

**GEOLOGY AND MINERALOGY OF THE PYROPHYLLITE DEPOSITS
SOUTH OF MANUELS, AVALON PENINSULA, NEWFOUNDLAND**

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HARVEY F. KEATS, B.Sc.

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GEOLOGY AND MINERALOGY OF THE PYROPHYLLITE DEPOSITS
SOUTH OF MANUELS, AVALON PENINSULA, NEWFOUNDLAND

by

 Harvey F. Keats, B.Sc.

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Abstract

The Late Precambrian (Hadrynian) Harbour Main Group of the eastern side of the Central Block of the Avalon Platform of Newfoundland consists predominantly of acidic volcanic rocks which are intruded on the west by quartz monzonite of the Holyrood Plutonic Series. Pyrophyllite deposits, containing mainly pyrophyllite, sericite and quartz, occur in the acidic volcanic rocks close to the Holyrood granite - Harbour Main contact. The deposits are localized by fault and shear zones. They were studied in the field in relation to the host rocks and in the laboratory by means of an X-ray diffraction technique involving the correlation of peak-height ratios with percentage ratios of mineral pairs. The percentages of pyrophyllite, sericite and quartz can be calculated from these ratios. This method can be adapted to a routine industrial analysis.

The alteration process responsible for the formation of the pyrophyllite deposits was one of metasomatic replacement by late stage hydrothermal solutions related to the Holyrood granite intrusion. The replacement, contemporaneous with deformation, involved the introduction of Si, K, and possibly Al, the movement of K, Na and Si within the alteration zones, and the migration of K, Na, Si and Mg away from the zones. The alteration took place at a total pressure of 1000 bars, a fluid pressure probably somewhat below this, and at a temperature below 380°C, possibly approaching 270°C.

CHAPTER I: INTRODUCTION

The thesis area lies about 15 miles southwest of St. John's, Newfoundland, within north latitudes $47^{\circ} 26'$ and $47^{\circ} 29' 30''$ and west longitudes $52^{\circ} 56' 20''$ and $52^{\circ} 57' 30''$, extending from a point about 2.5 miles south of Manuels to approximately 1.5 miles south of the Trans-Canada Highway (Figure I-1).

The area is made easily accessible by the road running southeast from Long Pond to Johnnies Pond and the Oval Pit area. The Trans-Canada Highway, the road running south from it past Dog Pond, and numerous trails and cut lines add to the ease of access. Field work in the central portion of the map area is made somewhat more difficult by dense vegetation, rough topography and an absence of trails.

The area contains the only known economic deposits of pyrophyllite in Canada. They occur in acidic volcanics and volcanic conglomerates of rhyolitic composition. Other economic deposits of this mineral in North America have had a more complex geological history, involving regional metamorphism; thus a study of the almost unmetamorphosed deposits south of Manuels may provide valuable information on the formation of pyrophyllite deposits.

Pyrophyllite and sericite have very similar optical properties, making them virtually impossible to distinguish visually. All previous work on the deposits was greatly hampered by this difficulty. This similarity between a valuable and an undesirable mineral, which complicated the task of hand-picking relatively pure pyrophyllite, was partly responsible

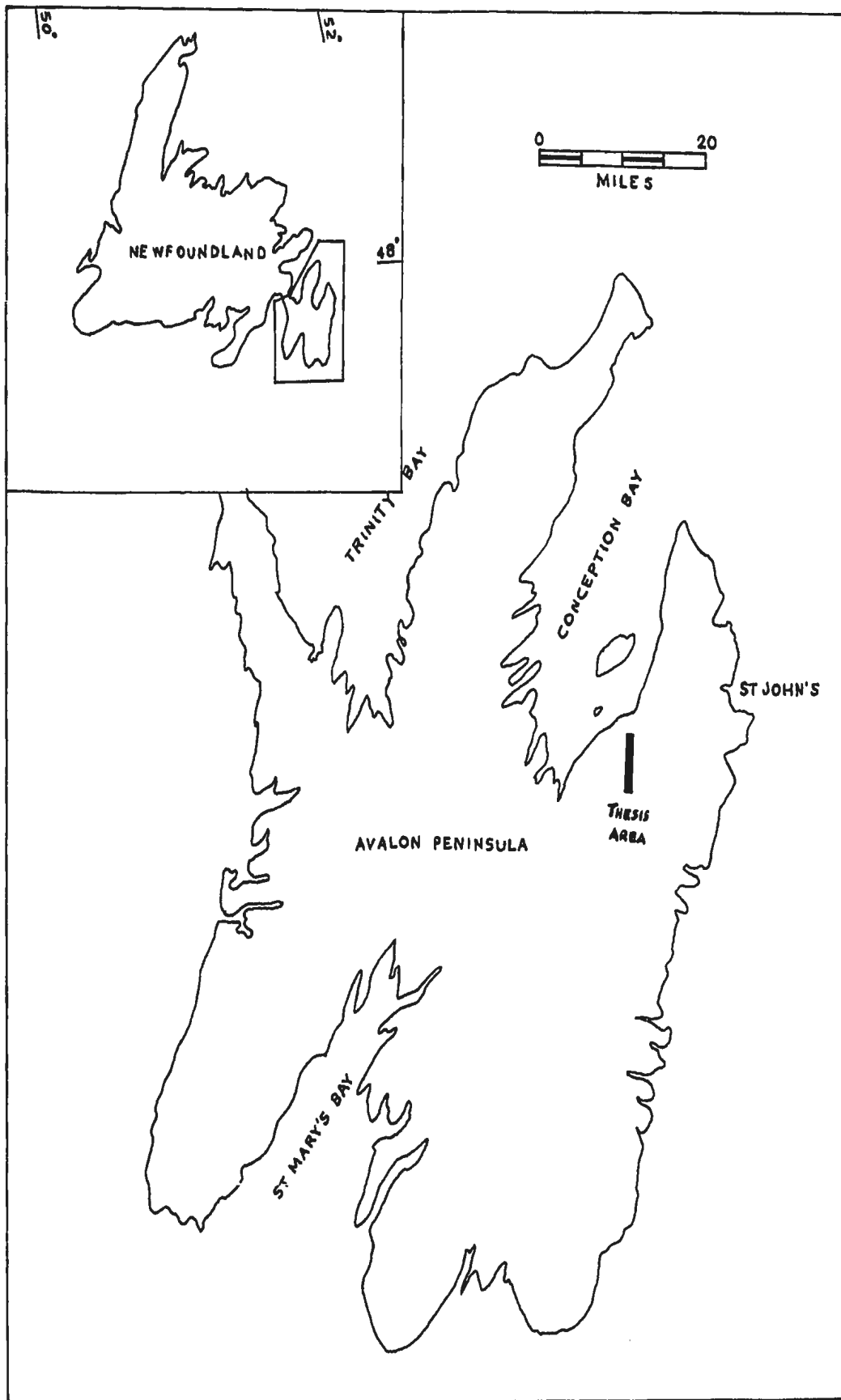


Figure I-1

for the area's intermittent mining history. This thesis presents a rapid and reliable method of semi-quantitative mineralogical analysis, which may help to solve this difficult problem.

Field work involved geological mapping of the host rocks of the pyrophyllite deposits to produce a detailed outcrop map showing original rock types. Some work was also done on the distribution of the pyrophyllite, sericite and quartz in the altered rocks as a whole and especially in the alteration zones. In particular, samples were taken across the alteration zones at the Oval Pit and the Dog Pond prospect (Map 1).

Laboratory time was divided between the development of a quantitative or semi-quantitative x-ray diffraction technique using standard samples from the pyrophyllite deposits, and the running of unknowns, particularly the detailed samples from the alteration zones.

CHAPTER II: PREVIOUS WORK

Geological Studies

The area studied by the writer has attracted attention many times since the late nineteenth century, when J. P. Howley, Newfoundland Government geologist, produced a sketch map (unpublished) in the first attempt to depict the geological relations of the pyrophyllite deposits.

In 1916, A. F. Buddington published a paper dealing mainly with the area studied by the present writer. He gave a fairly detailed description of the deposits and their host rocks and put forward a theory for their alterations. He concluded: "The pyrophyllite, pinite (i.e. impure sericite, HFK.), quartz-pyrophyllite schists of the Avondale (i.e. Harbour Main, HFK.) volcanics owe their formation to metasomatic replacement and alteration of previously silicified rhyolites or rhyolitic volcanics by thermal waters, under conditions of dynamic stress and intermediate temperatures and pressures, operating along channels primarily determined by fault or shear zones. Chemically, the salient features of these alterations have been the introduction of alumina, the more or less complete substitution of hydroxyl element in place of the alkalis, and the solution of soda. The solutions instrumental in causing these alterations may have been to a greater or lesser extent juvenile waters emanating from the intrusive granite batholith and monzonite stock at some period subsequent to their time of injection." (Buddington, 1916).

Later, Buddington (1919) published a second paper on the Precambrian rocks of the Avalon Peninsula in which he made a further contribution to the understanding of the alterations in the thesis area. Both papers were the

result of field work carried out in 1913-14 during a Princeton University Geological Expedition to Newfoundland.

In 1937, the pyrophyllite deposits south of Manuels were investigated by J. S. Vhay for the Newfoundland Department of Mines. His ideas on the origin of the deposits agree in substance with those of Buddington (1916).

In 1963 the present map area was included in a fairly detailed study by J. M. Dawson (Dawson, 1963). The most important part of the study relevant to the present work was the separation of the acidic conglomerates and tuffaceous slates into a distinct unit which he believed to lie unconformably above the altered volcanics and hence the Holyrood granite.

The southern 2.25 miles of the present map area was studied by G. H. Gale (Gale, 1966). He agreed with Dawson's classification of the volcanic sediments and their stratigraphic position. Parts of Gale's map have been incorporated in map 1.

Mining History

The Manuels pyrophyllite deposits have had an intermittent mining history. Although the presence of pyrophyllite in the area was known to J. P. Howley in the latter half of the nineteenth century, the first production from the Mine Hill prospect (Map 1) did not start until 1903, when a company was formed to mine the deposits. In 1904 an aerial tramway was installed to the railhead and a loading pier was built at Seal Cove, 8 miles west of Manuels. In the same year, 1750 tons of hand-picked pyrophyllite were shipped to the USA; in 1905, shipments increased to 6000

tons. Production ceased in 1905. In 1935, 30 tons of pyrophyllite were shipped ~~through~~^{by} the Canadian Alliance Corporation to a Montreal plant for an experimental grinding test (from the files of the Mines Branch, Department of Mines, Agriculture and Resources, Newfoundland. Exact reference unknown).

In 1938 the prospects were acquired by the Industrial Minerals Company of Newfoundland; production was reopened and in 1939 a mill was erected near Manuels to treat the ore. ~~Previously~~ Hand-sorted pyrophyllite was used for mill feed. In 1942 the Mine Hill pit was closed and the Oval Pit, north of Johnnies Pond was opened. Up to 1947, when it ceased operations, this company made regular shipments to the United Kingdom and smaller shipments to the United States, Canada, and elsewhere (Carr, 1958).

Newfoundland Minerals Limited, a subsidiary of American Encaustic Company Inc. of Lansdale, Pennsylvania (now the American Oelean Tile Company), entered the field in 1956. Milling operations were resumed in June of that year and the company has been making regular shipments of pyrophyllite to the parent company up to the present time. The mineral is being used in the production of a high quality bathroom tile. The pyrophyllite is removed in bulk and representative samples are chemically analysed for Al_2O_3 , Fe_2O_3 , K_2O and Na_2O to determine marketable material; any obvious siliceous or rhyolitic material is removed by hand-sorting as the ore passes through the mill on a conveyor belt.

CHAPTER III: GENERAL GEOLOGY

Introduction

The eastern part of the Avalon Peninsula can be divided into three blocks defined by two major fault zones, the Topsail fault zone and the more complex Holyrood-Brigus fault zone (Figure III-1), (Brueckner, 1969; Papezik, 1969). Displacement on the faults probably took place several times since, and possibly before, the emplacement of the Holyrood Plutonic Series (locally known as the Holyrood batholith or Holyrood granite).

The Western Block consists of acidic and basic volcanics of the Harbour Main Group, which are locally intruded by granitic rocks related to the Holyrood granite. The volcanics and intrusives are unconformably overlain by shale, mudstone, chert and sandstone of the Conception Group (McCartney, 1967). These grade upwards into black shales, red sandstones and conglomerates of the Hodgewater Group, all of Late Precambrian age.

The Eastern Block consists of a conformable sequence of basic and acidic volcanics of the Harbour Main Group, sediments of the Conception Group, and rocks of the Cabot Group, similar to the Hodgewater Group. The Holyrood granite does not outcrop in the Eastern Block.

The Middle Block is composed predominantly of rocks of the Holyrood Plutonic Series which intrude acidic to basic volcanics of the Harbour Main Group. The volcanics and intercalated volcanic sediments are found along the margins of the intrusion and in numerous roof pendants and xenoliths throughout the area.

In all but the Eastern Block, fossiliferous Cambro-Ordovician rocks rest unconformably on the above-mentioned Precambrian rocks of the eastern

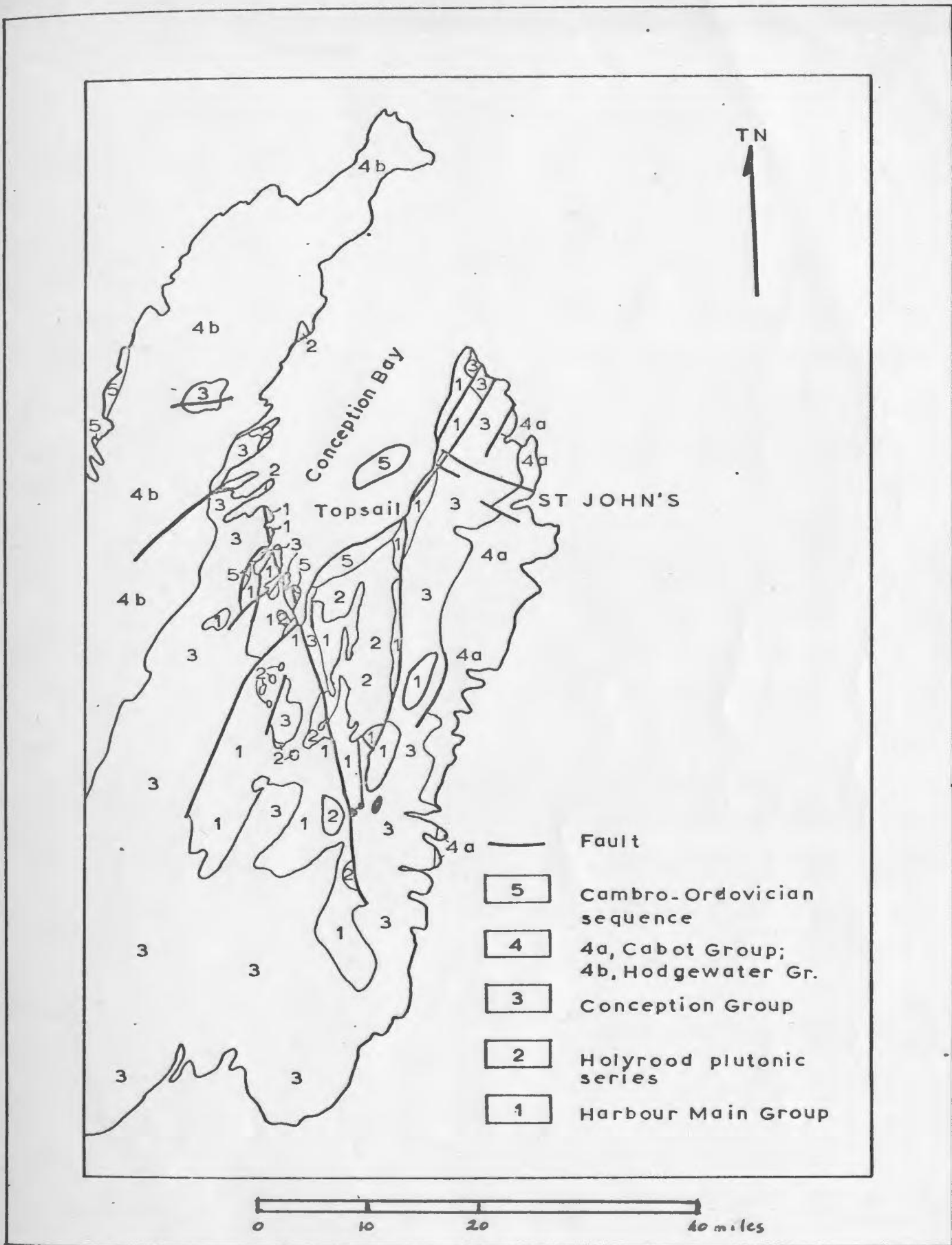


Figure III-1: Geology index map

part of the Avalon Peninsula.

The physiography of the Avalon Peninsula has been determined by differential erosion of rock units and by the northeasterly trending faults which dissect them (Buddington, 1916). The interior of the Peninsula consists of rounded hills 1000-1100 feet high, projecting above a plateau of 500-700 feet elevation; the edges of the plateau have been deeply dissected, as can be seen in the thesis area. The surface of the whole Peninsula was strongly modified by a local ice sheet in Pleistocene time.

The thesis area lies on the eastern margin of the Holyrood batholith, in the Central Block. It is dominated by a northerly-trending acidic volcanic belt which lies stratigraphically below more basic volcanic rocks to the east. The belt consists mainly of rhyolitic flows, with lesser amounts of acidic pyroclastics, volcanic sediments, and minor amounts of pillowed basaltic flows.

The greater part of the rhyolite belt has been sericitized and silicified; pyrophyllitization has taken place along several local fault- and shear-zones. The volcanics and volcanic sediments have been intruded by granitic rocks of the Holyrood batholith; volatiles, related to a late magmatic stage of this granite, are believed responsible for the alterations. There are two sets of diabase dykes, one older than and one younger than the Holyrood granite intrusion.

Harbour Main Group

Most of the rocks in the thesis area belong to the Harbour Main Group. The rocks of the group have been divided on a lithologic basis into

acidic pyroclastics, acidic flows, volcanic sediments, volcanics of predominantly andesitic composition, and basaltic flows.

Acidic Pyroclastics (Table IV-2)

Because of the discontinuous nature and often close spatial relationship of the volcanic breccias, lapilli tuffs and tuffs, they have been grouped under the same subdivision of the Harbour Main Group. Thin sections of the lapilli tuffs and tuffs show that they consist predominantly of fine-grained rhyolite fragments which have been devitrified, as shown by the frequent felsitic and spherulitic textures in the fragments. Fragments of quartz and sodic-plagioclase are present in a somewhat sericitized groundmass, together with fragments of partially and entirely altered feldspar showing no trace of twinning, which are probably K-feldspar. The rock fragments are often silicified and the groundmass highly sericitized. The alteration and the fine-grained nature of the rock fragments make further identification impossible.

Near the south end of Mine Hill there is an exposure of very coarse breccia which appears to be surrounded by rhyolitic flows, striking from westerly to northwesterly and dipping nearly vertically to the north or northeast. Most of the blocks of the breccia are 1 foot or less in diameter but a few blocks about 15 feet in diameter have been observed. Most of the fragments are rhyolitic but a few are andesitic. The groundmass consists of a fine-grained crystalline rock of probably andesitic composition; it cannot be identified accurately because the plagioclase microlites are too small and the whole groundmass has been highly chloritized and silicified, but a distinct pilotaxitic texture indicates its extrusive

origin. The few fragments of andesitic material are identical with the groundmass. The rhyolitic fragments are mostly felsitic but some are porphyritic with predominantly albite phenocrysts; both types show relic perlitic cracks in places.

Alteration of the breccia took place during the regional alteration and replacement, as evidenced by silicification and chloritization of the groundmass as well as silicification, sericitization and some pyrophyllitization of some of the rhyolitic fragments.

This conspicuous exposure, first noticed by Buddington (1916), is interpreted by Vhay (1937) as a tilted volcanic neck filled with explosion breccia. The narrow extensions to the west and northwest he considers to be breccia thrown out on the surface of the flows at the time the neck was filled. The present writer is in general agreement with this interpretation.

Acidic Flows (Table IV-1, Nos. 1-5)

Most of the acidic volcanics in the area show structural or textural evidence of being originally acidic flows. Among the criteria used to determine the nature of the rocks is flow banding, often accompanied by flow brecciation. The flow banding is usually outlined by small differences in grain size from band to band but is often accentuated by acicular intergrowths of quartz and feldspar which grew perpendicular to the flow banding (Plate III-1). Spherulites, radial aggregates of quartz and feldspar, are also found in flow banded rhyolites. Some of the coarsely flow-banded rhyolites have fine and coarse bands which exhibit a perfect



Plate III-1. (X 6.3, X nicols). Photomicrograph of flow banding in a rhyolite accentuated by acicular intergrowths of quartz and feldspar, perpendicular to the banding (a devitrification texture).

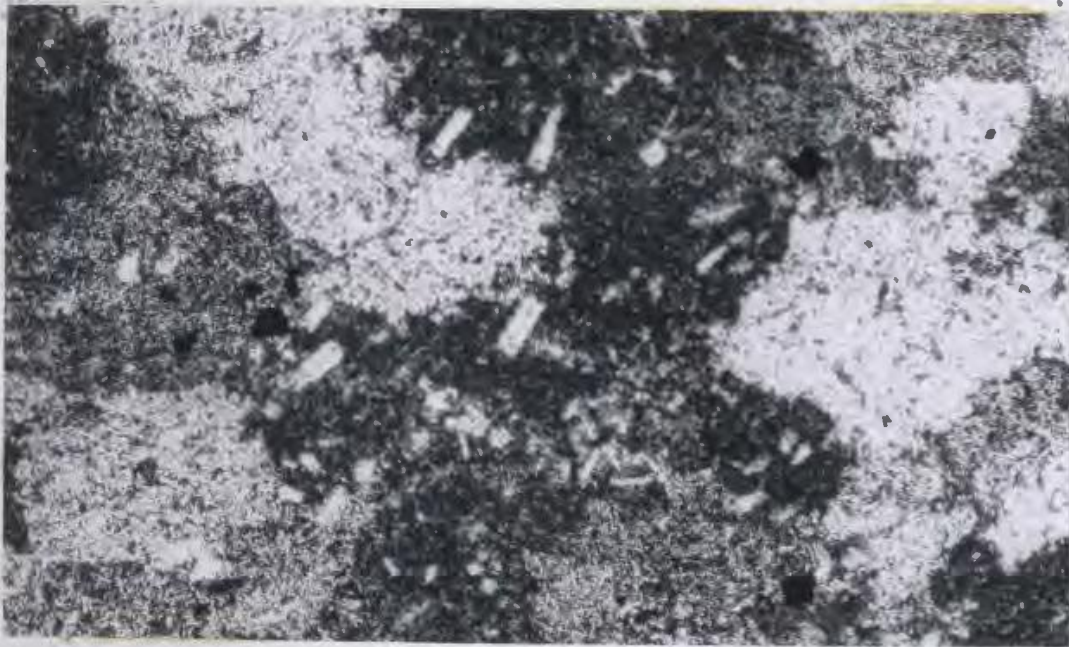


Plate III-2. (X16, X nicols). Photomicrograph of felsitic texture in a flow rhyolite (a devitrification texture).



Plate III-3. (X4, X nicols). Photomicrograph of a portion of a spherulite in a flow rhyolite (a devitrification texture).



Plate III-4. Photograph of a spherulite in a flow rhyolite (a devitrification texture).

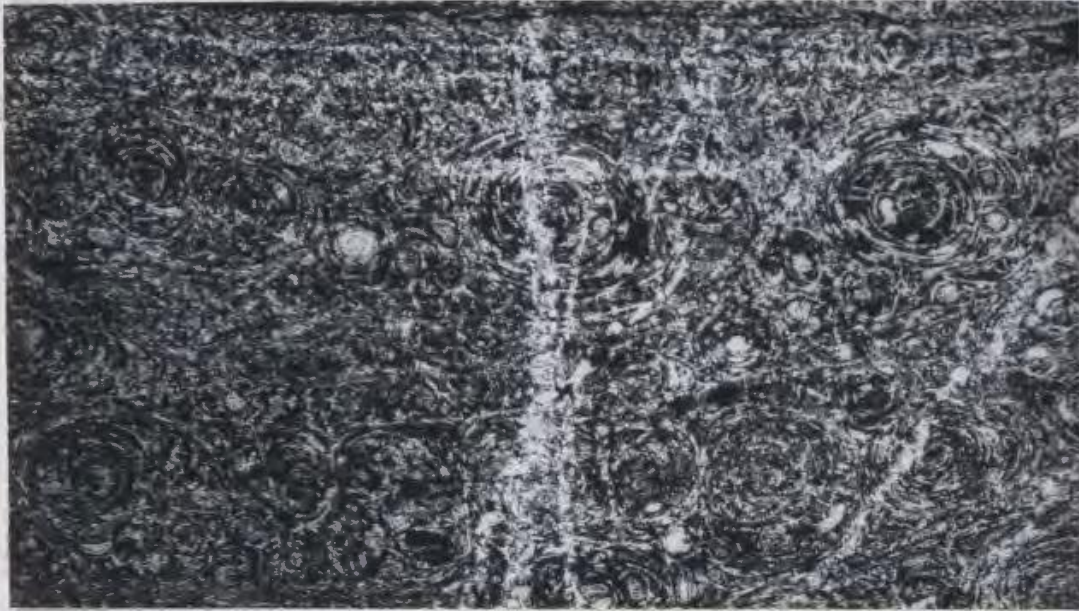


Plate III-5. (X4, plane polarized light). Photomicrograph of perlitic cracks excellently preserved in a flow rhyolite.

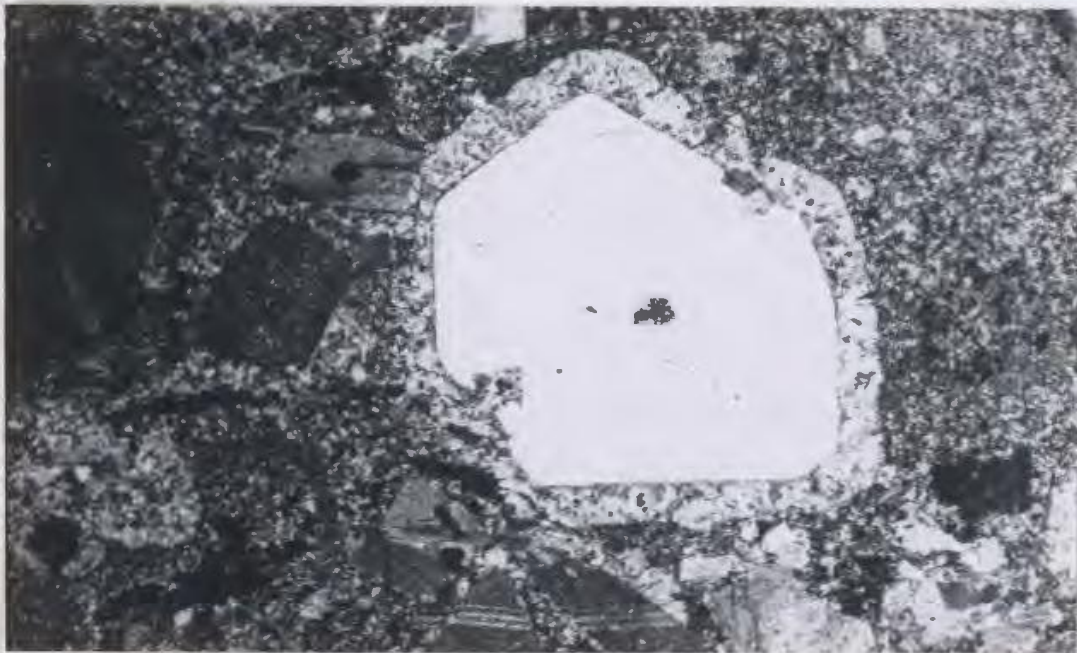


Plate III-6. (X4, X nicols). Photomicrograph of a quartz phenocryst, completely surrounded by a radial aggregate of quartz and feldspar, in a rhyodacite porphyry (a devitrification texture).

felsitic texture (Plate III-2). What appear first to be irregularly-shaped grains are actually mineral aggregates of quartz and feldspar microlites in optical continuity. All of these intergrowths of quartz and feldspar have been produced by the devitrification of glass.

Many of the flows in the area consist almost entirely of spherulites, ranging in size from microscopic to 2 or 3 inches in diameter (Plates III-3, 4). Buddington (1919) reported some spherulites as large as 22 inches in diameter in an outcrop which has been destroyed by the construction of the Trans-Canada Highway. No shards or eutaxitic textures were observed in thin section in any of the spherulitic rhyolites. Furthermore, many of the spherulitic rhyolites are associated with flows and show flow-banding or other flow structures. Thus, it was concluded that the spherulites were formed by devitrification of flows rather than of welded tuffs. Perlitic cracks are well-preserved in both the spherulitic and other acidic flows (Plate III-5).

Volcanic Sediments

The stratigraphically lowest volcanic sediments in the area are well-bedded and fairly well-sorted conglomerates made up of acidic fragments, together with some intercalated coarse acidic volcanic breccias and tuffs. South of the Oval Pit (Map 1), these grade upwards into first red and then green tuffaceous sediments, and again into conglomerates composed of acidic fragments. The tuffaceous sediments in the area consist of well-bedded mudstones, siltstones and volcanic greywackes or lithic tuffs, together with many intercalated acidic and intermediate tuffs. The composition of the

fine-grained mudstones and siltstones is not determinable because of the pervasive chloritic alteration and hematite staining. The volcanic greywackes are composed of a chaotic mixture of rhyolitic, andesitic and sedimentary rock fragments together with variable percentages of K-feldspar and plagioclase fragments. Many of the feldspar fragments are so highly sericitized that identification is difficult or impossible. Many of the volcanic greywackes are probably waterlain, airfall tuffs. There are also some acidic tuffs which are composed of rhyolitic fragments, sodic plagioclase and minor K-feldspar fragments, all of which are altered in varying degrees. Intercalated with all these rock types are tuff layers composed entirely of andesitic rock fragments in a highly chloritized groundmass. The fragments are themselves almost completely chloritized making an accurate identification impossible; their pilotaxitic texture, however, suggests an andesitic composition. Nearly all of the volcanic sediments are sericitized, chloritized or hematite is present to such a degree that an accurate identification of many of the constituents is almost impossible.

Volcanics of Predominantly Andesitic Composition

This subdivision of the Harbour Main Group consists mostly of andesitic flows and agglomerates, which contain rhyolitic fragments ranging from a fraction of an inch to 20 feet in diameter. Interbedded and often quite intimately intermixed with the andesitic flows are thin rhyolitic flows and lenses of siltstone and mudstone. These rocks were not examined in any great detail in the field since they have little bearing on the main problem of the thesis.

Microscopically as well as macroscopically, the rhyolitic blocks are identical to those in the rhyolite belt to the west. The mudstones and siltstones were not studied in thin section. The andesites are classified on the basis of their pilotaxitic and sometimes vitrophyric textures rather than by the An content of the plagioclase feldspar; albite twinning in the feldspars can be observed but wavy extinction, sericite alteration, and the fine-grained nature of the microlites prevented their exact identification. The andesites are highly chloritized and in most cases the original nature of even the dark minerals has been obscured. In one thin section, relatively fresh brown hornblende occurs as the main mafic mineral. Magnetite is abundant in all of the andesites. The presence of primary hornblende may indicate that at least some of the mafic rocks were originally hornblende andesites.

These andesites with blocks of rhyolite and interbedded rhyolite flows and sediments are found on the eastern side of the rhyolite belt and are best exposed in the northeast corner of the map area.

Basaltic Flows

Between the north end of Mine Hill and the road to Johnnies Pond (Map 1), there is a small exposure of pillowed basalt with a narrow band of sheared basic tuff. The basalt, locally massive, is partly amygdaloidal with quartz and calcite filling the vesicles. Chlorite is an abundant constituent of these rocks. They are also magnetic, indicating a fair percentage of magnetite.

Thin section work reveals that the basalts are high in chlorite and carbonate, which replace nearly all primary minerals. Magnetite and sphene

are fairly abundant, making up about 15 percent of the rock. The feldspars are highly sericitized and possibly saussuritized to the point where an An content is impossible to determine. In one thin section a few phenocrysts have been completely altered to chlorite, sphene and magnetite, but the crystal outlines suggest that they may have been originally amphiboles or possibly pyroxenes.

Microscopic examination shows that rocks which in hand specimen appear to be sheared basic tuffs are silicified and sericitized. Magnetite and sphene are also quite abundant making up about 15 percent of the rock. Practically all original textures have been obliterated except in a few areas of thin sections where vague relic textures of a basalt can be seen.

One other small outcrop of amygdaloidal basalt was found south of Trout Pond (Map 1). Both occurrences are believed to represent minor periods of basaltic volcanism during predominantly rhyolitic extrusions.

Holyrood Plutonic Series

The Holyrood Plutonic Series consists of a pink equigranular granite pluton with fringing stocks and marginal bodies of quartz monzonite and smaller marginal or overlying bodies of quartz-hornblende gabbro (McCartney, 1969). McCartney suggests "a single age of granitic intrusion accompanied by marginal hybridization to quartz monzonite and further suggests local conversion of some basaltic roof pendants to quartz-hornblende gabbro. This interpretation and the abundant granitic fragments in Conception conglomerate at Duffs lead to the conclusion that the granitic rocks are of Pre-Conception age. Granitic rocks recently yielded a Rb-Sr

isochron age of 574 ± 11 m.y." (McCartney 1969, pp. 121-122). Rose (1952), however, believes the Holyrood granite is intrusive into Conception Group rocks south of the present map area, which could suggest two periods of granitic intrusion. This problem remains unresolved.

Rocks of the Holyrood Plutonic Series in the thesis area consist of quartz monzonites and equivalent rhyodacite porphyries. The rocks are fairly fresh away from the intrusive contact and can be easily identified; near the contact, however, shearing, cataclasis and intense sericitization have practically obliterated all original granitic textures. Only some relic patches in thin section and hand specimens indicate the origin of the rocks.

The quartz monzonites have roughly equal amounts of microcline and plagioclase with a composition of An_{30} . The microcline has been altered to a very fine-grained brownish mineral which may be a clay mineral or incipient sericite. The plagioclase feldspars are relatively fresh. Quartz makes up about 15% of the rock.

The grain-size of the quartz monzonites is variable; some areas of even a single thin section are much finer grained than others. This texture and the fact that many of the feldspars are broken and somewhat strained suggest that cataclasis took place even a thousand feet away from the granite contact. Biotite or hornblende has not been observed in these rocks. Spene is very abundant, especially along fractures and in cataclastic zones.

A few intrusive rhyodacite porphyries are associated with the quartz monzonite. The phenocrysts indicate that the feldspar content is

very similar to the quartz monzonite. The phenocrysts, often surrounded by radiating quartz and feldspar intergrowths (Plate III-6), are set in a felsitic and spherulitic groundmass. Biotite, now completely altered to chlorite, occurs in the groundmass as small phenocrysts. Spene is a very common accessory mineral.

Diabase Dykes

As will be explained in a later section of this chapter, there are two ages of diabase dykes in the thesis area. Both sets of dykes, however, are very similar in having an intersertal texture with chlorite filling the interstices between the feldspars. Because of the sericitization or saussuritization of the feldspars in many of the early dykes and the fine-grained and poorly twinned plagioclase in the later ones, an An content has not been obtained. No primary mafic minerals remain in any of these rocks. Fine-grained spene, partially leucoxenised, makes up about 10 percent and magnetite from 5 to 10 percent of the dykes.

In the northern part of the outcrop area containing the pillowed basalts, north of Mine Hill, there are some coarse-grained basic rocks that occur in both massive and amygdaloidal forms. These rocks have an intergranular texture, with olivine making up about 35% of the total minerals. The olivine has been completely altered to chlorite, carbonate and magnetite but the original nature of the pseudomorphs is fairly well established. The plagioclase feldspars cannot be further identified because they have been highly sericitized or saussuritized. The vesicles are filled with quartz and calcite. The rock is considered to ^{have been} ~~be~~ a coarse-grained olivine diabase.

Metasomatism

The Harbour Main rhyolites in the thesis area have been intensely metasomatized. The rhyolites and conglomerates containing acidic fragments were affected by an early stage of silicification and a later stage of pyrophyllitization, sericitization and silicification, to be described in more detail in a later chapter. The degree of alteration decreases away from the granite contact, and intensely altered zones are closely related to this contact. Silicification and sericitization, however, are the only alterations of the granite itself along the sheared contact.

The pre-granite diabase dykes which cut highly altered rhyolites have been silicified, sericitized and chloritized almost to the point of making them unrecognizable in thin section. Other early diabase dykes, cutting relatively unaltered rhyolites, show the same type of alteration as above but much less intense. The post-granite dykes are relatively fresh except for the chlorite in the interstices of the plagioclase feldspars. The sheared basic tuff north of Mine Hill has been silicified, sericitized and chloritized. Even the andesites on the eastern side of the rhyolite belt have been somewhat sericitized, saussuritized and chloritized and show some carbonate alteration. Whether all this intense metasomatism is related to the same processes which are responsible for the alteration of the rhyolites is not known.

Structure

The general trend of major folds on the Avalon Peninsula is north-northeast; however the rhyolite belt under discussion has a northerly trend

and lies stratigraphically below a northerly-trending belt of andesites to the east (Dawson, 1963). Thus the rhyolite belt lies on the western limb of a large syncline. Volcanic sediments within the belt, however, are also folded. The rhyolites themselves may be folded as well but, as will be explained later, they probably reacted to the prevailing stresses more by faulting and shearing than by folding. Folding in the rhyolite is difficult to establish, since one cannot assume that flow-banding was originally horizontal.

The volcanic sediments in the area strike northerly and dip 30-40°E, except in the hinges of the southerly-plunging synclines, south of the Oval Pit and west of Mine Hill, where the beds strike approximately easterly and dip 30-40° southerly. East of the north end of Johnnies Pond the strike is northwest and the dip 85° southwest. The strike of the axial plane cleavage is close to northerly and the dip always close to vertical.

To the south of Dog Pond, volcanic sediments outcrop on the western limb of a syncline. The bedding strikes close to northerly and dips 40-50°E. The strike of the axial plane cleavage is also close to northerly and dips are always steeper to the east than the bedding and is usually 50°E. These cleavage-bedding relationships as well as cross-bedding and graded-bedding indicate that the beds are facing eastward. Since the bedding is almost as steep as the axial plane cleavage, it can be deduced that the volcanic sediments are on the western limb of very tight syncline, the core of which contains pyrophyllitized and sericitized rhyolites.

Strikes and dips of the flow-banding in the rhyolites are extremely variable and of very little significance. Strikes range from northerly to easterly and the dips from 60°E, W, S or N to vertical.

The schistosity or fracture-cleavage in the altered volcanics generally has a strike ranging from northerly to N 30°E, very similar to the axial plane cleavage in the volcanic sediments. It is often vertical or near vertical. In the smaller pyrophyllite showings, such as the Dog Pond area, the distribution of the pyrophyllite, sericite and quartz is related to this schistosity. At the Oval Pit and Mine Hill, however, the distribution of the three minerals varies in a northerly direction, related to an easterly-trending fault and shear zone, approximately perpendicular to the trend of the regional cleavage.

In the writer's opinion, faulting in the area is not as intensive and complex as previously reported. Nevertheless, there are local small scale faults with minor displacements in both the volcanic and sedimentary rocks, but they have very little significance except in fault zones which localize the alteration of the volcanics. West of Mine Hill there is a northwest-trending fault which separates sedimentary and volcanic rocks. At the southeast end of the mappable fault, granite is found intruded along and localized by it. The granite shows intensive shearing and cataclasis, indicating displacement on the fault subsequent to the intrusion. Practically everywhere near the Holyrood-Harbour Main contact the granite shows shearing and cataclasis indicating post-intrusion shearing along the contact.

Age Relations

Except for the explosion breccia in the postulated volcanic neck west of Johnnies Pond, the acidic pyroclastics are found interbedded between flows and are discontinuous along strike. The volcanic sedimentary rocks are believed to be interbedded between acid volcanics, contrary to the opinion of previous writers that at least some parts of them lie unconformably above altered rhyolites. Evidence for this conclusion includes the alteration of volcanic sediments along with the rhyolites, and the presence of altered and relatively fresh rhyolites lying stratigraphically above volcanic sediments.

The location of the andesites with blocks of rhyolite and interbedded rhyolitic flows and sediments between rhyolites to the west and andesites to the east, suggests that they have a particular stratigraphic significance. The blocks of rhyolite and occasional flows suggest a change from predominantly rhyolitic volcanism to a predominantly andesitic type, the latter represented by the northerly-trending andesite belt to the east of the present map area.

The contact relations between the pillowed basalts and the acidic volcanics are rather vague but since the basalts are found at different localities in the rhyolite belt, it is assumed that they represent local basic extrusions during predominantly acidic volcanism.

One set of basic dykes in the area intruded the Harbour Main volcanics prior to the granite intrusion, since they are altered along with the volcanics and are cut off by the granite. Another set intrudes the granite

and ^{is} ~~are~~ younger in age. This is indicated by the presence of granitic fragments in the dykes, chilling of the margins of the dykes in contact with the granite, and the presence of basic offshoots from the main dyke bodies into the granite. These relations are best observed in a large granite outcrop in the northwest corner of the map area.

Indirect evidence, such as proximity of the altered zones to the Holyrood granite contact, has led previous writers and the present writer to conclude that the alteration in the volcanics is related to the intrusive granite contact. A possible argument that the alteration may be related to a later, independent thermal event will be examined and disproved in a later chapter.

The Problem of the Black Hill Sequence

The "Black Hill Sequence", as defined by Dawson (1963), comprises all the rocks previously described in this chapter as "volcanic sediments". Vhay (1937) mapped the acidic conglomerates and associated rhyolitic breccias and tuffs south of the Oval Pit as part of the Harbour Main Group. He did so because these rocks are pyrophyllitized and sericitized along with the underlying Harbour Main rhyolites. He made the reservation, however, that these conglomerates may form the base of the overlying "tuffaceous slates", all of which he mapped as part of the Conception Group. This would make the volcanic sediments older than the Holyrood granite, which was presumably the cause of their alteration. Although he suspected that some of the "tuffaceous slates" (outcrop marked 1a + 1c, 1 mile south of the southern end of Johnnies Pond, Map 1) may lie stratigraphically between rhyolitic

rocks, he mapped all of the "tuffaceous slates" as part of the Conception Group, since they resembled other rocks of that group outcropping elsewhere on the Avalon Peninsula.

South of the present map area the Holyrood granite is reported to have an intrusive contact with the Conception Group (Rose, 1952). Dawson (1963) interpreted the altered acidic conglomerates, south of the Oval Pit, as basal conglomerates of the "tuffaceous slates", derived from underlying pyrophyllitized and sericitized rhyolites. This interpretation, the absence of any definite intrusive contact of the Holyrood granite with the "tuffaceous slates", and Rose's intrusive relationships to the south of the area (Rose, 1952), led Dawson to separate the acidic conglomerates and "tuffaceous slates" into a distinct unit, which he called the Black Hill Sequence. He placed this unit stratigraphically above the Harbour Main volcanics and the Holyrood granite. He suggested that the red members of this unit, which he believed to be at the base of it, may possibly be correlated with an upper unit of the Conception Group in the Western Block, the Hibbs Hole Formation.

The present writer is in partial agreement with Vhay (1937), that the acidic conglomerates south of the Oval Pit have been altered along with the rhyolites. The alteration, in the southern end of the Oval Pit, is gradational from highly altered rhyolites (dealt with in detail in a later chapter), into silicified and sericitized conglomerates to selectively altered conglomerates. Haloes around some of the sericitized pebbles in the selectively altered conglomerates are particularly indicative of alteration in place. Vhay's outcrop of pyrophyllitized conglomerate (Vhay, 1937, p. 7) has been destroyed by mining but about 600 feet south of the Oval Pit pyrophyllitization of other conglomerates has been observed by the writer.

Apart from the volcanic sediments which lie stratigraphically between rhyolites in the middle of the map area (Vhay, 1937) the volcanic sediments southwest of Dog Pond are also believed to underlie rhyolitic flows. As outlined in the section on structure, the cleavage-bedding relationships, cross-bedding and graded-bedding, all indicate that the sediments are facing eastward and the rhyolites lie in the core of a tightly folded syncline. The contact between the sediments and overlying flows is exposed in two outcrops, 6000 feet and 6500 feet south of Dog Pond (Map 1); the contact is not a fault as has been previously reported.

From the above evidence the writer concludes that the Black Hill Sequence, as defined by Dawson (1963), is not a distinct stratigraphic unit. It is further concluded that the "tuffaceous slates" do not belong to the Conception Group, as proposed by Vhay (1937), but instead are contemporaneous with the Harbour Main Group. The writer suggests that any similarities between the Hibbs Hole Formation and the red members of the volcanic sediments is strictly coincidental and reflects merely similar oxidizing conditions of sedimentation.

The volcanic sediments are interpreted as air-fall, water-lain tuffs and detrital volcanic material, deposited contemporaneous with volcanism. They were probably deposited in lakes or in the sea surrounding volcanic islands; the conglomerates containing acidic fragments are probably beach deposits.

CHAPTER IV: GEOLOGY OF THE PYROPHYLLITE DEPOSITS

Introduction

The main localities of economic interest in the rhyolite belt are alteration zones consisting mainly of pyrophyllite, sericite and quartz in widely varying proportions. Detailed mapping of the alteration zones is greatly complicated by the fact that the three principal minerals form extremely fine-grained aggregates. It is further complicated by the close similarity, both macro- and microscopic, between pyrophyllite and sericite. However, a reliable distinction between the two phyllosilicates is of economic importance, because sericite is an undesirable constituent of a marketable product. As conventional microscopic methods are of little use, a quantitative analytical method using x-ray diffraction was developed. This method involves the use of standard samples to construct calibration charts (Figure IV-1) from which the percentages of pyrophyllite with respect to sericite (P_s), quartz with respect to sericite (Q_s), and quartz with respect to pyrophyllite (Q_p) can be determined, ^{from} ~~having measured~~ prominent peak-height ratios on x-ray diffractograms of unknown samples. From these percentages, the percentage of each of pyrophyllite, sericite and quartz can be calculated. The details of the experimentation and the technique developed will be given in a later chapter.

The method proved quite reliable and was used to obtain modal analyses of samples collected at regular intervals across the Oval Pit and Dog Pond alteration zones. These cross-sections (Figures IV - 2,3) established the pattern of distribution of pyrophyllite, sericite and quartz in the alteration zones which proved useful in the interpretation of the origin of the deposits.

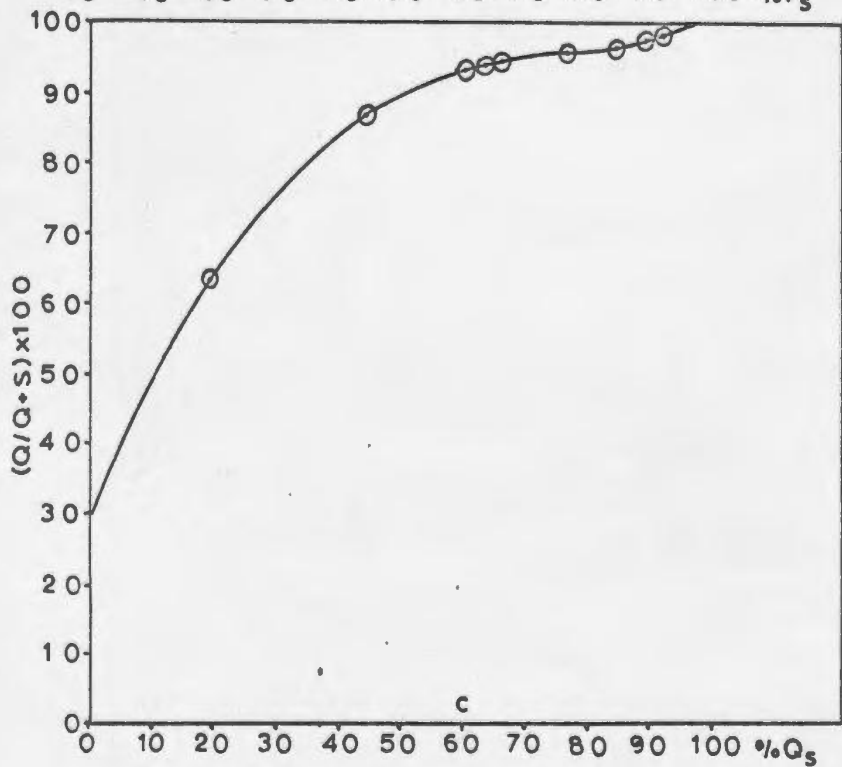
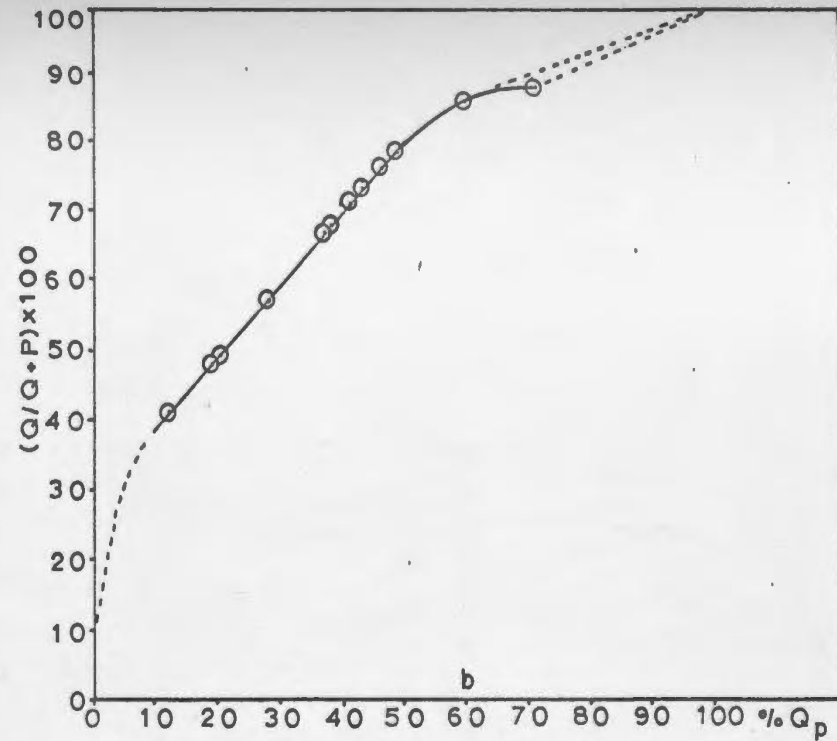
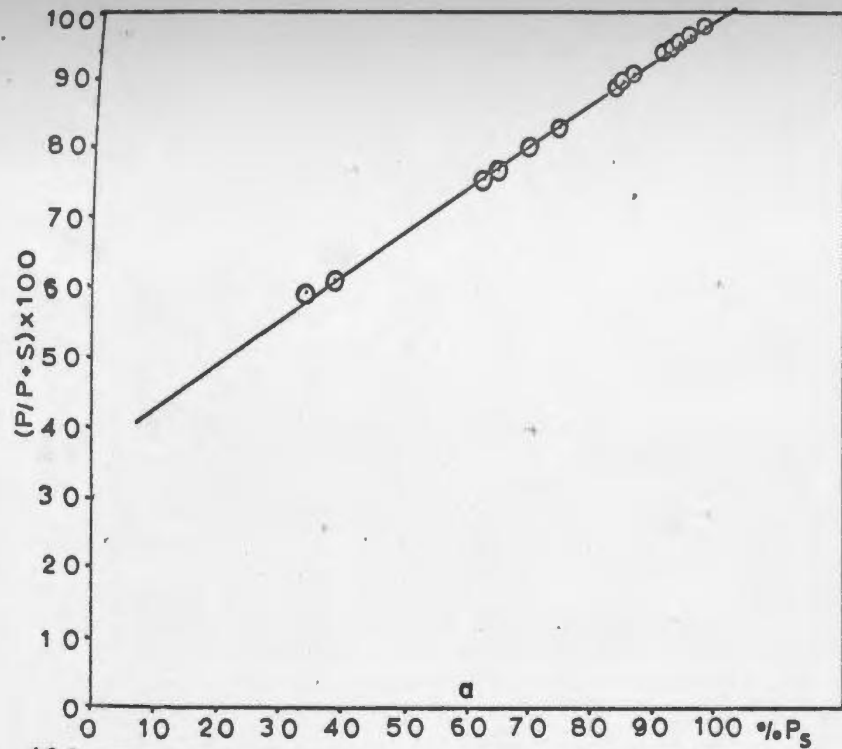
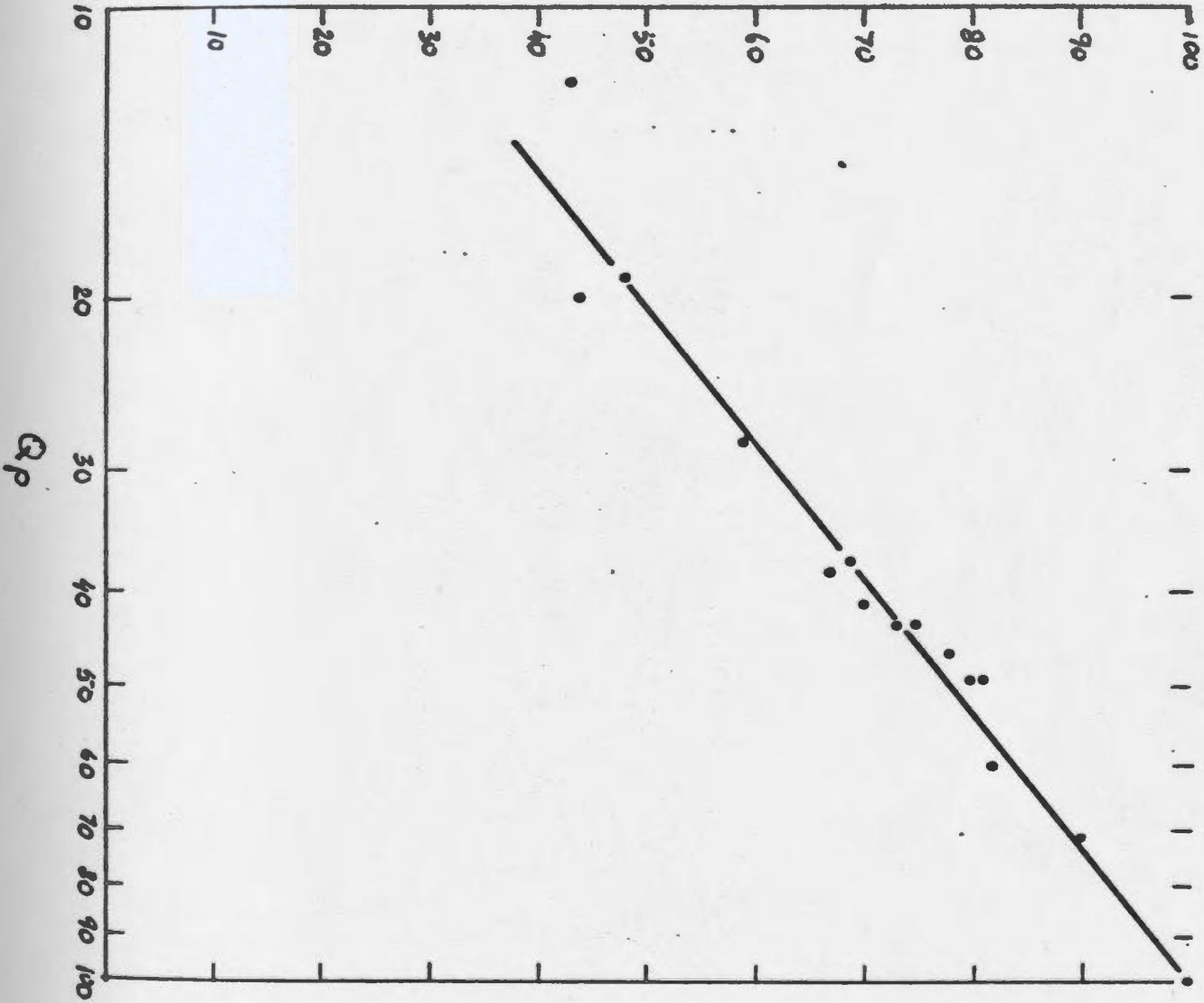


Figure IV-1: Calibration charts

- 1a, calibration chart for the mineral pair pyrophyllite-sericite
- 1b, calibration chart for the mineral pair pyrophyllite-quartz
- 1c, calibration chart for the mineral pair quartz-sericite

FIGURE IV-1a

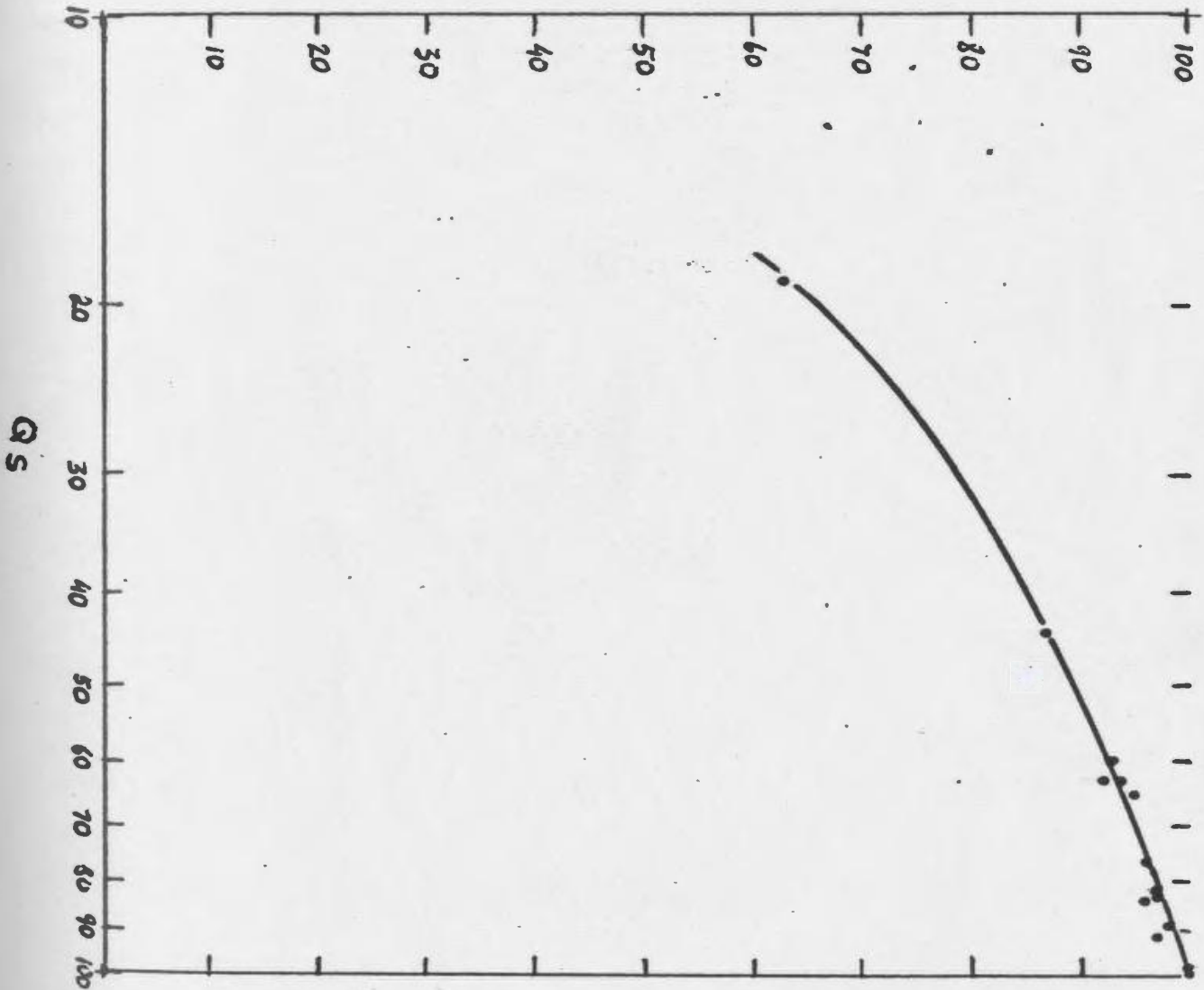
$$\left[\frac{Q}{Q+P} \right] \times 100$$



Calibration chart for the pair quartz-pyrophyllite.
Qp = proportion of quartz as % of (quartz + pyrophyllite)
 $\left[\frac{Q}{Q+P} \right] \times 100$: diffractometer peak height ratio.
Q = Qtz (10 $\bar{1}$ 1), P = Pyr. (002).

FIGURE IV-1b

$$\left[\frac{Q}{Q+S} \right] \times 100$$



Calibration chart for the pair quartz-sericite.
Qs = proportion of quartz as % of (quartz + sericite)
 $\left[\frac{Q}{Q+S} \right] \times 100$: diffractometer peak height ratio.
Q = Qtz (10 $\bar{1}$ 1), S = Ser. (002).

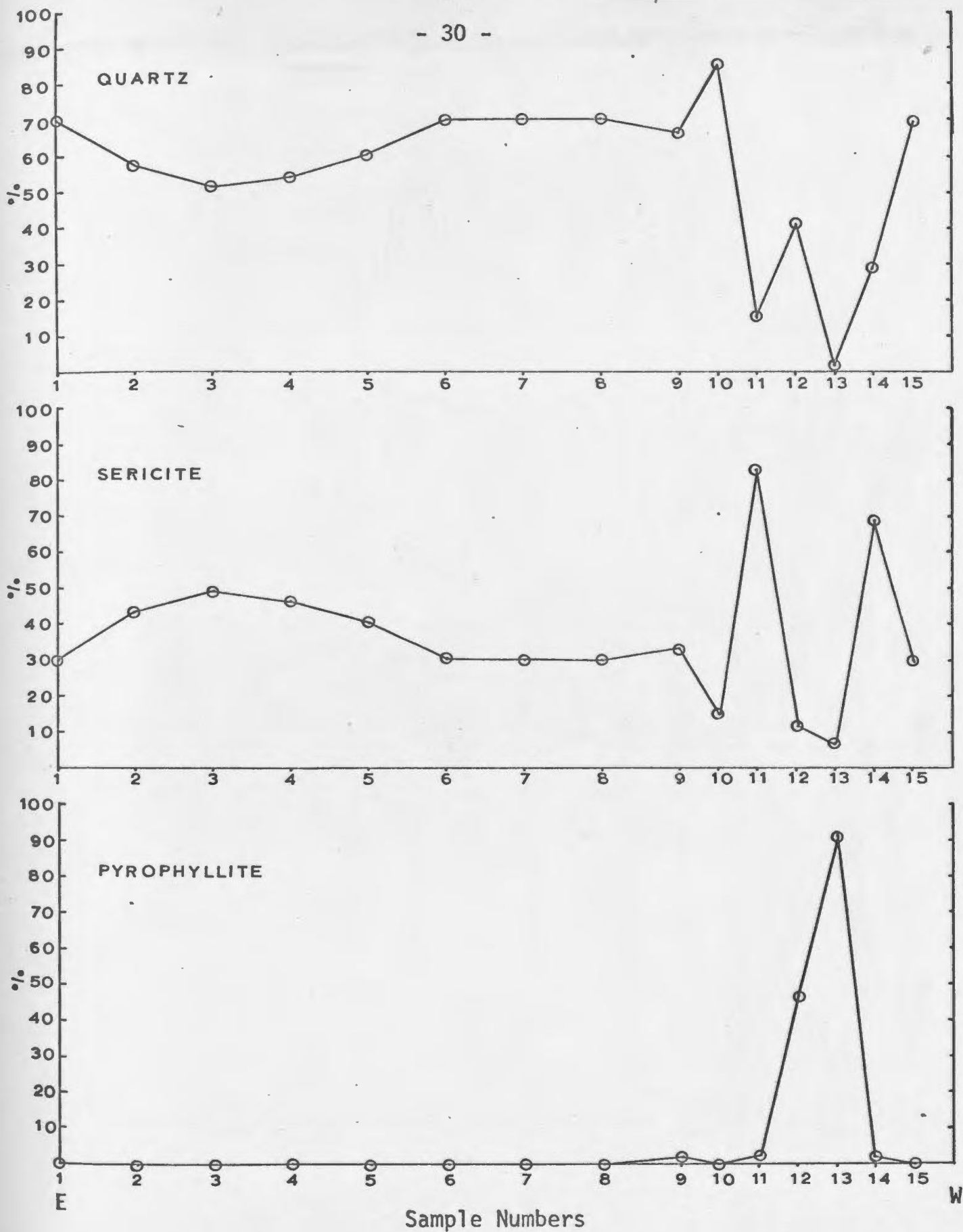


Figure IV-2: Dog Pond cross section

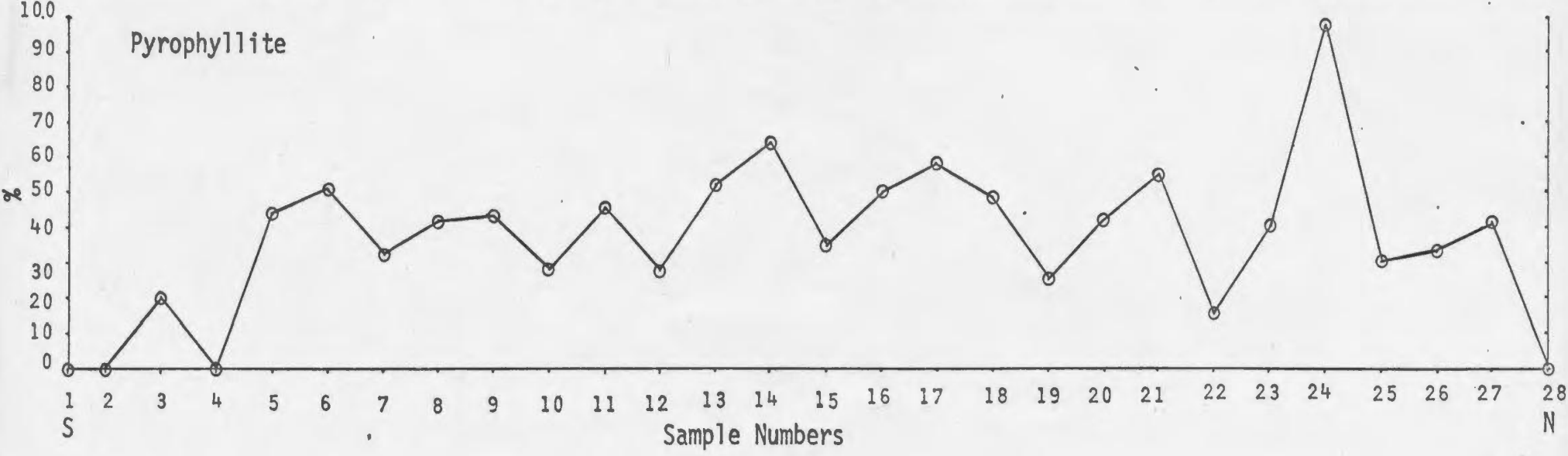
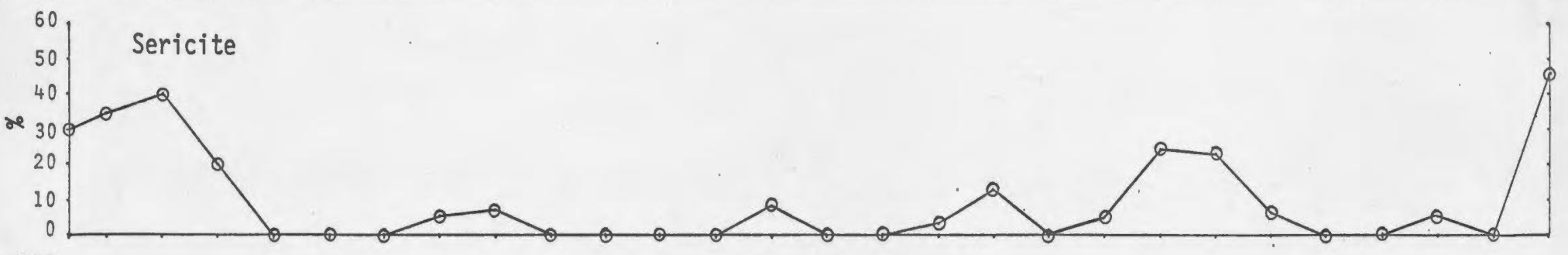
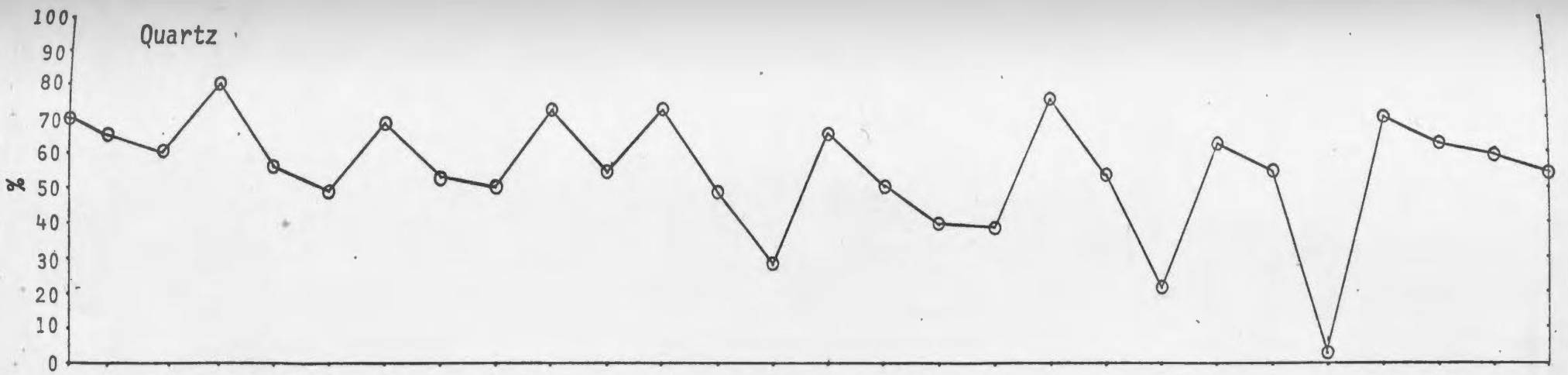


Figure IV-3: Oval Pit cross section

Geographical Distribution

All of the pyrophyllite deposits in the area, with the exception of Dog Pond, are located on the western side of the rhyolite belt near the granite contact. The Dog Pond prospect is believed to be underlain by granite at a shallow depth.

In the Dog Pond prospect, 6000 feet south of the Trans-Canada Highway (Map 1), practically pure pyrophyllite occurs in a 10 foot wide, 500 foot long lens which has a northerly strike and near-vertical dip. North of the Trans-Canada Highway and northeast of Trout Pond (Map 1), small pyrophyllite deposits have been opened by two shafts, an adit and an open cut. Further to the north there is a fairly large pyrophyllite deposit at Mine Hill, west of Johnnies Pond, as well as some low grade material near the eastern shore of Johnnies Pond (Map 1). The Mine Hill deposit contains several high grade lenses but on the whole the sericite content is too high for commercial exploitation. The only pyrophyllite deposit now being mined is the Oval Pit deposit, north of Johnnies Pond (Map 1). There are several high grade lenses north of the Oval Pit on the western side of the ridge but at least close to the surface they are not economic because of the high sericite and quartz content of the country rock and the low pyrophyllite to waste ratio.

Geologic Relations

All of the pyrophyllite deposits in the area are found in rocks of acidic composition, particularly in acidic flows. Pyrophyllite never occurs in "tuffaceous slates" but it is present in volcanic conglomerates containing acidic fragments at the base of and interbedded with "tuffaceous slates".

Vhay (1937) reported high grade pyrophyllite in conglomerates in the southern end of the Oval Pit but mining has left only sericitized conglomerates. However, about 200 feet south of the Oval Pit an exposure of highly pyrophyllitized and sericitized volcanic conglomerate can be seen. The "tuffaceous slates" are relatively unaltered except on the eastern margin of the Oval Pit where they have been bleached to a light green from the original dark green colour. Thin sections and x-ray diffraction *patterns* show that they have been altered to and replaced by chlorite and sericite. Sericite in particular is seen to be replacing grains and small veinlets of quartz.

The geologic distribution of the pyrophyllite is controlled by three factors: (1) proximity to the Holyrood granite, (2) acidic composition of the rocks and (3) structures in the rocks. The rhyolitic rocks were sheared and faulted in response to tectonic stresses more readily than the volcanic sediments which reacted by folding. The pyrophyllite is concentrated in zones of intense shearing, parallel to the axial plane cleavage in the volcanic sediments, or in fault and shear zones approximately perpendicular to the axial plane cleavage.

All of the low grade deposits (e.g. Dog Pond) trend parallel to the axial plane cleavage. At Mine Hill and the Oval Pit where there are two shear systems, one parallel to the axial plane cleavage and a more intense system approximately perpendicular to it, the alteration is more intensive and the percentage of pyrophyllite much higher, especially at the Oval Pit.

It will be shown later that the pyrophyllitization is hydrothermal in origin. The fault and shear zones, as well as the sheared granite contact,

acted as channelways for the hydrothermal solutions responsible for the alteration.

Form and Structure

The pyrophyllite in the thesis area occurs as single well-defined lenses or as a series of pockets and lenses making up a pyrophyllite zone. South of Dog Pond it occurs in a single well-defined lens which is about 500 feet long and varies from 6 to 15 feet wide. The center of the lens consists of about 70% pyrophyllite with occasional quartz-rich nodules (Figure IV-2). Outward from the center the pyrophyllite content decreases rapidly to 2 or 3 percent and the sericite content increases to 70 or 80 percent. Still further outwards the amount of sericite decreases to or below the level of sericite in the quartz-sericite schist to the east of the pyrophyllite lens; while the amount of quartz increases to 10 or 15% above the level of quartz in that rock. This single lens showing well-developed zoning best illustrates the distribution of pyrophyllite, sericite and quartz with respect to a particular channelway.

At the Oval Pit and Mine Hill the relationships are more complex since the pyrophyllite does not occur in one single lens but in a complex of pockets and lenses making up a pyrophyllite zone.

In view of the relatively poor exposure and low degree of pyrophyllite the other small pyrophyllite occurrences were not studied in detail.

At Mine Hill there are two directions of shearing or fracture cleavage. One direction is parallel to the axial plane cleavage in the

volcanic sediments and the general direction of cleavage in the rhyolites, N to N 30°E. There is another fault and shear system striking from easterly to ~~N~~ 120°~~E~~. Pyrophyllite-rich material occurs in pockets from 1 - 15 feet in diameter containing relatively unaltered siliceous nodules. It also occurs as thin sheets enclosing lenses of quartz-sericite-pyrophyllite rock oriented for the most part parallel to the easterly fault and shear system. There are also some branching lenses oriented parallel to the northerly-trending cleavage. Pyrophyllite often occurs as an interlacing network of thin laminae surrounding lenses of quartz-sericite-pyrophyllite rock or as "lenticles replacing the matrix between adjacent quartzose nodules. The pyrophyllite usually serves simply as a matrix for these nodules varying from a fraction of an inch to several feet in diameter" (Buddington, 1916). This elliptical or lenticular structure is also observed in quartz-sericite rock in which an aggregate of quartz and sericite acts as the matrix to quartz-rich nodules. The structure is characteristic in fact of many of the silicified and sericitized rhyolites in the area. The structure "may owe its origin to primary flowage phenomena, or to secondary dynamic forces, or probably to the former accentuated by the latter" (Buddington, 1916). The present writer favors the idea that it is a result of the combination of both processes, where cataclasis occurred contemporaneously with replacement.

In the Oval Pit area the pyrophyllite occurs in the same manner as at Mine Hill. However, the pyrophyllite to sericite ratio is much higher in the Oval Pit area. The high grade alteration zones at the Oval Pit are elongated parallel to the fault and shear zone trending 090° to 120°; the northerly regional cleavage is also observed in the area.

Detailed sampling of the Oval Pit on a line running N 10°E has revealed a general increase in the percentage of pyrophyllite from the margins of the alteration zone to the center, accompanied by a general decrease in the percentage of sericite (Figure IV-3). The fluctuations in the percentages reflect the complexity of the alteration zone and the difficulty of collecting a representative sample from an area with siliceous nodules in a pyrophyllitized and sericitized groundmass. Furthermore, some present low percentage areas of the Oval Pit are only remnants, left behind after large amounts of high grade material have been removed. Therefore, the present pattern has large deviations in detail from the original one.

In the main alteration zone there are numerous high grade pockets and lenses separated by rock with higher sericite and quartz content. Northward from a high sericite zone (samples 21 and 22, Figure IV-3), bordering the main alteration zone, is a very high grade lens containing practically pure pyrophyllite and 2 or 3 percent quartz; sericite, if present, is below detection level. Other exceptionally high grade lenses were probably present in the main alteration zone but have been removed by mining. Northward from the above lens the sericite content rises rapidly to over 40 percent; at this point the pyrophyllite content is nil or below the detection level.

Mineralogy

The minerals identified in the alteration zones are pyrophyllite $[Al_2Si_4O_{10}(OH)_2]$, sericite $[KA_2(AlSi_3O_{10})(OH)_2]$, quartz (SiO_2) , diaspore $[Al_2O_3(OH)_2]$, kaolinite $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$, barite $(BaSO_4)$ and rutile

(TiO₂). Most of the material in these zones consist of a fine-grained aggregate of pyrophyllite-sericite-quartz, pyrophyllite-quartz, pyrophyllite-sericite, or sericite-quartz.

Pyrophyllite commonly occurs as a very fine-grained aggregate but in some localities (e.g. North Carolina) it is formed as coarse radial aggregates; veins^{consisting} of a radial aggregate of pyrophyllite crystals are found cutting quartz-rich nodules in the Oval Pit area (Plate IV-1). Pyrophyllite is colorless in thin section, has a perfect basal cleavage, low to moderate relief and upper third order interference colors. The extinction is parallel or almost parallel to cleavage traces and parallel to elongate sections. Cleavage traces are parallel to the slower ray; elongate sections not showing cleavage are length slow. The interference figure is biaxial negative with a 2V of 53° to 60°.

Sericite is a phyllosilicate with very similar optical properties to pyrophyllite. The interference colors, upper second order, and the relief are lower for sericite but it is almost impossible to distinguish the two minerals when they occur in a fine-grained aggregate. The hardness of sericite is 2 1/2 on the cleavage and 4 across it, as compared to a hardness of 1 - 1 1/2 for pyrophyllite. Sericite is colorless or a pale shade of green, grey or brown. Using these properties highly sericitized rhyolite can sometimes be distinguished from highly pyrophyllitized rhyolite when the two minerals occur in a fine-grained aggregate. However, the hardness test is usually unreliable due to the variable quantities of associated quartz.

Buddington (1916) and Vhay (1937) describe the green alteration product often found in the matrix of spherulites and in some small alteration

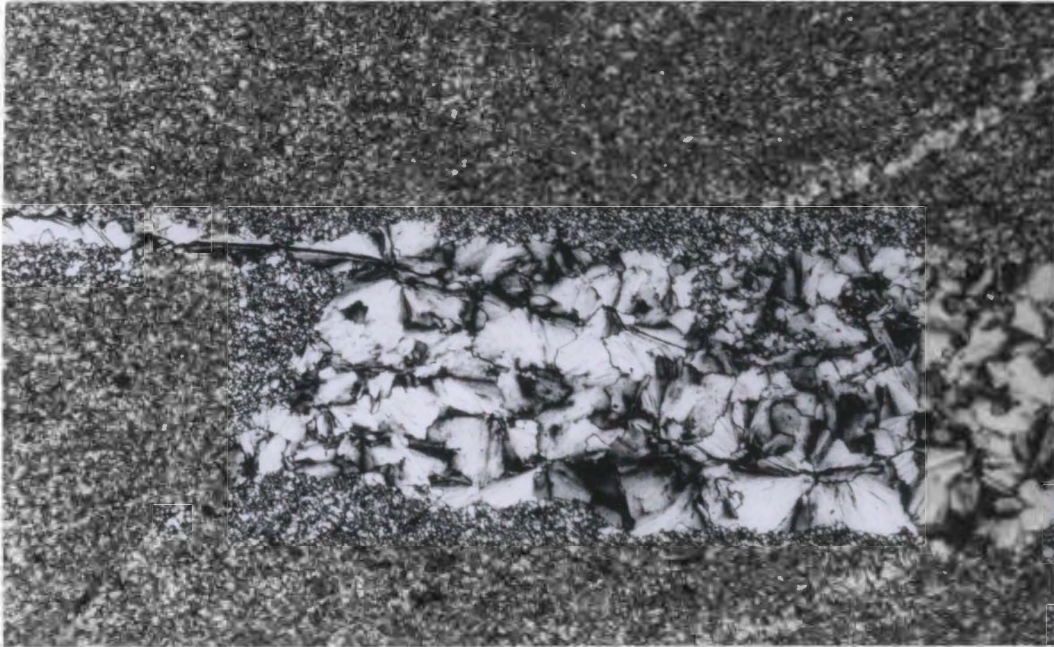


Plate IV-1. (X8, X nicols). Photomicrograph of a veinlet consisting of a radial aggregate of pyrophyllite crystals.



Plate IV-2. (X 6.3, X nicols). Photomicrograph of diaspore intimately intergrown with curved and distorted crystals of pyrophyllite.

zones as pinite, an impure variety of sericite. "Pinite", a descriptive term, is probably phengite, a member of a solid solution series in which the octahedral Al is replaced by Mg or Fe^{+2} and the tetrahedral Al by Si.

Quartz-rich nodules partially replaced by pyrophyllite, sericite, or pyrophyllite-sericite, occur in varying percentages throughout the deposits. Quartz also occurs as a replacement of rhyolite in much of the rhyolite belt as well as in later clear veins cutting the altered rocks.

Diaspore, intimately intergrown with curved and distorted tabular crystals of pyrophyllite (Plate IV-2), is found in nodules 1" - 4" in diameter sparsely distributed in practically pure pyrophyllite lenses. The mineral has good cleavage, high relief and upper third order interference colors. It is biaxial positive with a $2V$ of 84° . It is very brittle, has a conchoidal fracture and a hardness of $6\frac{1}{2}$ - 7. It is white or greyish in color and has a brilliant luster except on cleavage traces where it is pearly.

In the nodules diaspore is locally associated with barite which is found interstitial to diaspore and pyrophyllite crystals and as thin veinlets. Barite has three directions of cleavage at 90° and 78° . The relief is fairly high and the birefringence rather weak with maximum interference colors rarely above first order yellow or orange. The extinction is parallel to the best cleavage (001), but in (001) sections it is symmetrical. Barite is biaxial positive with a moderate axial angle. It is colorless to white and transparent, has a vitreous luster, perfect cleavage and a hardness of $3 - 3\frac{1}{2}$.

In the diaspore nodule kaolinite occurs as fine cloudy masses which have low relief and weak birefringence. Identification is not certain in thin section but a positive identification has been made by x-ray diffraction.

Rutile, most common in the diaspore nodules, forms small green prismatic crystals and irregular grains. The relief is very high and the extinction parallel. The interference colors are masked by the color of the mineral and by total reflection. Knee-shaped twins are very common and make certain the identification of the mineral.

Petrography

In thin section pyrophyllite and sericite have been observed replacing quartz-rich nodules in the alteration zones as well as silicified rhyolite on the margins of the alteration zones. Large clear quartz areas in the nodules have been partially recrystallized to a fine-grained aggregate and this aggregate has been selectively replaced by pyrophyllite and sericite. It is evident that there was a period of silicification prior to the formation of the phyllosilicates. This early silicification is probably connected with the widespread silicification in the rhyolite belt. Buddington believes the early silicification to be possibly genetically related to the extrusion of the rhyolites themselves (Buddington, 1916); the present writer believes it to be related to an early hydrothermal event since the silicification seems to be partially controlled by proximity to the Holyrood granite. Furthermore, there are isolated patches of almost completely unsilicified rhyolite in thoroughly silicified and sericitized rocks as well as in completely pyrophyllitized, sericitized and silicified rocks.

Small veinlets of quartz cut quartz-rich nodules and the highly altered rock surrounding them and are considered to have been formed at a late stage of the alteration to pyrophyllite and sericite but not after alteration ceased since the veinlets themselves are partially replaced along minute faults. They were probably formed by remobilization of quartz as a result of the formation of the phyllosilicates.

Pyrophyllitization and sericitization ^{are} ~~is~~ contemporaneous with deformation since the phyllosilicates are aligned subparallel to the cleavage with an increasingly random orientation away from individual cleavage planes. Deformation continued after the formation of the phyllosilicates, at least in some areas, since remnants of partially replaced quartz form "augen" in a matrix of pyrophyllite and sericite. Well-oriented flakes in the same thin-section, however, suggest considerable growth of the micas after the development of cleavage. It can only be concluded, therefore, that the alteration and deformation were contemporaneous, continuous processes, one facilitating the other, and that the process of alteration was one of replacement.

Chemistry

All of the fresh rhyolites analysed (samples 1-5, Table IV-1) are either Na- or K-Na rhyolites, the latter containing approximately equal percentages of K_2O and Na_2O . The percentage of Na_2O and the Na_2O/K_2O ratio in the pyrophyllitized and/or sericitized rhyolite are much lower than in the fresh rhyolites. The percentage of total alkalis is an indication of the sericite content, which increases outwards from the centers of the alteration zones. Since paragonite, $Na Al_2(AISi_3O_{10})(OH)_2$, is conspicuously

absent in the alteration zones and the widespread sericitized and silicified rhyolites, Na must occur as a substitution for K in sericite, a fact requiring the introduction of K into the system in order to reduce the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio. Mg, which is removed from the alteration zones, is localized in phengite, previously described as pinite, in minor shear zones and the matrix of spherulites. The 2.5 percent MgO in sample 14 (Table IV-1) is held only in phengite since chlorite does not occur in such rocks. The 1.9 percent in sample 15, a relatively fresh volcanic conglomerate, is accounted for by chlorite in the groundmass of the acidic pebbles; sericite occurs as an alteration of the groundmass and the pebbles but it is not known if it is the phengite variety.

The mobility of silica in the alteration zones is indicated by the fact that the percentage of SiO_2 in the highly pyrophyllitized material is significantly lower than the pyrophyllitized and sericitized rhyolite and considerably lower than the silicified rhyolite. Whether there has been an introduction of SiO_2 , apart from the early silicification, in the system as a whole is difficult to establish. Similarly it is difficult to establish if Al_2O_3 has been introduced into the highly pyrophyllitized areas or if the process was simply one of removal of SiO_2 , K_2O , and Na_2O . Although Al is considered to be one of the least mobile elements, the local concentrations of Al in the diaspore nodules suggest that some introduction of Al may have taken place.

Neither the writer's nor Buddington's samples (Figure IV-1) were chemically analysed for TiO_2 but an analysis of a silicified rhyolite breccia from the area (Papezik, 1970, personal communication) (Table IV-2)

shows 0.11 percent TiO_2 . Titania ranging from 0.52 to 0.90 percent has been reported in acidic volcanics of the Harbour Main Group in the Western Block (Papezik, 1969). This titanium content may account for the small amounts of rutile in the altered rocks.

TABLE IV-1: Rock Analyses

No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LOI	Total
1	78.76	12.42	1.06	0.56	0.27	0.29	5.68	0.53	99.57
2	78.30	11.44	0.76	1.40	0.14	3.35	3.62	0.98	99.99
3	73.28	16.00	1.32	0.58	0.16	0.70	7.43	0.19	99.66
4*	76.24	13.94	1.03	1.07	0.27	4.95	2.55	0.18	100.23
5*	80.60	11.27	1.03	0.66	0.31	4.68	1.16	0.60	100.31
6*	74.51	17.12	1.37	0.13	0.04	3.68	0.48	2.53	99.86
7*	72.10	21.51	0.54	0.49	0.04	2.21	0.42	3.32	100.63
8	84.52	11.91	0.17	0.18	0.07	0.43	0.10	2.10	99.48
9	70.50	24.28	0.28	0.08	0.17	0.24	0.20	4.30	100.05
10	80.34	16.17	0.15	0.12	0.18	0.18	0.09	2.82	100.05
11*	65.04	29.49	0.28	0.10	0.04	0.33	0.33	4.87	100.48
12*	88.09	9.53	0.20	0.58	0.05	n.d.	n.d.	1.72	100.17
13	61.28	31.38	0.32	0.16	0.04	0.93	0.40	5.30	99.81
14*	54.47	27.14	3.10	0.81	2.44	8.01	0.68	3.71	100.36
15	68.20	18.00	4.60	0.24	1.89	3.83	0.39	2.90	100.05
16	78.62	14.75	0.49	0.22	0.16	2.75	0.68	2.11	99.78

1. Flow rhyolite collected from an unreplaced remnant in altered rhyolite south of Dog Pond. A thin section reveals that it has been very slightly silicified, probably during the widespread early silicification.
2. Fresh rhyolite, except for some later fracture-filling calcite, collected from a rhyolite fragment in a volcanic mudflow about 3000' southeast of the southern end of Johnnies Pond.
3. Entirely fresh flow-banded rhyolite collected from the eastern side of the rhyolite belt 2500 ft. northeast of the Oval Pit.
- 4*. Slightly silicified dark-gray flow rhyolite collected at or near the present Trans-Canada Highway.
- 5*. Silicified drab spherulitic rhyolite collected about 2000' northeast of the Oval Pit.
- 6*. Pyrophyllitized and sericitized rhyolite collected from the matrix of silicified lenses at the present Oval Pit.

- 7*. Pyrophyllitized and sericitized rhyolite from Mine Hill. Matrix of spherulites.
8. Fine-grained aggregate of pyrophyllite, sericite and quartz from the Oval Pit (#10 on Oval Pit cross-section, Figure IV-3).
9. Pyrophyllitized matrix of quartz-rich nodules from detailed sampling of Oval Pit (#7, Figure IV-3).
10. Pyrophyllitized rhyolite from detailed sampling of Oval Pit (#14, Figure IV-3).
- 11*. Pyrophyllitized rhyolite from Mine Hill.
- 12*. Quartz-pyrophyllite nodule in high grade pyrophyllite (11*).
13. Practically pure pyrophyllite near a diaspore nodule, Oval Pit.
- 14*. Pinite—dark, dirty-green, waxy, matrix of spherulite, collected at or near the present Trans-Canada Highway.
15. Relatively fresh volcanic conglomerate from the south side of the Oval Pit (#1).
16. Sericitized volcanic conglomerate from the south side of the Oval Pit.

NOTE: Samples marked with an asterisk were collected and analysed by A.F. Buddington (1916). Writer's analyses by courtesy of American Olean Tile Company.

TABLE IV-2: Rock Analysis

SiO ₂	81.50
TiO ₂	0.11
Al ₂ O ₃	9.80
Fe ₂ O ₃	0.67
FeO	0.84
MnO	0.01
MgO	0.55
CaO	0.28
Na ₂ O	4.41
K ₂ O	0.96
P ₂ O ₅	0.04
CO ₂	0.00
H ₂ O	0.33 (total H ₂ O)
	<hr/>
	99.43

Silicified rhyolite breccia collected 1700 feet east of the creek flowing north from Little Pond, south side of highway, outcrop marked 1a. Note: Unpublished analysis from the files of V.S. Papezik, analyst, K. Ramlal, University of Manitoba.

CHAPTER V: DEVELOPMENT AND USE OF A SEMI-QUANTITATIVE X-RAY DIFFRACTION TECHNIQUE

Introduction

For reasons given previously, it was deemed expedient to develop a quantitative or semi-quantitative x-ray diffraction technique for the three-component system pyrophyllite-sericite-quartz. The writer attempted to develop a rapid method that could be adapted to a routine industrial use. After failure to develop an independent method and examination of several techniques used by other writers, it was decided to adopt and modify a method developed by Otalora and Hess (1969) for the purpose of the present study. The method is based on the change in peak-height ratios with concentration ratios of mineral pairs in a sample. Reasons for this will be given in a later section of this chapter.

Maximum peak intensities and reproducibility of these intensities are essential to any quantitative or semi-quantitative x-ray analysis of mineral pairs. Both these factors are controlled by the crystallite size of the samples being analysed. In general, maximum intensity and reproducibility are enhanced by a decrease in crystallite size. If the crystallite size is less than two microns, however, reproducibility is improved but only at the expense of intensity, which is reduced. It has been determined experimentally (Tatlock, 1966) that optimum reproducibility and near-maximum intensity are best attained where the maximum crystallite size is less than 40 microns and the minimum size is greater than 2 microns. It should be pointed out that particle size and crystallite size are two different properties since a coarsely-ground fine-grained rock may have a large particle size but a small crystallite size. A fine-grained rock must still be finely

ground, however, since in addition to a small crystallite size, random orientation is necessary for maximum peak intensities and reproducibility of these intensities. Preferred orientation is therefore undesirable and can be controlled by fine-grinding and careful sample packing.

The peak intensity of a mineral in a mixture varies with the concentration of the mineral and the ratio of the mass absorption coefficients of the mineral and the mixture. The theoretical relations are given by Klug and Alexander, 1954 (p. 410-416).

"Relations are expressed by the equation

$$I_1 = \frac{K_1 x_1}{\rho_1 [x_1(\mu_1^* - \mu_m^*) + \mu_m^*]}$$

I_1 is the peak intensity of the component, x_1 its weight fraction, and its corresponding absorption coefficient. μ_m^* is the mass absorption coefficient of the matrix, K_1 , a constant which depends upon the nature of component 1 and the geometry of the apparatus. The formula shows that in mineral assemblages with similar absorption coefficients, $\mu_1^* = \mu_m^*$, peak heights will change linearly with concentration. However, where $\mu_1^* \neq \mu_m^*$ the intensity-concentration curve is no longer linear" (Otalora and Hess, 1969, pp. 823-824).

"The mass absorption coefficient of any compound or composite material can be calculated from the relationship

$$\mu(\text{compound}) = \sum(\mu_i \cdot W_i)$$

where μ_i and W_i are individual mass absorption coefficients and weight

fractions" (Jenkins and DeVries, 1967, p. 16). Using this relationship the mass absorption coefficients of pyrophyllite, sericite and quartz were calculated as 33, 41 and 35, respectively.

Other Methods

Klug and Alexander (1954) and Bristol (1968) developed methods of indirect analysis which required the mixing of an internal standard with the sample to counter absorption effects. This method requires very careful and time-consuming weighing of samples and internal standard, an obvious disadvantage in a process suitable for a rapid industrial analysis. Tatlock (1966) developed a method in which he effectively correlated iron content with absorption in crystal mixtures and noted the effect of iron fluorescence on background intensity. He constructed intensity-concentration curves which he combined with background intensity curves to compensate for the absorption and fluorescence. Butler and Ragland (1969) used a modified version of Tatlock's method. The accuracy of both methods is dependent on the exact reproducibility of peak heights since absolute intensities are measured. Reproducibility is mostly dependent on a careful grinding technique that granulates sample powders to particle sizes allowing maximum diffraction intensities. Serious errors occur with inadequate grinding. The x-ray apparatus must also be carefully calibrated before use by standard powder mounts.

On the other hand, modal analysis of mineral concentration that treats the mineral phases of a rock as a series of mineral pairs (this writer's method) is less affected by deficiencies in grinding and requires neither calibration of the x-ray machine nor fixed instrument settings (Otalora and Hess, 1969).

Procedure

Sample Preparation

Samples were ground by Newfoundland Minerals Limited to pass a 100 mesh seive. About 50 grams of this 100 mesh material were spread evenly over a piece of 8 1/2" x 11" paper and divided into 1 inch squares, from each of which a small amount of material was removed making up enough to fill four standard aluminum holders. This material was ground by hand in an agate mortar and pestle for 5 or 10 minutes until all of it was judged to be a uniformly ground, sufficiently fine powder. This condition was usually reached when the powder became a soft, nearly frictionless material. Higher peak intensities and reproducibilities were obtained by this method than by grinding in a motor-driven mortar and pestle. A longer grinding time and non-uniformity of particle-size were two distinct disadvantages of the latter method when dealing with such small quantities of material.

Calibration Charts

Fifteen samples with chemical analyses for Al_2O_3 , Fe_2O_3 , K_2O and Na_2O , provided by Newfoundland Minerals Limited, were used as standard samples. The varying percentages of these oxides reflect varying percentages of pyrophyllite, sericite and quartz in the samples (Tables V-1 and V-2). Calculation of mineral percentages from oxide percentages was made, using average compositions of each of the minerals present (Deer, Howie and Zussman, 1962, pp. 16-18, 118). By assuming that all of the K_2O present went into the formation of sericite, fairly accurate results were obtained. Ten of the standard samples were later chemically analysed for SiO_2 and the results were used to check the preliminary calculations made without

TABLE V-1: Chemical Analyses of Standard Samples

No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	L.O.I.	Total
1	77.53	16.18	0.23	2.95	0.13	2.64	99.66
2	75.06	18.67	0.22	2.05	0.17	3.27	99.44
3	77.96	17.23	0.16	0.48	0.09	3.27	99.19
4	81.14	15.52	0.12	0.41	0.10	3.04	100.33
5	73.73	21.13	0.12	0.50	0.10	3.93	99.51
6	63.13	27.40	0.76	3.10	0.21	4.93	99.53
7	71.66	22.67	0.08	0.14	0.08	4.28	98.91
8	74.22	19.70	0.04	1.85	0.18	3.43	99.42
9	71.02	20.39	0.30	3.90	0.15	3.21	98.97
10	70.87	23.45	0.06	0.23	0.09	4.45	99.15
11	n.a	18.46	n.a	0.41	0.10	n.a	
12	n.a	17.84	n.a	0.72	0.12	n.a	
13	n.a	19.41	n.a	0.98	0.16	n.a	
14	n.a	16.91	n.a	0.85	0.10	n.a	
15	n.a	19.89	n.a	1.57	0.20	n.a	

Analyses supplied by Newfoundland Minerals Limited. SiO₂ analyses were done by the Department of Mines, Agriculture and Resources assay laboratory, Memorial University of Newfoundland.

TABLE V-2: Percentages of pyrophyllite, sericite and quartz calculated from chemical analyses (Table V-1).

Sample No.	a	b	c	d	e	f	g
1	20.16	32.27	47.57	77.53	12.98	15.31	49.24
2	40.00	22.43	37.57	75.06	25.75	10.65	38.56
3	54.39	5.25	40.36	77.96	35.02	2.49	40.45
4	49.24	4.49	46.27	81.14	31.70	2.13	47.31
5	67.80	5.47	26.73	73.73	43.65	2.60	27.48
6	57.61	33.91	8.48	63.13	37.09	16.11	9.93
7	77.63	3.10	19.27	71.66	50.00	1.47	20.19
8	46.10	20.24	33.66	74.22	29.68	9.61	34.93
9	23.17	42.67	34.26	71.02	14.92	20.27	35.83
10	79.24	2.52	18.24	70.87	51.01	1.20	18.66

a: calculated percentage of pyrophyllite

b: calculated percentage of sericite

c: calculated percentage of quartz: $Q = 100\% - (a + b)$

d: the total percentage of SiO_2 in each sample obtained from chemical analysis.

e: calculated percentage of SiO_2 in pyrophyllite

f: calculated percentage of SiO_2 in sericite

g: calculated percentage of free quartz: $Q = d - (e + f)$

Note: Compare results obtained without knowledge of the SiO_2 content (c) and results obtained using the total SiO_2 content (g).

TABLE V-3: Calculated mineral ratios and corresponding peak-height ratios.

Sample No.	P	S	Q	Ps	Qp	Qs	(P/P+S) x 100	(Q/Q+P) x 100	(Q/Q+S) x 100
1	20%	32%	48%	39%	71%	60%	61	90	92
2	40%	22%	38%	65%	49%	63%	80	81	94
3	54%	5%	41%	92%	43%	89%	95	73	98
4	49%	4%	47%	93%	49%		95	80	
5	68%	5%	29%	93%	28%	84%	95	59	96
6	58%	34%	8%	63%	12%	19%	69	43	63
7	78%	2%	20%	98%	20%	91%	98	44	97
8	46%	20%	34%	70%	43%	63%	79	75	92
9	23%	43%	34%	35%	60%	44%	61	82	87
10	79%	3%	18%	96%	19%		97	48	
11	60%	4%	36%	94%	38%		95	67	
12	54%	8%	38%	87%	41%	83%	94	70	97
13	56%	11%	33%	84%	37%	76%	92	69	96
14	49%	9%	42%	85%	46%	82%	91	78	97
15	50%	17%	33%	75%		65%	86		95

P: percent pyrophyllite

S: percent sericite

Q: percent quartz

Ps: pyrophyllite/sericite ratio

Qp: quartz/pyrophyllite ratio

Qs: quartz/sericite ratio

(P/P+S) x 100: peak-height ratio of pyrophyllite (002)/sericite (002)

(Q/Q+P) x 100: peak-height ratio of quartz (10T1)/pyrophyllite (002)

(Q/Q+S) x 100: peak-height ratio of quartz (10T1)/sericite (002)

TABLE V-4: Polynomial regression of degree 2, table of residuals.

Observation No.	Sample No.	x value	y value	y estimate	Residual
1	9	35.00000	61.00000	59.39359	1.60641
2	1	39.00000	61.00000	61.64050	-0.64050
3	6	63.00000	69.00000	75.89558	-6.89558
4	2	65.00000	80.00000	77.14337	2.85663
5	8	70.00000	79.00000	80.30312	-1.30312
6	15	75.00000	86.00000	83.52042	2.47958
7	13	84.00000	92.00000	89.45660	2.54340
8	14	85.00000	91.00000	90.12769	0.87231
9	12	87.00000	94.00000	91.47676	2.52324
10	3	92.00000	95.00000	94.88976	0.11024
11	5	93.00000	95.00000	95.57927	-0.57927
12	4	93.00000	95.00000	95.57927	-0.57927
13	11	94.00000	95.00000	96.27107	-1.27107
14	10	96.00000	97.00000	97.66159	-0.66159
15	7	98.00000	98.00000	99.06133	-1.06133

x: Ps

y: $(P/P+S) \times 100$

Note: x value and y estimate plotted against each other to construct a calibration chart for the mineral pair pyrophyllite-sericite.

TABLE V-5: Polynomial regression of degree 3, table of residuals.

Observation No.	Sample No.	x value	y value	y estimate	Residual
1	6	12.00000	43.00000	41.03506	1.96494
2	10	19.00000	48.00000	47.65514	0.34486
3	7	20.00000	44.00000	48.68214	-4.68214
4	5	28.00000	59.00000	57.33890	1.66110
5	13	37.00000	69.00000	67.31798	1.68202
6	11	38.00000	67.00000	68.39699	-1.39699
7	12	41.00000	70.00000	71.55884	-1.55884
8	8	43.00000	75.00000	73.58893	1.41107
9	3	43.00000	73.00000	73.58893	-0.58893
10	14	46.00000	78.00000	76.48703	1.51297
11	2	49.00000	81.00000	79.17230	1.82770
12	4	49.00000	80.00000	79.17230	0.82770
13	9	60.00000	82.00000	86.53581	-4.53581
14	1	71.00000	90.00000	88.46938	1.53062

x: Qp

y: $(Q/Q+P) \times 100$

Note: x value and y estimate plotted against each other to construct a calibration chart for the mineral pair quartz-pyrophyllite.

TABLE V-6: Polynomial regression of degree 3, table of residuals.

Observation No.	Sample No.	x value	y value	y estimate	Residuals
1	6	19.00000	63.00000	63.09814	-0.09814
2	9	44.00000	87.00000	86.42661	0.57339
3	1	60.00000	92.00000	92.82314	-0.82314
4	8	63.00000	92.00000	93.55374	-1.55374
5	2	63.00000	94.00000	93.55374	0.44626
6	15	65.00000	95.00000	93.98146	1.01854
7	13	76.00000	96.00000	95.73332	0.26668
8	14	82.00000	97.00000	96.47134	0.52866
9	12	83.00000	97.00000	96.59312	0.40688
10	5	84.00000	96.00000	96.71632	-0.71632
11	3	89.00000	98.00000	97.37587	0.62413
12	7	91.00000	97.00000	97.67226	-0.67226

x: Qs

y: $(Q/Q+S) \times 100$

Note: x value and y estimate plotted against each other to construct a calibration chart for the mineral pair quartz-sericite.

knowledge of the SiO_2 content (Table V-2). For further details of calculations, see appendix 1. From the calculated percentages of pyrophyllite, sericite and quartz the pyrophyllite/sericite ratio (Ps), quartz/pyrophyllite ratio (Qp), and quartz/sericite ratio (Qs) were calculated. [For example (sample 1, Table V-3): $20\% \text{ P} + 32\% \text{ S} = 52\%$
 $20/50 = 38.5$ percent pyrophyllite with respect to sericite.]

Using $\text{CuK}\alpha$ radiation and a Ni filter, four separate specimens of each sample, mounted in aluminum holders, were run at a scanning speed of $1^\circ 2\theta/\text{min}$. and a chart speed of $5^\circ 2\theta/\text{in}$. ^{on a Philips X-Ray diffractometer,} These scanning and chart speeds gave very sharp reproducible peaks and for the three minerals concerned slower speeds did not improve the results. The first holder was scanned from 8° to 30° to verify that only the three minerals, pyrophyllite, sericite and quartz were present. Three more runs were made of separate sample holders for which the peaks S(002), P(002), and Q(10T1) were scanned. The intensities were measured above a straight line through the background, and the average intensity for each of the peaks calculated. Since peak-height ratios were used in this technique, diffractometer parameters were varied to facilitate the measurement of peak heights. From the average intensity of S(002), P(002) and Q(10T1) for a given sample, the ratios $(\text{P}/\text{P}+\text{S}) \times 100$, $(\text{Q}/\text{Q}+\text{P}) \times 100$ and $(\text{Q}/\text{Q}+\text{S}) \times 100$ were calculated (Table V-3).

A polynomial regression analysis by Fortran IV computer was made for Ps against $(\text{P}/\text{P}+\text{S}) \times 100$ (Table V-4), Qp against $(\text{Q}/\text{Q}+\text{P}) \times 100$ (Table V-5) and Qs against $(\text{Q}/\text{Q}+\text{S}) \times 100$ (Table V-6), in order to obtain a best fit for the points. The x values and y estimates (Tables V-4, 5, 6) were plotted against each other to obtain three calibration charts (Figure IV-1)

from which P_s , Q_p and Q_s can be obtained for unknowns.

Modal Analysis of Unknowns

Unknown samples collected from the Oval Pit and Dog Pond alteration zones (Map 1) were run on an x-ray diffractometer at a scanning speed of $1^\circ 2\theta/\text{min}$. and a chart speed of $5^\circ 2\theta/\text{inch}$. Four separate specimens of each sample were analysed and the average intensities of the peaks $P(002)$, $S(002)$ and $Q(10\bar{1}1)$ were calculated. From these values, $(P/P+S) \times 100$, $(Q/Q+P) \times 100$, and $(Q/Q+S) \times 100$ were calculated. For a given value of $(P/P+S) \times 100$, for example, a value for P_s can be read directly from a calibration chart (Figure IV-1a). Similarly, values for Q_p and Q_s can be obtained from Figure IV-1b, c. By converting mineral ratios into numerical ratios the percentage of pyrophyllite, sericite and quartz in each sample can be calculated (Table V-7). It should be noted that for a three component system, only two calibration charts need be used; the third mineral percentage can be obtained by subtraction. For a two component system, a modal analysis can be read directly from one calibration chart.

The variations in the percentage of pyrophyllite, sericite and quartz in the Oval Pit and Dog Pond alteration zones were plotted against sample localities (Figures IV-2 and IV-3) and the results used in the study of the geology of the pyrophyllite deposits, dealt with in detail in chapter IV.

TABLE V-7: Percentage calculations from mineral ratios

<u>Mineral Pair</u>	<u>Peak-height ratios</u>	<u>Mineral ratios by calibration charts</u>	<u>Numerical ratios</u>
#4 (Figure IV-3)			
Pyrophyllite-sericite	67	48% - 52%	1:1.083
Pyrophyllite-quartz	91	25% - 75%	1:3.000
#18 (Figure IV-3)			
Pyrophyllite-sericite	97	95% - 5%	1:0.053
Pyrophyllite-quartz	70	60% - 40%	1:0.066
#28 (Figure IV-3)			
Quartz-sericite	91	54% - 40%	

Weight percent of minerals

	Pyrophyllite	Sericite	Quartz
#4	20%	40%	60%
#18	58%	3%	39%
#28	--	46%	54%

CHAPTER VI: THE ORIGIN OF THE PYROPHYLLITE DEPOSITS

Other Deposits

Before discussing the origin of the Manuels pyrophyllite deposits, reference should be made to the ideas of other writers on the origin of pyrophyllite deposits elsewhere.

Clapp (1914) described pyrophyllite deposits on the west side of Vancouver Island, British Columbia. According to Stuckey (1967), "both alunite and pyrophyllite occur in andesite, dacite, and associated pyroclastic rocks. ^{These rocks} ~~This series~~, and in particular its fragmental parts, has been metasomatically altered to quartz-sericite-chlorite rocks, quartz-sericite rocks, quartz-pyrophyllite rocks and quartz-alunite rocks. Clapp concluded that most of the mineralization was caused by hot sulphuric acid solutions of volcanic origin which were active during the accumulation of the pyroclastic rocks, and as a result of relatively shallow depths and low pressure. He postulated little change in the bulk composition of the original volcanic rocks and interpreted most of the new minerals as having been developed from feldspars. In general, however, the quartz-pyrophyllite rocks show a net gain in alumina, a loss of potash and either a loss or gain in silica." (Stuckey, 1967, pp. 14-15).

Jahns and Lance (1950) described pyrophyllite deposits, in the San Diequito area, California, which occur as an alteration of flows, tuffs and breccias of andesitic to rhyolitic composition. These rocks have been regionally metamorphosed prior to pyrophyllitization and silicification; the alteration is related to fracture and shear zones. Quartz and pyrophyllite, often of the same general age, are believed to be replacing

feldspars; the writers suggested that there has been an introduction of SiO_2 , Al_2O_3 and probably (OH). They concluded that the deposits were formed hydrothermally under conditions of intermediate temperatures and pressures.

The pyrophyllite deposits of North Carolina, the most important source of pyrophyllite in North America, have been described by J. L. Stuckey. Stuckey (1967) concluded that they were formed by metasomatic replacement of acid tuffs and breccias of rhyolitic and dacitic composition. He suggested that the pyrophyllitization was accompanied by the introduction of SiO_2 , Al_2O_3 and water and gave the following criteria as evidence of the replacement origin of the deposits:

1. Gradational contacts between pure pyrophyllite and unaltered country rocks.
2. The preservation of structures of the primary rocks in the mineralized rocks, such as bedding planes of the finer tuffs, and fragmental outlines of the coarser tuffs and breccias.
3. The presence of masses and lenses of practically pure or only partly altered country rocks, apparently unattached and completely surrounded, in the mineral bodies.
4. The introduction of some elements and the removal of others.
5. The lack of any noticeable change in the volume of the original rocks during the mineralization processes.
6. The massive and homogeneous structure of the pyrophyllite.

He deduced the following sequence of events:

1. The metamorphism of the volcanic fragmental and flow rocks in which the mineral bodies were later formed.
2. The silicification of volcanic fragmental and flow rocks by metasomatic processes as is indicated by the presence of original structures of the volcanics in the silicified materials, and by the presence of entirely surrounded fragments of only partly silicified volcanic rocks in the quartz areas.
3. The development of pyrite in the silicified areas, accompanying or immediately following the silicification of the volcanics.
4. The development of chloritoid to some extent in all the pyrophyllite bodies and in abundance in parts of these deposits that are near iron-rich formations.
5. The development of sericite by the replacement of previously silicified fragmental and flow rocks.
6. The development of pyrophyllite by replacement of the previously silicified and mineralized tuffs and breccias, closely associated with or immediately following the formation of the sericite.

Stuckey further concluded that the deposits formed under intermediate temperatures and pressures along lines of weakness, either fault zones or shear zones. He suggested that the solutions were furnished by igneous rocks that were intruded close to the surface but have not been exposed by erosion.

Zen (1961) minimized the role of hydrothermal solutions in the

formation of the pyrophyllite deposits of North Carolina and suggested that they represent equilibrium metamorphic assemblages. He considered the presence of 3-phase mineral assemblages -- quartz-kaolinite-pyrophyllite, pyrophyllite-andalusite-quartz, and kaolinite-diaspore-pyrophyllite -- in the ternary system $Al_2O_3 - SiO_2 - H_2O$ to indicate that water acted as a fixed component. He added, however, that this conclusion did not necessarily imply the absence of a free solution phase (hydrothermal solutions); it only implies that such a phase did not circulate freely through the system destroying the buffering mineral assemblages. He suggested that deep weathering of volcanics produced "saprolite" bodies which were buried by later volcanics and subsequently metamorphosed; during metamorphism the "saprolite" bodies acted as a closed system. The different mineral assemblages reflect relative concentrations of Al_2O_3 , SiO_2 and H_2O at different parts of the deposits.

In the Brooks Range area of Alaska, pyrophyllite occurs in quartzite and associated quartzitic conglomerates which unconformably overlie metamorphic rocks of the greenschist facies (Reed and Hemley, 1966). The conglomerates are at the base of a sequence of argillites and siltstones. The pyrophyllite occurs as a replacement of the original matrix (postulated to be kaolinite), quartz intergrowths, and detrital quartz grains. Locally, pyrophyllitization is so intense that all original textures have been destroyed. The pyrophyllite tends to be restricted to the conglomerates and quartzites but it does occur in both the overlying and underlying rocks; although it is confined to within a few feet of the contacts.

To explain the mineral assemblage, pyrophyllite-sericite-quartz, Reed and Hemley (1966) suggested that extensive weathering of the metamorphic

rocks provided a source for quartzite and conglomerate containing minor detrital clay minerals, particularly kaolinite type clays, but few feldspars or other mineral contaminants. During folding and low grade metamorphism, pyrophyllite was formed by reaction of kaolinite with associated quartz. From the experimental work of Hemley and Jones (1964) and later work by Hemley (Reed and Hemley, 1966), on the stability of kaolinite, the writers concluded that the pyrophyllite formed at about 300°C and possibly lower.

Experimental Work

Hemley and Jones (1964) established reaction curves for the system $K_2O - Al_2O_3 - SiO_2 - H_2O$ (Figure VI-1). Reaction curve 1 in Figure VI-1 represents the decomposition of K-feldspar to K-mica plus quartz, reaction curve 2 represents the decomposition of K-mica to kaolinite below about 350°C, reaction curve 3 represents the decomposition of K-mica to pyrophyllite above about 350°C. These reactions occur at low alkali-ion/ H^+ ratios. The experiments were carried out in the presence of quartz at a total pressure of 1000 bars. An increase in the total pressure favors the formation of pyrophyllite in a higher alkali-ion environment. Dissolved electrolytes and supersaturation with respect to quartz favours the formation of pyrophyllite at lower temperatures.

Superimposed on Figure VI-1 is the decomposition temperature of kaolinite to pyrophyllite in a pure-water environment. The reaction kaolinite + quartz = pyrophyllite took place in the region of 380°C, at 1000 bars PH_2O , in runs of moderate duration (a few weeks). In a later run (1 year) by Hemley (Reed and Hemley, 1966) pyrophyllite was produced from kaolinite plus quartz at 300°C and 1000 bars PH_2O . Reed and Hemley

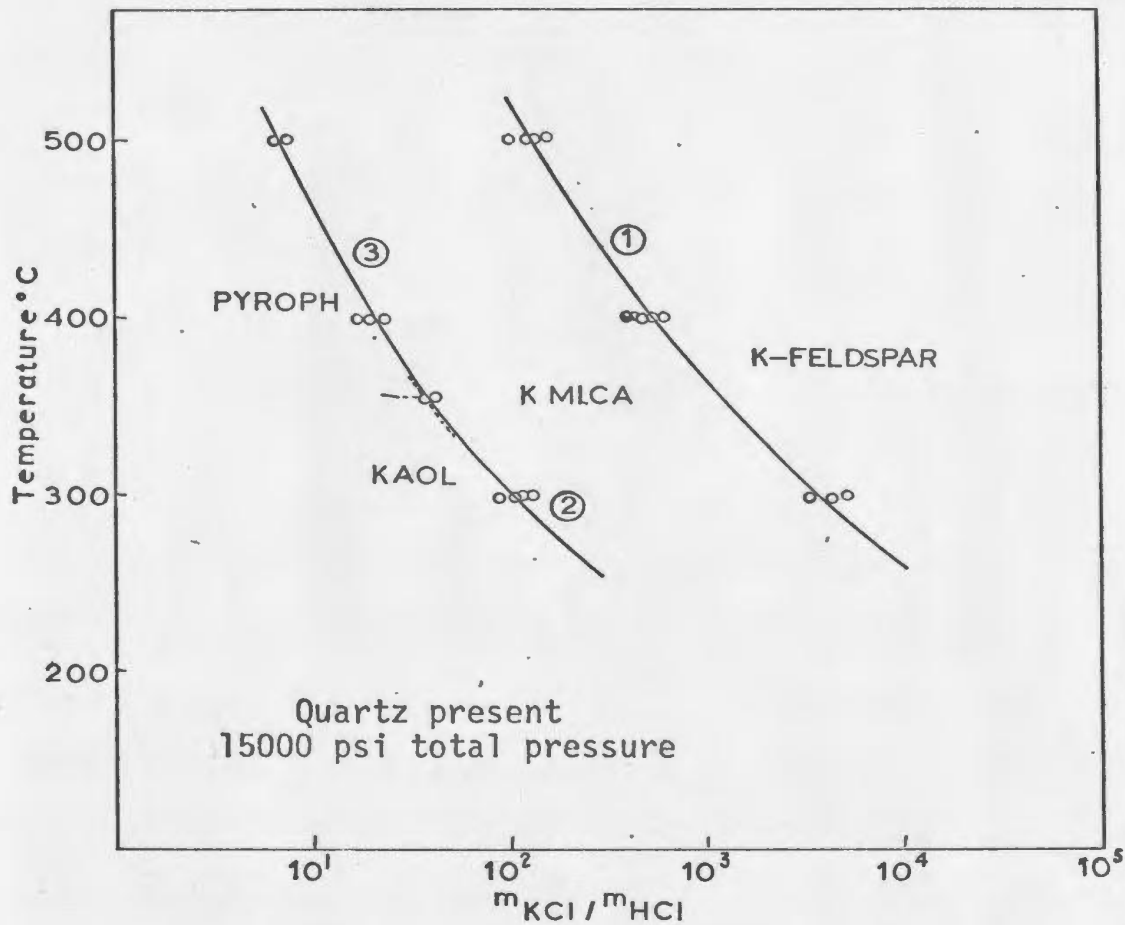


Figure VI-1: Reaction curves for the system $K_2O-Al_2O_3-SiO_2-H_2O$. The dashed line indicates experimental decomposition temperature of kaolinite in 0.5m KCl solution. Adopted from Hemley and Jones (1964).

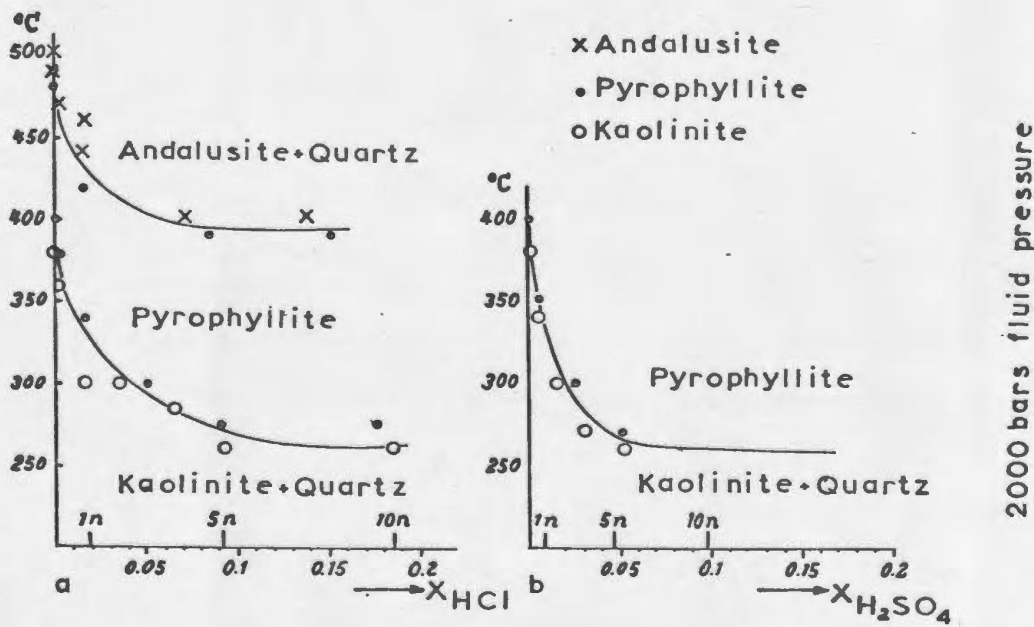


Figure VI-2a: Upper and lower temperature stability limits of pyrophyllite with different mole fractions of HCl in the fluid phase. Figure VI-2b: Lower temperature stability limit of pyrophyllite with different mole fractions of H_2SO_4 in the fluid phase (Althaus, 1966).

suggested that at lower water pressures and higher silica activities the upper stability limit of kaolinite would be further depressed. The kaolinite to pyrophyllite transition should also be favored by a large differential between total pressure and P_{H_2O} ; confining pressure favors the phase of higher density and lower hydration and entropy (Fyfe and others, 1958).

Experimental work by Althaus (1966) indicates that strong acids (HCl , H_2SO_4) bring about a relatively large decrease in both the upper and lower stability limits of pyrophyllite (Figures VI-2a, 2b). Mixtures of quartz and kaolinite were subjected to isochemical hydrothermal experiments at 2000 bars fluid pressure. The lower stability limit of pyrophyllite is decreased to about $275^{\circ}C$ in a 5N HCl solution, and the upper stability limit to $400^{\circ}C$ (Figure VI-2a). The lower stability limit of pyrophyllite is lowered to $270^{\circ}C$ in a 10N H_2SO_4 solution (Figure VI-2b).

Origin of the Manuels Deposits

Evidence for Replacement Origin

The field, microscopic and chemical evidence as well as x-ray diffraction modal analyses, indicate that the pyrophyllitization, sericitization, and silicification in the thesis area are the result of the metasomatic replacement of acidic pyroclastics and flows. In summary, the following criteria support the above conclusion:

1. The controls of the mineralization
 - (a) proximity to the Holyrood Granite
 - (b) acidic composition of the host rocks
 - (c) structures in the rocks: local fault and shear zones
 - (d) the degree of shearing.

2. The occurrence of pyrophyllite in a single well-defined lens (e.g. Dog Pond) or as a series of pockets and lenses to make up a pyrophyllite zone (e.g. Oval Pit area).
3. The massive and homogeneous structures of the mineralized rocks.
4. The preservation of primary structures in the mineralized rocks, such as pebbles of a conglomerate, fragments of a breccia, or flow structures.
5. Gradational contacts between highly pyrophyllitized rhyolite and unaltered country rock.
6. Zoning of the deposits (Figure IV - 2,3):
 - (a) a decrease in the percentage of pyrophyllite (sometimes associated with kaolinite and diaspore) outwards from the center, ~~reflecting a decrease in Al_2O_3~~ .
 - (b) an increase in the percentage of sericite and quartz outwards from the center, reflecting an increase in K_2O and SiO_2 .
 - (c) a marked increase in sericite on the margins of a single lens or alteration zone, reflecting an increase in K_2O , followed outwards by a marked increase in quartz, reflecting an increase in SiO_2 .
7. Replacement textures: rhyolite by quartz; quartz by sericite; quartz by pyrophyllite.
8. The occurrence of isolated patches of almost completely unaltered rhyolite in thoroughly silicified and sericitized rock.
9. The occurrence of isolated patches of relatively unaltered rhyolite in completely pyrophyllitized, sericitized and silicified rocks.

10. The introduction of some elements and the removal of others without any noticeable change in volume or porosity, as shown by the

~~analyses in Table IV-1~~; mineral and chemical composition of the rocks:
possible

- (a) /introduction of K into the system as a whole.
- (b) possible introduction of Al into the system as a whole.
- (c) removal of Si, K, and Na from the centers of the alteration zones and a more complex migration of these elements within the zones.
- (d) removal of Mg from the alteration zones and the concentration of that element in the mineral phengite in minor alteration zones.

The sequence of events ~~are~~^{is} believed to be as follows:

1. The silicification of the pyroclastics and flows by metasomatic processes. This is shown by the preservation of original textures and structures in silicified rock, by the presence of entirely surrounded fragments of relatively fresh rock in thoroughly silicified and sericitized rock, and by the later replacement of the quartz by phyllosilicates.

2. The replacement of quartz by pyrophyllite and sericite accompanied or immediately followed by further silicification of the margins of the alteration zones and possibly of the country rock.

Source of the Mineralizing Solutions

The close proximity of the alteration zones to the Holyrood granite - Harbour Main contact, the decrease in alteration away from the contact, the occurrence of the highly altered material in fault and shear zones, and the sericitization of the granite itself along its sheared contact with the Harbour Main group, indicate that the mineralizing solutions originated as late magmatic solutions emanating from the Holyrood granite.

Devonian and earlier Paleozoic granites which intrude Avalon platformal rocks in the Western Block may possibly intrude the Central Block but have not been exposed by erosion. It may be argued that the above relations could possibly hold if these younger granites were the source of the hydrothermal solutions; the sheared granite contact merely acted as a channelway for the solutions. To the north of the thesis area Lower Cambrian and younger beds unconformably overlie the Harbour Main group and the Holyrood granite of the Central Block. It is generally believed that the Central Block acted as a stable mass during Palaeozoic disturbances as shown by the lack of any regional cleavage in the Cambro-Ordovician sequence; the same rocks in the Western Block, however, have picked up a distinct regional cleavage. It has been earlier established that the replacement and deformation in the thesis area were contemporaneous processes. If the deformation of the Precambrian rocks, and hence the replacement, were Palaeozoic in age, the Palaeozoic rocks, the abundant shales in particular, would surely have picked up a regional cleavage. From the above evidence it can be firmly established that the replacement and deformation is Precambrian in age and is almost certainly related to the Holyrood granite.

Conditions of Formation of the Pyrophyllite Deposits

The process of formation of pyrophyllite in the thesis area was not simply the alteration of feldspars to sericite and hence to pyrophyllite and minor kaolinite as in the experiments of Hemley and Jones (1964). In fact, replacement of rhyolites by quartz and later replacement of quartz by phyllosilicates were probably the predominant processes. There was an overall introduction of SiO_2 , K_2O and possibly Al_2O_3 . Nevertheless, the

stability relations of pyrophyllite, sericite and kaolinite, as determined by Hemley and Jones (1964) are significant. The lower stability limit of pyrophyllite is probably significantly lower than 380° in the thesis area since quartz is so abundant in the system, which favors the formation of pyrophyllite at a lower temperature. The presence of barite in the diaspore nodules also strongly suggests the presence of H_2SO_4 in the hydrothermal solutions, further decreasing the lower stability limit of pyrophyllite.

Alunite $[KA_3(SO_4)_2(OH)_6]$, pyrophyllite and kaolinite are stable under acid conditions at 385°C (Hemley and others, 1969). Although barite, rather than alunite occurs with pyrophyllite and minor kaolinite in the Manuels deposits, the above stability relations may be relevant in this case.

The temperature-pressure conditions of formation of the Manuels pyrophyllite can only be deduced from experimental work and the geology of the deposits but the alteration may have taken place at a temperature below 380°C and possibly close to 270°C at a total pressure of 1000 bars and an even lower fluid pressure.

The increase in sericite outwards from the center of the alteration zones (Figures IV-2,3) can be explained by the leaching of alkalis from the centers of the zones, increasing the alkali-ion/ H^+ ratio in the margins of the zones, thus favoring the formation of sericite rather than pyrophyllite (Hemley and Jones, 1964). The silica leached from the centers of the alteration zones ^{was} ~~were~~ deposited on the margins of these zones and probably throughout much of the rhyolite belt.

Summary

Rocks of the thesis area belong to the Late Precambrian Harbour Main Group which is intruded by the Late Precambrian Holyrood Plutonic Series. The Harbour Main Group consists of acidic pyroclastics, acidic flows, volcanic sediments, volcanics of predominantly andesitic composition and basaltic flows. The Group is characterized by open upright folds and occupies the western limb of a major syncline. Associated with the folding is a fairly well-developed fracture cleavage associated with local shearing of the rhyolite. The Holyrood Plutonic Series, in the area, consist of quartz monzonite and associated rhyodacite porphyry.

The Manuel's pyrophyllite deposits are restricted to rocks of acidic composition and are localized by fault and shear zones closely associated with the Harbour Main - Holyrood granite contact. The alteration process was one of metasomatic replacement by late stage hydrothermal solutions, rich in Si, K and possibly Al, emanating from the Holyrood granite. The replacement, contemporaneous with deformation, involved not only the introduction of the above elements but also migration of K, Na, and Si within the alteration zones and of K, Na, Si, and Mg away from these zones. The alteration is believed to have taken place at a total pressure of about 1000 bars, a fluid pressure probably somewhat below this, and at a temperature below 380°C, possibly approaching 270°C.

Acknowledgments

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Appendix 1: Calculations of the percentage of pyrophyllite, sericite and quartz in standard samples from chemical analysis (Table V-1).

Given: (Deer, Howie and Zussman, 1962)

1% K ₂ O	≡	10.94%	Sericite
1% K ₂ O	≡	90.90%	Pyrophyllite
1% Al ₂ O ₃	≡	3.10%	Sericite
1% Al ₂ O ₃	≡	3.50%	Pyrophyllite

Sample #1 (Table V-1,2)

Sample contains 2.95% K₂O. Assume all K₂O in sericite

1% K ₂ O	≡	10.94%	Sericite (given)
2.95% K ₂ O	≡	32.27%	Sericite
1% Al ₂ O ₃	≡	3.1%	Sericite
1% Sericite	≡	.323%	Al ₂ O ₃
32.27% Sericite	≡	10.42%	Al ₂ O ₃

But sample contains 16.18% Al₂O₃; therefore,

16.18% — 10.42% = 5.76% Al₂O₃ in pyrophyllite

1% Al₂O₃ ≡ 3.5% pyrophyllite

5.76% Al₂O₃ ≡ 20.16% pyrophyllite

32.27% sericite + 20.16% pyrophyllite = 52.43% pyrophyllite + sericite

100.00% — 52.43% = 47.57% quartz in sample.

[The decimal places were used as calculated since the percentage of pyrophyllite, sericite and quartz are used in the following calculations; however, the decimal places are not significant.]

The above calculations were made without knowledge of the SiO₂ content of the sample. The accuracy of the results, however, are shown below by calculation of the percentage of SiO₂ in pyrophyllite and sericite using the percentages of these minerals calculated above. The percentage

of free quartz in the sample calculated with a knowledge of the total SiO_2 content compares favorably with the percentage of quartz calculated using only the percentage of Al_2O_3 and K_2O in the sample.

Given:

1% pyrophyllite \equiv .6438% SiO_2 (Deer, Howie and Zussman, 1962)

20.16% = the percentage of pyrophyllite calculated above

1% sericite \equiv .475% SiO_2 (Deer, Howie and Zussman, 1962)

32.27% = the percentage of sericite calculated above

77.53% = the total percentage of SiO_2 in the sample.

1% pyrophyllite \equiv .6438% SiO_2

20.16% pyrophyllite \equiv 12.98% SiO_2

1% sericite \equiv .475% SiO_2

32.27% sericite \equiv 15.31% SiO_2

12.98% SiO_2 in pyrophyllite + 15.31% SiO_2 in quartz = 28.29%.

77.53% SiO_2 available (by chemical analysis) - 28.29% = 49.24% free quartz.

Table 1

M.Sc. Thesis, Harvey F. Keats

Calculations of diffractometer peak ratios

(See Table V-3, p. 53 of thesis)

Sample	Measured diffractometer peak heights		
	Quartz (Q)	Pyrophyllite (P)	Sericite (S)
1	59.2	6.2	4.1
1	60.0	6.5	4.0
1	60.2	6.8	4.2
1	60.9	6.6	4.2

Peak Ratios:		% dev.*)
[P / (P+S)] x 100:	6.2 / 10.3 x 100 = 61.1	+ 0.2%
	6.5 / 10.5 x 100 = 61.9	+ 1.5%
	6.8 / 11.0 x 100 = 61.8	+ 1.3%
	6.6 / 10.8 x 100 = 61.1	+ 0.2%
	Average: 61.5	
	Reported by Keats: 61	
[Q / (Q+P)] x 100:	59.2 / 65.4 x 100 = 90.5	+ 0.6%
	60.0 / 66.5 x 100 = 90.2	+ 0.2%
	60.2 / 67.0 x 100 = 89.8	- 0.2%
	60.9 / 67.5 x 100 = 90.2	+ 0.2%
	Average: 90.2	
	Reported by Keats: 90	
[Q / (Q+S)] x 100:	59.2 / 63.3 x 100 = 93.5	+ 1.6%
	60.0 / 64.0 x 100 = 93.7	+ 1.8%
	60.2 / 64.4 x 100 = 93.4	+ 1.5%
	60.9 / 65.1 x 100 = 93.5	+ 1.6%
	Average: 93.5	
	Reported by Keats: 92	

*) % dev.: deviation from reported value in % of reported value.

Table 2

M.Sc. Thesis, Harvey F. Keats

Calculations of diffractometer peak ratios

(See Table V-3, p. 53 of thesis)

Sample	Measured diffractometer peak heights		
	Quartz (Q)	Pyrophyllite (P)	Sericite (S)
9	72.3	15.0	10.0
9	76.0	18.0	12.0
9	72.0	16.0	9.5
9	73.9	17.1	10.7

Peak Ratios:		% dev. *)
[P / (P+S)] x 100:	15.0 / 25.0 x 100 = 60.0	- 1.6%
	18.0 / 30.0 x 100 = 60.0	- 1.6%
	16.0 / 25.5 x 100 = 62.7	+ 2.8%
	17.1 / 27.8 x 100 = 61.5	+ 0.8%
	Average: 61.0	
Reported by Keats:	61	
[Q / (Q+P)] x 100:	72.3 / 87.3 x 100 = 82.8	+ 0.9%
	76.0 / 94.0 x 100 = 80.9	- 1.3%
	72.0 / 88.0 x 100 = 81.8	- 0.2%
	73.9 / 91.0 x 100 = 81.2	- 0.9%
	Average: 81.7	
Reported by Keats:	82	
[Q / (Q+S)] x 100:	72.3 / 82.3 x 100 = 87.9	+ 1.0%
	76.0 / 88.0 x 100 = 86.4	- 0.6%
	72.0 / 81.5 x 100 = 88.3	+ 1.5%
	73.9 / 84.6 x 100 = 87.4	+ 0.4%
	Average: 87.5	
Reported by Keats:	87	

*) % dev.: deviation from reported value in % of reported value.

Table 3

M.Sc. Thesis, Harvey F. Keats

Calculations of diffractometer peak ratios

(See Table V-3, p. 53 of Thesis)

Sample	Measured diffractometer peak heights		
	Quartz (Q)	Pyrophyllite (P)	Sericite (S)
12	62.0	26.6	2.2
12	72.0	33.1	2.2
12	74.2	32.0	2.0
12	76.0	28.8	2.0

Peak Ratios:		% dev. *)
[P / (P+S)] x 100:	26.6 / 28.8 x 100 = 92.4	- 1.7%
	33.1 / 35.3 x 100 = 93.8	- 0.2%
	32.0 / 34.0 x 100 = 94.1	+ 0.1%
	28.8 / 30.8 x 100 = 93.5	- 0.5%
	Average: 93.5	
Reported by Keats:	94	
[Q / (Q+P)] x 100:	62.0 / 88.6 x 100 = 70.0	0.0%
	72.0 / 105.1 x 100 = 68.5	- 2.1%
	74.2 / 106.2 x 100 = 69.9	- 0.1%
	76.0 / 104.8 x 100 = 72.5	+ 3.5%
	Average: 70.0	
Reported by Keats:	70	
[Q / (Q+S)] x 100:	62.0 / 64.2 x 100 = 96.6	- 0.4%
	72.0 / 74.2 x 100 = 97.0	0.0%
	74.2 / 76.2 x 100 = 97.4	+ 0.6%
	76.0 / 78.0 x 100 = 97.4	+ 0.6%
	Average: 97.1	
Reported by Keats:	97	

*) % dev.: deviation from reported value in % of reported value.

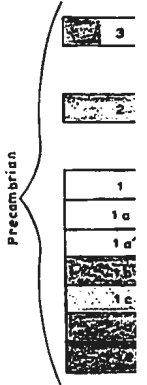
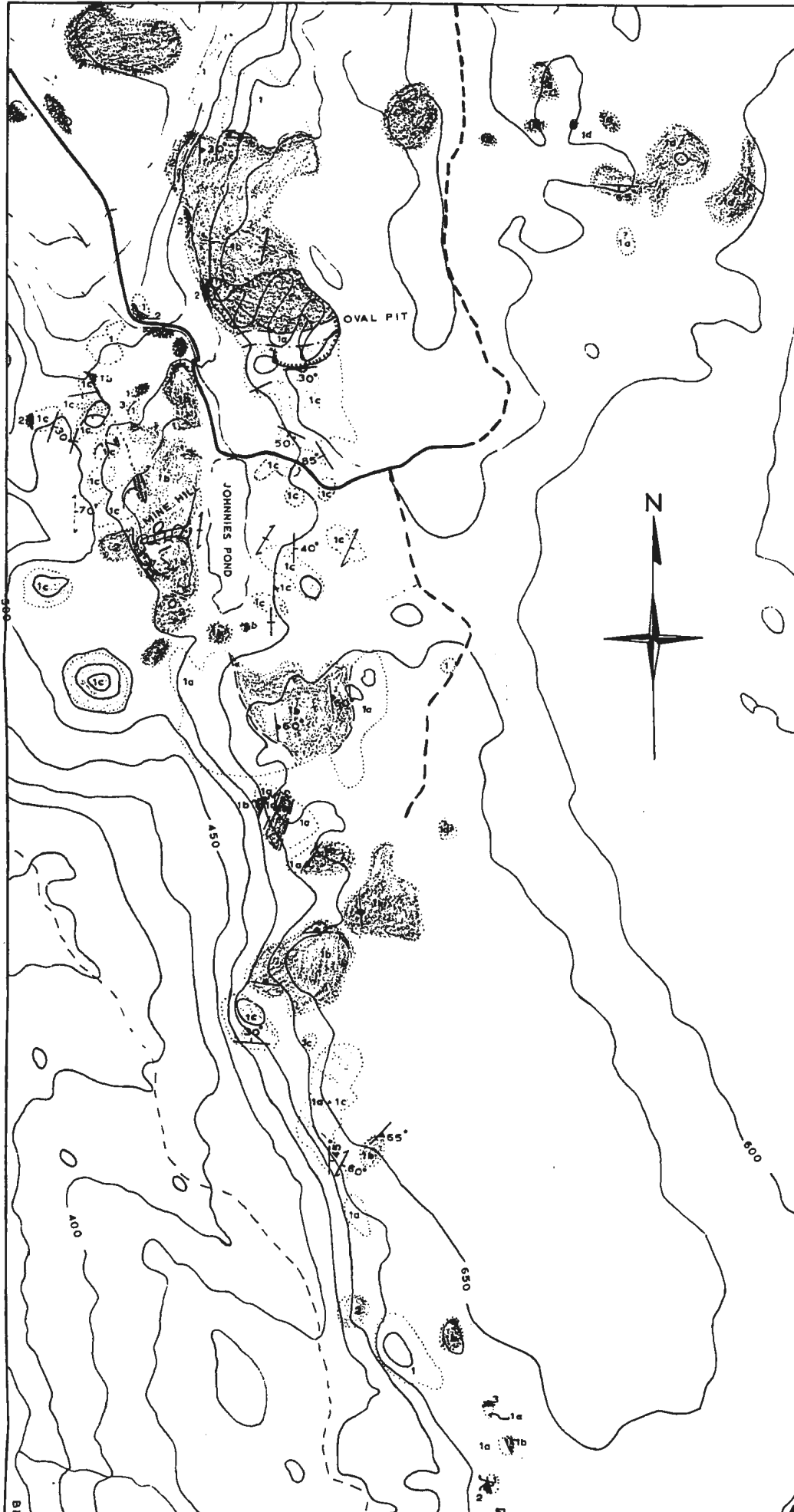
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- Rock c
- Geolor
- 155
- Limit
- Beddin
- Beddin
- Flow t
- Schist
- Fault
- Fault
- Quarry
- Shaft
- Trench
- Adit .
- Open c

GEOLOGY OF THE MANUELS PYROPHYLLITE DEPOSITS

CONTOUR INTERVAL 50 FEET

SCALE ONE INCH = 1000 FEET



LEGEND

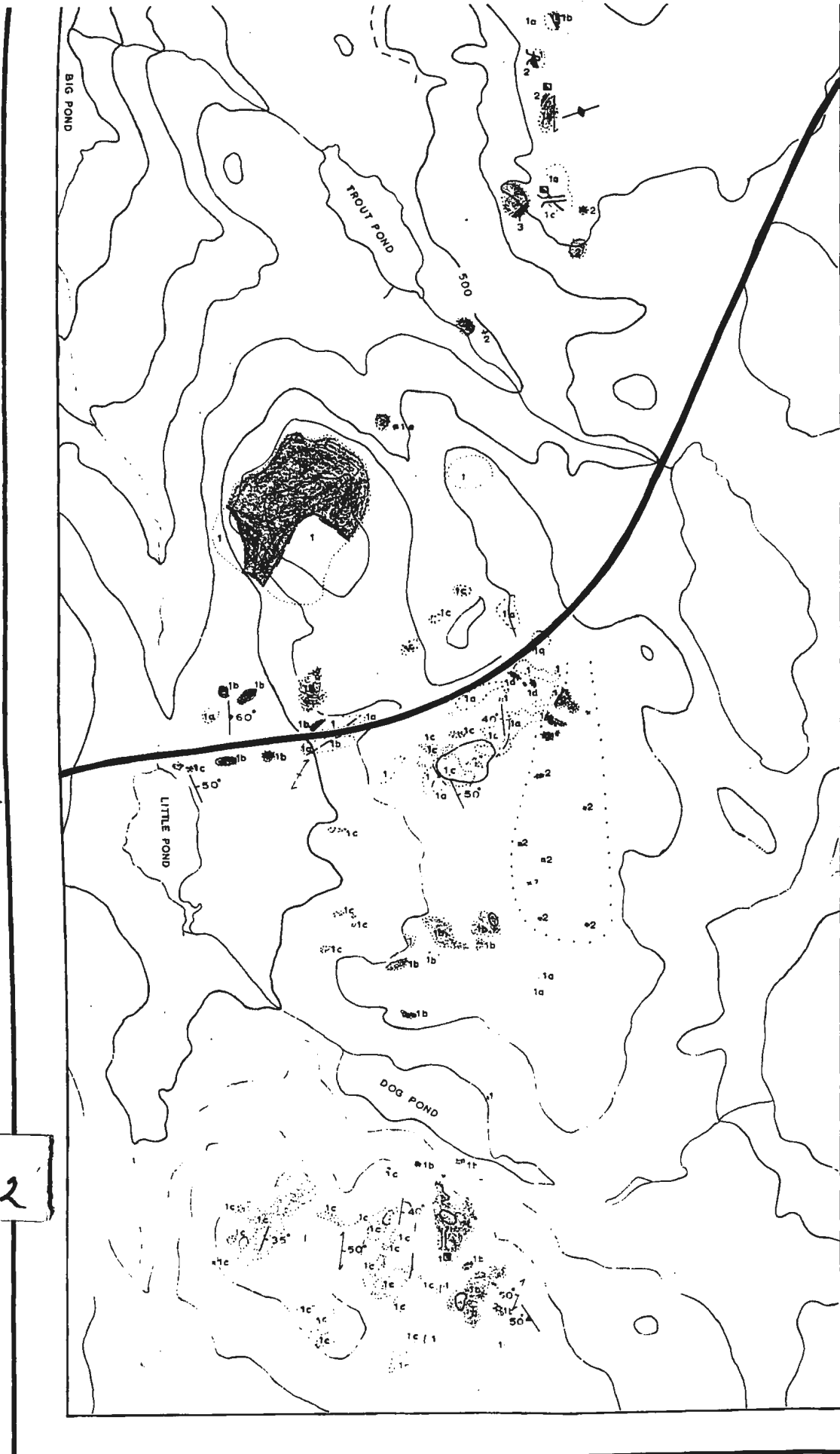
Precambrian		Dyabase dykes some of which are older than the Holyrood granite
		Holyrood granite: quartz monzonite with some rhyodacite porphyries
		Harbour Main Group: 1, rhyolitic volcanics, undivided; 1a, acidic pyroclastics — volcanic breccias, lapilli tuffs and tuffs; 1a', acidic pyroclastics — explosion breccia; 1b, rhyolitic flows — flow banded rhyolite, flow breccia, subvolcanic rhyolite, rhyolite porphyry (often flow banded); 1c, volcanic sediments — well-bedded mudstone, siltstone and volcanic greywacke with interbedded acidic, basic, and lithic tuffs; 1d, rocks of predominant andesitic composition containing blocks of rhyolite and interbedded by occasional rhyolitic flows and sediments; 1e, basaltic flows, often pillowed

- | | |
|---|--|
| Rock outcrop | |
| Geological boundary (defined, approximate, assumed, gradational)..... | |
| Limit of geological mapping | |
| Bedding, tops known | |
| Bedding, general trend (dip and top known) | |
| Flow banding (inclined, vertical) | |
| Schistosity, cleavage (inclined, vertical)..... | |
| Fault (defined, approximate, assumed) | |
| Fault and shear zone (width indicated) | |
| Quarry | |
| Shaft | |
| Trench | |
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| Open cut | |

500

Adit

Open cut



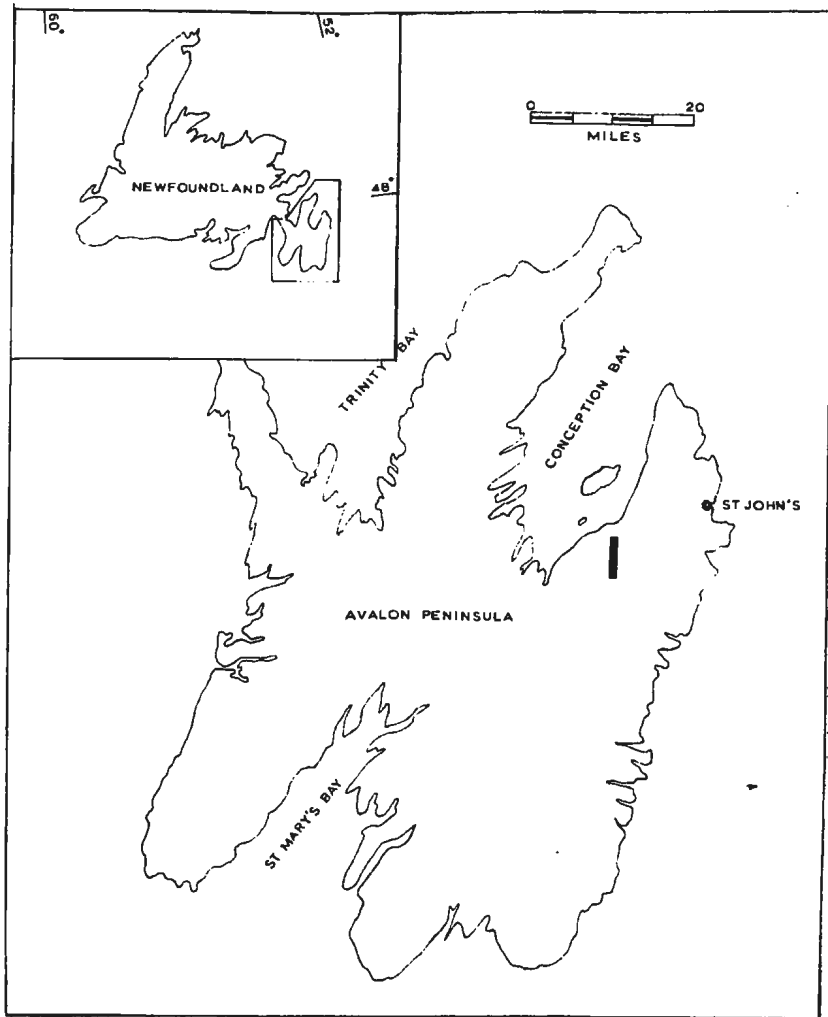
2 of 2

MEMO

Adit

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11
2



Geology by H.F. Keats

MSc

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MAP 1

