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THE ROLE OF REPLACEMENT
PROCESSES IN THE FORMATION
OF COMPLEX LITHIUM PEGMATITES

by

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Submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

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ABSTRACT

Field observations indicate that replacement processes are important in the formation of complex pegmatites. These processes and their role in the genesis of pegmatites have been studied using experimental and geochemical techniques. A laboratory method was adopted to investigate some of the more common replacements by reacting natural pegmatite minerals (albite, microcline and spodumene) with alkali halides (NaCl, KCl, LiF, Li_2CO_3, $KF.2H_2O$) under hydrothermal conditions, at temperatures ranging from 250 - 650°C and water vapour pressures of 15,000 to 39,000 p.s.i. These conditions are believed to be reasonable for natural pegmatite systems. Variations in temperature and pressure only alter the rate of the reaction, indicating that such replacement reactions can occur over a wide range of physical conditions, and may merely be related to the concentration of various alkalis and volatiles at successive stages in the pegmatite's genesis. Minor alkali (Li_2O, Rb_2O and Cs_2O) and fluorine contents of micas from the Preissac-Lacorne, Quebec and Black Hills, South Dakota, pegmatite regions were determined to evaluate their relative importance during differentiation. Li, Rb and Cs and F were found to increase steadily, and basic differences in these elements were found between the two pegmatites.

Experimental, geochemical and field observations are used to explain the formation of replacement bodies and the physical and chemical conditions of their replacement. It is believed that at a late stage in the genesis of complex pegmatites, an aqueous phase develops from the residual melt, leaving a silica-rich phase to form the quartz core. The aqueous phase, enriched in alkalis and fluorine, reacts with the crystallised microcline- and spodumene-bearing zones commonly surrounding the core to form albite, pollucite and lepidolite replacement bodies, depending on the elements present in the aqueous phase.

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION AND STATEMENT OF PROBLEM

During a preliminary field study of lithium pegmatites in the Preissac-Lacorne region of northwestern Quebec, certain textures suggestive of replacement reactions were observed. Among others, these included the replacement of spodumene by lepidolite and by albite.

A survey of pegmatite literature shows that such reactions, and others, have been recognised in many of the more complex pegmatites throughout the world, but both their mode of formation and their extent has aroused considerable controversy. The present study has therefore attempted to investigate and explain some of these problems of replacement and its role in pegmatite genesis.

The relative importance of replacement in the formation of complex pegmatites has been discussed for many years and from several different viewpoints. Cooper (1961), for example, discussing the very complex Bikita pegmatite of Rhodesia, recognises no appreciable effects of replacement. Schaller (1925), on the other hand, suggested that complex pegmatites crystallised initially as quartz and potash feldspar with minor plagioclase, but that other minerals were formed by a series of later hydrothermal solutions invading the pre-crystallised material. Both views presently have a number of adherents.

A major difficulty inherent in this problem is the recognition of conclusive criteria that replacement, both on a macroscopic and a microscopic scale, has taken place. On a macroscopic scale, replacement bodies are most easily recognised when they are discordant to the zonal structure of the pegmatite, and do not have the matching walls characteristic of fracture fillings where no replacement has taken place (Cameron et al, 1949). Obviously, all gradations between the two are to be expected, and indeed, fractures are probably the means by which many replacement bodies originated. However, in other cases replacement may have selectively occurred in only one zone, or possibly even in certain minerals of that zone. In such instances replacement is more subtle, and therefore more difficult to recognise within the background zonal structure of the pegmatite. These various types are shown diagrammatically in Figure 1.

On a smaller scale, the best evidence for replacement is pseudomorphism of structures or crystal forms. Corrosion and embayment of one crystal by another, although widely used, and well described by Bastin et al (1939), are poor criteria of replacement.

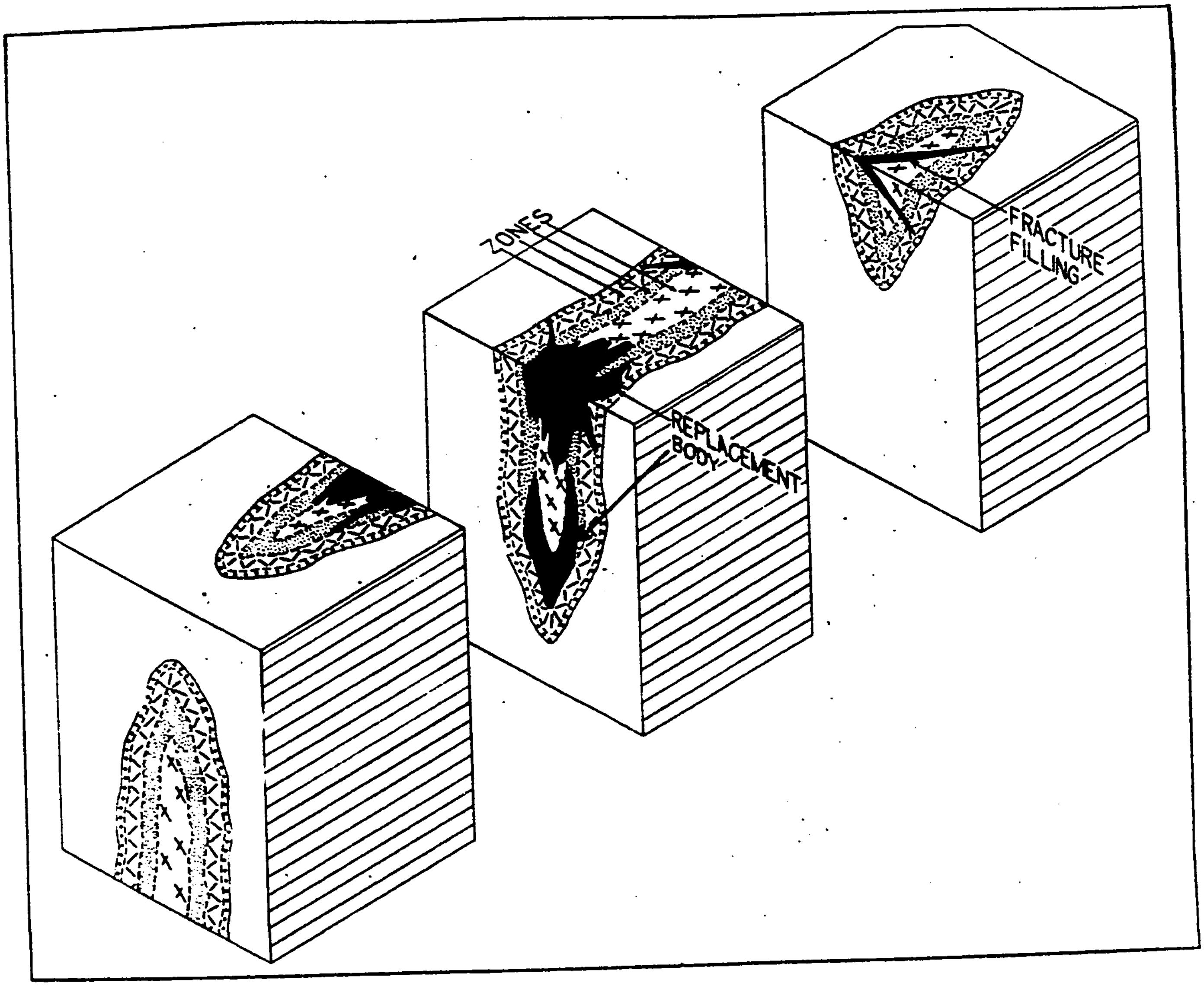

Figure 1. Idealised representation of zones, fracture fillings and two types of replacement body in a complex pegmatite. (After Cameron et al, 1949).

Cameron et al (1949) distinguished two important types of replacement: reaction replacement, involving reaction prior to the final consolidation of a pegmatite zone; and post-consolidation replacement, occurring after complete crystallisation. Obviously, the latter is more often characterised by cross-cutting relationships with earlier zones and is therefore easier to recognise. It may be the type controlled by fracturing and therefore discordant. Reaction replacement is more likely to occur throughout a complete internal shell of the crystallising pegmatite, and discordant structures, as a result, are uncommon. Here textural evidence alone must suffice.

Jahns (1955) has summarised the various views concerning the source of the fluids causing replacement, which may be applied to both the above types. These are as follows:-

1. Rest liquid of progressively changing composition, in disequilibrium with previously crystallised material. (Hitchen, 1935; Cameron et al, 1949; Page et al, 1953; Jahns et al, 1953; Page, 1954; Thurston, 1955; Sheridan, 1955).
2. Vapours, and especially their condensates, derived by resurgent boiling of the pegmatitic rest-liquid. (Bowen, 1933; Jahns, 1955).
3. Hydrothermal solutions formed by direct descent from the rest-liquid within the crystallising pegmatite. (Makinen, 1913; Fersman, 1931; Landes, 1933; Thurston, 1955).

4. Hydrothermal solutions immiscible with the rest-liquid and derived within and from it. (Neumann, 1948; Smith, 1949).
5. Liquid or gaseous solutions derived from sources outside the pegmatite body. (Schaller, 1925-7; Hess, 1925, 1933; Bjorlykke, 1937; Fisher, 1942).

Only the last of these requires an external source for the replacing fluids. In the first four cases the fluids are all products of the pegmatitic melt itself. The external source theory is probably the most easily discounted, because complex, rare-element pegmatites are now recognised as crystallisation products of a highly restricted or essentially closed system (Cameron et al, 1949; Jahns, 1955). Genetic theories requiring an external source are not compatible with the shell-like zoning pattern of many complex pegmatites, the geochemical behavior of many rare elements when traced from the walls inward, and the temperatures of formation of the zones when calculated by various means. The four remaining theories, involving an internal source, are more compatible with current geological knowledge about pegmatites, and can account for either reaction replacement or post-consolidation replacement. They will be discussed in a subsequent section of this study. Therefore the problems of replacement processes that require explanation are:-

1. The extent of replacement in the complex pegmatites.
2. The means by which the replacing fluid separated from

the original melt.

3. The composition of the fluids causing replacement at various stages in the pegmatite process.

4. The reasons why certain pegmatites exhibit extensive evidence of replacement, whereas others do not.

Many different types of replacement have been reported. Although interesting, some of these, such as replacement of silicate minerals by tantalates and Fe-Mn phosphates (Norton, 1962), have little bearing on the overall genesis of the pegmatite. Moreover, they are of minor quantitative importance, although they may be of considerable commercial significance. The present study concentrates on the major silicate replacement for which textural evidence has actually been observed. These include the following mineral transformations:-

Albite → Microcline
Microcline → Albite
Microcline → Spodumene
Microcline → Lepidolite
Spodumene → Lepidolite
Spodumene → Albite
Spodumene → Albite and Eucryptite
Spodumene → Microcline

There is no petrogenetic or quantitative significance to the order in which these reactions are listed. They include however, some, where a simple alkali exchange is involved with no severe change of crystal structure; and others, where a distinct change in silicate structure occurs.

Some experimental work on these transformations has been performed by other workers, using both natural pegmatite minerals and glasses as starting materials. The first work of this nature was performed by Gruner (1944) and O'Neil (1948), who, by reacting alkali-rich solutions and natural feldspars, obtained feldspars or micas depending on the pH of the system. Wyart and Sabatier (1956) and Scavnicar and Sabatier (1957) describe alkali-ion exchange reactions between natural feldspars and either anhydrous alkali chloride melts or alkali chloride solutions. They were able to transform soda feldspar to potash feldspar and vice versa. LiCl, when reacted with the feldspar, gave a variety of products:- an unstable lithium feldspar ($LiAlSi_3O_8$), iron spodumene ($LiFeSi_2O_6$) and eucryptite. The iron in the spodumene apparently came from the steel autoclave used in the experiments, and is therefore of no consequence to alterations observed in nature.

In this study, natural pegmatite minerals and solutions of various chlorides, carbonates and fluorides were used to examine qualitatively the conditions of the various reactions at different stages in the development of complex pegmatites.

Use of particular cations reacting in the solutions is based on evidence from fluid inclusions in pegmatites, and connate waters. Both of these show chlorides and carbonates to be abundant (Roedder, 1958; Orville, 1963). In particular, recent work by Yermakov (1964) showed that sodium and potassium chlorides are the most common contents of pegmatitic inclusions. Fluorides, although less abundant, are also present.

CHAPTER 2

SAMPLE LOCATIONS AND GEOLOGY

1. INTRODUCTION

Samples, both for use in the experimental work described in Chapter 3 and in the geochemical studies described in Chapter 4, were taken from pegmatites in two districts.

The Preissac-Lacorne district of northwestern Quebec was chosen because it is easily accessible and contains pegmatites with a wide range of geochemical complexity which have been extensively studied (Norman, 1945; Derry, 1950; Rowe, 1953; Ingham and Latulippe, 1955; Mulligan, 1965; Dawson, 1966).

The southern-Black Hills district of South Dakota was chosen because it contains many large, complex, lithium pegmatites which have been studied in great detail, thereby providing much background data for the present study (Page et al, 1953; Sheridan, 1955; Staatz, 1955; Norton et al, 1962, 1964; etc.).

The geology and sample locations of these two districts will be described in the following sections.

2. PREISSAC-LACORNE DISTRICT, NORTHWESTERN QUEBEC

The Preissac-Lacorne pegmatite district lies between Amos and Val d'Or in the Superior Province of the Canadian Shield (Figure 2). The pegmatites of this area are associated with the Archaean, Preissac-Lacorne batholith, which has intruded a series of Archaean sedimentary and volcanic rocks. All the Archaean rocks have been cut by a series of Proterozoic gabbro dykes, and in many places are covered by glacial deposits. Details of the general geology of the region may be found in Dawson (1966).

The batholith comprises three principal massifs, the Preissac, Lamotte and Lacorne, with a number of smaller associated stocks. The lithology of the massifs ranges from hornblende monzonite to what has been variously described as leucoadamellite or biotite-muscovite granite (Dawson, 1966).

Geochemical studies of the lithium content of the micas in each massif suggest that they were intruded in the order Preissac - Lamotte - Lacorne (Siroonian et al, 1959). Apparently due to this magmatic differentiation, the satellitic pegmatites become increasingly complex with each successive intrusion; the lithium and molybdenite pegmatites associated with the Lacorne massif being the richest in rare elements.

Around the Lacorne massif a distinct regional zonation of the pegmatites occurs. Heinrich (1953) has summarised examples of such zoning from many parts of the world, with the Preissac-Lacorne district representing one of these examples (Rowe, 1953). In districts having regional zoning, the

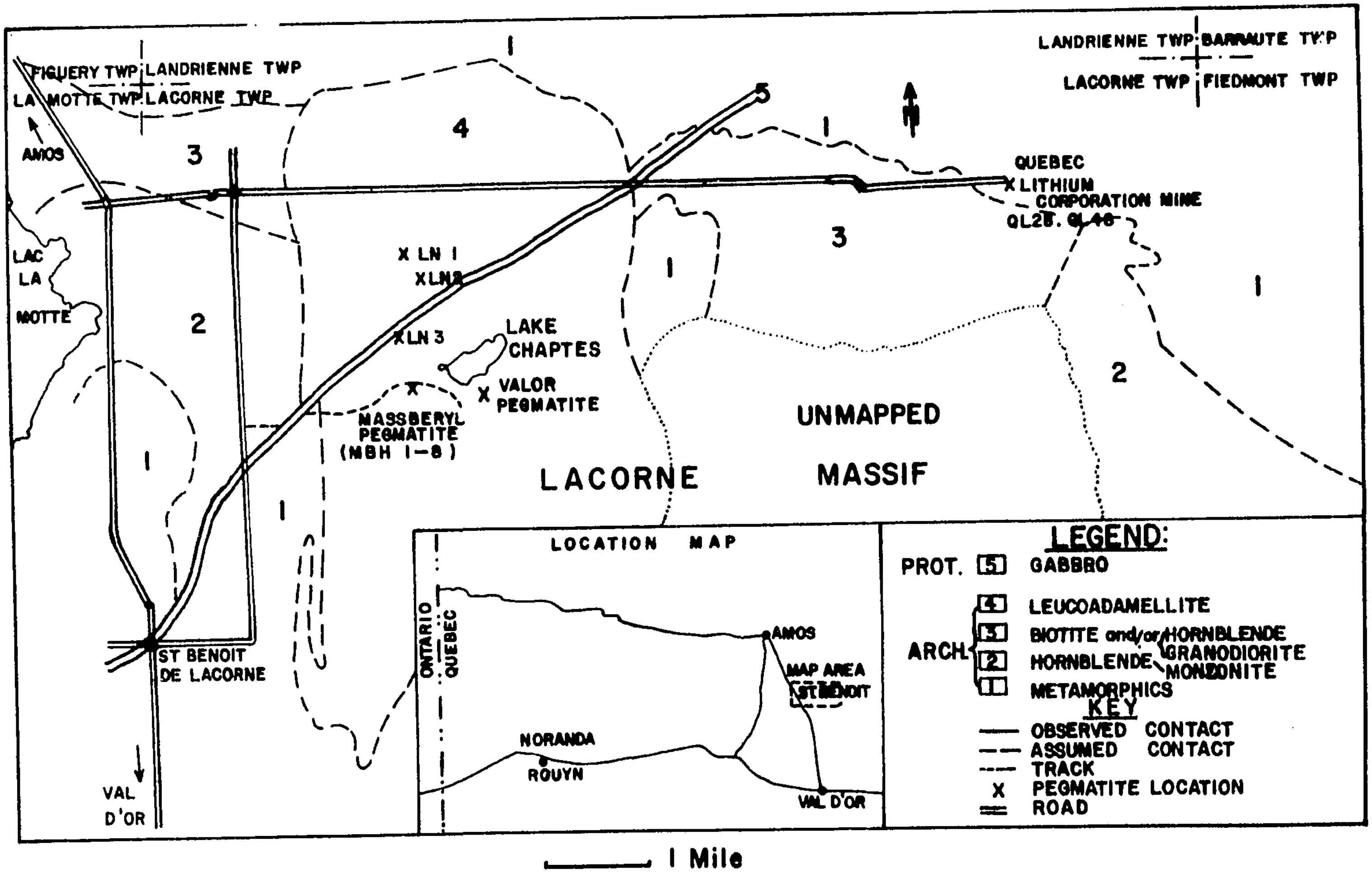

Figure 2. General geology and sample locations, Preissac-Lacorne district, northwestern Quebec. (After Dawson, 1966).

pegmatites become mineralogically more complex with increasing distance from the source batholith, as is the case around the Lacorne massif. The 'interior' pegmatites, lying within the batholith are either beryl-bearing, or barren of rare elements. The 'marginal' pegmatites, at the contact of the batholith and the country rocks, are spodumene-bearing, while the 'exterior' pegmatites, lying wholly within the country rocks, are spodumene- or molybdenite-bearing.

Nevertheless, neither the association of rare-element pegmatites with only the Lacorne massif, nor the regional zonation of pegmatites around it, is an infallible rule, and some exceptions to both generalizations have been recognised. Large spodumene pegmatites, for instance, have been found in the peridotite bordering the Lamotte massif, and the Valor pegmatite, an extremely complex spodumene-pollucite body, described below, lies within the Lacorne massif.

Considering the regional zonation and stages of pegmatite differentiation in the area, it appears to be a favourable location for the investigation of the geochemical differentiation of certain elements during the processes of pegmatite formation. Therefore, mica samples were taken from a series of barren, beryl- and spodumene-bearing pegmatites. The locations of all the pegmatites sampled are shown in Figure 2.

The barren pegmatites sampled (LN1, LN2, LN3) in the Lacorne granite, are three quartz, perthite, plagioclase, muscovite bodies occurring as irregular dykes and schlieren up to two feet wide.

Samples were taken from the Massberyl deposit (MBH1-8), which was extensively explored in the 1950's by a mining company for beryl. It consists of a series of interbranching pegmatite dykes up to twenty feet wide cutting the granite, and hence may be classified as an 'interior' pegmatite (Gevers, 1937). It is composed of quartz, plagioclase, perthite, muscovite beryl. In places it is distinctly zoned, having barren and beryl-bearing zones and quartz cores.

Two mica samples were taken from the spodumene pegmatites at the Quebec Lithium Corporation mine (QL26, QL48). These pegmatites are, in places, essentially homogeneous, with spodumene from wall to wall, but elsewhere are crudely zoned with spodumene restricted to the central portion of the bodies. They occur near the contact between the batholith and country rocks, and were mined for spodumene from 1956 to 1965. Due to the scarcity of mica, sampling from wall to wall across the dykes was not feasible.

The Valor beryllium - lithium - caesium pegmatite (Figures 2 and 3) is the most complex pegmatite in the area, but lies wholly within the Lacorne batholith. This pegmatite exhibits a wide range of mineralogy and contains several distinctly different mineral assemblages, which are described below in their probable petrogenetical order with reference to the samples taken from them.

The pegmatite is irregularly exposed over a N.W. to S.E. strike length of 350 feet, and dips essentially vertically throughout most of its length. A prominent bleached zone of contact one to two inches wide occurs in the granitic host rock around the pegmatite (Plate 1). This zone contains only quartz and feldspar, the micas of the granite having apparently migrated away from the pegmatite. The migration is assumed to be away from the pegmatite, as a granite xenolith occurring within the pegmatite has a central band of biotite and garnet apparently formed by the same mechanism.

At the south-eastern end of the exposure a border zone, composed essentially of quartz, beryl and muscovite (VMA14) with minor feldspar occurs (Plate 1).

The succeeding zone, which comprises the bulk of the pegmatite is, by definition, the wall zone. It contains quartz, clevelandite, spodumene and lepidolite, clevelandite occurring in radiating aggregates up to nine inches across (Plate 2). Spodumene is found as slender, lath-like crystals up to six feet long, but more generally one or two feet (Plate 3). These crystals are often bent and shattered. Spodumene, near the small fractures, has been altered to a pseudomorphic mass of green sericite (Plate 4). Lepidolite occurs mainly as coarse (up to two inches) purple or greyish-purple booklets (VMA2)associated with the clevelandite (Plate 2), but a

PLATES 1 - 8 FROM VALOR PEGMATITE, N.W. QUEBEC

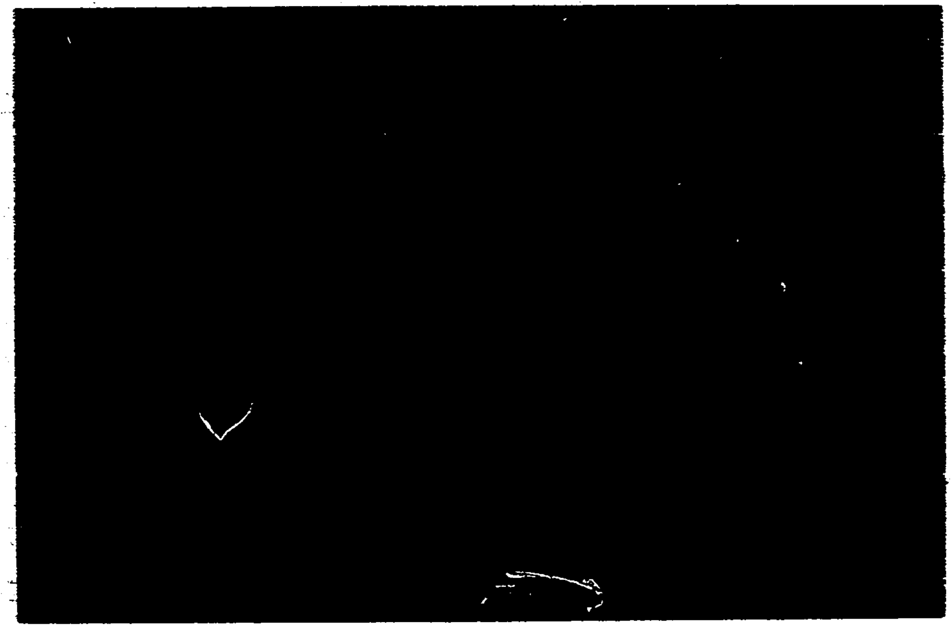

Plate 1. Contact of pegmatite and granite showing border zone assemblage and bleached zone of contact.

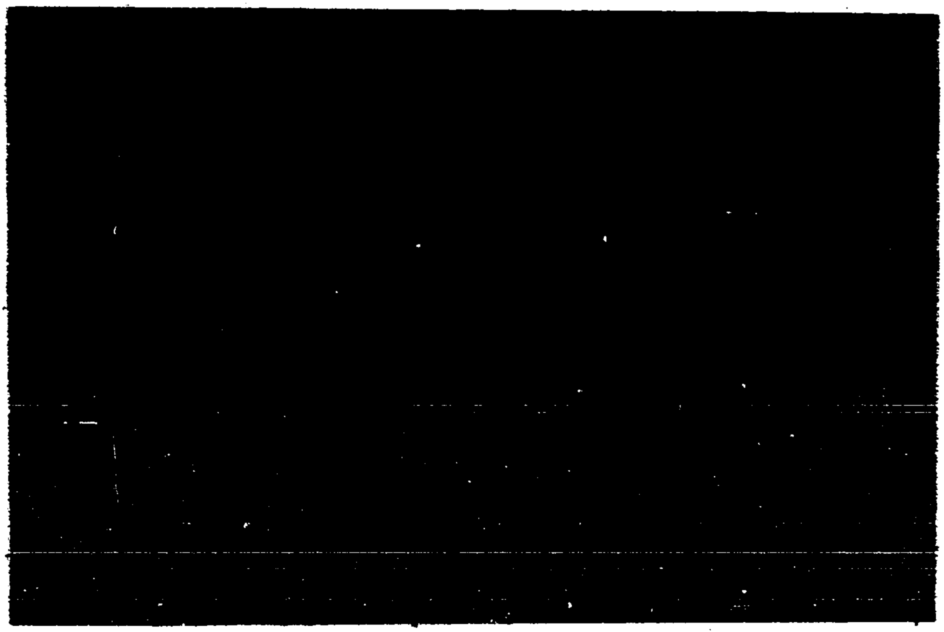

Plate 2. Wall zone assemblage showing radiating clevelandite, and coarse purple lepidolite.

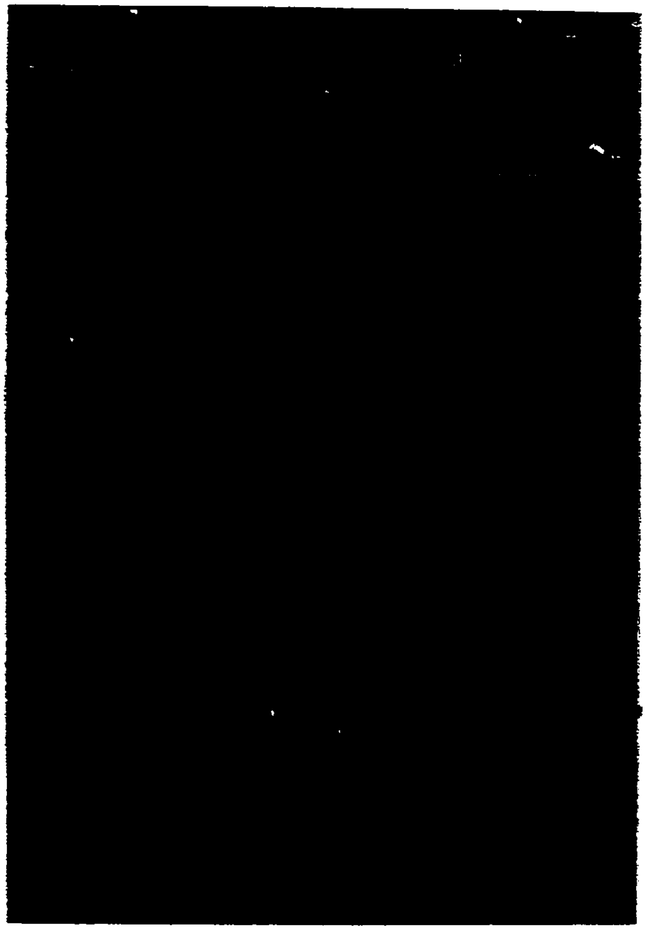

Plate 3. Spodumene in wall zone

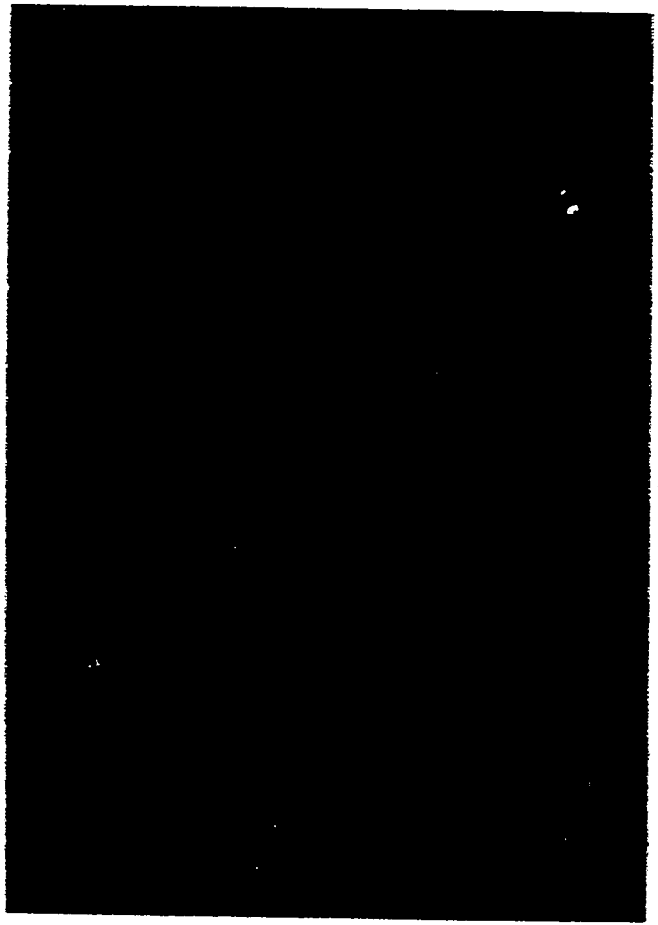

Plate 4. Spodumene altered to fine-grained sericite in the vicinity post-consolidation fractures.

finer-grained variety (VMA3) is found intimately mixed with some of the spodumene crystals (Plate 5).

Monomineralic bodies of three different compositions were also distinguished and mapped. Discrete pods of quartz up to ten feet long are scattered throughout this part of the exposure. Small pollucite bodies up to three feet across are also present here, and, although glassy and easily mistaken for quartz on freshly broken surfaces, are a distinctive dirty grey on weathered surfaces (Plate 6). The presence of Cs^+ may be detected by a simple field test (Mulligan, 1961). Pollucite bodies are commonly cut by veinlets of a fine-grained purple mica up to a quarter of an inch wide. This mica was initially thought to be a lepidolite, but subsequent analysis revealed the Li^+ content to be too low for its classification as a lepidolite. It appears, therefore, to be oncosine (EMG7), a form of muscovite described by Quensel (1957), from the Varutrask pegmatite in Sweden. A body of massive, fine-grained lepidolite (VMA1) occurs in the north-eastern part of the exposure against the granite contact. It transects both the barren pegmatite and the wall zone assemblage.

The zonal sequence described above fades out in both directions along the strike. At the southeastern extremity its place is taken by an aplitic assemblage containing schlieren of muscovite pegmatite (Plate 7), indicating that the body represents only the remnant keel of a larger pegmatite

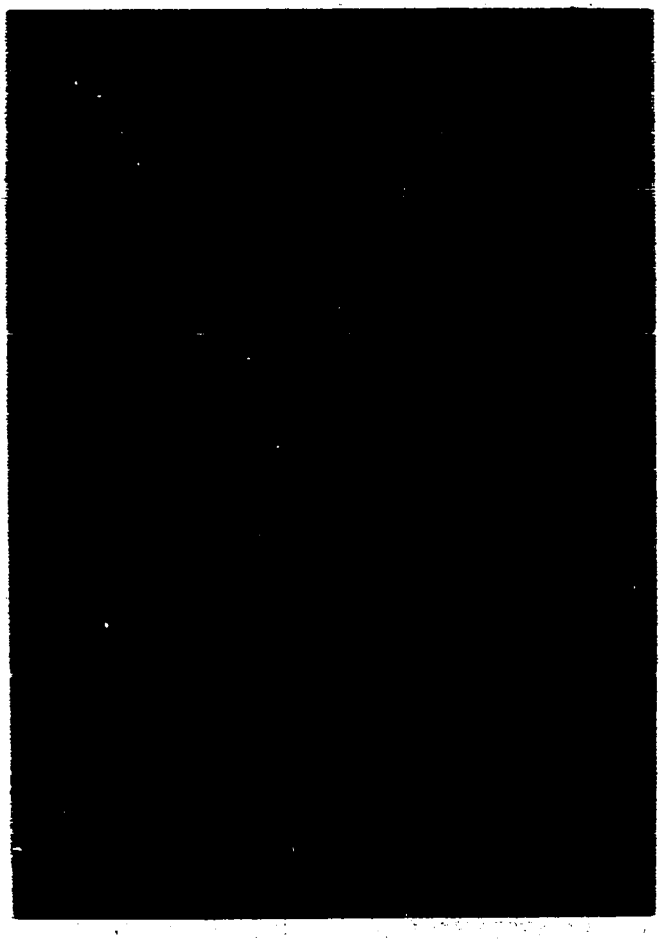

Plate 5. Spodumene in wall zone altered by fine-grained lepidolite.

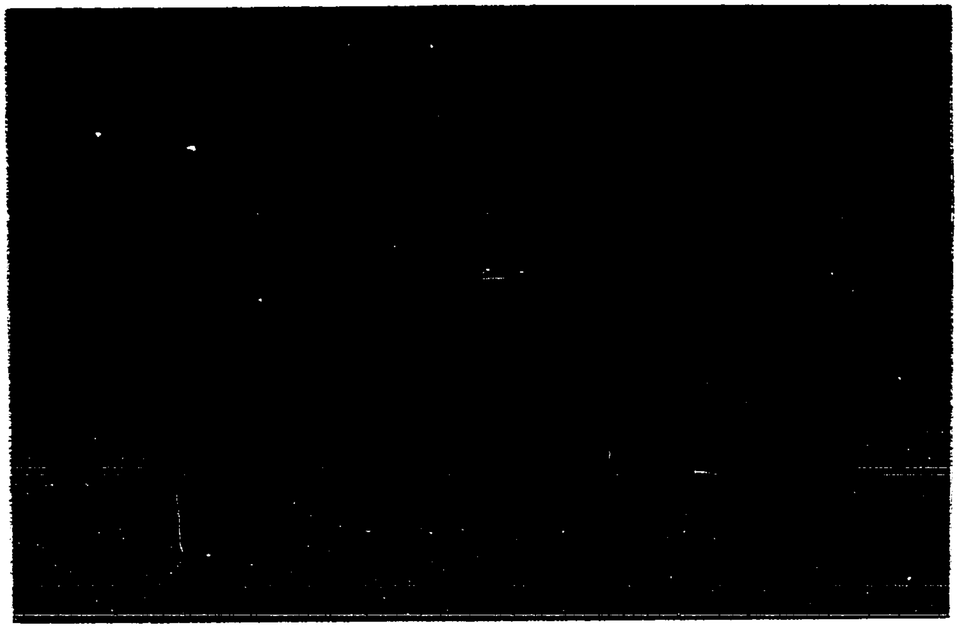

Plate 6. Grey-weathered pollucite cut by veins of oncosine.

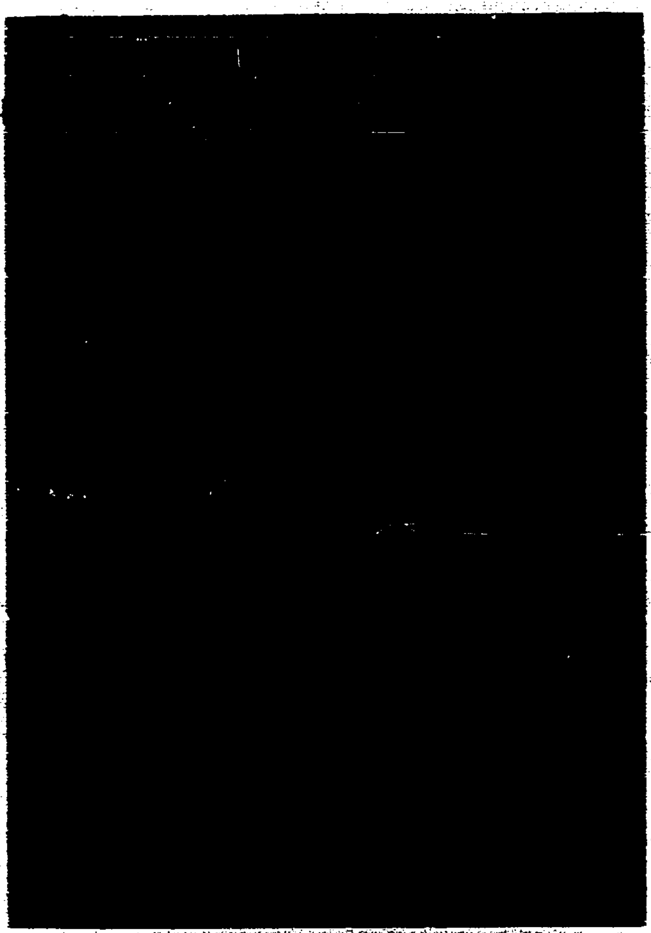

Plate 7. Aplite with pegmatite schlieren underneath the keel of the pegmatite.

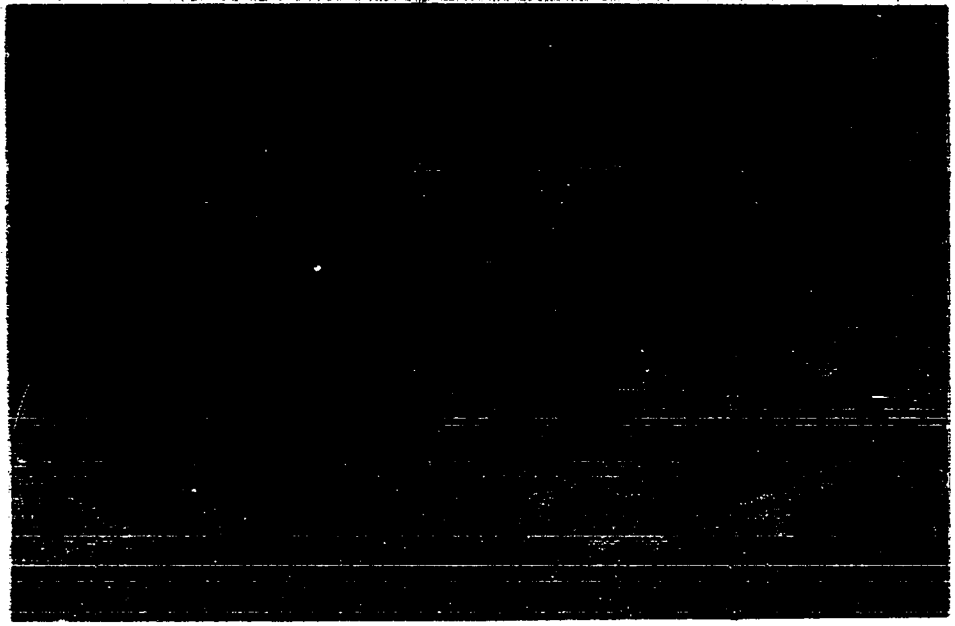

Plate 8. Contact of pegmatite and granite shown in section.

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work came from the beryl-bearing assemblage to the northwest. The locations of the mica samples used in the geochemical work are also shown on the accompanying map (Figure 3). Some of these have already been referred to.

3. SOUTHERN BLACK HILLS, SOUTH DAKOTA

This is one of the most famous pegmatite districts in the world, due to its large number of complex pegmatites, and the size and variety of the minerals they contain. Spodumene 'logs' up to 42 feet long have been reported (Schwartz, 1925).

Pegmatites and granitic intrusions are numerous throughout an area of about 250 square miles in the southern Black Hills, but pegmatites are most abundant around the Harney Peak granite, a small intrusion about ten miles in diameter (Figure 4). The Harney Peak granite is pegmatitic, with coarse and irregular-sized crystals up to one inch across. Due to the abundance of country rock inclusions in the intrusion, and pegmatite and granite bodies in the metamorphic country rocks, the contact between the granite and the surrounding metamorphic rocks is indistinct. Most of the large, complex pegmatites lie some distance from the contact, and, indeed, the area has a rough regional zonation as described for the Preissac-Lacorne district.

In contrast to the pegmatites of the previous district,

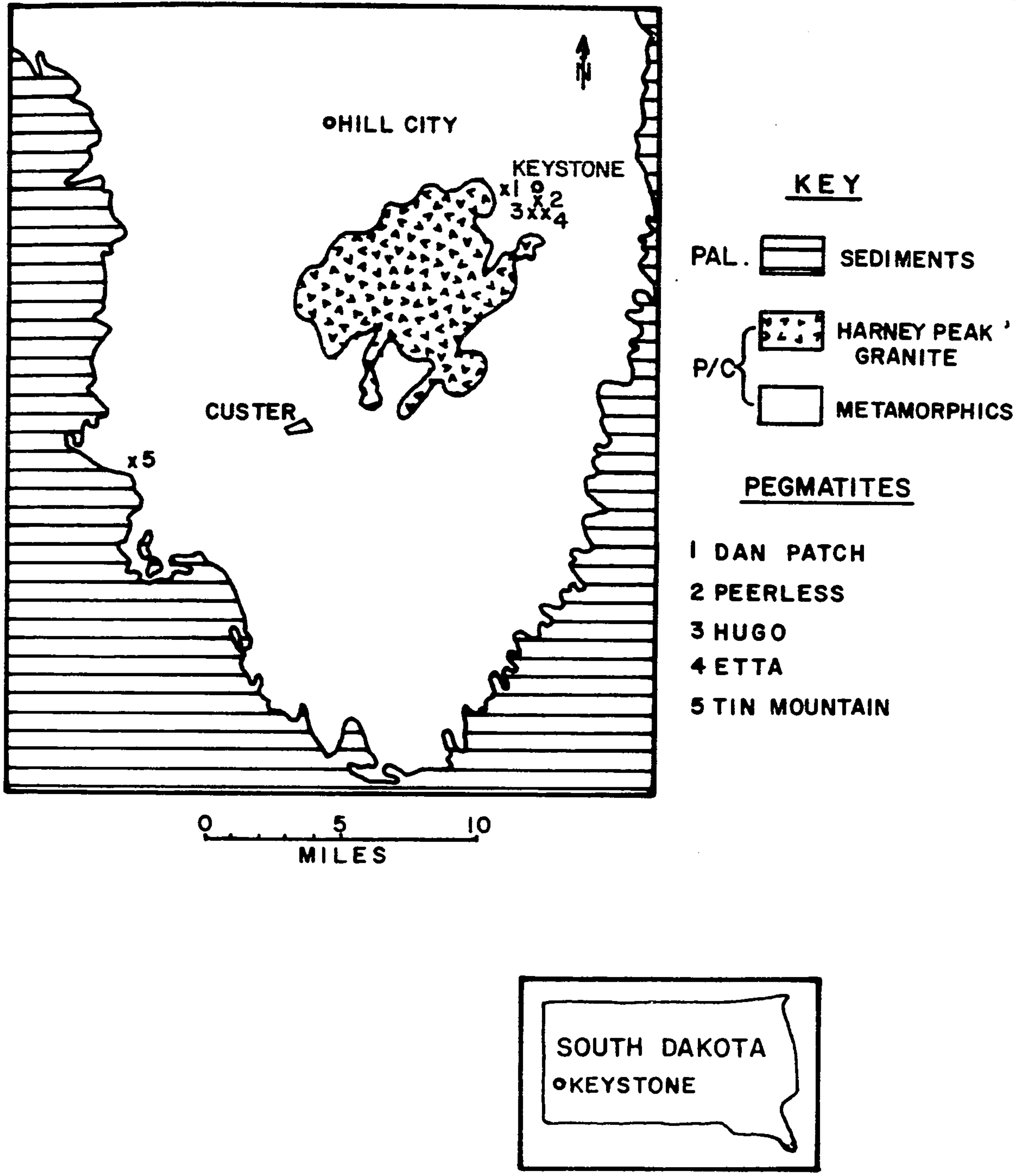

Figure 4. General geology and pegmatite locations, Black Hills district, South Dakota. (After Norton, 1964).

which are generally regularly-shaped dykes or flat-lying sills, the zoned pegmatites of the Black Hills are very irregular in shape. Such terms as tadpole-, teardrop-, and cigar-shaped have been used to describe them (Page et al, 1953). Many of the pegmatites contain several zones and replacement bodies that can be sampled to determine what chemical differentiation trends take place during the crystallisation of the successive zones. In addition, most of the complex pegmatites have been carefully mapped at various stages of mining, and numerous bulk chemical analyses, calculated from modal and chemical analyses, are available for them.

Samples were taken from several zones of the Hugo and Peerless pegmatites, and occasional samples from the Etta, Dan Patch and Tin Mountain deposits. Owing to the rarity of lepidolite in the Black Hills, all these specimens were of muscovite or lithian muscovite. The zonal sequence in each of these pegmatites is given in Table 1, with references to the workers who determined the sequence, and the source zone of each mica sample. The zones are listed from the walls inward, without significance as to their quantitative importance.

TABLE 1

ZONAL SEQUENCES OF BLACK HILLS PEGMATITES
WITH SAMPLE LOCATIONS

	ZONE	ASSEMBLAGE	SAMPLE
1. HUGO (Norton et al, 1962)	1.	Albite - quartz - muscovite	H5
	2.	Quartz - albite - muscovite	
	3.	Perthite - quartz - albite	H11
	4a.	Quartz - clevelandite - microcline - amblygonite	H10
	b.	Quartz - clevelandite	
	5.	Quartz - microcline - spodumene	
	6.	Quartz - microcline	
	7.	Clevelandite - microcline - Li-mica	
Replacement bodies	1.	Clevelandite - microcline - Li-mica	
	2.	Clevelandite - quartz - Li-mica	H2
2. PEERLESS (Sheridan et al, 1957)	1.	Quartz - muscovite - plagioclase	P2
	2.	Albite - quartz ± muscovite	
	3.	Clevelandite - quartz - muscovite	
	4.	Perthite - clevelandite - quartz	
	5.	Clevelandite - quartz	
	6a.	Quartz - microcline	
	b.	Quartz	
	7.	Li-mica - clevelandite	P1
Replacement bodies	1.	Li-mica - clevelandite - quartz	P4
	2.	Muscovite - clevelandite	

TABLE 1 CONT'D

	ZONE	ASSEMBLAGE	SAMPLE
3. ETTA (Norton et al, 1964)	1.	Microcline - biotite	
	2.	Quartz - muscovite	E3
	3.	Perthite - quartz - spodumene	
	4.	Perthite	
	5.	Quartz - spodumene	
	6.	Quartz	
4. TIN MOUNTAIN (Staatz et al, 1963)	1.	Muscovite - albite - quartz	
	2.	Albite - quartz - muscovite	
	3.	Perthite - quartz - albite	
	4.	Perthite	
	5.	Albite - quartz - spodumene	
	6.	Quartz - spodumene - Li-mica	TM1
fracture filling	1.	Quartz - spodumene	
5. DAN PATCH (Norton et al, 1964)	1.	Quartz - plagioclase - muscovite	DP4
	2.	Quartz - plagioclase - perthite	DP5
	3.	Quartz - perthite	
	4.	Quartz	

CHAPTER 3

EXPERIMENTAL METHODS AND RESULTS

1. INTRODUCTION

Two experimental methods were used to assess the effect of alkali halide solutions on pegmatite minerals. The initial method was a dynamic(1) technique using equipment designed by Dr. K. L. Currie at the Geological Survey of Canada in Ottawa. Solutions of alkali salts were passed over pegmatite minerals, simulating the origin of pegmatites as envisaged by Schaller (1925), with external fluids passing over pre-crystallised pegmatite, and thus forming a more complex body. However, a dynamic replacement mechanism can also occur if such fluids are generated within the crystallising pegmatite, and then transported along fractures within it. The method proved unsatisfactory, and will therefore only be briefly described.

The second approach was a static method using cold-seal pressure vessels (Tuttle, 1949). In order to have sufficient alkali halide present to produce replacement, the

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(1) A dynamic technique signifies that the system was not closed, but conditions changed so slowly that equilibrium is approximately attained. (Ermanovics, 1964).

natural minerals were mixed with alkali salts in certain proportions in the presence of water. Studies of the solubilities of these salts at high temperatures and pressures are limited, but from the available data (Clark, 1966), it appears that the concentrations of all the salts used would produce supersaturated solutions under the conditions of the experiments. Solid salt will therefore be present in all runs and the critical point of the solution will not be reached (Sourirajan and Kennedy, 1962), and two fluid phases will coexist. The advantage of this method is that experiments can be performed in small gold capsules in standard hydrothermal equipment.

Temperatures in both sets of experiments were in the range 250 - 650°C, a widely accepted range for pegmatite crystallisation (Jahns, 1955). Water vapour pressures ranged from 15,000 to 39,000 p.s.i., but were mainly at 2 kilobars (29,008 p.s.i.). The runs lasted from two days to two months.

2. DYNAMIC METHOD

a. PREPARATION OF STARTING MATERIALS

The pegmatite minerals used in this method were all from the Valor pegmatite described in the previous Chapter, and their locations may be seen in Figure 3. Analyses of the microcline and spodumene are shown in Table 2. The albite was not analysed as it is a coarse-grained clevelandite,

TABLE 2

ANALYSES OF MICROCLINE AND SPODUMENE USED IN HYDROTHERMAL EXPERIMENTS (IN WT.%) (1)

	MICROCLINE (M1)	SPODUMENE (S1)
LiO_2	64.42	62.60
Al_2O_3	18.04	26.44
Fe_2O_3	0.06	0.58
FeO	---	0.28
MgO	0.01	0.03
CaO	0.12	0.04
Na_2O	2.098 (2)	0.429
K_2O	13.90	0.40
H_2O^-	0.05	0.13
H_2O^+	0.51	0.51
CO_2	0.06	0.10
P_2O_5	0.01	0.04
Rb_2O	0.830	0.002
Cs_2O	0.053	0.032
MnO	0.005	0.17
Li_2O	0.017	7.586 (3)
TOTAL	100.18	99.39

TABLE 2 CONT'D

	No. of ions based on 8 oxygens	No. of ions based on 6 oxygens
Si	2.958	1.961
Al	.977	.975
Fe^{3+}	.002	.013
Fe^{2+}	---	.007
Mg	.0006	.0013
Ca	.0006	.0013
Na	.187	.026
K	.814	.0158
H	.171	.133
C	.0038	.0044
P	.0003	.0011
Rb	.024	.0046
Cs	.0022	.0008
Mn	---	.0045
Li	.0034	.956

Both samples were taken from the Valor pegmatite in the Preissac-Lacorne region of northwestern Quebec.

1. Analyst, K. Ramlal, University of Manitoba.

2. The microcline contains rather a high content of Na_2O, and under the microscope appeared slightly perthitic.

3. Ideally, spodumene should contain 8.05% Li_2O. However,

TABLE 2 CONT'D

published analyses are often in the range 5 - 7%, making the value shown here rather high. This could be due either to this spodumene being exceptionally pure, or to past methods of alkali analysis being inaccurate. Recent analyses published by Edgar (1968), also show high Li_2O content.

which is generally very pure. All minerals were ground to -5+10 mesh, and then purified by hand-picking. Even so, the microcline still had optically detectable traces of mica inclusions.

The salts used in the solutions were as follows:-

Li_2Co_3 K_2CO_3	Fisher Certified Reagents, each with impurities totalling 0.3%.
Na_2Co_3	British Drug Houses analytical reagent. No details of impurities are known, but are generally low in such reagent grades.

b. EXPERIMENTAL PROCEDURE

The alkali salts were dissolved in distilled water at room temperature. For one series of experiments lithium and potassium carbonates were dissolved together, and for the second series, lithium and sodium carbonates were similarly dissolved. These 'stock solutions' were made up in volumes of about 100 litres, and a sample of each was taken for analysis (Table 3).

The equipment and method used is described by Currie (1968), and the equipment is shown diagramatically in Figure 5.

Currie (1968) has shown that, using distilled water, a steady state, in which there is no noticeable change in the solubilities of the components, is reached in the system in a few hours. In the experiments described here, the solution was pumped into the system and brought up to the required temperature and pressure in a period of 20 to 30 minutes. It was then left overnight and collected at a flow rate of

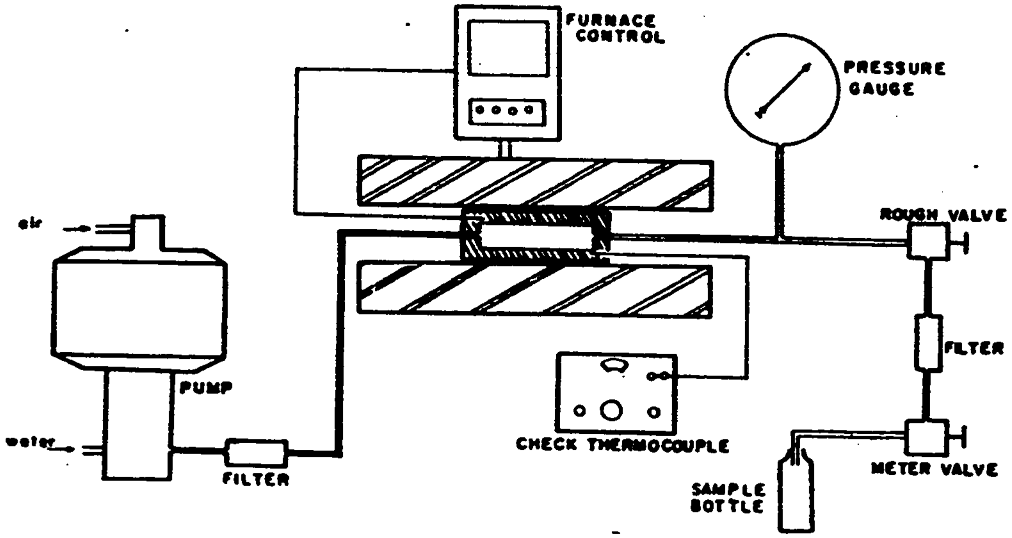


Figure 5. Diagrammatic representation of 'open system' hydrothermal equipment. (After Currie, 1968).

80 ml. per hour. Generally about 600 ml. were collected from each run. In two cases, the charge was again left overnight and another sample of the solution collected. A few ml. of solution were taken each time for pH measurement.

After each run, the pressure was released and the system allowed to cool. The solid charge was removed and stored, the bomb washed and scrubbed, and water pumped through the cooling tube to remove any traces of solution which might contaminate the following run.

c. IDENTIFICATION OF PRODUCTS

The solutions obtained from each run were analysed for SiO_2, Al_2O_3, K_2O, Na_2O and Li_2O by officers of the Geological Survey of Canada. Atomic absorption spectrophotometry was used to determine the alkalies, and a gravimetric method for SiO_2 and Al_2O_3.

The identity of the coarse mineral grains was checked using a petrographic microscope and a Philips high-angle X-ray diffractometer. Neither method indicated any change from the original material.

However, a fine-grained, grey material, identified as eucryptite, was found caked around the inside of the bomb at the termination of runs #4 and 5 (Table 3). Its formation in these experiments will be discussed below.

d. RESULTS

The results of these experiments are presented in Table 3.

TABLE 3

RESULTS OF HYDROTHERMAL EXPERIMENTS USING DYNAMIC METHOD

a). EXPERIMENTAL CONDITIONS

RUN NO.	MINERAL	STOCK SOLN	T C	P_{H_2O}(Kb).	SOLN NO
1	Spodumene	101	350	2	100, 102
2	Microcline	101	350	2	103
3	Albite	101	350	2	104
4	Microcline	101	450	2	105
5.	Spodumene	101	450	2	106
6.	Microcline	109	450	2	107, 108

b). SOLUTION ANALYSES IN P.P.M.

	pH	Si	Al	Na	K	Li
101	10.36	3.7	0.2	3.8	139	122
100	10.79	353	116	66.8	169	128
102	10.44	275	117	28.1	162	143
103	10.46	316	90	74.7	153	122
104	10.39	339	100	75.2	67.3	120
105	9.81	574	152	110	298	97
106	9.63	492	169	27.7	180	147
109	10.85	7.5	0.2	160	0.1	138

TABLE 3 CONT'D

	pH	Si	Al	Na	K	Li
107	10.08	537	153	245	213	120
108	10.20	627	138	237	277	125

RESULTS OBTAINED BY DR. K. L. CURRIE USING DISTILLED WATER

			Si	Al	Na	K
Albite	450 C	2,000 bars	60.7	180	200	1.8
Microcline	450 C	2,000 bars	553	154	127.7	193

In addition, results obtained by Dr. K. L. Currie by passing distilled water over albite and microcline at 450°C and 2kb. have been included for comparison with runs 3, 4 and 6.

e. DISCUSSION OF RESULTS

The alkali salts used in these experiments were dissolved in water at room temperature to the limits of their solubilities(Clark, 1966). In relation to the large amount of mineral in the bomb, insufficient salt was present in the solutions to have any marked effect, such as a phase change of the mineral, in these experiments. Dr. K. L. Currie (personal communication), found that a small amount of sample in the bomb is more likely to break down to a very fine powder which tends to be washed out of the bomb, and so large amounts of mineral had to be used in the present experiments.

A comparison of the results obtained from these experiments, and those obtained by Dr. Currie using distilled water, shows very little difference. Thus it appears that the only effect the solutions had was of leaching the components of the minerals in non-stoichiometric proportions. This has been discussed by Currie (1968), but is not relevant to pegmatite genesis.

pH measurements on starting solutions and solutions collected during a run, showed only insignificant changes, unrelated to changes of ions in the solutions.

The presence of small amounts of eucryptite in the bomb after runs 4 and 5 is thought to be due to the leaching of silica from spodumene. This type of formation of eucryptite is known to be achieved easily (Piotrowski, 1966). As mentioned earlier, the eucryptite was finely caked around the inside of the bomb and may easily have been formed during the first run with spodumene and not been removed despite scourings of the bomb with a brush. It seems unlikely that eucryptite was formed from microcline during run 4 as there is no detectable evidence of changes in the lithium concentration of the solution, sufficient for the formation of eucryptite from feldspar.

3. STATIC METHOD

a. PREPARATION OF STARTING MATERIALS

Descriptions of the minerals used are given in the previous section. For this method they were mechanically ground under acetone in an agate mortar to -100 mesh. After grinding, the size probably varied from -100 to 200 mesh. The powders were dried in an oven at 110 °C for two hours, and stored in sealed bottles.

The following additional salts were used in these experiments:-

LiF	British Drug Houses 'extra pure laboratory reagent', with trace amounts of Fe, SiO_2 and SO_4.
KCl	Analytical reagent from Mallinckrodt Chemical Works. No details of impurities are known.
NaCl	Fisher laboratory chemical. No details of impurities are known.

$KF.2H_2O$ Fisher Certified Reagent, with impurities (mostly CO_3) totalling 0.3%.

Both sodium and potassium chlorides were granular, and therefore had to be ground, dried in an oven, and stored in sealed bottles. With the exception of $KF.2H_2O$, all salts were premixed with the mineral powders in fixed proportions and stored in small vials in a desiccator until needed. Due to the deliquescence of $KF.2H_2O$, mixtures containing this material were freshly prepared in the gold capsules to ensure that the amount of water picked up was kept to a minimum. The silica used in several of the runs was obtained by gelling tetra-ethyl orthosilicate - $(C_2H_5)_4SiO_4$ (Roy, 1956).

b. EXPERIMENTAL PROCEDURE

All experiments were performed in sealed gold capsules using the technique described by Goranson (1931). The mineral and salt powder with distilled water in a weight ratio of 4:1, total solids to water, were placed in a gold capsule 3/4 inch in length and 3/32 inch I.D. and sealed in a carbon arc. The capsules were left in an oven at 110 °C for two hours and reweighed to ensure that the welded seal was effective.

Tuttle cold-seal pressure vessels (Tuttle, 1949), were used for all the runs. Temperatures were measured using chromel-alumel thermocouples, previously calibrated at the melting points of sodium chloride (800.4 °C) and zinc (419.4 °C), and recorded on a Honeywell multi-point potentiometer. Temperatures are believed to be accurate to 5 °C. At the temperatures used, the gold capsules do not weld together, and up to three capsules with different starting materials could be run in each pressure vessel.

Water vapour pressure was maintained by an air-operated pressure generator and measured with a Bourdon tube gauge. The actual pressure is believed to be ±4% of the recorded value.

At the end of each run, the bomb was quenched, first in a stream of air and then by immersion in water, and the capsules were removed and weighed. Any capsules showing a significant weight difference (0.0003 g.), were discarded.

c. IDENTIFICATION OF PRODUCTS

After each run the capsules were opened and the contents ground. All charges exuded water when opened, indicating that a gaseous phase was present.

Identification of the products with a petrographic microscope, using refractive index oils and crystal morphology, proved impossible, because the products appeared as a grey-black, cryptocrystalline mass with no recognisable crystals. In an attempt to determine if this was due to the excess alkali salts obscuring the silicate phases, the charges were washed several times in hot distilled water and filtered. However, no change was observed, and identification of the products had to be restricted to X-ray diffraction techniques. Because of the problem of lack of optical identification, it is possible that small amounts of phases in these experiments were overlooked.

A Philips high angle diffractometer operated at 35kV and 20mA with Ni-filtered, Cu radiation was used for X-ray identification. The goniometer was set to scan at 1° 2θ per minute, and the chart speed was 30 inches per hour. Identification of the products of the experiments was made by the following methods.

1. They could be compared with patterns obtained from the original starting materials, whose identity had already been confirmed by optical and chemical methods (Table 2).
2. New phases were identified using the standard ASTM card index of d-spacings, or with the spacings of pegmatite minerals found in the field. This method was especially valuable in the case of albite, eucryptite and lepidolite.

d. RESULTS

The results of the experiments are given in Table 4.

By using similar amounts of powder for each X-ray determination, a very rough estimate of the amount of each phase present in different experiments could be made. This was useful in runs where, although theoretically there was enough salt present to accomplish the transformation, the reaction was apparently not completed. Obviously, this method gives only a qualitative estimation of the relative amounts of phases present.

TABLE 4

RESULTS OF CLOSED SYSTEM EXPERIMENTAL WORK

Symbols used:-

Mic - microcline
San - sanidine
Euc - eucryptite
Spod - spodumene
Lep - lepidolite
Qtz - quartz
Alb - albite

R - run number
T - temperature
P - pressure
t - time
M/S - mineral/salt ratio in weight percent

Brackets and size of type indicate the relative amounts of the phases present. eg.

SPOD ALB EUC	Phases present in equal amounts.
SPOD (ALB EUC)	Spodumene > Albite and Eucryptite.
SPOD (Alb Euc)	Spodumene ≫ Albite and Eucryptite.
SPOD	Spodumene only

SPODUMENE AND K_2CO_3

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCT
3:1	DG33	350	20,000 p.s.i.	211	SAN EUC (SPOD)

TABLE 4 CONT'D

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCT
3:1	DG35	380	20,000 p.s.i.	211	SAN EUC (SPOD)
	DG34	400	22,500	211	" " "
	DG31	500	22,500	192	" " "
4:1	DG26	350	20,000	211	SAN EUC (SPOD)
	DG30	380	20,000	211	" " "
	DG27	400	22,500	211	" " "
	DG28	500	22,500	192	" " "
6:1	DG60	500	15,000	144	SAN EUC (SPOD)
7:1	DG76	415	13,500	552	SAN EUC SPOD
10:1	DG77	415	13,500	552	SPOD (SAN EUC)
14:1	DG61	500	15,000	144	SPOD (SAN EUC)

SPODUMENE + KCl (FIGURE 6)

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCT
4:1	MI23	250	2kb	336	SPOD (SAN EUC)
	MI21	250	2	672	" " "
	MI3	350	2	336	SAN EUC (SPOD)
	MI8	350	2	672	" " "
	MI4	400	2	168	" " "
	MI1	450	2	72	" " "
	MI20	450	2	336	" " "
	MI2	500	2	72	" " "

TABLE 4 CONT'D

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCT
4:1	MI24	500	2kb	168	SAN EUC (Spod)
	MI11	500	2	336	" " "
	MI9	500	2	672	" " "
	MI5	550	2	672	" " "
	MI25	600	2	168	" " "
	MI7	600	2	672	" " "
	MI22	650	2	72	" " "

SPODUMENE + KCl + SiO_2

MI represents Spodumene:KCl 4:1

MI was mixed with SiO_2 in the proportions shown below.

3:5:1	Y12	450	2kb	336	SAN (SPOD QTZ)
5:5:1	Y11	450	2	336	SAN (Spod)
10:1	Y13	450	2	672	" "

SPODUMENE + NaCl (FIGURES 7 AND 8)

4:1	LI1	250	2kb	72	SPOD
	LI2	300	2	72	"
	LI3	350	2	72	"
	LI8	350	2	672	SPOD (Alb Euc)
	LI4	400	2	72	SPOD
	LI15	400	2	168	SPOD (ALB EUC)
	LI5	450	2	72	" " "
	LI10	450	2	672	SPOD ALB EUC

TABLE 4 CONT'D

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCT
4:1	LI6	500	2kb	72	SPOD ALB EUC
	LI12	510	2	672	" " "
	LI11	550	2	1344	" " "
	LI14	600	2	672	ALB EUC (SPOD)
	LI13	650	2	672	ALB EUC (SPOD)
5:1	L222	250	2kb	336	SPOD
	L223	250	2	672	"
	L224	350	2	336	"
	L24	350	2	672	SPOD (Alb Euc)
	L213	400	2	168	" " "
	L220	450	2	336	SPOD (ALB EUC)
	L22	450	2	672	SPOD ALB EUC
	L225	500	2	168	SPOD (ALB EUC)
	L212	500	2	336	" " "
	L210	500	2	672	SPOD ALB EUC
	L23	550	2	1344	ALB EUC SPOD
	L25	600	2	168	SPOD ALB EUC
	L27	600	2	672	ALB EUC (SPOD)
	L221	650	2	336	SPOD ALB EUC
	L211	650	2	672	ALB EUC (SPOD)
SPODUMENE + Na_2CO_3					
5:1	DG96	385	20,000 p.s.i.	552	SPOD ALB EUC
6:1	DG95	465	20,000	216	" " "

TABLE 4 CONT'D

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCT
8:1	DG97	465	20,000 p.s.i.	552	SPOD ALB EUC
SPODUMENE + NaCl + SiO_2					
L2 represents Spodumene:NaCl 5:1					
L2 was mixed with SiO_2 in the proportions shown below.					
3:5:1	X11	550	2kb	336	SPOD ALB QTZ
4:5:1	X12	450	2	336	" " "
6:1	X13	350	2	672	SPOD (ALB)
10:1	X14	450	2	672	SPOD ALB
SPODUMENE + $KF.2H_2O$					
4:1	MLi	250	2kb	672	LEP
	ML2	350	2	672	"
	ML3	450	2	672	"
	ML4	550	2	672	"
2:1	DG52	390	28,000 p.s.i.	168	LEP
5:1	DG65	390	28,000	168	LEP
12.5:1	DG54	390	28,000	168	SPOD (Lep)
MICROCLINE + Li_2CO_3					
4:1	DG89	465	15,000 p.s.i.	93	MIC
5:1	DG86	465	15,000	93	"
6:1	DG88	465	15,000	93	"

TABLE 4 CONT'D

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCTS
8:1	DG87	420	20,000 p.s.i.	216	MIC
9:1	DG11	315	25,000	120	MIC
	DG9	320	35,000	220	"
	DG12	350	22,500	312	"
	DG7	370	30,000	294	"
	DG8	400	30,000	220	"
	DG10	445	27,500	120	"
	DG13	465	15,000	408	"

MICROCLINE + LiF

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCTS
4:1	E15	250	2kb	336	MIC
	E13	250	2	672	MIC (Lep)
	E16	350	2	336	LEP
	E11	450	2	336	"
	E18	550	2	672	"
	E12	650	2	336	"
5:1	Dg71	415	13,500 p.s.i.	552	LEP
	DG70	520	30,000	120	LEP (Mic)
6:1	DG81	425	22,000	72	MIC (LEP)
	DG80	465	17,500	72	MIC (LEP)
10:1	DG50	380	25,000 p.s.i.	166	MIC (LEP)
	DG48	435	25,000	48	" "

TABLE 4 CONT'D

M/S	R	T(°C)	P_{H_2O}	t(hrs)	PRODUCTS
10:1	DG47	510	25,000 p.s.i.	335	MIC LEP
15:1	DG44	380	25,000	166	MIC (Lep)
	DG43	435	25,000	48	" "
	DG45	510	25,000	335	MIC (LEP)

MICROCLINE + LiF + SiO_2

E1 represents microcline:LiF 4:1

E1 was mixed with SiO_2 in the proportions shown below.

2:5:1	Z12	450	2kb	336	LEP QTZ
6:1	Z11	550	2	336	LEP (QTZ)
9:1	Z13	350	2	672	LEP (Qtz)

e. DISCUSSION OF RESULTS

(1) LIMITATIONS OF EXPERIMENTS

Before discussing the significance of these results, and their pertinence to aspects of complex pegmatite genesis, their limitations should be noted.

(i) The experiments were not designed to explain in detail the chemistry and phase relations of pegmatite systems, but merely attempt to indicate possible conditions and processes that may have occurred in nature.

(ii) In all the reactions investigated, the number of variables is large. Variations in pressure, temperature and time may all be important. Where possible, the effects of some of these have been experimentally evaluated, but as it was not possible to study all the variables, it was decided to study several systems generally, in order to obtain an overall picture of conditions during late-stage pegmatite genesis, rather than one or two systems in great detail.

(iii) Pegmatites, especially the rare-element bearing variety, contain many other minor elements, which, if included in the experiments, may have drastically affected the results obtained.

(iv) Many of the reactions did not proceed to completion, although the alkali salt present was theoretically sufficient for a total mineral transformation. Reference to the temperature, time, yield curves (Figures 6, 7, 8) suggests that there is an increasing yield of products with increasing temperature

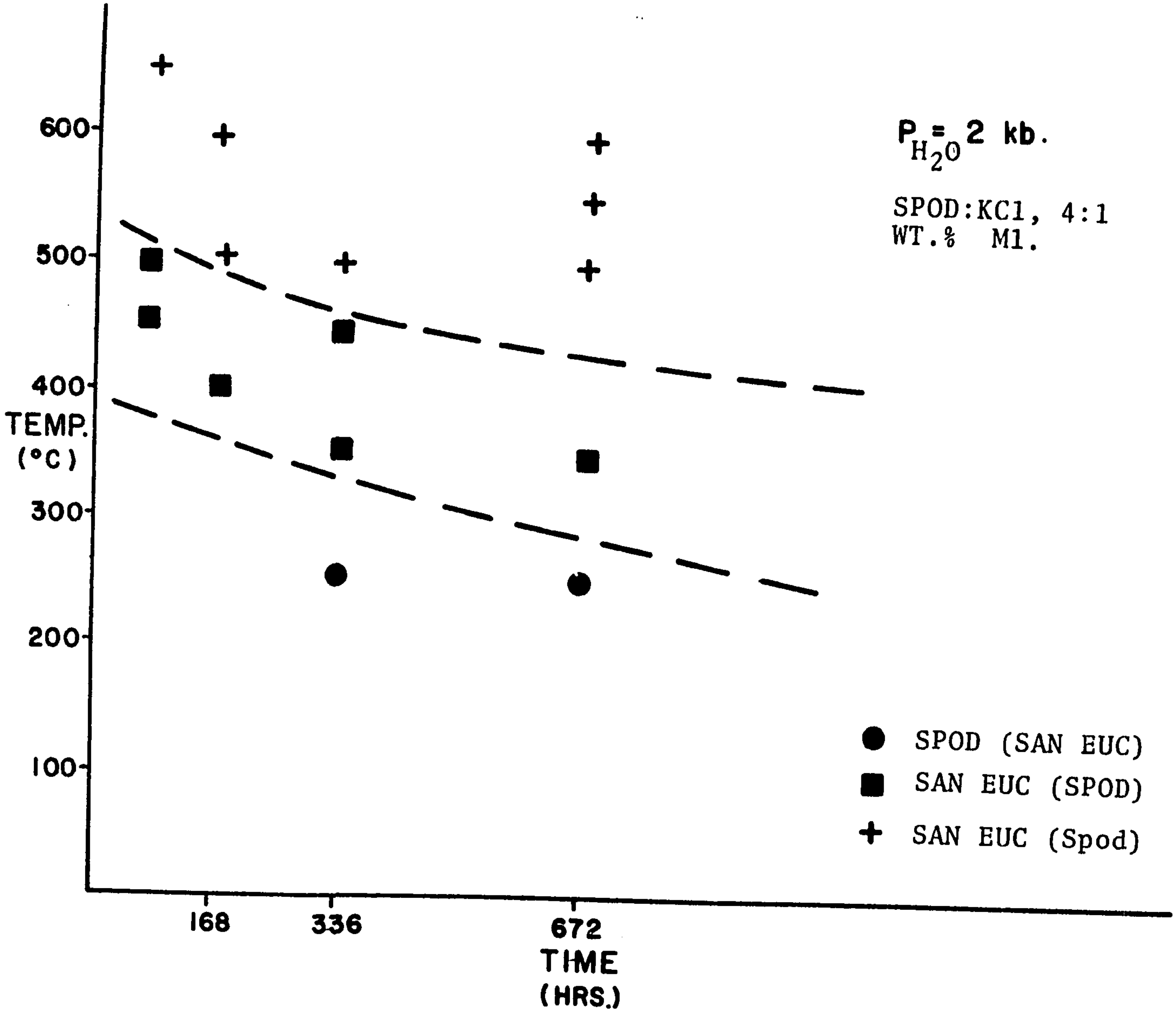


Figure 6. Temperature - time - yield curves for the reaction:-
$2LiAlSi_2O_6 + KCl \longrightarrow KAlSi_3O_8 + LiAlSiO_4 + LiCl$. (M1)

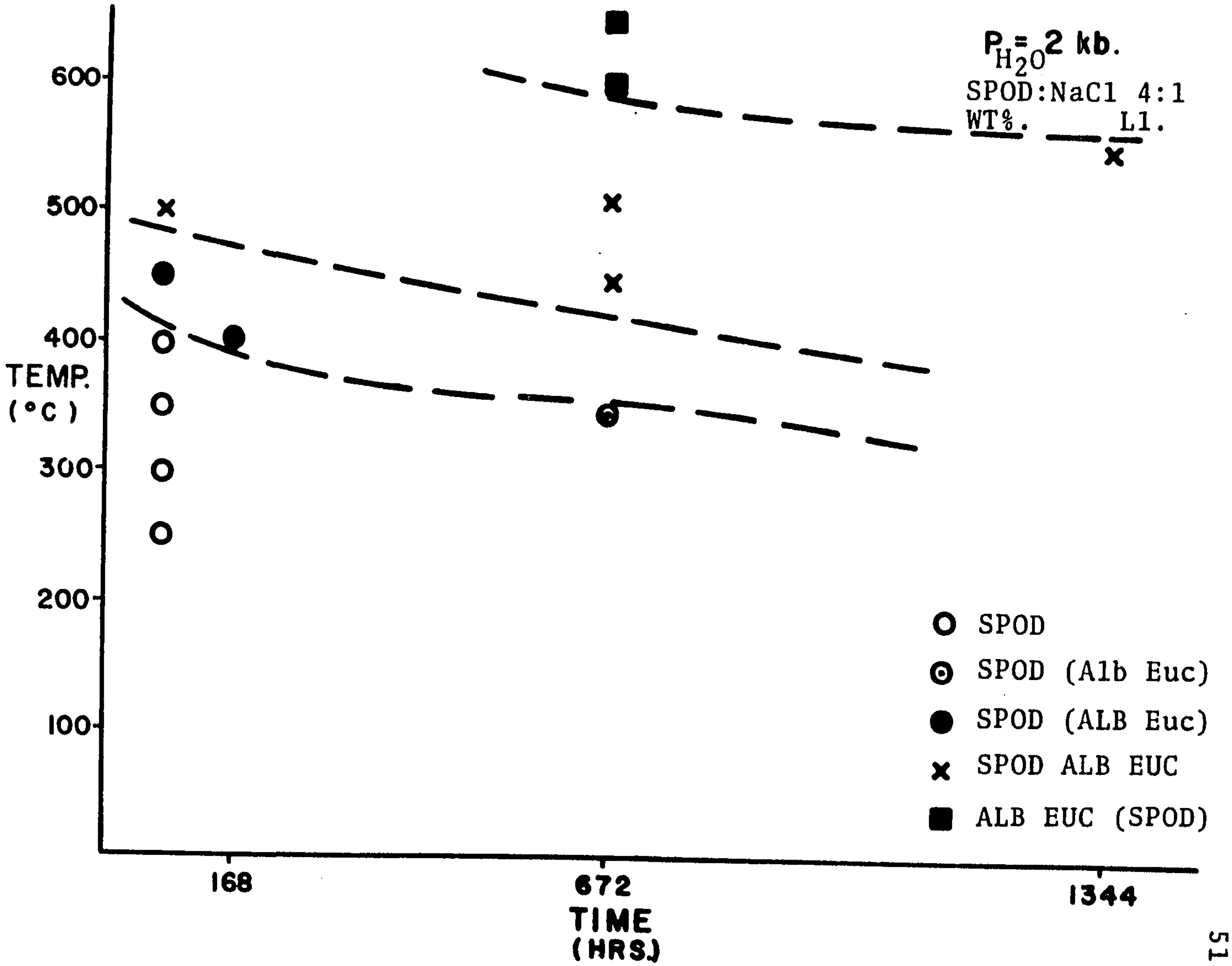


Figure 7. Temperature - time - yield curves for the reaction:- $2LiAlSi_2O_6 + NaCl \longrightarrow NaAlSi_3O_8 + LiAlSiO_4 + LiCl$ (L1).

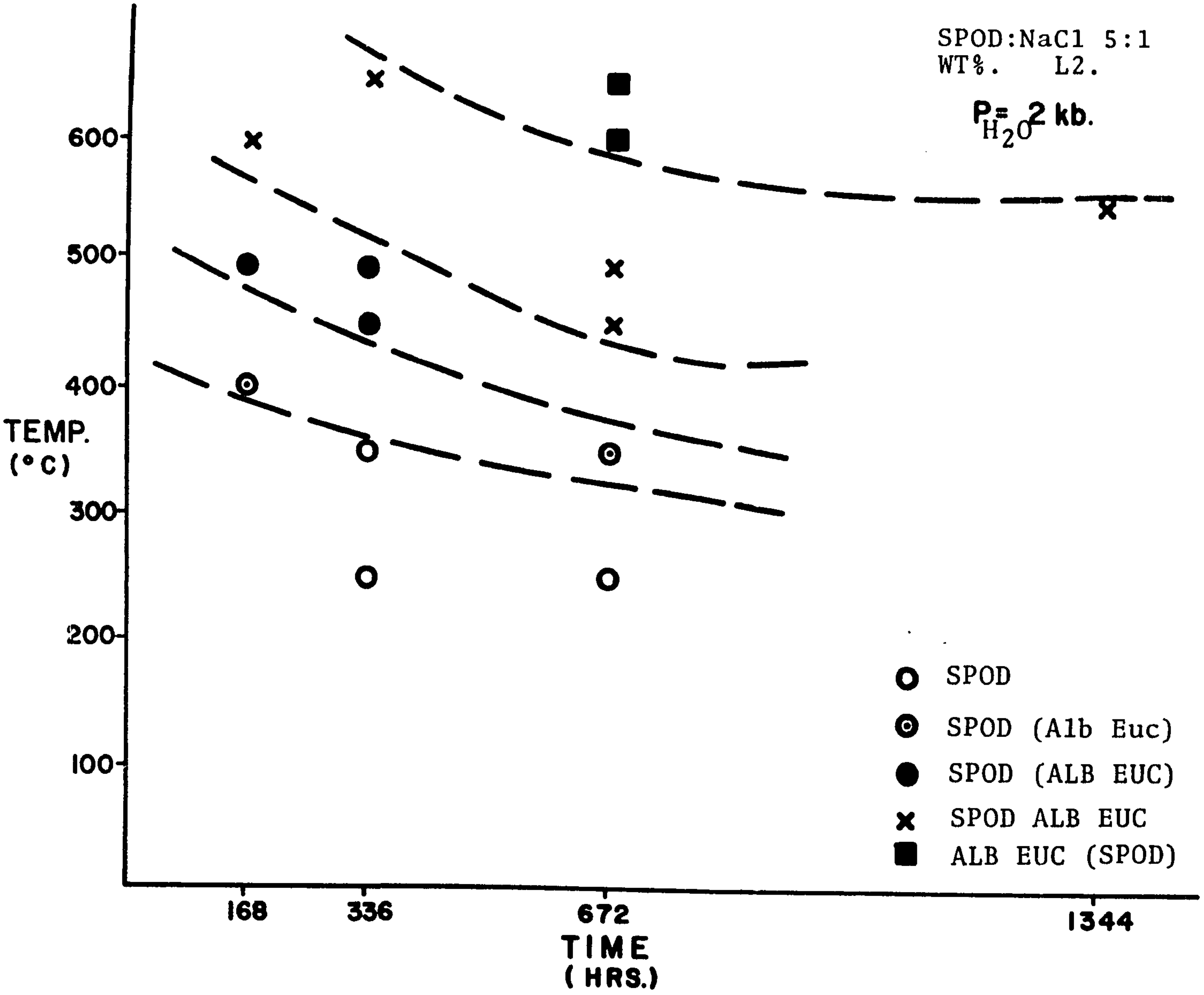


Figure 8. Temperature - time - yield curves for the reaction:-
$2LiAlSi_2O_6 + NaCl \longrightarrow NaAlSi_3O_8 + LiAlSiO_4 + LiCl.$ (L2)

and time, and that equilibrium may be established at some indefinite time.

(v) Definite temperatures, or small ranges of temperature, for given pressures, for each of these reactions to go to completion cannot be established from these experiments, as they occur at varying rates over the complete range of temperatures accepted for pegmatite formation (Jahns, 1955). It may, however, be concluded that within these limits, one of the basic factors determining whether these reactions will take place is the stage in the formation of a complex pegmatite at which a sufficient alkali concentration is reached.

For these reasons, the results of the experiments must be regarded as only qualitative to semi-quantitative and this should be borne in mind when interpreting their significance.

(2) SPODUMENE + K_2CO_3 AND SPODUMENE + KCl

These two reactions are discussed together, as there are no noticeable differences in the resulting products. In both cases the identifiable products are spodumene, sanidine and eucryptite, in varying proportions depending on reaction times and temperatures. At temperatures above 600 °C, the natural monoclinic α-spodumene is converted to tetragonal β-spodumene. This also occurred in other reaction systems and will not be referred to again. The transition has been discussed by Edgar (1968).

The reaction may be represented by the equation:-

$$2LiAlSi_2O_6 + K^+ + H_2O \longrightarrow KAlSi_3O_8 + LiAlSiO_4 + Li^+ + H_2O$$

In this reaction, and others described later, the excess alkali, in this case Li^+, is thought to be partly in solution and partly in the form of solid salt.

Sanidine, the monoclinic polymorph of $KAlSi_3O_8$, is a very rare mineral in pegmatites, being far more characteristic of high temperature volcanic assemblages. Nevertheless, it has been described from some shallow Tertiary pegmatites in New Mexico (Kelley and Branson, 1947), where it occurs in association with quartz and clevelandite in crystals up to 20 inches long. However, the large majority of pegmatites exposed today are Pre-cambrian or Palaeozoic in age, and typically contain the triclinic, low-temperature polymorph, microcline.

Microcline has yet to be synthesised, hydrothermally or in 'dry' systems, and even in runs made at 250°C and 2kb. in these experiments, sanidine is produced. However, Laves (1950) showed that the typical cross-hatch twinning on the albite and pericline laws, which is developed in the majority of microclines, is a logical consequence of inversion from a monoclinic symmetry. In addition, it has been demonstrated that a complete gradation exists between monoclinic sanidine and microcline showing maximum triclinicity (Goldsmith and Laves, 1954). Goldsmith (1953), has also shown that there is a strong tendency for sanidine to crystallise metastably in the stability field of microcline.

From the evidence given above, the presence of the high-temperature polymorph, sanidine, in the products of the present experiments is not, perhaps, surprising, and does not necessarily imply a high temperature of formation of the pegmatite. The presence of sanidine in these experiments may therefore represent microcline in nature, except that the subsequent inversion of sanidine to microcline has not taken place.

Eucryptite ($LiAlSiO_4$) is a very rare silica-deficient mineral, occurring only in lithium pegmatites, a silica-rich environment. Known occurrences in the western world are given by Mandarino and Harris (1965). The formation of eucryptite in lithium pegmatites could be due to one or more of the following mechanisms:-

a. Preferential concentration of silica in a vapour phase (Piotrowski, 1966).

b. Formation, through replacement by primary pegmatitic fluids, after the crystallisation of the quartz core.

c. Replacement by a later diagenetic leaching of spodumene.

d. Formation during a later period of metamorphism.

Of these, c and d appear to be the least likely. Diagenetic leaching of spodumene tends to remove Li_2O in solution and leave a pseudomorphic matte of sericite as seen in the Valor pegmatite and reported elsewhere (Pye, 1965). Later metamorphism has probably occurred in many of the older pegmatite districts, but eucryptite is still not found in these. However, it is a difficult mineral to identify and may have been overlooked in many cases. Ginzburg (1959) implies that it is a common pegmatite mineral in the U.S.S.R.

a. and b. are both plausible reasons for the formation of eucryptite by a silica-deficient phase in the crystallising pegmatite. It should be noted that both spodumene and eucryptite are rarely stoichiometric, and may be silica-rich or silica-poor (Skinner and Evans, 1960). It is possible that concentration of silica in a vapour phase may result in a silica-rich eucryptite. However, if this were a general mechanism, it should have occurred in many more pegmatites than the few in which eucryptite has been found. The author believes that a very late-stage formation after the crystallisation of the quartz core provides the most likely explanation.

However, the assemblage of minerals formed in this reaction has not been reported in nature, suggesting that replacement of spodumene by potassium-bearing solutions in a silica-deficient environment does not take place.

3. SPODUMENE + KCl + SiO_2

Runs made in this reaction with the addition of silica, showed that in the presence of sufficient silica, as indicated by the reaction below, eucryptite is not formed, and potassium-bearing solutions simply convert spodumene to sanidine. Incomplete reaction would leave spodumene and= potash feldspar together.

$$LiAlSi_2O_6 + SiO_2 + K^+ + H_2O \longrightarrow KAlSi_3O_8 + Li^+ + H_2O$$

The direct transformation of spodumene to microcline has been recognised in complex pegmatites. Norton (1962), for example, notices microcline pseudomorphically replacing spodumene in a replacement unit of the Hugo pegmatite in South Dakota. Pseudomorphic texture, such as this, is strong evidence for replacement, but the fact that potassium-bearing solutions have been shown to alter spodumene so easily in these experiments indicates that this reaction may be more common in complex pegmatites than previously envisaged. As mentioned earlier, replacement would be especially difficult to detect if it had occurred by reaction-replacement of an earlier-formed spodumene-bearing zone in a crystallising pegmatite.

The fact that replacement of spodumene by microcline occurs in nature, whereas its replacement by microcline and eucryptite apparently does not, suggests that any concentration of late-stage potassium, sufficient to alter spodumene to microcline, occurs when the pegmatitic fluid is still rich in silica. It is reasonable to assume that this would usually be prior to the crystallisation of most of the silica in the quartz core. The replacement unit in the Hugo pegmatite, in which this reaction apparently occurred, contains accessory quartz. This could either be due to remnant quartz from an earlier-formed zone, or quartz co-crystallised with microcline. The latter possibility may indicate that replacement occurred from a silica-rich fluid.

4. SPODUMENE + NaCl AND SPODUMENE + Na_2CO_3

No noticeable differences in products were detected using the two different salts, and the same type of reaction occurred as described for KCl and K_2CO_3. In this case albite and eucryptite were the products.

$$2LiAlSi_2O_6 + Na^+ + H_2O \longrightarrow NaAlSi_3O_8 + LiAlSiO_4 + Li^+$$

The assemblage albite and eucryptite has been found in complex pegmatites, but is very rare. Brush and Dana (1880), described the original albite-eucryptite intergrowth from the Branchville pegmatite in Connecticut. Stewart (1960) believes that it was formed by the alteration of spodumene in the manner outlined above. Such a reaction gives an equimolecular mixture, which contains 32.46 weight percent eucryptite. Brush and Dana found 32.1 weight percent at Branchville, strengthening the hypothesis that the intergrowth has formed by this type of replacement. A similar intergrowth has been described from the Centre Strafford pegmatite in New Hampshire (Mrose, 1953). Ginzburg (1959) describes such replacement from pegmatites in the U.S.S.R. but gives no exact localities.

As described previously for potassium-rich solutions, it must be assumed that this mineral transformation takes place when the pegmatite is deficient in silica. In such a silica-rich environment as an acid pegmatite, the most plausible explanation, once more, is replacement occurring after the crystallisation of the quartz core.

5. SPODUMENE + NaCl + SiO_2

Sodium-bearing solutions, acting on spodumene in the presence of excess silica, gave a variety of results depending on the silica concentrations and the length of the run. Some products contained crystalline quartz, and others just a mixture of spodumene and albite suggesting that the experiments were not sufficiently long to convert all the spodumene to albite. Eucryptite was not found. The reaction can be written as:-

$$LiAlSi_2O_6 + SiO_2 + Na^+ + H_2O \longrightarrow NaAlSi_3O_8 + Li^+ + H_2O$$

These reactions show that spodumene is readily converted directly to albite. Similarly Orville (1963) has shown that microcline can readily be converted to albite by a similar alkali-ion exchange reaction. Replacement of both spodumene and microcline by albite is very common in complex pegmatites, occurring both as clevelandite and sugary albite. Ginzburg (1959) states that "all spodumene pegmatites are more or less albitized." Hutchinson (1959), and Wright (1963) both recognise an albite replacement unit in the Montgary pegmatite in Manitoba. Numerous other examples have been described (Jahns, 1955; Quensel, 1957; Sheridan et al, 1957; Norton, 1962).

The results of these experiments indicate that a strongly alkaline aqueous solution reacting on spodumene or microcline provides a reasonable mechanism for the development of such replacement bodies. It has been suggested by Ginzburg (1959) that the formation of sugary albite, rather than clevelandite, is accompanied by a sudden pressure release.

The stages of pegmatite development at which this may occur are probably just prior to, or contemporaneous with, the crystallisation of the quartz core, when the melt is still sufficiently rich in silica to prevent the formation of encryptite. Field relationships also show that quartz cores cut albite replacement bodies.

6. SPODUMENE + $KF.2H_2O$

The only mineral formed by this reaction was lepidolite. A possible equation to represent the reaction is:-

$$2LiAlSi_2O_6 + KF.2H_2O \longrightarrow KLi_2AlSi_4O_{10}(OH,f)_2 + Al(OH)_3$$

This equation, however, is very generalised.

$KF.2H_2O$ was the only salt used which reacted with spodumene to give lepidolite. The importance of fluorine in the formation of lepidolites has been mentioned by several workers. Foster (1960), from published analyses of lepidolites and other lithia-bearing micas, found an approximate 1:1 ratio of Li_2O:F. Munoz (1968), using glasses as starting materials, could synthesise lepidolite only when fluorine was present in the system. A hydroxyl-rich lepidolite could not be produced. Because both OH^- and F^- have the same charge and ionic radii, F^- can readily substitute for $(OH)^-$ in the mica structure. No satisfactory explanation has yet been found for the importance of fluorine in the formation of lepidolite.

The experiments reported here, using a different approach from previous workers, are in agreement with the previous observation, as spodumene could only be transformed to lepidolite when both potassium and fluorine were present. This is probably also true in nature. This evidence suggests that spodumene alters to lepidolite in a pegmatite, only if a sufficient concentration of both elements builds up in the late-stage solutions.

The Valor pegmatite, described in a previous chapter, exhibits this type of replacement.

7. MICROCLINE + Li_2CO_3

No reaction was observed with microcline and lithium carbonate, although shifts in the "d" spacings of the feldspar, as shown by the X-ray diffractometer patterns, suggest that there may have been slight solution of microcline and reprecipitation of sanidine. No lepidolite was observed in this reaction, strengthening the apparent necessity of fluorine for the formation of lepidolite from microcline as well as spodumene. Another possible product of this reaction was the formation of an unstable lithium feldspar, $LiAlSi_3O_8$, as found by Scavnicar and Sabatier (1957) using lithium chloride, but this was not observed in the current experiments.

8. MICROCLINE + LiF

The action of lithium fluoride on microcline produced lepidolite, according to the possible reaction:-

$$4KAlSi_3O_8 + 6LiF \longrightarrow 3KLi_2AlSi_4O_{10}(F)_2 + KAlO_2$$

Once again, the equation is rather hypothetical due to lack of control in the identification of products. This re-emphasises the importance of fluorine in the production of lepidolite.

Replacement of microcline by lepidolite has been described in the lepidolite replacement bodies of the Montgary pegmatite by Wright (1963), who states that the contacts of these bodies range from knife-sharp to transitional over five feet. In the transitional parts purple rocks showing relict cleavages of microcline, somewhat obscured by many tiny lepidolite flakes, are observed. More extensive replacement results in an increase in the grain size of the lepidolite and gradual obliteration of relict microcline cleavages.

9. MICROCLINE + LiF + SiO_2

The few runs made in this reaction system yielded lepidolite and quartz. Earlier runs in the system without silica also formed lepidolite, showing that SiO_2 is not necessary for the formation of lepidolite by the alteration of microcline. It appears that this will also be the case in the alteration of spodumene by $KF.2H_2O$. Such transformations may therefore occur after the formation of the quartz core, resulting in essentially pure lepidolite bodies, as observed at Valor (Figure 3), Montgary (Hutchinson, 1959; Wright, 1963) and Varutrask (Quensel, 1957). Some minor quartz in these zones may be due either to excess silica present in the system, or to remnant quartz preserved after the alteration of earlier quartz-bearing zones. The latter possibility seems more likely, as the lepidolite bodies at Montgary have replaced a microcline-quartz zone.

In conclusion, the formation of lepidolite by alteration of microcline or spodumene may occur when a sufficient concentration of fluorine has built up in the system, either before or after the formation of the quartz core.

CHAPTER 4

GEOCHEMICAL METHODS AND RESULTS

1. INTRODUCTION

Variations in alkali and fluorine contents of pegmatite minerals may provide an indication both of geochemical trends during the differentiation sequence from pegmatites of simple to complex mineralogy, and of basic geochemical differences between pegmatite districts.

A series of micas from the Preissac-Lacorne and Black Hills pegmatite districts were analysed for alkali and fluorine contents. Alkali analyses were obtained commercially by an atomic absorption method, and fluorine analyses were performed by the author using an electron probe technique. The geology of the source pegmatites and pegmatite districts was described in Chaper 2, and the sample locations are shown in Figures 2, 3 and 4.

Because micas contain both $(OH)^-$ and K^+ ions, and may therefore have F^- substituting for the former and Rb^+ for the latter, they can be used to determine geochemical trends in pegmatites. Both fluorine and rubidium are recognised as important geochemical indicators in pegmatites (Ginzburg, 1960).

The analytical methods used and the results obtained are described and discussed in this chapter.

2. PREPARATION OF SAMPLES

The majority of the samples used were coarse-grained, and the micas were therefore very easily separated from their associated minerals. The crystals were crushed in a mortar to about 2 or 3 mm., and the clearest flakes, showing no iron staining, vegetable matter or associated mineral grains, were picked out with tweezers under a binocular microscope. These were then washed in acetone and mechanically ground. In some cases, the mica and associated mineral were so intimately mixed that they had to be roughly crushed together before the mica could be hand-picked.

3. ANALYTICAL METHOD

a. ALKALIES

Analysis of the alkali content of the micas was performed by Mr. K. Ramlal at the University of Manitoba using atomic absorption spectrophotometry.

b. FLUORINE

Wet chemical analysis for fluorine is notoriously lengthy and difficult. Darling (1967) used an electron probe fitted with a light element kit for fluorine analysis with satisfactory results, and this procedure was followed in the present study.

Mica flakes up to 1mm. across, separated in the manner described above, were used for probe analysis. The flakes were mounted in epoxy on glass slides, four samples to a slide. The flakes were allowed to settle in the epoxy, which then took one day to harden. The samples were then polished in four stages, and examined under a petrographic microscope to ensure that enough flakes of each specimen appeared on the surface, and that these were sufficiently smooth for analysis. The samples were then carbon-coated, each slide being coated with as near the same thickness of carbon as possible.

Five mica 'standards' were obtained from Dr. J. H. T. Rimsaite of the Geological Survey of Canada, and were prepared and mounted in the same way as the other specimens. They had been analysed for fluorine by J. G. Sen Gupta using a colourimetric method (Sen Gupta, 1968).

Due to the low atomic number of fluorine, the accessory 'light element kit' had to be used on the electron probe. The characteristic X-radiations of the light elements have long wavelengths which are more difficult to reflect and are more easily absorbed than those of the heavier elements. The reflecting crystal must have a large d-spacing, and a high vaccuum is required in the system to prevent excessive absorbtion. Even with these specifications, a fifty or twenty second count time was required due to the low number of counts being received.

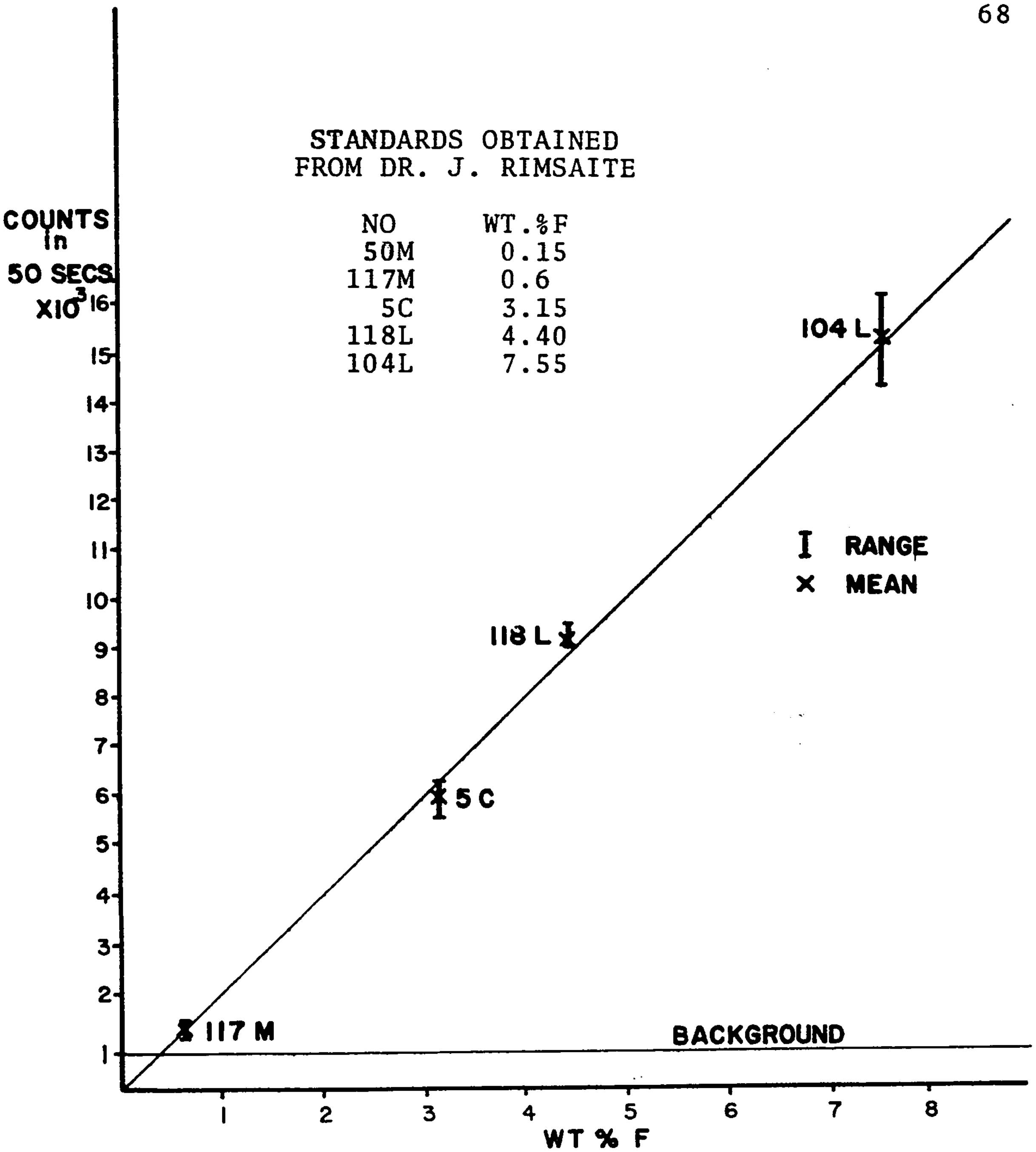
A fluorescent willemite crystal, mounted with the specimens, was used for focussing the beam and correcting drift. Willemite readings should be constant, and any change is due to drift of the beam. Hence willemite was measured at the beginning and end of each set of readings, and any difference was allocated proportionately to the intervening readings.

Three different flakes of each sample and standard were measured, with two counts being taken on each flake, and the mean value used. The counts obtained from the standards, plotted against the fluorine content determined chemically, are shown in Figure 9. From this graph, counts taken on the samples were used to determine the fluorine content. Because the background counts were high, fluorine contents lower than 0.40% were not detectable.

4. RESULTS

The results obtained are shown in Table 5. The results from the Preissac-Lacorne district have been arranged in order of the probable genetic sequence of pegmatite types. Those from the Black Hills district have been recorded in zonal sequence in cases where more than one zone was sampled.

Results obtained for fluorine are only semiquantitative. When analysing for an element with atomic number as low as that of fluorine, the limit of the electron probe's capabilities is approached, with the errors all building up to a maximum.



STANDARDS OBTAINED
FROM DR. J. RIMSAITE

NO	WT.%F
50M	0.15
117M	0.6
5C	3.15
118L	4.40
104L	7.55

Figure 9. Weight percentage of fluorine in mica standards plotted against counts obtained in a 50 second period.

TABLE 5

ANALYTICAL RESULTS

All results are given in weight percentages.

n.d. = not detectable

a. PREISSAC-LACORNE REGION

	K_2O	Na_2O	Li_2O	Rb_2O	Cs_2O	F	K_2O/Rb_2O	K_2O/Cs_2O
LN1	8.01		0.4037	.505	.017	n.d.	15.96	471.2
LN2	8.00		0.2992	.416	.019	n.d.	19.23	421.1
LN3	7.84		0.4101	.494	.023	n.d.	15.87	340.9
MBH1	7.75			.621	.046	-	12.48	168.5
MBH2	8.03		0.3606	.873	.027	0.26	9.20	297.4
MBH3	7.88			.906	.038	-	8.70	207.4
MBH4	7.84		0.3573	1.003	.072	0.72	7.82	108.9
MBH5	7.53			.910	.050	-	8.27	150.6
MBH6	7.73		0.3854	.951	.041	0.55	8.13	188.5

TABLE 5 CONT'D

	K_2O	Na_2O	Li_2O	Rb_2O	Cs_2O	F	K_2O/Rb_2O	K_2O/Cs_2O
MBH7	7.76			1.056	.082		7.35	94.6
MBH8	8.05		0.1959	1.057	.183	0.64	7.62	43.9
QL28						1.4		
QL46						1.15		
VP1	7.96		0.8449	.874	.048	0.78	9.11	165.8
VP2	8.03		0.8826	.850	.058	1.02	9.45	138.4
VP3	7.99		0.4381	.979	.068	0.58	8.16	117.5
VMA14	9.55	.477	1.287	1.310	.387	1.8	7.29	24.68
VMA2	10.19	.587	3.246	2.04	.541	2.65	4.995	18.84
VMA1	9.23	.697	1.50	2.297	.346	3.37	4.02	26.68
VMA3						4.85		
EMG7	7.958	.313	.921	1.084	.187	-	7.34	42.56

b. BLACK HILLS REGION, SOUTH DAKOTA

HUGO PEGMATITE

	K_2O	Na_2O	Li_2O	Rb_2O	Cs_2O	F	K_2O/Rb_2O	K_2O/Cs_2O
H5	9.21	.729	.387	.358	.017	.53	25.71	541.7
H11	9.43	.827	.161	..325	.014	.65	29.02	673.6

TABLE 5 CONT'D

	K_2O	Na_2O	Li_2O	Rb_2O	Cs_2O	F	K_2O/Rb_2O	K_2O/Cs_2O
H10	8.48	.686	.340	.411	.056	.85	20.6	151.4
H2	10.11	.537	.602	.540	.066	1.05	18.7	153.2
DAN PATCH								
DP4	10.01	.991	.107	.359	.013	n.d.	27.9	770.0
DP5	9.46	.829	.197	.390	.026	n.d.	24.3	363.8
PEERLESS								
P2	10.22		.1136	.5988	.1693	0.90	17.1	60.1
P1	9.63	.512	.147	.659	.053	0.92	14.6	181.7
P4	10.99	.422	.203	.706	.192	0.79	15.6	57.2
TIN MOUNTAIN								
TM1	10.54	.504	.254	1 .172	.283		9.1	37.4
ETTA								
E3			.1134	.0879	.001	0.58		

Analysts: F^-, C. W. Armstrong; remainder K. Ramlal, University of Manitoba

In addition, both standards and samples are markedly inhomogeneous (Rimsaite and Lachance, 1966). As a result, fluorine counts on different flakes of the same sample varied by as much as 40%. However, by using several flakes, and recording several counts on each, a semiquantitative average was obtained.

5. DISCUSSION OF RESULTS

a. PREISSAC-LACORNE DISTRICT

Pegmatites studied from this district include those of simple mineralogy, beryl- and spodumene-bearing varieties, and a complex spodumene - lepidolite - pollucite pegmatite. As both the regional and internal zoning patterns exhibit certain distinctive changes, variations within the district, and within the latter body will be discussed. Certain elements showing little or no change, or those for which results are incomplete, are not considered.

Each of these types of pegmatite represents a stage of differentiation of the end-product of the source magma, with increasingly complex mineralogy indicating a greater degree of differentiation. The various zones and replacement bodies of the Valor pegmatite represent extensions of this process by fractional crystallisation. In Figure 10 the various components of the micas are plotted against the source pegmatite, or pegmatite zone, arranged in their probable genetic sequence. Where several samples have been taken from one 'type' of

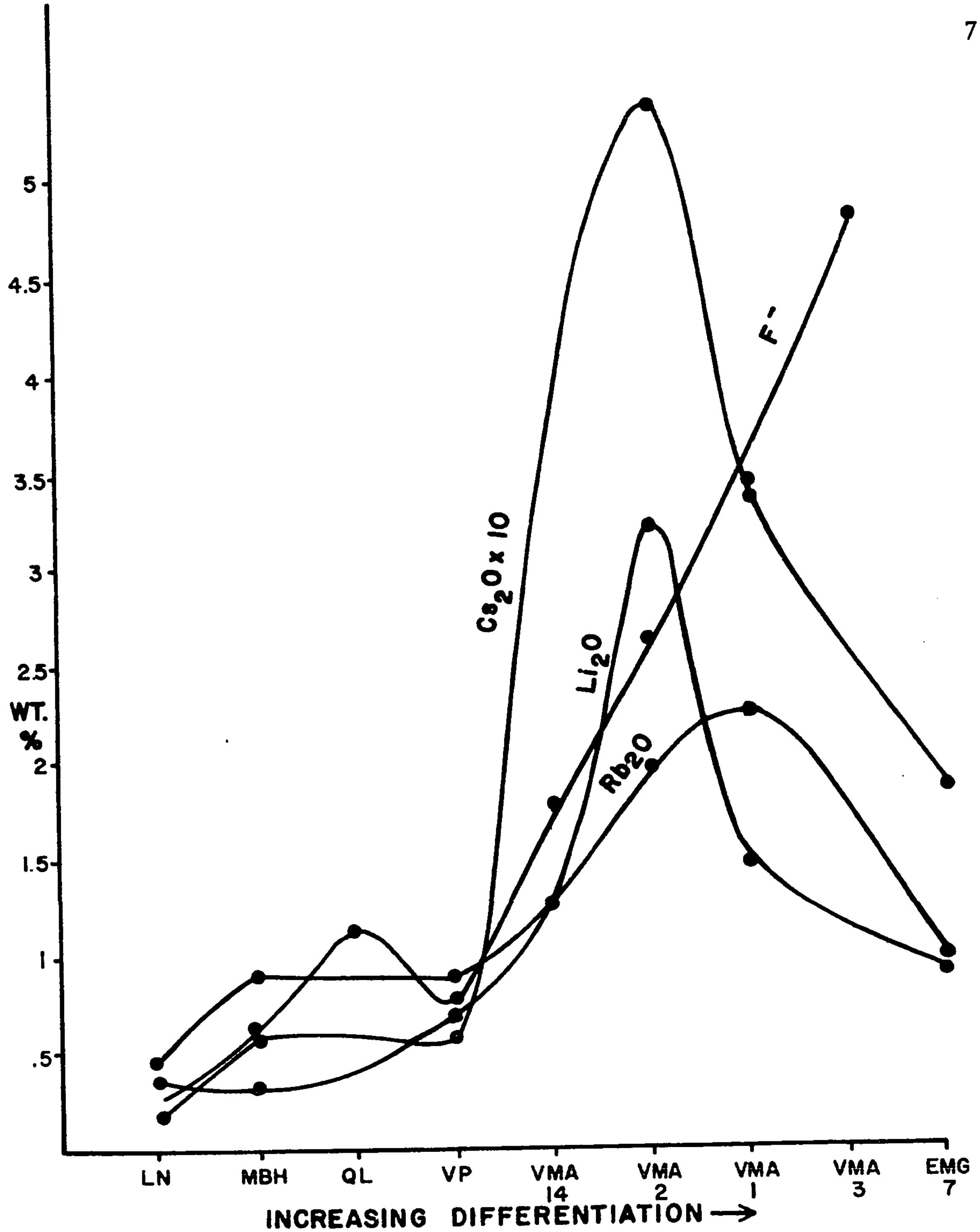


Figure 10. Weight percentages of alkalis and fluorine in pegmatitic micas from the Preissac-Lacorne district, plotted against genetic sequence.

pegmatite, a mean value has been used. A complication here is the fact that the border zone assemblage from the Valor pegmatite (VP), although occurring in a very late-stage pegmatite, could probably be better equated with the Massberyl assemblages (MBH), as its mineralogy is identical, and values obtained for minor alkali and fluorine content are very similar.

Cs_2O and Li_2O both increase erratically up to the stage of crystallisation of the coarse lepidolite (VMA2), in the wall zone of Valor, after which they steadily decrease. In the case of Cs_2O, it must be assumed that between the crystallisation of this lepidolite and the next one in the genetic sequence, the majority of the Cs_2O left in the melt crystallised as pollucite, leaving considerably less Cs_2O for incorporation in the later micas. This type of lepidolite (VMA2) also forms the bulk of the mica in the pegmatite, and it appears that most of the Li_2O was used here, leaving only minor amounts for the less well developed types forming subsequently.

Apart from in the fine-grained oncosine (EMG7), Rb_2O shows a steady increase. The oncosine appears to be rather unique, and was probably formed at a very late stage from the last residue of the pegmatite melt. In addition to increase in the absolute Rb_2O content with greater differentiation, the K_2O/Rb_2O ratio shows a steady decrease. This geochemical indicator is one of several described by Ginzburg (1960) as significant in the pegmatite process. Due to both elements having the same charge, and similar ionic radii (K^+1.33Å, Rb^+1.47Å), Rb^+ is the most likely ion to substitute for K^+ in potassium-bearing minerals. However, Rb^+ will increase during differentiation, as it has a slightly different radius, and this will be reflected in the K_2O/Rb_2O ratio. In the Preissac-Lacorne district, this ratio shows a steady decrease with increasing mineralogical complexity. It is interesting to note that Cs^+, which also occurs in the potassium-bearing minerals, shows a much more erratic change due to the dissimilarity of ionic size of K^+ (1.33Å) and Cs^+ (1.67Å).

F^-, substituting for $(OH)^-$ in the mica structure, shows a steady increase throughout both the regional and internal zonal sequences.

b. BLACK HILLS DISTRICT

Results from the Hugo pegmatite, from which samples were taken from four of the zones, are shown in Figure 11. Sample H5 was taken from the border zone, where chilling probably causes the results to reflect the composition of the pegmatite melt at the time of intrusion. The micas in the other zones show similar steady increases in Cs_2O, Rb_2O, Li_2O and F to those found in the Preissac-Lacorne area. Irregularities, such as the sudden decrease in Cs_2O are not encountered in these micas, but would not be expected due to the absence of pollucite in the pegmatite.

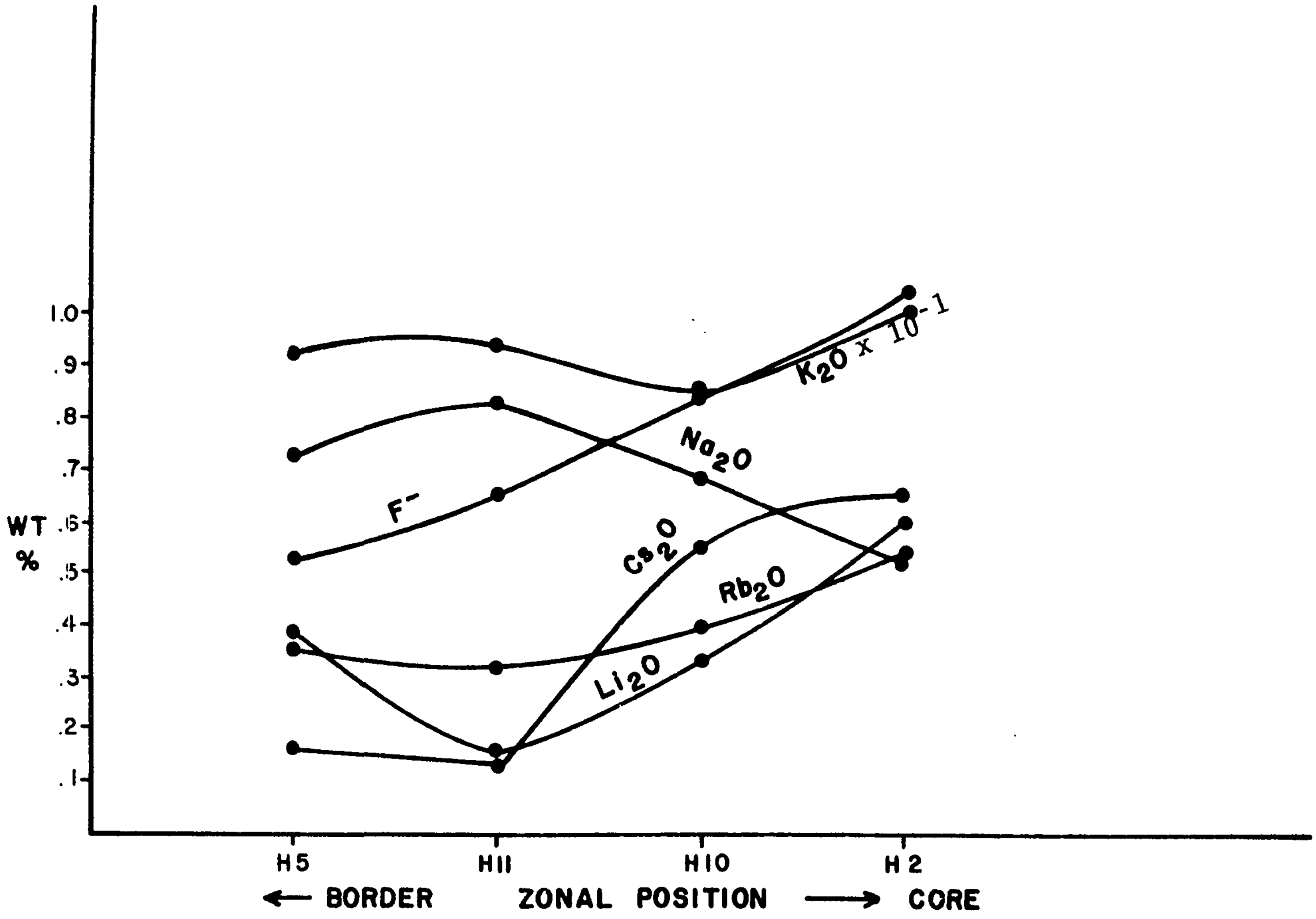


Figure 11. Weight percentages of alkalis and fluorine in pegmatitic micas from the Black Hills district, plotted against zonal position.

The results obtained for the minor alkalis from this and other pegmatites in the area show that minor alkali content is generally lower than at Preissac-Lacorne. This is surprising considering the large, complex, lithium pegmatites in the area but may indicate that the Preissac-Lacorne area is a geochemical province particularly rich in these rare alkalis.

Fluorine also appears to be generally lower, even in bodies such as the Etta pegmatite, where vast tonnages of spodumene show that lithium has been intensely concentrated. The Hugo and Peerless pegmatites, although large and well-zoned, only show fluorine contents comparable with those of the beryl pegmatites of the Preissac-Lacorne district.

During the early stages of this study, Rb_2O and Cs_2O were believed to be of significant importance in the formation of lepidolite. However, lepidolite was easily produced without these oxides in the experimental work described in Chapter 3, and despite the differences in minor alkalies in these two areas, both contain lepidolites and lithia micas. It seems that although the content of Cs_2O and Rb_2O in these micas may be high (in some cases higher than the lithia content), their presence is not essential for the formation of lepidolites.

c. CONCLUSIONS

The important conclusions to be drawn from the geochemical aspect of this study are:-

1. There are distinct basic geochemical differences between

pegmatite districts.

2. In any one pegmatite district, a guide to the complexity of a pegmatite, even if only the border zone is exposed, may be found in the range of Rb_2O contents or in the K_2O/Rb_2O ratios. Rb_2O is the best oxide to use, for unlike the others it is never lost from the system as a rubidium mineral, and substitutes easily for K_2O in the many pegmatitic potassium-bearing minerals. The latter will occur throughout most stages of pegmatite differentiation, the main exceptions being quartz cores and albite replacement bodies.

3. Fluorine steadily increases toward the late stages of pegmatite development, and this increase is important in the stage of formation of lepidolite.

CHAPTER 5

OVERALL DISCUSSION AND CONCLUSIONS

1. INTRODUCTION

The present experimental and geochemical studies have indicated some of the processes which may take place during the formation of complex, zoned, lithium pegmatites, and the possible reasons for these processes. A discussion of pegmatite crystallisation and the accompanying replacement is necessary as a basis for proposing a general model of pegmatite genesis. This model can then be related to some of the world's better-known pegmatites.

2. PEGMATITE CRYSTALLISATION AND ACCOMPANYING REPLACEMENT

In the introductory chapter, the principal theories for complex pegmatite genesis were briefly mentioned and discussed, particularly the problem of whether such bodies form in open or restricted systems. It was concluded that the bulk of the evidence (Jahns, 1955, etc.), suggests that such pegmatites were emplaced in one movement, and crystallised in a restricted system. The term 'restricted system' indicates that there is no significant addition of material after emplacement, but that material may escape from the system during crystallisation.

Evidence for a magmatic, as opposed to a metamorphic, origin for complex pegmatites was not considered in Chapter 1, as this has been extensively discussed in the literature (Cameron et al, 1949; Page et al, 1953; Jahns, 1955; Wright, 1963), where the overwhelming argument is for a magmatic source for the pegmatitic fluid.

On the assumption that the pegmatitic magmas are emplaced in restricted systems, the nature of such magmas at the time of their emplacement, and their subsequent mechanism of crystallisation can be discussed.

Acid magmas, producing granitic pegmatites, may contain up to 8-10% water (Goranson, 1931). Steam emitted in present-day volcanic regions is further evidence of fairly high water contents, although some of this may be of groundwater origin. By fractional crystallisation, a granitic magma containing only 1-2% water could become greatly enriched in an aqueous phase. Gevers (1937) suggests that only a small amount of water is taken up by the crystallisation of micas, and residual melts are therefore enriched in water. There will also be a concentration of certain rare elements and volatiles (Li, Rb, Cs, F etc.) that cannot be incorporated in the crystal structures of the cooling granite.

Despite the abundance of water in these melts, they must be essentially magmatic at the time of their emplacement.

The deformation of wall rocks around many complex pegmatites and the predominance of typical granitic minerals in the outer zones indicate a viscous silicate magma at the time of intrusion.

After emplacement of this water-rich magma, crystallisation begins from the walls inward by a process of fractionation, forming a series of roughly concentric zones. The number and sequence of these zones depends on a variety of factors, discussed in Section 3 of this chaper. In the early-formed zones, typical granitic minerals predominate, and the pegmatitic fluid becomes even richer in water and any other rare elements which may be present. At some stage of this process the fluid ceases to be essentially magmatic, and becomes essentially hydrothermal in character.

Page et al (1953) have related the stage of development of a hydrothermal fluid with both increasingly complex mineralogy and the formation of replacement features in pegmatites. Such a fluid is certainly in disequilibrium with pre-crystallised material, and may contain a higher concentration of certain elements and volatiles than a coexisting silicate magma. It would be far more fluid than the silicate phase, and therefore have more ability to penetrate along any channelways that may open up in pre-crystallised material. Such channelways might bring the hydrothermal fluid into contact with zones formed at an early stage in the pegmatite's formation, and these would be far more likely to be in disequilibrium with the fluid. Another possibility is that such a fluid may concentrate in one part of the contracting magma chamber, forming a limited replacement body.

The possibility that replacement occurs while the aqueous phase is still dissolved in the pegmatitic melt should also be considered. Fractional pegmatite crystallisation involves a stage when the pegmatitic rest liquid is in disequilibrium with the immediately pre-crystallised minerals, and reaction replacement may occur prior to the crystallisation of the next zone. The extent to which this can occur is uncertain, but may be related to the rate of cooling, initial concentration of alkalis, etc. Gevers (1937) has pointed out that many of the replacement features observed in pegmatites require very little actual exchange of material between pre-crystallised mineral and replacing fluid. These include the substitution of sodium for potassium or lithium (forming albite from microcline or spodumene), with little or no exchange of silica and alumina. Such alkali-ion exchange reactions are possible in a magmatic fluid, but for the reasons outlined in the preceding paragraphs, a hydrothermal fluid is probably a more favourable medium for these reactions. Replacement will therefore occur more commonly and extensively in the later stages of crystallisation of the pegmatite.

A distinct aqueous phase could separate from the melt by gradual change, liquid immiscibility or resurgent boiling. A gradual change from silicate melt to aqueous phase is the most difficult to conceive, as it does not explain factors such as the formation of quartz cores.

Smith (1949) has shown experimentally that silicate and aqueous phases become immiscible in the range 290 °C to 550 °C at accepted pressures for pegmatite genesis. This is merely the range in which the aqueous solution reaches a limiting solubility in the melt, and the actual temperature depends on the initial conditions of the pegmatite melt. Immiscibility appears to be a plausible explanation for the late-stage separation of two phases, and hence for the mechanism of replacement. A vapour phase, of course, would also be present.

The concentration of water and other volatiles during pegmatite crystallisation raises the vapour pressure, but the action of falling temperature tends to lower it. If concentration succeeds in raising the vapour pressure to the level of the confining pressure, resurgent or secondary boiling occurs. This is distinct from ordinary boiling in that it is in response to cooling rather than heating. Jahns (1955) envisages resurgent boiling as having a distillation effect on the residual pegmatite fluid, possibly removing alkalis and some silica and alumina, and leaving a silica-rich phase to form the quartz core. However, the same end result can also be formed by liquid immiscibility.

Due to lack of knowledge of the effect of solutes with different solubilities on the residual pegmatite fluid, the mechanism of separation is not known, but both liquid immiscibility and resurgent boiling may be considered as distinct possibilities. It is possible that either can occur under certain conditions.

3. FACTORS INFLUENCING PEGMATITE FORMATION

A general model for pegmatite formation must allow for variations in the bulk chemistry of pegmatite melts at the time of initial emplacement, and for variations in their development after emplacement. The few calculations that have been made of the bulk chemistry of individual pegmatites (Table 6) show substantial differences in the content of certain elements, particularly, and most important for the present approach, in alkalis and fluorine. These basic differences are due to a number of factors, some of which are interrelated.

a. The geochemical province in which the pegmatites are located.
b. The depth of intrusion of the parent magma.
c. The size of the intrusion.
d. The stage of withdrawal of the pegmatite melt from the magmatic hearth.
e. The size, shape and attitude of the pegmatite chamber.
f. The rate of cooling of the pegmatite melt.

g. The permeability of the wall rocks surrounding the pegmatite chamber.

Each of these will now be considered:

a. Both the studies described here, and others (Siroonian et al, 1959, etc.), have shown that definite differences may exist in the chemistry of unrelated granitic magmas. Such basic differences affect not only the mineralogy of the parent granite, but are reflected in the chemistry and mineralogy of any associated pegmatites. Siroonian et al (1959) concluded that lithium pegmatites are found only in geochemical provinces in which the parent granites contain a higher than average Li content.

b. The depth of intrusion of the parent magma may be important for several reasons. Shallow intrusions may be associated with fractures running to the surface, through which volatiles could escape entirely. Depth of intrusion also determines the rate of cooling of the granite. If the granite cools quickly, many elements that would normally concentrate in the pegmatite fraction may be incorporated in the lattices of typical granitic minerals. Lastly, Ginzburg (1960) has suggested that there may be an association of certain types of pegmatite with certain depths of intrusion.

c. The size of the intrusion also affects the rate of cooling, and the probability of a large pegmatite fraction being developed.

d. Pegmatite fractions 'tapped off' at successive stages from the crystallising magma have different bulk compositions, with the later fractions being more likely to contain the rare elements and volatiles, as these will have had more chance to be concentrated during differentiation. Pegmatites formed from the later fractions have a more complex mineralogy, and possibly also a more complex structure, than early-formed pegmatites. Heinrich (1953) suggests increased fluidity of successive fractions as a reason for the regional zonation of pegmatites discussed earlier (p. 10).

e. The attitude of the pegmatite body affects its final mineralogy and structure. In a steeply-dipping dyke much of the volatile fraction may migrate upwards and escape, whereas in a flat-lying sill the volatile fraction can migrate to the roof of the body, and therefore still affect the final nature of the pegmatite. No direct correlation can be made between size of pegmatites and their internal structure, as there are large homogeneous pegmatites, small zoned ones and vice versa. However, it seems that a pegmatite fluid crystallising in a large discrete chamber, as for example in the Black Hills, has more chance of differentiating than the narrow dykes found in many regions.

f. The size and shape of the pegmatite chamber is one of many factors determining the rate of cooling of the pegmatite melt. Others include proximity to the surface, conductance of enclosing rocks, etc. A slowly cooling pegmatite melt has more chance of concentrating rare elements and volatiles in the late stages, rather than their incorporation in the early-formed crystals.

g. The permeability of the wall rocks surrounding the pegmatite chamber may determine whether or not any of the volatiles in the pegmatite escape. Heinrich (1965) describes several localities in which Li-metasomatism has been observed, forming the lithian amphibole holmquistite in the wall rocks. Other volatiles may escape from the system, but unless they are 'fixed' in the minerals of the wall rocks, the extent of the loss is not known.

All these factors are important in determining the final characteristics of a pegmatite, and thus are relevant to any model which is proposed to explain these.

4. A MODEL FOR COMPLEX LITHIUM PEGMATITE FORMATION

This discussion will be restricted to the major mineral phases occurring in complex, lithium pegmatites, although in certain cases there may be an association between major and minor phases (Solodov, 1959).

The importance of alkalis at various stages in the development of complex pegmatites has been noted by several workers (Quensel, 1957; Brotzen, 1959; Ginzburg, 1960). Ginzburg (p. 114) states that -"geochemical evolution of the pegmatite process shows itself essentially in the change of the part played by alkalis at different stages in the process, and in the appearance of volatiles during the last stages." The dominant alkali(s) at a particular time determines the mineral(s) that crystallises. Both the experimental and geochemical studies described here supplement and corroborate these observation. The former demonstrate the ease with which various alkali-ion exchange reactions may take place in pegmatite systems, and the latter illustrate some of the changes in alkali and volatile content during the process of pegmatite differentiation. However, although the importance of alkalis has been noted, no attempt has been made to relate variations in initial alkali content to possible sequences of crystallisation and replacement.

The crystallisation of the early, outer zones of complex pegmatites appears to be a magmatic process, as the outer zones show variations in their quartz, plagioclase, perthite and muscovite contents. Initial crystallisation of spodumene commonly occurs after the formation of these zones, but in certain cases where the pegmatite melt is abnormally rich in lithium, spodumene crystallises earlier. The relationship between the amount of lithia in a pegmatite and the position of spodumene in the zonal sequence has been discussed by Solodov (1959).

WT. % Li_2O	POSITION OF SPODUMENE IN PEGMATITE
0.1 - 0.35	Only in inner zones.
0.35 - 1.0	Outside the zone of microcline, and in the inner zones.
>1.0	Throughout the pegmatite.

In the last case, the body may appear homogeneous. Some of the lithium pegmatites at the Quebec Lithium Corporation mine in the Preissac-Lacorne district (Chapter 2), containing 1% Li_2O, have spodumene from wall to wall and appear to be homogeneous. Closer examination, however, shows distinct variations in quartz, plagioclase and perthite content.

In many pegmatites, a microcline or microcline-quartz unit is found inside the spodumene-bearing zones. If sufficient potassium has concentrated in the residual pegmatite fluid for the formation of microcline, the fluid may be in disequilibrium with the enclosing spodumene zone, as the experimental studies have shown the ease with which K^+-bearing solutions replace spodumene. If replacement of spodumene by microcline occurred at this stage, it might be difficult to recognise, as it would occur throughout the solid pre-crystallised shell of the pegmatite, with no transecting features evident. Therefore it is possible that the outer parts of such microcline units formed by replacement, and subsequent parts by direct crystallisation. Any replacement of this nature would release lithium into the residual fluid.

The important units to consider after the formation of the microcline-bearing unit are the quartz core, and the lepidolite, albite and pollucite bodies which appear to be the ultimate product of the differentiation sequence of complex pegmatites. The relationships between these bodies have been variously interpreted by different workers.

Quensel (1957) suggests that the alkali bodies in the Varutrask pegmatite formed after the quartz core during what he calls a 'pneumatogenic stage' of pegmatite development. He defines pneumatogenic as occurring above the critical temperature of the aqueous solutions, between 600 C and 400 °C. The evidence he gives for an albite replacement unit forming after, and replacing the quartz core is that radiating aggregates of clevelandite are found in quartz. However, this texture has also been cited as evidence for co-crystallisation (Jahns, 1953). Hutchinson (1959) and Wright (1963), studying the Montgary pegmatite, both give evidence for veins of core quartz transecting pollucite and albite bodies, indicating that the core developed either later than, or contemporaneously with these bodies. Brotzen (1959) has reviewed the evidence from a number of localities, and concludes that various types of replacement body can be formed before or after the quartz core.

Evidence at contacts of replacement bodies and quartz cores is rather conflicting, and may indicate that this is the stage of pegmatite development at which the residual 'melt' separates into silica-rich and water-rich portions. Such a separation, either by resurgent boiling or liquid immiscibility, before the formation of the core and replacement bodies, gives a silica-rich phase which forms the core and an alkali-rich phase forming the replacement bodies. If all these bodies are formed roughly contemporaneously, the monomineralic nature of the core can be explained, and silica is still available for certain of the replacement reactions in which excess silica is necessary.

Experimental studies show that all the reactions investigated can occur between 250 °C and 650 °C, although at the lower temperatures they are slow. However, the rate of reaction need not necessarily be considered a problem when referred to natural occurrences. It therefore appears that temperature is not of prime importance in determining which of these reactions occur, and the order in which they occur. The basic factor appears to be the relative concentrations of alkalis and fluorine at different stages.

These replacement bodies are generally found at the core margin or at zonal contacts (Brotzen, 1959; Wright, 1963), and are likely to be distinctly interrelated. Elements released by the formation of an earlier replacement body are available for incorporation in later replacements; Li^+ and K^+ being used in the formation of lepidolite and Na^+ in albite. From both experiments and analytical studies described earlier, there appears to be a strong likelihood that a lepidolite replacement body is only found if a sufficient concentration of fluorine has built up in the system. Second generations of spodumene in replacement bodies (Quensel, 1957; Ginzburg, 1959), are believed due to an inadequate supply of fluorine to bond in micas with the lithium remaining in the system, and that which is released by microcline, albite and pollucite replacement of spodumene. Many lithium pegmatites have albite replacement bodies (Ginzburg, 1959), forming from both microcline and spodumene, but pollucite bodies are very rare, and seem to be found only in caesium-rich provinces, and in pegmatites that have attained a high degree of differentiation. In this way, the most likely order of formation of replacement bodies is albite - pollucite - lepidolite, because the Li^+ and K^+ required for lepidolite generation are released during the alteration of microcline and spodumene, and because lepidolite development by alteration of either of these minerals is independent of excess silica being present in the system. Therefore lepidolite may continue to form after the quartz core has crystallised. Unless it is formed merely by an alkali exchange with microcline, albite replacement requires excess silica in the system. Experimental studies of Na-rich solutions acting on spodumene indicate that, in a silica-deficient environment, the rare albite - eucryptite intergrowths form. The scarcity of the latter may mean that such replacement does not generally occur after the quartz core has ceased to crystallise.

The basically monomineralic nature of many replacement bodies is rather problematical, but may be due to a variety of hypothetical explanations.

1. If the hydrous fraction consists of liquid and vapour

phases, there may be preferential concentrations of different alkalis and volatiles in each phase. The vapour phase has a greater penetrative power in the pre-crystallised pegmatite than its co-existing liquid phase.

2. Preferential replacement of some pre-crystallised minerals by different alkali ions in the fluid.
3. At this stage, formation may be rapid, and only the dominant alkali at any one time may replace earlier-formed minerals.

The latter two possibilities could be investigated by further experimental studies. However, the fine-grained nature of the majority of these replacement bodies suggests rapid crystallisation about many scattered crystal nuclei, and therefore the third possibility seems realistic.

5. COMPARISON OF MODEL WITH OBSERVED SEQUENCES IN PEGMATITES

This scheme for pegmatite crystallisation and replacement can be compared with the zonal sequences of pegmatites of known bulk composition. However, despite their composition being known, the effects of the various factors outlined in Section 3 of this chapter should be remembered.

Bulk compositions of complex pegmatites are difficult to estimate due to:-

1. Variations in mineralogy between zones.
2. Their large and variable grain size.

3. Inadequate exposure.
4. Incorporation of minor elements in crystal structures.
5. Possible loss of some elements from the system.

However, a few bulk compositions have been calculated for pegmatites, and these may be used for comparison with one another. Unfortunately, bulk compositions have not been determined for the best-known examples of complex pegmatites - Bikita, Montgary and Varutrask - and consequently discussion of these must be restricted to a consideration of their observed sequences.

The estimated bulk compositions of the Hugo, Peerless and Pidlite pegmatites are shown in Table 6. The zonal sequences of the Hugo and Peerless pegmatites are shown in Table 1, and that of the Pidlite dyke, New Mexico, in Table 7. None of these pegmatites is particularly rich in lithium, but comparison of their compositions and their sequences of mineral assemblages shows some interesting features.

The Pidlite pegmatite contains only minor spodumene at the core margin, most of its lithium content has apparently been used in the formation of extensive lepidolite replacement bodies at the time of concentration of fluorine. From the arguments developed previously, it would seem that with Li_2O and F^- contents of 0.7 and 0.9 respectively, by the time Li_2O is sufficiently concentrated to form independent Li minerals, F^- had also concentrated to generate lepidolite

TABLE 6=

BULK COMPOSITIONS OF LITHIUM PEGMATITES

	1	2	3	4
SiO_2	74.5	77.0	77.0	73.05
Al_2O_3	14.8	13.7	12.5	17.21
Fe_2O_3				0.23
FeO				
MnO		0.5	0.9	
MgO				
CaO	0.2	0.6	0.2	1.29
Na_2O	3.3	5.0	3.5	5.02
K_2O	5.4	1.7	3.6	1.47
Li_2O	0.7	0.1	0.2	1.67
P_2O_5		0.5	0.9	
BeO		0.1		
F	0.9		0.1	
H_2O^+	0.6	0.6	0.5	

1. PIDLITE Dyke, Mora County, New Mexico. (Jahns, 1953).
2. PEERLESS pegmatite, South Dakota (Sheridan et al, 1957).
3. HUGO pegmatite, South Dakota (Norton et al, 1962).
4. NORTH LACORNE pegmatite, Quebec (Derry, 1950).

TABLE 7

ZONAL SEQUENCES OF COMPLEX LITHIUM PEGMATITES

PEGMATITE	ZONE	ASSEMBLAGE
1. PIDLITE (Jahns, 1953).	1.	Albite - quartz - muscovite - (perthite)
	2.	Perthite - quartz - albite - (muscovite)
	3.	Quartz - perthite
	4.	Quartz - (spodumene)
Replacement bodies	1.	Clevelandite - quartz - perthite - albite - lepidolite - muscovite
	2.	Albite - muscovite - lepidolite
	3.	Lepidolite - albite
2. MONTGARY (Wright, 1963).	1.	Quartz - albite
	2.	Perthite - quartz - plagioclase - muscovite
	3.	Spodumene - perthite - plagioclase - quartz
	4.	Spodumene - quartz
	5.	Microcline - quartz
	6.	Quartz
Replacement bodies	1.	Albite (replacing spodumene zones)
	2.	Lepidolite (replacing microclie - quartz zone)
	3.	Pollucite
3. VARUTRASK (Quensel, 1957)	1.	Quartz - muscovite (fine-grained)
	2.	Quartz - muscovite
	3.	Perthite - quartz - muscovite
	4.	Perthite - quartz - muscovite - spodumene
	5.	Quartz

TABLE 7 CONT'D

PEGMATITE	ZONE	ASSEMBLAGE
3. VARUTRASK (Cont'd)	1.	Lepidolite - (spodumene)
	2.	Pollucite - (lepidolite)
Replacement bodies	3.	Albite

rather than spodumene. The Hugo and Peerless pegmatites, although well-zoned, have a lower concentration of both Li_2O and F^-, and consequently only contain minor spodumene and lithia mica. The low fluorine content apparently determines that lithia mica, as opposed to lepidolite, forms. All three pegmatites have a high Na_2O content, and hence clevelandite replacement bodies are common. Cs_2O content has not been determined, but in the Black Hills, at least, this oxide is not abundant. This is undoubtedly why neither of the pegmatites from this area show pollucite replacement bodies, despite the exceptional differentiation during the formation of the zones.

A comparison of all three with the 'homogeneous' North Lacorne pegmatite (Table 6), shows that this pegmatite has a far higher content of Li_2O, and hence spodumene crystallises throughout the pegmatite. F^- was probably too low to permit the formation of lepidolite.

The mineralogy of the Montgary and Varutrask pegmatites (Table 7) indicates that they were exceptionally rich in Li, F and Cs. Geochemical studies described here have shown how all three of these elements are concentrated by differentiation. Initial concentration of Li^+ caused the formation of the spodumene-bearing zones, and subsequent concentration of all three elements allowed the formation of large replacement bodies. If the latter stage coincided with the development of an aqueous phase in the melt, their replacement nature can be more logically explained.

CHAPTER 6

CONCLUSIONS

1. Experimental studies, using natural pegmatite minerals and solutions that have been observed in fluid inclusions in pegmatites, have shown that a variety of alkali-ion exchange reactions are easily achieved in the laboratory under a wide range of hydrothermal conditions. These may represent a mechanism by which many replacement textures and bodies form at a late stage in complex pegmatite genesis.

2. The replacement reactions could not be related to a specific temperature or pressure. Rather, they are believed related to the concentration of specific alkalis and volatiles at different stages of pegmatite development. This may explain why they are not present in all complex pegmatites, and why they occur in different sequences. However, although the number of components in the systems studied makes them rather complex by experimental standards, they are still very simple in relation to the number of components in a crystallising pegmatite. The effect of this difference cannot be calculated, but it is probably an important factor.

3. It appears that most replacement reactions in pegmatites

are due to an aqueous phase, which might explain both the mobility of the phase and the concentration of certain elements in it. Such a phase may separate either by liquid immiscibility or by resurgent boiling. Insufficient data is available to decide which of these two possibilities is most likely, nor can it be determined whether one or more aqueous phases can be present.

4. The final 'character' of a pegmatite will depend on a variety of factors listed on p. 84 These will all be important in governing the nature and extent of any replacement bodies that form.

5. Geochemical work has verified certain strong trends in the differentiation sequences of pegmatites. The most important of these trends are the increase in Li_2O, Cs_2O, Rb_2O and F^- during the genetic sequence of pegmatite types.

6. Rb_2O content or a Rb_2O/K_2O ratio may be used to determine a geochemical sequence of pegmatites in any one geochemical province. Rb^+ is particularly useful as it commonly substitutes for K^+ in the numerous K-bearing minerals that form at many stages in the pegmatite process.

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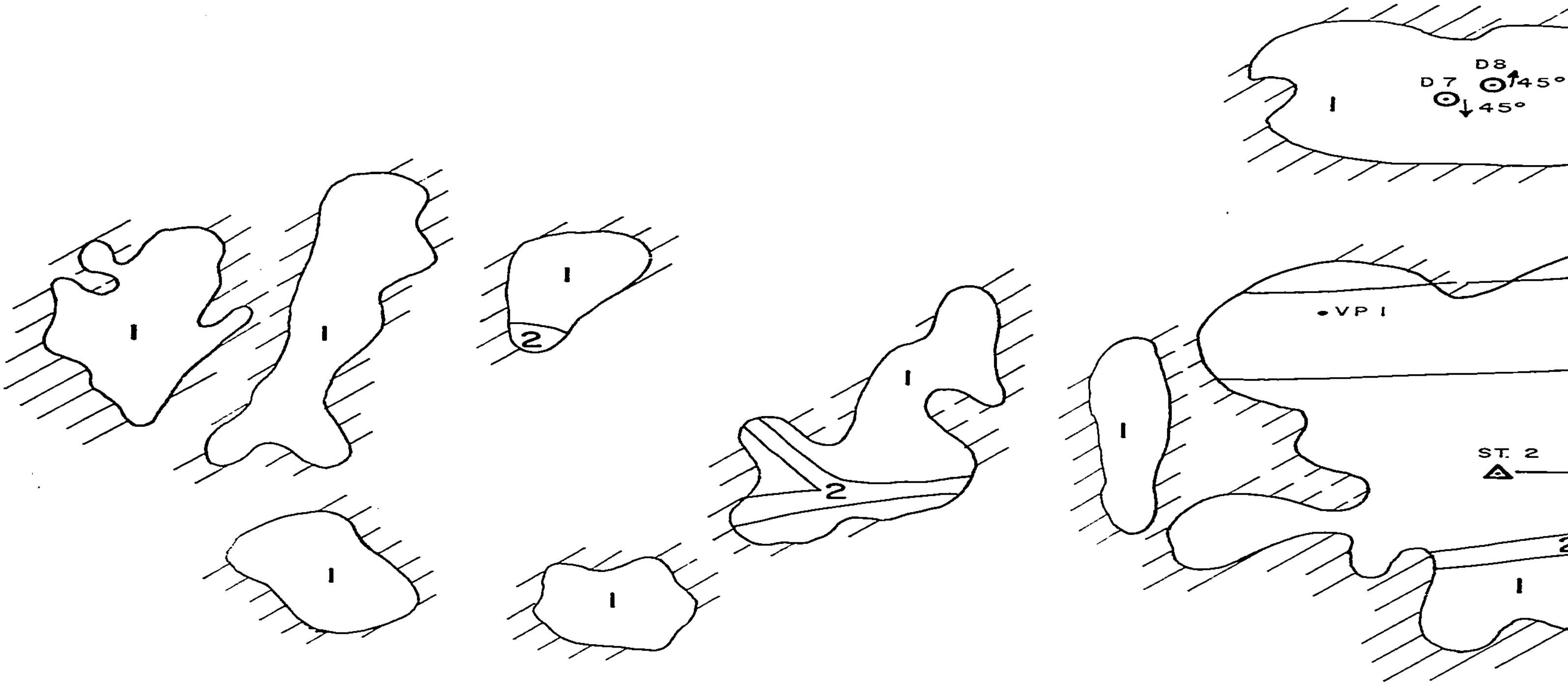

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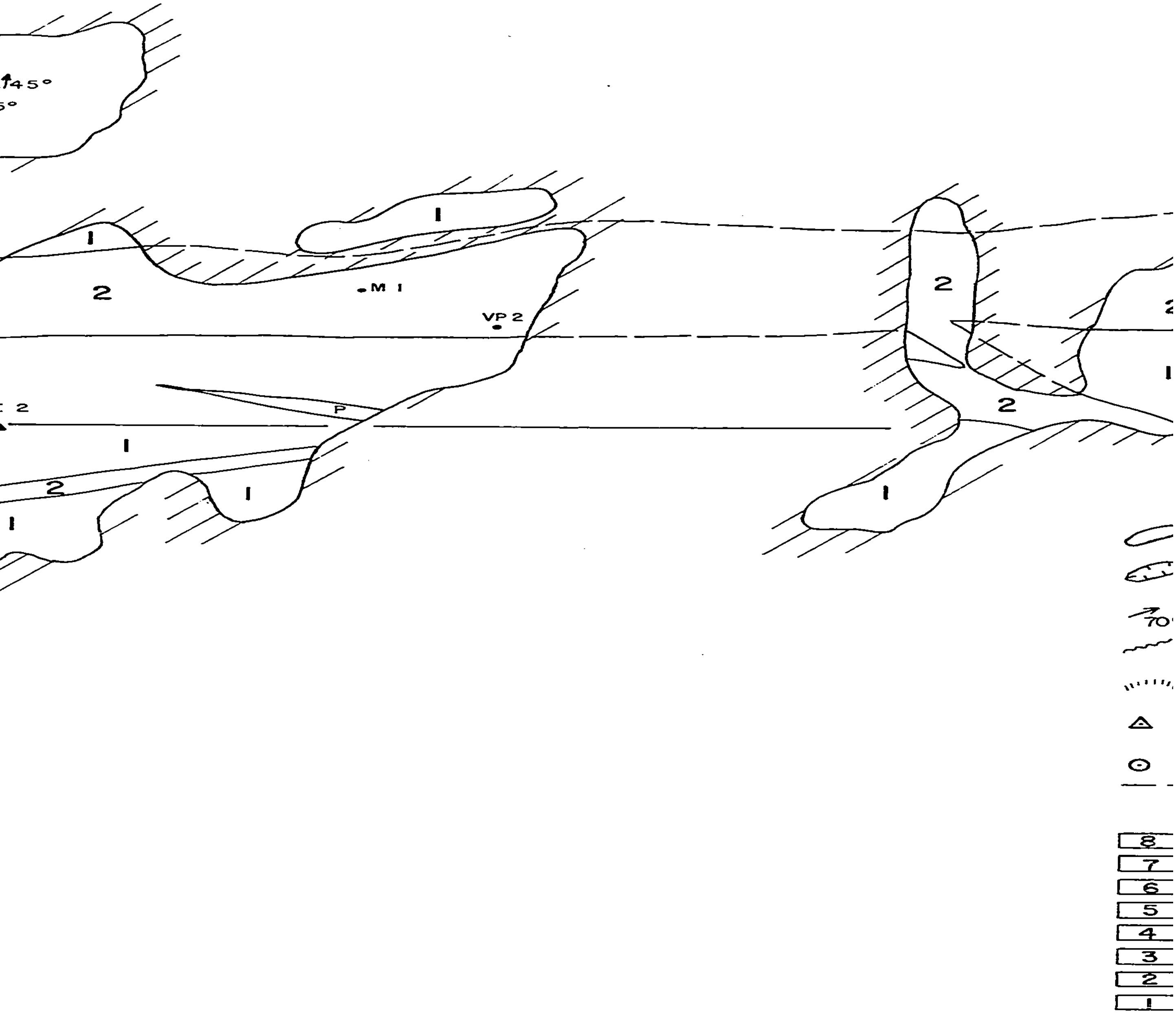

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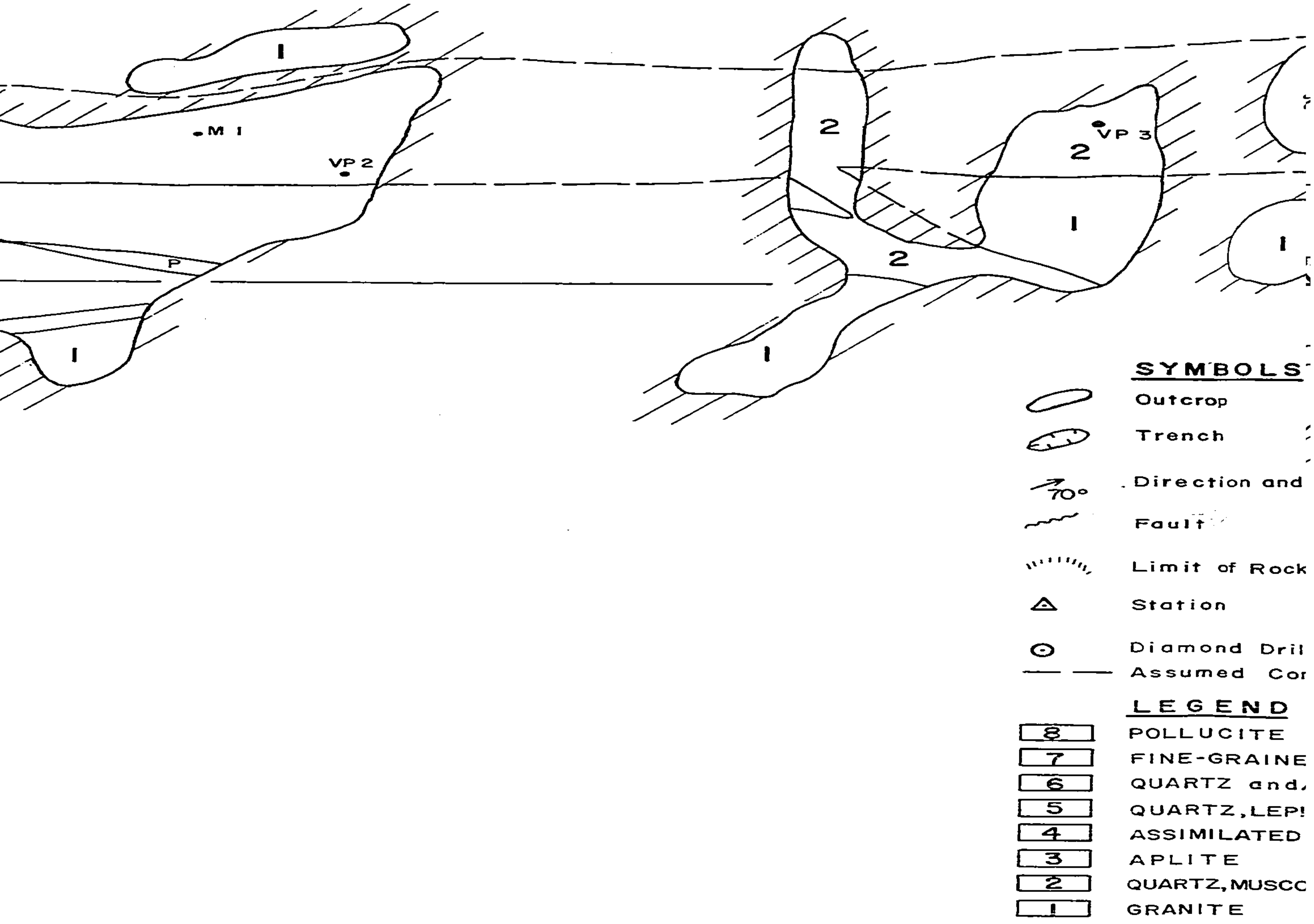
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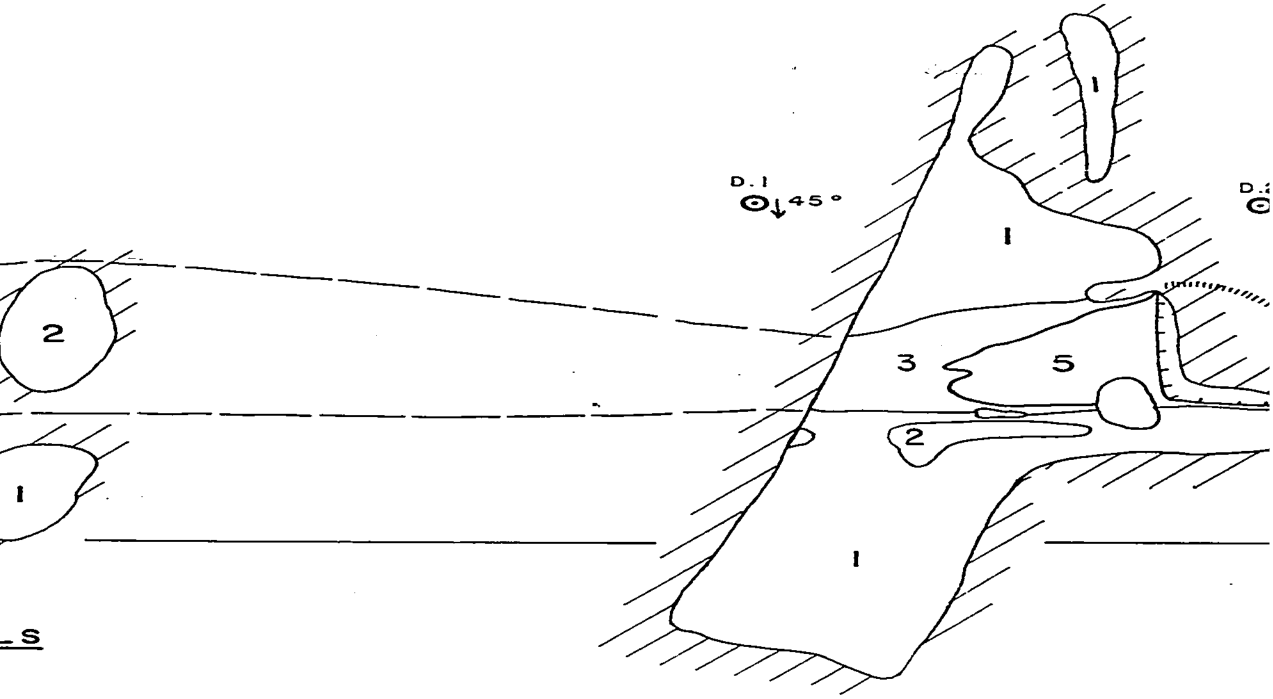
SYMBOLS
Outcrop
Trench
70°
Direction and
Fault
Limit of Rock
Station
Diamond Dril
Assumed Cor
LEGEND
8 POLLUCITE
7 FINE-GRAINE
6 QUARTZ and
5 QUARTZ, LEP
4 ASSIMILATED
3 APLITE
2 QUARTZ, MUSCO
1 GRANITE



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nd/or CLEVELANDITE
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ED MATERIAL—APLITIC

SCOVITE,PERTHITE,PLAGIOCLASE, PEGMATITE, ±BERYL

GEOLOGY
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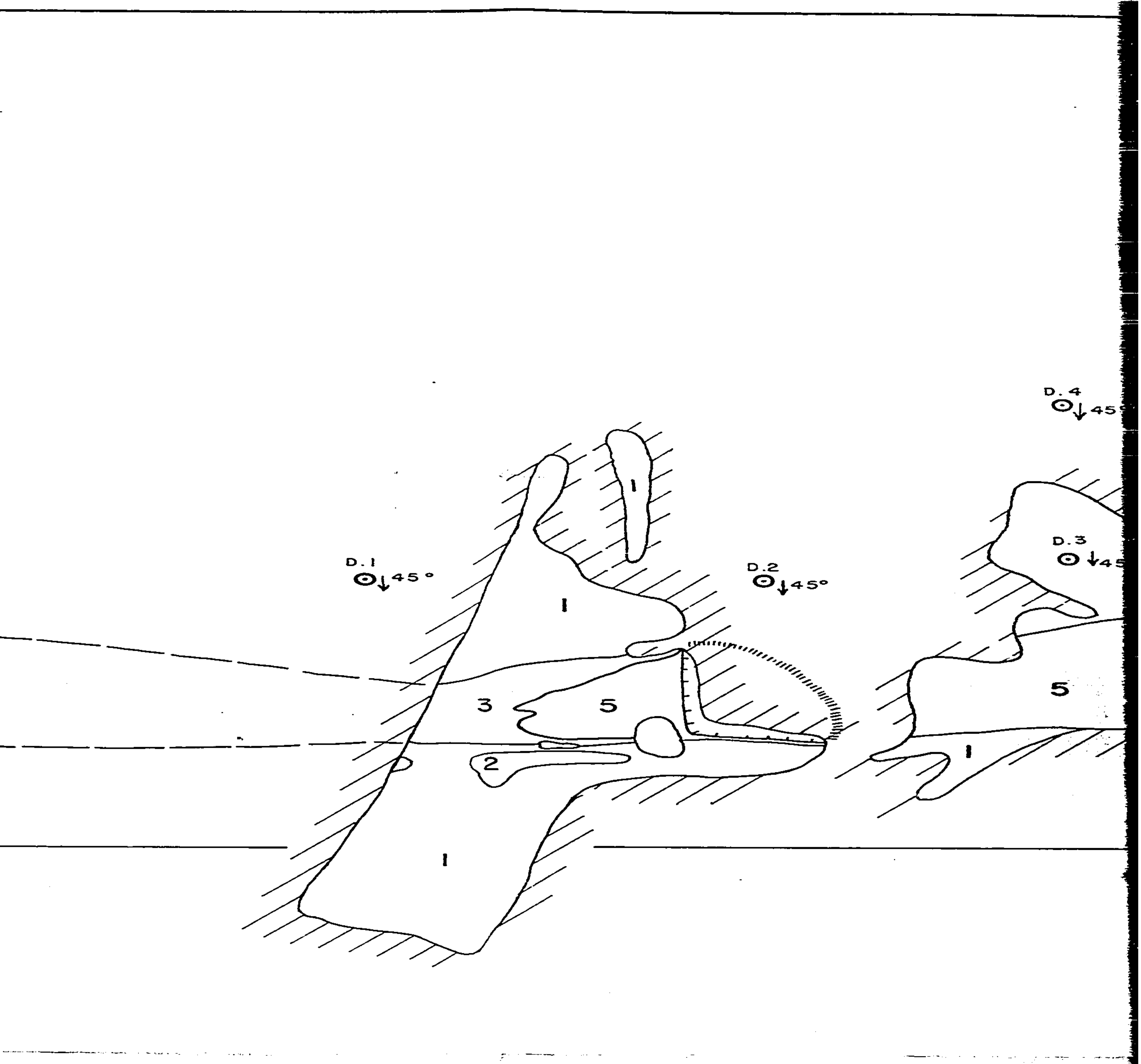


FIG. 3

GEOLOGY OF THE "VAL

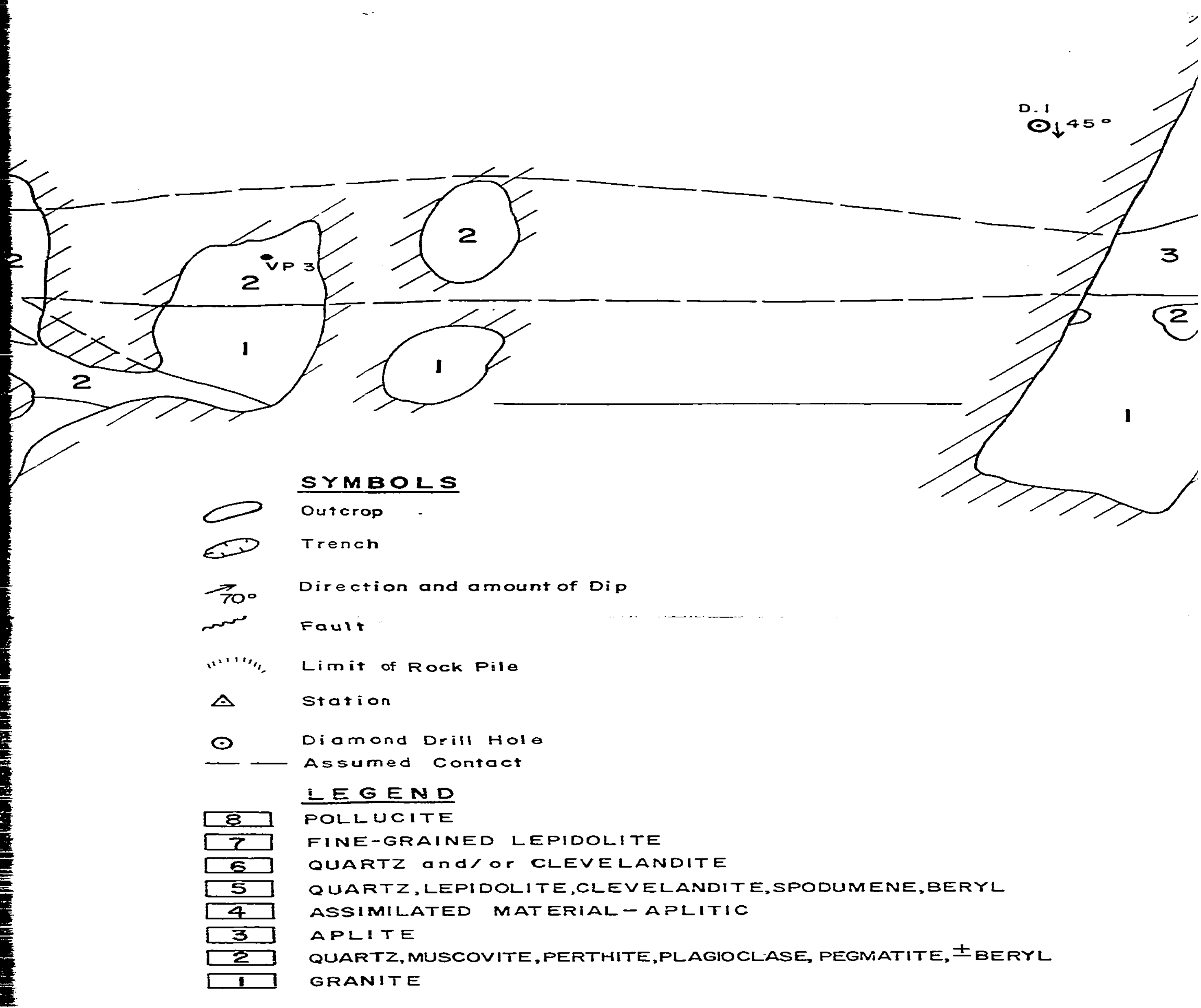
LITHIUM PEGMATIT

LACORNE TOWNSHIP,

(ALSO SHOWING SAMPLE LOCATI

DITE
ANDITE, SPODUMENE, BERYL
LITIC

LAGIOCLASE, PEGMATITE, ±BERYL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45°
2
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VP 3
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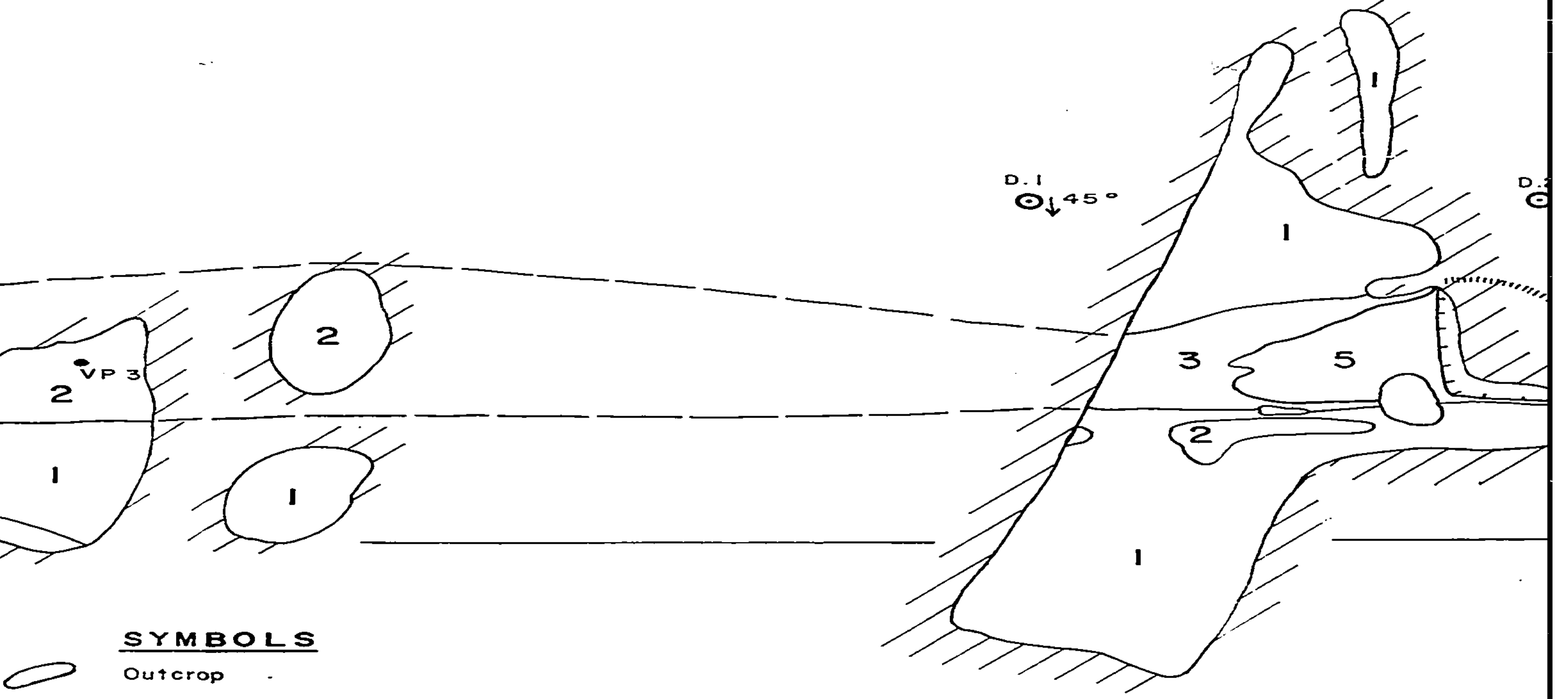
SYMBOLS
Outcrop
Trench
70°
Direction and amount of Dip
Fault
Limit of Rock Pile
Station
Diamond Drill Hole
Assumed Contact
LEGEND
8 POLLUCITE
7 FINE-GRAINED LEPIDOLITE
6 QUARTZ and/or CLEVELANDITE
5 QUARTZ, LEPIDOLITE, CLEVELANDITE, SPODUMENE, BERYL
4 ASSIMILATED MATERIAL – APLITIC
3 APLITE
2 QUARTZ, MUSCOVITE, PERTHITE, PLAGIOCLASE, PEGMATITE, ± BERYL
1 GRANITE



SYMBOLS

- Outcrop
- Trench
- Direction and amount of Dip (70°)
- Fault
- Limit of Rock Pile
- △ Station
- ⊙ Diamond Drill Hole
- — — Assumed Contact

LEGEND

8	POLLUCITE
7	FINE-GRAINED LEPIDOLITE
6	QUARTZ and/or CLEVELANDITE
5	QUARTZ, LEPIDOLITE, CLEVELANDITE, SPODUMENE, BERYL
4	ASSIMILATED MATERIAL – APLITIC
3	APLITE
2	QUARTZ, MUSCOVITE, PERTHITE, PLAGIOCLASE, PEGMATITE, ± BERYL
1	GRANITE

GEOLOG
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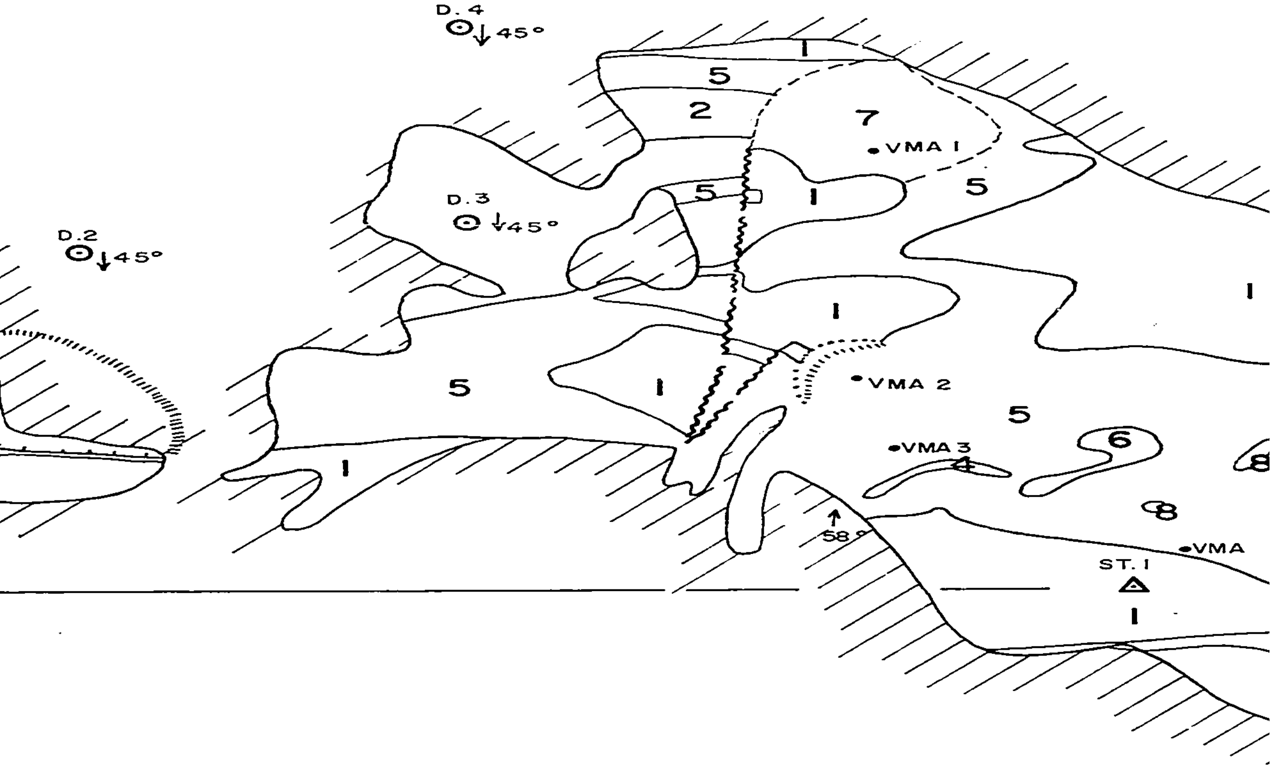


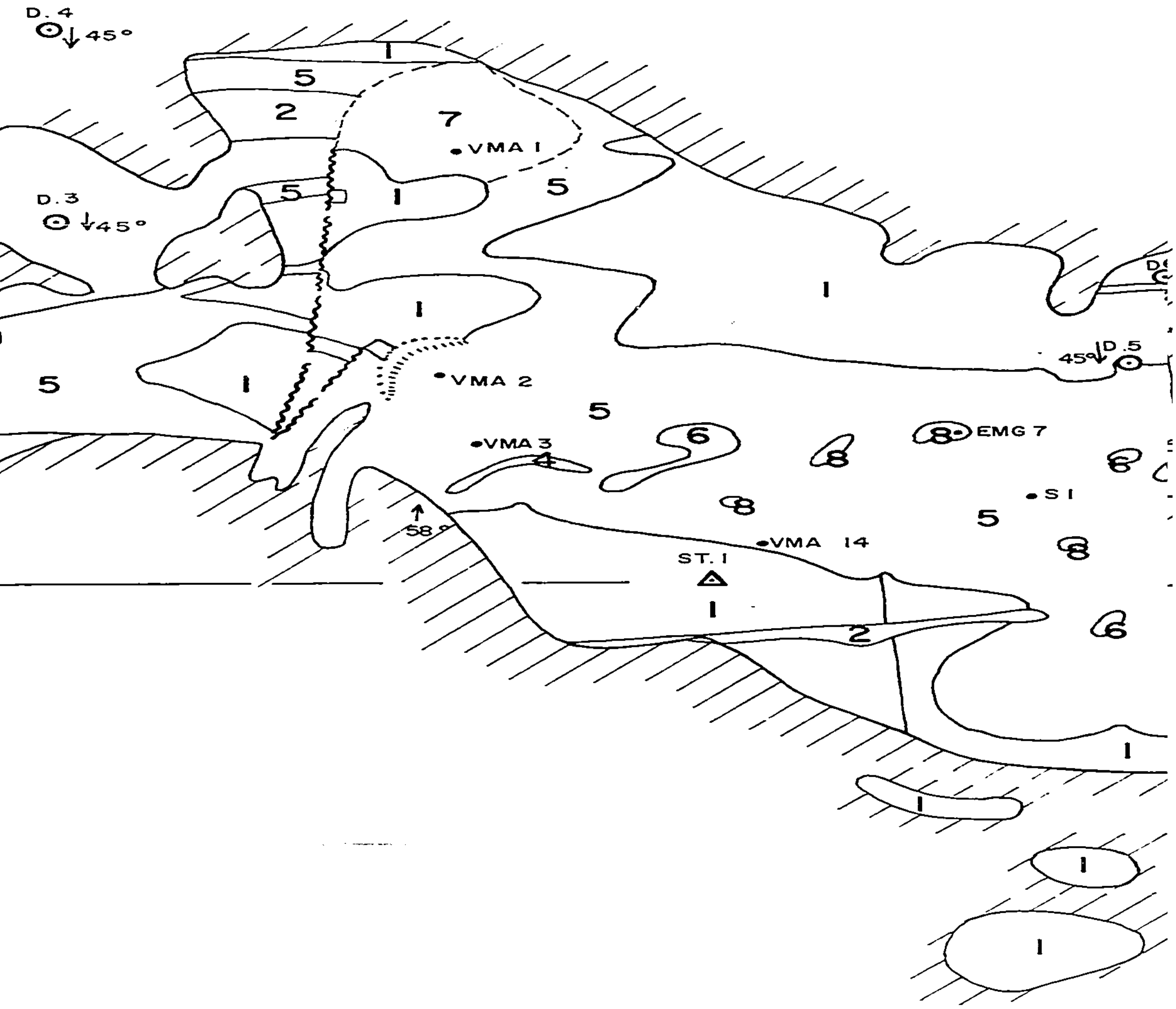
FIG. 3

OGY OF THE "VALOR"

IUM PEGMATITE,

RNE TOWNSHIP, P.Q.

SHOWING SAMPLE LOCATIONS)

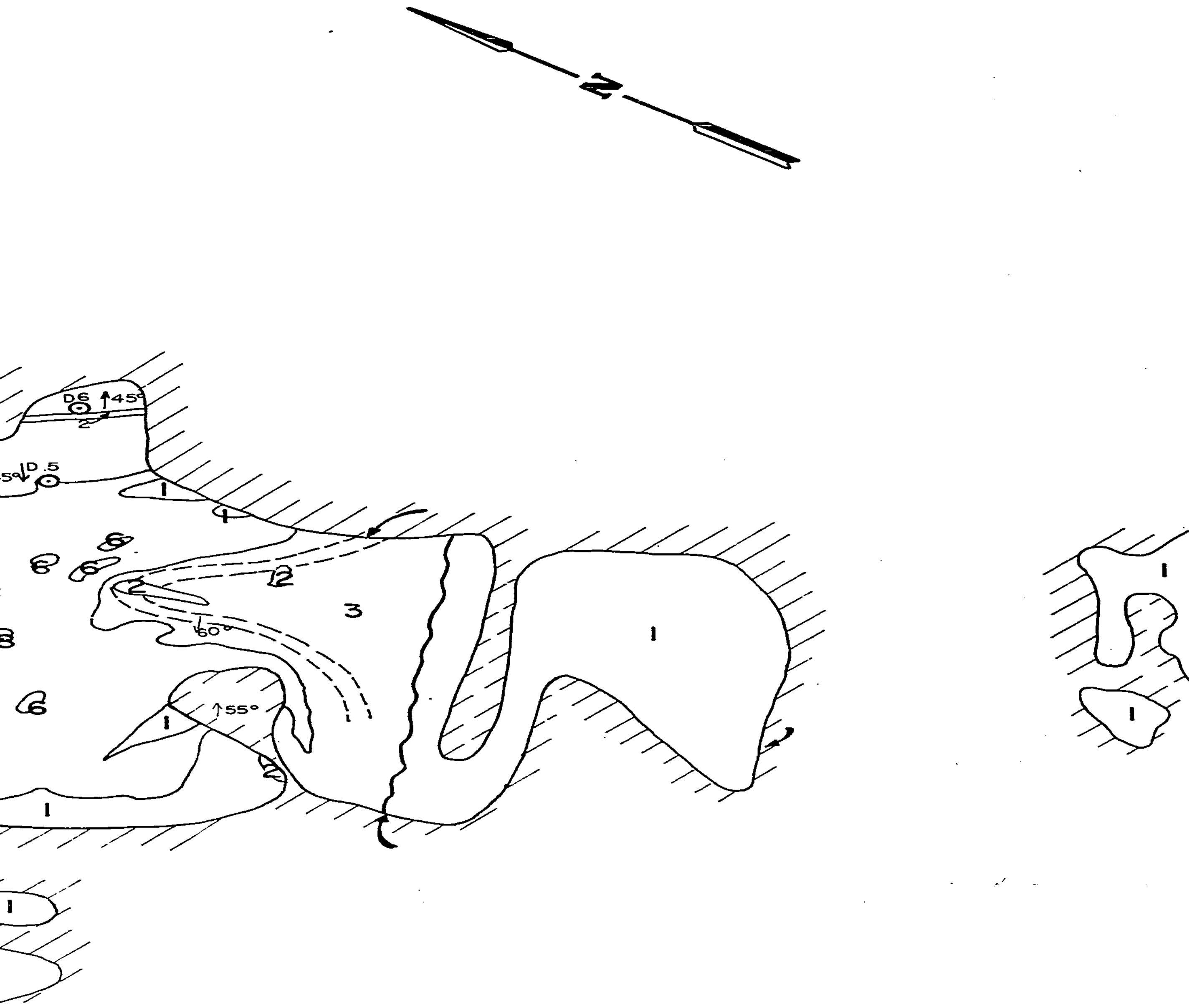


"VALOR"

ATITE,

SHIP, P.Q.

LOCATIONS)



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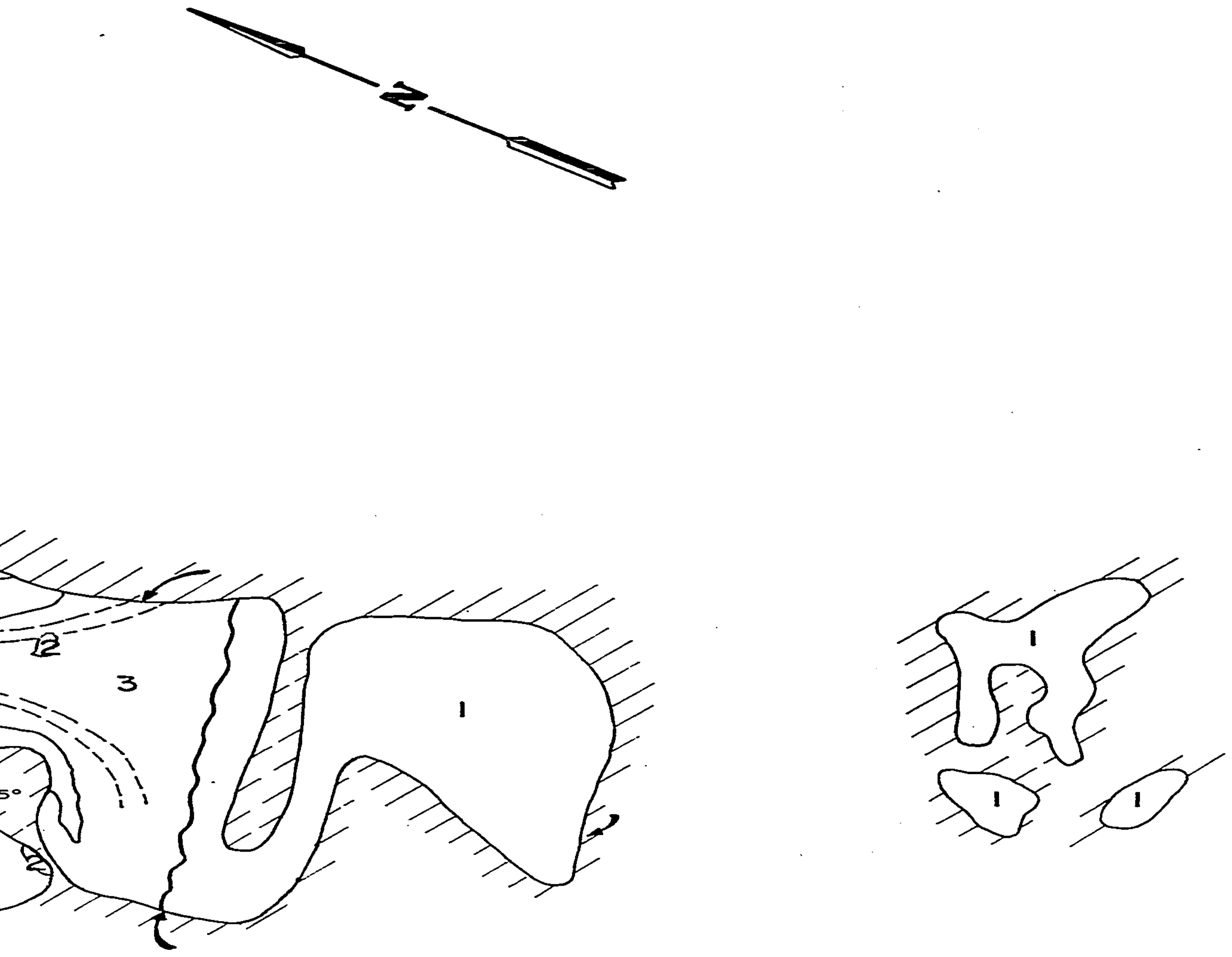
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