IMPROVED DATING OF CANADIAN PRECAMBRIAN DIKES

AND A REVISED POLAR WANDERING CURVE

by

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'3ignature of Author .. .--. Department of Earth and Planetary Sciences, June 25, 1971

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Certified by . . . **. . .** . */* **.** Thesis Supervisor

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Accepted by **. .** . **. .** *V.*

Chairman, Departmental Committee on Graduate Students

ABSTRACT

IMPROVED DATING OF CANADIAN PRECAMBRIAN DIKES AND A REVISED POLAR WANDERING CURVE

Todd Michael Gates

Submitted to the Department of Earth and Planetary Sciences on June 21, 1971 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Re-evaluation of Canadian dike swarms using Rb-Sr wholerock age data gives the following results:

The results show that in most cases the Rb-Sr mineral isochron age values are concordant with the Rb-Sr whole-rock age values and are clearly greater than K-Ar age values on the same material. The fact that the mineral isochron ages and the whole-rock ages by the Rb-Sr method are similar suggests that there has been no significant thermal overprinting of these particular dikes since their emplacement and solidification. Furthermore, the general scatter and lack of significant grouping of the lower K-Ar values similarly suggests that there was no single period of thermal resetting of the K-Ar ratios. It is observed that the K-Ar age values are greater in samples containing mica, and are more scattered and lower in samples in which potassium is contained in late-stage or principal phases other than mica. Therefore, it seems likely that significant loss of argon may result at near or normal surface temperatures and that the rate of diffusion is dependent on the mineralogy of the sample. It is concluded that reasonably good age determinations can be made on diabase dike rocks nf ancient age by the Rb-Sr whole-rock isochron method. This conclusion is based both on experimental results and the compatibility of the age values with known stratigraphic relationships.

By using these improved age values and confirming some of the existing paleomagnetic data, a revised Precambrian apparent polar wandering curve for the North American continent is proposed. The approach in this report is to determine average field directions for selected age intervals which contain correctly dated rock units suitable for paleomagnetic correlation. The results suggest that the rate of apparent polar wandering varies sinusoidally with time. Comparison with African paleomagnetic results suggests that during the Precambrian the North American and African continents were not connected and may have drifted independently.

It is shown that the K, Rb, and Sr contents of diabase dikes show lateral variations that reflect the nature of the environment intruded and therefore are not representative of the composition of the original magma. Variations in the initial Sr **/Sr86** ratios suggest.that contamination by radiogenic Sr⁸⁷-enriched Sr from the surrounding syenite country rock has occurred at the time of intrusion. Possible mechanisms such as recent contamination by migrating ground waters or minor assimilation of host rock are rejected as being the cause of crustal contamination. It is believed that the observed contamination is the result of trace element leaching, possibly by late stage deuteric fluids, which does not significantly affect the major element chemistry or mineralogy of the dike rock. A model is proposed that shows that crustal contamination may be a suitable explanation to account for the observed abundances of other incompatible elements in continental diabase. It is concluded that crustal contamination, with respect to the incompatible elements (Th, Pb, U, Cs, Rb, Ba, K, Sr) does occur and that before realistic models for the magmatic evolution of continental diabase can be proposed, it is necessary to know the nature and extent of crustal contamination.

Thesis Supervisor: Patrick M. Hurley, Professor of Geology

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SECTION III

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SECTION I

MEASUREMENT OF THE AGE OF CANADIAN PRECAMBRIAN

DIABASE DIKE SWARMS ¹

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Abstract

Re-evaluation of Canadian dike swarms using Rb-Sr wholerock age data give the following results:

The results show that in most cases the Rb-Sr mineral isochron age values are concordant with the Rb-Sr whole-rock age values and are clearly greater than K-Ar age values on the same material. The fact that the mineral isochron ages and the whole-rock ages by the Rb-Sr method are similar suggests that there has been no significant thermal overprinting of these particular dikes since their emplacement and solidification. Furthermore, the general scatter and lack of significant grouping of the lower K-Ar values similarly suggests that there was no single period of thermal resetting of the K-Ar ratios. It is observed that the K-Ar age values are greater in samples containing mica, and are more scattered and lower in samples in which potassium is contained in latestage or principal phases other than mica. Therefore, it

seems likely that significant loss of argon may result at near or normal surface temperatures and that the rate of diffusion is dependent on the mineralogy of the sample. It is concluded that reasonably good age determinations can be made on diabase dike rocks of ancient age by the Rb-Sr wholerock isochron method. This conclusion is based both on experimental results and the compatibility of the age values with known stratigraphic relationships.

Introduction

Recent studies have shown that the structural trends and magnetic properties of diabase dike swarms can be of significant use in problems of continental drift and polar wandering (Payne et al. 1965; Strangway 1964). These investigations have been limited, however, because of uncertainties in the age of the individual dikes and whether dike swarms result from a single event or represent multiple intrusions over extended periods of time.

In problems of continental- drift and polar wandering it is important that age measurements be related to the kind of correlation under consideration. Correlation **Of** structural and tectonic trends over hypothetically reconstructed protocontinents requires age determinations that express the time that the structure was formed. On the other hand, rock magnetism and the determination of paleomagnetic pole positions would require age determinations that represent the time the rock acquired its stable remanent magnetism. In this case the age required is the time of emplacement and solidification of the post-kinematic intrusive.

The present investigation concerns the dike swarms of the Canadian Shield. Most of the published ages are K-Ar analyses (Fahrig and Wanless 1963; Burwash et al. 1963, Leech 1966) which Stockwell (1970) has assumed provide reasonable ages. He has taken average age values determined from material which has produced reasonably concordant K-Ar ages. Since this method is notorious for giving low age values as the result of

argon loss, it was decided to check K-Ar determinations with values determined by the Rb-Sr method. After preliminary investigation of a single dike swarm, it was found that Rb-Sr whole-rock and mineral isochrons give essentially concordant and older ages than the K-Ar analyses. Earlier work by Van Schmus (1965) and Fairbairn et al. (1969) on the Nipissing diabase also showed that this approach was sound. Therefore, it was decided to re-evaluate many of the dike swarms of the Canadian Shield using the Rb-Sr whole-rock method.

Geologic Setting and Description of Dike Swarms The most recent and acceded sub-division **of** the Canadian Shield is that of Stockwell (1963) , who states that:

"The division of the Shield into structural provinces and subprovinces is useful for the purpose of description and discussion of the geology. The divisions are made mainly on the basis of important unconformities and overall structural characteristics, and each may contain rocks of widely different ages; but becuase of the close relationship between structural features and the last orogeny, the provinces correspond closely to orogenic divisions based on potassium-argon ages."

These divisions are shown in Figure **1.**

However, due to the widespread use of the K-Ar method there has been a tendency to conclude that most igneous and metamor-

Figure **1**

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phic rock units within a province are formed within too short an interval of time. This arises because large areas have been subjected to thermal or tectonic effects significant to reset the K-Ar systems but insufficient to significantly alter the rock systems.

Figures 2 and 3 show the regional distribution of the dike swarms studied. Exact sample localities and sample descriptions are reported by Gates (1971) or may be obtained on request. A summary of the field and laboratory observations is given in Table I. Although the Nipissing Sill was not studied it is included in Table **I** because of its probable relation to the Abitibi dike swarm.

Analytical Techniques

Potassium determinations were made by the atomic absorption method using a double beam, AC, premix Perkin-Elmer instrument, model 303. A description of the analytical details is given by Gates (1971). Errors are indicated by replicate analyses of W-1 which give an average value of 0.524 percent K with a standard deviation of analysis of .004.

Argon analyses were made in an all-glass gas purification train directly coupled to a MS-10 mass spectrometer which has been designated "GAIL". A description of the analytical details and instrumentation is given by Gates (1971). Replicate analyses of M.I.T. Standard Biotite B3203 show that argon determinations were in error, at most, by one percent.

Rb and Sr determinations were done using a 6"-radius mass

Figure 2

MILES

Figure 3

20 Table I

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positions

Intrudes Huronian sediments and Sudbury irruptive, Stratigraphic cut by Grenville Front, metanorphosed dikes probarelations bly related can be traced into the Grenville. $\overline{}$

SUDBURY (cont.)

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MACKENZIE SET III*

Strike N0°-30°W with dominant direction in the N20°-30°W range. Most extensive in the Slave Province, could form a continuous feature from the Bear Province cutting through the Slave, Churchill and into the southern portions of the Superior Province. Dike width generally greater than **100** ft. Dike length variable. In some cases individual dikes may extend for hundreds of miles.

Four whole-rock analyses fall on the Sudbury 1660 m.y. ? isochron. Data insufficient to make reliable age determination.

1000-1100 m.y. whole-rock (Burwash et al 1963) [see note **1]** 1315 m.y. Av. 4 biotite & 1 whole-rock (Fahrig and Wanless 1964) 1050 **±** 95 m.y. whole-rock (Wanless et al 1966) 1155 **± 100** m.y. Av. 10 whole-rock & 1 biotite (Leech 1966) 1550 **±** 170 m.y., 902 **± 100** m.y. whole-rock (Wanless et al 1968)

Intrudes Bear, Slave, and Churchill Provinces. Cuts all other dikes in Mackenzie area. Extension cuts little deformed supracrustal strata thought Middle Proterozoic (Stockwell 1970).

MACKENZIE SET III (cont.)

(Fahrig et al 1965)

[see note 2]

***** These are the most common dikes in the District of Mackenzie and are commonly referred to as the Mackenzie dikes. Since there are four different dike swarms in the Mackenzie area, this paper will use the guide lines set by Burwash et al (1963) when referring to individual swarms of the District of Mackenzie.

MACKENZIE SET II

Strike N-S to N30°E with dominant direction in the N20°-30°E range. Appear to be confined to the Slave Province. Generally less than 100 ft. in width and can be traced along strike for distances of 10-20 miles. Regional distribution uncertain.

 2067 ± 45 m.y. $[Sr^{87}/Sr^{86}]_o = .7037 \pm .0004$ (this study)

[see note 1]

2090 m.y. av. 4 whole-rock (Fahrig and Wanless 1963) **1570** m.y. whole-rock (Burwash et al 1963) **1155-1965** m.y. Gives age of intrusion as 2000-2100 m.y. (Leech 1966)

not done

Intrudes Archean basement.

MACKENZIE SET II (cont.)

not done

[see note 2]

note 1 The K-Ar listing is hopefully complete although there likely to be some omissions. Values underlined have been assigned to a particular dike swarm on available information. Since the reports containing these data make no direct reference to a particular dike swarm it is possible that some of these values may not be representative of that dike swarm.

MACKENZIE SET IV

Strike N30°-60°W with dominant direction in the N45°-60° range. Appear to be confined to the Slave Province. Little known about individual dikes. Regional distribution uncertain.

2174 ± 180 m.y.
$$
[Sr^{87}/Sr^{86}]_c = .7019 \pm .001
$$
 (this study)

1460-1955 m.y. Gives age of intrusion as 2000-2100 m.y. $\ddot{}$ (Leech 1966)

not done

Intrude Archean basement. Campbell (1948) gives two cases where dikes of Set IV are cut by dikes of Set II. Leech (1966) proposed that dikes of Setts II and IV are a conjugate set.

 $\mathbf{q} = \mathbf{q} \times \mathbf{q}$

MACKENZIE SET IV (cont.)

not done

Reference to the Mackenzie dikes is given by Henderson and Brown (1948, 1949, 1950a, 1950b, 1952a, 1952b), Stockwell and Kidd (1932), Stockwell (1933), and Jolliffee (1936, 1938, 1942, 1945, 1946). As these reports are given in general terms it is difficult to relate the dike descriptions to a particular dike swarm. It is apparent, however, that some of the dikes are quartz diabase and others are olivine diabase. Since no thin sections were available for this study, no attempt is made to classify the Mackenzie dikes of petrographic grounds. note 2

NIPISSING SILL

Is an undulating Sill up to 1000 ft. thick. It intrudes the Huronian sediments of southeastern Ontario from Sault Ste. Marie to Gowganda Lake.

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2155 ± 80 m.y. [\texttt{Sr}^{87}/\texttt{Sr}^{86}]_{\textsf{O}} = .7060 whole-rock
1700 ± 50 m.y. [Sr<sup>87</sup>/Sr<sup>85</sup>]<sub>o</sub> = .7145 mineral age
2162 ± 27 m;y.
[Sr87/Sr ]o =
.7061 ± .0005
                                                                   (Van Schmus 1965)
                      (Fairbairn 1967)
```
2095 mn.y. one biotite (London et al **1962)**

LONG $92°E$ LAT 19.51N (Symons **1970)**

intrudes Huronian sediments.

NIPISSING SILL (cont.)

Generally quartz diabase, containing mainly calcic labradorite, augite, with or without pigeonite, titaniferous magnetite (partly altered to leucoxene) and micrographic intergrowths of quartz and feldspar. Accessory minerals are red brown biotite, apatite, pyrite, phyrrhotite, and chalcopyrite. Some reports indicate that quartz free olivine diabase do occur (Fairbairn et al 1953). For detailed description see Robertson (1968).

ABITIBI

The individual dikes within the swarm show three trends. These trends have been described as ENEW, ENEN, and NNE (Larochelle 1966). Occur in a band roughly 150 miles wide which parallels the Grenville Front. Extends from Sault Ste. Marie (Ontario) to Lake Mistassini (Quebec). Number of dikes in the swarm is small, but individual dikes are large, up to 800 ft. wide and several hundred miles in length.

 1247 ± 68 m.y. $[{\rm Sr}^{87}/{\rm Sr}^{86}]_0 = .7045 \pm .0004$ ENEW trend 2262 ± 279 m.y. $[Sr^{87}/Sr^{86}]_0 = .7039 \pm .002$ ENEN trend $2227 \pm 125 \text{ m} \cdot \text{y}$. $[{\text{Sr}}^{87}/\text{Sr}^{86}]_0 = .7048 \pm .0008$ NNE trend (this study)

1230 m.y. av. 2 biotite (Fahrig and Wanless 1963) 1825 m.y., 1655 m.y. whole-rock (Wanless et al 1965) **± 60** m.y., 1935 **±** 35 m.y., biotite (Wanless et al 1968) **±** 165 m.y. whole-rock **±** 65 m.y. hornblende (Wanless et al 1970) **±** 90 m.y. whole-rock

Appears to be cut by Cobalt Front, but may be continuous beneath these flat lying Precambrian sediments (Strangway 1964). ABITIBI (cont.)

In the thin sections examined these dikes contain less calcic plagioclase, but are generally similar to the Nipissing diabase. Like the Nipissing diabase they appear to be a diverse group ranging from ophitic textured diabase to dioritic looking rocks and varying in composition from quartz diabase to olivine diabase. For detailed description see Prest (1952).

MACKENZIE SET I

Strike N70°E-EW. Appear to be confined to the Slave Province. Dike width ranges between 100-200 ft. Dike length may range from 50-100 miles. Regional distribution uncertain.

2692 ± 80 m.y.
$$
[Sr^{87}/Sr^{86}]_0 = .7128 \pm .0005
$$
 whole rock (this
\n1816 ± 4 m.y. $[Sr^{87}/Sr^{86}]_0 = .7130$ (metamorphic or study)
\nhydrothermal age?)

2250 m.y. whole-rock (Burwash et al 1963) 2310 m.y. hornblende 970-2390 m.y. age scatter using whole-rock and biotite samples. Gives age of intrusion as 2200-2400 m.y. (Leech 1966)

1570 **±** 115 m.y. whole-rock (Wanless 1970)

not done

Intrudes Archean basement.

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MACKENZIE SET I (cont.)

not done

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not done

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MATACHEWAN

Strike N-S. Extend from James Bay south to the $47th$ parallel, and from the Noranda area (Quebec) west to the Timmins area (Ontario). Dike width ranges from 100-200 ft. and individual dikes have been traced along strike for distances up to **100** miles.

2690
$$
\pm
$$
 93 m.y. $[Sr^{87}/Sr^{86}] = .7000 \pm .001$ (this study)

2485 m.y. whole-rock (Wanless et al **1965) 1930, 1760, 1500, 1325** whole-rock (Leech **1966)**

Intrudes Archean basement. Are cut by Abitibi dikes and may may be covered by Huronian sediments.

Quartz diabase. Frequently porphyritic with phenocrysts of white or pale green plagioclase in a fine grained dark green matrix. Are composed of labradorite, augite, with or without pigeonite, micrographic intergrowths of quartz and feldspar and titaniferous magnetite. Thin sections show much alteration. For detailed discussion see Prest (1952, 1957) and Lovell (1967).

spectrometer designated "IRIS". Standard isotope dilution methods were used. A description of the method including sample preparation, spike calibration, spiking, and method of calculation of the isotope dilution values is given by Reesman (1968). Replicate analyses of the Eimer and Amend Standard given an average Sr^{87}/Sr^{86} ratio of 0.7082 \pm .0002 normalized to a Sr^{86}/Sr^{88} ratio of 0.1194, with a standard deviation error for a single determination equal to .001. This value includes errors from sample heterogeneity, chemistry and instrumentation. Preliminary determinations of Rb and Sr were made by X-ray fluorescence, using procedures described in a report by Fairbairn (1966).

The best straight line fit for each isochron diagram, the intercept of each line on the Sr^{87}/Sr^{86} axis and the attendant errors, have been obtained from the least-squares computer program set up by York (1966). Ages have been computed using Rb^{87} $\lambda = 1.39 \times 10^{-11}$ yr⁻¹.

Mineral separations were done with S-tetrabromoethane, density 2.95, which efficiently separated pyroxene and plagioclase. The separated minerals were washed in acetone. All magnetite was removed with a hand magnet. Further separation to about 95% purity was accomplished using the Frantz magnetic separator. Grain sizes of the separated minerals varied from 150-250 microns depending on the grain size of the sample.
Comparison of Rb-Sr whole-rock, Rb-Sr mineral.and K-Ar wholerock age determinations, and an evaluation of the methods

The evaluation of the relative merits of the Rb-Sr and K-Ar methods of age determination was carried out on samples from the Matachewan dike swarm. This was chosen because:

- **1.** stratigraphically, it is the oldest dike swarm in the Superior Province. Therefore the possible detection of discordant relations is enhanced.
- 2. it occurs in an environment which is believed to have been tectonically stable since the close of the Kenoran Orogeny. This consideration hopefully eliminated the possibility of post-intrusion tectonic over-print. It should be mentioned that in some areas magnetic surveys reveal that the Matachewan dikes have been subjected to a considerable amount of faulting. In this study, however, an attempt has been made to avoid these areas.

3. access to sampling area is relatively easy.

The analytical data for the Rb-Sr determinations on the Matachewan dikes are given in Table II. An isochron plot of the whole-rock analyses is shown in Figure 4. The leastsquares isochron age for these samples is 2700 ± 100 m.y., and the initial ratio is .7000 ± .001.

The observed analytical scatter between duplicate runs, and in the isochron plot, is believed to be the result of the following factors.

TABLE II Analysis of Matechewan Whole-Rock and Mineral Samples.

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TABLE **II** (Cont'd.)

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TABLE II (Cont'd.)

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 $\label{eq:2.1} \frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\left(\frac{1}{\sqrt{2\pi}}\right)^{2\alpha} \frac{1}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2\pi}}\frac{$

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TABLE II (Cont'd.)

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- 1. Sample heterogeneity. In all cases where duplicate analyses have been made by the isotope dilution method, the observed variation is compatible with stated errors $(Sr^{87}/Sr^{86} \pm .001, Rb^{87}/Sr^{86} \pm 38)$ or else can be explained by sample heterogeneity. Samples R7524, R7536 and R7551 show variation within known analytical errors. On the other hand, samples R7530 and R7531 show variations in excess of these. When the Sr^{87}/Sr^{86} ratios are calculated to a common Rb^{87}/Sr^{86} ratio, the values are in good agreement. The sample heterogeneity may result from minor differences in the quantity of mica present.
- 2. Calculation of Sr^{87}/Sr^{86} ratios from Sr isotope dilution analysis. This procedure may make small contributions to the analytical error. However, samples R7537, R7547, **R7558** and R7551, which are unspiked aliquots, give values that are essentially identical with their spiked counterparts. Sample R7523 represents a duplicate analysis of a spiked and unspiked sample. Although the variation appears to be quite large (.0047), it may result from sample heterogeneity.
- **3.** Contamination from the host rock. It appears that the absolute abundances of Rb and Sr and the degree of scatter in the isochron are related to the nature of the intruded rock. The absolute abundance of Rb and Sr increases as the country rock becomes more acidic. This relationship is shown in Table III, and clearly indi-

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第159章 我们的人,他们的人都是一个人,他们的人都是一个人,他们的人都是一个人,他们的人都是一个人,他们的人都是一个人,他们的人都是一个人,他们的人都是一个人

cates the possibility of trace element contamination of the material of the dike, most of which must have occurred at time of emplacement.

The isochron plots of the Matachewan data support the conclusion that later contamination by Rb or Sr has not been sufficient to destroy the usefulness of the method. Figure 5 shows a plot of the analytical data for Matachewan samples that intrude Archean greenstone (metabasalts). The data points represent samples from the chilled margins and central portions of five dikes. The regional distribution of the dike samples covers about 3,000 square miles. Since the chemical compositions of the greenstone and diabase are similar, one would not expect a great deal of interaction between these two rock units. Although the amount of interaction cannot be determined from an isochron plot, the unusually low initial ratio and the statistical nature of the data points do indicate that there has been little contamination of the dike rocks during or since the time of emplacement.

In Figure 6 the analytical data are shown for Matachewan samples that intrude a metagrayacke. The metagrayacke is intermediate in composition and the samples are taken from the central portions of four parallel dikes. Within experimental uncertainties, the initial ratio and the ages for samples that.intrude metasediments and metabasalts are in good agreement. Based on these data alone it is reasonable to conclude that the Matachewan dikes were emplaced 2700 **±** 100 m.y. ago, possibly as a single event. The higher initial ratio of the

samples that intrude the metasediment may be significant although no positive comment can be made due to the nature of the analytical uncertainties.

Figure **7** shows the data for Matachewan samples that intrude a syenite. In this figure reference isochrons are plotted with different initial ratios and the same slope as in Figure 5. The samples are taken from the chilled margins and central portions of two parallel dikes. In most cases the data points fall above the whole-rock isochron determined in Figure 5 and exceed variations resulting from experimental uncertainty. This would indicate that Sr enriched in radiogenic Sr^{87} has at some time migrated into the dike systems. Wasserburg et $a1.$ (1964) have shown that diorite dike rocks can be enriched in radiogenic Sr during metamorphism. The Matachewan data, however, do not indicate any post-intrusion metamorphic event. The unlikelyhood of a metamorphic event is further supported by the known geology of the environment.

This would indicate either that the magma was isotopically heterogeneous at the time of solidification, or that over long periods of time basic rocks may act as a sink for migrating cations in a host environment in which they are more abundant.

The first possibility is not unlikely, and may occur during the end stages of dike solidification. A residual fluid phase might extract Sr^{87} enriched Sr from the country rock as suggested by Pankhurst (1969), and contaminate the dike, even causing isotopic variations within it.

The second possibility may result from the deposition of radiogenic Sr from surrounding areas by ground waters in recent times.

The isotopic evidence shows that samples closer to the contact generally have higher Sr^{87}/Sr^{86} ratios than would be predicted from the known whole-rock age. This would be expected for both the above alternatives. Neither of these processes, however, can be proved or disproved with the available data. The important point is that excess scatter of analytical data on the isochron'plots appears to be related to the host environment of the sample. Due to this scatter and the small spread in the Rb^{87}/Sr^{86} ratios, the determination of single sample whole-rock ages is very dependent on the initial ratio and may generate large errors. On the other hand, a statistical approach using a large number of samples for the development of whole-rock isochrons produces analytically more reliable results.

Figures 8-13 show mineral isochrons for the Matachewan samples. The large errors, resulting from lack of analytical resolution and the small spread in the Rb/Sr ratios, make interpretation of the individual isochrons difficult. When viewed as a group, however, the mineral isochrons appear to be generally concordant with the Rb/Sr whole-rock age. This relation is shown in Fig. 14. In this figure the Rb-Sr wholerock age for each sample is calculated using an assumed initial ratio. It is plotted against the Rb-Sr mineral isochron age. The line drawn with a slope of one represents the locus

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of concordant data. With the exception of sample R7538 the concordant nature of these data is indicated by the uniform distribution of points above and below this line. The crosshatched box in Fig. 14 represents the Rb-Sr whole-rock isochron age of 2.7 **±** 0.1 b.y. Within the limits of experimental uncertainties, both the individual Rb-Sr whole-rock and mineral isochron ages are concordant with this value.

Further indication of the concordant nature of these samples is given by a plot of the Rb-Sr mineral ages (Figures 15 and 16). These plots show that the plagioclase and pyroxene ages and initial ratios are in good agreement with the values determined by mineral isochron and whole-rock isochron methods.

The fact that the whole-rock isochron age, mineral isochron age and mineral age by the Rb-Sr method are similar, suggests that there has been no serious thermal overprinting of these particular dikes since approximately their time of emplacement. Thus it is believed that the best age for the Matachewan dike swarm is given by a least-squares fit through all of the whole-rock and mineral points from the data in Table II. **A** plot of these data is shown in Fig. 17. The least-squares isochron age given in this figure is 2690 ± 93 m.y. and the initial Sr⁸⁷/Sr⁸⁶ ratio is .7000 ± .001.

The analytical data for the K-Ar whole-rock age determinations are given in Table IV. When the K-Ar age values are compared with the Rb-Sr mineral isochron ayp or Rb-Sr wholerock age (Figures 18 and 19), it is clear that there has been

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Table IV K-Ar whole-rock and Rb-Sr mineral isochron ages for the Matachewan samples.

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some loss of radiogenic argon. Leech (1966) considered the problem of argon loss, and proposed Leech's Law: "Updating and uplifting have the same effect; old dykes and old ladies give younger ages". It has been shown that the Rb-Sr wholerock and mineral isochron ages are concordant. Therefore, it is unlikely that regional overprinting resulting from tectonic activity is a valid explanation for argon loss in the Matachewan samples. Furthermore, (as shown in Figures 18 and 19), the lack of significant grouping and general scattering of the lower K-Ar age values also suggests that there was no single period of thermal resetting of the K-Ar ratios.

As shown in Table I, a scatter of K-Ar ages similar to that observed in the Matachewan samples is characteristic for most of the dike swarms studied. The data presented indicate that thermal re-equilibration and argon loss resulting from regional tectonic activity is unlikely. Therefore, it is concluded that over long periods of time a diffusion loss of argon in dike rocks at near surface temperatures may result in a significant lowering of the age values.

Sample R7538 may be an exception. As shown in Figures 18 and 19, this sample appears to give younger and concordant K-Ar whole-rock, Rb-Sr whole-rock and Rb-Sr mineral isochron ages. The explanation may be localized faulting or simply lack of analytical resolution.

The argon retention within a rock appears to be dependent on its mineralogy. Diabase is commonly primarily of plagio-

clase, pyroxene and magnetite. None of these minerals freely accept potassium into their structure. If these are the only minerals present, potassium would tend to be excluded from them in the crystallization sequence and would probably concentrate in crystal defects or in intergranular residual glass. Neither of these sites is likely to retain argon.

Generally diabase contains mica or K-feldspar. If present, these minerals will incorporate most of the potassium into their structure. It is known that the argon retention of mica is greater than K-feldspar. Therefore, samples containing mica should give older ages than those containing K-feldspar. This is, in fact, found to be the case.

Thin-section examinations (Leech, 1966) show that the chilled margins of the Mackenzie dikes contain abundant biotite. These samples generally give older ages. On the other hand, the chilled margins of the Matachewan dikes contain no biotite and give younger ages. Biotite separated from some samples (Leech 1966) generally gave the oldest age for a particular dike swarm.

K-feldspar occurs with quartz as micrographic intergrowths. These are present in quantities up to 10 percent and occur in angular interspaces between laths of plagioclase crystals. Where K-feldspar is the dominant K-bearing mineral, younger ages are always obtained.

Surprisingly old ages are obtained from highly altered and sericitized samples. The reason for this is probably the occurrence of mica (muscovite). Sample R7550 (Matachewan)

gives a K-Ar age of 2715 m.y. which agrees well with the Rb-Sr whole-rock isochron age, and mineral isochron age. This rock contains about 15 percent altered pyroxene and 85 percent relic plagioclase. No micrographic intergrowths of Kfeldspar and quartz are present. The pyroxene has been altered to amphibole, chlorite, and epidote. Sericite has almost completely replaced the plagioclase. The Mackenzie dikes (Leech 1966) show the same trend: older ages are generally obtained from highly sericitized samples. Since these samples give old ages, their highly altered appearance is probably due to deuteric fluids and not the result of subsequent metamorphism.

Re-Evaluation of Canadian dike swarms using Rb-Sr whole-rock age data

The data presented have shown that the K-Ar method of age determination is generally unreliable when applied to diabase dike rocks. Therefore, the remainder of this report is devoted to the re-evaluation of the Canadian dike swarms using the Rb-Sr whole-rock ages.

Sudbury Dike Swarm:

The samples analyzed were obtained from A. Larochelle (1967) and the age determined in this study is directly applicable to the pole positions which he determined. Table V gives the isotope dilution analyses for the Sudbury samples. The isochron (Figure 20) shows an age of 1660 **±** 145 m.y. and initial Sr^{87}/Sr^{85} of .7040 \pm .0004. This age would indicate that the

M.I.T. No.	Sr ⁸⁶	Sr a.	Rb ⁸⁷	Rb	Sr ⁸⁷ /Sr ⁸⁶	Rb ⁸⁷ /Sr ⁸⁶
R7776	34.3	354.8	9.44	33.3	7109	.2721
R7777	41.3	427.3	6.33	22.35	.7073	.1515
R7778	45.4	469.4	5.99	21.1	.7079	.1304
R7779	39.1	404.2	5.06	17.86	.7065	.1279
R7780	50.15	518.5	5.29	18.67	,7068	.1043
R7781	42.48	439.2	5.49	19.39	.7065	.1278
R7782	28.45	294.2	8.02	28.33	.7111	.2787
R7783	33.02	341.5	8.43	29.8	.7096	.2524
R7784	33.77	349.2	7.91	27.95	.7098	.2317
R7785	34.8	359.3	7.80	27.5	.7082	.2216
R7786	36.5	377.0	8.14	28.7	.7089	.2206
R7787	33.6	335.9	9.20	32.5	.7105	.2707
R7788	45.08	466.3	2.95	10.42	.7130	$.0647*$
R7789	32.9	340.3	9.26	32.7	.7104	.2782
R7790	47.1	486.9	4.99	17.63	.7067	.1047
R7791	35.13	363.3	9.19	32.5	.7096	.2586

Analysis of Sudbury whole-rock samples. TABLE V

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TABLE V. (cont'd.)

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* Omitted from isochron.

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Sudbury dike swarm was emplaced towards the close of the Hudsonian Orogeny.

Mackenzie Set III Dike Swarm:

All of the samples for the Mackenzie dikes (Sets I-IV) were obtained from the Geochronology Laboratory of the University of Alberta. Consequently, the Rb-Sr whole-rock determinations of this study may be compared directly with the K-Ar results of Burwash et al. (1963) and Leech (1966) (Table I).

The isotope dilution analyses for the Mackenzie Set III dike swarm is given in Table VI and the isochron plot is shown in Fig. 21. Because of the limited number of samples and the very small spread in the Rb^{87}/sr^{86} ratio, a least-squares computation was omitted.

Similarities in pole positions and chemical composition (Table I) suggest that the Sudbury dikes represent an extension of the Mackenzie Set III dike swarm. This possibility is supported by the similar spread in the Rb^{87}/Sr^{86} ratios of the two swarms and the fact that the data points for the Mackenzie Set III samples fall on the Sudbury reference isochron (Figure 21).

Abitibi Dike Swarm:

As with the Sudbury dike swarm, most of the Abitibi samples (R7745-R7775) were obtained from Larochelle (1966), so that the age determined in this study is directly applicable to his pole positions.

The isotope dilution analyses for the Abitibi dike swarm

TABLE VI Analysis of Mackenzie Set III whole-rock samples.

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are given in Table VII. Figures 22-24 show the isochron plots for the various trends (Table I) of the Abitibi dikes. Different pole positions (Larochelle 1966) relative to the trend of the dike would indicate that the dikes were not emplaced at the same time. Furthermore, the variation in chemical composition and the occurrence of both olivine diabase and quartz diabase would suggest that the swarm did not result from a common magmatic source. The isotopic evidence shows that within experimental limits all the Abitibi samples analyzed, regardless of dike trend, appear to be roughly isochronous (2147 **± 68** m.y.). It is possible, however, that multiple intrusions over an interval as large as 200 m.y. may be undetectable because of the small spread in the Rb^{87}/Sr^{86} ratio (Figures 22-24).

As shown in Table I, petrographic and chemical similarities between the Abitibi and Nipissing diabase suggest possible correlation. The excellent agreement for the age of the Nipissing diabase 2162 **±** 27 m.y. and 2155 **±** 80 m.y. (Van Schmus 1965; Fairbairn et al. 1969), with that of the Abitibi dike swarm, increases the likelihood of common origin. The fact that the Abitibi dikes predominantly intrude the Archean basement and the Nipissing diabase occurs mainly as sills in the post Archean Huronian sediments indicates stratigraphic control of intrusion in this region rather than emplacement controlled by regional fracture systems.

Paleomagnetic measurements, although not in agreement, do not rule out the possibility that the Nipissing and Abitibi diabase

TABLE VII Analysis of Abitibi whole-rock samples.

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TABLE VII (Cont'd.)

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TABLE VII (Cont'd.)

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are related.

Mackenzie Set II and IV Dike Swarms:

Tables VIII and IX give the isotope dilution analyses of the Mackenzie Set II and IV dike swarms, respectively. The isochron for the Set II data (Figure 25) gives an age of 2067 \pm 45 m.y. and an initial Sr^{87}/Sr^{86} value of .7037 \pm .0004. The isochron for the Set IV data (Figure 26) gives an age of 2174 **±** 180 m.y. and initial Sr8 7/Sr8 6 of .7019 **±** .001. These data support the observation of Leech (1966) that the Mackenzie Set II and IV dikes are conjugate. Within the limits of analytical uncertainties, the ages of these two swarms are identical. Therefore, if it is assumed that these dikes are conjugate and comagmatic, the best age is obtained by a composite of the analytical data from both swarms. This has been done and is shown in an isochron plot (Figure 27), which gives an age of 2093 \pm 86 m.y. and initial $\text{Sr}^{87}/\text{Sr}^{86}$ of .7030 ± .0006.

Mackenzie Set I Dike Swarm:

Table X gives the analytical data for the Mackenzie Set I dike swarm. Relative to the average Rb concentration for this swarm, samples R8004 and R8005 show Rb enrichments of 5 and 11 times, respectively, and appear also to have been slightly depleted in Sr. Since these samples were obtained from narrow dikes which intrude a granite, it is likely that the anomalous Rb contents result from trace element migration.

TABLE VIII Analysis of Mackenzie Set II whole-rock samples.

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* Not included in average and omitted from isochron.

TABLE IX Analysis of Mackenzie Set IV whole-rock samples.

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* Not included in average and omitted from isochron.

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TABLE X. Analysis of Mackenzie Set I whole-rock samples.

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TABLE X. $(cont'd.)$

M.I.T. No.	Sr^{86}	sr	Rb^{87}	Rb	Sr ⁸⁷ /Sr ⁸⁶	Rb^{87}/Sr^{86}
R8005*	13.06	137.0	72.02	254.6	.8523	5.4512
\sim R8006	\blacksquare	\blacksquare	5.02	17.73	$\overline{}$	$\overline{}$
Average		182		22		

* Not included in average.

Whether this reflects a metamorphic event or is the result of continuous diffusion over a long period of time is not known.

Figure 28 shows an isochron plot for both the high and low Rb samples. Since the high Rb samples give an impossibly high initial ratio and a geologically unacceptable age, they are considered unreliable and believed not to reflect the time of emplacement. On the other hand, the low Rb samples give a low initial Sr^{87}/Sr^{86} ratio of .7028 ± .0005 and geologically acceptable age of 2692 **±** 80 m.y. This age probably reflects the time of dike solidification. The identidal age of the Matachewan dike swarm is noteworthy.

A summary of the radiometric ages determined in this study is shown in Table XI. Where applicable, other well dated rock units are shown. The cross-cutting and age relations of these rock units and the field relations as given in Table I lend credence to the conclusion that the ages determined in this study are geologically valid.

Summary and Conclusions

It has been shown that for the Matachewan dike swarm the single sample whole-rock and mineral isochron ages are concordant within the limits of analytical uncertainties, and are clearly greater than K-Ar age values for the same materials. The fact that the mineral isochron ages and wholerock ages by the Rb-Sr method are similar, suggests that there has been no significant thermal overprinting of these particular dikes since the time of their emplacement and so-

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Table XI Geologic succession a‼d summary of radiometric age values.

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lidification. Similarly the general scattering and lack of significant grouping of the lower K-Ar age values further suggests that there was no single period of thermal resetting of the K-Ar ratios. It appears that the K-Ar age values are greater in samples containing mica, and are more scattered and lower in samples in which the potassium appears to be contained in late-stage or principal phases other than mica. It is likely that the lower K-Ar ages are due to potassium being in sites that are not stable with respect to the retention of argon at normal surface temperatures.

It is found that some of the scatter of the data on the whole-rock isochron plots is the result of a minor amount of contamination from the surrounding country rocks. The degree of scatter appears to be directly related to the absolute abundance of trace elements in the surrounding environment. Because of this and the small spread in the Rb^{87}/Sr^{86} ratio, it is necessary that a large number of analyses be made on a set of dikes in order to achieve a precise dating by the Rb-Sr whole-rock isochron method. This will disclose statistically the nature of the scatter and monitor the whole-rock isochron age value. Using this method it is concluded that reasonably good age determinations can be made on diabase dike rocks of ancient age. This conclusion in based both on experimental results and the compatibility of the age values with known stratigraphic relationships.

The Rb-Sr age values and the initial Sr⁸⁷/Sr⁸⁶ ratio for the individual dike swarms are:

Acknowledgments

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SECTION II

REVISED NORTH AMERICAN POLAR WANDERING

CURVE, PRECAMBRIAN TO PRESENT¹

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Abstract

Using new additions to radiometric and paleomagnetic data a revised Precambrian apparent polar wandering curve for the North American continent is porposed. The approach in this report is to determine avarage field directions for selected age intervals which contain correctly dated rock units suitable for paleomagnetic correlation. The results suggest that the rate of apparent polar wandering varies sinusoidally with time. Comparison with African paleomagnetic results suggests that during the Precambrian the North American and African continents were not connected and may have drifted independently.

Introduction

Using available paleomagnetic and age data, Spall (1971c) has recently proposed apparent Precambrian polar wandering rates and an apparent polar wandering curve for the North American continent. Improved radiometric age measurements and confirmation of critical paleomagnetic pole positions suggest an alternative interpretation of the data. Therefore, the purpose of this report is to re-evaluate the usable data and propose a revised Precambrian North American polar wandering curve.

A discussion of the difficulties encountered in the interpretation of Precambrian pole positions is given by Spall (1971c) and is summarized below:

> (a) lack of precise geologic and/or magnetic age control;

- (b) possible rotation of rock unit after formation;
- (c) lack of rigorous laboratory demagnetization tests in early studies;
- (d) subjective nature of selecting the most meaningful pole position for a particular rock unit.

Due to these inherent difficulties and the obvious decrease in resolution with increasing age, it seems unrealistic to attempt meaningful interpretation of radiometric and paleomagnetic data over short age intervals (± 100 m.y.), unless the data show agreement within the limits of experimental uncertainty.

Since diabase dikes and other basaltic rock samples account for many of the North American pole positions, their radiometric and magnetic properties are critical. Strangway (1964) has shown that the magnetic properties of dike rocks yield stable and probably reliable results. It has also been shown that the remnant magnetization of diabase dikes is probably acquired at the time of dike emplacement and solidification, and that due to low temperature argon diffusion, K-Ar age values given in the literature are generally not representative of this time. On the other hand, the concordant nature of Rb-Sr whole-rock and mineral isochron ages and the compatibility with known stratigraphic relations strongly suggests that age values determined by the Rb-Sr method are representative of the time dike rocks acquired their stable remnant magnetism. Therefore, it is believed that Rb-Sr age values are more suitabl. for making paleomagnetic correlations (Gates 1971). Since Rb-Sr age values are generally greater than K-Ar age values and in

some cases indicate a reversal in the present geologic succession, it is obvious that the rates of polar wandering and the polar wandering curve proposed by Spall need revision.

In this report the data are grouped and averaged within age intervals that contain rock units dated by or stratigraphically correlated with Rb-Sr age determinations. Where these are not available the oldest K-Ar age value given for a particular rock unit is used as an approximate indication of the age of intrusion. Within a particular age interval an average pole position is determined from the available data. Assuming that a minimum amount of polar wandering has occurred between age intervals (McElhinny et al 1968) and that the younger end of the Precambrian curve is connected to the polar wandering curve established for the Phanerozoic, a plot of the average pole positions then defines a first approximation of the eventual North American polar wandering curve. This curve can then be modified in light of available data within a particular age interval.

Summary of New Data

Paleomagnetic

In an attempt to better define the ancient portion of the North American Precambrian polar wandering curve, the magnetic properties of the Matachewan, Nipissing and Abitibi diabase were studied. Since the results of the study are in general agreement with those of other workers, a lengthy discussion of the results and possible implications is unnecessary. Therefore, only a brief description of analytical procedures

and tabulation of experimental data are given (Table I and Figure **1).** For a complete discussion and interpretation of the magnetic results for these diabases the reader is referred to the references given in Table IV.

Radiometric

A summary of new Rb-Sr age values for some of the diabase dikes of the Canadian Shield is given in Table II. These results may serve as a foundation on which other radiometric and paleomagnetic studies can be based. A complete discussion of the radiometric age relations (Rb-Sr and K-Ar) for these dike rocks is given by Gates (1971)

Revised Precambrian Polar Wandering Curve Average Curve

Table III gives the average paleomagnetic pole positions for the selected age intervals. The individual pole positions within a particular age interval are given in Table IV. For the purpose of illustrating an approximate Phanerozoic polar wandering curve, the average pole positions for the Cambrian and Permian (Table III) have been determined from data given by Strangway (1970). Figure 2 shows a plot of the data from Tables III and IV and gives an apparent polar wandering curve drawn through the average pole positions. Except for its damped amplitude, which results from averaging, this curve is not significantly different in shape from that proposed by Spall.

Table I

Paleomagnetic Results* (stable components)

Table I (cont.)

Paleomagnetic Results* (stable components)

 $D = average declination$

 $I = average inclination$

 k = Fisher kappa (indication of the dispersion of the directions of magnetization (Irving 1964))

* All samples were orientated in the field with a Brunton compass. In the laboratory, cylinders one inch in diameter and one inch high were cored from the samples. The remnant magnetization was measured with a spinner magnetometer as described by Hood (1956). Each sample was subjected to A.C. demagnetization from 0-800 oersteds in 50-100 oersted intervals.

Table II

Sunmmary of Rb-Sr Diabase Dikes Whole-Rock Data for Some of the Canadian Shield

* For classification of Mackenzie dikes see Burwash et al (1963)

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Table III

Average Paleomagnetic Pole Positions, Early Precambrian to Present

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Table IV

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Summary of North American Precambrian Pole Positions

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Summary of North American Precambrian Pole Positions

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Precambrian pole positions and an average apparent polar wandering curve.

Key and Legend to Figure 2

- **1.** Matachewan diabase dikes
- 2. Cobalt Group sediments
- **3.** Soudan iron ores and andesites
- 4. Stillwater Complex
- 5. Nipissing diabase sill
- 6. Abitibi diabase dikes
- 7. Marathon diabase dikes
- 8. Negaunee iron ore
- 9. Gunflint Iron Formation
- 10. White River diabase dikes
- 11. Mackenzie diabase dieks
- 12. Sudbury diabase dikes
- 13. Molson diabase dikes
- 14. St. Francois Mts. (volcanics and tuffs)
- 15. Southeastern Missouri igneous rocks
- 16. Corker Island Complex
- 17. Front Range, Colorado
- 18. Arbuckle Granites, Oklahoma
- 19. Mickikeman Anorthosite, Labrador
- 20. Barron Quartzite
- 21. Sioux Quartzite
- 22. Coppermine lavas
- 23. Muskox
- 24. Belt Series (Missoula Group)
- 25. Belt Series (Grinnell Argilite)

Key and Legend to Figure 2 (cont.)

- 26. Belt Series average
- **27.** Grand Canyon Series
- 28. Keweenawan rocks
- **29.** Copper Harbor lavas
- 30. Nonesuch Shale and Freda Sandstone
- 31. Duluth gabbro
- 32. Duluth diabase
- 33. Beaver Bay basalts
- 34. Allard Lake anorthosite
- 35. Central Arizona diabase dikes
- 36. Portage Lake lava series
- 37. Pikes Peak granite
- 38. Michigan diabase dikes
- **39.** Copper Harbor basalts
- 40. Duluth gabbro complex
- 41. Mamainse Pt. lavas
- 42. Logan diabase (I)
- 43. Logan diabase (II)
- 44. Alona Bay lavas
- 45. Mellen Wisconsin gabbro
- 46. Beaver Bay Complex

Key and Legend to Figure 2 (cont.)

Interpretation of Polar Path through:

1000-1400 m.y. Interval.

According to the age relations given in Table IV, the 1000- 1400 m.y. age group shows agreement only in the younger 1000- 1200 m.y. age interval. The rock units in this interval are the Keweenawan basaltic rocks, Arizona diabase, Pikes Peak granite, Nonesuch shale, and Freda sandstone. Since it is considered unrealistic to interpret results over short age intervals, the rock units in this sequence (1000-1200 m.y.) that show general age and paleomagnetic agreement have been grouped together and interpreted as representing "normal scatter" for a 1100 m.y. pole position as shown in Figure 3. Because of the assumption that this segment of the curve is connected to the Phanerozoic polar wandering curve, the proposed southerly polar migration (DuBois 1962) at this time is likely. It is unlikely, however, that over this short span of time, the magnitude of polar wandering could have been as great as indicated by DuBois.

Disagreement in the pole positions of the Grand Canyon Series, Belt Series, Michigan dikes, Allard Lake anorthosite, and Alona Bay lavas may result from the inherent difficulties previously mentioned. It is possible, however, that in some cases the disagreement results simply from placing a particular rock unit in the wrong age interval. This is particularly true for rock units for which the apparent age is close to the low or high limits of an age interval. Although the available data do not warrant a modification of the age relations shown in Table IV, it is interesting to speculate on possible changes.

Figure **3**

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Therefore, if the radiometric and paleomagnetic data suggest the possible placing of a rock unit into another age interval, the possible modification will be discussed with the age interval affected.

1400-1800 m.y. Interval

In this interval two age groupings are indicated and suggest an easterly polar movement between 1600 m.y. and 1450 m.y. (Figure 3). The 1450 m.y. pole position is based on radiometric and paleomagnetic data from the Arbuckle Granites, southeastern Missouri igneous rocks, Corker Island Complex, St. Francois Mountain (volcanics and tuffs), Mickikeman Anorthosite, and Front Range rocks (Colorado). The 1660 m.y. pole position is based on the data from the Sudbury and Mackenzie dike swarms. An easterly direction of polar wandering during this time interval is opposite to that proposed by Spall. It is, however, believed to be correct in light of improved age values.

Although the age of the Mackenzie dikes is not precisely known, it is believed related to the intrusion of the Sudbury dike swarm dated by Rb-Sr method at 1660 m.y. The suggested correlation of these dike swarms is based on the similarities of major element composition, paleomagnetic pole positions, dike trend and possible co-magnetic nature indicated from isotopic studies.

The Grand Canyon and Belt Series pole positions which are included in the 1000-1400 m.y. age interval may border the lower limit of the 1400-1800 m.y. interval. This would explain the similarity between their pole positions and that of the rock units grouped at 1450 m.y. A possible correlation, however, requires that the upper limit of the cited radiometric ages for the Grand Canyon and Belt Series be used. An alternative suggestion (Spall 1971) is that the Grand Canyon and Belt Series pole positions are only suggestive of field direction due to limited, or lack of, laboratory demagnetization tests.

1800-2200 m.y. Interval

Polar migration during this age interval is difficult to interpret due to limited data and inconsistency in the pole positions for the Abitibi diabase. Therefore, the following interpretation is only a suggested polar path, and the discussion is given only to indicate possible areas of future research.

Recent Rb-Sr whole-rock age determinations indicate that the Nipissing and Abitibi diabase are related in time and possibly in origin (Gates 1971). This explains why the ENEN and NNE trending Abitibi dikes* give pole positions similar to that of the Nipissing diabase. Therefore, using these results, a 2150 m.y. pole position as shown in Figure 3 is suggested.

Variations in the chemical composition of the Abitibi dikes ranging from quartz to olivine tholeiite indicate the possibility of more than one period of intrusion. This may be a valid explanation for the differences in the Abitibi pole positions, but Rb-Sr whole-rock isotopic studies indicate that if multiple intrusions occurred, their duration was short (± 100 m.y.). The

^{*} For classification of Abitibi dikes see Larochelle (1966).

required rate of apparent polar migration over this short time interval may be realistic; however, an alternative possibility is suggested.

A compilation of the K-Ar values (Gates 1971) determined by the Geological Survey of Canada shows that the measured K-Ar age values for the Abitibi dikes range from about 1250 m.y. to 2050 m.y. with a significant grouping at about 1800 m.y. Because of the Rb-Sr whole-rock results, it is not likely that this age variation is the result of multiple intrusions. These results do, however, strongly suggest that thermal overprinting of most of the Abitibi dikes occurred at about 1800 m.y. Therefore, it is possible that the ambient temperature was great enough to not only out-gas the diabase, but also reset the remnant magnetism. This possibility is supported by the age and pole position obtained for the Marathon diabase dikes (Figure 2). From these assumptions and the data for the Abitibi main ENEW trending diabase dikes and the Marathon diabase dikes,-an 1800 m.y. pole position as shown in Figure 3 is suggested.

Although the available data are insufficient to propose a pole position for a time period within the 1800-2200 m.y. interval, the pole positions for the White River diabase dikes and Gunflint Iron Formation suggest an apparent polar route through the western United States as shown in Figure 3. If the apparent polar wandering curve for the $1800-2000$ m.y. age interval is approximately correct, it would suggest that future work on the age of the Molson and Michigan diabase dikes is necessary. This is particularly true for the Molson dikes which may have

been slightly metamorphosed (Fahrig et al 1965).

Assuming the maximum cited age of 1700 m.y., the pole positions for the Barron and Sioux quartzites may be consistent with the proposed 1800 m.y. pole position. These rock units were not demagnetized and precise age measurements are lacking so that the data for these quartzites are not given much weight as yet.

2200-2600 m.y. Age Interval.

General inconsistency and lack of data prevent the estimation of a pole position for this time interval. Therefore, the 2400 m.y. average pole position given in Figure 2 is considered as being suggestive only.

Greater than 2600 Age Interval.

Rb-Sr whole-rock measurements indicate that the age of the Matachewan diabase dikes is 2690 m.y. Therefore, the average of the Matachewan pole positions is chosen to be representative of the 2690 m.y. pole position, as given in Figure 3.

Discussion and Conclusions

Using the available and new data, a revised apparent Precambrian polar wandering curve is proposed, as shown in Figure 3. The rates of apparent polar wandering determined from this curve are given in Table V. A plot of these rates vs. age (Figure 4) suggests that the apparent rate of polar wandering may be governed by some natural process which varies sinusoidally with time. This observation may support the mechanism of polar wandering proposed by Goldreich and Toomre

Table V

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Apparent Rates of Polar Wandering

Figure 4

(1969). They suggest that on a geologic time scale, gradual redistribution of density inhomogeneities within the earth may produce large angular displacements of the earth's rotational axis relative to the entire mantle. It should be noted, however, that a simple harmonic expression of the polar wandering rate would indicate a uniform rate of convection and redistribution of mass within the earth. This may be an unlikely situation (Toomre, personal comrunication) and an understanding of alternative mechanisms such as the dynamic nature of the core, total crustal sliding, continental drift or some combination of the above is required before further speculation is possible.

A comparison of the North American polar wandering curve and the paleomagnetic results from Africa (Gough et al 1964, McElhinny et al 1968) suggests that during the Precambrian the North American and African continents were not connected and may have drifted independently. An illustrative example of the general inconsistencies leading to this conclusion is given by a comparison of the 2600 m.y. pole positions. The 2600 m.y. pole position for the North American continent indicated that the continent was located near the equator and rotated about 180° from its present orientation. Pole positions of similar age for the African continent, although not in interval agreement, would place Africa in the Northern hemisphere near the north pole and rotate it **900-1800** counterclockwise relative to its present orientation. None of these possible orientations results in a construction similar to that proposed by Bullard et al (1965). Depending on the amount one chooses to rotate

the African continent, the closest approximation to a Bullardtype reconstruction indicates that the western to northern coast of Africa was in some way connected or at least very close to the southern part of North America. If the western coast of Africa is connected to the southern part of North America the location of South America presents obvious difficulties.

Similar inconsistencies in the apparent rates of polar wandering, although possibly produced by rotation of a single large proto-continent, suggest that North America and Africa drifted relative to each other during the Precambrian. This would also tend to support the concept of independently drifting early continental masses, and the concept of the existence of at least two proto-continents (DuToit 1937).

This discussion is obviously speculative in nature and very dependent on the reliability of the available data and the assumed dipolar nature of the magnetic field. With the refinement of Precambrian polar wandering curves for other continents it is believed that this approach will lend itself to the investigation of early continental histroy and the relative distribution of proto-continents over the earth's surface.

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SECTION III

K, Rb, Sr, **AND** Sr ISOTOPIC EVIDENCE FOR **NEAR SURFACE CRUSTAL** CONTAMINATION OF DIABASE DIKES'

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It is shown that the K, Rb, and Sr contents of diabase dikes show lateral variations that reflect the nature of the environment intruded and therefore are not representative of the composition of the original magma. Variations in the initial Sr^{87}/Sr^{86} ratios suggest that contamination by radiogenic $Sr⁸⁷$ -enriched Sr from the surrounding syenite country rock has occurred at the time of intrusion. Possible mechanisms such as recent contamination by migrating ground waters or minor assimilation of host rock are rejected as being the cause of crustal contamination. It is believed that the observed contamination is the result of trace element leaching, possibly by late stage deuteric fluids, which does not significantly affect the major element chemistry or mineralogy of the dike rock. A model is proposed that shows that crustal contamination may be a suitable explanation to account for the observed abundances of other incompatible elements in continental diabase. It is concluded that crustal contamination, with respect to the incompatible elements (Th, Pb, U, Cs, Rb, Ba, K, Sr) does occur and that before realistic models for the magmatic evolution of continental diabase can be proposed, it is necessary to know the nature and extent of crustal contamination.

Introduction

The development of geochemical models for the magmatic evolution of continental basaltic rocks generally assumes that their compositions have not been significantly modified during transfer from depth. If this assumption is valid, then variations within a single rock type are generally attributed to crystal-liquid fractionation, degree of partial melting of the source rock, inhomogeneity of the source rock, or mantle wallrock reaction (Harris 1957, Green and Ringwood 1967).

If, on the other hand, variations in chemical composition can be shown to result, at least in part, from near surface crustal contamination, then the above models must be modified. It is the purpose of this report to show that lateral variations in the trace element content of diabase dikes, which reflect the composition of the host rock, may at least explain some of the trace element differences between continental and oceanic basalts.

If trace element exhange between these magmas and their host environment can be as great as suggested in the near surface environment, it seems likely that greater exchange and contamination may have occurred during their rise from depth. The variables used to indicate the extent and nature of near surface crustal contamination are K, Rb, Sr, Sr^{87}/Sr^{86} , and the rare-earth elements (REE).

Sampling

The trend and general location of the dike swarms studied is shown in Figure **1.** The Mackenzie and Sudbury samples were analyzed for REE only. The Matachewan dike swarm of eastern Ontario was chosen for more detailed study. These dikes strike north-south. They extend from James Bay south to the 47th parallel and from the Noranda area (Quebec) west to the Timmins area (Ontario) (Figure 1). The dike width ranges from 100-200 feet and individual dikes have been traced along strike for distances up to 100 miles.

These diabases are frequently porphyritic with phenocrysts of white or pale green plagioclase in a fine-grained, dark-green matrix. They are composed of labradorite, augite, titaniferous magnetite, granophyric intergrowths of quartz and feldspar, and may contain pigeonite. Thin sections show varying degrees of alteration which, based on isotopic evidence (Gates 1971), is believed to be due to late stage deuteric fluids and not the result of subsequent metamorphism. For detailed petrographic discussion see Prest (1952, 1957) and Lovell (1967).

This dike swarm is probably the oldest in the Superior Province. It intrudes only the Archean basement. The Rb-Sr whole-rock isochron age for these samples is 2690 ± 93 m.y. (Gates 1971). General sample localities are shown in Figure 2. Figures 3 and 4 show detailed sampling of diabase and country rock across contacts.

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Figure **3**

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Detailed sampling of diabase in greenstone country rock.

Figure 4

Analytical Techniques

Potassium determinations were made by the atomic absorption method using a double beam, AC, premix Perkin-Elmer instrument, model 303. A description of the analytical details is given by Gates (1971). Errors are indicated by replicate analyses of W-1 which give an average value of 0.524 percent K with a standard deviation of the mean of analyses of 0.004.

Rb and Sr determinations were done using a 6" radius mass spectrometer. Standard isotope dilution methods were used. A description of the method, including sample preparation, spike calibration, spiking, and method of calculation of the isotope dilution values is given by Reesman (1968). Replicate analyses of the Eimer and Amend SrCO₃ standard give an average $Sr⁸⁷/Sr⁸⁶$ ratio of 0.7082 \pm .0002 (standard deviation of the mean) normalized to a $Sr⁸⁶/Sr⁸⁸$ ratio of 0.1194, with a standard deviation error for a single determination equal to .001. This includes errors from sample heterogeneity, chemistry and instrumentation. X-ray fluorescence procedures are described in a report by Fairbairn (1966).

The best straight line fit for each isochron diagram, the intercept of each line on the Sr⁸⁷/Sr⁸⁶ axis and the attendant errors, have been obtained from the least-squares computer program set up by York (1966). Ages have been computed using Rb^{87} = 1.39 x 10^{-11} yr⁻¹.

Composite samples of 15 Sudbury dikes, 13 Matachewan dikes, and four Mackenzie dikes were analyzed by the neutron activation method as outlined by Gordon et al (1968). The rare-earth

analyses are presented as chondrite-normalized.abundance patterns in which the abscissa gives the REE as a function of increasing atomic number and the ordinate gives the amount REE in rock/amount REE in chondrites. The presentation of data in such a manner is done primarily to remove the even-odd effect of the Oddo-Harkins rule (Coryell et al 1963).

Results and Interpretations

The K, Rb, Sr, and Sr isotopic results for the Matachewan samples are given in Table I. This table indicates whether the sample was collected from a dike that intruded syenite or greenstone and gives the distance to the closest contact.

If near surface crustal contamination resulting from the migration of K, Rb, and Sr has had any significant effect on these dikes, it is assumed that the samples intruding the syenite would be most affected. This assumption is based on the average K, Rb, and Sr concentrations of six syenite samples (this study) which are 55454 ppm, 115 ppm, and 414 ppm respectively. These amounts are significantly greater than the average K, Rb, and Sr concentrations for a composite of 70 samples from the Noranda, Kirkland Lake and Michipicoten greenstone belts which are 2120 ppm, 5.9 ppm, and 175 ppm respectively (Hart et al 1970). Furthermore, the mineralogy of greenstone (metabasalts) and diabase is similar, whereas the mineralogy of syenite is very different. Therefore, if the country rock and diabase systems have not remained closed during or since the time of dike emplacement and there has been transfer of K, Rb, and Sr,

Sample	K (ppm)	Rb (ppm)	Sr (ppm)	(Sr ⁸⁷ / Sr^{86} _O	Distance to con- tact (ft)	Notes
R7523	3220	14	163	.6991	40	DB
R7524	2850	15	163	.6995	20	DB
R7537	5100	19	150	.7007	10	DB
R7538	8450	43	183	.6992	5	DB
R7539	5730	26	220	.6973	60	DB
R7541	11460	39	160	.7010	5	DB
R7543	10000	38	166	.7006	50	DB
R7547	4200	15	124	.7000	$\boldsymbol{2}$	DB
R7548	8300	33	143	.7007	50	DB
R7550	7200	28	128	.7004	5	DB
R7551	11200	44	144	.6993	50	DB
R7530		52	241	.6985	40	DS
R7531		77	308	.7002	40	DS
R7536		117	566	.7925	10	DS
R7692	14313	65	328		20	DS
R7693	11000	60	287	.7012	33	DS
R7694	9570	57	247	.7002	60	DS
R7695	11200	68	349	.7026	47	DS
R7704	11810	$80+$	382 [†]		$\mathbf{1}$	DS
R7705	3846	20^{t}	112^{\dagger}		75	DS
R7706	13400	60	380	.7036	$\mathbf{1}$	DS
R7698	63255	128^\dagger	457^{t}		250	${\tt S}$
R7699	52570	119^{\dagger}	267^{\dagger}		150	S

Table I

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K, Rb, Sr, and Sr Isotopic Experimental Results

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Table I (cont.)

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K, Rb, Sr, and Sr Isotopic Experimental Results

*DB = diabase intrudes basalt (greenstone); $DS = diabase$ intrudes syenite; S = syenite.

Determinations done by XRF.

it would be expected that the effects would be. the most pronounced in samples taken from dikes that intrude syenite.

By assuming that the dikes of the Matachewan dike swarm approximate an isochronous and comagmatic event, the absolute abundance of K, Rb, and Sr can be used as a measure of the amount of contamination. It is seen (Table I) that the average content of K (10735 ppm), Rb **(66** ppm), and Sr (320 ppm) for samples intruding syenite is significantly greater than that for samples intruding greenstone, K(7065 ppm), Rb (27 ppm) and Sr (159 ppm). This strongly suggests that near surface crustal contamination has occurred.

This data and the Sr isotopic data show large amounts of K, Rb, and Sr contamination but only slightly higher Sr^{87}/Sr^{86} ratios in dike rocks that intrude syenite. This requires the contaminating cations to have had only a short residence time in the syenite. Therefore, it is likely that contamination occurred at the time of dike emplacement which was shortly after the emplacement of the syenite.

An alternative means of contaminating is recent deposition of K, Rb, and Sr from migrating ground waters. This explanation is unlikely, however, since the amount of deposited Sr required would generate higher $Sr⁸⁷/Sr⁸⁶$ ratios than are observed.

Figures 5-7 show plots of K, Rb, and Sr vs. distance from the contact. In these figures the solid line drawn between points shows the nature of this diffusion for samples taken from a single dike. These plots show that the abundance

of K, Rb, and Sr in dike rocks that intrude syenite country rock is generally greater in samples taken close to the contact. As will be shown later, fractionation toward the center of a cooling dike would be expected to result in enrichment of K, Rb and Sr away from the contact. Therefore, it is likely that the higher abundance of K, Rb, and Sr in dike rocks that intrude syenite is the result of K, Rb, and Sr transferred from the syenite into the diabase.

It is possible that the observed variations in K, Rb, and Sr are the result of partial melting and assimilation of the syenite at the time of intrusion. This would easily explain the differences, since it would result in two different rock types which should not be expected to be similar. Although it is not possible to prove uniquely or disprove the possibility of contamination by syenite assimilation, it is believed that other processes, such as the selective leaching of mobile cations by residual fluids, or simple diffusion, are primarily responsible for the observed variations. These alternatives are favored because field and petrographic observations suggest that syenite assimilation has not been significant. in the field it is found that contacts between syenite and diabase are sharp with well defined chilled margins. Thin section examination shows that although samples intruding syenite generally are much altered and sericitized, and contain larger amounts of granophyre in thin section, they are in many cases essentially identical to samples from dikes that intrude greenstone. Therefore, it is proposed that the variations in K, Rb, and Sr

are the result of the migration of these mobile cations from the syenite into the diabase without significant change in the general chemistry or mineralogy of the dike rock.

Figure 8 clearly shows that K and Rb have been removed from the syenite near the contact and apparently redeposited in the diabase. The behavior of Sr near the contact is not clear. It is interesting to note, however, that because of the combined effects of Rb and Sr, the Rb/Sr ratio in syenite samples near the contact has been reduced. The reason that dikes show greater enrichment near the contact may simply reflect a lag in the diffusion of K, Rb, and Sr into the dike.

The relationship for dike rock intruding greenstone is not clear. Figures 5-7 indicate that the amounts of K, Rb, and Sr present are not related to the distance from the contact and, therefore, are probably uninfluenced by the greenstone. Because of the similarities in chemical composition and mineralogy of the greenstones and diabase, it might be expected that there would be little interaction between these rock types. This being the case, it would be expected that the concentrations of K, Rb, and Sr would increase towards the center of the dike as a result of fractionation.

The fractionation of dikes from the contact towards the center is in many places clearly evident. Im its most pronounced form it results in granophyric pods vhich generally occur in the central portions of dikes. In other dikes it is not as easily detected and can only be inferred by textural, relations and the general increase in grain size towards the

center of the dike. Figure 9 shows what is believed to be the result of inward fractionation of a dike during cooling. In this figure K and Rb show an enrichment towards the center of the dike of roughly 100 percent while the Sr content increases only about 10 percent. The relative amounts of enrichment are explained by K and Rb being more strongly fractionated into residual liquids than Sr. This relation is shown for the Rb/Sr ratio which increases towards the center of the dike (Figure 9).

A comparison of the Sr isotopic ratio is made by measuring the present Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} and calculating the initial $Sr⁸⁷/Sr⁸⁶$ using the known age of 2690 m.y. The results are given in Table I and shown graphically in Figure 10 which gives a plot of the initial Sr^{87}/Sr^{86} vs. distance from the contact. Figure 11 shows a histogram for the initial Sr⁸⁷/Sr⁸⁶ relative to the rock intruded. These figures clearly show that dike rocks intruding syenite have incorporated Sr which has been enriched in radiogenic $Sr⁸⁷$. Furthermore, it appears that the amount of $Sr⁸⁷$ -enriched Sr incorporated into the dike is dependent on the distance from the contact. On the other hand, the Sr isotopic composition for samples intruding greenstone shows no influence from the country rock and tends to cluster, within the limits of experimental uncertainties (.001) around the initial $Sr⁸⁷/Sr⁸⁶$ value of .7000 determined by isochron plots (Gates 1971). From these data it is concluded that the migration of Sr , enriched in radiogenic $Sr⁸⁷$, from the surrounding country rock can result in higher $Sr⁸⁷/Sr⁸⁶$

Figure 10

RE Content, Normative Rock Type and Age of Some Canadian Dikes

 \star Determined from chemical analysis given by Fahrig et al (1965).

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ratios in dike rocks despite a lack of later metamorphism (Wasserburg et al 1964). A particular enrichment in radiogenic Sr⁸⁷ may have resulted from isotopic fractionation in a process similar to that described by Pankhurst (1969).

The rare earth analyses, age and normative rock type for composite samples of the Mackenzie, Matachewan, and Sudbury dikes are given in Table II. These samples were analyzed to determine if the REE content of dike rocks have any relation to the age of the dike or its chemistry. The results are shown graphically in Figure 12, and indicate that rock chemistry and not the time of intrusion is probably responsible for the absolute abundance and pattern of REE. This conclusion is supported by the analyses of five Mesozoic diabases (Philpotts and Schnetzler 1968). Their work showed that the REE pattern for Mesozoic dikes fell within a limited range which is bounded by the upper and lower limits for the differentiation range of the Palisade Sill. This range is shown in Figure 12. It is seen that, with the exception of the Sudbury diabase, the REE content of the Precambrian dikes falls within the Palisade differentiation range. The normative classification of the Sudbury diabase as an alkaline olivine diabase shows that it is chemically different from the other diabase studied. This difference may account for its higher absolute abundance of REE (see Table IV, Figure 14). The fact that the Mesozoic and Precambrian diabase dikes have essentially the same REE abundances and patterns suggests that the source region for these rocks has not changed in this respect throughout geologic time.

Figure 12

Although there is no proof that there has been crustal contamination it is interesting to speculate on the general similarities in REE patterns for most continental rock types. Continental rocks generally show light REE enrichment regardless of rock type (i.e., basalts, granites, and sediments). The important question is whether contamination by crustal rocks similar to that shown for K, Rb, and Sr has had any influence on the observed REE patterns for crustal rocks. The answer to this question may place some restrictions on the amount of inhomogeneity in the mantle source region.

Model for Crustal Contamination

A model is proposed that attempts to account for the generally higher contents of incompatible elements in continental diabase by crustal contamination of a magma which was originally like that of ocean ridge tholeiites found today. This model implies a mantle of uniform and depleted composition and is obviously an end member approximation. Because it compares the most depleted crustal basalts (ocean ridge tholeiites) with the most enriched crustal basalts (continental), it shows the maximum amount of crustal contamination required. Any variations which take into account a more enriched source region, crystal-liquid fractionation or varying degrees of partial melting will lead to smaller degrees of crustal contamination.

A summary of the major element chemistry (taken from the literature) and the calculated norms for continental diabase dikes and sills, continental flood basalt and oceanic tholeiites

is shown in Table III. Detailed listing of the analyses used are given by Gates (1971) and may be obtained on request. Figure 13 shows the normative relations on the basalt tetrahedron (Yoder and Tilly 1962). It is immediately apparent that diabase dikes and sills are essentially identical to continental flood basalts. This is to be expected, however, since in some areas erosional dissection into prevolcanic basement has revealed a clear connection between the surface flows and diabase dikes (Turner and Verhoogen 1969). Oceanic tholeiites do show small and probably significant differences but are in general very similar to continental diabase in major element chemistry (excluding potassium).

Table IV contains the norms for some Canadian diabases, calculated from chemical analyses reported by Fahrig et al (1965). Figure 14 shows the normative relations on the basalt tetrahedron. If Figure 13 is compared with Figure 14, it is immediately apparent that the normative composition of Canadian diabase scatters uniformly around that of oceanic tholeiites. Again this clearly shows that continental diabase and oceanic tholeiites are similar in their major element chemistry.

On the other hand, the observed differences in incompatible and rare-earth elements is significant as shown in Table V. The relative amount of enrichment for these elements in continental diabase relative to oceanic tholeiites is shown by the dashed line in Figure 15.

Due to the similarities in the major element chemistry and using reasoning similar to that of Gast (1968) and Hart et

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Table III

Summary of Major Element Averages and Calculated Norms

Table IV

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Canadian Shield Diabase Norms

Table V

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Average Content of Incompatible and Rare-Earth Elements for Continental Diabase, Ocean Ridge Tholeiites and Shales

Table V (cont.)

Average Content of Incompatible and Rare-Earth Elements for Continental Diabase, Ocean Ridge Tholeiites and Shales

Diabase* = incompatible and rare-earth elements from average tholeiite plus 30% incompatible and rare-earth elements from shale.

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Figure 15

al (1970) it is unlikely that the observed variations in incompatible elements can be explained by variations in the degree of partial melting of a single source rock or subsequent fracionation. This would indicate that either the source region for continental diabase is enriched relative to that of oceanic tholeiites or that the amount of incompatible elements (Green and Ringwood 1967) present in continental diabase is partially the result of crustal contamination.

To evaluate the contamination of continental diabase it is necessary to know the abundance of incompatible elements in an average continental rock or crust. Since it is difficult to integrate the abundance of all crustal rocks, it is assumed that the content of REE (Haskin et al 1968) and the incompatible elements (Turekian and Wedepohl 1961) found in shales may represent a rough approximation of average crustal material. These values are given in Table V.

To compare the differences in incompatible and rare-earth elements a semi-log, normalized abundance pattern similar to that used for the REE is used (Figure 15). The amount of enrichment of continental diabase relative to ocean ridge tholeiites which have been contaminated by 30 percent of the incompatible and RE elements from shale is shown by the solid line. If crustal contamination of magma which was originally like ocean ridge tholeiites is actually the cause of the observed abundances in continental diabase, the solid line should be horizontal with a relative enrichment of one as shown.

It is immediately apparent that the heavy REE of continental diabase appear to be depleted relative to ocean ridge tholeiites. It is obvious that crustal contamination can only increase the relative depletion. Because of this difficulty it is unlikely that crustal contamination is a suitable explanation for the observed differences in REE.

The incompatible elements, however, show normalized values which indicate that crustal contamination is likely. These elements are known to be very mobile and it is possible that late stage fluids have selectively extracted these elements from the surrounding environment. This process has been shown to be likely for K, Rb, and Sr. Therefore, it is realistic to assume that this type of mechanism may be at least partially responsible for the high abundance of the other incompatible elements in continental diabase.

The calculations shown graphically in Figure 15 assume a 1:1 mass relation between diabase and contaminants from the shale. Since the volume of crustal rocks greatly exceeds the volume of diabase it is possible that the degree of crustal contamination is much less than 30 percent.

The purpose of this model is to show that the observed abundances of incompatible elements may be the result of crustal contamination. The model is given to illustrate that it is possible to extend the observations for K, Rb, and Sr to other incompatible elements and obtain valid and consistent results.

Conclusions

It has been shown that K, Rb, and Sr contents of diabase dikes show variations that reflect the nature of the environment intruded and, therefore, are not representative of composition of the original magma. Furthermore, the observed variations in the initial Sr^{87}/Sr^{86} ratios of these basic rocks appear to have resulted from contamination by radiogenic Sr⁸⁷enriched Sr from the surrounding country rock at the time of intrusion. Because of the large amount of contamination and only slightly higher initial $Sr⁸⁷/Sr⁸⁶$ ratios it is unlikely that recent deposition from ground waters is a valid explanation. Similarly, the field and petrographic evidence suggests that partial syenite assimilation is not a suitable explanation of the observed variations. Therefore, it is believed that the variations in K, Rb, and Sr are the result of the migration of these mobile cations from the country rock into the diabase without significant change in the general chemistry or mineralogy of the dike rock. It is believed that a possible mechanism for cation exchange is selective leaching from the surrounding country rock by late stage deuteric fluid from the intruding diabase.

Using a crustal contamination model it is seen that it is possible to extend the observations for K, Rb, and Sr to other incompatible elements and obtain valid and consistent results. These results indicate that the amounts of incompatible elements present in continental diabase may be at least partially the result of crustal contamination. Therefore, it is unlikely

that it is necessary to have higher degrees of mantle heterogeneity than required to account for the observed major element variations in oceanic basalts. These results would indicate that before realistic models for the magmatic evolution of continental diabase can be proposed it is necessary to know the nature and extent of crustal contamination.

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APPENDIX A

LOCATION AND DESCRIPTION OF SAMPLES

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FIGURE 2. Sample Locations for Abitibi Dikes (Larochelle 1966)

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FIGURE 3. Sample Locations for Sudbury Dikes

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FIGURE 4. Sample Area For Mackenzie Dikes (Burwash 1963)

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FIGURE 6 Sample Locations Mackenzie Dikes Lac de Gras Area (Leech 1966)

After R.E. FOLINSBEE

194 FIGURE 7. Sample Locations For Mackenzie

Dikes Point Lake Area (Leech 1966)

(After Fraser et al)

APPENDIX B

MAJOR ELEMENT SUMMARY

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Major Element Summary for Diabase Dikes and Sills

(8) Fleischer, M. 1969: U.S.G.S. rock standard W-1 (Mesozoic)

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Table 1 (cont.)

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Major Element Summary for Diabase Dikes and Sills

Table 2

Constituents	1	$\overline{2}$	3	4	5	66	Average	
SiO ₂	54.1	50.61	49.98	50.66	50.75	50.39	50.58	
Al_2O_3	13.65	13.58	13.74	14.28	13.80	14.80	13.9	
Fe ₂ O ₃	3.68	3.19	2.37	3.41	4.65	3.38	3.23	
FeO	8.91	10.39	11.60	8.58	6.20	8.31	9.77	
MnO	0.17	0.16	0.24	0.12	0.10	0.20	0.17	
CaO	6.95	9.45	8.21	8.60	8.90	10.93	9.08	
MgO	3.28	5.46	4.78	6.92	7.10	6.03	5.62	
Na ₂ O	3.31	2.60	2.92	2.92	2.85	2.93	2.79	
K ₂ O	1.68	0.72	1.29	0.72	0.85	0.57	0.82	
TiO ₂	2.23	1.91	2.87	1.30	1.15	0.96	1.79	

Major Element Summary for Continental Basalts

(1) Flanagan, F.J. 1969: U.S.G.S. rock standard BCR-1

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- (2) Turner, F.J., Verhoogen, J. 1960: Average Decan basalt
- (3) Turner, F.J., Verhoogen, J. 1960: Oregon basalt
- (4) Turner, F.J., Verhoogen, J. 1960: New Jersey basalt
- (5) Turner, F.J., Verhoogen, J. 1960: South African basalts
- (6) Turner, F.J., Verhoogen, J. 1960: Australian basalts

Table 3

Constituents	\mathbf{I}	$\overline{2}$	3	4	5	6		8
SiO ₂	50.01	50.53	49.9	49.78	50.25	51.81	51.13	49.34
A12O3	16.18	15.17	17.28	16.92	16.09	15.56	15.20	17.04
Fe ₂ O ₃	2.32	0.89	1.93	1.94	2.72	3.56	1.16	1.99
FeO	7.07	8.20	7.00	7.32	7.20	6.39	7.64	6.82
MnO	0.17	0.13	0.16	0.16	0.19	0.17	0.18	0.17
CaO	11.33	11.6	11.51	11.34	11.81	9.35	11.89	11.72
MqO	7.71	8.65	7.90	8.18	7.02	7.10	10.45	7.19
Na ₂ O	2.79	2.4	2.77	2.77	2.81	3.87	1.81	2.73
K ₂ O	0.22	0.24	0.16	0.16	0.20	0.11	0.19	0.16
TiO ₂	1.37	1.22	1.23	1.29	1.56	1.88	0.35	1.49

Major Element Summary for Oceanic Tholeiites

(1) Engel, A.E.J., Enge 1, C.G. 1970: Average oceanic tholeiite

- (2) Aumento, F. 1969: Mid-Atlantic Ridge basalts
- Engel, **A.E.J.,** Engel, C.G. 1964a: Mid-Atlantic Ridge basalts **(3)**
- Engel, A.E.J., Engel, (4) Mid-Atlantic Ridge basalts
- 5) Engel, A.E.J., Engel, C.G. 1964b: Basalts from East Pacific Rise
- Engel, A.E.J., Engel, (6) Indian Ocean basalts, Carlsberg Ridge
- Engel, A.E.J., Engel, (7) Indian Ocean basalts, Abyssal Hill
- Engel, A.E.J., Engel, C.G., and Havens, R.G. 1965: Average oceanic basalts **(8)**

Table 3 (cont.)

Constituents	9	10	11	12	13	14	Average
SiO ₂	49.21	48.39	50.11	47.0	48.61	49.58	49.57
$\mathrm{Al}_2\mathrm{O}_3$	15.81	19.85	15.35	15.7	16.04	15.15	16.37
Fe ₂ O ₃	2.21	1.77	2.93	4.9	1.94	2.15	2.21
FeO	7.19	5.05	5.55	5.0	6.28	8.40	6.73
MnO	0.16	0.08	0.14	$\frac{1}{2}$ and $\frac{1}{2}$ and $\frac{1}{2}$	0.15	0.18	0.17
CaO	11.14	12.32	8.94	7.5	11.52	11.04	11.11
MgO	8.53	7.11	8.24	10.3	9.50	7.82	8.13
Na ₂ O	2.71	2.37	3.55	3.0	2.72	2.74	2.80
K ₂ O	0.26	0.05	0.07	0.14	0.57	0.17	0.20
TiO ₂	1.39	0.89	1.31	1.2	1.45	1.60	1.34

Major Element Summary for Oceanic Tholeiites

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APPENDIX **C**

INCOMPATIBLE **AND** RARE-EARTH **ELEMENTS--SUMMARY**

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Average Content of Incompatible and Rare-Earth Elements in Continental Diabase

(2) Karroo diabase: (Philpotts and Schnetzler, 1968)

(3) Mackenzie diabase: (this study)

(4) Sudbury diabase; (this study)

Table 1 (cont.)

Average Content of Incompatible and Rare-Earth Elements *in* Continental Diabase

(5) Matachewan diabase (this study)

(6) Abitibi diabase (this study)

(7) Red Hill diabase, Tasmania (Philpotts and Schnetzler 1968)

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(8) W-1 (Fleischer 1969)

Table 1 (cont.)

Average Content of Incompatible and Rare-Earth Elements in Continental Diabase

(9) Ferra diabase, Antarctica (Philpotts and Schnetzler 1968)

(10) Nipissing diabase (Fairbairn et al 1953)

(11) Mackenzie dikes Set I - IV (this study)

Average Content of Incompatible and Rare-Earth Elements in Oceanic Tholeiites

Table 2

(1) Submarine basalts (Hart 1969)

(2) Oceanic tholeiites (Aumento 1969)

(3) Fresh basalts, oceanic (Melson et al 1968)

(4) Oceanic dolerite (Melson et al 1968)

* Not included in average.

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Average Content of Incompatible and Rare-Earth Elements in Oceanic Tholeiites

(5) Oceanic greenstone (Melson et al 1968)

(6) Mylonitized basalt (Melson et al 1968)

(7) Oceanic tholeiite (Engel et al 1965)

(8) Mid-Atlantic ridge and East Pacific rise (Tatsumoto 1966)

* Not included in average.

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Table 2 (cont.)

Average Content Element of Incompatible and Rare-Earth in Oceanic Tholeiites

(9) Oceanic basalts (Tatsumoto <u>et al</u> 1965)

(10) Oceanic basalts (Frey et al 1968)

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APPENDIX **D**

ANALYSIS OF E&A STANDARD

Date	Sr^{87}/Sr^{86}	Sr ⁸⁶ /Sr ⁸⁸	$(Sr^{87}/Sr^{86})N$
7/4/69	.7065	.1198	.7077
7/7/69	.7086	.1193	.7083
7/13/69	.7083	.1194	.7083
7/14/69	.7085	.1193	.7082
10/25/69	.7058	.1203	.7085
10/26/69	.7089	.1192	.7083
11/28/69	.7119	.1182	.7083
12/2/69	.7099	.1189	.7084
1/29/70	.7065	.1200	.7083
2/14/70	.7030	.1211	$.7080*$
2/28/70	.7047	.1205	.7079
3/6/70	.7013	.1216	.7078
3/21/70	.7026	.1212	.7080
4/25/70	.7029	.1211	.7079
6/16/70	.7025	.1214	.7084
7/10/70	.7020	.1215	.7082
9/10/70	.7076	.1197	$.7084*$
9/15/70	.7030	.1212	$.7083*$
9/23/70	.7020	.1215	.7082
10/15/70	.7048	.1205	.7080
11/22/70	.7048	.1205	.7080
1/20/71	.7028	.1213	.7084
		Ave.	$.7082 \pm .0002$

TABLE **1.** Analysis of A and E Standard

* Source modified

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APPENDIX E

DEVELOPMENT OF THE Ar SYSTEM

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DEVELOPMENT OF THE AR SYSTEM

Development of the present M.I.T. argon system (designated GAIL) spanned a ten month period. The system is shown schematically in Figure 1 and the following text contains a detailed description of the development and general use of the individual sections. The step by step operating procedures are given in the appendix of this report.

FURNACE SECTION

Fusion Furnace

The furnace consists of a detachtable, water-cooled pyrex bell and male ground glass ball joint. It is connected to the system by insertion of the male joint into the female joint and sealed with Apiezon Hard Wax. The dimensions and geometry of the fusion furnace are shown in Figure 2.

The crucible holder is made of recrystallized alumina. It is 40 mm long with a diameter of 30 mm. Such crucibles can be commercially purchased from Morgan Refractories in England. A molybdenum rod screwed into the base of the crucible holder provides support. The lower part of this rod is screwed into a stainless steel base resting on the bottom of the fusion furnace. The seal in the furnace is broken by heating the joint with a heating tape above **850** at which point the wax becomes pliable. By repeated heating and cooling the joint may be opened and resealed in about 20 minutes. This type of furnace design has only one major disadvantage: It is non-bakable. This feature, however, is not of great impor-

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FIGURE 2. Furnace Section

tance since the primary purpose is not to approach the minimum limits of argon analysis with this equipment. With this one handicap this furnace design is believed to be superior to any other in use. It has the following advantages:

- 1) rapid loading
- 2) easy to clean
- **3)** no glassblowing experience necessary
- 4) minimum difficulty achieving air-tight seals
- 5) efficient cooling during fusion

Fusion of the sample is accomplished by induction. The induction coil is fitted over the top of the furnace and the hose connections for water cooling made. Because the water flow under operating conditions produced enough pressure to cause the plastic tubing to slide off the inlet system, the hose connections had to be secured to the furnace with a small length of tightly twisted wire. Larger commercial screw type fasteners were tried but they became too hot during fusion and caused the plastic tubing to melt. By valving off a mercury seal stopcock connected directly to the furnace outlet, the furnace may be isolated from the remainder of the system. This feature is valuable since it greatly reduces the volume of the system, thus producing shorter pump-down times. This is particularly important during spike calibration. It also aids in precisely determining whether a leak in the furnace section is in the furnace seal or some other portion of the furnace section.

Spike Release

The spike release in included in the furnace section to insure uniform mixing during fusion. It was observed that during fusion metallic ions would be plated onto the cooler bell jar. Some of the radiogenic argon could be absorbed by this film, but spiking prior to fusion eliminates the chance of undetected radiogenic argon loss. The spike release is shown in Figure 3. It consists of a **303** ± 1 cc resevoir and a 0.1033 cc pipette. This gives a proportional release of 3.41×10^{-4} parts/release and a half-use of 2033 releases. The spike itself was obtained in 1955 from Oak Ridge and is about 90% Ar^{38} -enriched. The exact ratios were determined by repeated analyses of the spike and are

> $Ar^{38}/Ar^{40} = 12.3365$ $Ar^{36}/Ar^{38} = 0.00086$

The spike volume was checked with weighed biotite M.I.T. standard B3203. The measured volume of the first spike release of 6.31×10^{-6} cc Ar³⁸ compares well with the calculated volume of 6.303×10^{-6} cc Ar³⁸. Figure 4 shows that repeated measurements using B3203 fall very close to the calculated decay curve.

Mechanical Forepump

The forepump in the furnace section produces the initial evacuation. In this way the gas purification system is never exposed to atmospheric pressures greater than a few microns of Hg. This procedure reduces memory, background and pumpdown time.

ampoule

FIGURE 4. Spike release curve

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Hg manometer

The use of the Hg manometer in the furnace section is twofold. First, it estimates the amount of gases liberated during fusion. This was generally on the order of 0.5 - 1.0 cm Hg for Precambrian dikes. Second, it indicates when the sample is completely fused. It was observed that during fusion the manometer registers an initial rapid drop, the rate of which decreases after a certain temperature (about 900°C). Complete fusion of every sample is produced by increasing the temperature until no noticeable drop in the manometer can be observed with time.

U-Tubes

Each section of the gas train and the line leading to the mass spectrometer contains a U-tube constructed of 13mm O.D. pyrex tubing. They are 20 cm high and 5.5 cm wide. Their purpose is to freeze-out volatiles such as H_2O , CO_2 , CO and hydrocarbons.

PRIMARY GAS PURIFICATION SECTION

Charcoal Finger

The charcoal finger, as shown in Figure 5, draws the sample from the furnace section into the Primary Gas Purification Section. By cooling with liquid nitrogen and pumping, it can also extract hydrogen from the sample. The charcoal finger is directly connected to a Hg-seal stopcock so that it can be valved off after the sample is released into the purification

FIGURE 6.

section.

ChemicaZ Furnaces

The Copper-Copper Oxide Furnace is a mixture of these two components in the ratio **1:1.** As shown in Figure 6, the chemicals are held by a molybdenum crucible suspended in a vycor tube. The copper is reagent grade and can be obtained from any chemical supply house. The copper metal is that of shavings produced by drilling into a copper bar. The combined weight of the components is about five grams. In the presence of H_2 and O_2 and at 500°C the chemicals react in the coupled reaction $CuO + H_2 = Cu + H_2O$

$$
Cu + \frac{1}{2}O_2 = CuO
$$

H₂ + $\frac{1}{2}O_2 = H_2O$

The water is frozen-out in the liquid nitrogen-cooled U-tube. Formation of one to four standard cc of hydrogen may occur during normal fusion by reduction of water vapor on hot metal or sample (Hart, 1960).

The Titanium Furnace contains about 10 grams of Titanium sponge. This furnace is identical to the Copper-Copper Oxide Furnace shown in Figure 6. The titanium sponge can be obtained commercially from E.I. duPont de Nemours and Co., Delaware. By maintaining a temperature of 900°C for one hour, all non-noble gases except hydrogen are removed. The furnace is then slowly cooled to room temperature. As the temperature cools through the 450-300° range, hydrogen reacts with the titanium and is removed.

SECONDARY GAS PURIFICATION SECTION

This section was incorporated into the original design to allow extremely dirty samples a second exposure to a Titanium furnace. It was found, however, that gas purification in the primary section was adequate. The Secondary Gas Purification Section now serves as a temporary storage area.

The Titanium furnace is identical to the one used in the Primary Gas Purification Section. As stated above, it was never used, but it is, nonetheless, a potentially valuable feature. By the nature of the samples so far run (diabase volcanics, shales, biotites) the gas produced has been relatively clean. If this system is used in the future to analyze carbonates, a secondary Titanium furnace may be necessary.

Charcoal Finger

The charcoal finger is very similar to that in the Primary Gas Purification Section, the only differences being that, 1) it contains two grams of activated charcoal instead of four grams, and 2) there is no means of isolating it from the rest of the section. This is not an important feature since the sample is quite pure at this point and out-gassing of the charcoal is not a problem.

Expansion Resevoir - Storage BuZb

This device stores gas for duplicate analysis and decreases the pressure. The volume of the bulb is one liter; about three times that of the Secondary Gas Purification Section.

This resevoir is evacuated to a pressure of $2-3 \times 10^{-7}$ mm Hg and isolated from the remainder of the section. In the event of excessive pressure, the sample can expand into the bulb. This expansion generally decreases the total pressure to the point that there is no fear of burning-out the filament in the mass spectrometer. After the gas equilibrates, the resevoir can be closed and a fraction of the sample introduced into the mass spectrometer. This decreases the pressure by expansion and maintains a gas reserve for duplicate analyses. Duplicate analyses of this type only check background corrections. It is sufficient to say here that inaccurate background corrections could cause a three percent reduction in radiogenic argon due to excessive atmospheric argon correction.

Pressure Gauge

The pressure gauge used is a Veeco RG-75P ion gauge and Expanded Range Vacuum Gauge Control Panel Type RG-31X. The ion gauge is connected to the Secondary Gas Purification Section with a ground-glass joint and sealed with Apiezon Hard Wax. This type of pressure gauge is highly recommended but does have one major disadvantage: If it is turned on in the presence of the sample, isotopic fractionation occurs.

VACUUM SYSTEM

Welch Duo-Seal Model 1400 forepumps are used for the initial evacuation of the Furnace Section and as a back-up for the mercury diffusion pump. The high vacuum is obtained with

a single stage mercury diffusion pump separated from the purification system by a large cold trap.

STOPCOCKS

Corning two-way four mm mercury-seal evacuated bulb stopcocks are used throughout the system except where high vacuum was maintained during down time. At such points (spike release, inlet valve to mass spectrometer) Granville-Phillips Type C Ultra-High vacuum valves are used. Stopcocks make it impossible to bake-out the entire system, although partial baking of the surrounding glassware can be achieved with a propane torch. The initial out-gassing of the stopcocks involves evacuation of the vacuum bulb and repeated turning of the stopcock. High vacuum in a system using stopcocks may never be achieved unless they are properly out-gassed. Once the stopcock is out-gassed it leaks only if subjected to a high pressure gradient across the valve. There is virtually no leakage into the valve due to the mercury seal. As shown in Figure **1,** there is one point that is under a high pressure gradient. This is the valve used to flood the Furnace Section with N_2 and for initial evacuation. The pressure gradient into the system is greatly reduced by using the double stopcock method with evacuated area between.

When stopcocks are properly out-gassed, they require no special treatment if used in a high vacuum environment. The lowest pressure that can be achieved with a stopcock system is in the low 10⁻⁷ mm Hg range. This corresponds to the vapor pressure of most commercial high vacuum stopcock grease.

MASS SPECTROMETER

The MS-10 is a two-inch 180° velocity focusing mass spectrometer distributed by Associated Electrical Inductries, Ltd., Manchester, England. Experimentation indicated that the MS-10 required a separate vacuum system in order to decrease the background to a workable level. The vacuum pump used is a 40 liter Vacion ion pump which maintained a steady state pressure of less than 10⁻⁹ mm Hg. Prior to gas analysis the Vacion pump is valved off and the background correction determined. At masses 40 and **36** the background grows with time and the ratio of 40:36 is in no way close to that of air argon. It is assumed therefore that the presence of masses 40 and **36** in the mass spectrometer is due to volatile hydrocarbons. The growth of the background after the Vacion pump is valved off probably results from interaction of ions with the inner surfaces of the mass spectrometer. The background corrections are determined as a function of time $(i.e.$ on a recorder) and plotted forward in time to the point where the gas was introduced into the mass spectrometer. Corrections thus determined accounted for about 0.5 percent and 30 percent of the final Ar^{40} and Ar^{36} readings, respectively.

Figure 2 shows the recording method. Background readings are plotted forward in time to t_0 and sample readings are plotted back to t_0 . t_0 represents any convenient vertical line on the record chart, usually coinciding with the time the sample was introduced into the mass spectrometer. By assuming linearity in the rate of growth or decay, this me-

thod results in isochronous readings for both sample and background. The assumption of linearity is not always valid because introducing the sample into the mass spectrometer produces a greater number of ions which can interact with the inner surfaces of the mass spectrometer. To check for linearity the following test was devised. t_0 was chosen to coincide with the time the sample was let into the mass spectrometer and a final answer calculated. Then different t_0 values were chosen covering the entire time of the total run and a final answer calculated using the background corrections at these different values of t_0 . All the final answers were compared and it was found that the standard deviation was less than one percent. There were no systematic errors which were a function of the position of t_0 with respect to the introduction of the sample into the mass spectrometer.

Detailed operating instructions for the MS-10 are found in the Instruction Manual, Publication 2032-69, distributed by Associated Electrical Industries, Ltd., Instrumentation Division, Manchester, England. During calibration of the instrument the following settings gave the most sensitive and sta- ble results

ARGON ANALYTICAL DETAILS

The appendix of this report contains detailed procedures used for argon analysis.

POTASSIUM ANALYTICAL DETAILS

INSTRUMENTATION AND STANDARDS

Potassium determinations by the atomic absorption method were made on a double beam, AC, pre-mix Perkin-Elmer instrument, model 303. This method has the following advantages: minimum spectral interferences; low chemical interferences; uses a larger proportion of the atoms present than excitation methods, and generally produces a higher degree of precision than other methods (Kahn, 1966).

The standards used bracketed the concentrations from zero to 10 ppm/ml at one ppm/ml intervals. This range corresponds to operating concentrations between 10 to 100 times the instrument sensitivity, where the sensitivity is defined as the con- centration of an element in water solution which will produce an absorption of one percent. In other words, a sample containing 1 ppm/ml should ideally produce an absorption of 10 percent and a sample containing 10 ppm/ml should produce an absorption of 100 percent. Since most diabases contain between 0.2 - 2.0 percent potassium, a dilution equivalent to 0.5 grams dissolved in one liter will generally produce ppm/ ml concentrations which are bracketed by the standards. To compensate for chemical interference and matrix effects, stanwere made which approximated the composition of the samples analyzed. This was achieved by adding elements to the standard solution until its total chemistry equaled an average 0.5 gram diabase dissolved in 1000 ml of 0.2 N HC1. The added elements and their percent concentration are listed below.

Major elements added to standard solutions

Silica is not added because it evaporates as silicon tetrafluoride upon dissolution in HF acid. The Primary Solution, containing only the above elements, was carefully checked to determine any possible potassium contamination, and none was found within the detection limit of the instrument. To the above Primary Solution known quantities of potassium were added covering the concentration ranges stated earlier. Potassium analyses were always duplicated and the results averaged. The results never varied by more than three percent. The standard solution, W-l, was run with every series of potassium determinations and the results of replicate runs are shown below.

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APPENDIX F

ARGON ANALYSIS CHECK LIST

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ARGON ANALYSIS CHECK LIST

PREPARATION OF SAMPLE

Greater than 40 mesh samples are loaded into the small molybdenum crucibles. Sample weight should be such that the amount of radiogenic $Ar^{4,0}$ liberated during fusion is about 6^{-10} x 10^{-5} cc. This can be easily estimated by knowing the percentage of K and approximate age of the sample. Using sample grains greater than 40 mesh reduces possible argon loss during grinding. It has been found that grinding decreases the apparent age of a sample by as much as 15%. This decrease is probably related to the argon which is loosely held in crystal defects and crystal boundaries. (Data for this grinding experiment are included at the end of this section.) It should be noted that using a small number of large pieces has disadvantages. Most important of these is the ability to select a representative sample. The portions used for potassium and argon analysis must be identical. This is generally not difficult to achieve for fine grained rocks like basalts, diabases, rhyolites and most shales. It is exceedingly difficult for coarse grained rocks. When the latter are used it is recommended that the K/Ar analysis be done on pure mineral separates. The molybdenum crucibles may be cleaned prior to use by heating to red heat in a vacuum. It is found, however, that there is no noticeable difference in analyses if uncleaned crucibles are used.

RESEALING AND EVACUATION OF FURNACE SECTION

The furnace is resealed by plugging in the heating tape which is left wrapped around the female portion of the groundglass ball joint. The water-cooled furnace section and attached male ground-glass ball joint are lowered onto the female joint. The hard wax becomes pliable after about fifteen minutes of heating. The upper furnace section is then seated into the lower furnace section by twisting and applying a reasonable amount of downward pressure. The number of complete revolutions necessary to achieve a proper seal varies. The ease with which the upper portion can be turned usually is a good indicator. The upper portion initially turns with some difficulty. As turning continues, the resistance decreases. This is because the wax is becoming more fluid and the irregularities on the surface of the joint are being smoothed out. When the upper portion turns freely, a good seal has generally, but not always, been made. The heating tape is now unplugged and the upper portion of the furnace centered with respect to the alumina crucible. While the joint cools, the furnace is held in position by the clamp provided.

It is important that the pressure in the furnace section not be greater or less than one atmosphere. If so, rivulets form in the seal and a leak results.

When the seal has cooled and the wax becomes hard the furnace section is evacuated with the fore pump. The fore pump for this evacuation is not the same one used to maintain the diffusion pump. It is located next to the furnace section.

Access to this pump is through the double stopcocks located directly above the pump. This access is also used to flood the furnace section with N_2 prior to breaking the furnace seal. The initial pump-down is not done through the purification section. Using this procedure the purification section never sees gas pressures greater than a few microns of Hg. The importance of this can be demonstrated in the following manner. Assume that the volume of the furnace section is one liter and that air at one atmosphere has been let into this section. Since atmospheric air contains about 1% argon there is a potential contamination of 10 cc argon, most of which is $Ar^{4,0}$. The amount of radiogenic argon produced during fusion is on the order of 10^{-5} cc. This means that if one millionth of the air contamination remains after pumpdown, air argon and sample argon will be present in equal amounts. This example is somewhat exaggerated but the point should be clear, nonetheless. If, on the other hand, the initial pressure in the purification section is reduced by 106 by the fore pump, needless air contamination is eliminated. An alternative method is repeated flushing with N_2 . This reduces atmospheric argon by successive dilutions but does, however, require longer pump-down time.

The best method for evacuating the furnace section and removing atmospheric argon is as follows. Once the furnace is resealed, flood the furnace section with N_2 at 3 psi (this is the pressure maintained on the laboratory nitrogen supply so that no adjustment should be necessary). Evacuate the

furnace section with the fore pump and flood with N_2 again. Once again evacuate the furnace section. This double N_2 flushing technique should reduce the original amount of argon by 12 orders of magnitude. Following the first pump-down with the fore pump the furnace seal is checked for tightness. Valve off the pump and record the level of the Hg manometer. If the manometer level does not fall over a five minute period, generally, the furnace seal is good. It should be noted that rapidly changing atmospheric conditions can produce anomalous movements of the manometer. Leaks in the seal are usually very obvious and are indicated by a $steady$ and continuous drop. If this occurs flood the furnace section with N_2 at three atmospheres. To achieve the desired pressure of one atmosphere in the furnace section disconnect the vacuum hose from the N_2 supply. The N_2 in the furnace section will then rush out and equilibrate with atmospheric pressure. This process takes about two seconds, at which time one of the double stopcocks is valved off. At this point connect the heating tape and start again.

The final check of the seal will now be described but first a short preface is necessary. Generally, this point in the operation coincides with the termination of a routine mass spectrometer run. It is necessary that the purification section be at a pressure in the 10^{-6} range and open to the diffusion pump. Be certain that the Granville-Phillips valve to the mass spectrometer is valved off. To attain this pressure all three U-tubes in the purification system must be cooled

with liquid nitrogen. It is also advisable to set the charcoal heater at 300°C and place them over the charcoal fingers. This procedure reduces memory effects and decreases the overall pump-down time. At this point the second check of the furnace seal is made. Open the stopcock between the furnace and the purification sections. The entire gas train is now open to the diffusion pumps and, within 10 minutes, should attain a pressure in the 10^{-4} range. The pressure should drop from the 10^{-4} range down to the low 10^{-5} and possibly 10^{-6} range within another 10 minutes. If this happens one can be very confident that the furnace seal is tight. The final check is done by valving off the diffusion pump and observing the reading on the ion gauge. If no rapid pressure increase is observed the seal is tight. Slow increases in pressure can be ignored since they are related to natural outgassing processes.

The liquid nitrogen is now removed from the U-tubes. If the ion gauge is left on, an initial increase in pressure will be observed. This increase changes, and for a short period of time the pressure actually decreases. This is due to the liberation and evacuation of CO and $CO₂$ which have been frozen-out in the U-tubes. The slight decrease in pressure is followed by a very rapid increase. This is due to the melting of water and the liberation of water vapor. At this point it is unlikely that the ion gauge registers any reading. The charcoal heaters can now be turned down to 200° C and baked-out over night. (The settings of the various

heaters are listed at the end of this section along with standard techniques that should be used).

PREPARATION OF GAS TRAIN PRIOR 'TO FUSION

This part of the operation generally begins in the morning. It takes between 5-8 hours to complete the run and reload the furnace. The entire gas train is open to the diffusion pump and the charcoal heaters are at 200°C. Increase the temperature of the charcoal heaters to 300°C. Turn on the copper heater and Ti heater so that the temperatures are 500°C and 1000°C, respectively. Check to see that the inner valve of the spike release is closed. Open the outer valve. Slip the induction coil over the fusion furnace and center it with the clamp provided. It is important not to subject the furnace to unnecessary rough treatment. Connect the water cooling tubes to the stems on the Fusion Furnace. The inlet should be connected to the lower stem and the drain to the upper stem. The furnace breaks if the order is reversed. This is because cooling is insufficient due to the formation of air pockets. To secure the tubes to the stems, take short lengths of wire and twist them around the connection. Check that the drain valve is open and turn on the water inlet valve. Repeated checks of the water flow are necessary as water pressure in the Green Building varies. The rate of flow should be rapid but not so rapid that it forces the tubes off the stems.

Prior to baking the chemical furnaces, the pressure must

be reduced. This is done by placing one pint dewars on all four U-tubes using the clamps provided. The dewars are filled with liquid nitrogen. The U-tube under the table is filled with a funnel through the hole in the table. Within 10 minutes, the pressure should drop to 10⁻⁵ range. Remove the heater from the second charcoal finger. After it has cooled to room temperature cool it with liquid nitrogen. Using the second charcoal finger as an additional pump shortens the operation by about one hour. By this time the copper and Ti heaters should be operating at temperatures of 500°C and 1000° C, respectively. Raise the Cu heater over the Cu-CuO furnace and the Ti heater over the primary Ti furnace. The pressure begins to increase, and when the Ti sponge comes to a dull red heat the ion gauge will not register. This is the only procedure necessary to bake-out the chemical furnaces in the primary clean-up stage. Lower the heaters and valve-off the primary clean-up section from the diffusion pump. Move the heater to the Ti furnace in the secondary clean-up section. Raise it. The Cu heater is raised and lowered by hand, using the clamp provided. The Ti heater is raised and lowered with the lab jacks fastened to the table. When the Ti sponge in the secondary Ti furnace comes to a dull red heat lower the heater and reduce the temperature to **90⁰ C.** This procedure completes the bake-out. The pressure should decrease to less than 3×10^{-6} mm Hg within 30 minutes. This is the maximum usable pressure. Generally the pressure will fall to the middle 10^{-7} range.

SPIKING

When the pressure has dropped below 3×10^{-6} mm Hg, valve off the furnace section from the diffusion pump. Mark the level of the manometer with a felt tipped marker. Lower the heater on the first charcoal finger. The sample is now ready to spike. Close the outer valve to the pipette using 15 foot pounds on the torsion wrench. Open the inner valve of the pipette and allow the spike to equilibrate for five minutes. Close the inner valve and open the outer valve. Record the spike number on paper provided on the pipette. Equilibrate the spike in the furnace section for five minutes.

FUSION OF THE SAMPLE AND OPERATION OF THE LEPEL

Turn on the water valve located on the wall. The water pressure should be greater than 40 psi or the generator will not function. Leave the two switches on the back of the Lepel on "Cont" and turn on the switch at the rear left side of the Lepel. If nothing happens, check the water pressure or the circuit breaker located in the hall.

Come to the front of the Lepel. Check that all dials are set at zero. Check the water flow in the fusion furnace. Push the start button on the face of the Lepel. When the "Plate Ready" light comes on, push the start button on the switch located on the floor. Wait until the "Plate On" light appears and turn the "Power Control" to **65.** Turn the "Grid Control" to 20 and let the sample warm for about five minutes. The "Grid Control" can be now increased at the rate of one

unit per minute until fusion is complete. Depending on the sample, the rate of heating can be varied. Caution should be exercised as samples explode if the gases are liberated too rapidly. In all cases to date, complete fusion has been achieved by using the manometer as a guide. When the molybdenum crucible containing the sample comes to a dull red heat the manometer registers a noticeable drop corresponding to a temperature of about 900°C. Slowly increase the "Grid Control" until there is no noticeable drop in the manometer. The crucible at this point is usually cherry red to light yellow and the temperature ranges are between $1000 - 1200^{\circ}C$. At this temperature complete fusion is generally achieved. Under no conditions should the "Grid Control" be turned over 40. The sample remains at this temperature for five minutes to insure uniform mixing of spike and sample.

Turn the Lepel off in the following manner. "Grid Control" to zero; "Plate Control" to zero; both panel and floor switches off; switch at rear left of Lepel to "off" and water off. The sample then is allowed to cool for five minutes.

TRANSFERRING SAMPLE FROM SECTION TO *SECTION* AND USE OF CHARCOAL FINGERS

The charcoal fingers are loaded with activated charcoal which is held in place by quartz wool. Activated charcoal has a very large surface area and can adsorb large quantities of gas when cooled with liquid nitrogen. The charcoal fingers serve mainly to move the sample from one section to

another by cooling and warming the activated charcoal. Once the sample is adsorbed onto the charcoal, only the more volatile gases (i.e. hydrogen) can be pumped off.

When the furnace has cooled, the primary clean-up section is valved off from the diffusion pump. The charcoal finger is cooled with liquid nitrogen and the valve between the furnace section and the primary clean-up section opened. The charcoal finger adsorbs the sample. Within 15 minutes the manometer attains its original height. The furnace section is valved off and the primary clean-up section opened to the diffusion pump. At this stage the ion gauge generally does not register. It has, therefore, been standard practice to pump on the charcoal finger until the pressure is 1×10^{-4} mm Hg. At this pressure the sample is ready for purification in the primary clean-up section, the secondary clean-up section is ready for its second bake-out, and the **MS-10** filament is turned on.

SECOND BAKE-OUT OF SECONDARY CLEAN-UP SECTION

To save time, the second bake-out and purification of the sample are done concurrently. Valve-off the primary cleanup section and the storage bulb valve of the secondary cleanup section. The pressure in the secondary clean-up section should fall rapidly to the low 10^{-6} or high 10^{-7} region before the storage bulb is valved off.

Lower the liquid nitrogen on the charcoal finger in the secondary clean-up section and allow the finger to warm to

room temperature. Replace the charcoal heater, which should still be set at 300°C, and bake the charcoal finger for one hour. After one-half hour of baking remove the liquid nitrogen from the U-tube in the secondary clean-up section. When the U-tube has reached room temperature (15 minutes) replace the liquid nitrogen on the U-tube. Wait another 15 minutes to lower the charcoal heater. This point should coincide with turning off the Cu and Ti heaters.

As the charcoal finger cools, the pressure in the secondary clean-up section decreases to the low 10^{-6} region. This procedure produces the lowest pressure in the shortest amount of time.

TURNING ON THE **MS-10** FILAMENT

Before the filament is turned on, the U-tube in the mass spectrometer section is cooled with liquid nitrogen to freeze out any volatiles present. Go to the **MS-10** control panel and turn the filament switch from "off" to "on". The pressure on the Vacion control (which should be reading in the black region off scale) rises as the filament warms up and then falls off again.

GAS PURIFICATION IN PRIMARY CLEAN-UP SECTION

During the gas purification process the primary clean-up section is isolated from the other sections of the gas train. Lower the liquid nitrogen on the charcoal finger and warm to room temperature. Avoid the formation of ice on the outer

surface of the charcoal finger. The best method to prevent such formation is to warm with room temperature water held in a dewar. If ice does form, the charcoal finger becomes insulated and slows the warming process. When the finger has warmed to the point where ice does not form, clamp the dewar in position. The heaters for the chemical furnaces, which should still be at operating temperature, are raised over the furnaces and left there for one hour. During this time the Cu-CuO furnace combines H_2 and O_2 by an oxidation-reduction reaction to form water, which is frozen out in the U-tube.

At 1000°C the Ti furnace absorbs all non-noble gases except hydrogen. After the charcoal finger has warmed and equilibrated for 20 minutes, it is valved off from the remainder of the primary clean-up section. If it is not valved off; it continues to outgas and chokes the Ti sponge. After one hour turn off the heaters and allow them to cool slowly in position. This is not important for the Cu furnace, but is is easier to remove when it is cool. The Ti furnace, however, absorbs hydrogen as the temperature cools through the 500 -300°C range.

When the heaters have cooled for one-half hour, lower them and let the chemical furnaces cool to room temperature. This completes the purification process. Ideally the remaining gas should be argon and small quantities of other inert gases. The actual composition of the gas has been found to be 70% argon, 20% nitrogen and 10% oxygen.

FINAL PREPARATION OF SAMPLE BEFORE INTRODUCTION

INTO THE MS-10

Check the pressure in the secondary clean-up section to see that it is in the low 10^{-6} range. Valve off the diffusion pump and cool the charcoal finger with liquid nitrogen. Open the stopcock between the secondary and primary clean-up sections. Allow 15 minutes for the sample to be adsorbed onto the charcoal finger and valve off the primary clean-up section. Open the valve to the diffusion pump and pump for five minutes. The pressure should fall to the low 10-6 region. Valve off the diffusion pump and warm the charcoal finger to room temperature with water. The pressure at this point is quickly checked by rapidly turning the ion gauge on and then off. The ion gauge should not be left on longer than one second or isotopic fractionation of the sample occurs. The pressure reading should be less than 1×10^{-4} . If the pressure exceeds this, open the storage bulb and recheck the pressure. If the pressure is till too high, it can be lowered by two alternative methods. The first is to use the secondary Ti furnace and further clean the sample. This takes an additional two hours. The second is to close off the storage bulb and pump the remainder of the section down. Then, valving off the pump, open the storage bulb and check the pressure again. This process is repeated until the pressure is less than 1×10^{-4} and takes about five minutes. The latter method is quicker but has the disadvantage that large portions of the sample are lost. The sample is now ready to let into the mass spectrometer.

INTRODUCTION OF SAMPLE INTO MASS SPECTROMETER

The mass spectrometer is on and the sample is in the secondary clean-up section. Valve off the vacion and record the background. (Recording methods and mass spectrometer settings are contained in the main text of this report). Valve off the storage bulb and open the Granville-Phillips valve with a torsion wrench. Close the valve when the Ar^{40} reading exceeds 800 units on the chart. Proceed with recording as described in text. When the first run is complete, open the vacion and the reserve bulb valves. Wait five minutes. Repeat the above process three times. This completes the run. Place the charcoal heaters on the charcoal fingers and start again.

Heater Settings

Due to the heat of the furnaces, the wire connections are quickly oxidized. This changes their resistance. Therefore, the current to the heater is changed. Hence, it is necessary to make daily checks of the temperature settings.

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Analytical Data for Grinding Experiment using Sample R7524

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K-Ar Age (m.y.)

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BIOGRAPHICAL SKETCH

The author was born August 23, 1943 in Milwaukee, Wisconsin. He received his secondary education at Maine Township High School, Park Ridge, Illinois. After receiving a B.S. degree in geology from Michigan State University in December 1965, he was conmmissioned into the United States Environmental Science Services Administration and served on active duty for three years.

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The author was married to Susan Jo Dail, January 29, 1966 and has one daughter, Gail Luellen.