

GEOLOGICAL
SURVEY
OF
CANADA

DEPARTMENT OF MINES
AND TECHNICAL SURVEYS

This document was produced
by scanning the original publication.

Ce document est le produit d'une
numérisation par balayage
de la publication originale.

BULLETIN 85

**POTASSIUM-ARGON DATING OF ROCKS
NORTH AND SOUTH
OF THE GRENVILLE FRONT IN
THE VAL D'OR REGION, QUEBEC**

N. J. Snelling

POTASSIUM-ARGON DATING OF ROCKS
NORTH AND SOUTH OF THE
GRENVILLE FRONT IN THE
VAL D'OR REGION, QUEBEC

8,000-1968-1874

55441-0-1



GEOLOGICAL SURVEY
OF CANADA

BULLETIN 85

POTASSIUM-ARGON DATING OF
ROCKS NORTH AND SOUTH
OF THE GRENVILLE FRONT IN
THE VAL D'OR REGION, QUEBEC

By
N. J. Snelling

DEPARTMENT OF
MINES AND TECHNICAL SURVEYS
CANADA

ROGER DUHAMEL, F.R.S.C.
QUEEN'S PRINTER AND CONTROLLER OF STATIONERY
OTTAWA, 1962

(French edition available)

Price 75 cents Cat. No. M42-85

PREFACE

The nature of the "Grenville Front" is a problem that has long puzzled geologists. In some places it is a fault zone and in others a zone of transition whose nature is far from clearly understood.

In this bulletin the author presents the results of a series of age determinations that represent a new approach to the problem. The Superior rocks to the north of the front are older by more than 1,000,000,000 years than the Grenville rocks to the south, but at or close to the actual front are rocks of intermediate ages. The significance of these data is discussed by the author.

J. M. HARRISON,
Director, Geological Survey of Canada

OTTAWA, May 2, 1962

CONTENTS

	PAGE
<i>Introduction</i>	1
Acknowledgments	1
<i>General geology</i>	3
The Grenville province	3
The Superior province	4
Results of previous age determinations	6
The nature of the boundary between the Grenville and Superior provinces	6
<i>Age determinations</i>	8
Mineralogy, petrology, and location of samples	8
True and apparent ages	10
<i>Geological interpretation of age data</i>	13
Age determinations on rocks from the Superior province	13
Age determinations on rocks from the Grenville province	15
The Grenville front	15
<i>Conclusions</i>	18
<i>References</i>	19
Appendix A. Experimental methods	21
B. The radioactivity of potassium	26

Illustrations

Figure 1. Location and apparent age of samples, Val d'Or area, Quebec	2
2. Argon extraction apparatus	22

POTASSIUM-ARGON DATING OF ROCKS NORTH AND SOUTH OF THE GRENVILLE FRONT IN THE VAL D'OR REGION, QUEBEC

Abstract

The potassium-argon method of geological age measurement was applied to a study of the relative ages of micaceous minerals from igneous and metamorphic rocks of the Superior and Grenville provinces of the Canadian Shield. The metamorphic rocks on either side of the boundary between these provinces were sampled in detail, as were the various facies of the Preissac-Lacorne batholith and associated metamorphic country rocks.

Although biotites appear to lose a fraction of their radiogenic argon (about 10 per cent), the ages determined may be successfully employed to date metamorphic episodes. The following time-sequence of events in the Val d'Or region is suggested:

1. The Preissac-Lacorne batholith was emplaced at least 2,635 million years ago, based on the average age determined for muscovites from the batholith.

2. This date, 2,635 million years, may be taken as the lower limit of the age of the orogenic episode that brought about the deformation and metamorphism of the rocks of the Abitibi Group.

3. The metamorphism of the Pontiac schist and the granitization of the Ottawa Mountain granite belt occurred somewhat later but was certainly initiated over 2,000 million years ago.

4. Metamorphism of garnet gneisses of the Grenville province occurred from 850 to 1,000 million years ago. This is in substantial agreement with dates obtained on pegmatitic micas and uraninites from elsewhere in the Grenville province.

An abrupt change in age from 950 to 2,205 million years has been found between the Grenville and Superior provinces, within a maximum distance of 5 miles, corresponding to a sharply defined change in the degree of metamorphism. Biotite from a single schist outcrop within this 5-mile interval yielded an intermediate age of 1,695 million years.

Résumé

La détermination de l'âge géologique par la méthode au potassium-argon a servi à étudier les âges relatifs de minéraux micacés en provenance de roches ignées et métamorphiques des provinces Supérieure et de Grenville du bouclier canadien. Les roches métamorphiques réparties des deux côtés de la limite entre ces deux provinces ont été échantillonnées en détail, et il en a été de même des divers faciès du batholithe de Preissac-Lacorne ainsi que des roches métamorphiques encaissantes qui lui sont associées.

Bien que les biotites semblent perdre une fraction de leur argon radio-génique (environ 10 p. 100), les âges déterminés peuvent servir à établir avec succès l'âge de certains épisodes métamorphiques. Voici ce qu'on propose comme chronologie des événements dans la région de Val-d'Or:

1. Le batholithe de Preissac-Lacorne a été mis en place il y a au moins 2,635,000,000 d'années, compte tenu de l'âge moyen déterminé sur des muscovites du batholithe.

2. Cette période de 2,635,000,000 d'années peut être considérée comme la limite inférieure de l'âge du phénomène orogénique qui a provoqué la déformation et le métamorphisme des roches du groupe Abitibi.

3. Le métamorphisme du schiste de Pontiac et la granitisation de la zone granitique des montagnes ottawaiennes se sont produits à une époque un peu plus récente, mais ces phénomènes se sont sûrement amorcés il y a plus de deux milliards d'années.

4. Quant au métamorphisme des gneiss à grenat de la province de Grenville, il s'est produit il y a 850 millions à un milliard d'années. Ces âges concordent sensiblement avec les datations faites à partir de micas et uraninites pegmatitiques en provenance d'autres endroits de la province de Grenville.

On a noté un changement abrupt de l'âge, soit de 950 millions à 2,205,000,000 d'années, entre la province de Grenville et la province Supérieure, sur une distance de moins de cinq milles et cet écart correspond à un changement très marqué dans le degré de métamorphisme. La biotite d'un affleurement de schiste, le seul dans les limites de cet intervalle de cinq milles; date d'un âge intermédiaire, soit 1,695,000,000 d'années.

INTRODUCTION

This bulletin is an account of the application of the potassium-argon method of age determination to a study of the relative ages of igneous and metamorphic rocks in the Grenville and Superior provinces of the Canadian Shield. It is particularly concerned with age relations in the vicinity of the Grenville front, which divides the two provinces. As part of the study, micas from a wide variety of rocks on both sides of the Grenville front were dated. Special attention was paid to different facies of the Preissac-Lacorne batholith because the field relationships of these rocks and the metamorphic country rocks had been studied in detail and it was hoped this would facilitate interpretation of ages of micas separated from them.

When this investigation was initiated it was necessary for the writer to construct an additional vacuum line for extraction and purification of argon. Details of this apparatus and some notes on its efficacy, together with experimental procedures, are given in Appendix A. General data of the decay rates of potassium-40 and of the branching ratio of K^{40} to Ar^{40} and Ca^{40} , together with equations used in computing ages from analytical data, are summarized in Appendix B.

Acknowledgments

The investigation was made at the suggestion of R. K. Wanless to whom the writer is deeply indebted for his help and encouragement throughout the progress of the work. Special thanks are also due to K. R. Dawson who selected many of the specimens used for age determinations and who freely gave of his knowledge and experience of the geology and petrology of the area investigated; to R. J. Trail for X-ray diffraction examination of the specimens; and to Sydney Abbey who carried out the potassium determinations.

The financial assistance provided through a Post-doctorate Fellowship by the National Research Council of Canada is gratefully acknowledged.

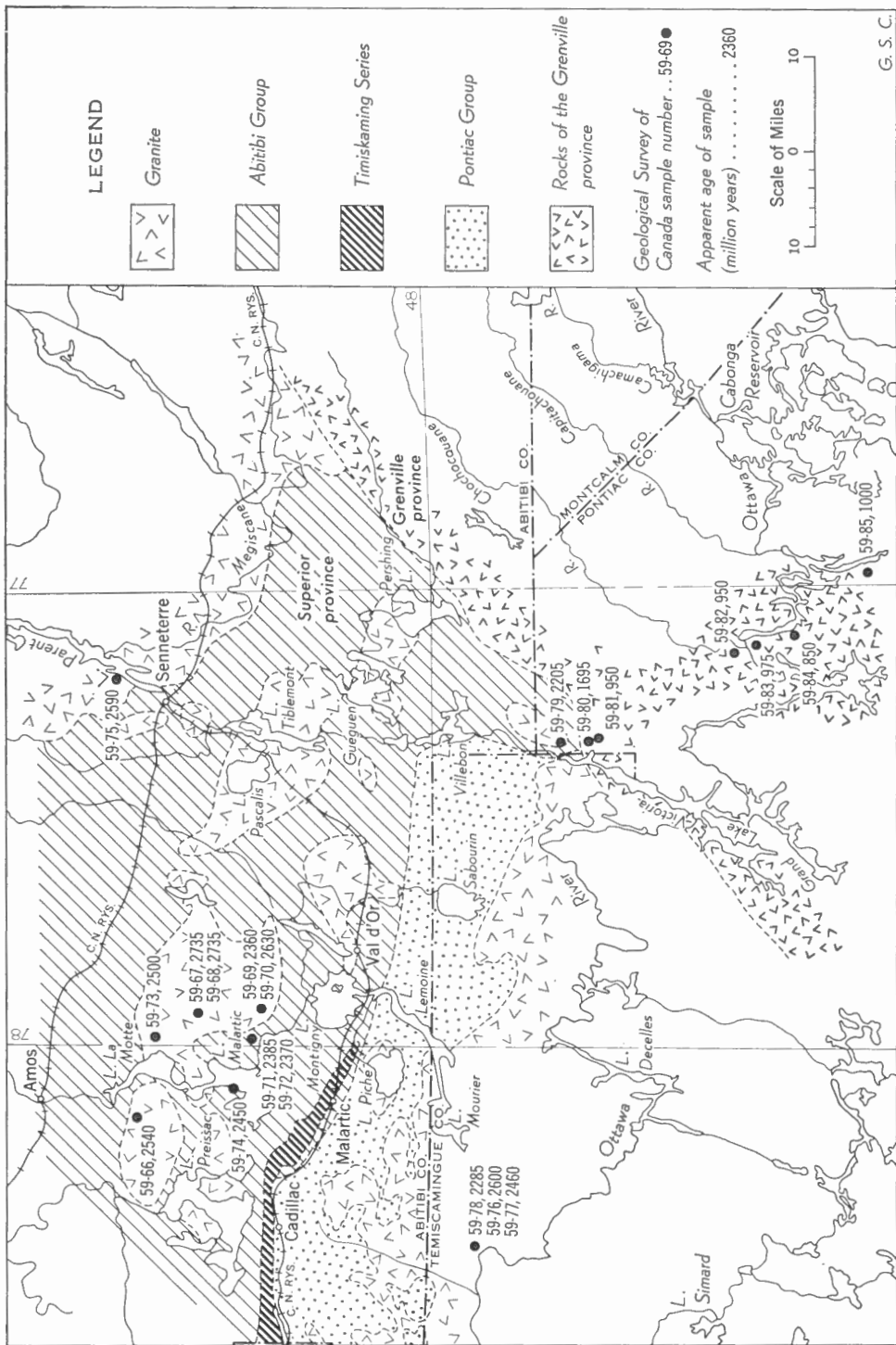


Figure 1. Location and apparent age of samples, Val d'Or area, Quebec.

GENERAL GEOLOGY

The investigated area lies athwart the boundary between the Superior and Grenville provinces in the vicinity of Grand Lake Victoria in western Quebec (*see* Fig. 1). The samples used for age determinations were collected by K. R. Dawson and the writer within the area bounded by latitudes 47° to 49°N and longitudes 77° to 78°30'W. In this region, the tectonic and plutonic characteristics of the rocks in the Grenville province are pronouncedly different from those in the Superior province. In the Grenville province the characteristics are those of the migmatitic infrastructure of a mobile belt, deformation is of a plastic kind, the grade of regional metamorphism is high, and the dominant rock types are gneisses intimately permeated and penetrated by granitic material. In contrast the rocks of the Superior province, though strongly folded, exhibit only a low grade of regional metamorphism and granitic activity is limited to the emplacement of diapiric plutons with local and well-defined thermal aureoles.

Table of Formations

Era	Province	Lithology	Ages of Metamorphism and Intrusion
Proterozoic	Grenville	Granitic intrusions and pegmatite -----intrusive contact-----	
Proterozoic or Archæan		Gneiss complex orthogneiss paragneiss limestone, quartzite -----Grenville Front-----	850, 895, 950, 975, 1000 1695
Archæan	Superior	Granitic intrusions and pegmatite Preissac-Lacorne batholith Other granitic intrusions -----intrusive contact----- Timiskaming Series -----unconformity----- Abitibi Group Pontiac Group	2540, 2735, 2735, 2310, 2630, 2370, 2500, 2450 2590, 2205, 2290, 2600 2385 2460

The Grenville Province

Age determinations were made on biotites from gneisses occurring in the Cawatose map-area (Whal and Osborne, 1950)¹ and in the Canimitti map-area (Gillies, 1952). Whal and Osborne divided the gneisses of the Cawatose area

¹Names and/or dates in parentheses are those of references cited at the end of this report.

into two main groups: those of igneous origin which are mainly biotite-granite-orthogneisses, and those of sedimentary origin which include biotite, biotite-garnet, and hornblende paragneisses. Mixed gneisses or migmatites are also abundant. The grade of regional metamorphism is high, the mineral assemblages indicating metamorphism under conditions of the sillimanite-almantine subfacies of the amphibolite facies. Gillies mapped and named the gneisses of the Canimitti area on a purely mineralogical basis and found the most common rock types to be biotite, garnet, and hypersthene-gneisses, acidic orthogneisses, and migmatites. The occurrence of hypersthene-gneisses suggests that the metamorphic grade is somewhat higher in the Canimitti area than in the Cawatose area to the south. Chemical analyses of a hypersthene-gneiss and a garnet-gneiss suggest that these rocks are metamorphosed greywackes. Metamorphosed mature sediments (crystalline limestones, quartzites, and aluminous sillimanite-schists) which are so characteristic of the type area of the Grenville Series, have not been found in the Canimitti area and are known from only one part of the Cawatose area. Their absence prompted Wahl, Osborne, and Gillies to consider the possibility that these gneisses were the highly metamorphosed correlatives of the immature metasediments and intermediate and basic meta-volcanic rocks that are characteristic of the Superior province to the north, but because of their tectonic and plutonic characteristics the gneisses were eventually assigned to the Grenville province.

Crystallization of the rocks in this part of the Grenville province probably occurred within a temperature range of 500°C to 700°C. This metamorphic episode caused crystallization under conditions of the amphibolite and granulite facies over a large area and must have been associated with an orogeny of major importance.

The Superior Province

In the area studied, the rocks of the Superior province consist mainly of basic and intermediate volcanic and immature sedimentary rocks that have been deformed and subjected to low-grade regional metamorphism. These contain many important metalliferous ore deposits (Stockwell, 1957, pp. 45-52), whose presence has undoubtedly stimulated research into the stratigraphy and structure of this region (Wilson, 1956).

Wilson has shown that the Precambrian rocks there occur in three east-west-trending belts: to the north a highly folded, widespread, conformable volcanic succession, usually called Keewatin but named by him the Abitibi Group; to the south the siliceous mica schists with some interbedded volcanic rocks of the Pontiac Group, which occur in a zone about 10 miles wide and 100 miles long; and between these a synclinorium, more than 125 miles long, of Timiskaming conglomerate and greywacke. These sedimentary and volcanic rocks have been intruded by numerous granitic bodies but only the Preissac-Lacorne batholith has been investigated in detail (Dawson, report in preparation).

Abitibi Group. The most common rocks in this group are intermediate and basic volcanic rocks, together with lesser amounts of greywacke and some conglomerates. These rocks have been deformed and subjected to regional low-grade metamorphism under temperature-pressure conditions of the muscovite-chlorite subfacies of the albite-epidote-amphibolite facies. The Preissac-Lacorne batholith intrudes members of the Abitibi Group and has an extensive thermal aureole. Biotite has crystallized in pelitic schists within this aureole and some pelitic schists also contain garnet, staurolite, and sillimanite.

Pontiac Group. Wilson (1918, pp. 93-97) described the petrography of the rocks of this group. The dominant rock type is a siliceous mica schist; there are also hornblende schists and conglomerates. These rocks have suffered regional metamorphism, the metamorphic grade being somewhat higher than that exhibited by the members of the Abitibi Group. The mineral assemblages in members of the Pontiac Group indicate metamorphic conditions of the muscovite-biotite subfacies and the almandine-amphibolite facies. The rocks of the Pontiac Group are bounded to the south by granitic gneisses, but the boundary is indefinite; a transitional zone about 2 miles wide contains an increasing proportion of irregular masses of granite, aplite, and pegmatite intruding the schists until finally only isolated blocks of schist can be found. This great belt of banded gneisses and granite, named the Ottawa Mountain granite belt by Wilson, separates the rocks of the Abitibi and Pontiac Groups and Timiskaming Series from the Grenville province between Grand Lake Victoria and Lake Timiskaming.

The Timiskaming Series. The rocks of the Timiskaming Series consist of interbedded conglomerate and greywacke: the conglomerate predominates at the base, and the greywacke in the upper sections. This series rests unconformably on members of both the Pontiac and Abitibi Groups, which Wilson suggests are stratigraphically equivalent. Thus the rocks of the Timiskaming Series are obviously stratigraphically younger than the members of the Abitibi and Pontiac Groups and, as the conglomerates of the Timiskaming Series contain rock types that can be matched both lithologically and with regard to metamorphic grade with members of these groups, the Timiskaming Series was probably deposited after the metamorphic episodes that affected the Abitibi and Pontiac Groups. The conglomerates of the Timiskaming contain boulders and pebbles of granitic rocks, and the series is also intruded by various granites. On the basis of claimed lithological similarities among these granitic pebbles and intrusions, Wilson (1956) proposed certain time relationships between granitic activity, orogeny, and the deposition and deformation of the Timiskaming Series. However, detailed knowledge of the petrology of the various granites of this region is so scanty that his correlations must be regarded as rather speculative.

The Preissac-Lacorne batholith. This batholith is one of several that occur in this part of the Superior province. Dawson (report in preparation) has shown that it is a multicomponent body but the different components are believed to

have a close genetic relationship and to have been intruded over a relatively short period of time. Brief accounts of the geology and petrology of this batholith are to be found in papers by Tremblay (1950), Dawson (1954), and Buddington (1959). As previously mentioned (p. 4), the batholith is intrusive into rocks of the Abitibi Group, and has caused extensive thermal metamorphism. Pegmatites, younger than the various components of the batholith, are numerous and are believed to be late differentiates. Some of the pegmatites are characterized by beryl, molybdenite, and spodumene, and have provided mineral deposits of economic value. These ore-bearing pegmatites occur in incomplete concentric zones around the Lacorne massive and there is a suggestion of zoning with beryl in the centre, molybdenite at the outside, and spodumene between (Tremblay, 1950).

Results of Previous Age Determinations from this Area

The few age determinations previously made are restricted to the Superior province, no determinations have been made on rocks or minerals occurring in the parts of the Grenville province under investigation. Shillibeer and Cumming (1956) reported ages¹ of 2,168 and 2,190 million years on micas from the Lacorne massive by the potassium-argon method. These results are significantly lower than those obtained from the same body during the present investigations. Unfortunately Shillibeer and Cumming give no account of their experimental methods so that discussion of the discrepancy would be rather fruitless. Wilson, Russell, and Farquhar (1956) have made age determinations on galenas occurring in this part of the Superior province and their results indicate that the galena deposits investigated were at least 2,000 million years old.

Age determinations on minerals occurring elsewhere in the Grenville province (Lowdon, 1960) have given results ranging from 800 to 1,300 million years. With one exception, all determinations so far have been made on minerals occurring in pegmatites and intrusive granites and syenites, and only set a younger limit to the geological age of the terrain in which they occur.

The Nature of the Boundary Between the Grenville and Superior Provinces

The few age determinations that are available suggest that regional metamorphism, igneous activity, and mineralization affected the Superior and Grenville provinces at very different times, and consequently much speculation has been made as to the geological relationships between the two provinces. As may be expected, most of this speculation has centred on the nature of the geological boundary. At Grand Lake Victoria it is assumed to be a fault because of the

¹These ages were calculated from the Ar^{40}/K^{40} ratios reported by Shillibeer and Cumming using the following decay constants:

$$\lambda_e = 0.585 \times 10^{-10} \text{ yr}^{-1}, \lambda_\beta = 4.715 \times 10^{-10} \text{ yr}^{-1}, \lambda / \lambda = 0.1241$$

apparent abrupt change in trends of formations in the two provinces, and because of the contrast in tectonic, metamorphic, and plutonic features on either side of the boundary (Norman, 1947). Some geologists believe this to be part of a great fault system (generally termed the Grenville front) which they believe extends from the north shore of Lake Huron northeastwards for more than 700 miles to Lake Mistassini and which forms the northwestern boundary of the Grenville province. However, by no means all of this zone has been mapped or even traversed, and other geologists maintain that the faults so far established are of local importance only and that elsewhere the boundary between these two great geological units is gradational. Deland (1956) has provided very convincing evidence that the Grenville front in the Surprise Lake area is a transitional zone about 2 miles wide, where mappable rock-units pass from a lower to a higher grade of regional metamorphism, the higher grade rocks being in the Grenville province and the lower grade rocks in the Superior province.

Thus it may be that the rocks of the Superior and Grenville provinces were formed and metamorphosed at much the same time but that subsequently the rocks in what is now the Grenville province suffered a further episode or episodes of more intense metamorphism. If this were so, the Grenville front would be the boundary of the zone in which this later metamorphism occurred.

Erratum

Last line of footnote on p. 6 should read:

$$\lambda_e = 0.585 \times 10^{-10} \text{ yr}^{-1}, \lambda_\beta = 4.715 \times 10^{-10} \text{ yr}^{-1}, \lambda_e/\lambda_\beta = 0.1241$$

AGE DETERMINATIONS

Samples for age determination were limited to those rocks containing sufficient mica to supply a measurable amount of argon. Care was taken to secure fresh rock samples free from surface alteration. Outcrops sampled were those in which the field evidence permitted the best assessment of age relative to surrounding rocks. Normally rocks were selected only if they contained fresh unchloritized biotite but some age determinations were made on chloritized biotite in the hope that the results would throw some light on the effects and significance of this common type of alteration. From one granite it was possible to separate samples of coeval biotite and muscovite; samples of coeval muscovite and lepidolite were obtained from a pegmatite.

Separation and purification of the micas was achieved by means of Franz Isodynamic separators and the usual heavy liquids. As far as possible the use of heavy liquids was kept to a minimum.

Mineralogy, Petrology, and Location of Samples

- GSC 59-66 Muscovite from granite pegmatite: Figury twp., rge. 1, lot 28; $\gamma=\beta=1.596$.¹
- GSC 59-67 Lepidolite from granite pegmatite: Lacorne twp., rge. 8, lot 21; $\gamma=\beta=1.571$.
- GSC 59-68 Muscovite from same pegmatite as GSC 59-67; $\gamma=\beta=1.572$.
- GSC 59-69 Biotite from muscovite-biotite granodiorite: Vassan twp., rge. 7, lot 17; $\gamma=\beta=1.649$. X-ray diffraction analysis indicated that material used consisted of 20% to 30% chlorite.
- GSC 59-70 Unaltered muscovite from same granodiorite as GSC 59-69; $\gamma=\beta=1.596$.
- GSC 59-71 Biotite from biotite schist, Lacorne Molybdenite Mine, Lacorne twp., rge. 1, lot 1; $\gamma=\beta=1.600$; X-ray diffraction analysis revealed no chlorite. This biotite schist is the result of thermal metamorphism, caused by granitic rocks of the Preissac-Lacorne batholith which was superimposed on low-grade sericite-chlorite-schist of Abitibi Group.
- GSC 59-72 Biotite from biotite granodiorite, close to schist of GSC 59-71; $\gamma=\beta=1.622$; X-ray diffraction examination detected no chlorite; modal analysis² of the parent rock showed: quartz 25.5, plagioclase (An₁₅) 54.6, microcline 3.6, biotite 12.4, epidote 1.7, apatite 0.3.
- GSC 59-73 Biotite from hornblende-biotite granodiorite: Lacorne twp., rge. 9, lot 1; $\gamma=\beta=1.620$; X-ray diffraction examination detected no chlorite; mode: quartz 16.4, plagioclase (An₁₅) 47.0, biotite 8.9, hornblende 8.3, glaucophane 1.1, epidote 3.0, sphene 0.4, apatite 0.3.

¹ All refractive index determinations are assumed to have a precision of ± 0.002 .

² All modal analyses were made by K. R. Dawson and are given in volume per cent.

- GSC 59-74 Unaltered biotite from biotite granodiorite: Malartic twp., rge. 9; mode: quartz 23.8, plagioclase (An_{33}) 60.7, biotite 7.7, epidote 7.4, iron oxides 0.4, hornblende 0.3.
- GSC 59-78 Biotite from biotite granodiorite: Beraud twp., Rapid 7 road, 23 miles south of Cadillac; X-ray diffraction analysis detected no chlorite; mode: quartz 23.6, microcline 10.8, plagioclase 58.6, biotite 6.3, hornblende 0.2, epidote 0.4.
- GSC 59-76 Chloritized biotite from biotite-quartz monzonite: Beraud twp., Rapid 7 road, 24 miles south of Cadillac; mode: quartz 28.9, plagioclase 28.9, microcline 37.9, chlorite 4.1, muscovite 1.9, epidote 0.1; chlorite occurs as pseudomorphs after biotite and has $\gamma=\beta=1.650$.
- GSC 59-77 Unaltered biotite from quartz-biotite-muscovite schist of Pontiac Group: Beraud twp., Rapid 7 road, 23 miles south of Cadillac; $\gamma=\beta=1.631$.
- GSC 59-79 Biotite from hornblende-biotite-quartz syenite: Freville twp., on highway 58 about half-way between mile posts 144 and 145; X-ray diffraction examination detected no chlorite; $\gamma=\beta=1.628$.
- GSC 59-75 Biotite from coarse-grained foliated biotite granodiorite: Montgay twp., rge. 1, lot 41, north of Senneterre; $\gamma=\beta=1.640$; X-ray diffraction examination detected no chlorite.
- GSC 59-84 Biotite from garnet-gneiss consisting essentially of garnet, biotite, quartz, and andesine; $\gamma=\beta=1.638$; from roadside exposure on highway 58, by mile post 112, La Verendrye Provincial Park, Cawatose map-area; X-ray diffraction examination detected no chlorite.
- GSC 59-85 Biotite from lens-shaped body of coarse granitic gneiss in hornblende gneiss; $\gamma=\beta=1.636$; X-ray diffraction examination detected no chlorite; granitic gneiss consists essentially of quartz, sodic plagioclase, and biotite with minor amounts of sillimanite replacing biotite, from road-cut on Quebec highway 58 by mile post 107, La Verendrye Provincial Park, Cawatose map-area.
- GSC 59-83 Biotite from medium-grained garnet gneiss consisting of garnet, biotite, quartz, and sodic feldspar; $\gamma=\beta=1.634$; X-ray diffraction analysis detected no chlorite; specimen collected from roadside quarry on highway 58, $1\frac{1}{2}$ miles south of the Ottawa River bridge between mile posts 116 and 117, La Verendrye Provincial Park, Canimitti map-area.
- GSC 59-82 Biotite from orthogneiss (shown as Older Granite on Cawatose map) consisting of quartz, perthite, sodic plagioclase, and biotite; $\gamma=\beta=1.650$; X-ray diffraction examination detected no chlorite; from roadside exposure $\frac{1}{2}$ mile north of mile post 120, highway 58, La Verendrye Provincial Park, Canimitti map-area.
- GSC 59-81 Biotite from garnet-biotite gneiss in road-cut at mile post 139 on highway 58; $\gamma=\beta=1.632$; X-ray diffraction analysis detected no

chlorite; because of extensive deposits of glacial sand exact position of boundary between Grenville and Superior provinces cannot be precisely located along highway 58, however highway must cross the Grenville front almost at right angles somewhere between mile posts 139 and 144. This rock is the first gneiss of 'Grenville aspect' encountered south of the locality of GSC 59-79.

GSC 59-80 Biotite from muscovite-biotite schist consisting entirely of mica, quartz, and oligoclase: $\gamma=\beta=1.638$; X-ray diffraction examination detected no chlorite; from road-side exposure about 100 yards south of mile post 142 on highway 58. This is the only known exposure along highway 58 between localities GSC 59-79 in the Superior province and GSC 59-81 in the Grenville province.

True and Apparent Ages

Table I contains all the age determinations carried out during this investigation. It is divided into three parts: (A) ages from the Preissac-Lacorne batholith, (B) ages from other rocks in the Superior province, and (C) ages from rocks in the Grenville province. It should be emphasized that these are apparent ages that will be equal to the true age of the mineral only if (1) the mineral was formed in an interval of time short compared with its age, (2) there have been no preferential gains or losses of either daughter or parent element in the mineral by processes other than radioactive decay of the parent, (3) proper corrections can be made for the amount of daughter product (if any) incorporated in the mineral at the time of its formation, and (4) the decay constant of the parent element is accurately known.

When considering the relation between the true and apparent ages of a mineral or rock some form of control and reference is obviously necessary, and normally age determinations are made on several minerals by different methods. However, in the present study the only available control lay in the thorough and systematic field and laboratory investigation of the Preissac-Lacorne batholith which had established a relative sequence of events, including deformation, multiple intrusion, and metamorphism. Examination of the apparent ages in Table I(A) immediately reveals an appreciable spread of values that cannot be attributed entirely to experimental errors. Although the batholith is composed of several bodies, it is unlikely that the spread is due to intrusions occurring at intervals over so long a period of time, partly because of its magnitude—nearly 500 million years—and partly because the pegmatites, which are undoubtedly the youngest rocks of the complex, have the greatest apparent ages. As we are dealing with micas that crystallized from magma, it is safe to assume that they were formed in a short interval of time compared with the age of the parent rock and it is unlikely that any argon was incorporated in the micas during crystallization for the argon atom is relatively large and is electrostatically neutral, and argon is a gas. The most likely explanation is that some of the micas have suffered slight but

Table I
Age Determinations of Micas

Specimen No.	Rock type	Mineral	% K	% Radiogenic argon	ml Radiogenic Ar ⁴⁰ /gm mica at S.T.P. × 10 ⁻³	Apparent age (million yrs.)	Averages as indicated
A. Preissac-Lacorne batholith, Superior province							
GSC 59-66	Pegmatite	Muscovite	8.06	86	1.74	2540	
59-67	Pegmatite	Lepidolite	6.87	100	1.70	2735	
59-68	Pegmatite	Muscovite	7.30	96	1.80	2735	
59-69	'Granite'	Biotite	5.78	94	1.00	2240	
59-69	'Granite'	Biotite	5.78	93	1.03	2285	2310
59-69	'Granite'	Biotite	5.78	91	1.13	2405	
59-70	'Granite'	Muscovite	7.87	96	1.81	2610	2630
59-70	'Granite'	Muscovite	7.87	95	1.84	2650	
59-71	Schist	Biotite	5.55	97	1.13	2455	2385
59-71	Schist	Biotite	5.55	91	1.01	2310	
59-72	'Granite'	Biotite	6.78	86	1.29	2370	
59-73	'Granite'	Biotite	6.72	98	1.40	2500	
59-74	'Granite'	Biotite	6.73	88	1.36	2450	
B. Other areas, Superior province							
GSC 59-78	'Granite'	Biotite	7.25	100	1.30	2290	2285
59-78	'Granite'	Biotite	7.25	94	1.29	2285	
59-76	'Granite'	Chloritized biotite	1.67	72	0.382	2600	
59-77	Pontiac schist	Biotite	7.09	100	1.44	2460	
59-79	'Granite'	Biotite	7.19	92	1.21	2205	
59-75	Granitic gneiss	Biotite	7.28	95	1.63	2590	
C. Grenville province							
GSC 59-84	Gneiss	Biotite	7.89	73	0.341	850	
59-85	Gneiss	Biotite	7.81	94	0.413	1000	
59-83	Gneiss	Biotite	8.00	92	0.425	975	
59-82	Gneiss	Biotite	7.32	80	0.337	895	
59-81	Gneiss	Biotite	7.59	68	0.409	950	
59-80	Schist	Biotite	7.39	93	0.804	1680	1695
59-80	Schist	Biotite	7.39	97	0.823	1705	

varied loss of argon. This would satisfactorily explain the difference of more than 300 million years between the apparent ages of muscovite GSC 59-70 (2,630 m.y.) and of biotite GSC 59-69 (2,310 m.y.), micas that occur as primary minerals in the same rock and undoubtedly crystallized at the same time. Aldrich and Wetherill (1958) have also concluded that K-Ar ages are sometimes affected by argon leakage from having compared K-Ar and Rb-Sr ages of the same mica and U-Pb ages of cogenetic uranium-bearing minerals such as zircon and uraninite. Fortunately, the amount of argon loss appears to be small and it is believed that the apparent ages of micas are rarely lower than their true ages by more than 10 per cent. The highest ages from the Preissac-Lacorne batholith are given by white micas, and the literature reveals that muscovites and lepidolites tend to give higher ages than cogenetic biotites. This can probably be correlated in part, with the greater resistance of the white micas to secondary alteration caused by hydrothermal solutions and weathering—processes that readily cause the alteration of biotite to chlorite—and in part, with the fact that the stability of a biotite is dependent not only on hydrostatic pressure and temperature but also on the partial pressure of oxygen. Slight, post-crystallization variations in the partial pressure of oxygen will induce appropriate changes in the composition of a biotite during the resultant recrystallization and any argon present could well be lost. Unfortunately such recrystallization, unlike chloritization, may not be detected during petrographic and mineralogical examination (Wones and Eugster, 1959, p. 132).

In a metamorphic rock the true and apparent ages of a mica may differ considerably for in this rock we have to contend not only with a possible slight loss of argon but also with the chance that some argon was incorporated in the mica as it grew, a possibility that is enhanced because many of the micas present in metamorphic rocks have probably crystallized from a clay mineral nucleus that may well have been potassic and hence have contained some argon. In simple thermal metamorphism it should be possible to tell whether or not argon generated before metamorphism is trapped or retained by the newly formed mica for it is generally possible to obtain an age for the igneous rock that caused the thermal metamorphism. Unfortunately this is not possible in regionally metamorphosed rocks and when, as in the present rock, no other method of age determination is available it is necessary to make as many determinations as possible on micas from different rock types, from different metamorphic grades, and from as large an area as possible. If the apparent ages so determined are in reasonable agreement, then it seems safe to assume that this is the age of metamorphism. Discordance among the apparent ages would suggest either that some argon was retained or incorporated during metamorphism or that the rocks had been subjected to more than one metamorphic episode.

During the present investigation age determinations were made on biotite from a thermally metamorphosed rock adjacent to the Preissac-Lacorne batholith and on biotites from regionally metamorphosed gneisses of the Grenville province. The results are discussed in the following section.

GEOLOGICAL INTERPRETATION OF AGE DATA

Age Determinations on Rocks from the Superior Province

Most of the determinations from the Superior province have been made on rocks from the Preissac-Lacorne batholith and, as indicated above, the results suggest that the biotites in particular have lost some of their radiogenic argon. It is suggested that, pending age determinations by other methods, an age of 2,635 million years be assigned to the Preissac-Lacorne batholith. This is the average of the determinations made on muscovites and may well have to be revised (probably slightly upwards) in the light of future research. The remaining age determinations are all within 15 per cent of this suggested age. It is obvious that possible differences in age of the components and facies of the batholith are masked by such factors as the inherent limits of accuracy of the potassium-argon method and by variations in the argon retentivity of the individual micas.

It is of interest to note that the apparent age of biotite (GSC 59-71: 2,385 m.y.) from a mica schist is very close to that of biotite (GSC 59-72; 2,370 m.y.) from an adjacent body of biotite granodiorite. Although both determinations are lower than the suggested age of the batholith, they at least suggest that biotite (GSC 59-71), which crystallized as the result of thermal metamorphism, did not incorporate or retain any significant amount of radiogenic argon.

As there can be no doubt that the rocks of the Abitibi Group were folded and subjected to low-grade regional metamorphism before the intrusion of the Preissac-Lacorne batholith, the proposed age of the batholith also sets a younger limit to the orogenic episode (if such it was) that caused the deformation and metamorphism of the rocks of the Abitibi Group.

Age determinations on other rocks within the Superior province are given in part B of Table I; the determinations from the Pontiac mica schist and intruding granites are considered first. The age determinations were made on biotites from rocks occurring within the transitional zone between the ungranitized Pontiac mica schists and the granites of the Ottawa Mountain granite belt, in the hope that the results would indicate the age of metamorphism and granitization. Excluding, for the moment, consideration of GSC 59-76 (2,600 m.y.), which is a chloritized biotite, the apparent ages indicate that regional metamorphism of the Pontiac schist (GSC 59-77) occurred 2,460 million years ago and intrusion by granitic rocks (GSC 59-78) about 2,285 million years ago. The determination of the relation between these apparent ages and the true ages however is impossible when only two determinations by the same method are available. Most geologists would probably maintain, on the basis of the field relationships and by analogy with other metamorphosed terrains, that metamorphism and granitic intrusion occurred in this area at much the same time making it necessary to suggest either that the result for GSC 59-78 is too low because of argon leakage or that the result for GSC 59-77 is too high because some argon was incorporated during metamorphic

crystallization. With only two determinations one cannot decide in favour of either of the possible interpretations. The results do suggest, though only faintly, that metamorphism of the Pontiac schists and granitization in the Ottawa Mountain granite belt occurred a little later than the deformation and metamorphism that affected the rocks of the Abitibi Group (the Abitibi metamorphism). Thus the apparent age of GSC 59-78 is a little more than 13 per cent lower than the suggested age of the Preissac-Lacorne batholith and that age may itself be lower than the true age of the batholith rather than higher. The batholith was intruded after deformation and metamorphism of the Abitibi Group in contrast to the granites in the Pontiac Group which were probably intruded contemporaneously with metamorphism. Thus the apparent age of the biotite GSC 59-78 is probably much more than 13 per cent lower than the age of the Abitibi metamorphism. This is an extreme and, because of the fresh unchloritized nature of the biotite GSC 59-78, rather an unlikely discrepancy. However, more age determinations are necessary from these rocks before any definite pronouncements may be made. If there was any difference in time between the metamorphism that affected the Abitibi Group and that which affected the Pontiac Group it was probably only slight—perhaps of the order of 100 million years or less. More important is the definite indication provided by these two determinations that the metamorphism of the Pontiac Group and the formation of the Ottawa Mountain granite belt occurred, or perhaps one should say was initiated, more than 2,000 million years ago..

The two remaining age determinations from the Superior province further confirm the great antiquity of the rocks in this region. Biotite GSC 59-79 (2,205 m.y.) was separated from a quartz syenite that occurs as a stock-like body at the northern end of Grand Lake Victoria (Tiphane and Dawson, 1950). The stock intrudes members of the Abitibi Group but is within 5 miles of garnet gneisses of the Grenville province. It is highly probable that this quartz syenite is younger than the granitic rocks of the Preissac-Lacorne batholith for even if this apparent age is due to the loss of 10 per cent of argon from the biotite its true age would still be only 2,450 million years. Biotite GSC 59-75 (2,590 m.y.) was separated from a foliated granite occurring in an extensive and, geologically, a virtually unknown area of foliated gneiss and granite that occurs along the northeastern margin of the Abitibi Group. The relations of the rocks of the Abitibi Group to these granites and gneisses are unknown, but the apparent age of GSC 59-75 suggests that it may well have been a product of the same orogenic episode that deformed the Abitibi Group and saw the emplacement of the Preissac-Lacorne batholith.

Consideration of the apparent age obtained for biotite GSC 59-76 (2,600 m.y.) was excluded from the above discussion because this specimen has been almost completely altered to chlorite. This chloritized biotite came from a granite occurring in the same general area as GSC 59-78 and 59-77 and if it is assumed (and it is surely not an unreasonable assumption) that the granites in this restricted

area are all of much the same age, then the apparent age of GSC 59-76 would indicate that in this case at least chloritization has not caused any significant preferential loss of either argon or potassium.

Age Determinations on Rocks from the Grenville Province

Age determinations on biotites from rocks occurring in the Grenville province are listed in part C of Table I. Determinations GSC 59-84 and 59-85 are from the Cawatose map-area and GSC 59-83 and 59-82 are from the Canimitti map-area. Also included is the result of an age determination on a biotite GSC 59-80 separated from a schistose rock occurring as an isolated outcrop in the vicinity of the boundary between Grenville and Superior provinces. The four micas from the Grenville province were separated from various gneisses that possibly differed slightly in metamorphic grade, and were collected over a distance of about 30 miles. Their apparent ages fall within a narrow range of values suggesting that the last major metamorphism suffered by these rocks occurred between 850 and 1,000 million years ago. The spread in the apparent ages can best be explained as being the result of experimental errors and slight variable amounts of preferential argon leakage. It is very satisfying to note the agreement between the ages obtained on metamorphic biotites and those obtained on pegmatite micas and uraninite occurring in the southwestern part of the Grenville province (Lowdon, 1960). Although ages determined on pegmatitic minerals can only set a younger limit to the geological age of any particular terrain it has been usual to assume that the emplacement of such pegmatites occurred during the final stages of the orogeny responsible for the regional metamorphism. These results undoubtedly help to substantiate the validity of this assumption as a working hypothesis. Quirke, *et al.* (1960) have reported a potassium-argon age determination on a biotite from a paragneiss occurring in the Grenville province at Lake Kawwachigomau in the vicinity of Lake Mistassini, some 400 miles northeast of the Val d'Or region. Their study yielded a result of 1,000 million years. Thus there can be no doubt that the regional metamorphism that caused the crystallization of rocks under the conditions of the amphibolite and granulite facies in the Grenville province affected a huge area of the earth's surface and was probably associated with an orogeny of major importance.

The Grenville Front

The results of this study have confirmed that in the Grand Lake Victoria area an abrupt change in age across the Grenville front corresponds to a sharply defined change in degree of metamorphism. Sample GSC 59-81 gives an age of 950 million years and is within the equivalent of 5 miles, measured normal to the front, of GSC 59-79 whose age is 2,205 million years. Sample GSC 59-80, which was taken from the only intervening outcrop along the road, yielded an intermediate age of 1,695 million years. The nature of the Grenville front has already been briefly

discussed and is now considered further in the light of the age determinations given in this report together with those recently published by Quirke, *et al.*

As stated, Quirke, *et al.* report a potassium-argon age of 1,000 million years from the metamorphic complex within the Grenville province southeast of Lake Mistassini. The Grenville front in this region is undoubtedly a fault zone (Norman, 1940) and separates the 1,000 million-year-old metamorphic complex from the less highly metamorphosed Keewatin-type sedimentary and volcanic rocks of the Sam Gunner Group, which are in turn intruded by the Takwa intrusive complex of granitic rocks and overlain, together with the Takwa granites, by the relatively unmetamorphosed sediments of the Mistassini Group. A biotite from a granitic gneiss of the Takwa complex has given a potassium-argon age of 1,605 million years and a rubidium-strontium age of 1,670 million years. In interpreting their results, Quirke and his colleagues seem loath to accept the age of the Takwa complex as being of primary origin and instead put forward two suggestions. They propose that the rocks of the Sam Gunner Group and the Takwa complex were formed more than 1,600 million years ago and that their apparent age is possibly due (1) to an orogeny that occurred about 1,600 million years ago and caused the complete loss of radiogenic argon and strontium from the biotite of the Takwa granite-gneiss, and (2) to partial loss of radiogenic argon and strontium from this biotite due to the orogeny that recrystallized the rocks of the Grenville province 1,000 million years ago. Such explanations are obviously applicable to biotite GSC 59-80 and one could suggest that this mineral originally crystallized over 2,000 million years ago, perhaps during the metamorphism of the rocks of the Abitibi and Pontiac Groups. Later, rocks in the vicinity of what is now the Grenville front were involved in the 1,000 million-year-old orogeny of the Grenville province and suffered partial loss of radiogenic argon to produce an age intermediate between those of the Superior province and those characteristic of the Grenville province. These speculations do not shed much light on the nature of the Grenville front itself. If it is accepted as a major fault formed soon after the 1,000 million-year-old metamorphism, then it is possible that during the fault movements any adjacent older rocks would be heated up and perhaps partly recrystallized with the partial preferential loss of any radiogenic argon they may have contained. If the front is looked upon as a metamorphic isograd marking the limits of the effects of a 1,000 million-year-old metamorphism superimposed on older rocks, then one would expect ages intermediate between the original age and the 1,000 million-year-old age to be found along the front. However, the possibility cannot be overlooked that there is present in this part of the Canadian Shield a 1,600 to 1,700 million-year-old orogenic belt. Ages of this order of magnitude have been reported by Goldich, *et al.* (1957) from the Thompson Formation of Minnesota and from other formations in northern Wisconsin and in Michigan; somewhat dubious ages of this order are also known from the Sudbury complex. In Quebec we have the 1,695 million-year age obtained during this investigation, the 1,600 million-year age from the Takwa intrusive complex, a

1,580 million-year-old date from the gneisses west of Wabush Lake (Hurley, *et al.*, 1958), and a 1,400 million-year date from the Menihek slate (Quirke, *et al.*, 1960). If an orogenic belt of this order of age does exist it must be very narrow in the Grand Lake Victoria region, most of it may perhaps have been faulted out. Further age determination studies northwest of the Grenville front in eastern Quebec will be necessary to determine its existence and magnitude in other parts of Quebec. The Grenville front itself remains one of the greatest problems in Canadian geology and its solution must await additional field studies supplemented by the radioactive dating of as many samples as possible by all the available methods.

CONCLUSIONS

1. This research has been concerned with the extraction and determination of radiogenic argon from micas and the application of the geological ages so determined to a study of a specific geological problem.

2. The potassium-argon method was satisfactorily applied to various igneous rocks. Age determinations on biotites from metamorphic rocks indicate that this method can be used to date metamorphic episodes.

3. The results suggest that many micas, and in particular biotites, suffer slight loss of their radiogenic argon during geological time with the result that their apparent ages are slightly lower than their true ages.

4. Age determinations on micas from igneous and metamorphic rocks of the Superior province indicate that this geological unit was formed more than 2,000 million years ago. Age determinations in the Grenville province indicate that a major episode of regional metamorphism, granitization, and orogeny occurred about 1,000 million years ago.

5. As defined by age data, the contact between these two provinces in the Grand Lake Victoria region is gradational and is less than 5 miles wide.

REFERENCES

- Abbey, Sydney, and Maxwell, J. A.
1960: Determination of potassium in micas; *Chemistry in Canada*, September, p. 37.
- Aldrich, L. T.
1956: Measurements of radioactive ages of rocks; *Science*, 123, pp. 871-875.
- Aldrich, L. T., and Nier, A. O.
1948: Argon 40 in potassium minerals; *Phys. Rev.*, 74, p. 876.
- Aldrich, L. T., and Wetherill, G. W.
1958: Geochronology by radioactive decay; *Ann. Rev. Nuclear Sci.*, 8, pp. 257-298.
Annual Reviews Inc., Palo Alto, Calif.
- Birch, Francis
1951: Recent work on the radioactivity of potassium; *J. Geophys. Res.*, 56, pp. 107-126.
- Buddington, A. F.
1959: Granite emplacement with special reference to North America; *Bull. Geol. Soc. Amer.*, 70, pp. 671-747.
- Campbell, N. R., and Wood, A.
1906: The radioactivity of the alkali metals; *Proc. Cambridge Phil. Soc.*, 14, pp. 15-21.
- Carr, D. R., and Kulp, J. L.
1957: Potassium-argon method of geochronometry; *Bull. Geol. Soc. Amer.*, 68, pp. 763-784.
- Dawson, K. R.
1954: Structural features of the Preissac-Lacorne Batholith, Abitibi County, Quebec; *Geol. Surv., Canada*, Paper 53-4.
- Deland, A. N.
1956: The boundary between the Timiskaming and Grenville Sub-provinces in the Surprise Lake Area, Quebec; *Geol. Assoc. Can. Proc.*, 8, pp. 127-141.
- Evans, R. D.
1940: Introduction to atomic nucleus; *Mass. Inst. Technol.*, class notes.
- Fermi, E.
1934: *Zeit. für Physik*, 88, pp. 161-177.
- Gillies, N. B.
1952: Canimitti River Area, Pontiac County; *Que. Dept. Mines*, Geol. Rept. 52.
- Goldich, S. S., Baadsgaard, H., and Nier, A. O.
1957: Investigations in A⁴⁰/K⁴⁰ Dating; *Trans. Am. Geophys. Union*, 38, pp. 547-551.
- Hurley, P.M., et al.
1957: Variations in isotopic abundances of Strontium, Calcium, and Argon, and related topics; *U.S. Atomic Energy Comm.*, NYO-3937, Fourth Ann. Prog. Rept., 1956-1957. Contract AT (30-1)-1381.
1958: Variations in the isotopic abundances of Strontium, Calcium, and Argon, and related topics; *U.S. Atomic Energy Comm.*, NYO-3938, Fifth Ann. Prog. Rept., 1957-1958. Contract AT (30-1)-1381.
- Inghram, M. G.
1954: Stable isotope dilution analysis; *Ann. Rev. Nuclear Science*, 4, p. 81. Annual Reviews Inc., Palo Alto, Calif.
- Lipson, Joseph
1958: Potassium-argon dating of sedimentary rocks; *Bull. Geol. Soc. Amer.*, 69, pp. 137-150.
- Lowdon, J. A., et al.
1960: Age determinations by the Geological Survey of Canada, Report I, Isotopic Ages; Part II by S. C. Robinson; *Geol. Surv., Canada*, Paper 60-17.
- Norman, G. W. H.
1940: Thrust faulting of Grenville Gneisses northwestward against the Mistassini Series of Mistassini Lake, Quebec; *J. Geol.*, 48, pp. 119-128.
1947: Vauquelin, Pershing, and Haig Townships, Abitibi County, Quebec; *Geol. Surv., Canada*, Paper 47-12.

- Quirke, T. T., Goldich, S. S., and Krueger, H. W.
1960: Composition and age of the Temiscamie iron-formation, Mistassini Territory, Quebec, Canada; *Econ. Geol.*, 55, pp. 311-326.
- Shillibeer, H. A., and Cumming, G. L.
1956: The bearing of age determinations on the relation between the Keewatin and Grenville Provinces. The Grenville Problem; *Roy. Soc. Can.*, Spec. Publ. No. I.
- Smythe, W. R., and Hemmendinger, A.
1937: The radioactive isotope of potassium; *Phys. Rev.*, 51, pp. 178-182.
- Stockwell, C. H.
1957: (Editor) Geology and Economic Minerals of Canada; *Geol. Surv., Canada*, Econ. Geol. Ser. 1 (Fourth Ed.).
- Thompson, F. C., and Rowlands, S.
1943: Dual Decay of Potassium; *Nature*, 152, p. 103.
- Tilton, G. R., and Davis, G. L.
1959: Geochronology; *Researches in Geochemistry*, New York, John Wiley and Sons.
- Tiphane, M., and Dawson, K. R.
1950: Villebon Map-sheet, Quebec; *Geol. Surv., Canada*, Map 998A.
- Tremblay, L. P.
1950: Fiedmont Map-area, Abitibi County, Quebec; *Geol. Surv., Canada*, Mem. 253.
- Wahl, W. G., and Osborne, F. F.
1950: Cawatose Map-area, Pontiac County; *Que. Dept. Mines*, Geol. Rept. 44.
- Wanless, R. K., and Thode, H. G.
1953: A mass spectrometer for high precision isotope ratio determinations; *J. Sci. Inst.*, 30, pp. 395-398.
- Wassberg, G. J., and Hayden, R. J.
1955: A⁴⁰-K⁴⁰ Dating; *Geochim. et Cosmochim. Acta*, 7, pp. 51-60.
- Wilson, J. T., Russell, R. D., and Farquhar, R. M.
1956: Radioactivity and age of minerals; *Encyclopedia of Physics*, vol. 47, Ed. S. Flugge, Geophysics I. Spinger-Verlag, Berlin, Göttingen, and Heidelberg.
- Wilson, M. E.
1918: Timiskaming County, Quebec; *Geol. Surv., Canada*, Mem. 103.
1956: Early Precambrian rocks of the Timiskaming Region, Quebec and Ontario, Canada; *Bull. Geol. Soc. Amer.*, 67, pp. 1397-1430.
- Wones, D. R., and Eugster, H. P.
1959: Biotites on the join Phlogopite (KMg₃AlSi₃O₁₀(OH)₂)-Annite (KFe₃AlSi₃O₁₀(OH)₂); *Carnegie Inst. Wash.*, Ann. Rept. Director Geophys. Lab., 1958-1959.

Appendix A

EXPERIMENTAL METHODS

The extraction and determination of radiogenic argon. The radiogenic argon was extracted from its host minerals by fusion with sodium hydroxide in a vacuum system. A known amount of Ar^{38} was introduced to the system as an isotopic tracer and the evolved gases were cleaned up by hot CuO and hot titanium sponge; water, which was given off during the fusion and was also formed as a by-product of the clean-up process, was absorbed by magnesium-perchlorate or frozen out in liquid nitrogen traps. The amount of Ar^{40} was determined by mass spectrometric analysis, the response of the mass spectrometer to the known amount of Ar^{38} being utilized as a standard with which to compare its response to the unknown amount of Ar^{40} . Corrections for possible atmospheric argon contamination in the sample were based on observed ion currents at mass 36 and an appropriate contribution was subtracted from the amount of Ar^{40} determined. The remaining Ar^{40} was then assumed to be entirely radiogenic. The percentage of radiogenic argon for each determination is given in Table I, in most specimens it exceeded 90 per cent. In addition to the mass spectrometric determination using the introduced Ar^{38} as a standard, the volume of gas at S.T.P. was determined, after nearly all the fusions, by expansion into a calibrated McLeod gauge. The amount of gas was subsequently corrected for the introduced tracer and for atmospheric argon as determined by mass spectrometric analysis, the remaining gas was assumed to be radiogenic argon, and the age calculated on this assumption. The two ages, i.e., the isotope dilution and volumetric, agreed to within 10 per cent in over two thirds of the determinations. Such agreement can be regarded as being very satisfactory considering that, except in a few cases, the evolved gases were put through the clean-up procedure only once.

The vacuum apparatus for the extraction and purification of radiogenic argon is shown diagrammatically in Figure 2. It was constructed of pyrex glass except for the reaction vessel which was nickel. As far as possible mercury cut-offs were used rather than vacuum stopcocks, and except for the stopcock connecting the reaction vessel to the manifold (Sc_1), the other stopcocks could be isolated from the vacuum line by mercury cut-offs once a satisfactory vacuum had been attained.

The procedure used for the extraction and determination of radiogenic argon was as follows. About 5 gms of mica and 30 to 40 gms of sodium hydroxide were placed in the nickel crucible. The crucible was then bolted onto the vacuum line and a vacuum tight seal obtained with an aluminium gasket. The sodium hydroxide had previously been fused under vacuum at 700°C and was kept in a desiccator until required. The grain size of the micas analyzed differed from sample to sample but was sufficiently fine to pass a 50 sieve but too coarse to pass a 150 sieve. Very finely ground samples were avoided partly because of the risk of some secondary sericite being present, the result perhaps of alteration of feldspars long

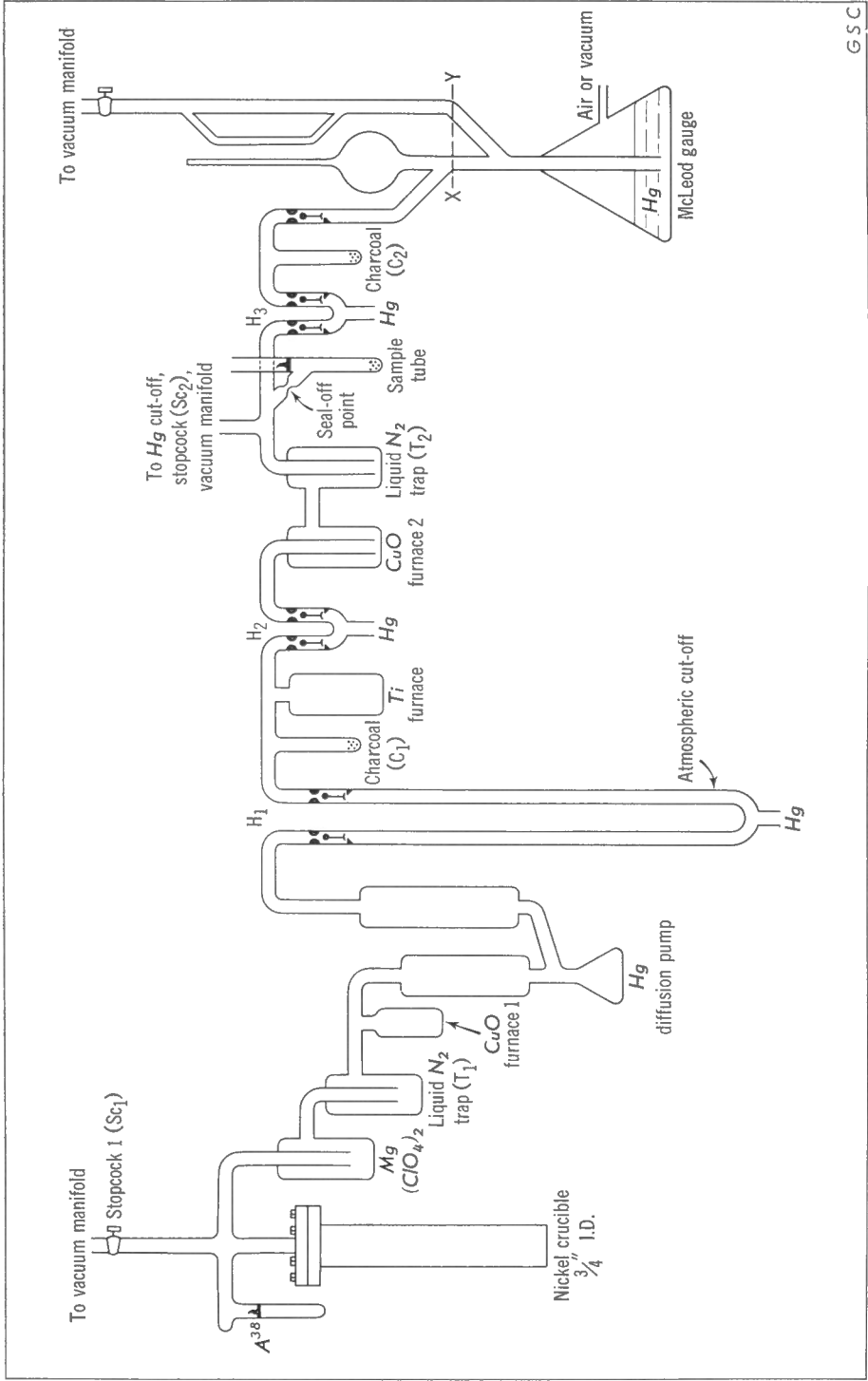


Figure 2. Argon extraction apparatus.

after the crystallization of the primary mica, and partly because of the tendency of fine powders to blow up out of the reaction vessel during its evacuation and outgassing. A sample tube containing the isotopic tracer or spike (in most cases about 10^{-4} c.c. of Ar^{38} at S.T.P.) was attached to the vacuum line for each determination in the position indicated together with sample tubes containing about 0.1 gms of activated charcoal on which the argon could be absorbed at the end of the extraction and purification procedure. These sample tubes could be isolated from the vacuum line at the seal-off point with a torch and then removed for mass spectrometric analysis. Several sample tubes were attached to the vacuum line at a time so that the section of the apparatus to the right of the atmospheric cut-off could be kept under vacuum throughout several argon extractions.

Before commencing the extraction of argon from a sample the apparatus was outgassed for 12 to 18 hours. During this period the CuO furnaces were kept at a temperature of 450°C in order to remove absorbed air and the magnesium perchlorate trap was kept at 200°C in order to rejuvenate the desiccant. The sample tubes and charcoal traps were kept at 180°C by small resistance furnaces and the whole apparatus was periodically flamed. The nickel crucible and its contents were outgassed by heating at 250°C . By rigorously following this procedure a satisfactory vacuum of 10^{-6} mm of Hg was regularly obtained; the extraction of argon was never commenced until this degree of vacuum had been reached. With the attainment of a satisfactory vacuum the nickel reaction vessel was isolated from the rest of the apparatus by raising the atmospheric cut-off H_1 and shutting the stopcock Sc_1 . The crucible was then heated to 800°C in a Fieldner resistance furnace. The total time of heating was usually about 7 hours and the crucible was maintained at a temperature in excess of 600°C for at least 4 hours. With biotites a vigorous reaction commenced at about 400°C with the evolution of considerable amounts of hydrogen. This hydrogen was oxidized in the CuO furnace 1 which was maintained at a temperature between 450°C and 500°C throughout the fusion period. Water so formed together with water given off during the reaction was absorbed in the magnesium perchlorate traps which had been allowed to cool to room temperature following outgassing and rejuvenation. There was nothing to suggest that hydrogen was formed in any quantity during either blank fusions or muscovite fusions indicating that the hydrogen evolved during biotite fusions was the result of reduction of the OH group of the biotite by ferrous iron which is invariably a major constituent of this mineral. As soon as the fusion was proceeding quietly the isotopic tracer was released and allowed to mix with the evolving gases. At the end of the fusion period the cold trap T_1 was immersed in liquid nitrogen in order to freeze out any unabsorbed water, the mercury cut-off H_2 was raised, the atmospheric cut-off H_1 was lowered, and the remaining gas was taken up on the activated charcoal, cooled by liquid nitrogen, in trap C_1 . In order to ensure complete transfer of gases from the furnace section into the titanium furnace section of the line the mercury diffusion pump was also set in operation. An hour was usually allowed for this transfer after which the mercury in the atmospheric cut-off was raised and the gas sample left isolated

in the titanium furnace section of the line overnight. During this fusion and transfer procedure, which normally took the whole of one working day, the sections of the vacuum line not in use were continuously pumped through stopcock Sc₂.

Removal of the remaining non-inert gases was achieved by allowing the gas to stand in contact with hot titanium sponge. Complete release of the gas from the charcoal trap C₁ was ensured by immersing the trap in hot water, the evolved gas then stood in contact with about 15 grams of titanium sponge contained in a small quartz crucible and heated to red heat by a small 500-watt induction unit. About 20 minutes was usually allowed for this process. According to Hurley (1957), gases other than the inert gases are readily taken up by hot titanium, however there appears to be a risk that hydrogen taken up at a lower temperature may be given off again at higher temperatures and because of this the gas sample was further purified by standing in contact with hot CuO in order to remove as far as possible all traces of hydrogen. This was done by raising the mercury in the cut-off H₃ and in the cut-off between the purification train and the stopcock Sc₂, allowing the titanium to cool slowly, and then lowering the mercury in the cut-off H₂. The gas was allowed to remain in contact with CuO at 450°C in furnace 2 for at least 30 minutes, water formed by the oxidation of any hydrogen present being frozen out in the liquid nitrogen cold trap T₂. The complete removal of hydrogen is most important for its presence during mass spectrometric analysis appears to enhance the 36 peak which introduces a considerable error in the correction for contaminating atmospheric argon (Carr and Kulp, 1957). With the completion of the clean-up procedure the mercury in cut-off H₃ was lowered and the remaining gas absorbed onto activated charcoal, cooled by liquid nitrogen, in trap C₂. On completion of the transfer the mercury in cut-off H₃ was raised and the gas allowed to expand into the calibrated McLeod gauge where its pressure and volume were determined. Following this estimate of the volume of the gas it was absorbed onto the charcoal in the sample tube which was then sealed off and removed for mass spectrometric analysis. This clean-up procedure could be completed in a morning and the remainder of the day spent preparing the apparatus for the next determination. After removal from the vacuum line the isotopic composition of the argon was determined by mass spectrometric analysis.

Isotopic tracer preparation and calibration. The isotopic tracer used in the present set of argon determinations was obtained from neutron irradiated KCl. The argon, which had been extracted and purified in a manner similar to that described above, had the following isotopic composition: Ar⁴⁰ 6.42%, Ar³⁹ 2.40%, Ar³⁸ 90.98%, and Ar³⁶ 0.191%. The apparatus and methods used in the preparation of the isotopic tracers were virtually the same as used by Wasserburg and Hayden (1955). The method of calibration was essentially the same as described by Carr and Kulp (1957) and Lipson (1958).

Mass spectrometer. The mass spectrometer used was a Nier type having a 10-inch radius of curvature and a 90 degree deflection. The ion current signal at the collector was amplified by an Applied Physics Corporation Model 30 vibrating reed electrometer and fed to a Brown Electronic Recorder. The sample introduction system was essentially the same as described by Wanless and Thode, 1953.

A low background was obtained in the mass region of interest by frequent baking without opening the instrument to atmospheric pressure. Corrections for mass discrimination effects in the mass spectrometer were based on calibration analyses carried out on atmospheric argon.

Potassium determinations. Potassium was determined by a flame photometric method. The sample was decomposed by hydrofluoric and sulphuric acids, evaporated to dryness, and the residue ignited. The ignited residue was then leached with distilled water and the potassium content of the resultant solution was determined using a Beckman DU spectrophotometer with a flame photometer attachment. The determination of potassium in micas is the subject of a separate publication by other members of the Geological Survey of Canada (Abbey and Maxwell, 1960).

Precision. The potassium percentages given in Table I are, in all specimens, the average of two determinations, and a precision of 1 per cent in the range of 1 to 10 per cent of potassium is normal. The spike calibrations are also reproducible to within 1 or 2 per cent. Replicate determinations on radiogenic argon from very old samples indicate an order of reproducibility in the range of 5 to 10 per cent. The overall precision of the method however is dependent on many additional factors and operations that are difficult to evaluate singly and which, when taken together, may cancel each other out. Thus recourse must be made to replicate determinations in order to obtain some idea of the precision of the age determinations. The results so far indicate that the apparent ages can be quoted with an average deviation of the order of $\pm 5\%$ in the age range considered in this study.

Appendix B

THE RADIOACTIVITY OF POTASSIUM

Introductory remarks. The potassium-argon method of determining the age of a mineral utilizes the dual decay exhibited by the radioactive isotope of potassium, K^{40} , to Ar^{40} and Ca^{40} . This process of radioactive decay results in the accumulation of measurable amounts of Ar^{40} in potassium-rich minerals at a rate that is governed by two nuclear constants; these are the total decay constant, λ , which determines the rate at which K^{40} disintegrates and λ_e , the K electron capture decay constant. The isotopic composition of potassium is known and does not appear to vary with either origin or location so that determination of the total potassium content immediately gives the amount of K^{40} . If the two nuclear constants are known it is only necessary to determine the amount of radiogenic argon and the potassium content in order to calculate an apparent age for any potassic mineral. The advantages of this method of age determination lie in the wide distribution and common occurrence of potassium-rich minerals, in the fact that the half-life of K^{40} (1.3×10^9 years) is suitable for dating almost the entire range of geological time, and in the relative ease with which the amount of radiogenic argon present in minerals can be determined by the method of isotope dilution (Ingram, 1954, and Aldrich, 1956).

The decay constants of K^{40} . The spontaneous emission of β -rays or electrons by potassium was first recorded in 1906 (Campbell and Wood) though the radioactive isotope was not definitely identified as K^{40} until 1937 (Smythe and Hemmendinger). Meanwhile Fermi's theory of β decay (1934) had suggested the likelihood of an additional process in which the atomic nucleus captured an electron from the innermost K orbit—a process termed K capture—but the first experimental evidence of this suspected type of decay was not reported until 1943 (Thompson and Rowlands). Evans (1940) was one of the first to suggest that the age of a potassium-bearing mineral could be calculated from its Ar^{40} content and Aldrich and Nier (1948) were able to show a relation between the Ar^{40}/K^{40} ratio of a mineral and its age, but obviously little could be achieved in applying this radioactive system to geological age determination until agreement could be obtained concerning the decay constants involved. Adequate accounts of the difficulties faced in determining these decay constants and of the uncertainties associated with the constants at present being used for age calculations are to be found in the reviews by Birch (1951), Aldrich and Wetherill (1958), and Tilton and Davis (1959). In this paper all calculations have been made using the following constants: for K capture $\lambda_e = 0.585 \times 10^{-10} \text{ yr}^{-1}$, for β emission $\lambda_\beta = 4.715 \times 10^{-10} \text{ yr}^{-1}$, giving a total decay constant $= 5.30 \times 10^{-10} \text{ yr}^{-1}$, and a branching ratio $R = \lambda_e / \lambda_\beta = 0.1241$ (Aldrich and Wetherill, 1958).

The calculation of the age. The age of the mineral determined by the potassium-argon method is calculated as follows:

Let N_0 = number of K^{40} atoms present at time $t = 0$

N = number of K^{40} atoms present after time t

N' = number of Ar^{40} and Ca^{40} atoms produced during a time t

N'_{Ar} = number of Ar^{40} atoms produced during time t

The number of Ar^{40} atoms produced will be given by

$$\frac{\lambda_e}{\lambda_e + \lambda_\beta} \cdot N' = N'_{Ar} \quad (1)$$

Assuming that $N' = 0$ when $t = 0$ we have

$$N = N_0 e^{-\lambda t} \quad (2)$$

$$N_0 = N e^{\lambda t} \quad (3)$$

$$\text{and } N' = N_0 - N = N[e^{\lambda t} - 1] \quad (4)$$

from (1)

$$N'_{Ar} = \frac{\lambda_e}{\lambda_e + \lambda_\beta} N[e^{\lambda t} - 1] \quad (5)$$

and

$$e^{\lambda t} = 1 + \frac{\lambda_e + \lambda_\beta}{\lambda_e} \frac{N'_{Ar}}{N} \quad (6)$$

solving (6) for t we get,

$$t = \frac{1}{\lambda} \ln \left[1 + \frac{R + 1}{R} \frac{Ar^{40}}{K^{40}} \right] \quad (7)$$

where R is the branching ratio and is equal to $\lambda_e / \lambda_\beta$. Substitution of the appropriate numerical values in equation (7) yields

$$t = 1.887 \times 10^9 \ln \left[1 + 9.058 \frac{Ar^{40}}{K^{40}} \right] \quad (8)$$

The substitution of the number of atoms of Ar^{40} and K^{40} in (8) will yield the age in years.