VAPOUR FRACTIONATION AND K/Rb RATIOS OR MELT PHASES IN THE ONAPING FORMATION, SUDBURY, ONTARIO.

VAPOUR FRACTIONATION AND K/Rb RATIOS OF MELT PHASES IN THE ONAPING FORMATION SUDBURY, ONTARIO.

BY

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ABSTRACT

The process of vapour fractionation during impact fusion of country rocks is discussed in relation to absolute loss and relative loss. The factors which determine the amount of vapour fractionation are considered in an equilibrium thermodynamic model. The model is tested upon the relative vapour fractionation of Rb with respect to K. Application of the model to crater studies leads to sampling concepts and the statistical validity of differences in measured compositions of melt rock and adjacent country rocks.

The petrography and K/Rb ratios of twelve samples of melt phases in the Onaping formation, Sudbury, Ontario are presented. The data is discussed in the light of theoretical model for vapour fractionation.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. J. H. Crocket for suggesting a study of K/Rb ratios in the Onaping formation and for his critical appraisal of this document. I wish to express my gratitude to Michael Marchand and Dr. D. M. Shaw for fruitful discussions concerning crater phenomena and K/Rb relations.

Walter Gibbins aided the author in the sample preparation and analysis. John Muysson introduced the author to atomic absorption spectroscopy. Mr. H. D. Falkiner made the thin sections and Len Falkiner and Frank Tebay provided X-ray diffractometer traces.

The author claims complete responsibility for the vapour fractionation models in Part A.

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INTRODUCTION

The original purpose of this study was to examine the K/Rb relations in the melt phases of the Onaping Formation, Sudbury Ontario in the light of possible vapour fractionation during high temperature fusion. The author found that the literature contains a multitude of references to vapour fractionation processes but no rigourous theoretical evaluation of the process. Furthermore there is a dearth of experimental data on trace element behaviour during vapour fractionation.

The literature on theoretical and experimental vapour fractionation is summarized in Philpotts (1965). A recent paper by Blander et al (1970) has discussed vapour fractionation in a qualitative evalation of factors but it of little quanlitative value.

As a consequence this report is divided into two parts: Part A in which a theoretical basis for the prediction of vapour fractionation trends is derived. Part B in which data for the Onaping Formation are presented and evaluated.

PART A

I

IMPACT FUSION AND NON IDEALITY

(1) Impact Fusion Process

During a large meteorite impact, a relatively small volume of rock near the impacting body will be subjected to shock pressures in excess 500Kb, which is sufficient to produce melting of the rock such impact-melted material has been found in several forms: (1) individual bodies composed of mixtures of glass and rock and mineral fragments which are ejected from the crater and aerodynamically shaped before deposition (Fladen). (2) glass-rich breccias containing numerous shocked rock fragments which make up part of the breccia lens within the crater. (3) relatively thick uniform layers resembling sills, associated with breccias but composed of completely crystalline rock with few or no inclusions. The third form, impact melt layers reflect their formation by sudden high-temperature fusion of the target rock, rapid injection and rapid cooling.

Temperatures during impact fusion are estimated to be in excess of 2000^{o} K [1]. Rates of cooling of molten material ejected from the crater may be calculated if the initial temperature, specific heat, density and

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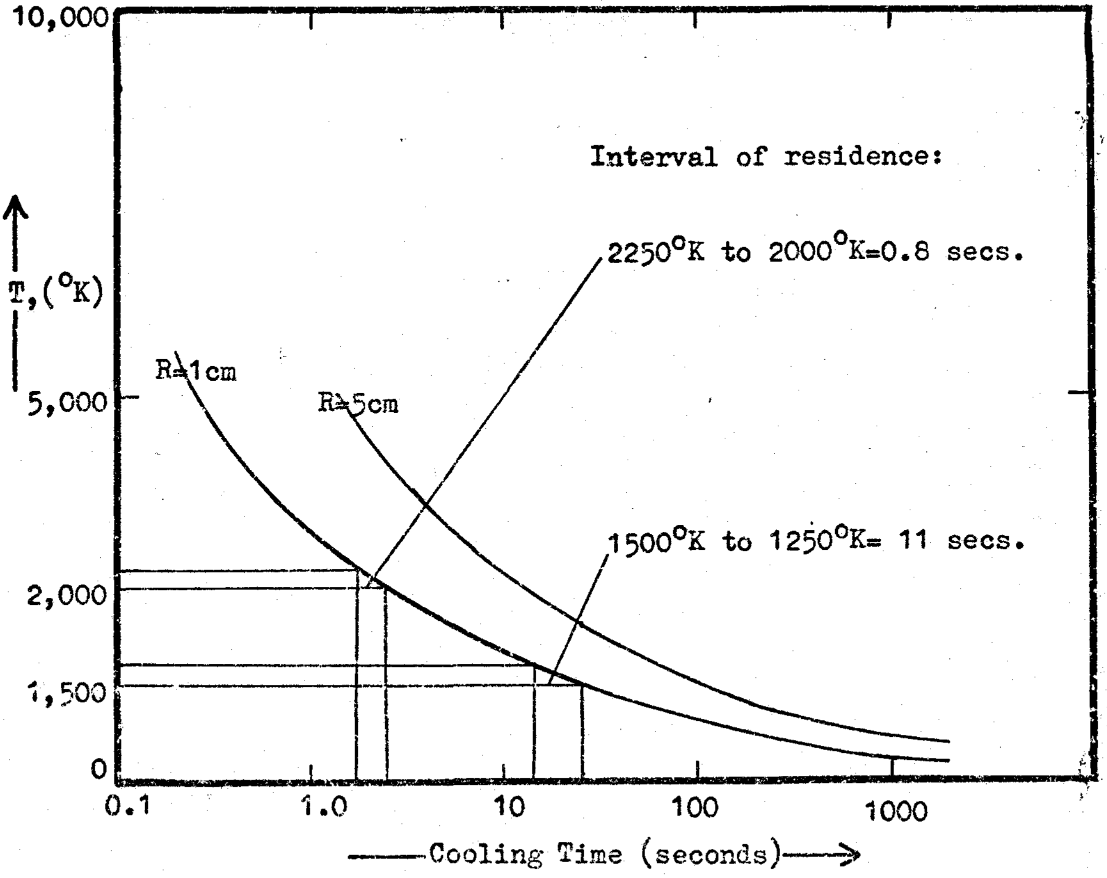
[1] Textures have been found indicating the decomposition of zircon and sphene in crater rocks. The temperature of decomposition of these minerals is in excess of 1800^{o}K.

radius of the Fladen is known (Greenland and Lovering 1962). The object rapidly loses temperature until the rate of cooling decreases at lower temperatures. An object of tektite composition with a radius of 5 cm cools from 2000° K to 1000°K in three minutes. The interval during which the impact melt layers would remain molten is unknown but the petrographic features indicate rapid quenching. The interval of residence of the melt rock at a temperature would increase with decreasing temperature (see Fig. 1.)

Fig. 1: The Rate of Cooling of Fladen.

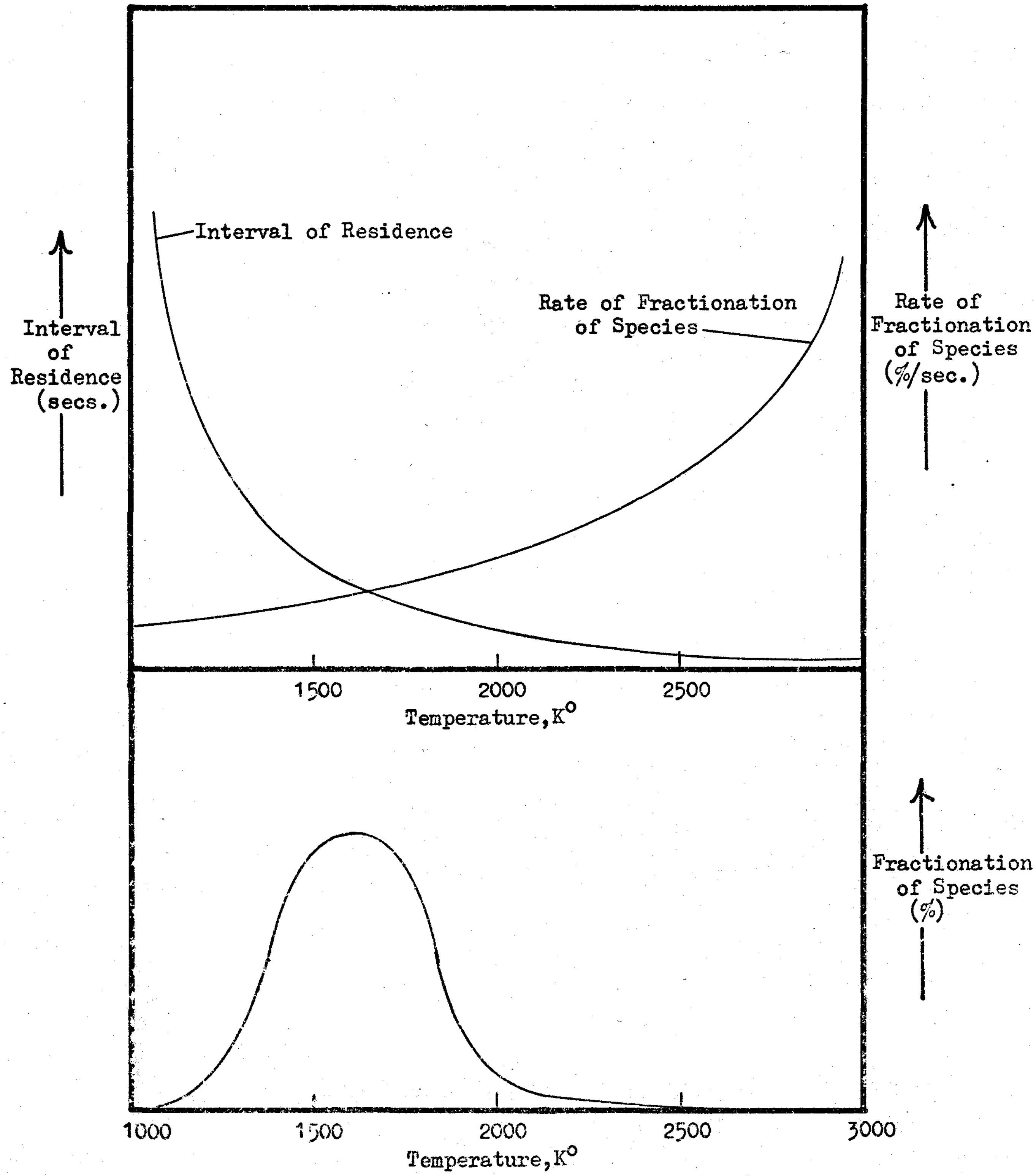


The relations between the impact melt and the ambient atmosphere are important to the vapour fractionation process. It is safe to assume that the Fladen were in contact with a normal terrestrial atmosphere during fractionation. Dence (1968) has suggested that impact melt layers are material melted close to the penetrating meteorite and that their location indicates the approximate depth of penetration of the meteorite into the target rock. Vapour fractionation of the impact melt layer would be governed by the surface area exposed to the atmosphere and the surface cooling effects.

(2) Kinetics

Obviously the impact fusion process is a non-equilibrium process in natural situations. The variation in temperature of the melt body would render vapour fractionation non-equilibrium. It is the author's contention that time is the major control on the absolute loss of species by vapour fractionation. The interplay of the rate of fractionation and the rate of cooling would define the temperature range over which significant vapour fractionation occurs. The relationship between these factors is illustrated for a hypothetical system in Fig. 2. The author contends therefore that significant vapour fractionation may be approximated as an equilibrium process operating over a range of temperature and that these temperatures are lower than the temperature of fusion.

Fig. 2: The Kinetics of Vapour Fractionation in a Hypothetical System



II

ABSOLUTE VAPOUR FRACTIONATION MODEL

Laying kinetic considerations aside, we may express equilibrium vapour fractionation in terms of a thermodynamic system. Consider the fractionation reaction

$$\text{(1)} \qquad A \text{ oxide (liquid)} \longrightarrow {}_mB \text{ (vapour)} + nO_2 \text{ (vapour)}$$

A = metal oxide in the silicate liquid

B = the vapour species of the metal

nO_2 = the oxygen derived from the breakdown of the liquid oxide

B species may be the pure metal if there are no stable oxides or B may be an oxide of different stoichiometry from A.

At equilibrium, Shick (1960) uses the relation

$$\text{(2)} \qquad \Delta G_T = -RT \ln \left[\frac{(f_B)^m (fo_2)^n}{a_A} \right]$$

f_B = fugacity of B in the vapour

fo_2 = fugacity of oxygen in the vapour

a_A = the activity of the metal oxide in the silicate liquid

The activity of the oxide is a function of the concentration in the melt, the stoichiometry of the oxide and the SiO_2 content of the melt.

$$\text{(3)} \qquad a_A = (N_A+)(N_o2-)$$

Masson et al (1970)

$$\text{(4)} \qquad N_A+ = \frac{\text{moles of } A^+}{\sum \text{moles of all cations}}$$

$$\text{(5)} \qquad N_o2 = \frac{\text{moles of } O^{z-}}{\sum \text{moles of all anions}}$$

a_A is directly dependent upon concentration

a_A is also related to silica content by the relation

$$\text{(6)} \qquad \frac{1}{N_{SiO_2}} = \frac{1 - \dfrac{1}{\left[\dfrac{1}{3} + \dfrac{a_A}{K_{11}(1 - a_A)} \right]}}{1 - a_A}$$

N_{SiO_2} = mole fraction of SiO_2

K_{11} = is a function of the properties of the metal and is specific to each metal.

The effect of K_{11} on the activity of a metal oxide in a metal oxide - silicate liquid binary system is illustrated in Fig. 1 of Masson et al (1970)

The value of K_{11} for some metals is tabulated below

	K_{11}
CaO	0.0016
PbO	0.196
MnO	0.25
CoO	2.0
SnO	2.55

Assuming B behaves as an ideal gas then

$$X_B = \frac{f_B}{P_B^o} \qquad (7)$$

X_B = the mole fraction of B in the vapour

P_B^o = the vapour pressure of pure B in the vapour

P_B^o is a function of T and will increase with increasing T.

Substituting (2) in (7) we have,

$$X_B = \frac{1}{P_B^o} \cdot \left[\frac{a_A}{(fo_2)^n} \cdot \exp\left(\frac{-G_T}{RT} \right) \right]^{\frac{1}{m}} \qquad (8)$$

Factors which would increase X_B are

- increased activity = larger concentration, lower SiO_2
- increased temperature
- smaller ΔG ($\Delta G > 0$)
- decreased fo_2

- decreased P^o_B
- decreased N_{SiO_2}

Similarily, to decrease X_B

- decreased activity = smaller concentration, higher SiO_2
- decreased temperature
- larger ΔG $(\Delta G > 0)$
- increased fo_2
- increased P^o_B
- increased N_{SiO_2}

Data for $_A$ and G are not available for most metal oxides. The value of fo_2 is difficult to estimate. Therefore equation (8) has limited use except for the relative vapour fractionation of chemically similar species such as K and Rb.

III

RELATIVE VAPOUR FRACTIONATION MODEL

(1) Model

The model for the relative vapour fractionation of two elements is derived from the equilibrium absolute vapour fractionation expression in the following manner:

Consider two geochemically similar elements K and Rb. The vapour reactions analogous to equation (1) are;

$$K_2 O_2 (\ell) \longrightarrow 2 K (g) + O_2(g)$$
$$Rb_2 O_2 (\ell) \longrightarrow 2 Rb (g) + O_2(g)$$

The ΔG_T for these reactions may be calculated up to 1500°K. Considering equation (2), the value for fo_2 in the vapour above the melt rock will be the same for K and Rb.

Evaluating the activity of the oxide in the melts it is safe to assume that No^2 will be the same for both oxides and that N_{A^+} for the cations will be directly proportional to the moles of the cations K and Rb^+ in the melt. The effect of K_{11} upon the activity of the oxide is considered the same for both elements due to the chemical similarity. This assumption is not strictly true and invalid for elements which are not closely related chemically . The assumption that the vapour phases of K and Rb are ideal (equation(7)) is unecessary provided these phases are equally non-ideal.

The values of P^o for K and Rb are available from the Handbook of Chemistry and Physics.

One further simplification may be obtained by multiplying the ratio of mole fractions by the atomic weights of the elements involved. The resulting parameter is $\left(\frac{K}{Rb}\right)_v$ the weight ratio of the elements in the vapour.

Therefore dividing equation (8) for K by equation (8) for Rb, simplifying with the assumption made above and multiplying by atomic weights we obtain:

$$(9) \qquad \left(\frac{K}{R_b}\right)_v = \frac{\text{atomic wt K}}{\text{atomic wt R}_b} \cdot \frac{P^o_{Rb}}{P^o_K} \cdot \frac{N_{K}+}{N_{Rb}+} \cdot \left[\exp\left(\frac{\Delta G_{Rb} - \Delta G_K}{RT}\right)\right]^{\frac{1}{2}}$$

$$\frac{N_K+}{N_{Rb}} = \frac{\text{moles K}}{\text{moles Rb}} = \frac{\text{ppmK}}{\text{ppmRb}} \cdot \frac{\text{atomic wt Rb}}{\text{atomic wt K}}$$

$$(10) \qquad \left(\frac{K}{Rb}\right)_v = \left(\frac{K}{Rb}\right)_l \cdot \frac{P^o_{Rb}}{P^o_K}\left[\exp\left(\frac{\Delta G_{Rb} - \Delta G_K}{RT}\right)\right]^{\frac{1}{2}}$$

where $\left(\frac{K}{Rb}\right)_l$ = the $\frac{K}{Rb}$ in the liquid melt

$\left(\frac{K}{Rb}\right)_l$ will change as the melt loses K and Rb according to the ratio in the vapour $({}^K/Rb)\,v$. The initial $({}^K/Rb)_l$ will be that of the target rock, $({}^K/Rb)t$. The expression for $({}^K/Rb)\,v$ corrected for the loss of the elements is:

$$(10) \qquad \frac{K}{Rb\ v} = \left(\frac{100\left(\frac{K}{Rb}\right)_t - \left(\frac{K}{Rb}\right)_u \cdot \Delta Rb}{100 - Rb}\right)\left(\frac{P^o_{Rb}}{P^o_K}\left[\exp\left(\frac{\Delta G_{Rb} - \Delta G_k}{RT}\right)\right]^{\frac{1}{2}}\right)$$

$$\text{where } \Delta Rb = \frac{Rb_t - Rb}{Rb_t} \cdot 100$$

ΔRb is the percent loss of Rb by fractionation from the target rock.

The second term in the product on the right hand side of the equation (10) will be a constant at equilibrium.

So setting

$$(11) \qquad \frac{P^o_{Rb}}{P^o_K}\left[\exp\left(\frac{\Delta G_{Rb} - \Delta G_K}{RT}\right)\right]^{\frac{1}{2}} = C$$

and rearranging equation (10) we obtain

$$(12) \quad \left(\frac{K}{Rb}\right)_v = \frac{100.C. \left(\frac{K}{Rb}\right)_t}{100 + (C - 1)\Delta Rb}$$

therefore substituting (12) in the expression for $\left(\frac{K}{Rb}\right)_l$

$$(13) \quad \left(\frac{K}{Rb}\right)_l = \frac{100}{100 + (C-1)\Delta Rb} \cdot \left(\frac{K}{Rb}\right)_t$$

rearranging (13) we obtain:

$$(14) \quad \frac{\left(\frac{K}{Rb}\right)_l}{\left(\frac{K}{Rb}\right)_t} = \frac{100}{100 + (C-1)\Delta Rb}$$

(2) <u>The Relative Vapour Fractionation Coefficient</u>

For convenience, the ratio of $^K/Rb$ in the melt to $^K/Rb$ in the target rock shall be defined as the relative vapour fractionation coefficient, Dv.

where $$\left(\frac{K}{Rb}\right)_l = Dv \cdot \left(\frac{K}{Rb}\right)_t$$

and $$Dv = \frac{100}{100 + (C - 1)\Delta Rb}$$

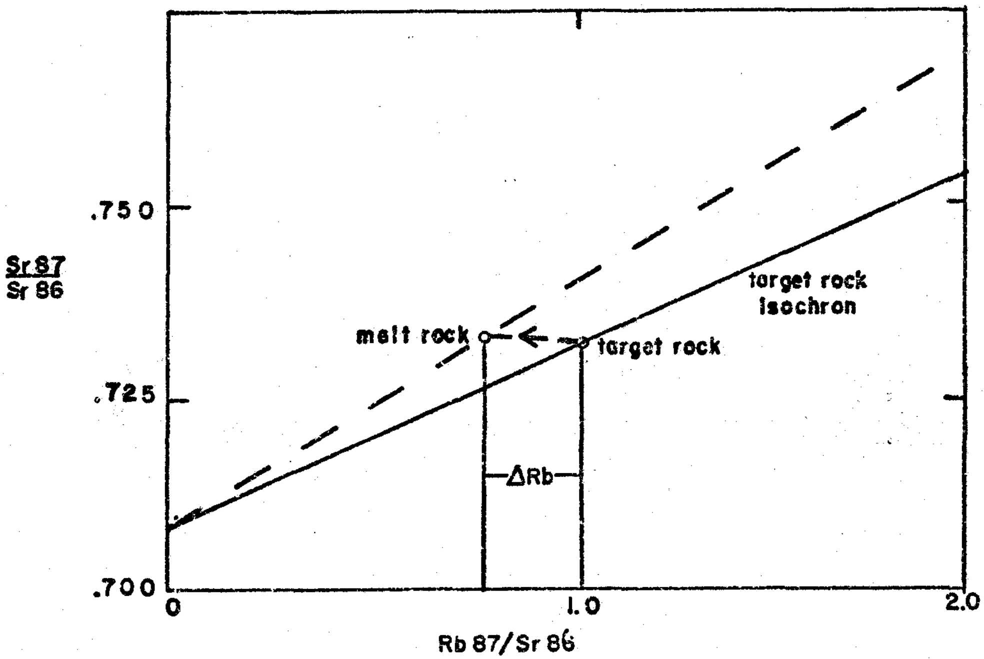
for equilibrium vapour fractionation at constant T resulting in a loss of ΔRb in % Rb.

The ratio of $^K/Rb$ measured in a melt rock to $^K/Rb$ measured in the target rock is the observed Dv of the vapour fractionation process. The ΔRb may be calculated from the decrease of Rb^{87}/Sr^{86} ratio in the melt rock from the Rb^{87}/Sr^{86} value on the target rock isochron corresponding to the same Sr^{87}/Sr^{86} ratio as the melt rock. The relations of Rb/Sr and Rb are illustrated in Fig.-3. The calculation of Rb assumes no vapour fractionation of Sr or Sr isotopes which is substantiated in experimental work by Lippet and Wasserburg (1964) and Schnetzler et al (1966).

The calculation of ΔRb also assumes insignificant modification of the Sr $^{87}/86$ ratio by Rb 87 decay since the impact and no post-impact homogenization of Sr isotopes by metamorphic events. The method would be limited to recent impact melts in target rocks with higher Sr isotopic ratios due to greater age.

The values of C could then be calculated and referred to a plot of C versus T calculated from thermodynamic data using equation (11). The value of T obtained is the effective temperature of equilibrium vapour fractionation. It may be used in calculations of vapour fractionation for other elements.

Fig. 3: Rb87/Sr86 Shift by Vapour Fractionation



(3) Experimental Evidence

There is no experimental evidence to support the theory of relative vapour fractionation of Rb with respect to K in high temperature melting processes. Studies by Lippet and Wasserburg (1964) and Schetzler et al (1966) describe fractionation of Rb with respect to Sr in high temperature melting of microcline and tektites respectively. Experimental fusion of terrestrial rocks by Lovering (1960) and Friedman et al (1960) resulted in losses of K in amounts from 6 to 13%. The average loss of K observed was 10%. The estimated average loss of Rb reported by Schnetzler et al (1966) was 25%. The fusions were performed under atmosphetic pressure, at temperatures between 1500-2500°K. Therefore an estimated Dv from this experimental data is 1.2.

IV

APPLICATION OF THE MODEL TO CRATER STUDIES

(1) Processes which modify $K/_{Rb}$ in Melt Rocks

Four processes effect the composition of melts rocks the impact fusion of target rocks:

(1) The addition of meteoric material

(2) Vapour fractionation of components of the target rock

(3) Differences between the composition of the target rock actually melted and the calculated composition of the adjacent county rocks.

(4) Alteration after consolidation

The addition of meteoritic material would not significantly change the $K/_{Rb}$ of the melt because of the low concentrations of K and Rb in meteorites Process (4), the hydrothermal alteration of fine grained rocks has been studied by Ellis and Mahon (1966). The authors report that the hydrothermal solutions are enriched in Rb and have lower $K/_{Rb}$ values than that of the rocks from which the solutions are derived. Significant loss of the alkalais only occurs at temperatures greater than 450°C at 500 bars. Hydrothermal alteration could result in higher $K/_{Rb}$ ratios therefore sampling of altered melt rocks should be avoided.

The differences between the composition of the target rock and calculated composition of adjacent country rock is a serious problem for which there exists no corrective method. If the country rock about the crater has not been deeply eroded since the formation of the melt, then a reasonable estimate of the composition may be obtained be representative sampling. Another method would be the analysis of country rock below the melt sampled by coring. A third method applicable to deeply eroded craters such as Sudbury would involve the analysis of major lithologies of crystalline inclusions in the impact breccias.

(2) Sampling and Analytical Determination of Dv

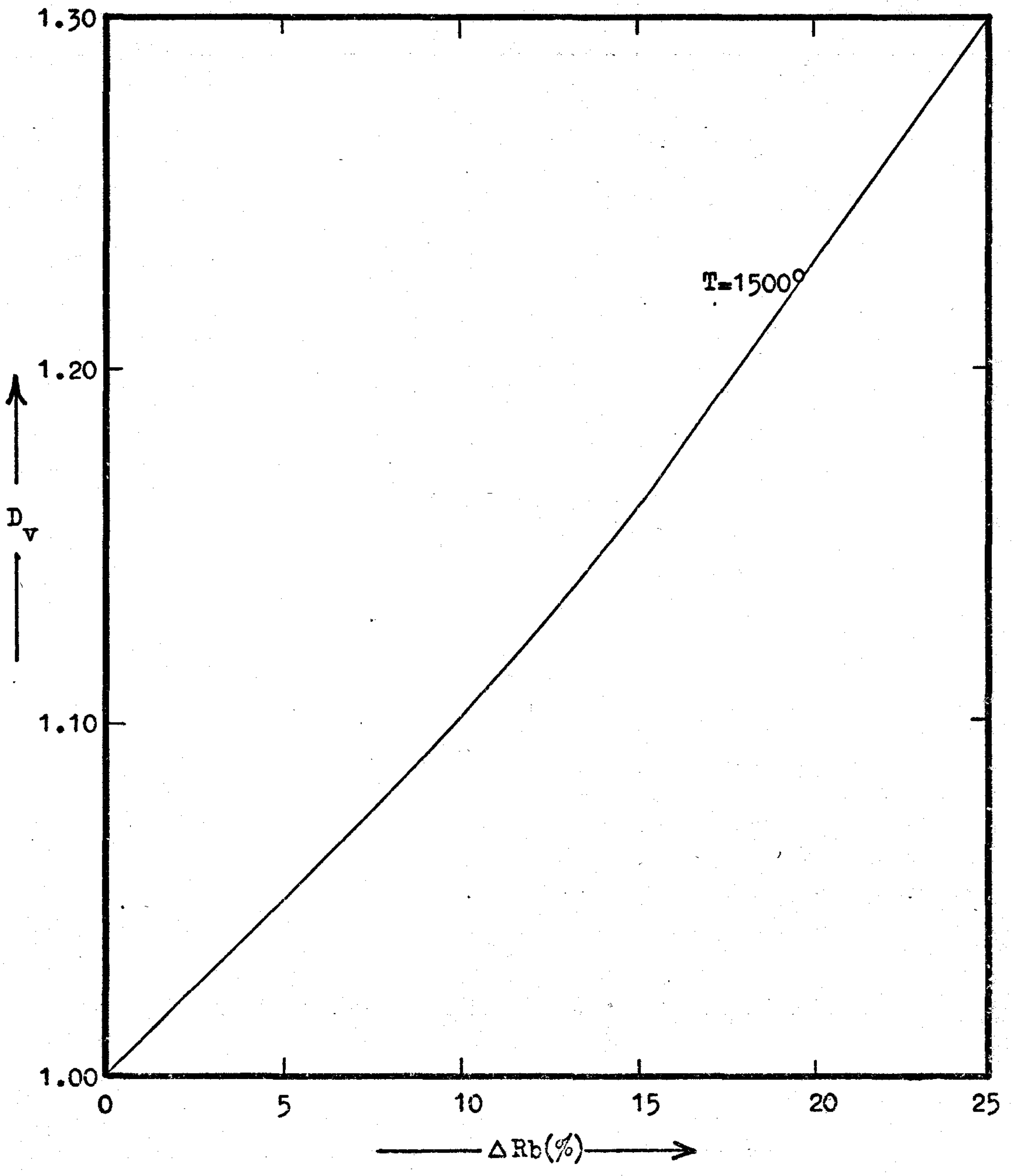
Let us consider the sampling of melt and adjacent country rocks with the purpose of measuring Dv the change in K/Rb of the melt by vapour fractionation. Applying the theoretical value of Dv for a reasonable estimate of effective temperature and Rb, we may see the expected measurable change in $K/_{Rb}$ and evaluate the sampling requirement. The $K/_{Rb}$ distribution in the target rock will be provided by the data of Bostock (1966) for the country rocks adjacent to the Clearwater Lake Craters. Based on 23 samples, the mean $K/_{Rb}$ of the country rocks is 274 with a standard deviation of 76. Evaluating Dv at $T = 1500^{\circ}K$ results in Fig.-4, a plot of Dv versus Rb. If the country rocks were uniformly fractionally vapourized, losing 15% Rb, then the $K/_{Rb}$ of the derived melt rocks would be increased by a factor of Dv = 1.16. Applying Dv to the original ratios results in a mean $K/_{Rb} = 318$ and a standard deviation of 88 for the melt rock.

The difference between two populations for which the sample mean and standard deviations is known may be tested by student's t function.

$$t_{df} = \frac{\overline{X_1} - \overline{X_2}}{(S_1^2/N_1) + (S_2^2/N_2)}$$

Dixon and Massey
pp 119

Fig. 4: D_v, Relative Vapour Fractionation Coefficient



$$df = \frac{(S_1^2/N_1) + S_2^2/N_2)^2}{\frac{(S_1^2/N_1)^2}{N_1} + \frac{(S_2^2/N_2)^2}{N_2}}$$

Where subscript 1 = melt rock

$S_1 = 88$

$\bar{X}_1 = 318$

$N_1 = 23$

subscript 2 = country rock

$S_2 = 76$

$\bar{X} = 274$

$N_2 = 23$

$df = 45$

$t = 1.82$

The difference between the means is significant at the 90% confidence level but not at the 95% confidence level. The confidence level will increase by taking more samples.

In the case of a crater with a very hetrogeneous target rock, the variances of target rocks increases so that many more samples are required to reach the 95% confidence level.

The actual difference of mean K/Rb at Clearwater Lake for the melt rock and country rock is 14 based upon 7 samples and 23 samples respectively. The difference is not significant at the 60% confidence level.

V

DISCUSSION

The author has attempted in this part of the study to evaluate the factors which control absolute and relative vapour fractionation in a silicate melt. In summary, these factors are

(1) Temperature of effective vapour fractionation
(2) G_T for the vapourization reaction
(3) Silica content of the melt
(4) Concentration of the species
(5) Fugacity of oxygen in the ambient atmosphere

The author has also attempted to determine the factors which control the measured composition of melt rocks relative to the target rocks. The factors are in decreasing importance:

(1) Sampling method and number of samples
(2) Degree of vapour fractionation
(3) Uniformity of vapour fractionation in the melt
(4) Post-impact hydrothermal alteration
(5) Melt contribution of meteoritic material

The effect of factors (1), (3) (4) and (5) unless controlled will mask any real trends effected by the vapour fractionation process.

PART B

I

SAMPLE LOCALITY

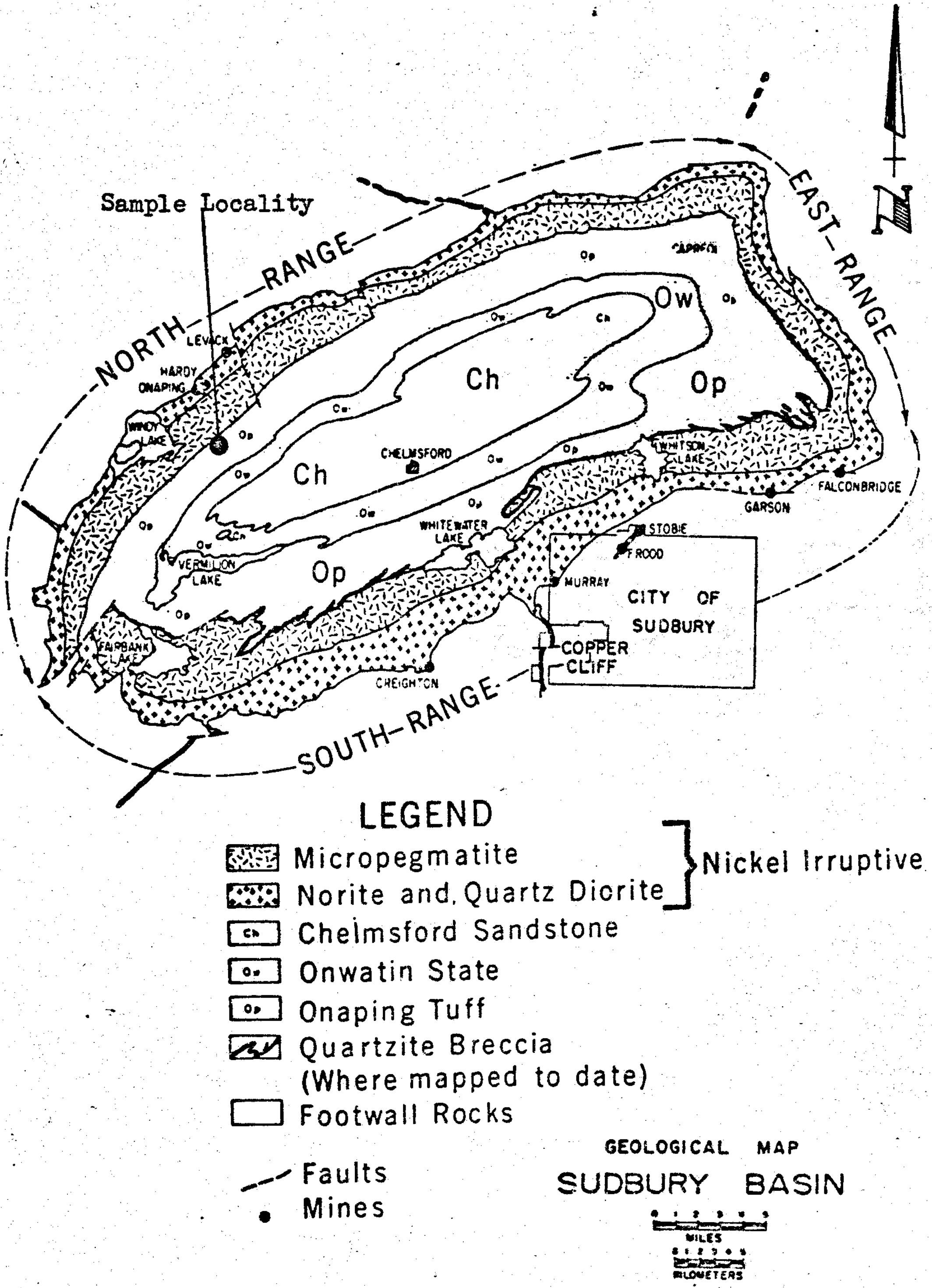
(1) General Geology

The Sudbury area is part of the southern structural province and is located between the Superior province to the north and the Grenville province to the south. The Sudbury basin is about ten miles north of the Grenville front and lies essentially at the intersection of the three structural provinces. The general geology of the Sudbury Irruptive is illustrated in Fig.-5.

The Sudbury structure is an elliptical basin approximately 35 miles long and 17 miles across; the long axis trends east-northeast. From the outside in the rocks in the Sudbury basin are the Nickel irruptive and the Whitewater sedimentary series. The Nickel Irruptive is divided into the lower norite and the upper granophyre or micropegmatite.

The Whitewater series under lies the centre of the Sudbury basin. From oldest to youngest, the sediments are the Onaping Formation, the Onwatin Slate and the Chelmsford sandstone. The Onaping formation, approximately 4000 feet thick has been described in detail by Burrows and Rickaby (1929) Williams (1956) and French (1968 1970). French (1970) summarizes the conclusions of previous workers that the Onaping formation: (1) contains numerous fragments devitrifiedglassy material; (2) also contains numerous inclusions of basement rocks up to several meters in size, (3) exhibits a

Fig. 5: General Geology and Sample Locality



uniform gradation in fragment size with larger blocks at the base and fine material at the upper contact; (4) exhibits a concentric zoning of rock types with respect to the basin margin; (5) cannot be definitely correlated with formations outside the Sudbury basin (6) was apparently deposited as a single unit during a brief period.

The contact zone between the micropegmatite and the typical inclusion bearing black Onaping consists of several rock units of widely varing aspect and chemistry whose field relations are complex and not fully understood at this time. Three of these contact lithologies are quartzite breccia, the grey Onaping and the aphanitic melt rocks. A schematic section of the Onaping formation is presented in Fig.-6.

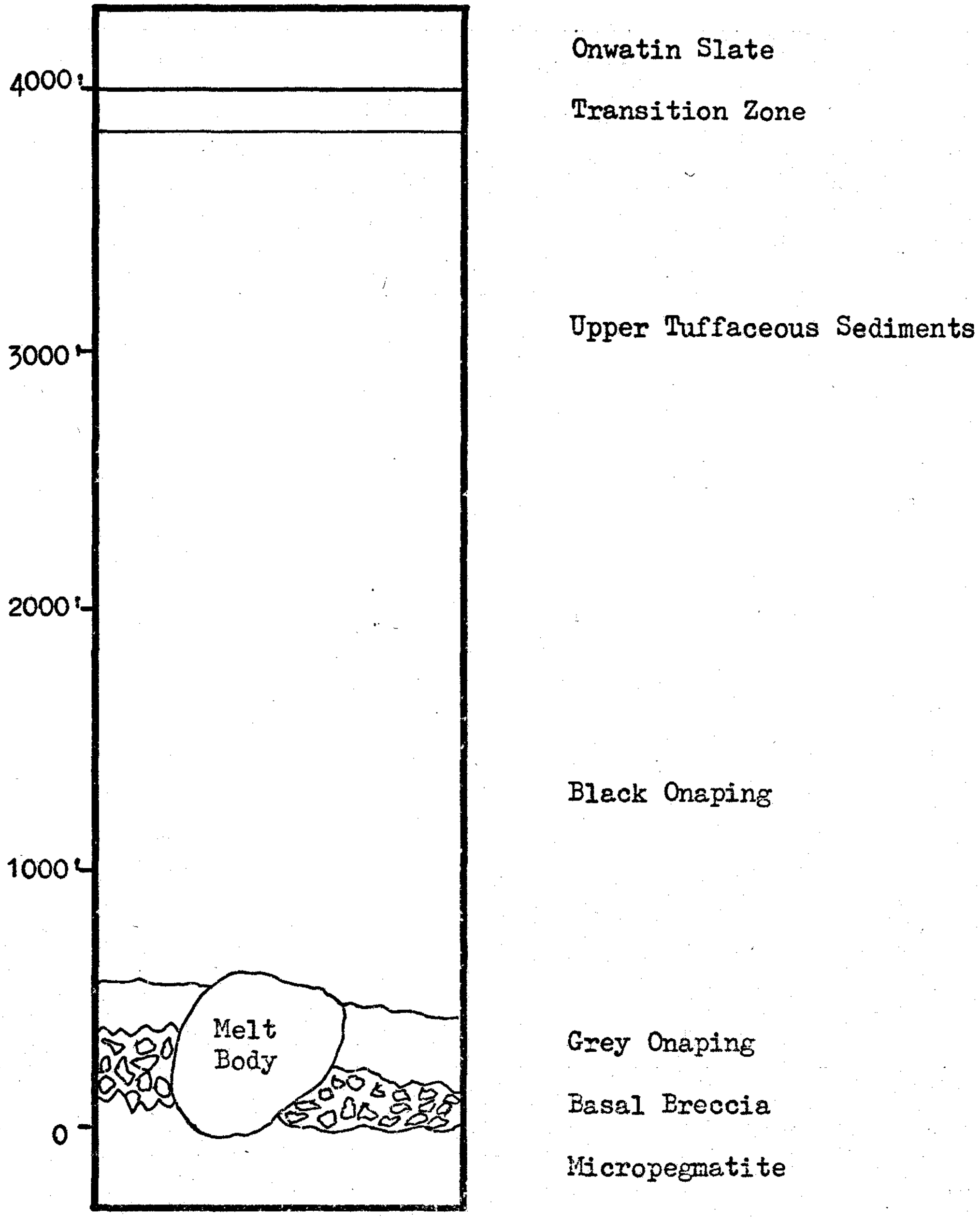
The grey Onaping overlies and is interbedded with the discontinuous breccias. The rock is very hard and cherty looking and weathers to a light grey. Inclusions are typically large, up to two feet and large glass rich fragments are common. The rock does not contain carbon.

The aphanitic melt body occurs with intrusive contacts into the grey Onaping and black Onaping and the basal breccia. The melt rock consists of isolated quartzite and quartzofeldspathic inclusion in an aphanitic or devitrified glass matrix.

The black Onaping which makes up the majority of the Onaping formation overlies the grey Onaping. The black Onaping consists of crystalline and glassy inclusions in a carbonaceous matrix. The black Onaping has a characteristic black colour due to the content of amorphous carbon of approximately 0.5%. The maximum size of inclusions decreases up section to a very fine grained highly carbonaceous argillite which is immediately overlain by the laminated Onwatin Slate.

French (1968) has found petrographic evidence for an impact origin of the Onaping formation in the crystalline inclusions of the grey and black

Fig. 6: Schematic Section of the Onaping Formation



Onaping. Inclusions has been shock metamorphased to the following stages (French 1970)

(1) Planar features in quartz and feldspar
(2) Selective recrystallization of feldspar
(3) Plastic deformation of feldspar and recrystallization of quartz.
(4) Eutectic melting between quartz and feldspar
(5) Heterogeneous melting
(6) Complete melting, mixing and accretion

Glassy inclusions of completely melted country rock are commonly flow banded and aerodynamically shaped by flight. The glassy inclusions are termed Fladen by analogy to the glassy bombs formed at the Ries Crater, Germany.

(2) Sample Location

Samples of the grey Onaping and black Onaping were taken at the High Falls type locality for the Onaping formation, lots 7 and 8, concession IV Dowling township. Four grab samples of the grey Onaping and seventeen samples of black Onaping were collected. A traverse was run from the contact of the grey Onaping, 2600 feet up the section of the black Onaping sampling at 300 foot intervals. The lithology did not vary perceptably in the nature of the inclusions, size of the inclusion or carbon content. The rock is massive and unfoliated but minor zones of shearing and associated iron staining were noted.

The samples of melt rock and stage 5 inclusions were kindly provided by Walter Peredery. The melt body sampled occurs as an intrusive body within the grey and black Onaping lots 8 and 9, concessions IV and V. The melt rocks also have an intrusive contact with the basal breccia, or quartzite breccia (Stevenson 1960, 1961, 1963).

(3) Petrography

The specimens analysed were examined in hand specimens and thin section. Some specimens which were too fine grained to be examined in thin section were stained for K-bearing phases using HF and sodium cobaltinitrate The following are brief descriptions of sample types

(a) Fladen

Glassy material in inclusions occurs in two habits: (1) shards containing minor crystalline inclusions (2) accretionary tims surrounding large fragments of shock metamorphased basement rock, (cored inclusions). The size of fragments in the lower 2000 feet of the black Onaping is roughly:

$60\% < 1 \text{ mm} < 13\% < 2 \text{ mm} < 12\% < 4 \text{ mm} < 15\%$

The estimated amount of glass fragments (stage 6) as a percentage of all fragments seems to increase up section from about 25% to 90%. The degree of shock metamorphism of non-glassy fragments also appears to increase up section .

The shards have embayed outlines and occasionally are surrounded by accrertionary rims of carbonaceous material and mineral fragments oriented tangential to the shard outlines. Fragments are not commonly in contact but are supported by the carbonaceous matrix.

The most common glassy fragment consists of elongate grains of quartz and feldspar less than 0.1 mm in length in an axiolitic devitrification texture. The second most common form is flow banded and consist of varying amounts of quartz, feldspar and chlorite. The flow bands have devitrified into spherulites of quartz, feldspar, chlorite and occasionally, pyroxene. Axiolitic devitrification occurs to a minor extent in this form. The flow bands may be traced for several centimeters in larger specimens but are commonly truncated or discontinuous. The flow bands envelop mineral and rock fragment inclusions within the glass.

Mafic glasses are relatively rare and recrystallize completely to spherulites of feldspar, pyroxene and chlorite. A few almost isotropic flow banded inclusion-bearing shards are present. The devitrification products are so fine-grained as to appear isotropic under crossed nicols.

Radiating acicular crystals of actinolite occur ubiquitously in fragments of all kinds. Opaques and carbonaceous material are also included in the fladen.

GG1 Green glassy inclusion in the Black Onaping about 400 feet south of the High Falls Park along the bush road. The sample is massive with no flow banding but small inclusions of carbonaceous material.

GG2 Cored inclusion 4 cm in diameter within the grey Onaping at a road cut on Highway 144 at High Falls. The glassy rim 1.5 cm thick is flow banded and contains carbonaceous material The crystaline core 1 cm in diameter consists of leucocratic mineral which is probably feldspar.

GG3 Green glassy inclusion 9 cm X 9 cm X 3 cm from the black Onaping in High Falls park. The inclusion is aerodynamically shaped and contains flows bands up to 8 cm long. The average width of the flow bands is 50-100μ. Numerous mineral inclusions, among them shock metamorphosed quartz and eutectic-melted quartz and feldspar. The K-bearing phase which is irresolvable in thin section occurs in continuous flow bands.

GG4 Green glassy inclusion collected from the black Onaping in the High Falls park. Flow bands of K-feldspar and inclusions 2 mm in width and flow bands of plagioclase and quartz 1 mm in width the flow bands are truncated at the fragment outline and the outline is embayed. Carbonaceous matrix material is included to a larger extent than GG3.

GG5 Green glassy flow-banded inclusion collected at the same location as GG1

(b) Melt Rocks

The melt rocks under study were supplied by Walter Peredery. The melt body occurs with intrusive contact into the basal breccias and the grey and black Onaping. The melt rock contains fragments of country rock which has been shock metamorphosed.

DW248-69

A chill phase of the melt rock. Specimen size prevented petrographic study.

DW 61-69

A chill phase of the melt rock at the contact with the basal breccia. Sample size limited the petrographic investigation.

DW 245-70

Common melt rock. Contains numerous quartzofeldspathic rock inclusions up to 3 cm in diameter. The matrix consists of an intergrowth of untwinned altered laths of plagioclase and alkalai feldspar with anhedral quartz. Well developed laths of clinopyroxene is the accessory mafic mineral. The grain size is uniform and not larger than 0.3 mm. The K-feldspar is uniformly distributed throughout the rock.

DW 108-70

Altered (?) melt rock. The rock is free of large inclusions. Needle-like crystals of light grey mineral up to 5 mm long with no preferred orientation occur in hand specimen. The mineral is quartz and the crystals seem to truncate fine grained quartz feldspar and clinopyroxene formed prior to alteration. The matrix consists of subhedral to euhedral quartz in local subparallel orientation isolated in a ground mass of very fine grained feldspar. The quartz grains are approximately 0.2 mm in length. Accessary minerals are clinopyroxene and opaques The K-feldspar is uniformly distributed in the rock.

DW 431-70

Melt rock vesicular (?). The rock contains crystalline inclusions and pockets of carbonaceous material (vesicles?) The carbonaceous material if graphite which has probably formed from amorphous carbon assimilated by the melt during intrusion. The rock is quite find grained and has a blue colour. Staining indicates that the K-bearing phase is evenly disseminated through the rock in grains sizes 100μ.

(c) Crystalline Inclusions

Three crystalline inclusions from the black Onaping were analysed. The classification of degrees of shock metamorphism is that of French (1970).

P 110-68

Blue glass. An inclusion-bearing fragment consisting of anorthoclase and chlorite. The feldspar of the blue glass has been heated to a sufficiently high temperature to disorder the structure. The feldpsar melted in situ and has not flowed. This corresponds to stage (5) heterogeneous melting.

DW 27-69

Inclusion containing quartz and plagioclase in spherulitic regrowth and incipient flow. Interpreted as stage 5 heretogeneous melting.

XL - 1

Crystalline inclusion from the same location as GG1 and GG5. The fragment is quartzofeldspathic with K-Feldspar rimming quartz and plagioclase grains. The fragment is interpreted as stage 3, plastic deformation of feldspar and recrystallization of quartz.

(d) Whole Rock

In order to compare the abundance and distribution between inclusion and host rock, two whole rock determinations were performed

Grey Onaping -B06

Fragments in stages of shock metamorphism of 2-4 usually less than 1 cm diameter in a matrix of microcrystalline quartz of grain size 10-20μ. There appears to be no actual melt phase in the fragments. The feldspars are highly altered, actinolite and chlorite are ubiquitous as overgrowths. Large blebs of disseminated marcasite, pyrite, pyrrohotite, sphalerite and chalcopyrite occur with associated carbonate and sphene, (Desborough and Larsen (1970). The K-bearing phases are restricted to shocked fragments and to a minor degree rimming several inclusions. The rim habit may be material accreted by the fragments in flight subsequent to impact.

Black Onaping - B26

Same location as GG1, GG5 and XL-1. The estimated amount of carbon matrix by volume is a maximum of 1%. Silicate minerals vary from sub-microscopic in the matrix to inclusions 1 cm in diameter. The fragment size distribution is:

$62\% < 1\,\mathrm{mm} < 6\% < 2\mathrm{mm} < 14\% < 4\mathrm{m} < 18\%$

Approxiamately 80% of the fragments are glassy. One-half of all the inclusions contain potassium bearing phases.

II

ANALYTICAL METHOD

(1) Sample Preparation

The inclusions to be analysed were chosen on the basis of glassy appearence in hand specimen, relative lack of crystalline inclusions, size and lack of alteration. The samples crushed weighed at least 50 grams. The inclusions were chiseled from slabs sawed from field samples and contamination from the matrix is considered to be less than 1%. Samples were crushed either in hand mortar (if sample weight was small) or a Spex shatterbox.

(2) Sample Analysis

The potassium and rubidium abundances were determined by atomic absorption spectroscopy on a Perkin-Elmer model 303 with a rotary sampling table and a DCR-1 digital readout and paper printout. Samples were read a minimum of eight times and the data was processed by a computer deck which averages blank-corrected data and rejects readings with deviations greater than five percent from the mean. The level of rejections for potassiums analyses did not exceed ten percent of the readings. Energy drift during some of the rubidium analyses was caused by the instability of the Osram vapour discharge lamp. Levels of rejections from the mean for GG3, P110-68, GG1, DW 61-69A, DW 108-70, DW 431-70, DW 27-69 and GG5 were high but the data has significance due to the large number of readings (13). Precision of the method for potassium is ± 0.10. Precision of the method for rubidium is ± 5 ppm with a detection limit of 20 ppm.

Standard solutions were made up from Specpure KCl and Rb Cl. Accuracy of the method was checked against USGS standard rocks GSP-1 G2 and W1. Analytical data of the standard rocks is presented in table 1. Analytical data for the samples is presented in table 2. Replicate K determinations are presented in table 3. Sample procedure and instrument settings are presented in Appendix tables A and B.

Table 1 ANALYTICAL DATA: USGS STANDARD ROCKS

	POTASSIUM Weight %				Rubidium ppm		
	Run 1	Run 2	Run 3	Recommended	Run 1	Run 2	Recommended
W1			0.55	0.53[1]			
G2	3.76		3.78	3.74[2]	167		170[2]
GSP-1		4.58	4.58	4.55[2]		265	263[2]

1. Fleischer, M., 1969 GCA 33 pp 65-79
2. Flanagan, F.J., 1969 GCA 33 pp 81-120

Table 2 ANALYTICAL DATA OF SAMPLES

Sample	K wt%	Rb ppm	$K/_{Rb}$
GG1	4.59	170	270
GG2	8.77	293	300
GG3	5.12	220	230
GG4	4.61	193	239
GG5	0.35	—	—
DW 248-69	2.99	95	315
DW 61-69	3.07	115	270
DW 245-70	2.28	89	256
DW 108-70	2.59	95	270
DW 431-70	1.00	—	—
P 110-68	5.12	145	350
DW 27-69	0.74	—	—
XL1	2.83	89	333
B06	0.96	25	384
B26	1.92	59	325

— indicates the Rb concentration was below 20 ppm

Table 3 REPLICATE POTASSIUM DETERMINATIONS

	Runs 1 + 2	Run 3	Average
Sample	K wt %	K wt %	K wt %
GG3	5.12	5.17	5.14
XL-1	2.83	2.94	2.88
DW 245-70	2.28	2.30	2.29
DW 431-70	1.00	1.07	1.03
DW 108-70	2.59	2.65	2.62
DW 61-69	3.07	3.10	3.08

III

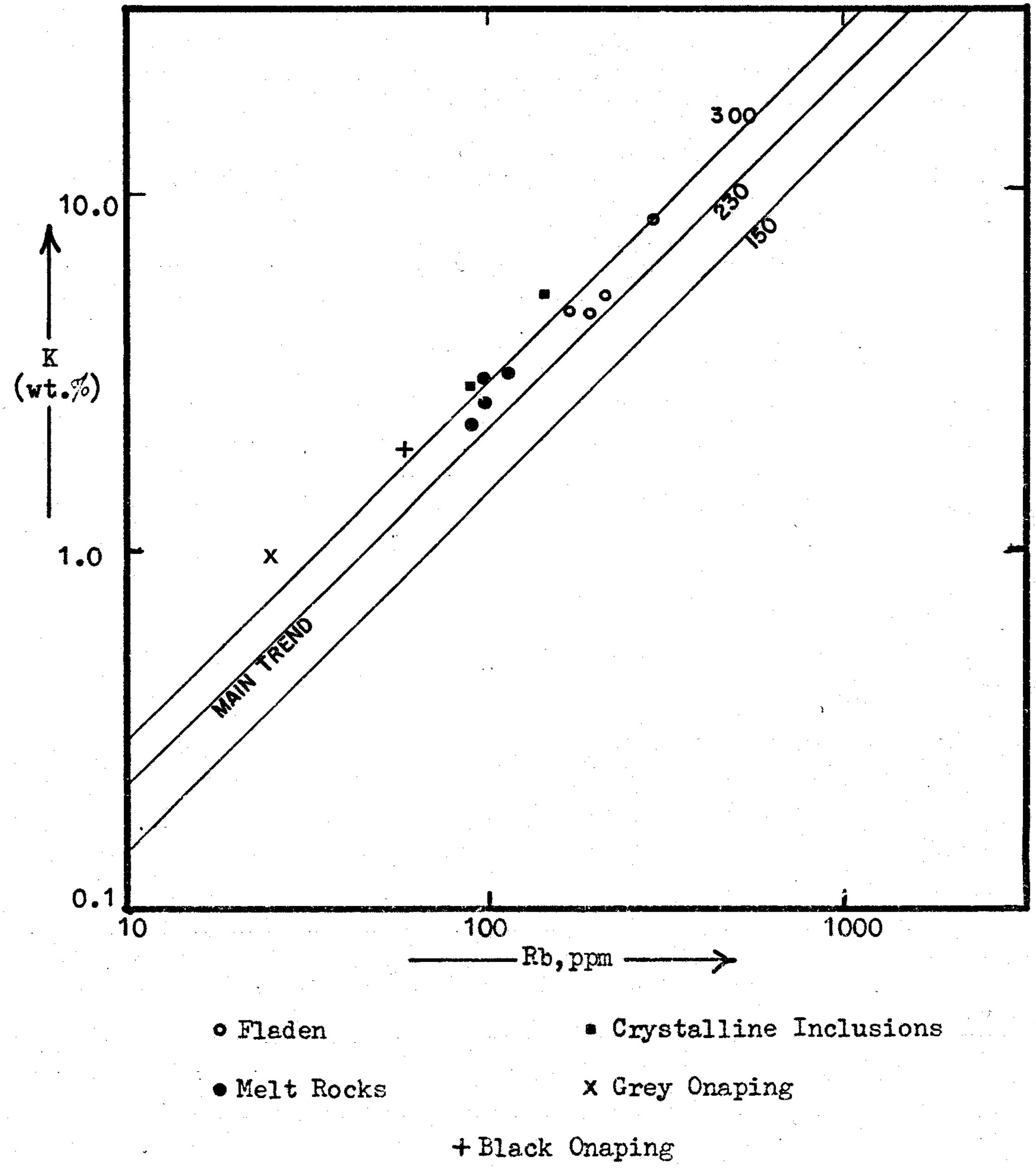
DISCUSSION

The calculated K/$_{Rb}$ of the samples is plotted on the graph of K versus Rb on logarithimic coordinates (Fig 7). The trends on the graph are those proposed by Shaw (1968). The samples which deviate from the main trend are P110-68, XL-1, B06 and B 26. The deviations connot be attributed to vapour fractionation because none of these samples exceed stage 5 (see page 23) and hence would not be predicted to be vapour fractionated. Perversely, the K/Rb for the melt phases fall within the boundaries of the main trend.

The cause of the apparent discrepancy between K/Rb of the melt phases and crystalline phases is probably inadequate sampling. The variations in abundances of K and Rb indicate the heterogenaity of the target rock. The valuation of the K-Rb ratio may be due to (1) variations in the original K-Rb of the inclusions (2) vapour fractionation (3) alkalai metasomatism during devitrification amd metamorphism. The variations due to mechanisms (1) and (2) can not be discussed due to inadequate data.

The possibility of alkalai metasomatism cannot be discounted as a significant process. Stevenson (1961) has noted Na-metasomatism to occur in quartzite fragments of the basal breccia. Scott (1971) has shown that alkalai exchange between glass and aqueous phase occurs during devitrification of ignimbrites. K in the aqueous phase exchanges with Na in the glass phase with resulting changes in the K content of up to 4 weight percent in the rock. Ellis abd Mahon (1967) have shown that Rb is enriched in hydrothermal solutions with respect to K,

Fig. 7: Sample K/Rb Ratios and Igneous Trends



If Rb follows K in exchange with Na during devitrification, then changes in Rb content of the glass may be in the order of 200 ppm or less. Rb is enriched with respect to potassium in clay minerals which are formed during devitrification. Chlorite in devitrified glass of the Onaping formation is possibly the metamorphosed equivalent of the clay minerals.

The Fladen of the Onaping formation have an average Rb content of 190 ppm with a standard deviation of 70. (data;9 samples this study, French (1971). The grey Onaping has an average Rb content of 76 ppm S=36 based on 9 samples (data; this study,French (1971), Fairbarin et al (1968). The shocked unmelted inclusions have an average Rb content of 144 ppm S = 71 based on 13 samples (data; this study, French (1971). The fladen are apparently enriched in Rb in comparison to the grey Onaping (significance 99.9%) and the unmelted inclusions (significance 80%)

The possibility of metasomatism of unmelted inclusions is suggested by French et al (1971). The apparent loss of radiogenic Sr is ascribed to extensive shock damage of minerals thus creating open systems. The author suggests that Rb may be preferentially leached from shocked metamorphosed inclusions and preferentially incorporated in glassy inclusions during devitrification. Although no evidence is available to justify the suggestion, the process would account for the observed higher K/Rb in shocked fragments and higher abundances of Rb in the glassy inclusions.

The K/Rb for the melt rock samples vary from 256 to 315. The abundance of Rb ranges from 89 to 115 ppm. The chilled phases have similar K contents which are higher than that of the common melt rock.

The altered (?) melt rock contains more K than the analagous common melt rock and a slightly higher K/Rb. Thr narrow range of Rb content and abundance is quite similar to values reported for the micropegmatite by Fairbairn et al (1965) and Souch et al (1969). The melt rock is similar in composition to the micropegmatite in major element composition (W. Peredery personal communication) so the rocks may be cogenetic.

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APPENDIX A

1. Weigh one gram of rock powder 100 mesh into weighing bottle
2. Dry for one hour in oven at 110°C
3. Dry in dessicator for one hour
4. Calibrate balance = 0, after 5 minutes
5. Weigh to 5 decimal places allowing 1 minute to reach equilibrium onffree swing.
6. Weigh into teflon dish - moisten to paste
7. Add five drops 1:1 HNO_3
   15 ml conc HF
   5 ml conc $HClO_4$
8. Cover dishes, digest on water bath overnight
9. Remove covers, evaporate to white $HClO_4$ fumes
10. Transfer to sand bath evaporate to mush
11. Transfer salts to the 100 ml beaker with aid of 13 ml 6NHCl
12. Dissolve by strong heating on hot plate
13. Transfer to volumetric flask
14. Add 20 ml NaCl buffer solution in 1MHcl
15. Make up to 100 ml with distilled water
16. Transfer to plastic bottles. Determine Rb
17. Take a 10 ml aliquot of sample solution and put it in 500 ml volumetric flask
18. Add 50 ml NaCl buffer solution in 1 in HCl
19. Make up to 500 ml with 1 N HCl
20. Agitate well and transfer to plastic bottles. Determine K

APPENDIX B

INSTRUMENTAL PROCEDURE

POTASSIUM

Spectrograph:	lamp ... hollow cathode
	wavelength setting ... 383
Rotary Table:	flush ... 6 secs
	read ... 6 secs
DCR1:	average ... 4X

RUBIDIUM

Spectrograph:	source ... 500 ma
	silt ... 5
	wavelength ... 390
	range ... vis
	lamp ... osram vapour discharge
Rotary Table	flush ... 6 secs
	read ... 22½ secs
DCR1:	mode ... concentration
	concentration ... 9700
	curvature ... 225
	noise suppression ... 3
	average ... 4X