A: Non Rare-Earth Elements; Fig. 25B: Rare Earth Elements.



# VARIATION COEFFICIENTS

VARIATION COEFFICIENTS



(B)

Rare Earth Elements (REE):

REE abundances in the Traveler Rhyolite are unaffected by deuteric changes, even in the few extensively altered specimens (see Fig. 25A). This is also true for the tectonically sheared granitic sample (Sample #81), and for the weathered crust sample (Sample #190-W). However, the sample of hydrothermally altered granite (#240) shows a depletion in HREE (Lu concentration is 0.6 of the average concentration in the Doubletop facies of Katahdin Granite), whereas the sample from the contact with the layered pegmatite-aplite (#134-2) shows a considerable enrichment in HREE (Lu is 2.4 times higher than the average content in the Katahdin Granite-Doubletop Facies). Since these postmagmatic changes are easily detectable in the field, I conclude that the REE abundance variations reflect variations imprinted by magmatic processes alone.

#### Scandium (Sc):

The Sc variation in the tested rhyolites and granites is within the limits of analytical precision, except for Sample #134-2 (contact with the aplite-pegmatite dike), which shows an enrichment of approximately 1.4 times the average Katahdin Granite-Doubletop Facies.

#### Cobalt (Co):

The variation coefficient of Co in rhyolites (24%) does not correlate with the degree of deuteric alteration; the dispersion is most likely a primary feature caused by a Fig. 26. Plot of Rare-Earth Elemental Abundances of Variedly Affected Samples of Doubletop Facies of Katahdin Granite Normalized to an Average of 8 Fresh Samples of Doubletop Facies of Katahdin Granite. See Text For Further Discussion.

Legend:	Sample	134 - 2	_	From Contact With Layered
				Aplite-Pegmatite Dike
	Sample	240	-	Strongly Reddened and Hydro-
				thermaly Altered
	Sample	190W		Weathered Rind From Around
				a Fresh Sample 190F
	Sample	81	_	Sheared, Ground and Silici-
				fied Sample From a Fault Zone


statistical variation in the modal content of clinopyroxene, opaques, and fayalite. The variation of Co in altered granitic rocks is within the limits of analytical precision, except for enrichment in Sample #240 (hydrothermally altered zone) of 1.4 times the average Katahdin Granite-Doubletop Facies (KGD).

### Rubidium(Rb):

Rb abundances in granites and rhyolites are very uniform with a marked depletion found only in extremely altered samples, e.g., in hydrothermally recrystallized rhyolites (Sample #M-14)(L. Lopes, 1972). A significant depletion of 0.5 times the average Katahdin Granite-Doubletop Facies is also found in the tectonically sheared granite (Sample #81) and in the hydrothermally altered granite (Sample #240) (about 0.65 times the KGD).

### Cesium (Cs):

Cs seems to be a very sensitive indicator of postmagmatic changes, as documented by large variation coefficients of 50 to 70% for the rhyolitic and granitic rocks. Cs is usually depleted in altered rocks but its abundance is enriched in the weathered crust sample (#190-W).

#### Hafnium (Hf):

All Hf variations are within the limits of analytical precision, except for the sample from the contact with the layered pegmatite-aplite, which shows an enrichment of 1.35 times above the average Katahdin Granite-Doubletop facies.

### Tantalum (Ta):

Ta is next to Cs the most variable element. Its variation coefficient in rhyolites is about 35%. Although the variation coefficient in KGD is only about 15%, all altered samples show a significant depletion (about 20-50%) except for the weathered crust sample which is within normal limits. The large variation of Ta abundances may be due to the relative solubility of tantalum fluoride.

## Thorium (Th):

Th variations in the rhyolites and granites are within the limits of analytical precision. Only two samples from near the contact with the pegmatite-aplite dike show an enrichment by about 42-50%.

#### Uranium (U):

It was difficult to assess the variation of U abundances, primarily because of the low analytical precision (about  $\pm$ 20%). However, there is a strong indication that U abundances are sensitive to deuteric alterations; for example, the U content in the weathered crust sample #190-W) and in the sample from the contact with the pegmatite-aplite dike (#134-2) is twice as high as the average KGD facies. These results show that the abundances of Cs, Ta and U are strongly influenced by deuteric changes. For this reason Cs, Ta and U variations cannot be used as indicators of fractional crystallization. However, REE, Sc, Co, Rb, Hf and Th abundances vary within the limits of analytical precision and these elements are a reliable source of information on magmatic processes.

On inspection of Figure 25B, there is a gradual increase of variation coefficients from Lu to La for the granites of Doubletop facies. I believe that this gradual increase of uncertainty from Lu to La (except for Eu) is due to the statistical variation between samples; e.g., unequal distribution of monazite or allanite in the analyzed samples. Strong evidence for such apparent sample heterogeneity is that the smallest and the coarsest samples yield the largest From the known distribution of REE in these deviations. accessory minerals, the difference between average and extreme values (normalized to Lu) can be explained by the weight variation of +1:6600 for allanite or +1:17000 for monazite. These variation ranges are approximate, based on estimated La partition coefficients of allanite and monazite (3700 and 9500, respectively; Lee and Bastron, 1967; Nagasawa, 1970; Lee et al., 1973).

#### D. Layered Pegmatite-Aplite

Upon fractionation of hydrous magmas, the continually evolving and escaping volatile-rich gaseous phase may

carry with it an unknown (but appreciable) amount of trace elements and may thus, during the late magmatic states, cause important changes in their abundances otherwise attributable to crystal fractionation processes. Further understanding of the effect of the exsolving hydrous phase on TE abundances is thought to be gained by a geochemical study of coexisting pegmatite and aplite within a layered pegmatite-aplite dike (Sample #134). As will be shown later, the aplite of this dike represents approximately 20% residual magma differentiated from the parental Debsconeag Granodiorite (DGD) melt. The associated pegmatite is a coarse crystalline rock, formed by a crystal growth from the hydrous vapor phase which was purged from the crystallizing magmas (Jahns, Tuttle, 1963; Luth, Tuttle, 1966; Jahns, Burnham, 1969).

Sample #134 comes from the upper part of a 0.5 m wide, layered aplite-pegmatite dike, exposed in the stream bed of the Katahdin Stream (elevation 395 m), approximately at the base of Mt. Owl and 0.5 km above the Katahdin Stream Campground. The dike intrudes the Doubletop Facies of Katahdin Granite.

A 2 cm thick and 30 cm long slab obtained from this sample was further divided into a sequence of the following eight blocks:

134-1 5 cm long block of Doubletop facies of Katahdin Granite - 4 cm away from the contact;

134-2 4 cm long block of Doubletop facies of Katahdin Granite - from the contact;

- 134-3 2 cm wide aplitic zone;
- 134-4 3.5 cm long block, half the thickness of the pegmatitic zone;
- 134-5 Ditto; and
- 134-6,7,8 4 cm long consecutive blocks of the main aplitic zone.



Trace element variations across Sample #134 are shown on Figs. 27, 28, 29A, 29B, and 29C. The REE chrondrite normalized distribution patterns are illustrated in Fig. 27. Fig. 28 shows relative REE distributions of AP3 (average of the four aplitic samples: #134-3, 134-6, 134-7 and 134-8, and PEG3 (average of the two pegmatitic samples: 134-4 and 134-5) with respect to their parental DGD magma and the relative distribution of PEG3 compared to AP3. Fig. 27. Chondrite-Normalized Rare Earth Element Abundances in 6 Samples Taken From Across a Layered Pegmatite Aplite Dike.



Fig. 28. Plot of Average Rare Earth Elemental Abundances in Aplites and Pegmatites Normalized to Debsconeag Granodiorite (Presumed Parental Magma) and Rare Earth Element Abundances of Pegmatite Normalized to Aplite.



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Concentration profiles of the individual trace elements across the analyzed portion of the layered dike are shown on Figs. 29A, 29B, and 29C. They are compared with average abundances in the Doubletop facies of KG with superimposed +3 standard deviations (99% confidence limit).

The diagrams are largely self-explanatory, but some general conclusions can be drawn:

- REE are always more abundant in pegmatites than in coexisting aplites. Light RE(LRE) are two to three times more enriched in the pegmatitic phase than heavy Re(HRE) (Gd-Lu) which show only mild enrichment (1.35 times);
- 2) In Sample #134-1, 6 cm from the contact, only La, among the REE, shows marked enrichment relative to the average granite;
- 3) Near the vicinity of the contact, the granite (Sample #134-2) is strongly enriched in HRE (Ho-Lu: 2.2 times).
- 4) Except for Eu, Sc, and Co, there is a considerable enrichment of the other trace elements in the aplitic zone immediately adjacent to pegmatite;
- 5) Co abundances in both aplites and pegmatites are identical. There is no exchange of Co between the wall rock and the dike;
- 6) Sc, Th tend to be enriched in the wall rock; Th is relatively depleted in the pegmatites; Sc abundances in pegmatites and aplites are similar.

Fig. 29A,B,C. Variation of Elemental Abundances Across Analyzed Portion of a Layered Aplite-Pegmatite Dike. On Abscissa Are Plotted Average Doubletop Facies of Katahdin Granite and Individual Segments of Sample # 134, e.g. 134-1 to 134-8. Average Doubletop Facies of Katahdin Granite is Plotted With ±3 Standard Deviations (99% Confidence Interval).

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(B)

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7) Rb abundances in the main aplitic zone and in the pegmatitic zone are identical; original Rb abundances in the wall rock are unaffected.

The comparison of TE abundances in coexisting aplite and pegmatite emphatically points to a diverse behavior of some of the elements during the late stages of evolution of hydrous granitic magmas. REE, Hf, Ta and U are preferentially incorporated in pegmatites whereas Cs and Th tend to be enriched The best indicators of fractionation during the in aplites. stages of vapor phase separation are the abundances of Rb, Sr. Sc and Co; their excess relative pegmatite abundances in percent of the average aplite (3%, -8%, 13% and 30%, resp.) indicate their equal mobility in both the evolving vapor phase and the magma. Abundances of Rb and Sc, and possibly of Sr, are also valued for their passivity during The unique signifithe postmagmatic alteration processes. cance of the Rb and Sr behavior will be reemphasized later (see discussion on TR-KG sequence).

#### E. Results

Trace elemental abundances of the studied samples are given in Table 7 and the REE abundances normalized to a chrondrite average (Haskin et al., 1968) are plotted in Figs. 30, 31, 32 and 33. Based on petrography, it is possible to arrange all the rock samples into two groups, with further subdivisions based on their Sc abundances:

Table	7. Trace	Element G	eochemisti	ry. Samp	les Arran	ged in As	cending N	umeric Oro	der and A	lphabetica	ally.
Sample Symbol	: 4	29*	29*	41	43	46	51	64	69	74	81
Rock Unit	: HIP	KGD	KGD	KGD	KGW	TRP	TRP	KGS	KGCH	KGÐ	KŒD
Sc	5.68	27.68	27.24	25.27	26.01	22.19	32.43	27.71	24.60	26.98	21.38
Cr	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
Co	5.98	1.27	1.19	0.93	0.51	0.28	2.11	0.67	0.71	1.08	1.07
Rb	68.80	189.7	NA	182.5	236.2	180.2	169.0	202.2	NA	212.5	87.42
Cs	2.23	10.47	9.19	7.58	9.33	8.09	8.73	8.46	9.73	8.87	1.09
$\operatorname{Hf}$	3.91	10.55	10.12	9.87	6.35	9.86	11.42	10.74	8.04	8.83	8.73
Ta	0.37	1.37	1.58	1.62	1.60	1.32	1.38	1.12	2.32	1.33	0.93
Th	7.23	16.68	NA	14.54	14.72	15.20	14.16	16.07	NA	12.68	12.45
U	0.90	2.77	2.23	3.06	5.74	2.83	4.57	1.87	4.08	2.47	2.23
$\mathbf{Sr}$	540	67	NA	63	26	45	NA	59	NA	68	NA
La	19.87	58.77	57.33	51.11	47.34	52.22	47.74	35.61	48.08	32.59	41.17
Ce	44.32	126.0	123.2	117.2	123.4	130.0	120.4	74.16	107.5	65.16	82.79
Nd	16.69	55.99	54.02	50.76	52.39	66.44	55.65	34.30	46.40	31.21	38.11
Sm	3.21	12.24	11.60	11.06	12.38	15.07	13.75	8.07	10.16	7.07	8.53
Eu	0.88	1.30	1.30	1.25	0.68	1.70	2.00	1.13	1.25	1.02	1.25
Gd	2.67	12.52	12.20	11.17	10.84	14.91	14.80	8.45	10.52	8.00	9.48
Ho	0.41	2.48	2.10	2.30	2.80	2.98	2.69	1.91	2.06	1.74	1.92
Yb	0.94	6.35	5.96	6.41	7.01	7.28	7.28	5.24	6.09	5.37	4.90
Lu	0.15	1.02	0.98	1.05	1.17	1.20	1.19	0.84	1.05	0.90	0.83

\* Duplicate analyses.

NA Not analyzed.

BD Analyzed, but below detection limit. From counting statistics the detection limit for Cr is 4 ppm. All data in ppm.

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Sample Symbol	:	115	121	127A	134–1	134-2	134-3	134-4	134–5	134-6	134-7	134-8
Rock Unit	:	KGD	KGCT	HQD	KŒ	KGÐ	AP3	PEG3	PEG3	AP3	AP3	AP3
Sc		24.92	15,93	12.23	33.68	39.70	9,65	17.28	13.66	13.40	12.56	11.86
Cr		BD	BD	167.7	BD	BD	BD	BD	BD	BD	BD	BD
Co		1.28	1.71	20.08	0.82	1.11	0.23	0.20	0.15	0.13	0.14	0.11
Rb		183.8	210.8	76.18	219.2	213.5	201.7	267.0	277.2	307.4	285.8	277.2
Cs		5.02	8.85	2.92	6.01	6.10	4.64	6.82	6.61	13.15	11.45	11.41
$\operatorname{Hf}$		8.93	6.56	4.29	9.87	12.59	1.70	13.55	2.19	5.63	4.95	4.57
Ta		1.74	1.64	0.67	1.12	1.45	2.43	9.58	2.64	2.56	1.43	1.58
Th		15.94	16.67	7.97	20.24	22.15	24.66	17.69	13.23	33.79	29.73	30,58
U		4.07	6.02	2.26	2.66	6.54	7.89	22.71	9.28	9.60	7.32	5.36
Sr		79	NA	NA	70	78	26	24	NA	NA	. NA	NA
ไล		46.35	41 61	34 63	94 62	190 0	11 69	33-30	41 87	14 94	9.26	10 12
Ce		97.58	92.93	66.55	183.1	130.9	21.53	79.88	83.45	33.02	23.19	24 25
Nd		42.55	41.11	27.34	79.24	57.02	12.70	34.72	38.34	19.88	14.49	15.58
Sm		9.74	8.74	4.32	15.42	14.13	4.32	10.59	12.02	7.95	5.76	5.42
Eu		1.08	0.94	1.18	1.08	1.02	0.29	0.30	0.43	0.15	0.16	0.17
Gd		10.95	9.21	4.28	12.46	15.15	8.06	9.74	12.74	9.89	7.91	8.85
Ho		2.19	1.92	0.50	2.67	5.36	3.58	4.24	5.26	4.07	3.31	3.34
Yb		6.31	5.37	1.01	6.55	13.27	14.43	16.62	18.45	15.75	12.36	10.44
Lu		1.06	0.89	0.17	0.99	2.11	2.22	2.81	3.01	5.21	1.84	1.58

Table 7. Trace Element Geochemistry. (Cont.)

NA Not analyzed.

BD Analyzed, but below detection limit. From counting statistics the detection limit for Cr is 4 ppm.

Sample Symbol	: 145	150	166	190F*	190\**	198	209	214	215	216	217
Rock Unit	: AP2	KGD	DGÐ	KGD	KGD	KGCT	KGD	TRP	TRP	TRP	TRBC
$\mathbf{Sc}$	41.04	26.00	12.02	28,26	26.38	21.27	25,17	25,25	24,07	26.94	33.57
Cr	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD	BD
Co	0.40	1.12	3,95	1.07	1.00	1.83	0.96	1.72	1.59	3.79	2.15
Rb	377.0	191.3	135.8	194.3	203.7	NA	179.6	160.5	200.0	143.2	189.8
Cs	7.16	9.36	7.62	10.96	13.10	8.38	11.15	8.17	10.71	2.50	11.72
Hf	7.84	9.27	6.77	8.61	7.96	9.82	10.76	9.32	9.47	15.12	14.53
Ta	4.23	1.35	1.27	1.51	1.47	2.19	1.59	1.30	1.24	1.39	1.70
Th	19.22	14.90	20.07	13.75	14.83	NA	10.89	12.50	15.70	12.90	15.33
U	15.07	2.65	3.32	4,58	6.13	3.03	2.51	6.23	5.58	3.98	4.21
$\mathbf{Sr}$	8	60	186	62	NA	NA	66	74	51	84	78
La	15.35	65.10	57.53	44.38	44.75	41.71	36.06	57.83	53.35	52.69	54.24
Ce	29.45	133.8	104.3	101.8	102.0	96.15	84.94	131.7	134.5	121.1	127.9
Nd	16.39	57.92	40.04	45.93	45.40	43.94	41.41	57.70	58,99	56.34	55.70
Sm	5.09	12.40	6.85	11.55	10.76	9.09	9.48	13.13	13.77	13.29	12.96
Eu	0.08	1.27	1.03	1.27	1.21	1.57	1.24	1.53	1.44	2.16	1.88
Gd	5.39	12.32	8.57	12.31	10.81	9.23	9.97	14.67	13.57	14.19	12.55
Ho	2.09	2.48	1.69	2.38	2.40	1.76	2.14	2.94	2.88	2.55	2.81
Yb	8.51	6.48	4.92	5.60	5.24	4.95	5.57	7.49	7.02	6.91	7.97
Lu	1.44	1.05	0.75	1.00	0.91	0.80	0.90	1.25	1.12	1.14	1.30

Table 7. Trace Element Geochemistry. (Cont.)

NA Not analyzed.

BD Analyzed, but below detection limit. From counting statistics the detection limit for Cr is 4 ppm.

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Fresh sample Weathered crust

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Sample Symbol	: 219	220	235	238	240	244	247	6291	KM1	KM2	KM6
Rock Unit	: TRBC	TRBC	HQD	HQD	KGD	MG*	KR**	EPG***	KGS	KGCT	KGS
											یون باعد دربیر همه پخیر می بخش ها بخش ا
Sc	29.37	27.53	13.81	14.14	23.46	4.66	29.22	3.32	27 62	19.83	26 95
Cr	BD	BD	101.6	115.5	BD	BD	BD	BD	BD	BD	20.95 BD
Co	3.05	1.56	16.95	17.23	1.55	1.88	0.61	3.50	0.89	2.12	0.91
Rb	137.5	165.2	56,93	59.91	117.9	148.1	145.5	121.8	166.9	206.0	192.6
Cs	15.61	3.09	1.08	1.30	1.21	4.22	2.02	1.85	8.05	9.25	16.10
$\operatorname{Hf}$	15.36	12.55	4.34	4.10	9.53	3.55	10.22	5.97	10.29	12,26	11.35
Ta	1.17	1.78	0.39	0.67	0.75	2.25	1.74	1.68	1.45	1.30	1.64
Th	12.86	14.68	6.29	6.13	16.35	19.55	15.66	12.76	17.08	15.57	16.24
U	7.50	4.11	1.22	1.68	2.99	5.77	4.26	1.88	4.94	6.75	5.49
$\mathbf{Sr}$	88	63	883	NA	NA	77	50	424	NA	NA	NA
La	56.68	47.14	29,24	24.43	53.10	21.51	52.44	32.98	57.10	34.77	49.85
Ce	131.8	117.8	54.31	52.85	122.5	42.79	125.8	60.70	133.4	75.54	111.2
Nd	60.82	52.76	23.57	22.10	54.60	16.55	53.86	19.72	59.89	37.87	52.93
Sm	13.76	12.29	4.36	4.26	10.99	4.37	12.17	3.50	11.56	7.91	11.29
Eu	1.92	1.74	1.26	1.19	1.29	0.49	1.29	0.68	1.12	1.18	1.33
Gd	15.25	13.70	4.08	3.95	9.49	4.95	10.54	2.68	13.51	7.72	12.34
Ho	2.89	2.70	0.48	0.54	1.56	1.33	1.80	0.35	2.02	2.10	2.49
Yb	7.62	6.81	1.33	1.46	3.47	4.0	4.65	0.89	5.36	5.55	6.11
Lu	1.28	1.13	0.22	0.23	0.57	0.67	0.77	0.12	0.84	0.86	0.94

Table 7. Trace Element Geochemistry. (Cont.)

\* MG = Moxie Granite

\*\* KR = Kineo Rhyolite

\*\*\*EPG= Echo Pond Granite

BD = Analyzed, but below detection limit. From counting statistics the detection limit for Cr is 4 ppm. NA = Not analyzed.

10010	1 110000		د مسید. مدر سه سار بنی سه می مدر مید			بني والدة والناة التلك تعليك وولي والبور مجمع فينيه ا	وهجر جمال منده بدرها محدد ويها محد وجد ومنغ و	بنو ومبيريتين ويدر ويو عمو ويبد وينه مبيد به	سه مبني مص 100 منه من و100 ميرد 100 مي د	اخصا صدا يتهد ونبو خلته سبب عبيه تبلية كلب ب	ويجبه بالقبة وتست كتبته ومحد أأكله وملك فالم
Sample Symbol	: KM7	KM9	NNP2	PP1	PP235	PP379	TR3 <sup>(1)</sup>	$TR8^{(1)}$	$\operatorname{TR10}^{(1)}$	G-2*	G-2*
Rock Unit	: AP1	KGCH	Lexington Granite	$PPG^{(2)}$	<sub>PPG</sub> (2)	$PPG^{(2)}$	TRBC	TRBC	TRBC	USGS-ST	USGS-ST
Sc	27.30	24.87	3.53	38.13	51.71	51.56	29.23	33.50	33.27	3.87	3.83
Cr	BD	BD	BD	222.8	227.6	75.8	NA	NA	. NA	8.25	NA
Co	0.26	1.30	1.63	54,50	46.20	45.73	2.16	2.26	2.00	4.66	4.62
Rb	290.5	176.0	290.4	BD	BD	BD	181.6	202.6	180.4	177.0	NA
Cs	8.06	13.59	17.69	0.33	0.79	0.88	2,98	12.97	18.14	1.34	1.33
Hf	5.75	9.76	2.80	0.75	0.76	1.78	12.10	14.44	15.02	8.81	8.41
Ta	2.01	1.47	2.25	0.04	1.03	0.32	1.28	2.70	2.35	1.01	1.07
Th	15.83	14.02	8.47	BD	1.90	0.59	14.37	14.99	14.22	23.52	NA
U ·	5.84	2.74	4.04	BD	0.65	0.33	NA	NA	NA	2.67	2.03
Sr	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
La	28.03	38,89	18.62	0.64	19.28	5,83	57.64	65.31	58.68	81.54	81.48
Ce	80.71	86,96	40.23	1.00	41.65	14.19	114.8	129.5	113.0	163.7	161.3
Nd	35.42	41.08	14.95	0.62	20.58	8.75	55.78	64.25	57.44	49.16	47.80
Sm	9.84	10.49	4.21	0.22	4.76	2.66	14.02	15.26	13.91	7.18	6.99
Eu	0.17	1.24	0.52	0.60	1,96	1.13	1.84	2.15	1.90	1.27	1.29
Gd	14.28	9.73	3.17	0.63	5.27	3.04	12.69	14.20	12.28	4.10	4.08
Ho	3.21	2.76	0.44	0.15	1.01	0.70	NA	NA	NA	0.51	0.48
Yb	8.32	5.72	0.94	0.49	3.18	2.01	6.83	7.81	7.89	0.64	0.76
Lu	1.35	0.89	0.15	0.084	0.52	0.33	1.17	1.16	1.09	0.115	0.112

Table 7. Trace Element Geochemistry. (Cont.)

(1) According to L. Lopez, 1972.

(2) Pierce Pond Gabbro.

(\*) Duplicate analyses.

NA Not analyzed.

BD Analyzed, but below detection limit. From counting statistics the detection limit for Cr is 4 ppm, for Rb 8 ppm, for Th 0.2 ppm and for U 0.1 ppm.

Fig. 30. Chondrite-Normalized Rare Earth Element Abundances in Traveler Rhyolite - Katahdin Granite Magmatic Sequence.

Legend:	TRBC	-	Traveler	Rhyolite	: Black Cat Member
	$\mathrm{TRP}$	-	Traveler	Rhyolite	: Pogy Member
	KGD	-	Katahdin	Granite:	Doubletop Facies
	KGW	-	Katahdin	Granite:	Wassataquoik Facies
	KGS		Katahdin	Granite:	Summit Facies
	KGCH	-	Katahdin	Granite:	Chimney Facies
	KGCT	-	Katahdin	Granite:	Cathedral Facies
	AP1	-	Katahdin	Granite:	Aplite Dike # 1
	AP2	-	Katahdin	Granite:	Aplite Dike # 2



TR-KG SEQUENCE

Fig. 31. Chondrite-Normalized Rare Earth Abundances For Horserace Quartz Diorite - Harrington Lake Porphyry Magma Sequence.



Fig. 32. Chondrite-Normalized Rare Earth Element Abundances in Lexington Granite (NNP-2), Moxie Granite (244) And Echo Pond Granite (6291).



Fig. 33. Chondrite-Normalized Rare Earth Element Abundances in Samples of Pierce Pond Gabbro.

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PIERCE POND GABBRO

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#### Acidic Rocks:

- High Sc Content (15-42 ppm)
  - Traveler Rhyolite (TR)
  - Katahdin Granite (KG)
  - Kineo Rhyolite (KR)
- Intermediate Sc Content (5-15 ppm)
  - Horserace Quartz Diorite (HQD)
  - Harrington Lake Porphyry (HLP)
  - Debsconeag Granodiorite (DGD)
- Low Sc Content (<5 ppm)
  - Granite from Moxie Pluton (MG)
  - Lexington Granite (LG)
  - Echo Pond Granite (EPG)

#### Basic Rocks:

• Pierce Pond Gabbro (PPG) (Sc = 38-52 ppm)

Scandium abundances are thus an important petrogenetic discriminator between rocks of distinct magmatic associations. The different Sc abundance levels appear to be of fundamental nature, allowing Sc to be used as a geochemical guide in identifying various igneous provinces in northcentral Maine.

# 1. <u>High Scandium Rocks: TR-KG Sequence and Kineo</u> Rhyolite

#### a. General Statement

To demonstrate the uniqueness of the Sc abundances in the TR-KG sequence, Table 8 lists Sc abundances in a variety of granitic rocks of different origin. From this table, it follows that the usual range of Sc abundances in acidic rocks is between 2 and 5 ppm, although it may reach up to 15 ppm. Hence, the unusually high Sc abundances

# Table 8A

### Scandium\*

Table 21-E-2. Content of Sc in igneous rocks\*

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Rock type	Sc, ppm	Method	Reference
Granite G-1	2.7-2.8	NA	cf. FRYCKLUND and FLEISCHER (1962)
Granite G-1	2.4	NA	NORMAN and HASKINS (1968)
Granite G-1	2.83	NA	BRUNFELT and SLEINNES (1966)
Granite G-2	3.4	NA	BRUNFELT and SLEINNES (1966)
Granites (191, av.; 60-70% SiO,)	10	NA	NORMAN and HASKINS (1968)
Granites (221, av.; > 70% SiO <sub>2</sub> )	2.8	NA	NORMAN and HASKINS (1968)
Granites (27, av.; Finland)	6.9	NA	NORMAN and HASKINS (1968)
Granites (~75)	19	S	BORISENKO (1959), BORISENKO and Rodionov (1961), Sahama (1945) Ahrens (1954), Tongeren (1938
Granites, low Ca	7	S	TUREKIAN and WEDEPOHL (1961)
Granites, high Ca	14	S	TUREKIAN and WEDEPOHL (1961)
Granitoids, U.S.S.R., av.	2.7	S	VLASOV (1966a)
Rhyolites (24, av.)	5	S	FRYCKLUND and FLEISCHER (1962
Rhyolites (av., 67% SiO2)	9.2	NA	NORMAN and HASKINS (1968)
Obsidian	5.7	NA	NORMAN and HASKINS (1968)
Granodiorites (7)	28	S	BORISENKO and RODIONOV (1961)
Granodiorite GTM-1	5.6	NA	BRUNFELT and SLEINNES (1966)
Granodiorite	15.5	S	MEL'NICHENKO and MOGAROVSKY (1966)
Trachyte (2)	2.56.9	NA	NORMAN and HASKINS (1968)
Frachyandesite	7.7	NA	NORMAN and HASKINS (1968)
Syenites (8, av.)	1	S	BORISENKO and RODIONOV (1961)
Syenites, Lapland	2	S	<b>Sahama</b> (1945)
Rhyodacites (32, av.)	14	S	FRYCKLUND and FLEISCHER (1962
Dacites (68, av.)	21	S	FRYCKLUND and FLEISCHER (1962
Duartz latites (14, av.)	11	S	FRYCKLUND and FLEISCHER (1962
Andesites (72, av.)	34	S	FRYCKLIND and FLEISCHER (1962
Andesite AGV-1	11.5	NA	BRUNFELT and SLEINNES (1966)
Andesites	1—10	S	Goldschmidt (1934, 1954), VAN TONGEBEN (1938)
ntermediate rocks (85, av., <60% SiO.)	15	NA	NORMAN and HASKINS (1968)
Basalts (99, av.)	38	S	FRYCKLUND and FLEISCHER (1962
Sasalts, continental (282, av.)	30±1	NA	NORMAN and HASKINS (1968)
Tholeiitic basalts, oceanic (8)	3550	NA	NORMAN and HASKINS (1968)
Basalts	23—92	S	NOCEOLDS and ALLEN (1959), GUNN (1966), PATTERSON and SWAINE (1958), TURERIAN and WEDEPOHL (1961), ENGEL and ENGEL (1965), COX and HORNUNG (1966)

\*) From the Handbook of Geochemistry, ed. Wedepohl (1970)

# SCANDIUM ABUNDANCES

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IK TYPE	AVG. PPM	RANGE	# OF SAMPLES
LER RHYOLITE - BLACK CAT UNIT	31	27 - 34	6
LER RHYOLITE - POGY UNIT	26	22 - 32	5
)IN GRANITE	25	20 - 33	21
)IN GRANITE - APLITE	34	27 - 41	2
RHYOLITE	29		1
DIORITE	28	22 - 41	5
ACE QUARTZ DIORITE	13	12 - 14	3
POND GABBRO	47	38 - 52	3
GRANITE	5		1
STON GRANITE	4		1
YOND GRANITE	3		1
IGTON LAKE PORPHYRY	6		l

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determined in the TR-KG rocks (15-42 ppm) strongly imply their genetic relationship and furthermore the special and unique conditions during the magma formation stage--mainly a subordinate role of minerals with high preference for Sc, i.e., mafic silicates.

The group of acidic rocks with high Sc content includes all rocks of the earlier voluminous episode, namely the Katahdin Granite (KG), and the two largest rhyolitic localities of the Piscataquis Volcanic Belt--the Traveler Rhyolite (TR) and the Kineo Rhyolite (KR). Based on the identical stratigraphic position and similar major trace element composition of other rhyolites contained in the Piscataquis Volcanic Belt, it is fair to say that the entire Piscataquis belt is part of the TR-KG sequence.

The main geological, petrological and mineralogical features of the TR-KG sequence are summarized below:

<u>TR</u> - Traveler Rhyolite (Fig. 4) is part of a caldera collapse structure which forms a 215 km<sup>2</sup> large, tectonically sunken block of rhyolitic ignimbrites occurring on the northern side of Katahdin Pluton. The emplacement of the volcanics preceded the KG intrusion as evidenced by the contact relationships. The TR consists of two units: the older, extensively hydrothermally altered Pogy Member (TRP), contains 20-25% phenocrysts, of which 60% are plagioclase, 30% quartz, 8% clinopyroxene and biotite, and 2% opaques. The overlying Black Cat Member (TRBC) is less altered and contains a lesser amount of phenocrysts (5 to 15%), of which 75% are plagioclase, 20% clinopyroxene, and 4% opaques.

<u>KG</u> - Katahdin Granite makes up about 95% of the Katahdin Pluton (Fig. 14) which extends over an area of approximately 1330 km<sup>2</sup>. This granitic body is mineralogically and chemically homogeneous, consisting of 34% alkali feldspar, 35% quartz, 25% plagioclase, and 6% biotite. Six textural types-also called facies of KG--were identified: the main Doubletop facies (KGD) grades upward via Chimney facies (KGCH) into Summit facies (KGS) and laterally into South Brother facies (KGSB) and Wassataquoik facies (KGW); up to 50 m wide, rare porphyritic dikes of Cathedral facies (KGCT) cross-cut most of the other facies of KG. Thin, up to 1 m wide, aplitic dikes are frequent.

Since major element abundances of both rhyolites and granites of different facies are very similar (Table 4), no differentiation path is therefore indicated. From the AFM plot the only distinct unit is TRBC which is also the least differentiated. TE abundances are in accord with the major element variations, in that among the TR-KG group TRBC has the highest Sc, Co and Eu abundances and the lowest Rb abundance. Using TRBC as the parental magma, the fractionation model for other rhyolites and granites will be discussed in detail.

## b. Trace Element Evaluation of the Voluminous Magmatic Episode: Traveler Rhyolite-Katahdin Granite

The similar distribution of TE in both TR and KG (Fig. 30) implies not only their cogenetic relationship, but also

their independent origin from the younger HQD-HLP episode (Fig. 31). In order to demonstrate plausibility of the cogenetic origin and in order to allow quantitative assessment of the processes leading to the formation of the TR-KG sequence, it became apparent that evaluation of TE abundance variations in terms of a fractional crystallization model is necessary.

Table 9 gives average TE abundances of each of the nine rock units that are to be considered for the fractionation model, i.e., TRBC, TRP, KGS, KGCH, KGD, KGCT, KGW, AP1, and AP2. In order to avoid undue propagation of analytical errors and minimize the effect of postmagmatic changes, this model will only use elements with the largest abundance variations and the least susceptibility to deuteric alteration. Based on the results of comparative studies of altered and alteration-free samples (see section on "Postmagmatic Changes") and on TE variations as given in Table 9, the selected elements are Co, Rb, Hf, Sr, and Eu.

Using a surface equilibration model, the degree of fractionation F (weight proportion of residual melt with respect to the initial parental magma) and mean partition coefficient (MPC: summation of fractional mineral/liquid partition coefficients) are related as expressed by Rayleigh distillation law (model B2 of Albarede, Bottinga, 1972):

(1)  $\ln C/Co = (MPC-1) \ln F$ 

C and Co refer to trace element abundances in the daughter and parental magma.

Table	- 9
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	TRBC	TRP	KGS	KGD	KGCH	КССТ	KGW	AP-1	AP - 2
Sc	31.07	26.18	27.26	26.44	24.74	19.01	26.01	27.30	41.04
Со	2.20	1.90	0.82	1.11	1.01	1.89	0.51	0.26	0.40
Rb	162.90	170.60	187.22	190.51	176.03	208.39	236.23	290.50	377.02
Cs	10.75	7.64	10.87	9.08	11.66	8.83	9.33	8.06	7.16
Hf	14.00	11.04	10.79	9.56	8.90	9.54	6.35	5.75	7,84
Та	1.83	1.32	1.40	1.51	1.90	1.71	1.60	2.01	4.23
Th	14.41	14.09	16.46	14.20	14,02	16.12	14.72	15.83	19.22
U	5.27	4.64	4.10	3.04	3.41	5,27	5.74	5.84	15.07
Sr	76	64	59	66.4	N.A.	N.A.	26	N.A.	8
La Ce Nd Sm Eu Gd Ho Yb Lu	171.56 139.14 96.32 75.69 27.60 54.00 40.00 37.44 34.92	159.90 144.93 98.37 76.24 25.62 57.94 40.11 35.98 34.75	144.00 120.77 81.73 56.94 17.28 45.91 30.58 27.85 25.68	148.36 120.71 79.12 58.80 17.66 44.90 31.80 30.28 29.26	131.78110.5072.9157.0418.0940.6634.4729.5128.53	119.28 100.05 68.29 47.40 17.86 35.03 27.52 26.43 24.99	143.47 140.18 87.31 68.38 9.90 43.54 39.99 35.05 34.30	84.94 91.72 59.03 54.38 2.47 57.34 45.82 41.60 39.76	46.52 33.47 27.31 28.10 1.17 21.65 29.89 42.54 42.42
Number of Samples	6	5	3	8	2	3	1	1	1

Average Elemental Abundances in TR-KG Sequence
In the course of model calculations, the mean partition coefficient of each element is let to be a constant during the fractionation of the entire sequence. This corollary is substantiated by the fact that the major element composition of the melt, the crystallization temperature, as well as the relative proportion of minerals crystallizing from the magma, remain virtually unchanged during the crystallization process (see previous chapter).

However, the Rayleigh equations cannot be solved for F and MPC's simultaneously. The model calculation, therefore, requires two steps: in the <u>first</u> step, an apparent solution satisfying the set of equations described below is obtained. For this purpose, the Rayleigh equation can be rewritten as follows:

(2)  $\ln C/Co = ((MPC-1)/Q)*(Q*ln F)$ The constant Q relates relative (or apparent) and actual sets of values:

- (3) RMPC = ((MPC-1)/Q)+1
- (4) RF = RF = F \* Q

In the <u>second</u> step, the constant Q is evaluated through comparison of RMPC's and MPC's, which are estimated from published values of PC's (Table 12).

For the five selected elements (Co, Rb, Hf, Sr and Eu) and nine members of the fractionation sequence (TRBC, TRP, KGCH, KGD, KGCT, KGW, AP1 and AP2) there are thirty-seven equations which interrelate twelve unknown parameters (5 MPC's and 8 F's). This set of thirty-seven equations is solved by an iterative numerical method by subsequent approximations with assumed initial values of RMPC's equal 2 for all five elements.

From the solution which usually converges in three iterations, the newly calculated daughter abundances are compared with the actual (observed) TE abundances. If there is more than a 20% difference between any calculated and observed value, the data point with the largest deviation is rejected and the computation cycle is repeated until all the data points satisfy the 20% allowed deviation. A flow chart showing how the final solution was obtained is shown on Fig. 34.

The final solution, including the eight rejected data points, are graphically illustrated in Figs. 35A, B, and C. The initial unrestricted (no data points rejected), as well as the final solutions are given in Table 10. The fast convergence of the above methods indirectly proves the validity of the initial corollary (constant MPC's). Other solutions satisfying the initial set of thirty-seven equations can be obtained from equation (3). Table 11 lists several such sets for different assumed values of Q which are so chosen that they would yield apparent MPC's for Rb as given at the top of Table 11.

Fig. 34. Flowchart for the Iterative Method Used in Calculating Mean Partition Coefficients And Degrees of Fractionation. See Text For Further Explanation.



FIGURE 34

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## Table 10

## Calculated Mean Partition Coefficients

Initial	2.905	$0.\frac{\text{Rb}}{480}$	$2.\frac{\text{Hf}}{183}$	$2.\frac{\mathrm{Sr}}{187}$	$1.\frac{Eu}{566}$
Final	3.182	0.489	2.424	2.079	2.410

## Calculated Wt. Fraction of Residual Liquid

Initial	$\frac{\text{TRP}}{0.894}$	KGS 0.739	$0\frac{\text{KGD}}{.757}$	$\frac{\text{KGCH}}{0.739}$	$0\frac{\text{KGCT}}{.750}$	$0\frac{\mathrm{KGW}}{.477}$	0.323	0.251
Final	0.899	0.775	0.766	0.754	0.703	0.512	0.348	0.155

Calculated apparent mean partition coefficients and apparent fractions of residual liquid for Traveler Rhyolite-Katahdin Granite fractionation sequence. Fig. 35A,B,C. Final Solution of Iterative Calculations For Traveler Rhyolite - Katahdin Granite Magmatic Sequence. Excluded Data Points Are Encircled. See Text And Table 34 For Further Explanation And Discussion.



(A)



(B)



(C)

Table 11

Rb	0.000	0.100	0.200	0.300	0.400	0.500	0.600	0.700	0.800	0.900	0.49*
Sr	3.118	2.906	2.694	2.482	2.271	2.059	1.847	1.635	1.424	1.212	2.08
Co	5.275	4.847	4.420	3.992	3.565	3.137	2.710	2.282	1.855	1.428	3.18
Hf	3.784	3.506	3.227	2.949	2.671	2.392	2.114	1.835	1.557	1.278	2.42
Eu	3.765	3.488	3.212	2.935	2.659	2.382	2.106	1.829	1.553	1.276	2.41

\* The last column gives solutions from Table 10.

Calculated apparent MPC's of Sr, Co, Hf, and Eu corresponding to different assumed apparent MPC (Rb). (See text for further explanation). During the second step, the actual MPC's for Rb, Sr, and Co are estimated for an average KGD assemblage (Table 12). Combining the results of Tables 11 and 12, the best set of MPC's is MPC(Rb) = 0.500(Table 11); from this, the constant Q of equations (3) and (4) is equal to 0.98 or approx. to 1. The value of Q being equal approx. 1 is only coincidental and is the result of the "lucky" choice of 2 as the initial (seed) values of RMPC's. Therefore, the solutions obtained in Table 19 represent the best MPC's and F's.

The abundances of the TR-KG sequence support a model of fractionation from the TRBC-type parental magma in the following succession: TRBC-TRP-(KGS, KGD, KGCH)-KGCT-AP1-AP2. The TE abundances also indicate that KGS-KGD-KGCH crystallized from the same magma. Figures 36 and 37 show variations of REE and Sc, Cs, Ta, Th, and U as a function of the proportion of the residual liquid. For the discussion of these variations, see the section "Comparison of Aplites".

#### c. Kineo Rhyolite

Among other rhyolitic occurrences within the Piscataquis Volcanic Belt, Sample #247 of the Kineo volcanic center (Rankin, 1968) was studied as a comparison to the TR (Fig. 3, and Fig. 38). The TE data and REE chondrite normalized distribution of this Kineo sample are given in Table 7 and Fig. 39. The Kineo REE pattern is essentially identical with the pattern of KGD except for a significant depletion in HREE. If KGD is assumed as the parental magma, the only common

Table	12	
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	Mineral Proportions	PC(Rb)		PC(Sr)			PC(Co)		
	wt %	low	high	pref.*	low	high	pref.*	low	high
Bi	8	2.2	4.4	3.1	0.1	1.0	0.2	12	30
P1	25	0.1	0.2	0.15	5.0	7.0	7.0	0.05	0.50
Af	35	0.3	0.7	0.5	2.0	5.0	3.8	0.05	0.50
Mt	1	0.0	0.0	0.0	0,0	0.0	0.0	10	50
MPC		0.306	0.647	0.461	1.958	3.580	3.096	1.090	3,200

Estimated MPC's of Rb, Sr, Co for TR-KG Sequence

\* Preferred Values

Sources:

	Rb	Sr	Со
Bi	1, 8, 13	1, 12, 13	8, 12
P1	1, 4, 6, 8, 11, 13	1, 3, 4, 5, 6, 7, 8, 11, 13	4
Af	1, 2	1, 3	**)
Mt	*)	*)	7, 9, 10

1. Philpotts, Schnetzler, 1970

- 2. Noble, Hedge, 1970
- 3. Nagasawa, 1971
- 4. Dudas et al., 1971
- 5. Korringa, Noble, 1971
- 6. Ewart, Taylor, 1968
- 7. Ewart et al., 1973

- 8. Higuchi, Nagasawa, 1969
- 9. Duncan, Taylor, 1968 10. Paster et al., 1974
- 11. Nagasawa, Schnetzler, 1971
- 12. De Albuquerque, 1974, and Ewart, Taylor, 1968
- 13. Lyakhovich, 1972
- \*) PC assumed to be zero \*\*) PC assumed to be equal to PC of plagioclase

Fig. 36. Chondrite-Normalized Abundances And Their Variation For Selected Rare Earth Elements in The Traveler Rhyolite - Katahdin Granite Magmatic Sequence.



Fig. 37. Variation of Abundances of Th, Ta, Sc, U, and Cs in The Traveler Rhyolite - Katahdin Granite Magmatic Sequence.



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Fig. 38. Inferred Volcanic Centers in The Piscataquis Volcanic Belt (Fig. 27-1. of Rankin, 1968).



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FIGURE 27-1. Generalized geologic map showing volcanic centers and geologic setting of the Piscataquis volcanic belt. Modified from Boucot (1961; written

communication, 1966), Boucot and others (1964a), Doyle (1967), and Rankin (unpublished data).

(from Rankin, 1968)

Fig. 39. Chondrite-Normalized Rare Earth Element Abundances in Kineo Rhyolite.

Legend: ØTR - Average Abundances in Traveler Rhyolite

- KGD Average of Katahdin Granite: Doubletop Facies
- KR Kineo Rhyolite



mineral which can cause such a depletion is garnet. Using Rayleigh distribution law, it appears that a removal of 0.7% garnet will reproduce the Kineo rhyolitic HREE abundances (PC(Lu) = 30; PC(Yb) = 40; PC)Ho) = 35; Schnetzler, Philpotts, 1970). However, garnet does not occur in the Kineo center but it is abundant in the nearby Cold Stream center and in the Big Spencer center (Fig. 38; Rankin, 1968). Consequently, garnet may have been a fractionating mineral crystallizing in place of biotite. As both garnet and biotite have strong preference for Sc, no change in Sc abundances is observed.

Other TE's are not inconsistent with the proposed derivation of Kineo Rhyolite from KGD magma. Although they are within the limits of twice the TRBC variation coefficients (Fig. 25A), they show a considerable scatter. Rb abundances--the best indicators of fractionation (see preceding section)--are also in favor of this model. The average Rb abundances of TRBC and KGD (163 ppm and 191 ppm, resp.) compare poorly with 146 ppm of Sample #247 but agree well with the average value of 181 ppm obtained for Kineo Rhyolite by Fullagar and Bottino, 1968.

Due to the large variation coefficients of some TE's (Figs. 25A and B) and taking into account that only one sample was analyzed, a detailed evaluation of Kineo Rhyolite petrogenesis cannot, therefore, be formulated. Further geochemical and petrological studies of other rhyolitic occurrences and mineral separates, namely that of garnet, are needed.

#### 2. Intermediate Scandium Rocks: HQD-HLP Sequence

### a. General Statement

Rock units of intermediate Sc abundances (5 to 15 ppm) are found only as minor igneous bodies emplaced near the West Branch Penobscot River fault system (Fig. 14). The close association of these bodies with the fault suggests tectonically controlled intrusions. This younger igneous episode consists of the Harrington Lake Porphyry (HLP), the Horserace Quartz Diorite (HQD), and the Debsconeag Granodiorite (DGD) (Fig. 14). The main geological, petrological and mineralogical features of these bodies are summarized below:

HLP - Harrington Lake Porphyry: The semi-arcuate, silllike intrusion of HLP  $(3.8 \text{ km}^2)$  lies outside the main body of the Katahdin Pluton (KP) Although a direct contact with Katahdin Granite (KG) is presumed, the contact relationship The only geological link between HLP and remains unknown. other members of the younger episode is provided by rare inclusions of hornblende quartz diorite found in HLP. These inclusions are believed to be identical with marginal facies If this correlation is correct, HLP represents a of HQD. younger phase of the HQD-HLP sequence. Mineralogically, the unit is composed of extremely altered, fine grained matrix with abundant plagioclase and subordinate hornblende phenocrysts.

<u>HQD-Horserace Quartz Diorite:</u> HQD forms a small, elongated stock (5.7 km<sup>2</sup>) which is entirely enclosed within the Doubletop facies of KG. This intrusion is accompanied by a prominent, apophysical dike swarm, traceable on each side of the stock for a distance of at least 10 to 15 km along the West Branch Penobscot River fault system. The HQD body is compositionally zoned, with gradational change from biotite-bearing hornblende quartz diorite near the margins to hornblende-bearing biotite granodiorite in the center.

<u>DGD-Debsconeag Granodiorite:</u> DGD is a medium grained, hornblende-bearing biotite granodiorite which occurs in two separate bodies within the Doubletop facies of KG (Griscom personal communication). Near the vicinity of the suspected margins, the grain size of DGD tends to be finer and the content of biotite increases to 15%.

The major element variation within the younger episode implies the following fractionation sequence: HQD-HLP-DGD (Fig. 23A, B, C). This differentiation sequence will be further examined on the basis of trace element geochemistry. Five samples from the younger episode were analyzed for trace elements: two samples are from the marginal facies of HQD (#235 and 238), one each from HLP (#4) and DGD (#166), and one from the dike swarm (#127A). Their trace element abundances are given in Table 7 and their chondrite normalized REE distributions are plotted in Fig. 31.

# b. Trace Element Evaluation of the Younger Magmatic Episode

On the basis of the most "primitive" TE and ME abundances (lowest Fe/Mg ratio, highest Cr and Co abundances), Sample #127A is considered to represent a parental magma from which the younger igneous episode might have evolved.

Although the TE abundances of the HQD marginal zone are similar to the assumed parental magma, they cannot be explained in terms of a simple fractionation model; for example, abundances of Co and Cr favor direct fractionation of HQD-margin from Sample #127A by the removal of mafic minerals, but the lower Rb and higher Sc abundances do not support this model. This seemingly contradictory behavior can best be reconciled if a partial cumulative nature of the marginal zone is assumed. Provided that Sample #127A represents the composition of the original magma and that the magma did not change during the crystallization of the settling crystals, the fraction of cumulus can be estimated from the following mass balance equation:

> (HQD - margin) = (1-x)(127A) + (x)(MPC)(127A)x = fraction of cumulus

The mean partition coefficients for Lu and Rb, calculated for a Cpx, Hb, Pl assemblage from PC's of Dudas et al., 1971; Philpotts, Schnetzler, 1970; Schnetzler, Philpotts, 1970; and Nagasawa, Schnetzler, 1971, are both equal to 0.2: PC(La-Cpx) PC(La-Hb) PC(La-Pl) 0.2; PC(Rb-Cpx) 0.02; PC(Rb-Hb) 1.3; PC(Rb-P1) = 0.05-0.15; e.g., MPC(Rb) = 0.02; if plagioclase is dominant. The estimated fraction of cumulus is 0.28 and 0.29, respectively. Based on the average value (0.28), Table 13 lists calculated mean partitions coefficients for other trace elements. This table also shows literature values of PC for Cpx, Hb, Pl and zircon. The calculated MPC's can be reconstituted from 95% Pl, 5% Hb. and 0.4% zircon, or from 70% Pl, 30% Cpx and 0.4% zircon. The actual mineral proportion is probably somewhere between these two estimates, as both, Cpx and Hb, were identified in HQD-margin rocks (Cpx forms frequent cores of Hb grains). The observed differences of Cr, Cs, and U cannot be reconciled by this model. Cr was probably removed by opaques and Cs and U were apparently lost during the late crystallization stages if the model is to be valid. However, the above model for the derivation of HQD is consistent with petrological (Fig. 24) and field observations.

The REE distribution pattern of HLP compared with the presumed parental magma is similar, but the absolute REE abundances are approximately 30% lower. Since this depletion indicates mainly a removal of accessory minerals (or amphibole), REE can provide only qualitative evidence of the genetic relationship of HLP-HQD. Also depleted in HLP with respect to HQD are Cr, Cs, Co and Sr, which were possibly removed by mafic silicates, opaques and feldspars. The depletion in Rb is most likely due to the extensive hydrothermal alteration.

#### Table 13

	Parent #127A	HQD Margin Ø	Calcul- ated MPC's <sup>*</sup>	PC(P1)**	PC(Cpx)**	PC (Hb)**	PC(Zr)**
Sc Cr Co Rb Cs Hf Ta Th U	12.23 167.66 20.08 76.18 2.92 4.29 0.67 7.97 2.26	$     \begin{array}{r}       13.98 \\       108.51 \\       17.09 \\       58.42 \\       1.19 \\       4.22 \\       0.53 \\       6.21 \\       1.45 \\     \end{array} $	$\begin{array}{c} 1.51 \\ (-0.26) \\ 0.47 \\ 0.17 \\ (-1.12) \\ 0.94 \\ 0.25 \\ 0.21 \\ (-0.28) \end{array}$	  0.06-0.46     	6.2-17.0 0.8-9.7 2.3-8.0 0.03    	2.7-260 0.5-70 3.9-12 0.4  	  ?  ? ? ?
La Nd Eu Gd Ho Lu	104.94 45.56 17.16 17.18 7.13 4.86	$81.32 \\ 38.06 \\ 17.74 \\ 16.13 \\ 7.31 \\ 6.66$	0.20 0.41 1.12 0.78 1.09 2.32	0.28-0.49 0.14-0.29 0.75-4.20 0.11-0.24 0.10-0.17 0.06-0.11	0.07-0.33 0.94-1.3 1.1-2.0 2.1-1.4 2.4-1.14 1.8-1.3	0.13-0.41 1.0-4.5 1.4-5.9 2.0-10.9 2.4-13.5 1.8-6.3	4 4 10 100 500

## Derivation of HQD-Margin from Sample #127A

REE in chondrite normalized values, others in ppm.

- \* MPC's are calculated for 73% parent (#127A) and 27% cumulus (See text for explanation).
- \*\* PC for plagioclase are after Dudas et al., 1971.
  - PC for Hb and Cpx: non-REE are for dacites after Ewart et al., 1972; Ewart, Taylor, 1968; and Philpotts, Schnetzler, 1970 REE are for dacite after Schnetzler, Philpotts, 1970; and Nagasawa, Schnetzler, 1971.

Using the rate of REE depletion obtained from the fractionation of KG from TR, the REE abundances of HLP can be explained in terms of fractionation from HQD by the removal of 35 to 40% crystals. Sc, Cr and Co abundances also imply that HLP can be derived from Sample #127A by removing approximately 30 to 40% crystalline material. The calculated MPC's required by this model are: 2.5 (Sc), 3.37 (Co), 6.88 (Cr), and 2.10 (Sr). These MPC's can be reconstituted from 15 to 20% of mafic silicates, 80% plagioclase, and 3 to 4% opaques (compare with Table 13). The mineralogical composition of fractionating crystals is similar to the HQD marginal zone.

TE abundances in DGD differ considerably from TE abundances in either HLP or HQD. The REE are characterized by enrichment in HRE (4.5), LRE (1.7), and by a large negative Eu anomaly (Fig. 31). Also, in DGD the abundance of Rb is significantly higher (1.8 times) and Co and Sr are lower. The abundances of REE, Sc, Co and Rb preclude a fractionation model from the TR magma. The simplest model for the origin of the DGD magma is the mixing of HLP and TRtype magmas with subsequent surface equilibrium fractionation of Cpx and Pl. The model for the derivation of DGD magma is illustrated in Table 14. The first step of the proposed model is mixing 40% TRBC and 60% HLP designated as DGD-1. DGD-2 is derived from DGD-1 by removal of 28% crystals consisting of 80% Pl and 20% Cpx (typical TRBC assemblage). For most elements, the calculated (DGD-2) and observed

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	DGD	DGD-1	CPX*	PL*	DGD-2
	Observed	Calculated	PC	PC	Calculated
Sc	12.02	15.84	10		11.40
C0	3,95	4.45	6		4.16
Rh	135.84	106.44		0.17	141.37
Cs	7.62	5.64	- 4	0.11	7.61
нf	6.77	7.95		0.15	10.61
Та	1.27	0.95		0.20	1.25
Th	20.07	10.10		0.05	13,84
U	3.32	2,65		0.20	3.49
Sr	186	354	0.50	3.50	190
La	174.33	104.76	0.2	0.3	132.71
Nd	66.74	55.22	1.0	0.2	68.14
Eu	14.86	16.67	1.7	1.3	14.71
Gd	34.43	28.04	2.0	0.1	33.26
Но	24.08	19.52	1.8	0.1	23.46
Lu	22.18	16.61	1.5	0.09	20.42

Derivation of DGD from HLP

For References See Table 13.

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\* Preferred Average Values.

abundances are in close agreement and therefore support the validity of the proposed model.

However, the discrepancies for Hf and Th remain unexplained. The poor agreement between calculated and observed values for La and Ce may be interpreted as an accidental concentration of accessory allanite (see end of "Postmagmatic Changes", subchapter).

#### c. Summary of the HLP-HQD Sequence

TE abundances support the hypothesis of cogenetic relationships of intrusive bodies of the younger igneous The dike swarm represents the parental magma from episode. which the HQD may have been derived. The marginal facies of HQD is formed by a combination of 73% parental magma and 27% cumulat crystals. HLP appears to be a product of the differentiation of HQD magma by fractional removal of 40% crystalline material. The model for the origin of DGD magma proposed mixing 40% TRBC and 60% HLP magmas with the subsequent removal of approximately 30% crystals. This model is consistent with the hypothesis that HQD-type magmatism-possibly of upper mantle origin--supplied the necessary heat to allow melting of sedimentary rocks and thereby generating TRBC.

During its rise to the Earth's surface, the HQD magma differentiated and in some regions the differentiated melt mixed with TRBC melt. The geological position of DGD in the center of Katahdin Pluton as well as its ME chemistry and mineralogy conform with the proposed model. HLP was probably extruded as the last magmatic event.

#### 3. Comparison of Aplites

TE abundances of aplitic samples of both HQD-HLP and TR-KG sequences, respectively, are derived from highly differentiated magmas. With respect to the parental KGD magma, Sample #145 (AP1) represents 20% residual melt and Sample KM-7 (AP2) approximately 45% of the same parental magma. The average of aplitic samples #134-3, 134-6, 134-7, and 134-8 (AP3) represents approximately 20% of the DGD parental magma. If our fractionation estimates are correct, we may expect a reasonable agreement (within factor 2) between their mean partition coefficients.

Using observed TE abundances in aplites and in their assumed parental magmas and the above estimates of degree of fractionation, the mean partition coefficients are calculated from the Rayleigh distribution law:

MPC = (ln C/Co)/lnF) + 1

The calculated mean partition coefficients (MPC's) presented in Table 15 and Fig. 40 are remarkably similar and provide additional support in favor of the employed models.

#### Discussion:

REE - Light REE are removed at a higher rate than heavy REE which tend to be enriched in the residual melts. Lyakhovich and Balanova (1971) have shown that REE are preferentially

Tab	)le	15
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	AP≂1 from KGD	AP≂2 from KGD	AP-2 from TRBC	AP <del>~</del> 3 from DGD	TR <del>.</del> KG Sequence from Table 10	Baker**
	F=0.454	F=0,202	F=0.155	F=0.200		
Sc Co Rb Cs Hf Ta Th U Sr	0.96 2.84 0.47 1.15 1.64 0.64 0.86 0.17 N.A.	0.73 0.64 0.57 0.85 1.12 0.36 0.81 0.00 2.32	$\begin{array}{c} 0.85\\ 1.91\\ 0.55\\ 1.21\\ 1.31\\ 0.55\\ 0.85\\ 0.44\\ 2.21 \end{array}$	0.97 3.12 0.52 0.72 1.18 0.76 0.72 0.51 2.22	0.91* 3.18 0.49  2.42 0.57* 0.89*  2.08	1.74 2.30 0.40  0.52 0.40 0.40 
La Ce	1.71 1.35	1.73	1.70	2.02 1.84		
Nd S-	1.37	1.67	1.68	1,55		
Eu	3.49	2.70	2.70	2.15	2.41	0.86
Gd	0.69	1.46	1.49	0.98		
Но	0.54	1.04	1.16	0.33		
Yb	0.60	0.79	0.93	0.40		
Lu	0.61	0.//	0.90	0.40		

# Calculated MPC's for Katahdin Pluton Aplites

\* Average Values

\*\* Personal Communication; Data Obtained for West African Rift Benmoreites Fig. 40. Calculated Rare Earth Element Mean Partition Coefficients For AP1, AP2, and AP3.



concentrated in accessory minerals: LREE in allanite and monazite; the intermediate REE (Sm, Gd) in apatite and sphene; and HREE in zircon and xenotime. The striking difference between the mean partition coefficients of LREE and the value of MPC of Lu being considerably less than 1 needs further explanation. Xenotime is a rare mineral and its role in controlling HREE is most likely minimal, because of the preference of phophorous for apatite and the higher level of HREE concentration needed for xenotime saturation. The second possibility is that zircon crystallization is suppressed because of Zr loss with the exsolving vapor phase. The alternative explanation that the activity of Zr in the melt is somehow lowered is regarded as unlikely. This inferred possible Zr loss is further supported by observed abundances of Hf; Hf abundances in the TR-KG sequence first decrease logarithmically with fractionation and, as fractionation reaches more than 40-50%, the trend reverses indicating no further removal of zircons (Fig. 35B). HREE follow a similar trend (Fig. 36). Because pegmatites are more frequently associated with DGD, another source of information consistent with the proposed Zr vapor phase removal is obtained from the lower values of calculated mean partition coefficients for HREE and Hf in DGD aplites due to the higher loss of Zr in DGD.

The mean partition coefficient for Eu is dependent upon oxygen fugacity; therefore, the reducing KGD magma has a higher MPC (Eu) than the more oxidizing DGD magma (see

Fig. 41. Abundances of Rare Earth Elements in Aplites Normalized to Their Respective Granitic Parents. Data on Susamyr Batholith Are From Balashov (1963). Data on Eagle Peak Pluton And Red Lake Pluton (Both of Sierra Nevada Batholith) Are From Noyes (1976).


estimates of  $f(O_2)$  in earlier chapters). Fig. 41 shows a relative distribution of REE in aplites normalized to their presumed parental rocks of different magmatic environments. This figure shows that the proposed model for REE during progressive differentiation is generally applicable. The tendency of HREE enrichment in late stage magmas is also supported by the comparison of sphene, monazite and apatite from both granites and granitic pegmatites (Fleischer, Altschuler, 1969).

Sc: The calculated mean partition coefficient of Sc, nearly equal to 1, is a consequence of the constant rate of 8 wt.% of biotite with PC equal to 10-15.

Co: The variable, estimated mean partition coefficient of DGD and KGD reflects a different oxidizing environment controlling the crystallization of magnetites. A higher removal rate is therefore observed for the more oxidizing DGD sequence.

Rb: The similar mean partition coefficients of all aplites, caused by constant fractional removal of alkali feldspar, plagioclase and biotite: 35% AF (PC=0.8); 25% PL (PC=0.2); and 8% Bi (PC=3).

Cs: The relative mobility of Cs during alteration is thought to be responsible for the large variations.

Hf: Removed by zircon during the early fractionation stages; in the late stages, Hf is concentrated in the melt.

Ta: Ta is always enriched in the residual magmas; perhaps slightly fractionating into vapor phase or lost via deuteric alteration.

Th: This is a good indicator of fractional crystallization with a constant mean partition coefficient equal to 0.8.

U: Uranium in aplites tends to be enriched in residual magmas. The mean partition coefficient is always less than 0.5.

Sr: The constant rate of removal of Sr is a consequence of the constant fractional removal of feldspars: 35% of alkali feldspar (PC=3 to 4) and 25% plagioclase (PC=4 to 6) with a mean PC of 2.05 to 2.90.

In conclusion, the comparison of aplites shows that the mean partition coefficient may be employed as a useful indicator of fractionation for late-stage differentiation processes of granitic melts.

4. Low Sc Acidic Rocks (45 ppm Sc)

This group consists of granites from the Lexington Pluton, the Moxie Pluton, and the Echo Pond Pluton (Vermont) (see Fig. 3). Their TE abundances are given in Table 7 and Fig. 32.

All three granitic bodies were analyzed in order to determine the areal extent of the TR-KG igneous complex. The low Sc abundances in the granites of this group (3-5 ppm), as well as the dissimilar abundances of REE, Co, Rb, Hf, Ta and Th (see Figs. 30, 32; Table 7), indicate distinct differences between the TR-KG igneous complex and the other Lower Devonian acidic plutonic rocks. Since these differences cannot be easily reconciled in terms of any simple fractionation sequence, it is assumed that the TR-KG igneous complex does not extend beyond the limits of the Katahdin Pluton and the Piscataquis Volcanic Belt.

# 5. Basic Rocks

The close association of acidic and gabbroic bodies in the Greenville Plutonic Belt (Fig. 2) may possibly suggest that the granitic melts were derived by differentiation from a parental basic magma. In order to evaluate this possibility, gabbroic samples from Pierce Pond Pluton were analyzed as representative gabbroic rocks of the plutonic belt. The analytical data are given in Table 7 and their chondrite normalized patterns are plotted on Fig. 33.

For a detailed description of the geology, petrology and mineralogy of the Pierce Pond Pluton, see P. Lyttle, 1975. The TE abundances imply an adcumulitic origin of Sample #PP-1 and the orthocumulitic nature of Samples #PP-235 and PP-379. The TE abundances of the latter samples are similar to the oceanic island tholeites or to the high alumina basalts of active orogenic belts (Schilling, 1973; Lopez, 1974), which may indicate that the Greenville Plutonic Belt was formed near a plate margin. Until further work is done, however, this conclusion must be regarded as tentative.

The possible derivation of granitic melts from the gabbroic magma can be demonstrated only for the granite of Moxie Pluton. Here, the similar REE distribution, except for a strong Eu anomaly, in Samples #244 (Moxie Granite) and PP-235 (Pierce Pond Gabbro) suggests the possibility of a cogenetic relationship. From the observed abundances of Rb, Ta, Th and U in granite of the Moxie Pluton, the degree of fractionation needed for the granite can be calculated by assuming that these elements are totally concentrated in the residual melt. The calculated degree of fractionation, expressed in terms of the removal of crystals, is: Rb-96%, Ta-86%, Th-97%, and U-94%, which is consistent with the strong Eu anomaly (removal of plagioclases) as well as with the depletion of Co, Cr and Sc (removal of mafic silicates). Such a large gabbro/granite volume ratio is supported by field observation (Espenshade, 1969). The large volume of the TR-KG igneous complex, as well as its distinct TE abundances, makes a derivation of the TR-KG sequence from a parental gabbroic magma unlikely.

# F. Origin of TR-KG

The petrologic evidence outlined in the previous chapters suggests that the TR-KG complex was formed by the partial melting (approximately 20%) of sedimentary rocks at a depth of 25-30 km. Since the low regional metamorphic grade (a chlorite zone) precludes exposure of the parental rocks, the REE content of the parental rocks may, instead, be deduced from data obtained by Cullers et al. (1974) for meta-sedimentary Silurian strata of the Rangeley and Perry Mountain Formations. According to Moench (1974), the Rangeley formation represents massive, graded conglomerates, sandstones and shales, whereas the overlying Perry Mtn. formation consists of reworked shales and siltstones. Provided that most of the geosynclinal sediments in northwestern and northcentral Maine were originated from a lithologically similar source (Naylor-personal communication), the sedimentary rocks parental to the TR-KG sequence may have similar REE abundances.

Fig. 42 shows REE patterns of the average REE contents of the Rangeley and Perry Mt. Formations (Cullers et al., 1974) as well as the 1:1 mixture of these two averages and the average Black Cat unit of the Traveler Rhyolite.

Based on a general resemblance of REE patterns, it is conceivable that TRBC magma could have been derived by a partial melting of sediments. In order to illustrate this possibility further, in the table below, calculated mean partition coefficients are given for individual REE's on the assumption that TRBC represents a 20% melt formed in equilibrium with a residue derived from either the Rangeley Formation or the 1:1 mixture of the Rangeley and Perry Mt. Formations. These mean partition coefficients were obtained from the equation: Fig. 42. Average Abundances of Rare Earth Elements in Rangeley, Perry Mountain And 1:1 Mixture of Rangeley And Perry Mountain Formations. Data From Cullers and Others, 1974.



#### 1:1Rangeley (Rangeley/Perry Mt.) La .79 .35 Ce .74 .34 .62 .29 Sm1.04 Eu .62 .64 .39 Gd Ho .43 .32 Yb .32 .34 Lu .43 .45

# $MPC = 1.25 \times (Sediment - 20\% TRBC) / TRBC$

Mean Partition Coefficients for TRBC and Its Residue for Two Different Parent Sources

The validity of either model requires that the calculated mean partition coefficients can be reconstituted from the known partition coefficients of minerals which may be present in the residue. From experimental studies of Winkler (1957), Winkler and v. Platten (1958, 1959, 1960), such a residue in equilibrium with the anatectic melt is likely to contain plagioclase, alkali feldspar, quartz, biotite, sillimanite or kyanite, cordierite, opaques and undisclosed amounts of accessory minerals (monazite, apatite or zircon, etc.). From published data by Dudas et al., 1971; Nagasawa and Schnetzler, 1971; Higuchi and Nagasawa, 1969, the REE partition coefficients of plagioclase (except for Eu), alkali feldspar and biotite, have nearly uniform values (0.1-0.3). REE content in quartz, kyanite and opaques is essentially negligible and can, for all purposes, be ignored. Assuming that octahedrally coordinated Mg or Fe have similar preference for REE, the REE partition coefficients of cordierite can then be estimated from REE partition coefficients of orthopyroxene. Since OPX has 50% octahedral sites and cordierite only 18%, we may expect that REE partition coefficients of cordierite have a similar relative distribution but with absolute values approximately 2.75 times lower than PC's of orthopyroxene, e.g., PC(La) 0.05, PC(Sm) 0.09, PC(Dy) 0.15, PC(Lu) 0.33 (Nagasawa and Schnetzler, 1971).

Taking into account the uncertainty due to the relative content of the residual minerals (typically quartz 30%, plagioclase 35%, alkali feldspar 10%, biotite 10%, cordierite 15%), then, the MPC's calculated above for 1:1 (Rangeley/Perry Mt.) represent values well within the range of feasibility and, consequently, provide a convincing qualitative evidence for the genetic relationship of TRBC magma and the geosynclinal sediments of northcentral Maine.

### V. SUMMARY

The geological setting, major and trace element geochemistry, as well as the intensive parameters deduced from the coexisting mineral assemblages, show that the Traveler Rhyolite-Katahdin Pluton igneous complex consists of two penecontemporaneous but genetically independent igneous episodes. The earlier voluminous episode includes thick ignimbrite deposits of Traveler Rhyolite and six textural facies of Katahdin Granite. The younger sequence consists of several minor bodies of Horserace Quartz Diorite, Harrington Lake Porphyry and Debsconeag Granodiorite.

The unusually high Sc abundances (15-42 ppm) of both members of the earlier magmatic episode demonstrate their close genetic relationship and contrast sharply with the lower Sc content (5-15 ppm) of the younger series. Modeling of Co, Rb, Hf, Sr and Eu abundances provides a strong evidence that the Katahdin Granite is derived from the Traveler Rhyolite magma by a fractional removal of 25% of alkali feldspar (35 wt.%), plagioclase (25 wt.%), quartz (31 wt.%), biotite (8 wt.%), and magnetite (1 wt.%), with the following estimated mean (bulk) partition coefficients: 3.18, 2.42, 2.08 and 2.41, respectively. The estimated temperature, water pressure and logarithm of oxygen fugacity for Traveler Rhyolite (800<sup>O</sup>C, 1100 bars and 15.00) and for Katahdin Granite (710<sup>o</sup>C, 1200 bars and 17.25) are

consistent with the model, that the Katahdin Granite represents a solidifed magma chamber underneath the Traveler volcano. Both oxygen fugacity estimates lie slightly below the QFM buffer curve which is in agreement with relative values of Eu and Sr mean partition coefficients.

The magma source of the earlier episode is best explained by a partial fusion of Appalachian eugeosynclinal sediments, a model which is consistent with several lines of evidence as discussed below:

1. A conspicuous absence of mafic or intermediate rocks associated with the earlier episode, as well as homogeneous major element composition and relatively constant petrology throughout the Traveler Rhyolite and Katahdin Granite, imply a steady state melting process as the only possible mechanism to generate such large quantities of acidic magma.

2. Based on major element geochemistry, it is deduced that at the time of its formation the Traveler Rhyolite magma was under 8 Kb total pressure (depth of 25-30 km), 4 Kb water pressure, a temperature of 810<sup>o</sup>C, and in equilibrium with two feldspars and quartz.

3. Oxygen fugacity of the magma was maintained through equilibrium with graphite which is common in Appalachian eugeosynclinal sediments.

4. High Sc abundances imply special conditions during the formation of the Traveler Rhyolite magma, namely the subordinate role of minerals with high preference for Sc, such as mafic silicates. The range of Sc abundances in the Traveler Rhyolite and Katahdin Granite is typical of basalts and basaltic andesites, but not of granites.

5. The REE abundances of the Traveler Rhyolite magma are consistent with the postulated anatectic origin of the TR magma from the Appalachian eugeosynclinal sediments.

6. The strontium isotope initial ratio of 0.7100 (Fullagar, Bottino, 1968) is also consistent with the partial fusion of preexisting sediments.

The petrology, mineralogy and crystallization path of the younger magmatic episode, i.e., HQD, HLP and DGD, is much more varied even though it underlies only approximately 5% of the Katahdin Pluton. In contrast with the earlier TR-KG magmatic episode, the evolution of the younger sequence was controlled by an oxidizing environment. Trace element abundances show that both, the Horserace Quartz Diorite and the Harrington Lake Porphyry, are genetically unrelated to the earlier episode, and that the Debsconeag Granodiorite is best explained by mixing of 40% Traveler magma and 60% Harrington Lake Porphyry. The presented data do not provide sufficient constraint about the origin of the magma of the younger episode. However, the major and trace element abundances are consistent with calc-alkaline associations of continental margins. If this inference is correct, then the younger episode may represent magma derived from a subducting oceanic crust.

In conclusion, Fig. 34 illustrates schematically the possible time sequence for the origin of the Traveler Rhyolite-Katahdin Pluton igneous complex. Mafic magma of mantle origin (possibly derived along a subducting plate) raises the temperature near the base of the crust causing its partial fusion. The resulting melt of rhyolitic composition is then pushed up into shallow levels within the crust. From there it is rapidly moved to the surface through violent ash flow eruptions. The residual melt fractionates and, on crystallization, forms the Katahdin Granite which is in turn intruded by smaller intrusions of quartz diorite (HQD) and granodiorite (DGD).

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Fig. 43. Schematic Illustration of The Evolution of The Traveler Rhyolite - Katahdin Pluton Igneous Complex.

> Legend: TR - Traveler Rhyolite TRBC- Traveler Rhyolite: Black Cat Member TRP - Traveler Rhyolite: Pogy Member KG - Katahdin Granite KGD - Katahdin Granite: Doubletop Facies KGS - Katahdin Granite: Summit Facies HQD - Horserace Quartz Diorite HLP - Harrington Lake Porphyry DGD - Debsconeag Granodiorite













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