

A RUBIDIUM-STRONTIUM ISOTOPIC INVESTIGATION OF THE
POSSIBILITY OF DATING HYDROTHERMAL MINERAL DEPOSITS

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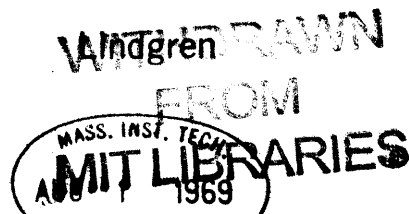
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ABSTRACT

The analyses of the strontium isotopic compositions of strontium-rich, rubidium-poor, gangue minerals from various vein-type hydrothermal mineral deposits have demonstrated that the gangue strontium is either largely derived from the wallrocks, or else has largely exchanged with the wallrock strontium.

The analyses of syenite country rocks and altered syenitic rocks from the ore zone at Kirkland Lake, Ontario, have yielded whole rock isochron ages of about 2000 m.y. that are indistinguishable from one another. These rock samples have all been highly carbonatized. When the carbonate material was leached from these samples and the rock materials were re-analyzed the syenite country rocks yielded an isochron age of 2260 ± 88 m.y. and the rocks of the alteration zone yielded isochron ages of about 1800 m.y. Both of these ages are reasonable with respect to the geology of the Kirkland Lake area.

The analyses of trace amounts of Rb and Sr in samples of massive sulfide ores from Noranda, Quebec have shown that these ores contain sufficiently large amounts of Rb and Sr, and sufficiently large Rb/Sr ratios, to make the dating of these ores possible, if the problems of sample contamination during processing can be overcome.

The analyses of trace amounts of Rb and Sr in samples of gold-quartz from Porcupine, Ontario, have yielded less promising results than have the sulfide analyses.

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PART ONE
(Intended for Publication)

AN INVESTIGATION OF THE STRONTIUM ISOTOPIC COMPOSITIONS
OF STRONTIUM-RICH, RUBIDIUM-POOR, GANGUE MINERALS FROM
VEIN-TYPE HYDROTHERMAL MINERAL DEPOSITS

R. H. REESMAN

ABSTRACT

Strontium isotopic analyses have been made on strontium-rich, rubidium-poor, gangue minerals from several vein-type hydrothermal mineral deposits. These minerals were from deposits in which: 1) Tertiary mineralization occurs within rocks of Tertiary age, 2) Tertiary mineralization occurs within rocks of Precambrian age, and 3) the mineralization is Precambrian. The results of these analyses show that the gangue strontium was derived, at least to a very large extent, from the rocks of the host environment.

INTRODUCTION

Measurements of the $\text{Sr}^{87}/\text{Sr}^{86}$ isotopic compositions of a series of strontium-rich, rubidium-poor, gangue minerals from some vein-type hydrothermal mineral deposits have been made in order to gain information concerning the possible origins of the gangue material. If these materials are of primary magmatic origins (i.e. derived directly from subcrustal sources having Rb/Sr ratios similar to those in the source regions of basalts), and if the strontium compositions of the gangue minerals faithfully represent the initial strontium compositions of the mineralizing fluids, then the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios should reflect the strontium compositions of the source regions.

In a study of the strontium isotopic compositions of basaltic rocks Faure and Hurley (7) found that both the

oceanic and continental types had uniformly low $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of less than about 0.708. Because these rocks are very low in rubidium these ratios are believed to characterize the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the source region of these rocks at the time of their formation. This source region is believed to be either the lower crust or the upper mantle. From the Rb and Sr concentrations measured in these samples Faure and Hurley determined that the Rb/Sr ratio in the source region of these rocks is about 0.04 and that the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of this region has grown to its present value of about 0.708 from an initial value of about 0.700 at the time of its formation 4500 million years ago. Therefore, gangue minerals containing strontium derived directly from this region should be expected to have $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of not more than about 0.708 for the more recent deposits and the ratios should decrease with the increasing age of the mineralization.

Faure and Hurley also calculated the approximate Rb/Sr composition of the upper continental crust from a consideration of the average Rb/Sr compositions of the various crustal rock types, as determined from the analyses of many previous workers, and by weighting these analyses with respect to the approximate amounts of each of the rock types in the crust. Their best estimate for the Rb/Sr composition for the upper continental crust is 0.25. By assuming an average age for the crust of 2000 million years Faure and Hurley then calculated that the average $\text{Sr}^{87}/\text{Sr}^{86}$ composition

of the upper continental crust at the present time is about 0.725. Therefore, if the gangue minerals contain strontium which was derived from pre-existing upper crustal materials having Rb/Sr ratios approximating the upper crustal average, then the gangue strontium should show $\text{Sr}^{87}/\text{Sr}^{86}$ ratios significantly greater than 0.708. If the gangue strontium was derived from crustal materials of near basaltic composition, or from very young crustal materials, the minerals may show $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of very near 0.708, but if the gangue strontium was derived from old sialic (Rb-rich) upper crustal materials the minerals should show ratios greater, possibly considerably greater, than 0.708.

The samples chosen for this investigation were from deposits in which: 1) Tertiary mineralization occurs within rocks of Tertiary age, 2) Tertiary mineralization occurs within rocks of Precambrian age, and 3) the mineralization is Precambrian. Fluorite was the preferred gangue mineral as it is generally accepted that the fluorine is of magmatic, and thus possibly deep-seated, origin. Because of a lack of adequate fluorite samples the measurements were extended to two other strontium-rich minerals, barite and calcite. For this survey investigation samples were selected from among those available in the Lindgren Collection of Ores and Minerals in the Department of Geology and Geophysics at M.I.T.

Three different mass spectrometers of similar design were used to make the isotopic measurements. In the tables

to follow the instrument used for a particular analysis is identified alongside the sample number. During the period in which these analyses were made the operation of each instrument was monitored by the periodic analysis of a standard sample of SrCO_3 (Eimer and Amend, lot number 492327). The measured ratios of $\text{Sr}^{87}/\text{Sr}^{86}$ were normalized to a value of $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$. The standard analyses are listed in Table 1. Also given in this table are the designations of each of the instruments. The analyses made on "Nancy" were the first measurements to be made on this machine after it was assembled, as a consequence relatively more standard analyses were made on this instrument than were made on either of the other two. Experience has shown that the precision of the normalized values of $\text{Sr}^{87}/\text{Sr}^{86}$ is $\pm 0.1\%$.

TERTIARY MINERALIZATION IN TERTIARY ROCKS

The samples of Tertiary mineralization occurring within rocks of Tertiary age came from locations in Colorado, Arizona, Montana and the Philippines. The results of the analyses are listed in Table 2. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the gangue minerals range from 0.705 to 0.711. One sample of andesitic country rock from the Telluride district, Colorado, has a $\text{Sr}^{87}/\text{Sr}^{86}$ composition of 0.709. This sample was not from the same locality as was the calcite sample from the Telluride district, it was analyzed solely to gain some idea of the present strontium isotopic composition of the Tertiary volcanics.

Table 1.

Replicate analyses of strontium isotopic standard.

Record No.	$\text{Sr}^{86}/\text{Sr}^{88}(1)$	$\text{Sr}^{87}/\text{Sr}^{86}(1)$	$\text{Sr}^{87}/\text{Sr}^{86}(2)$
3364(S) ⁽³⁾	0.1191	0.7094	0.7084
3372(L)	0.1202	0.7059	0.7083
3404(L)	0.1186	0.7104	0.7080
3411(S)	0.1195	0.7077	0.7077
3715(N)	0.1193	0.7090	0.7087
3745(N)	0.1186	0.7109	0.7085
3770(N)	0.1188	0.7104	0.7086
3799(N)	0.1187	0.7110	0.7089
3811(N)	0.1189	0.7100	0.7085

(1) Measured value.

(2) Normalized to $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$

(3) The mass spectrometers used in this study have all been given names. S denotes "Sally", L denotes "Lulu", and N denotes "Nancy".

The main conclusions which can be drawn from the results of these analyses is that both the gangue minerals and the country rock sample show $\text{Sr}^{87}/\text{Sr}^{86}$ ratios which are compatible with an origin in a deep-seated source region in Tertiary times. The gangue mineral ratios are also compatible with an origin in rocks of Tertiary age which were derived directly from a deep-seated source. The Tertiary gangue strontium ratios are not compatible with a derivation through the remobilization of pre-existing upper crustal materials of greater than 1000 m.y. age, having average Rb/Sr ratios in excess of 0.20, and having average $\text{Sr}^{87}/\text{Sr}^{86}$ compositions in excess of 0.702. The implications of this last proposition will now be discussed.

Cripple Creek district, Colorado. - In the Cripple Creek district a plug of latite-phonolite tuffs and breccias is exposed within a Precambrian terrain comprised of granite and granitic gneisses and schists. The gangue minerals were associated with mineralization in the Tertiary volcanics. The granitic country rocks of this area have yielded K-Ar and Rb-Sr ages of 1000 to 1200 m.y. (2,8,22). This age is the youngest recognized Precambrian event in this region (14). The maximum Rb/Sr composition of 0.20 that such basement rocks could have if they were the source rocks for the gangue strontium is less than either the average Rb/Sr value of 0.25 of the upper continental crust (7) or the average of 0.25 and greater of rocks with compositions more sialic than the average of the upper continental

Table 2.

Tertiary mineralization in Tertiary rocks.

Sample No.	Sample and Locality	86/88	87/86	87/86 _N ⁽¹⁾
R5293	(S) ⁽²⁾ Calcite	0.1194	0.7076	0.7076
"	(L) Liberty Bell Mine Telluride, Colorado	0.1196	0.7069	0.7075 ⁽³⁾
R5297	(S) Andesitic country rock	0.1192	0.7095	0.7088
"	(L) Smuggler vein Telluride, Colorado	0.1181	0.7127	0.7088
R5299	(S) Fluorite Mineral Rock Mine Cripple Creek, Colorado	0.1185	0.7074	0.7048
R5300	(S) Fluorite Rice vein, 1700' level Eagles shaft Cripple Creek, Colorado	0.1189	0.7088	0.7073
R5301	(L) Fluorite Portland Mine Cripple Creek, Colorado	0.1191	0.7077	0.7068
R5304	(S) Calcite Tom Reed Mine Mohave County, Ariz.	0.1199	0.7101	0.7115
R5305	(S) Fluorite Limestone-fluorite ore Maginnis Mine Judith Mts., Montana	0.1191	0.7103	0.7094
R5306	(S) Calcite from sample R5305, above	0.1186	0.7098	0.7075
R5307	(L) Fluorite Maginnis Mine Judith Mts., Montana	0.1192	0.7104	0.7098
R5432	(L) Pink calcite Balatoc Mine Baguio Mining District Luzon, Philippines	0.1196	0.7042	0.7049

(1) Normalized to $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$.

(2) See footnote (3), Table 1 for instrument designations.

(3) All duplicate analyses were made on two different instruments.

crust given by both Faure and Hurley (7) and Turekian and Wedepohl (34). It is significantly less than the average Rb/Sr ratio of about 1.0 given for rocks of granitic compositions by Hurley, Hughes, Faure, Fairbairn and Pinson (15). The maximum $\text{Sr}^{87}/\text{Sr}^{86}$ composition of 0.702 that any pre-existing sialic source rocks could have, if the previously given conditions for age and Rb/Sr composition were both met, is too low for the basement rocks of this area. From the data given by Faure and Hurley these rocks should have had an initial $\text{Sr}^{87}/\text{Sr}^{86}$ of about 0.704 to 0.706 if they had been derived from a deep-seated source 1000 m.y. ago. If they were derived from pre-existing sialic rocks then their initial $\text{Sr}^{87}/\text{Sr}^{86}$ compositions should have been greater than the upper mantle value at that time, since sialic crustal materials generally have Rb/Sr values greater than that of the upper mantle. In Tertiary times the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of these rocks would have been significantly greater than their initial compositions, and thus significantly greater than 0.702. The granitic gneisses and schists of this area are older than the granitic rocks just discussed, and are believed to correlate with rocks further to the north which have been dated by Hedge, Peterman and Braddock (14) as 1700 m.y.

From the evidence available from the rocks of the Cripple Creek district, then, it appears very improbable that any of the pre-Tertiary rocks of this district could

have been the source rocks of the Tertiary gangue strontium. With the Precambrian basement rocks ruled out as a possible source for the Tertiary gangue strontium, two possible sources of this material remain. One possible source is the source region of the volcanics, presumed to be either the lower crust or the upper mantle. The alternative source is the volcanics themselves. During the whole of Tertiary time, about 70 m.y., rocks having an average Rb/Sr composition approximately the same as the crustal average would increase in their $\text{Sr}^{87}/\text{Sr}^{86}$ composition only about 0.001 over their initial strontium composition; this difference would not be discernable in the analyses carried out here.

Moorbath, Hurley and Fairbairn (20) measured the initial strontium compositions of some mineralized Laramide intrusives from the southwestern United States and found that these compositions were in the range $\text{Sr}^{87}/\text{Sr}^{86} = 0.705$ to 0.709. One sample of fluorite from the Cripple Creek district also gave a strontium composition within this range. From this data Moorbath et al concluded that both the intrusives and the fluorite were derived from a deep-seated source region. The arguments presented above suggest that their conclusion regarding the strontium in the fluorite may not be correct in so far as the immediate source of this component is concerned; their conclusion is most probably correct with respect to the ultimate source of this component in Tertiary time.

Oatman district, Arizona. - The mineralization in the Tom Reed mine occurs in Tertiary andesites which cover a basement of Precambrian gneisses and schists. Gilletti and Damon (9) have obtained Rb-Sr ages of 1200 to 1350 m.y. from three biotite samples from these Precambrian rocks. The same type of argument can be applied to the rocks of the Oatman district as was previously applied to the rocks of the Cripple Creek district and, as in the case of the Cripple Creek district, it is very improbable that the Precambrian basement rocks of the Oatman district could have been the source of the Tertiary gangue strontium. Once again, the possible alternative sources for this gangue strontium are the source region of the volcanic rocks or the volcanic rocks themselves.

Telluride district, Colorado. - In the Telluride district the conclusions are less clear than in either of the two districts just discussed. In this district a series of Tertiary volcanics of acid to basic composition overlies a series of Paleozoic and Mesozoic sediments. The ore mineralization occurs in the volcanics. Some Precambrian rocks are exposed in the area. The ages of these Precambrian rocks are uncertain, but Rb-Sr and K-Ar ages from Precambrian granitic rocks in areas surrounding this region are about 1400 m.y., an age which appears to be ubiquitous to a large part of the southwestern United States (1,21). It would be difficult to adequately assess the possibility that the sediments underlying this district were the source

rocks of the Tertiary gangue strontium, therefore such a possibility cannot be ruled out in this district. In the Telluride district, then, there are three possible sources of the Tertiary gangue strontium. These sources are the assumed deep-seated source region of the volcanics, the volcanics themselves, or the underlying sediments.

Judith Mountains, Montana. - In the Maginnis mine the ore mineralization is associated with a Tertiary rhyolite porphyry at the contact with an underlying Carboniferous limestone. The analyses of the two fluorite samples from this mine give $\text{Sr}^{87}/\text{Sr}^{86}$ compositions that are within the range of strontium compositions measured in limestones of less than 1000 m.y. age by Powell (24). In this district the underlying Carboniferous limestone cannot be ruled out as a possible source of the Tertiary gangue strontium.

Baguio district, Philippines. - In the Balatoc mine, on Luzon, the ore mineralization occurs in a volcanic neck filled with Tertiary andesite breccia. The country rocks consist of older diorites of early Tertiary (?) age. These diorites cannot be ruled out as the source of the Tertiary gangue strontium because of a lack of adequate information about them.

Conclusions of the analyses of Tertiary mineralization in Tertiary rocks. - The analyses of the strontium isotopic compositions of the gangue minerals associated with Tertiary mineralization occurring within rocks of Tertiary age have yielded $\text{Sr}^{87}/\text{Sr}^{86}$ ratios that are

compatible with a derivation either from a source region similar in Rb/Sr composition to that of the source region of the Tertiary rocks or from the Tertiary rocks themselves. In the two districts in which adequate information is available on the pre-Tertiary crustal rocks these rocks can be ruled out as possible sources of the gangue strontium. In three of the districts there is insufficient information concerning the pre-Tertiary crustal rocks to rule them out as possible sources of the gangue strontium. However, because the gangue strontium compositions are all compatible with a derivation either from a deep-seated source region or from the Tertiary rocks themselves, and because the pre-Tertiary rocks can be ruled out as possible sources of the gangue strontium in the two districts in which adequate information about these rocks is available, it is neither necessary nor logical to assume that the pre-Tertiary crustal rocks in the remaining three districts were the sources of the Tertiary gangue strontium.

TERTIARY MINERALIZATION IN PRECAMBRIAN ROCKS

Samples of Tertiary mineralization in Precambrian rocks were selected from three areas in Colorado. In these three locations Tertiary dikes and stocks invade Precambrian granite and schist. The mineralization occurs in veins in the Precambrian rocks. The results of these analyses are listed in Table 3.

The $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the gangue minerals are much greater than would be expected for rubidium-

Table 3.Tertiary mineralization in Precambrian rocks.

<u>Sample No.</u>	<u>Sample and Locality</u>	<u>86/88</u>	<u>87/86</u>	<u>87/86_N</u> ⁽¹⁾
R5347 (L) ⁽²⁾	Barite Hiawatha Mine Chaffee County, Colo.	0.1193	0.7258	0.7255
R5348 (L)	Barite American Flag Mine Gilpin County, Colo.	0.1190	0.7235	0.7242
R5349 (L)	Fluorite Big Indian Mine Georgetown, Colo.	0.1193	0.7310	0.7298
R5350 (L)	Granite (Precambrian) Burleigh Tunnel Georgetown, Colo.	0.1197	0.7777	0.7787

(1) Normalized to $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$

(2) See footnote (3), Table 1, for instrument designations.

deficient phases which had incorporated only primary Tertiary strontium, that is, strontium with an isotopic composition of about 0.708.

The granitic rocks of the Georgetown district have yielded Rb-Sr whole rock ages of about 1700 m.y. (14, 23). 1700 m.y. old rocks having Rb/Sr ratios equal to or greater than the average of the upper continental crust (0.25) would have had $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of 0.720 or greater in Tertiary time. This is in good agreement with the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the Tertiary gangue strontium from the Georgetown district. The sample of granitic rock listed in Table 3 was from the same rock unit which enclosed sample R5349 but was from another mine in the same area. Geologic conditions similar to those of the Georgetown district are associated with each of the other two gangue samples listed in Table 3.

Conclusions of the analyses of Tertiary mineralization in Precambrian rocks. - The $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the Tertiary gangue minerals in Precambrian rocks are clearly too great to be compatible with a derivation from a deep-seated source region. They are also too great to be compatible with a derivation from the associated Tertiary rocks. Tertiary rocks having Rb/Sr ratios as great as the average given for granites (15) would increase only about 0.003 in the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions during the whole of Tertiary time. The strontium isotopic compositions of the gangue minerals are, however, compatible with a derivation

from pre-existing materials similar in composition and age to the granitic host rocks in these three districts.

PRECAMBRIAN MINERALIZATION

Precambrian gangue minerals were examined from the Kirkland Lake, Porcupine and Cobalt districts of Ontario. The results of these analyses are listed in Table 4.

The $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the Kirkland Lake and Porcupine gangue samples lie in the range 0.704 to 0.707. These ratios may be slightly greater than would be expected for rubidium-deficient phases which contained only primary strontium of Precambrian ages, but the data to support this inference are not compelling.

Kirkland Lake district. - At Kirkland Lake a syncline of Timiskaming sediments and volcanics has been intruded by syenites. The mineralization occurs principally in the syenites. The time of host rock alteration in this district is believed to have been about 1800 m.y. ago (27). From the data given by Faure and Hurley (7), and discussed earlier, the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the lower crust or upper mantle source region should have been about 0.704 to 0.705 at 1800 m.y. ago. Purdy and York (25) have dated the Otto stock, a syenitic intrusion which is exposed about three miles south of the Kirkland Lake district, and have obtained an age of 1830 m.y. and initial $\text{Sr}^{87}/\text{Sr}^{86}$ composition of 0.704. This initial ratio is in good agreement with the probable lower crustal or upper mantle composition at that time. The Precambrian gangue strontium

Table 4.

Precambrian mineralization.

Sample No.	Sample and Locality	86/88	87/86	87/86 _N ⁽¹⁾
R5419 (N) ⁽²⁾	Calcite Lake Shore Mine Kirkland Lake, Ontario	0.1192	0.7046	0.7039
R5420 (S)	Calcite Lake Shore Mine Kirkland Lake, Ontario	0.1204	0.7035	0.7065
R5421 (N)	Calcite Lake Shore Mine Kirkland Lake, Ontario	0.1190	0.7054	0.7043
R5422 (N)	Barite from coexisting barite and calcite Lake Shore Mine Kirkland Lake, Ontario			0.705
R5423 (N)	Calcite from sample R5422, above	0.1200	0.7038	0.7056
R5456 (N)	Slightly mineralized porphyry wallrock Lake Shore Mine Kirkland Lake, Ontario	0.1183	0.7216	0.7184
R5457 (S)	Calcite	0.1197	0.7051	0.7061
" (N)	Vipond Mine Porcupine, Ontario	0.1192	0.7080	0.7074 ⁽³⁾
R5458 (N)	Calcite Moneta Mine Porcupine, Ontario	0.1188	0.7067	0.7049
R5351 (L)	Calcite	0.1197	0.7102	0.7112
" (N)	Nipissing Mine Cobalt, Ontario	0.1188	0.7127	0.7108

(1) Normalized to $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$.

(2) See footnote (3), Table 1, for instrument designations.

(3) All duplicate analyses were made on two different instruments.

compositions in the Kirkland Lake district may be slightly greater than the composition of the presumed deep-seated source region at the time of mineralization, but the differences involved are slight. Because several different rock types might possibly have been source rocks for the gangue strontium, and because adequate data concerning their Rb/Sr and $\text{Sr}^{87}/\text{Sr}^{86}$ compositions are not available, no definite conclusions can be drawn about the possible crustal sources of the gangue strontium in this district.

Porcupine district. - At Porcupine Keewatin volcanics and Timiskaming sediments have been deformed into a syncline, and this structure has in turn been intruded by quartz porphyries. The mineralization may be genetically related to the porphyries although it occurs mainly in the volcanics and sediments. As in the Kirkland Lake district no definite conclusions can be drawn with respect to the possible crustal sources of the gangue strontium.

Cobalt district. - In this district Keewatin volcanics and schists are overlain by conglomerate and graywacke of the Cobalt series. These rocks are all overlain by Keewatin diabase. The ore veins occur in the diabase and in some of the underlying rocks. The $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the calcite sample from this district is clearly too great to have been derived directly from a deep-seated source. Once again, however, the available information concerning the rock compositions and time relationships is too sparse to lead to any definite conclusions regarding the possible crustal sources of the gangue strontium.

Conclusions of the analyses of Precambrian mineralization. - The $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the Precambrian gangue minerals appear to be slightly greater than would be compatible with a primary deep-seated derivation of this material. The available information concerning the crustal rocks in the three districts sampled is insufficient to allow any conclusions to be drawn about the possible crustal source rocks of this gangue strontium.

SUMMARY AND CONCLUSIONS

The strontium isotopic compositions of the gangue minerals from Tertiary mineralization occurring within rocks of Tertiary age are compatible with a derivation either from a deep-seated source region similar in Rb/Sr and $\text{Sr}^{87}/\text{Sr}^{86}$ compositions to the source regions of basalts, or from the Tertiary host rocks themselves. The strontium isotopic compositions are not compatible with a derivation from the pre-Tertiary crustal rocks in the districts from which these samples were taken.

The strontium isotopic compositions of the Tertiary gangue minerals occurring within rocks of Precambrian age are not compatible with a derivation either from a deep-seated source region in Tertiary time or from the associated Tertiary rocks. The strontium compositions are compatible with a derivation from the Precambrian host rocks.

The strontium isotopic compositions of the Precambrian gangue minerals appear to be slightly greater than would

be compatible with a derivation from a deep-seated source region, but this evidence is not conclusive.

The only conclusion that is compatible with the information obtained from all three types of deposits is that the gangue strontium was derived, at least to a large extent, from the host rocks of the mineralization. There is no evidence which requires a source for the gangue strontium outside of the host environment.

This conclusion is in agreement with the earlier conclusions of Schwartz (30) and Schmitt (28). Both of these workers compared the chemical analyses of large numbers of rock samples from hydrothermal alteration zones with the chemical analyses of their unaltered equivalents, and from these comparisons both workers concluded that in most instances the data indicated that the mineral-forming elements in the alteration products were largely derived from the host environment. Schmitt believed that this was especially true for the alkali and alkaline earth elements.

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THE Rb-Sr ANALYSES OF SOME SULFIDE MINERALIZATION

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The analyses of sulfide ores reveal that they contain low concentrations of Rb and Sr. The Rb/Sr ratios appear to be adequate for dating these ores.

1. INTRODUCTION

Eleven samples of massive sulfide ores from the Noranda district, Quebec, have been analyzed for Rb and Sr by isotope dilution mass spectrometry. The purpose of these analyses was to determine whether or not these sulfides contain adequate amounts of Rb and Sr, and adequate Rb/Sr ratios, to permit an age analysis by the Rb-Sr method. The premise of this approach is that the Rb and Sr found in the sulfides should represent material which was present in the mineralizing fluids and which was included in the minerals at the time of their formation. If the mineralizing fluids were essentially homogeneous with respect to strontium isotopic composition it should be possible to obtain an isochron age from the sulfide minerals. This age would approximate the time of mineral formation.

Most of the samples consisted of intimate mixtures of chalcopyrite, pyrite, pyrrhotite and sphalerite. Two

samples were almost all sphalerite. The samples containing only copper and iron sulfides were powdered, then roasted in air in a stainless steel pan to drive off the sulfur. They were then dissolved in vycor distilled 2N HCl on a steam bath. The powdered sphalerite samples were dissolved directly in vycor distilled 1:1 HNO₃ on the steam bath. A combination of the above two procedures was used to dissolve the samples which contained a combination of copper, iron and zinc sulfides.

Because of the low abundances of Rb and Sr in the sulfides very large samples were dissolved. The average sample size was about 35 grams. Owing to the large quantities of copper, iron and zinc in the solutions, the samples were passed through two different ion exchange columns. The first column contained 500 ml of Dowex 50-8X resin and was used to separate the major metallic elements from the solutions. The second column contained about 100 ml of the same type resin and was used to separate the Rb and Sr. About 3500 ml of vycor distilled 2N HCl were required to elute each sample through both columns.

All the sample analyses were made on a 6-inch, 60°-sector, single filament mass spectrometer. The Sr concentration and Sr⁸⁷/Sr⁸⁶ composition of each sample were both determined from a single Sr⁸⁴-spiked analysis. All Sr⁸⁷/Sr⁸⁶ ratios were normalized to Sr⁸⁶/Sr⁸⁸ = 0.1194.

2. DISCUSSION OF RESULTS

Listed in Table 1 are the results of the sample analyses, including three duplicates. Also shown in the table are the results of two blank analyses which were made at different times to monitor the contamination levels in the sample preparation procedure.

The Rb concentrations in the sulfides range from 0.01 to 1 ppm and the Sr concentrations range from 0.1 to 1 ppm. The Rb/Sr ratios range from about 0.03 to about 1. The precision of the duplicate analyses is poor and this is probably due to the effects of uncontrollable contamination of the samples during processing. As can be seen from the table the Sr blanks are particularly high and differ by nearly 100%. The strontium isotopic composition of the contamination is unknown, therefore its' effect on the measured $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the samples cannot be estimated. The high blank values are probably due largely to the very large volumes of reagents used during the sample preparation. The three duplicate analyses were made on samples which were among the highest in both Rb and Sr concentrations. The relative errors in the analyses of the samples with lower Rb and Sr concentrations are probably considerably greater than those for the duplicates shown here because of the effects of the high contamination levels.

Shown in Figure 1 is an isochron-type plot of the sulfide analyses. These analyses show a large degree of

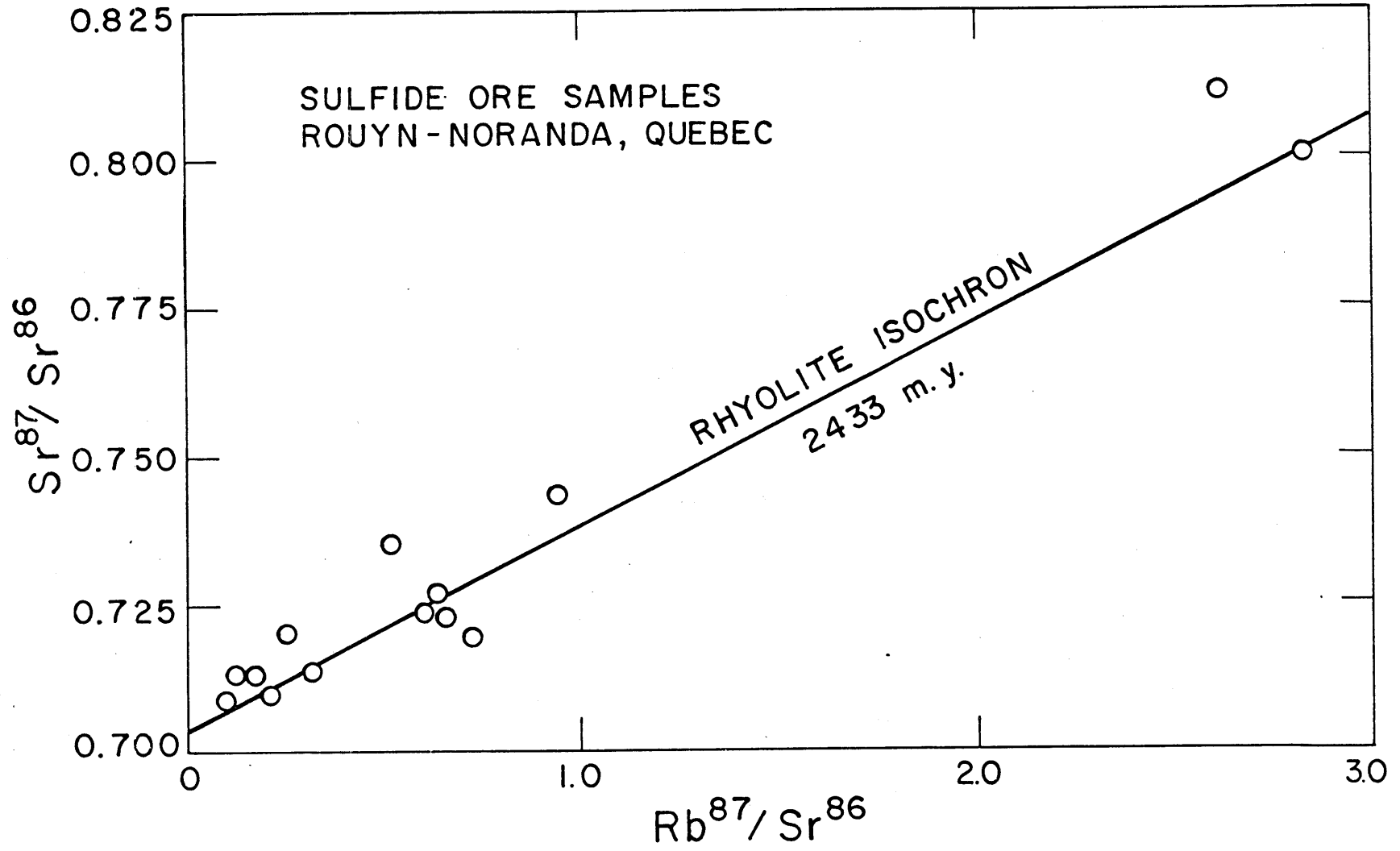
TABLE 1

Analyses of sulfide ores, Noranda, Quebec

Sample No.	Rb _{ppm}	Sr _{ppm}	Rb ⁸⁷ /Sr ⁸⁶	Sr ⁸⁷ /Sr ⁸⁶
R6572	0.200	0.898	0.645	0.7265
"	0.164	0.661	0.719	0.7191
R6710	0.059	0.997	0.171	0.7133
"	0.064	0.862	0.215	0.7098
R6711	0.992	1.106	2.623	0.8116
"	0.910	0.943	2.819	0.8008
R6977	0.05	1.09	0.133	0.7126
R6978	0.05	0.154	0.943	0.7432
R6979	0.089	0.486	0.529	0.7346
R6981	0.025	0.135	0.536	0.7232
R6983	0.070	0.631	0.323	0.7138
R6985	0.066	0.288	0.664	0.7226
R6986	0.015	0.166	0.256	0.7204
R6988	0.012	0.334	0.104	0.7091
Blank	0.037*	0.339*		
"	0.023*	0.745*		

*Blank analyses given in micrograms per analysis.

FIGURE 1



scatter on the diagram, much of which is undoubtedly due to the quality of the analyses, and no attempt has been made to calculate an age from these sample points. Also shown on the diagram is a Rb-Sr whole rock isochron obtained from the rhyolite host rocks at Noranda (1). This isochron is shown so that comparisons can be made between it and the sulfide sample points. The sulfides show a trend similar to the rhyolite isochron. The degree to which this apparent correlation is due to uniformity of the initial strontium isotopic compositions in the sulfides and to the contemporaneity of their formation has yet to be determined. The spread of the $\text{Rb}^{87}/\text{Sr}^{86}$ values should be great enough to permit the age analyses of these sulfides; sample R6711 is particularly encouraging in this respect.

3. CONCLUSIONS

The massive sulfide ores from Noranda contain concentrations of Rb and Sr of 1 ppm, or less, and Rb/Sr ratios up to about 1. Although these Rb/Sr ratios are low they should be great enough to permit the age analyses of the sulfide minerals if the problem of analytical precision can be overcome; this problem may be largely one of sophistication in the analytical procedures. The question of whether or not isochron analyses can be performed on sulfide samples has yet to be answered, and this answer must await the required improvement in the analytical precision.

Not until a large number of reliable determinations have been made can any conclusions be drawn as to whether or not the sulfide minerals in a particular deposit, or in a particular zone in a deposit, incorporated strontium of a uniform isotopic composition.

It is not yet known which sulfide minerals are the more enriched in Rb, although the samples with the greatest Rb/Sr ratios in this study were composed largely of chalcopyrite and pyrrhotite.

It may be some time before it can be determined if the direct dating of sulfide minerals by the Rb-Sr method is feasible. The ability to obtain such age measurements, however, would be of great benefit in determining the absolute ages of mineral deposits, especially those of Precambrian age. The problem is an interesting one, and one which merits further attention.

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A Rb-Sr INVESTIGATION OF THE TIME OF MINERALIZATION
AT KIRKLAND LAKE, ONTARIO

INTRODUCTION

The Kirkland Lake gold mining district is located in Tech township in eastern Ontario, about 130 miles north of North Bay (see map, Figure II*). In terms of production it has been the second largest gold camp in Ontario. The major part of the ore has been produced from seven mines in and near the town of Kirkland Lake. Underground production has now ceased at all but one of these mines; the one remaining active mine is the Macassa mine, located at the extreme western end of the district.

The host rocks around the ore zone have undergone widespread, low grade alteration; they have been altered from a composition comprised largely of feldspar to one comprised predominantly of sericite, chlorite and carbonates. During the time of alteration these rocks did not remain closed chemical systems, but rather were open to exchange with the hydrothermal fluids. It would be expected that the fluid components would have had a large degree of mobility at the time of alteration and that there would have been a large degree of mixing and homogenization of the original fluid components with the components derived from the wallrocks. Thus when the alteration minerals formed they would have incorporated strontium whose isotopic composition was essentially homogeneous, over at least moderately large areas, and therefore the alteration

*All figures and tables referred to are in Part Two of this report.

minerals should have formed a new radiometric system which is distinguishable from the pre-existing wall rock system. These alteration minerals are extremely fine-grained, however, and it is not feasible to separate the various minerals from the rocks. The principal Rb-bearing phase in the altered rocks is the sericite; the other phases are Rb-poor and although they may contain significant amounts of Sr this strontium should have a composition which is the same as the initial strontium composition incorporated by the sericite, thus the whole rock analyses of the altered rocks should yield an age which is the sericite age and the inclusion of the strontium from the Rb-poor phases should have no effect on the measured age.

GEOLOGY

The Kirkland Lake district, which is located in the Superior province of North America, lies near the western end of a highly disturbed, east-west trending shear zone, the western termination of which lies near Kenagami Lake (see map, Figure III) and which extends eastward to the Ontario-Quebec boundary, and thence into Quebec. Major faults lie in and along this zone, and faults also transect the zone. The Kirkland Lake fault is a major feature in the western part of the shear zone and has been the major factor in the control and localization of the ores.

The country rocks of the region are all of Precambrian age and consist of volcanics, sediments and intrusives. The sediments and volcanics have been severely folded and faulted. They have been subdivided into two age groups

on the basis of field evidence, and are separated from one another by an angular and erosional unconformity. The older group is classified as Keewatin and the younger is classified as Timiskaming. Fairbairn (1965,1966) has dated volcanics from both groups in the Kirkland Lake area by the rubidium-strontium whole rock method and has found the isochrons obtained to be indistinguishable from one another. Fairbairn's age for the Keewatin is 2376 ± 40 m.y. with an initial ratio of 0.7032, and his age for the Timiskaming is 2368 ± 48 m.y. with an initial ratio of 0.7026. As pointed out by Fairbairn, the error limits on the isochrons would allow more than sufficient time for the unconformity to develop.

The Keewatin and lower Timiskaming series have been intruded by gabbro and diorite bodies, and all of these rocks have been intruded by rocks of acid to basic composition. These latter intrusives have been classified as Algomian age and it is in these rocks that most of the Kirkland Lake ores occur. Purdy and York (1967) have dated the Otto Stock, a syenitic body which is exposed about 4 miles south of the Kirkland Lake district, and on the north edge of the Round Lake pluton, and have obtained a Rb-Sr age of 1730 m.y. with an initial ratio of 0.7046. However, Purdy and York used a decay constant for Rb^{87} of $1.47 \times 10^{-10} \text{yr}^{-1}$; their age for the Otto stock recalculated using the decay constant of this study ($1.39 \times 10^{-10} \text{yr}^{-1}$) is 1830 m.y. Purdy and York also obtained a Rb-Sr age for

the Round Lake pluton of 2520 m.y. (when recalculated using a decay constant of $1.39 \times 10^{-10} \text{ yr}^{-1}$) with a $\text{Sr}^{87}/\text{Sr}^{86}$ initial ratio of 0.7015; Fairbairn (1966) obtained a Rb-Sr age of 2530 m.y. and initial ratio of 0.7031 for this same body.

In the Kirkland Lake district the host rocks for the ore are in an Algonian syenitic stock. These rocks were intruded in three stages; the oldest is an augite syenite, this was intruded by a syenite, and both of these rock types were intruded by a syenite porphyry.

In the vicinity of Kirkland Lake the entire structure has been sliced in two by the Kirkland Lake fault, which is known in the mining camp as the Main Break. The ore zone is mostly localized in the fault zone. The faulting and fracturing of the rocks provided the fissures through which the mineralizing fluids gained access to the rocks. The syenitic intrusives were more brittle than the surrounding country rocks and consequently were fractured to a greater extent than were the surrounding rocks. The syenite porphyry was the most brittle of all the rocks, causing it to be fractured to a much greater extent than any of the other rocks. As a consequence, the syenite porphyry became the major host rock for the gold mineralization.

The ores at Kirkland Lake have been termed mesothermal by Lindgren (1933). The principal ore mineral is native gold, which occurs in the quartz vein and fracture vein and fracture fillings in the syenitic intrusives.

The hydrothermal alteration of the syenitic wallrocks has produced a rock that is characteristically reddish in color, owing to the development of iron oxides. Chlorite,

sericite, carbonates, quartz and leucoxene have developed in the rocks.

All the rocks in the syenitic stock have been severely carbonatized. Much of this carbonate developed at the time of hydrothermal alteration, but an examination of thin sections made from these samples indicates that a part of the carbonate was also developed in post-alteration fractures. It will be shown later that this carbonate mineralization seriously detracts from the quality of the whole rock age analyses.

SAMPLES

Most of the samples examined from the Kirkland Lake district were collected from the Macassa mine. These samples consisted of syenite country rock, and of altered syenite and altered syenite porphyry. The altered syenite samples were collected from the 4625' and 4750' levels along the North Branch of the Main Break (see figures IV and V). All the samples were taken from within a few feet of the fault plane, with the exception of sample R6462 which was taken from highly fractured ground about 75' from the fault. The strike length along which these samples were taken was about 500'. The altered syenite porphyry samples were collected from the 4625', 4750' and 4900' levels along the '04 Break (see figures IV, V and VI). All the samples were taken from within a very few feet of the fault surface. The strike length along which these samples were taken was about 1200'. The syenite country rock samples were all

taken from a large syenitic mass which is located between the two fault planes.

Six samples of alteration zone rock were selected from among those available in the Lindgren Collection at M.I.T. These samples were from four other mines in the district that are no longer open.

ANALYTICAL PROCEDURES

The analytical procedures used in this study were the standard procedures which are in use in the M.I.T. geochronology laboratory and which have been discussed by previous workers (see for example, Bence 1966). The strontium concentration and strontium isotopic composition of each sample were both made from a single Sr^{84} spiked analysis. All measured values of $\text{Sr}^{87}/\text{Sr}^{86}$ were normalized to a value of $\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$. The Rb^{87} decay constant used in the age calculations is $1.39 \times 10^{-10} \text{yr}^{-1}$. All the isochron analyses were made using the cubic least squares method of York (1966). For the purposes of the isochron analyses the errors on the measured $\text{Rb}^{87}/\text{Sr}^{86}$ ratios were taken to be 2% and the errors on the measured $\text{Sr}^{87}/\text{Sr}^{86}$ ratios were taken to be 0.1%. These errors are based on the analyses of many previous workers in the M.I.T. laboratory over a period of several years.

WHOLE ROCK ANALYSES

Syenite. Eight samples of syenite country rock from the Macassa mine were analyzed for Rb and Sr. The results of these analyses are listed in Table VI. These results are shown diagrammatically in Figure IX; the error limits for each analysis are given by the size of the rectangle given for each point. The samples show a large amount of scatter on the isochron plot; this is most probably due to the masking effect of the strontium contained in the carbonate mineralization, as will be discussed later. The least squares isochron age for these points is 2034 ± 108 m.y. and the initial strontium ratio is 0.7072 ± 0.0017 .

Altered Syenite. Eight samples of altered syenite from the Macassa mine were analyzed for Rb and Sr and the results are listed in Table VII; they are shown diagrammatically in Figure X. The least squares isochron age for these samples, minus sample R6458, is 1983 ± 116 m.y. and the initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio is 0.7068 ± 0.0020 . This isochron cannot be considered to be different than that for the syenite samples, within the limits of the isochron errors. Sample R6458 was excluded from the age calculation in order to obtain

the highest age value from these samples, since the purpose of this part of the study is to determine whether or not a younger age can be obtained from the rocks of the alteration zone than is obtained from the country rocks. Also, as will be shown later, this sample may not properly belong with the other samples on this plot. The inclusion of R6458 in the isochron age would lower it about 50 m.y.

As in the case of the syenite samples, the altered syenite samples show a large degree of scatter on the isochron plot, and this is probably due to the masking effects of the carbonate strontium.

Altered Intrusive. Six samples of altered intrusive rock from the main ore zone were selected from among those available in the Lindgren Collection at M.I.T. These samples were selected at random and are from four different mines that are no longer open. These samples were used to test the premise that all the altered rocks should yield approximately the same isochron age. The results of these analyses are listed in Table VIII, and they are shown diagrammatically in Figure XI. The least squares isochron age is 1917 ± 106 m.y. and the initial ratio is 0.7048 ± 0.0011 . Within the limits of the errors on the isochrons both this isochron and the altered syenite isochron are identical, and although both of these isochrons may suggest a lower age than does the syenite isochron, all three of the isochrons are indistinguishable from one another, within the limits of the isochron errors.

Conclusions of Whole Rock Analyses. Three suites of

whole rock samples from the Kirkland Lake district have been analyzed for Rb and Sr. These suites consisted of samples of syenite and altered syenite from the Macassa mine and a suite of altered syenitic rocks selected at random from various places throughout the alteration zone of the district. All three isochrons are of rather poor quality and within the limits of the errors on the isochrons they are indistinguishable from one another. The two suites of altered samples may give isochron ages that are slightly lower than that obtained from the suite of syenite samples, but there is no clear evidence to support this inference.

Two possibilities are suggested by the isochron analyses reported in this section. One possibility is that there was no large scale mixing and homogenization of the strontium in the alteration zone at the time of alteration, and the other possibility is that the alteration occurred only a very short time after the emplacement of the host rocks.

A third possibility not suggested by the foregoing analyses is suggested by the fact that all of these rock samples have been intensely carbonatized, leading to the development of calcite and dolomite in the rocks. This carbonate material would probably contain significant amounts of strontium which would not necessarily be a part of the radiogenic processes presently at work in the rocks, and this carbonate strontium might be masking the

correct isochron analyses of the rock samples. This possibility will now be investigated.

INVESTIGATION OF CARBONATE STRONTIUM

Leaching Experiment on Four Kirkland Lake Syenite

Samples. As a preliminary test of the effects of the carbonate strontium on the whole rock analyses one split of each of four samples of the syenite country rock was leached with 2N HCl and one split of each sample was leached with glacial acetic acid in order to determine the differences in amounts and compositions of Sr (and Rb) leached from the rocks by the two acids, and to determine the relative effects on the isochron analyses of the leached samples; a split of one sample was also leached with 6N HCl. The leaching procedure consisted of digesting the samples in 30 ml of acid for 20 minutes at room temperature. The filter papers used to filter two of the 2N HCl leached solutions were also examined for Rb to determine whether or not any insoluble Rb salts were being precipitated during the filtering process. These filter papers were boiled in 40 ml of demineralized water for 30 minutes, then the water was spiked with Rb spike and the solutions analyzed.

The results of all the analyses made in the leaching experiment are listed in Table IX, as are the whole rock sample analyses. These results show that the amount of Rb remaining in the filter papers was negligible. The

2N HCl leached more Sr and Rb from the rocks than did the acetic acid, and in general the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the 2N HCl leach were somewhat greater than were those of the glacial acetic acid leach. The amount and composition of the Sr leached by the 6N HCl was identical with that leached by the 2N HCl, although the amount of Rb leached by the 6N HCl would appear to be somewhat greater than that leached by the 2N HCl.

The greater $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the materials leached by the 2N HCl and the 6N HCl when compared with that leached by the glacial acetic acid are probably due to small amounts of radiogenic Sr^{87} being leached by the HCl as evidenced by the greater amounts of Rb leached. This will be discussed more fully in a later section. The greater amounts of Sr leached by the HCl when compared with that leached by the glacial acetic acid are most probably due to the fact that the HCl would tend to react to a greater extent with any dolomite present.

The results of the leached sample analyses are shown diagrammatically in Figure XII, along with the whole rock sample analyses. All three points corresponding to the three analyses of the same numbered sample are shown by the same symbol within the rectangles. The numbered point represents the whole rock sample; the point farthest up the isochron represents the sample after leaching with 2N HCl; the intermediate point represents the sample after it was leached with glacial acetic acid. The size of each

rectangle corresponds with the limits of the analytical errors for each point. Within the limits of these errors the three points for each sample fall on a straight line; this would be expected since the analyses of the materials leached from each numbered sample by both acids are rather similar. There appears to be a tendency for the samples leached with glacial acetic acid to give slightly lower $\text{Rb}^{87}/\text{Sr}^{86}$ ratios than would be expected, when compared with those of the unleached samples and the samples leached with 2N HCl, but it is not possible to say with certainty whether this slight effect is real or not.

The quality of the leaching analyses can be determined in two ways. One method is to extend tie-lines between the whole-rock and leached sample points and to extend these lines back to the line $\text{Rb}^{87}/\text{Sr}^{86} = 0$, on the isochron plot. Within the limits of the analytical errors each tie-line should intersect the line $\text{Rb}^{87}/\text{Sr}^{86} = 0$ at the value of the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the material leached from the sample. The other method is to calculate the material balance from the three sets of measurements made on each sample (i.e. whole rock, leached rock, and leached solution). This second method is quite sensitive to both the strontium concentrations and compositions in all three fractions of the sample.

In this study all three fractions of thirteen of the samples which were leached were analyzed. It will be seen later that when the graphical test of the quality of the

leaching analyses was applied to these samples three of them yielded poor tie-line linearity. When the arithmetic test was applied all of the samples gave excellent material balances. The reason for the three discrepant samples is discussed when the sample analyses are discussed.

The results of this leaching experiment suggest that improved isochron linearity might be obtained by removing the carbonate Sr; they also indicate that either 2N HCl or glacial acetic acid might yield satisfactory results, although the 2N HCl might be expected to give greater increase in linearity due to the fact that it would more completely remove the carbonate Sr than would the glacial acetic acid.

2N HCl was used to leach two groups of samples in the following section, glacial acetic acid was used to leach one group to test the theory that either acid should yield approximately the same isochron results.

LEACHED ROCK ANALYSES

Leached Syenite. Splits of all eight of the syenite samples previously analyzed as whole rocks were leached with 2N HCl and re-analyzed, splits of seven of these samples were leached and analyzed in duplicate. The results of these analyses are listed in Table X and they are shown diagrammatically in Figure XIII. All fifteen of the leached rock analyses are shown on the isochron plot so that a visual comparison can be made of the duplicate analyses. In the lower part of the diagram where the

error rectangles for several samples overlap similar symbols have been used for each of the sets of duplicates to help in distinguishing among the various samples. The agreement between the seven sets of duplicates is considered to be good.

The least squares isochron age for these samples is 2260 ± 88 m.y. and the initial ratio is 0.7017 ± 0.0022 . The linearity of this isochron is markedly improved over that of the whole rock syenite isochron (Figure IX). In Figure XIII it can be seen that fourteen of the fifteen points fall on the computed isochron. It is unfortunate that the spread in the Rb^{87}/Sr^{86} ratios for these samples is not greater, but these samples are composed predominantly of feldspar, with only minor biotite, etc., therefore the rather restricted range of Rb^{87}/Sr^{86} ratios is not surprising.

Listed in Table XI are the analyses of the solutions leached from these samples.

When the graphical test for the quality of the leaching analyses was applied to the eight syenite samples it was found that five of the samples gave excellent agreement. The tie-lines for samples R6475, R6476 and R6493 gave ordinate intercepts significantly below the Sr^{87}/Sr^{86} ratios measured in the leached solutions; for all three samples these intercepts were close to 0.710. When the arithmetic test was applied all eight leached syenite samples gave excellent agreement.

One possible reason for the non-linearity of the tie-line points for samples R6475, R6476 and R6493 could be due to errors in the Rb analyses of the leached samples. As can be seen in Table XI, from 1% to 3% of the Rb was leached from these rocks. If a 1% to 3% correction is made in the Rb/Sr values for these samples the linearity of the tie-line points is greatly increased. However, the radiogenic Sr^{87} occupies Rb lattice positions in the minerals, and because of the differences in the ionic sizes and charges of Rb and Sr, the radiogenic Sr^{87} is metastable in these Rb positions. It can therefore be assumed that if up to 3% of the Rb was leached from the samples than at least as much, if not more, Sr^{87} was also leached; the effect of this would be that the position of the leached rock point would not change relative to the position of the tie-line. However, the leaching of radiogenic Sr^{87} from the rock would also give greater than correct $\text{Sr}^{87}/\text{Sr}^{86}$ ratios in the material leached from the samples. An examination of Table XI will reveal that the 87/86 ratios of the material leached from samples R6475, R6476 and R6493 are somewhat greater than those of the other samples. And, although the analyses of the other samples indicate that approximately the same amount of Rb was leached from all the samples, considerably less Sr was leached from the three samples in question. Therefore, the effect of the addition of radiogenic Sr^{87} to these leached solutions would be more severe than with the

other samples. Also the Rb/Sr ratios of these three samples are the highest of all the samples, thus relatively more Sr^{87} was available for leaching from the samples. Calculations show that the leaching of 2% to 3% of the radiogenic Sr^{87} would easily account for the non-linearities observed in two of the three samples. For sample R6493 the leaching of 4% to 5% of the radiogenic Sr^{87} would be necessary to account for the non-linearity observed.

It will also be seen in Table VII and in Table XII, to follow, that the altered syenite porphyry sample which gave the greatest $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in the leached material (sample R6446) also had the greatest Rb/Sr ratio of all the altered syenite samples and next to the lowest amount of Sr leached. This greater $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in the leached material is also probably due to the relative effects of leached radiogenic Sr^{87} .

It would appear, therefore, that the non-linearities in the tie-lines for samples R6475, R6476 and R6493 are due to the greater than correct $\text{Sr}^{87}/\text{Sr}^{86}$ ratios in the leached solutions and are not due to the incorrect relative positions of the leached sample points on the isochron plot. The leaching of radiogenic Sr^{87} from the samples has probably had no more than a very minor effect on the leached sample isochrons, as is evidenced by the linearity of most of the tie-lines for both the leached syenite samples discussed here, and the leached altered syenite samples to be

discussed in the next section.

It is believed that the isochron age obtained from the leached syenite samples is the correct age of this body. This age (2260 m.y.) must be considered to be close to the maximum age for this body, within the limits of error placed on the isochron, since it is known from field relations to intrude the Timiskaming rocks which have been dated by Fairbairn as 2368 ± 48 m.y.

Leached Altered Syenite. Splits of four of the altered syenite samples showing approximate linearity in Figure X (samples R6444, R6446, R6462 and R6468) were leached with 2N HCl and re-analyzed, as was sample R6458. An isochron through the four best points, before leaching, gives an age of 1855 ± 79 m.y. and an initial ratio of 0.7071 ± 0.0014 .

The results of the leached rock analyses are listed in Table XII. The values for the leached rock analyses are plotted in Figure XIV; also shown on this figure are the values for the whole rock samples and the tie-lines showing the shift of the points with leaching. The isochron age for the four linear samples is 1826 ± 36 m.y. with an initial ratio of 0.7067 ± 0.0008 . The linearity of these four samples has been increased by the removal of the carbonate Sr while sample R6458 has been displaced further from the isochron, this may indicate that sample R6458 does not belong in the same group as the other samples.

When both the arithmetic and graphical tests for the quality of the leaching analyses were applied to these samples all five gave excellent agreement.

When compared with the leached syenite isochron (Figure XIII), the leached altered syenite isochron gives a significantly younger age than does that of the leached syenite.

Leached Altered Syenite Porphyry. Eight samples of altered syenite porphyry were leached with glacial acetic acid and then analyzed for Rb and Sr. Whole rock analyses were not made on any of these samples. The purpose of these analyses was to test the premise that any of the leached rocks of the alteration zone should yield approximately the same isochron age as that obtained from the leached altered syenite samples, and that either 2N HCl or glacial acetic acid should yield about the same leaching results.

The results of these analyses are listed in Table XIII and they are shown diagrammatically in Figure XV. These samples show a fair degree of scatter on the isochron plot. The least squares isochron age given by these samples is 1734 ± 122 m.y. and the initial ratio is 0.7044 ± 0.0012 . Within the limits of error placed on this isochron it gives an age identical with that given by the leached altered syenite isochron.

Conclusions of Leached Rock Analyses. Three suites of carbonatized rocks from the Macassa mine have been leached and analyzed for Rb and Sr. These suites consisted of splits of the syenite and altered syenite samples which had been previously analyzed as whole rocks and

a suite of altered syenite porphyry samples which have not been analyzed as whole rocks. The syenite and altered syenite samples were leached with 2N HCl; the altered syenite samples were leached with glacial acetic acid. The results of these analyses yield isochrons with greater linearity than those yielded by the whole rock samples. When the two isochrons obtained from the suites of altered rocks are compared it is seen that they give identical ages within the limits of the errors on the isochrons; when these two isochrons are compared with the isochron obtained from the leached syenite country rock it is seen that the rocks of the alteration zone yielded significantly younger ages than do the country rock samples.

DISCUSSION OF RESULTS

Leached Samples. The splits of the whole rock samples from which the carbonate minerals have been removed by leaching show increased linearity on the isochron plots, compared with the unleached samples, and the leached altered sample plots yielded significantly younger ages than do the unaltered samples; these younger ages are believed to represent the time of alteration. The mechanism which produced these younger ages is as follows.

At the time of alteration the original host rock minerals (chiefly feldspars) were destroyed and the alteration minerals sericite, chlorite, carbonates, etc., were formed. During this time the alteration zone did not remain a closed chemical system but rather was open to exchange with

the hydrothermal fluids. Because of the highly fractured nature of the wallrocks the various components of the fluids would have had great mobility, consequently there would have been large scale mixing and homogenization of the original fluid components with the components derived from the wallrocks. When the alteration minerals formed they incorporated strontium whose isotopic composition was homogeneous, or nearly so, thus forming a radiometric system distinguishable from the pre-existing wallrock system. The sericite is the principal Rb-bearing phase in this younger system and thus it is also the principal phase which contains the radiogenic Sr^{87} generated since the time of alteration. It is the sericite, therefore, which dates the time of alteration.

The examination of thin sections made from the altered samples reveals that there was post-alteration fracturing of the host rocks and that these later fractures were filled with carbonates and some quartz. Thus the rocks as a whole have not remained closed chemical systems since the time of alteration. There is no evidence, however, that the sericite mineralization has been affected by this later fracture filling or that any other Rb-bearing phases were formed in the post-alteration fractures. Therefore, the radiometric system formed at the time of alteration has not been disturbed since that time.

The carbonates which were formed at the time of hydrothermal alteration would have incorporated strontium whose

isotopic composition was the same as that incorporated by the other alteration minerals. This strontium would act merely as a diluent and its inclusion in or exclusion from the whole rock analyses would not affect the age analyses. The post-alteration carbonate, however, most probably incorporated strontium whose isotopic composition was not similar to that incorporated by the alteration minerals and the inclusion of this strontium in the whole rock analyses could affect the age analyses significantly. By removing all of the carbonate mineralization by leaching and analyzing the leached rock material the correct age of the alteration minerals (i.e. the sericite) is obtained; the Rb and the radiogenic Sr^{87} measured in the leached rocks comes primarily from the sericite, and the $\text{Sr}^{87}/\text{Sr}^{86}$ composition which is estimated from the isochron analysis is the initial strontium composition which was incorporated by all the alteration minerals.

The ages calculated from the two suites of leached altered rock isochrons agree within the limits of the isochron errors, and this correspondence of ages indicates that this is the true age of the alteration. The two suites of altered rocks were collected from two separate fault zones which are roughly parallel and which range in separation from about 400 to 500 feet (see discussion of "Samples"). The alteration zones around these two faults do not overlap and there are no significant structural breaks between them that would have enabled the

hydrothermal fluids in the two fault zones to intermix. Each of the fault zones can therefore be considered to have been isolated from the other at the time of alteration, thus the alteration minerals which developed in each of the fault zones were separate but contemporaneous systems. The slight difference in the initial ratios of the two leached altered rock isochrons may be an indication that the two fault zones were indeed isolated from one another with respect to the strontium isotopic homogenization.

The leached altered syenite porphyry samples appear to show more scatter on the isochron plot (Figure XV) than do the leached altered syenite samples (Figure XIV). This relationship may be more apparent than real because the scales of the two diagrams differ by a factor of 5. The scatter of the sample points on the plots may indicate that the strontium isotopic homogenization was not complete in either of the two fault zones or else the distance over which the homogenization occurred was exceeded during the collection of the samples; the data presented here are insufficient to distinguish between these two possibilities.

Leached Carbonate. It has been shown that the carbonate mineralization in the rock samples detracts from the quality of the isochron analyses, and that this must be due to the post-alteration fracture fillings since the carbonate which was formed at the time of alteration should have no effect on the age analyses. The actual composition of the post-alteration carbonate cannot be measured, but it

must have a greater $\text{Sr}^{87}/\text{Sr}^{86}$ composition than the carbonate formed at the time of alteration. The alteration carbonate would have a strontium isotopic composition similar to the initial compositions calculated from the isochron analyses. In the case of the leached altered syenite this composition is about 0.707. From Table XII it can be seen that the $\text{Sr}^{87}/\text{Sr}^{86}$ of the leached carbonate is in the range of 0.713 to 0.719. It was also shown earlier that a part of these higher ratios in the leached materials are probably due to excess radiogenic Sr^{87} leached from the rock minerals, as is evidenced by the small amounts of Rb leached. For most of the solutions, however, this excess Sr^{87} would raise the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions by about 0.001 to 0.003. This is clearly too small an increase to account for the observed strontium compositions in the solutions; the rest of these greater $\text{Sr}^{87}/\text{Sr}^{86}$ compositions in the solutions must be due to the relatively greater Sr^{87} content of the post-alteration carbonate compared with the composition of the alteration carbonate.

SUMMARY AND CONCLUSIONS

The analyses of a suite of syenite country rock samples and two suites of altered syenitic samples from the Kirkland Lake district have yielded Rb-Sr whole rock isochrons of rather poor quality and indistinguishable age (about 2000 m.y.), although it might be inferred that the altered rocks tended to give lower ages than did the country rocks. These rocks have all been intensely carbonatized; this

carbonate material is of at least two generations, and it contains significant amounts of strontium. When the syenite and altered syenite samples were leached with dilute acid and re-analyzed the linearities of the two isochrons were improved and the two rock types yielded significantly different ages. The leached syenite samples yielded an age of 2260 ± 88 m.y. and the leached altered syenite samples yielded an age of 1826 ± 36 m.y. A suite of altered syenite porphyry samples was leached with dilute acid and re-analyzed. These samples yielded an isochron age of 1734 ± 122 m.y., an age which is identical with that measured for the leached altered syenite samples, within the limits of the isochron errors.

It is believed that the leached syenite isochron age of 2260 ± 88 m.y. is the true age of this intrusive body. It cannot be older as it intrudes Timiskaming rocks which have been dated by Fairbairn as 2368 m.y. It is also believed that the leached altered syenite and the leached altered syenite isochrons approximate the time of hydrothermal alteration and, by inference, the time of mineralization. The younger ages measured in the altered rocks are due to the fact that these rocks are composed of alteration products which incorporated strontium of an approximately uniform isotopic composition. The correspondence of the ages from the two different rock types, collected from two different fault zones, lends support to the validity of the ages measured.

The data presented here are not sufficient to make any reliable estimation about the extent over which the strontium isotopic compositions were homogenized at the time of alteration. It would appear that this homogenization must have occurred over areas of comparable sizes to the ones over which the altered syenite and altered syenite prophyry samples were taken, that is, up to about 1200' along the strike of the faults and up to about 300' in height; the distances away from the fault zones at which the samples were taken were negligible.

Probably the best way to test for the actual extent over which homogenization occurred would be to collect samples from along several isolated, or semi-isolated, faults of varying extents and to compare the quality of the isochron analyses obtained from each suite of samples. Because of the uniformity of the alteration throughout both the lateral and vertical extent of the mineralized area in the Kirkland Lake district, and because the wallrock alteration is not zoned mineralogically, the Macassa mine should provide an ideal setting in which to carry out this type of study.

Listed in Table XIV are the ages measured in this study along with the ages of other rock units in the Kirkland Lake area that have been measured previously by other workers. The 2260 m.y. age for the syenite is geologically reasonable when compared with the age of the folded Timiskaming rocks which it intrudes. The 1830 m.y. age of the Otto stock indicates that there was igneous activity in the area at about the same time that has been measured for the time of hydrothermal alteration in the Kirkland Lake district, about 1800 m.y. ago.

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INTRODUCTION

The classical method of determining the ages of ore deposits is to obtain the ages of the associated country rocks and then to bracket the time of mineralization through field relations. This procedure gives the maximum-minimum time span in which the mineralization must have occurred.

Age determinations on ore minerals have been made by the helium method (Hurley, 1954); in this method the concentrations of uranium, thorium and radium in the sample are measured, as is the volume of helium produced through the radioactive decay of these elements; the method is subject to large errors.

In recent years the lead-lead age technique has been used to date galena samples from various ore bodies. Such ages, however, more nearly correspond to the time of separation of the lead from its uranium and thorium parents, and these ages may or may not correspond to the time of emplacement of the leads in their present locations. Also, there is the problem of the contamination of these leads with crustal lead during the passage of the mineralizing solutions through the country rocks.

Recently Turek (1966) has dated gold mineralization in western Australia by using the Rb-Sr whole rock method of samples of rocks associated with the gold ores. These samples contained the Rb-rich phases biotite, muscovite,

and sericite, presumably formed contemporaneously (or nearly so) with the gold mineralization, and the ages measured are considered to represent the time of gold mineralization. Ohmoto, et al, (1966) measured the K-Ar and Rb-Sr age of muscovite which was found intergrown with sulfide mineralization, and the ages of some albite-actinolite mixtures from late-stage hydrothermal veins, at Providencia, Mexico, and have taken these ages to represent the time of mineralization. McDowell and Kulp (1967) measured the K-Ar ages of five unaltered monzonite host rock samples and two biotite-argillic alteration samples from the Robinson district, Nevada, and have shown that within the limits of analytical error the intrusion and hydrothermal alteration of the host rocks were contemporaneous. Since the geological evidence indicated that the alteration and mineralization were contemporaneous, McDowell and Kulp deduced that the intrusion, alteration, and ore deposition were genetically related.

In the first part of the present study strontium-rich, rubidium-poor, gangue minerals (fluorite, calcite and barite) from some hydrothermal vein-type mineral deposits were analyzed for their strontium isotopic compositions. If the strontium in these minerals were derived solely from primary magmatic sources (i.e. primary subcrustal source regions having Rb/Sr ratios similar to those in the source regions of basalts), this should be reflected in uniformly low (less than about 0.710) Sr^{87}/Sr^{86} ratios

in the minerals. The measurement of such ratios in samples from various deposits would then provide another parameter for characterizing the nature of the mineralizing fluids and their source regions. Such measurements might also provide a means of applying a correction to measurements made on carbonate-flooded rocks from ore zones. If the strontium were derived in part, or in toto, from pre-existing, Rb-rich, crustal rocks, this might be apparent from the gangue $\text{Sr}^{87}/\text{Sr}^{86}$ ratios.

In the latter part of this study three different approaches were made to the problem of dating ore mineralization.

The first approach consisted of comparing age analyses of samples of fresh and altered wallrocks associated with the gold ores at Kirkland Lake, Ontario. The alteration zone rocks have undergone widespread, low-grade alteration, and the rocks are comprised predominantly of alteration products. If these alteration products were formed at a time significantly later than the formation of the host rocks, and if they incorporated strontium of approximately uniform isotopic composition, then these altered rocks should contain a mixture of materials of two different ages, with the younger age predominating. The age analyses of these rocks should yield ages which approach that of the younger material; these ages will approximate the time of alteration and, by inference, the time of mineralization.

The second approach to the problem of dating ore mineralization consisted of measuring trace amounts of Rb and Sr in massive sulfide samples from the Rouyn-Noranda district of Quebec. The premise of this approach is that these trace elements in the ores represent the compositions of these elements in the mineralizing fluids and that the ages measured should be the age of the mineralizing fluids and thus the age of the ore minerals.

The third approach consisted of measuring trace amounts of Rb and Sr in samples of gold-quartz from the Porcupine district, Ontario.

CHAPTER I
ANALYTICAL PROCEDURES

General

All rubidium and strontium concentrations were measured by isotope dilution using a mass spectrometer. In the early part of this work, when only strontium isotopic compositions were determined, these determinations were made directly on the unspiked samples. The later analyses of compositions and concentrations of strontium were both made from a single spiked sample.

In general, the standard analytical procedures in use in the M.I.T. Geochronology Laboratory were used throughout this investigation, although some modifications of these procedures were necessary in handling the extremely large samples of sulfide ores. The last detailed discussion of these standard procedures was given by Bence (1966). However, since that time some minor changes in these procedures have taken place, therefore the discussion will be repeated here in considerable detail.

Sample Preparation

The whole rock samples were first scrubbed with a stiff-bristled brush, using demineralized water, to remove any surface dirt, after which the samples were rinsed with demineralized water and dried with acetone. The samples were then broken up on a clean steel plate using a small sledge hammer. The resultant rock chips were put through a small jaw crusher and further reduced in size to about

10 mesh. Between each sample the plates of the jaw crusher were loosened and the assembly cleaned of rock dust and fragments by means of a compressed air jet. Fine-grinding of the samples was accomplished by means of a PICA blender mill; the grinding vials used in this mill were disassembled between each sample and cleaned by means of a test tube brush using soap and water, followed by a tap water rinse, then followed by two successive rinsings with 2N HCl and demineralized water, and finally an acetone rinse.

The approximate concentrations of rubidium and strontium, which must be known in order to be able to properly spike the samples, were obtained by means of X-ray fluorescence. The instrument used in this laboratory is a Norelco unit equipped with a molybdenum tube and a topaz crystal. The 2θ peaks for Rb and Sr were scanned at $1/2^\circ$ per minute and peak intensities compared with those obtained from standard granite G-1 (256 ppm Sr and 219 ppm Rb). Although the precision for these runs was low (several percent) they were quite adequate for spiking purposes. Because the concentrations of rubidium and strontium in the sulfide ores were below the limits of detectability of this instrument, the samples were prepared and spiked using an assumed concentration of 0.5 to 1.0 ppm.

In general, whole-rock sample sizes were used which contained about 100 μg Sr, the Rb content was usually less, perhaps 50 μg on the average. The amount of Sr and Rb in the sulfide samples was only a few micrograms.

The gangue minerals examined at the beginning of this study were prepared in much the same way as the whole rocks, except that the initial sample crushing was done with a clean steel mortar and pestle, rather than with the jaw crusher.

The massive sulfide samples were first crushed with a clean steel mortar and pestle followed by a fine grinding in the PICA blender mill. The powdered sample was then placed in a clean stainless steel pan and roasted over a Bunsen burner to convert the sulfides to oxides, which were then weighed out for analysis.

Chemistry

Isotope Dilution Techniques. An isotope dilution analysis is an addition analysis in which a precisely measured volume of a "spike" solution, whose concentration and isotopic composition are precisely known, is added to a precisely weighed sample. The samples are weighed on an analytical balance and the spikes are dispensed by means of pyrex pipettes calibrated to National Bureau of Standards tolerances ($\pm 0.2\%$).

The spiking ratio used for strontium in this study was $\text{Sr}^{84}/\text{Sr}^{86} = 1.0$. The optimum spiking ratio for rubidium (based on normal and spike compositions) is $\text{Rb}^{85}/\text{Rb}^{87}$ equals 0.85; in general, however, a ratio closer to 1.0 was used as it was still close to the optimum ratio and it also reduced instrumental measuring errors to a minimum.

Spike Solutions. Three Sr^{84} -enriched spikes and three Rb^{87} -enriched spikes were used in this investigation. Two of the Sr^{84} spikes and two of the Rb^{87} spikes used were the same as those described by Bence (1966); one Sr^{84} spike contained 1.036 micrograms Sr^{84}/ml while the other Sr^{84} spike contained 4.85 micrograms Sr^{84}/ml ; one Rb^{87} spike contained 2.89 micrograms Rb/ml while the other Rb^{87} spike contained 14.47 micrograms Rb/ml . During the course of this study the supplies of these spikes were exhausted, and a new Sr spike containing 1.95 micrograms Sr^{84}/ml and a new Rb spike containing 11.305 micrograms Rb/ml were prepared by the laboratory staff.

Spikes used in this laboratory were obtained as pure, isotopically-enriched salts from Oak Ridge National Laboratory. The spikes were dissolved in 2N HCl and the solutions were then calibrated against standard shelf solutions of precisely known concentration and isotopic composition. The calibration of spike solutions has been detailed by Shields (1964).

Reagents used in the dissolution of samples were reagent grade HF, triple distilled HClO_4 , vycor distilled 2N HCl, vycor distilled HNO_3 , reagent grade (A.C.S.) ethyl acetate, and reagent grade (A.C.S.) acetic acid. The HF, HClO_4 , ethyl acetate and acetic acid were obtained commercially; the HCl and HNO_3 were vycor distilled at M.I.T. from reagent grade acids.

Samples were digested in platinum; stirring rods were

teflon. The centrifuge tubes used were vycor. The ion exchange columns were vycor and polypropylene. Ion exchange fractions were collected and evaporated in 100 ml polypropylene beakers. The samples were ignited and stored in 5 ml vycor beakers. All reagents, spike solutions and shelf solutions prepared in this laboratory were stored in polyethylene containers.

Sample Digestion Procedure. Weighed whole-rock samples were placed in clean platinum dishes and moistened with demineralized water. The appropriate amounts of spike were added, and then the samples were digested on a steambath using 20 ml HF and 2 ml HClO_4 per gram of sample. When the samples had been taken nearly to dryness a second aliquot of HF was added, and the samples again digested until nearly dry. At this point 20 ml of vycor distilled 6N HCl were added and the sample residue taken into solution.

Separation of Rubidium. The alkali perchlorates are sparingly soluble in concentrated acid, so the result of the previous step is that while most of the sample material was taken up into solution the alkalies were not. The solution and residue were then washed into a vycor centrifuge tube with a few ml of 6N HCl and centrifuged. The clear liquid was decanted back into the platinum dish and the precipitate was washed into a clean vycor dish with two or three washings of 2-3 ml each of ethyl acetate. Potassium perchlorate is slightly soluble in ethyl acetate;

therefore, when the ethyl acetate was decanted from the dish some of the potassium was removed from the sample. The dish was then placed on a warm hot plate and the sample dried. It was then taken into solution with 2 or 3 ml of 2N HCl and washed into a clean 5 ml vycor beaker and evaporated to dryness on the hot plate.

Separation of Strontium. A few ml of carrier-free Sr^{85} tracer were added to the decantate returned to the platinum dish from the centrifuge and the sample was placed on the ion exchange column. The columns used were of vycor glass and each contained about 100 ml of Dowex 50-8X, 200-400 mesh, H^+ resin. Approximately 800 ml of 2N HCl were required to elute a strontium sample through one of these columns. The position of the strontium on the column was monitored by means of the Sr^{85} tracer. The samples were collected in 40 ml fractions and the two or three fractions showing the greatest tracer activity were evaporated down and combined for the strontium sample.

Procedure for Leaching Carbonate from Whole Rock Samples. All of the whole rock samples from the Kirkland Lake district of Ontario contained carbonate minerals (calcite and dolomite) which were introduced during and/or after the alteration of the rocks. Whole rock analyses were made on most of these samples, then selected samples were leached with either 2N HCl or reagent grade glacial acetic acid to determine the effect of the carbonate on the age analyses. The following leaching procedure was used.

A few grams, generally about $1\frac{1}{2}$, of sample were weighed into a clean polypropylene beaker. 20 ml of acid were added and the mixture stirred with a teflon stirring rod. The samples were allowed to digest for 10 minutes, at room temperature, with occasional stirring, then 10 ml more acid were added, the samples stirred again and allowed to digest for another 10 minutes with occasional stirring. None of the samples showed any visible effervescence at the end of the 20 minute period. The samples were then filtered. The samples and filter paper were washed with three 5-ml aliquots of demineralized water; these washings were added to the filtered solutions. The leached samples were dried and then reanalyzed by isotope dilution mass spectrometry. The leached solutions from some of the leached samples were also analyzed.

Preparation of Sulfide Samples. The previously oxidized ores were weighed out and placed into platinum dishes. Because of the very large sample size (30 to 50 grams) each sample was split into two portions and placed into two platinum dishes. 100 ml of 6N HCl were placed into each dish and the samples were digested on the steam bath until a sludge began to form. 200 ml 2N HCl were then added and the digestion continued. Usually another aliquot of 150 ml of 2N HCl was required to bring the samples into solution. When the samples had been evaporated down until the sludge again began to form they were removed from the steam bath and just enough 2N HCl added to bring the

chlorides in the cooled sample into solution. Usually a residue of quartz and some free sulfur remained. This residue was filtered off and both the residue and filter were washed with a few ml of demineralized water. This washing was added to the chloride solution. The two halves of the sample were combined and at this point the Rb and Sr spikes, as well as the Sr⁸⁵ tracer, were added.

Because of the low concentrations of Rb present in the sulfide ore samples, the method of rubidium separation used for the whole rock samples could not be used, as it required a visible perchlorate precipitate. Therefore the rubidium separation had to be made on the ion exchange column also. Because of the extremely large amounts of iron and copper present, the samples could not be placed directly on the regular exchange column without the danger of overloading the resin. Therefore, a large ion exchange column was constructed from a 1000 ml polyethylene graduate. This column contained about 500 ml of Dowex resin. About 1200 ml of 2N HCl were required to elute most of the iron and copper through the column; another 3000 ml were required to elute the rubidium and strontium. This last volume was collected and evaporated down to about 40 ml and this was placed on the normal ion exchange column. At the time these analyses were made a radioactive Rb tracer was not available commercially, so the entire volume of solution taken from the column after the emergence of the iron band and before the

emergence of the strontium was combined and evaporated down for the rubidium sample.

Sample Ignition. All rubidium and strontium samples were transferred to 5 ml vycor beakers after they had been evaporated down to small volumes. The rubidium samples which had been separated as perchlorates were dried on a hot plate, then ignited over a Bunsen burner to eliminate the perchlorate. The rubidium and strontium samples which had been separated on the ion exchange columns were each treated with a few drops of perchloric acid to oxidize any resin which may have been present in the sample, evaporated to dryness, and then ignited. Two or three ml of 1:1 vycor distilled HNO_3 were added to each sample to convert them to nitrates, the samples were evaporated to dryness, and then stored until such time as they could be analyzed on the mass spectrometer.

Mass Spectrometry

In the course of this investigation three different mass spectrometers were used. These are all 6-inch, 60° sector, single filament, solid source, Neir-type instruments. Cary Model 31 vibrating reed electrometers are used to amplify the ion beam current, and the VRE output is recorded on Brown strip chart recorders. Each vacuum system consists of a mercury diffusion pump backed by an oil-sealed mechanical fore pump. A liquid nitrogen cold trap, for cryogenic pumping of condensibles, is located between the mercury pump and the analyzer tube. Pressures

less than 5×10^{-6} mm Hg are necessary for rubidium runs, and pressures less than 1×10^{-6} mm Hg are necessary for strontium runs. During the first part of this work measurements were made by continuous magnetic scanning over the appropriate mass ranges; later in this study magnetic peak hopping was used for most runs.

Filaments of tantalum ribbon, 0.020" wide and 0.001" thick, were employed for all analyses. Each filament was monitored for cleanliness in the mass spectrometer before it was used for making an analysis. Each sample, stored in a vycor beaker, was taken into solution in one drop of vycor distilled 1:1 HNO_3 , and loaded onto the filament with a clean vycor pipette tip. A 1-ampere electric current was passed through the filament until the sample was evaporated to dryness.

Calculation of Strontium Isotopic Composition

Natural strontium has the following isotopic ratios (Nier, 1938):

$$\text{Sr}^{86}/\text{Sr}^{88} = 0.1194$$

$$\text{Sr}^{84}/\text{Sr}^{86} = 0.006783$$

The composition of the Sr^{84} spike used in this study was measured several times in the M.I.T. Geochronology Laboratory by several different workers; the average of these measurements gave the following isotopic ratios for the spike, and these were the ones used in this study:

$$\text{Sr}^{86}/\text{Sr}^{84} = 0.04685$$

$$\text{Sr}^{87}/\text{Sr}^{84} = 0.01574$$

$$\text{Sr}^{88}/\text{Sr}^{84} = 0.13875$$

A mixture of sample and spike strontium will have an isotopic composition which is a mixture of the sample and spike compositions and which depends on the relative amounts of sample and spike in the mixture. The approximate composition of the mixture can be measured on the mass spectrometer, and from this measurement the correct isotopic composition of the mixture and the relative amounts of sample and spike in the mixture can be calculated, as can the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the sample.

The following discussion is largely a revision of the discussion given by Van Schmus (1966). In this discussion the subscripts M, sa and sp refer to the mixture, the sample and the spike respectively. An asterisk (*) after a subscript indicates that the quantity referred to is only an approximate one as will be explained later in the discussion.

From the mass spectrometer measurements the ratios $(84/86)_{M^*}$, $(87/86)_{M^*}$ and $(88/86)_{M^*}$ can be calculated. If mass discrimination did not occur during the analysis these ratios would be the true isotopic ratios in the mixture, but discrimination almost invariably occurs. From the measured ratios it is necessary to determine the fraction of each ratio due to the spike, the fraction of each ratio due to the sample, the $87/86$ composition of the sample, and the amount of discrimination that has occurred.

These values can be found in the following manner. A plot is made of $(\text{Sr}^{84}/\text{Sr}^{86})_M$ vs $\text{Sr}^{84}_{sa}/\text{Sr}^{86}_M$. From the

isotopic ratios given at the beginning of this section this plot must have end values of

$$(84/86)_M = 21.34 \text{ at } 84_{sa}/86_M = 0$$

$$84_{sa}/86_M = 0.0568 \text{ at } (84/86)_M = 0$$

Since most of the strontium samples were spiked to give an $(84/86)_M$ of about 1.0 a large scale plot of the range of $(84/86)_M$ from 0.5 to 1.5 was prepared (Figure I). From the chart the value of $84_{sa^*}/86_M$ which corresponds to the value of $(84/86)_{M^*}$ is found. Then the following subtraction can be made:

$$\frac{84_{M^*}}{86_M} - \frac{84_{sa^*}}{86_M} = \frac{84_{sp^*}}{86_M} \quad (1)$$

Then

$$\frac{84_{sp^*}}{86_M} \times \left(\frac{86}{84} \right)_{sp} = \frac{86_{sp^*}}{86_M} \quad (2)$$

and

$$\left(\frac{86}{86} \right)_M - \frac{86_{sp^*}}{86_M} = \frac{86_{sa^*}}{86_M} \quad (3)$$

where $(86/86)_M$ must obviously be 1.0000.

In the same manner:

$$\frac{84_{sp^*}}{86_M} \times \left(\frac{88}{84} \right)_{sp} = \frac{88_{sp^*}}{86_M} \quad (4)$$

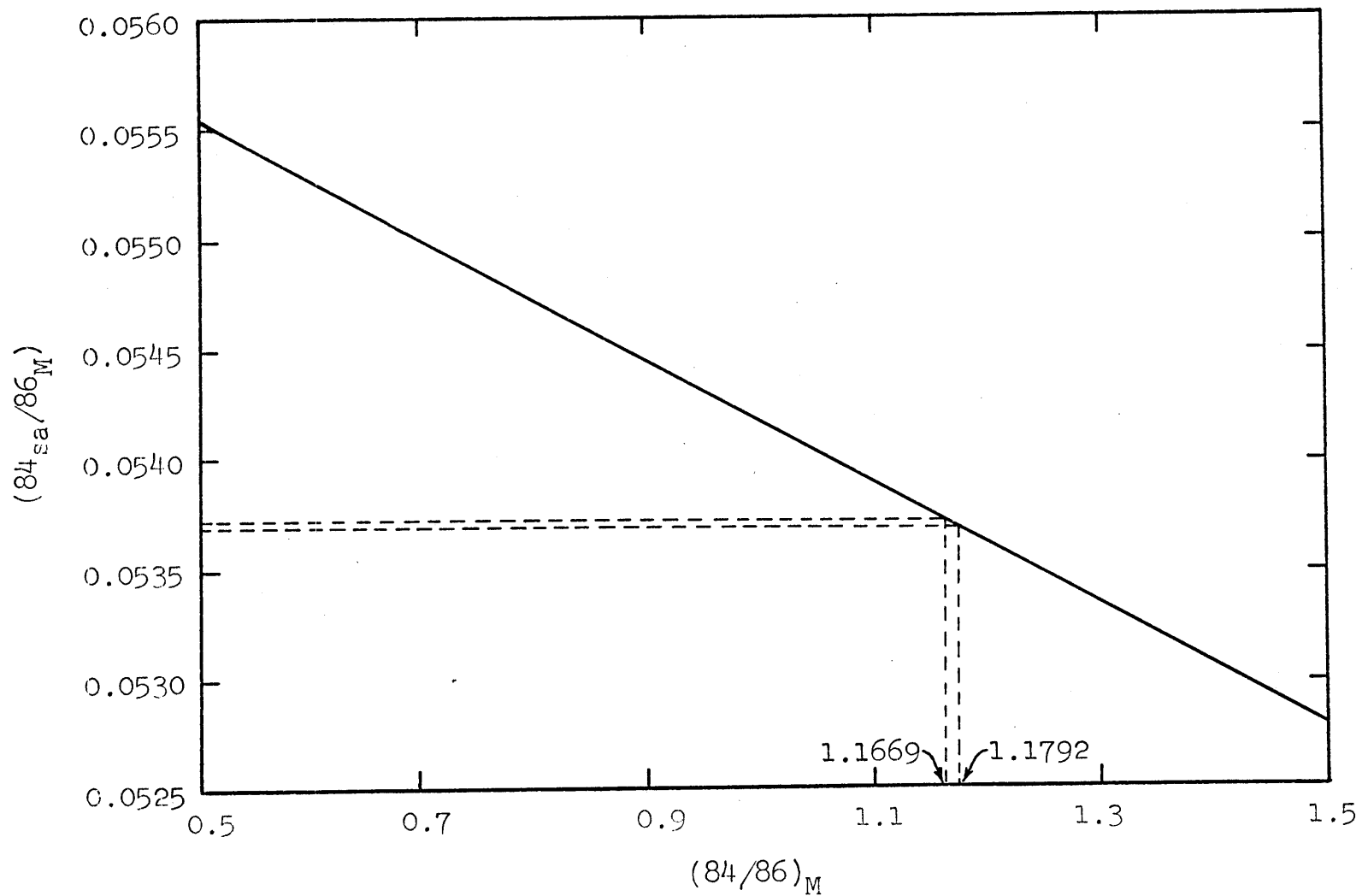
and

$$\left(\frac{88}{86} \right)_M - \frac{88_{sp^*}}{86_M} = \frac{88_{sa^*}}{86_M} \quad (5)$$

Dividing (3) by (5):

$$\frac{86_{sa^*}}{86_M} \bigg/ \frac{88_{sa^*}}{86_M} = \left(\frac{86}{88} \right)_{sa^*} \quad (6)$$

FIGURE I
PLOT OF $(84/86)_M$ vs $(84_{sa}/86_M)$ FOR A MIXTURE OF
NORMAL AND SPIKE STRONTIUM



where $(86/88)_{sa^*}$ is the measured ratio of the sample 86/88 in the mixture.

In this first trial calculation the corresponding $(87/86)_{sa^*}$ calculation is ignored.

By use of the ratio obtained in (5) the measured ratios of the mixture can be corrected for mass discrimination. In this study all strontium runs were corrected to $(86/88)_{sa} = 0.1194$, therefore the normalization factors are:

$$\left(\frac{88}{86}\right)_{saN} = \frac{(86/88)_{sa^*}}{0.1194} \quad (7)$$

where the subscript N denotes a normalized value. Also:

$$\left(\frac{84}{86}\right)_{saN} = \frac{1}{(88/86)_{saN}} \quad (8)$$

since the $(84/86)_{sa}$ correction is equal in amount to the $(88/86)_{sa}$ correction but is in the opposite direction.

Similarly the $(87/86)_{sa}$ correction can be shown to be:

$$\left(\frac{87}{86}\right)_{saN} = \frac{(86/88)_{sa^*} + \frac{0.1194 - (86/88)_{sa^*}}{2}}{0.1194} \quad (9)$$

or, one half the $(86/88)_{sa}$ correction.

The factors found in (7), (8) and (9) are applied to the originally measured ratios to correct them for mass discrimination and the entire procedure through step (6) is repeated, this time yielding the correct quantities. In this second iteration the same types of calculations that are shown in the first six steps are also applied to the $(87/86)_M$ ratio, i.e.:

$$\frac{84_{sp}}{86_M} \times \left(\frac{87}{84}\right)_{sp} = \frac{87_{sp}}{86_M} \quad (10)$$

and

$$\left(\frac{87}{86}\right)_M - \frac{87_{sp}}{86_M} = \frac{87_{sa}}{86_M} \quad (11)$$

The correct, normalized value for the sample (87/86) is then found from the results of (11) and (3), i.e.:

$$\frac{87_{sa}}{86_M} \bigg/ \frac{86_{sa}}{86_M} = \left(\frac{87}{86}\right)_{saN} \quad (12)$$

The following numerical example will illustrate the method. The ratios calculated from a mass spectrometer run were found to be:

$$(84/86)_{M^*} = 1.1792$$

$$(87/86)_{M^*} = 0.7262$$

$$(88/86)_{M^*} = 8.0075$$

From the graph the value of $84_{sa^*}/86_M$ corresponding to $84_{M^*}/86_M$ is found to be 0.0537. Then from (1):

$$84_{sp^*}/86_M = 1.1255$$

from (2)

$$86_{sp^*}/86_M = 0.0527$$

from (3)

$$86_{sa^*}/86_M = 0.9473$$

from (4)

$$88_{sp^*}/86_M = 0.1561$$

from (5)

$$88_{sa^*}/86_M = 7.8514$$

These numbers can be conveniently tabulated as follows:

<u>84/86</u>	<u>86/86</u>	<u>87/86</u>	<u>88/86</u>
1.1792 m*	1.0000 M	0.7262 M*	8.0075 M*
-0.0537 sa*	-0.0527 sp*		-0.1561 sp*
<hr/>	<hr/>		<hr/>
1.1255 sp*	0.9473 sa*		7.8514 sa*

and from (6):

$$(86/88)_{sa*} = 0.12065$$

The corresponding normalization factors are then found to be:

from (7)

$$(88/86)_{saN} = 1.0147$$

from (8)

$$(84/86)_{saN} = 0.98964$$

and from (9)

$$(87/86)_{saN} = 1.00524$$

Applying these correction factors to the originally measured ratios and referring back to the graph, the second iteration is made:

<u>84/86</u>	<u>86/86</u>	<u>87/86</u>	<u>88/86</u>
1.1669 M	1.0000 M	0.7300 M	8.0913 M
-0.0537 sa	-0.0522 sp	-0.0175 sp	-0.1545 sp
<hr/>	<hr/>	<hr/>	<hr/>
1.1132 sp	0.9478 sa	0.7125 sa	7.9368 sa

Now, again, from (6):

$$(86/88)_{saN} = 0.1194$$

and from (11):

$$(87/86)_{saN} = 0.7532$$

which are the correctly normalized values for the sample isotopic composition.

Calculation of Strontium and Rubidium Concentrations
from Isotope Dilution Analyses

Strontium. The concentration of Sr^{86} in ppm in a sample can be calculated from the following equation:

$$\text{Sr}^{86}_{\text{ppm}} = \frac{(\text{Sr}^{84}_{\text{ugm/ml Spike}})(\text{ml Spike})}{\text{Sample weight in grams}} \left(\frac{^{86}_{\text{sa}}}{^{84}_{\text{sp}}} \right) \left(\frac{\text{at.wt.}^{86}}{\text{at.wt.}^{84}} \right) \quad (13)$$

where the quantity $(^{86}_{\text{sa}}/^{84}_{\text{sp}})$ is the isotopic ratio of the sample Sr^{86} to the spike Sr^{84} in the mixture and can be found by dividing the results of (3) by the results of (1), after the ratios have been correctly normalized, i.e.:

$$\frac{^{86}_{\text{sa}}}{^{86}_{\text{M}}} \bigg/ \frac{^{84}_{\text{sp}}}{^{86}_{\text{M}}} = \frac{^{86}_{\text{sa}}}{^{84}_{\text{sp}}} \quad (14)$$

The concentration of total strontium in ppm in the sample can be found from the following equation:

$$\text{Sr}_{\text{ppm total}} = \text{Sr}^{86}_{\text{ppm}} / \text{Weight } \% \text{ Sr}^{86} \quad (15)$$

The weight percent of Sr^{86} in natural strontium is, however, a function of the $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the sample, since all the other isotopic ratios are constant. In this laboratory a large scale plot of weight % vs $\text{Sr}^{87}/\text{Sr}^{86}$ has been prepared and the weight % Sr^{86} corresponding to the measured $\text{Sr}^{87}/\text{Sr}^{86}$ in a given sample can be easily found from the chart.

Rubidium. Natural rubidium has the isotopic fractions:

$$\text{Rb}^{85} = 0.7215$$

$$\text{Rb}^{87} = 0.2785$$

and has a total atomic weight of 85.56. The rubidium spike in use in this study had the isotopic fractions:

$$\text{Rb}^{85} = 0.0082$$

$$\text{Rb}^{87} = 0.9918$$

and had a total atomic weight of 86.99.

A mixture of natural (sample) and spike rubidium has the following relation:

$$\frac{85_M}{87_M} = \frac{85_{sa} + 85_{sp}}{87_{sa} + 87_{sp}} \quad (16)$$

where the subscripts M, sa and sp once again refer to the mixture, the sample and the spike, respectively. This equation can also be written:

$$\frac{85_M}{87_M} = \frac{F_{85n}(N) + F_{85s}(S)}{F_{87n}(N) + F_{87s}(S)} \quad (17)$$

where the quantities F_{85n} , F_{85s} , F_{87n} and F_{87s} are the isotopic fractions of natural 85, spike 85, natural 87 and spike 87, respectively, and where the quantities N and S are the percentages of natural (sample) and spike rubidium in the mixture, respectively. By substituting the isotopic fractions into (17):

$$\frac{85_M}{87_M} = \frac{0.7215 N + 0.0082 S}{0.2785 N + 0.9918 S} \quad (18)$$

and then rearranging:

$$\frac{N}{S} = \frac{0.9836}{0.7215 - 0.2785(85_M/87_M)} \quad (19)$$

where now $(85_M/87_M)$ is the isotopic ratio of the mixture 85 to 87 and is measured on the mass spectrometer, and

where the ratio N/S is to be determined. Then the total rubidium, in ppm, in the sample can be calculated by the following equation:

$$Rb_{sa} = \frac{(Rb_{ugm/ml \text{ Spike}})(ml \text{ Spike})}{\text{Sample weight in grams}} \left(\frac{N}{S} \right) \frac{\text{At.wt.Normal Rb}}{\text{At.wt.Spike Rb}} \quad (20)$$

Since rubidium has only two isotopes, only one isotopic ratio can be measured, consequently no correction for mass discrimination is possible.

Principles of the Rubidium-Strontium Age Method

Natural strontium has four stable isotopes - Sr^{84} , Sr^{86} , Sr^{87} , and Sr^{88} . Natural rubidium has two isotopes - Rb^{85} and Rb^{87} ; Rb^{85} is stable, but Rb^{87} is radioactive and decays to Sr^{87} with a half-life of approximately 5×10^{10} years. In a chemical system which has remained closed with respect to rubidium and strontium since its formation the amount of Sr^{87} increases with time. Therefore, if the present abundances of Rb^{87} and Sr^{87} in the system are measured, and if the initial abundance of Sr^{87} in the sample can be determined, the age of the system can be calculated.

The age equation is:

$$(Sr^{87}/Sr^{86})_p - (Sr^{87}/Sr^{86})_o = (Rb^{87}/Sr^{86})_p (e^{\lambda t} - 1) \quad (21)$$

where:

$(Sr^{87}/Sr^{86})_p$ is the atomic ratio of Sr^{87} to Sr^{86} in the system at the present time.

$(Sr^{87}/Sr^{86})_o$ is the atomic ratio of Sr^{87} to Sr^{86} in the system at the time of formation.

$(\text{Rb}^{87}/\text{Sr}^{86})_p$ is the atomic ratio of Rb^{87} to Sr^{86} in the system at the present time.

λ is the decay constant for Rb^{87} , and is taken to be $1.39 \times 10^{-11} \text{ years}^{-1}$.

t is the age of the system in years.

The quantities $(\text{Sr}^{87}/\text{Sr}^{86})_p$ and $(\text{Rb}^{87}/\text{Sr}^{86})_p$ can be measured in the laboratory. The value of λ can also be measured. $(\text{Sr}^{87}/\text{Sr}^{86})_o$ cannot be measured directly, however, and since t is the quantity to be determined, the above equation contains two unknowns. By measuring two or more chemically closed systems (samples) which originated at the same time and which incorporated strontium of the same isotopic composition a separate equation can be set up for each system and the values for $(\text{Sr}^{87}/\text{Sr}^{86})_o$ and t determined.

If equation (21) is rearranged:

$$(\text{Sr}^{87}/\text{Sr}^{86})_p = (e^{\lambda t} - 1)(\text{Rb}^{87}/\text{Sr}^{86})_p + (\text{Sr}^{87}/\text{Sr}^{86})_o \quad (22)$$

this can easily be seen to be of the form:

$$y = mx + b$$

which is the equation of a straight line; x and y are the measurable quantities, m is the slope of the line, and b is the y intercept at $x = 0$. Chemically closed samples which originated at the same time and which incorporated strontium of the same initial composition should all fall on a straight line defined by equation (22). A plot of such samples is termed an isochron. The age of the samples can be calculated from the slope of the line and $(\text{Sr}^{87}/\text{Sr}^{86})_o$.

can be found from the y intercept at $x = 0$, which is the value for $\text{Sr}^{87}/\text{Sr}^{86}$ which all of the samples would have had before any decay of the rubidium had occurred. The isochron method of age analysis was first introduced by Nicolaysen (1961).

Analytical Precision

Replicate Analyses of Strontium Standard. It is general practice in the M.I.T. Geochronology Laboratory to monitor the operation of the mass spectrometers by analyzing a strontium isotopic standard at frequent intervals. The standard sample employed is a spec-pure SrCO_3 (Eimer and Amend, lot number 492327). During the course of this investigation three different mass spectrometers were used for measuring the strontium isotopic ratios, while most of the spiked strontium runs were made on one of the instruments (Sally). All the standard runs made by this investigator are listed in Table I. These runs were made during two different periods of investigation which were separated by a period of inactivity of two years. Since these standard runs were made on three different instruments it is not possible to calculate a standard deviation from the values listed in the table. It can be seen, however, that the runs are all in fairly good agreement, with the exception of the three highest values. The three values of 0.709 were obtained from the first three standard runs made on one instrument (Sally) after

it had stood idle for nearly three months, with the exception of one rubidium run which was made during that period.

During the period of this investigation other standard runs were made on these instruments by other workers. However, the standard runs listed here are thought to be representative of the period of investigation, and, furthermore, since there is undoubtedly some degree of personality involved in the setting of baselines and in the reading of peak heights, the exclusion of runs made by other workers is believed to more satisfactorily monitor both the instrument and the operator during the course of this study.

Because all the standard runs listed in Table I were not made on the same instrument a standard deviation cannot be calculated for all the measurements. Nine of the standard analyses made during the second part of the investigation were made on one instrument (Sally), however, so a standard deviation can be calculated for the analyses made during this period. The formula used for this calculation is:

$$\sigma = \pm \sqrt{\frac{\sum_{i=1}^n |X_i - \bar{X}|^2}{n-1}}$$

where X_i is the value of a particular analysis, \bar{X} is the average of all the analyses, and n is the number of analyses. σ is the 65 2/3% confidence limit and 2σ is the 99% confidence limit. These values are given at the bottom of Table I.

TABLE I

Replicate Analyses of Strontium Isotopic Standard

<u>Record</u>	<u>Date</u>	<u>(86/88)_{measured}</u>	<u>(87/86)_{normalized}</u>
3372(L)*	2 Nov 63	0.1202	0.7083
3404(L)	29 Nov 63	0.1186	0.7080
3715(N)	11 May 64	0.1193	0.7087
3745(N)	22 May 64	0.1186	0.7085
3770(N)	4 Jun 64	0.1188	0.7086
3799(N)	24 Jun 64	0.1187	0.7089
3811(N)	29 Jun 64	0.1189	0.7085
4974(S)	3 Nov 66	0.1194	0.7091
4991(S)	19 Nov 66	0.1194	0.7090
5066(S)	12 Jan 67	0.1191	0.7091
5197(S)	30 Mar 67	0.1187	0.7081
5245(S)	3 May 67	0.1188	0.7084
5260(S)	10 May 67	0.1193	0.7085
5364(S)	22 Jun 67	0.1196	0.7081
5538(S)	8 Sep 67	0.1183	0.7083
5639(S)	20 Nov 67	0.1190	0.7085
5671(N)	11 Dec 67	0.1183	0.7083
5678(N)	14 Dec 67	0.1181	0.7083
5685(N)	22 Dec 67	0.1193	0.7091
5713(N)	15 Jan 68	0.1198	0.7084
5747(N)	31 Jan 68	0.1182	0.7084

Standard deviations for record numbers 4974(S) through 5639(S) (See text):

(86/88): Average = 0.1191 $\sigma = \pm 0.0004$ $2\sigma = \pm 0.0008$

(87/86): Average = 0.7086 $\sigma = \pm 0.0004$ $2\sigma = \pm 0.0008$

* The mass spectrometers in the M.I.T. laboratory have all been given names; L denotes "Lulu", N denotes "Nancy", and S denotes "Sally".

Blank Analyses. Contamination in the M.I.T. Geochronology Laboratory has historically been quite low (generally $\ll 1$ μgm per analyses for both Rb and Sr) and therefore is insignificant where normal rock analyses are concerned. During the course of this investigation only one blank analysis was made on the whole-rock analysis procedure. This blank gave 0.030 μgm per analysis for Rb and 0.032 μgm per analysis for Sr. During the preparation of both the massive sulfide ore samples and the gold-quartz samples, where very large quantities of reagents were used, other blank analyses were made for these particular procedures. These blank analyses are listed and discussed along with the corresponding sample analyses.

Duplicate Sample Analyses. Duplicate analyses for strontium were made on three individual rock samples and duplicate analyses for rubidium were made on four rock samples, as a check on the validity of the measurements. These duplicate analyses were made several months apart. The results of these analyses are shown in Table II. Shown at the bottom of the table are the standard deviations which have been calculated for these duplicate analyses, although admittedly the number of duplicates is small. In general it may be said that the results are in good agreement, with the possible exception of the Sr determinations for sample R6496; past experience would suggest that the differences in these analyses is probably real.

TABLE II

Duplicate Sample Analyses

Sample No.	Rb _{ppm}	Diff $X_1 - X_2$	Diff ² $(X_1 - X_2)^2$	Sr _{ppm}	Diff $X_1 - X_2$	Diff ² $(X_1 - X_2)^2$	$(87/86)_N$	Diff $x_1 - x_2$	Diff ² $(x_1 - x_2)^2$
R6494	223 223	0	0	581 572	9	81	0.7424 0.7422	0.0002	0.00000004
R6495	209 210	1	1	725 723	2	4	0.7322 0.7318	0.0004	0.00000016
R6497	247 248	1	1	587 589	2	4	0.7440 0.7435	0.0005	0.00000025
R6499	196 193	3	9						
			11			89			0.00000045

$$S.D. = \pm \sqrt{\frac{11}{8}} = \pm 1.17^*$$

$$S.D. = \pm \sqrt{\frac{89}{6}} = \pm 3.85$$

$$S.D. = \pm \sqrt{\frac{0.00000045}{6}} = \pm 0.0002$$

$$* S.D. = \pm \sqrt{\frac{\sum_{i=1}^n (x_i' - x_i'')^2}{2n}}$$

From Youden (1951)

Sources of Error

The sources of error in rubidium and strontium isotopic analyses can be summarized as follows:

1. Inhomogeneous sample material - this can lead to random errors in both the Rb and Sr concentration determinations, as well as leading to errors in the $\text{Sr}^{87}/\text{Sr}^{86}$ isotopic ratio measurements, for the sample as a whole.
2. Error in sample weighing - this can lead to random errors in the Rb and Sr determinations. (If the weighing error is due to a biased balance, however, the errors will be systematic.) In the calculation of the age of a sample, or its position on an isochron plot, weighing errors have no effect.
3. Loss of sample after weighing and before spiking - for homogeneous sample material this type of error produces the same result as a random error in sample weighing.
4. Error in spiking - this type of error will lead to random errors in the measured concentration of Rb or Sr, and will also lead to an error in the calculated age for a sample and in its position on an isochron plot; it will not affect the $\text{Sr}^{87}/\text{Sr}^{86}$ measurement. Improperly calibrated spikes can be classed under this heading, although in this case the errors will be

systematic for all analyses made using the improper spike.

5. Instrumental errors - these errors include non-linearity in the measuring system, improper scale factors, improperly functioning equipment, and extreme isotopic fractionation during the analyses. These errors can be either random or systematic and affect measurements of both concentration and isotopic composition. For normal rock analyses these errors are not usually important, unless they are extremely large. In the determinations of very small quantities of Rb and Sr, where the sample-spike ratios are often very poor, as in the case of the sulfide and quartz analyses reported in the latter part of this study, these instrumental errors can become quite important.
6. Variable and uncontrollable contamination by Rb and Sr - this type of error can be quite serious when analyzing for very small amounts of these elements and will lead to errors in both the Rb and Sr concentration determinations as well as to errors in the Sr isotopic determinations since the isotopic composition of the contaminating Sr is also unknown.

Least Squares Analyses of Isochrons

All the isochrons in this study were analyzed by the cubic least squares method of York (1966). For the purposes of these analyses the errors in the $\text{Sr}^{87}/\text{Sr}^{86}$ measurements were taken to be 0.1%, and the errors in the $\text{Rb}^{87}/\text{Sr}^{86}$ measurements were taken to be 2.0%. These error limits are based on the analyses of many individual workers in this laboratory over a period of several years. The least squares analyses were carried out on facilities provided by the Computation Center at the Massachusetts Institute of Technology. I wish to especially thank Mr. C.M. Spooner who modified the least squares program for the I.B.M. 360 Computer.

CHAPTER II

REVIEW OF THE HYDROTHERMAL PROCESSES OF GOLD DEPOSITION

The mechanisms for the transport and precipitation of gold by hydrothermal processes are poorly understood. For background purposes a very brief review of some of the ideas that have been put forward on this topic will be given.

There is abundant experimental evidence to show that gold can be transported in either acid or alkaline solutions; see for example Frondel (1938), Linder and Gruner (1939) and Krauskopf (1951). There is some disagreement, however, on whether the ore-forming fluids are acid or alkaline, although the majority of geologists today appear to accept the idea that such fluids are alkaline.

Bowen (1933) suggested that the residual liquid from a crystallizing magma might boil off with the formation of an initially acid solution. As this solution moves outward from the magma it would become neutral or alkaline by reaction with the wallrocks of the veins, fissures, etc. According to Frondel (1938) the gold in such a fluid would be carried in true solution as long as the fluid was acid, later on in the alkaline fluid the gold would be carried in colloidal form. Graton (1940) argued that an initially acid residual liquid would largely remain acid after leaving the magma chamber and would still be acid when it reached the surface of the earth. His argument was based on the belief that after the earliest part of the fluid

had reacted with the wallrocks the later fluids would be effectively prevented from further reaction. Since most of the theories of hydrothermal ore formation require the action of very large volumes of fluids, the bulk of these fluids would have to be acid, according to Graton, if they did indeed leave the magma chamber in that condition. Graton believed, instead, that the ore-forming fluids must be alkaline when they leave the magma chamber because the alteration effects of magmatic and hydrothermal solutions (e.g. sericitization, carbonatization, albitization, etc.) all show the effects of alkalic introduction.

Smith (1943) also has stated that the residual magmatic fluids must be alkaline since they should be in equilibrium with the silicate rocks with which they are in contact, and that the hydrolysis of the alkali silicates, bringing soluble hydroxides into solution, would be the more important reaction since there are greater quantities of alkali than acid elements in igneous rocks. Further, according to Smith, most ore deposits of igneous origin are formed at depths where the pressures are too great for a separate vapor phase to exist, consequently there would be no boiling off of components as suggested by Bowen.

Whether the fluids leave the chamber as acidic or alkaline, it appears to be generally accepted that most of the transport is accomplished under alkaline conditions. As was stated before, there is abundant evidence that gold is soluble in alkaline solutions. Krauskopf (1951) states

that these solutions must contain sulfur, and that in such solutions AuS^- is very stable and can be carried in very dilute solutions even near the neutral point. Smith (1943) says, however, that AuS^- is not stable above 40°C , but rather must be carried as the thiosulfide at higher temperatures.

The colloidal transport has found favor among many geologists, perhaps because it would provide a mechanism for moving larger quantities of gold than would normal solution transport. Frondel has shown that gold sols, when protected by colloidal silica, are stable in hydrothermal solutions at high temperatures even despite high concentrations of electrolytes. Colloidal transport aided by colloidal silica protection of the gold would appear to be a favorable mechanism if the proposal of Bichan (1941) is valid. He proposed that the mineralizing fluids drawn off from the magma chamber are "silicothermal", that is, fluids in which the principal ingredient is silica. But there is a question as to how much silica is actually present in hydrothermal fluids, especially at their point of origin.

Schmitt (1954) has discussed the nature of silica in hydrothermal vein fillings and replacements and has argued that in most of the occurrences examined the amounts of silica, as well as most of the other major elements associated with the wallrock alterations and vein fillings, could have easily been derived from the wallrocks themselves.

By comparing chemical analyses of unaltered and altered wallrocks he shows that in most instances silica, as well as the alkalies and alkaline earths, is lost by the wallrocks during alteration and that the vein fillings gain in these components. Consequently there would be no need to call upon the hydrothermal fluids to carry these materials in from an external source, and Schmitt further contends that there is little, if any, evidence to support the belief that these materials were deposited by the fluids. In a similar type of study Schwartz (1939) has shown that the analyses of hydrothermal alteration products generally show a small net loss of silica and alumina, and greater losses of iron, MgO, CaO and Na₂O, while K₂O and combined water usually show a net gain, when compared with the unaltered rocks.

Smith (1963), however, has made analyses that show that fluid inclusions from quartz-carbonate-sulfide ore deposits usually contain salts of Na, Ca, K, Mg, etc., in amounts of 5-20%, and occasionally reaching amounts of up to 50%. He has used these data to argue that they represent the concentrations of these materials in the hydrothermal mineralizing fluids at the time of deposition. While this is undoubtedly very near to the truth, these analyses do not give any indication as to the original source(s) of these constituents.

The mechanisms involved in the deposition of gold from hydrothermal fluids quite obviously depend in the

first instance on the nature of the gold in the fluid. AuCl_4^- in an acid solution could be precipitated as the native metal by reaction with H_2S or some other reducing agent as the fluid becomes more neutral or alkaline. Gold carried in an alkaline solution as AuS^- would be precipitated, according to Krauskopf, by either falling temperature or falling pressure, or both. Gold carried as the thio-sulfide would be precipitated by a lowering of the sulfide concentration in the solution; this could be brought about by reaction of the fluid with the wallrocks, loss of H_2O by boiling, or by dilution of the fluids with meteoric waters (Smith, 1943). It is also possible that the gold thus forced out of solution may appear in colloidal form, rather than as a precipitate, and be transported in this manner down to quite low temperatures.

According to Frondel the precipitation of colloidal gold carried in an alkaline solution could be brought about by a decrease in temperature at a constant concentration of electrolytes, variations in type and concentration of electrolytes, or by a change from alkaline to acid conditions in the solution. Also, crystal faces or gel surfaces exposed to fluids could remove colloidal gold.

Whatever the mode(s) of transport and deposition, studies of hydrothermal gold deposits offer abundant evidence that the gold was deposited quite late in the mineral sequence, often being one of the last constituents to form, and that this deposition must have occurred at rather low

temperatures, certainly below 573°C , the inversion point of quartz.

The major concern of this study, however, is not the how and why of mineralization, but rather, when.

CHAPTER III

INVESTIGATION OF THE STRONTIUM ISOTOPIC COMPOSITIONS OF
STRONTIUM-RICH, RUBIDIUM-POOR, GANGUE MINERALS FROM
VEIN-TYPE HYDROTHERMAL MINERAL DEPOSITSIntroduction

Measurements of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of a series of strontium-rich, rubidium-poor, gangue minerals from some vein-type hydrothermal mineral deposits were made in order to gain information concerning the possible origins of these deposits. If such deposits are of primary magmatic origins (i.e. derived directly from subcrustal sources having Rb/Sr ratios similar to those in the source regions of basalts), and if the strontium compositions in the gangue minerals faithfully represent the initial strontium compositions of the mineralizing fluids, then the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios should reflect the strontium compositions of the source regions.

In a study of the strontium isotopic compositions of basaltic rocks of recent origins Faure (1961) found that both the oceanic and continental types of basalts had uniformly low $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of about 0.708. Because these rocks are low in rubidium this ratio is believed to characterize the present $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in the upper mantle, which is assumed to be the source region for these rocks. From the Rb and Sr concentrations measured in these samples Faure determined that the upper mantle $\text{Sr}^{87}/\text{Sr}^{86}$ composition has slowly grown to its present value from an initial value of about 0.700 at the time of its formation

4500 million years ago. Therefore, gangue minerals containing strontium derived directly from this subcrustal source should be expected to have $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of about 0.708 for the more recent deposits and the ratios should decrease with the increasing age of the mineralization.

Faure also calculated the approximate Rb/Sr composition of the continental crust from a consideration of the average Rb/Sr compositions of the various crustal rock types, as determined from the analyses of many previous workers, and by weighting these analyses with respect to the approximate amounts of each of the rock types in the crust. His best estimate for the Rb/Sr composition of the continental crust is 0.25. By assuming an average age for the crust of 2000 m.y. Faure then calculated that the average $\text{Sr}^{87}/\text{Sr}^{86}$ composition of the continental crust at the present time is about 0.725. Therefore if the gangue minerals contain strontium which was derived from pre-existing crustal materials which had Rb/Sr ratios approximating the crustal average, then the gangue strontium should show $\text{Sr}^{87}/\text{Sr}^{86}$ ratios greater than 0.708. If the gangue minerals were derived from crustal materials of basaltic composition they should show $\text{Sr}^{87}/\text{Sr}^{86}$ ratios very near to 0.708, but if they were derived from more sialic (Rb-rich) crustal materials they should show ratios greater, possibly considerably greater, than 0.708.

The samples chosen for this investigation were from deposits in which 1) Tertiary mineralization lies within rocks of Tertiary age, 2) Tertiary mineralization lies within rocks of Precambrian age, and 3) the mineralization is Precambrian. Fluorite was the preferred gangue mineral as it is generally accepted that the fluorine at least is of magmatic origin. Because of a lack of adequate fluorite samples the measurements were extended to two other strontium-rich minerals - barite and calcite. For this survey investigation samples were selected from among those available in the Lindgren Collection of Ores and Minerals in the Department of Geology and Geophysics at M.I.T.

Results and Discussion

Tertiary Mineralization in Tertiary Rocks. The first type of occurrence examined was that of Tertiary mineralization lying within rocks of Tertiary age. The samples tested came from locations in Colorado, Arizona, Montana and the Philippines. The results of these analyses are listed in Table III. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios lie in the range 0.705 to 0.708, with an average of about 0.707. One sample of andesitic country rock from the Telluride district has an $87/86$ ratio of 0.709. This sample was not from the same locality as was the calcite sample analyzed from the Telluride district; it was analyzed solely to gain some idea of the present strontium isotopic composition of the Tertiary volcanics.

TABLE III

Tertiary Mineralization in Tertiary Rocks

Sample No.	Sample and Locality	86/88	87/86	87/86 _N
R5293	Calcite Liberty Bell Mine Telluride, Colo.	0.1194 0.1196	0.7076 0.7069	0.7076 0.7075
R5297	Andesitic country rock Smuggler vein Telluride, Colo.	0.1192 0.1181	0.7095 0.7127	0.7088 0.7088
R5298	Fluorite Cripple Creek, Colo.	0.1192	0.7084	0.7078
R5299	Fluorite Mineral Rock Mine Cripple Creek, Colo.	0.1185	0.7074	0.7048
R5300	Fluorite Rice vein, 1700' level Eagles shaft Cripple Creek, Colo.	0.1189	0.7088	0.7073
R5301	Fluorite Portland Mine Cripple Creek, Colo.	0.1191	0.7077	0.7068
R5304	Calcite Tom Reed Mine Mohave County, Ariz.	0.1199	0.7101	0.7115
R5305	Fluorite Limestone-fluorite ore Maginnis Mine Judith Mts., Mont.	0.1191	0.7103	0.7094
R5306	Calcite from sample R5305, above	0.1186	0.7098	0.7075
R5307	Fluorite Maginnis Mine Judith Mts., Mont.	0.1192	0.7104	0.7098
R5432	Pink calcite Balatoc Mine Baguio Mining District Phillippines	0.1196	0.7042	0.7049

The main conclusions which can be drawn from the results of these analyses is that both the gangue minerals and the country rock sample show ratios which are compatible with an origin in a homogeneous subcrustal source region in Tertiary times; the gangue mineral ratios are also compatible with an origin in rocks of Tertiary age which were derived directly from a subcrustal source. The Tertiary gangue strontium ratios are not compatible with a derivation through the remobilization of pre-existing sialic crustal materials of greater than 1000 m.y. age, having average Rb/Sr ratios in excess of 0.20, and having average $\text{Sr}^{87}/\text{Sr}^{86}$ compositions in excess of 0.702. The implications of this last proposition will now be discussed in some detail.

In the Cripple Creek district of Colorado a plug of Tertiary latite-phonolite tuffs and breccias is exposed within a Precambrian terrain comprised of granite, gneiss and schist. The gangue samples analyzed here were associated with mineralization in the Tertiary volcanics. The granitic country rocks of this area have yielded K-Ar and Rb-Sr ages of 1000 - 1200 m.y. (Aldrich, et al, 1958; Giffin and Kulp, 1960; and Pearson, et al, 1966). This age is the youngest recognized Precambrian event in this region (Hedge, et al, 1967). The maximum Rb/Sr composition of 0.20 that such basement rocks could have if they were the source rocks for the gangue strontium is less than either the average Rb/Sr value of 0.25 for the continental

crust given by Faure (1961) or the average of 0.25 and greater given by both Faure and Turekian and Wedepohl (1961) for rocks with compositions more sialic than the average continental crust. It is significantly less than the average Rb/Sr ratio of about 1.0 given for granitic rocks by Hurley, et al (1962). The maximum $\text{Sr}^{87}/\text{Sr}^{86}$ composition of 0.702 that any pre-existing sialic source rocks could have, if the previously given conditions for age and Rb/Sr composition were both met, is also too low for the basement rocks of this area. From the data given by Faure these rocks should have had an initial $\text{Sr}^{87}/\text{Sr}^{86}$ composition of 0.704 to 0.706 if they had been derived from an upper mantle source 1000 m.y. ago; if they were derived from pre-existing sialic materials then their initial $\text{Sr}^{87}/\text{Sr}^{86}$ composition should have been greater than the upper mantle value since sialic crustal materials generally have Rb/Sr values greater than that of the upper mantle. In Tertiary times the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of these rocks would have been significantly greater than the initial compositions. The granitic gneisses and schists of this area are older than the granitic rocks just discussed, and are believed to correlate with rocks further to the north which have been dated by Hedge, et al, (1967) as 1700 m.y.

From the evidence available on the rocks of the Cripple Creek district it appears very improbable that any of the pre-Tertiary rocks of this district could have been the source rocks for the Tertiary gangue strontium.

With the Precambrian basement rocks ruled out as a possible source for the Tertiary gangue strontium, we are left with two possible alternatives as to the source of this material. One possible source is the source region of the volcanics themselves (presumed to be the upper mantle). The other possible source is the volcanics. During the whole of Tertiary time, about 70 m.y., rocks having an average Rb/Sr composition approximately the same as the crustal average would increase in their $\text{Sr}^{87}/\text{Sr}^{86}$ composition only about 0.001 over their initial strontium composition; this increase would not be discernable in the analyses carried out here.

The mineralization in the Tom Reed mine, in the Oatman district of Arizona, occurs in Tertiary andesites which cover a basement of Precambrian granitic gneisses and schists. Rb-Sr ages on three biotite samples from these Precambrian rocks have yielded ages of 1200 to 1350 m.y. (Giletti and Damon, 1961). The same type of argument can be applied to these rocks as was previously applied in the case of the Precambrian rocks of the Cripple Creek district, and as in the case of the Cripple Creek district it is very improbable that the basement rocks of the Oatman district could have been the source of the Tertiary gangue strontium. Once again, the possible alternative sources for this gangue strontium are either the source region of the volcanic rocks or the volcanic rocks themselves.

In the Telluride district in southwestern Colorado the conclusions are less clear than in either of the two districts just discussed. Here a series of Tertiary volcanics of basic to acid composition overlies a series of Paleozoic and Mesozoic sediments; the ore mineralization occurs in the volcanics. Some Precambrian rocks are exposed in the area; the age of these rocks is uncertain, but Rb-Sr and K-Ar ages from Precambrian granitic rocks in areas surrounding this region have yielded ages of about 1400 m.y., an age which appears to be ubiquitous to a large part of the southwestern U.S. (Aldrich, et al, 1957; Mose and Bickford, 1968). It would be difficult to adequately assess the possibility that the sediments underlying this district were the source rocks for the Tertiary gangue strontium, therefore this possibility cannot be ruled out in this district. In the Telluride district, then, there are three possible sources for the Tertiary gangue strontium - the assumed subcrustal source region of the volcanics, the volcanics themselves, or the underlying sediments.

In the Maginnis mine in Montana the ore mineralization is associated with a Tertiary rhyolite porphyry at the contact with an underlying Carboniferous limestone. The analyses of the two fluorite samples from this mine give $\text{Sr}^{87}/\text{Sr}^{86}$ compositions that are within the range of strontium compositions measured by Powell (1962) in limestones less than 1000 m.y. in age. In this district the

underlying Carboniferous limestone cannot be ruled out as a possible source for the Tertiary gangue strontium.

In the Baguio mine in the Philippines the ore mineralization occurs in a volcanic neck filled with Tertiary andesite breccia. The country rock here consists of older diorites of uncertain age; these diorites cannot be ruled out as the source of the Tertiary gangue strontium because of a lack of adequate information about them.

The analyses of the strontium isotopic compositions in the gangue minerals associated with Tertiary mineralization lying within rocks of Tertiary age have yielded $87/86$ ratios that are compatible with a derivation of the gangue strontium from either a homogeneous subcrustal source region having an average Rb/Sr ratio similar to that of the source regions of basalts or from the Tertiary host rocks themselves. In the two districts in which adequate information is available concerning the pre-Tertiary crustal rocks these rocks can be ruled out as possible sources of the gangue strontium. In three of the districts there is insufficient information concerning the pre-Tertiary crustal rocks to rule them out as possible sources of the gangue strontium. However, because the gangue ratios are all compatible with a derivation from either a subcrustal source region or from the Tertiary rocks themselves, and because the pre-Tertiary rocks can be ruled out as possible sources of the gangue strontium in the two districts in which adequate information about these rocks is available, it is neither necessary

nor logical to assume that the pre-Tertiary crustal rocks in the remaining three districts were the sources of the Tertiary gangue strontium.

Tertiary Mineralization in Precambrian Rocks. Samples of Tertiary mineralization in Precambrian rocks were selected from the area in and near the Georgetown district in the Front Range of Colorado. Here a series of Tertiary dikes and stocks invade Precambrian granite and schist. The mineralization occurs in dikes in the Precambrian rocks. Table IV shows the results of these analyses.

The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the gangue minerals are much greater than would be expected for rubidium-deficient phases which had incorporated only primary Tertiary strontium, that is, strontium with an $87/86$ isotopic composition of about 0.708. The one sample of granitic rock listed in the table was from the same body which enclosed sample R5349, but was from another mine in the same area.

The granitic rocks of the Georgetown district have yielded Rb-Sr whole rock ages of about 1700 m.y. (Peterman, et al, 1965; Hedge, et al, 1967). 1700 m.y. old rocks having Rb/Sr ratios equal to or greater than the average of the continental crust (0.25) would have had $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of 0.720 or greater in Tertiary time; this is in good agreement with the $87/86$ ratios found in the Tertiary gangue strontium from the rocks of the Georgetown district.

TABLE IV

Tertiary Mineralization in Precambrian Rocks

<u>Sample No.</u>	<u>Sample and Locality</u>	<u>86/88</u>	<u>87/86</u>	<u>87/86_N</u>
R5347	Barite Hiawatha Mine Chaffee County, Colo.	0.1193	0.7258	0.7255
R5348	Barite American Flag Mine Gilpin County, Colo.	0.1190	0.7235	0.7242
R5349	Fluorite Big Indian Mine Georgetown, Colo.	0.1193	0.7310	0.7298
R5350	Granite (Precambrian) Burleigh Tunnel Georgetown, Colo.	0.1197	0.7777	0.7787

The strontium $^{87}/^{86}$ ratios of the Tertiary gangue minerals in the Precambrian rocks of the Georgetown district are clearly too great to be compatible with a derivation from either a subcrustal source region or from the associated Tertiary rocks themselves. They are, however, compatible with a derivation from pre-existing sialic crustal materials similar in composition to the granitic host rocks of the district.

Precambrian Mineralization. Precambrian mineralization was examined in specimens of gangue from the Kirkland Lake and the Porcupine districts of Ontario. At Kirkland Lake a syncline of Timiskaming sediments and volcanics has been intruded by syenites. The gold mineralization occurs in quartz-filled fractures in the syenites. A more complete discussion of the Kirkland Lake geology is given in Chapter IV. In the Porcupine district Keewatin volcanics and Timiskaming sediments have been deformed into a syncline, and this structure has in turn been intruded by quartz porphyries. The gold mineralization is believed to be genetically related to the porphyries although it occurs mainly in the volcanics and sediments.

The results of the analyses of the Precambrian gangue mineralization are listed in Table V. The $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the Kirkland Lake and Porcupine samples lie in the range 0.704 to 0.707. These ratios may be slightly greater than would be expected for rubidium-deficient phases which contained only primary strontium. For example, the time of

TABLE V

Precambrian Mineralization

<u>Sample No.</u>	<u>Sample and Locality</u>	<u>86/88</u>	<u>87/86</u>	<u>87/86_N</u>
R5419	Calcite Lake Shore Mine Kirkland Lake, Ontario	0.1192	0.7046	0.7039
R5420	Calcite Lake Shore Mine Kirkland Lake, Ontario	0.1204	0.7035	0.7065
R5421	Reddish calcite Lake Shore Mine Kirkland Lake, Ontario	0.1190	0.7054	0.7043
R5422	Barite from coexisting barite and calcite Lake Shore Mine Kirkland Lake, Ontario			0.705
R5423	Calcite from sample R5422, above	0.1200	0.7038	0.7056
R5456	Slightly mineralized porphyry wallrock Lake Shore Mine Kirkland Lake, Ontario	0.1183	0.7216	0.7184
R5457	Calcite Vipond Mine Porcupine, Ontario	0.1197 0.1192	0.7051 0.7080	0.7061 0.7074
R5458	Calcite Moneta Mine Porcupine, Ontario	0.1188	0.7067	0.7049
R5351	Calcite Nipissing, Ontario	0.1197 0.1188	0.7102 0.7127	0.7112 0.7108

host rock alteration in the Kirkland Lake district has been dated as about 1800 m.y. ago, as is discussed in Chapter IV of this report. From the data given by Faure, and discussed earlier in this chapter, the upper mantle value of $\text{Sr}^{87}/\text{Sr}^{86}$ should have been about 0.704 - 0.705 at 1800 m.y. ago. Also, about three miles to the south of the Kirkland Lake district lies the syenitic Otto stock which has been dated as 1830 m.y. with an initial $\text{Sr}^{87}/\text{Sr}^{86}$ composition of 0.704 (Purdy and York, 1967), this initial ratio is in good agreement with the upper mantle composition at that time based on the data of Faure. However, there is probably not enough difference between the model upper mantle strontium composition and the gangue strontium compositions measured here to be able to say with certainty that a real difference exists. The only exception to this last statement is the one sample of calcite analyzed from the Nipissing district of Ontario. The $\text{Sr}^{87}/\text{Sr}^{86}$ value measured for this sample is not compatible with a derivation in a subcrustal source region because this ratio is greater than even the present day value in the upper mantle.

The conclusions which can be drawn from the analyses of the Precambrian gangue strontium are not entirely convincing. The data appear to favor a derivation of the strontium from a source other than the upper mantle, but the differences in composition involved are slight.

Summary and Conclusions

The strontium isotopic compositions of the gangue minerals from Tertiary mineralization lying within rocks of Tertiary age are compatible with either a derivation from a homogeneous subcrustal source region having an average Rb/Sr composition similar to that of the source region of basalts or from the Tertiary host rocks themselves. The strontium compositions are not compatible with a derivation from the pre-Tertiary crustal rocks.

The strontium isotopic compositions of the gangue minerals from Tertiary mineralization lying with rocks of Precambrian age are not compatible with a derivation from a subcrustal source region in Tertiary time; they are, however, compatible with a derivation from Precambrian granitic rocks with Rb/Sr compositions similar to those of the Precambrian host rocks.

The strontium isotopic compositions of the gangue minerals from Precambrian mineralization appear to give evidence that the strontium may have been derived from a source other than a subcrustal region, but this evidence is not conclusive.

The only conclusion that is compatible with the information obtained from all three types of deposits is that the strontium was either derived from the rocks of the host environment or else largely exchanged with the strontium in the host rocks. There is no evidence which compels

us to search for the source of this strontium outside of the host environment. This conclusion is in agreement with the earlier conclusions of Schwartz (1939) and Schmitt (1954). Both of these workers compared the chemical analyses of large numbers of rock samples from hydrothermal alteration zones with their unaltered equivalents, and from these comparisons both workers concluded that in most instances most of the mineral-forming elements in the alteration products were most probably derived from the host environment; Schmitt believed that this was especially true for the alkali and alkaline earth elements.

The strontium isotopic compositions of the gangue minerals therefore largely reflect the strontium isotopic compositions of the host rocks at the time of mineralization; they are not representative of the original strontium isotopic compositions of the hydrothermal mineralizing fluids.

CHAPTER IV

INVESTIGATIONS OF THE POSSIBILITY OF DATING
HYDROTHERMAL MINERAL DEPOSITS

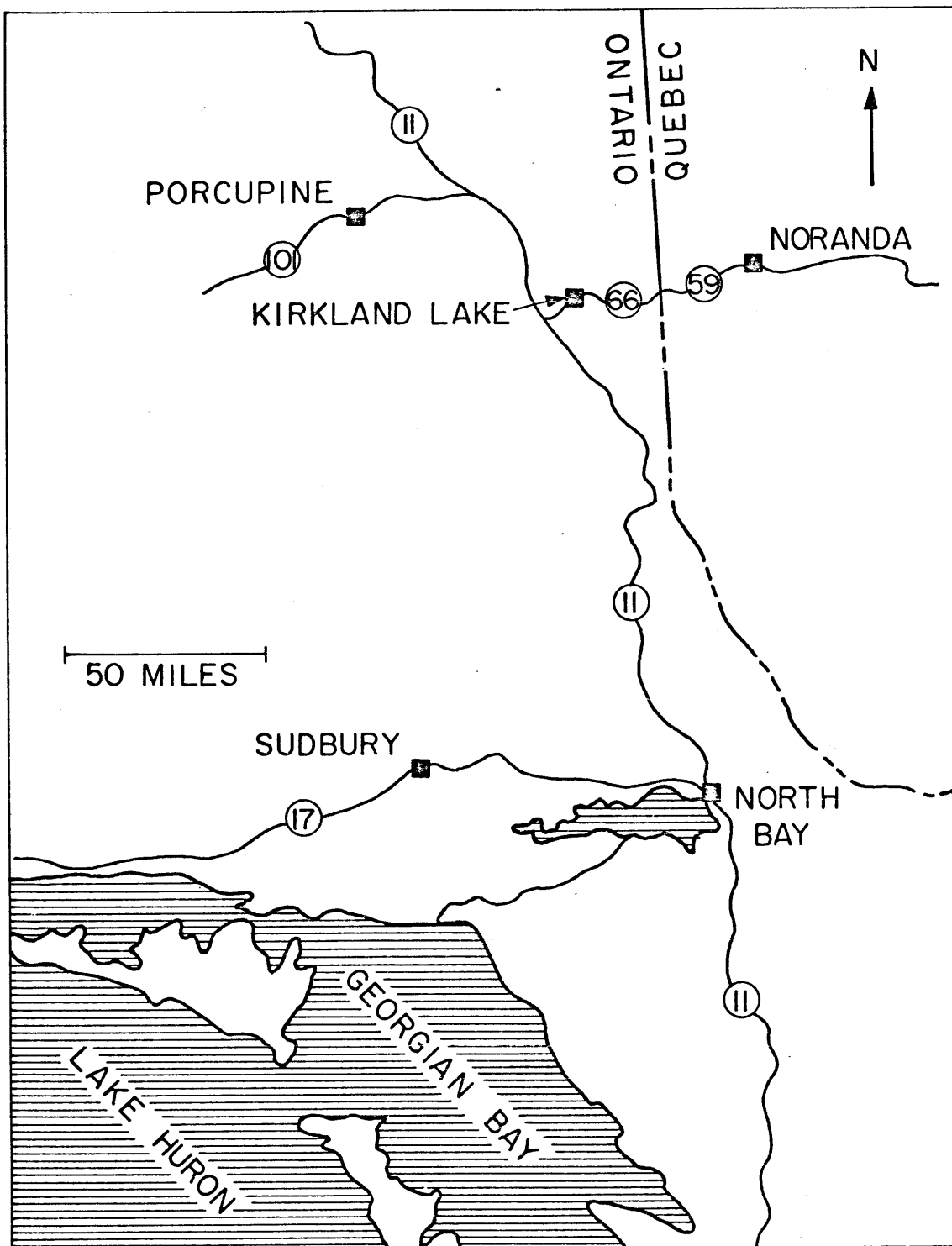
Part A: The Kirkland Lake District, Ontario

Introduction

The Kirkland Lake gold mining district is located in Teck township in eastern Ontario, about 130 miles north of North Bay (see map, Figure II). In terms of production it has been the second largest gold camp in Ontario. The major part of the ore has been produced from seven mines in and near the town of Kirkland Lake. Underground production has now ceased at all but one of these mines; the one remaining active mine is the Macassa mine, located at the extreme western end of the district.

The host rocks around the ore zone have undergone widespread, low grade alteration; they have been altered from a composition comprised predominantly of feldspar to one comprised predominantly of sericite, chlorite and carbonates. During the time of alteration these rocks did not remain closed chemical systems, but rather were open to exchange with the hydrothermal fluids. If there was a large degree of mixing in the fluids at the time of alteration, and if the strontium isotopic composition of the fluids and that of the strontium derived from the wall-rocks were largely homogenized, then the sericite and chlorite alteration products which incorporated this

FIGURE II



LOCATION MAP OF THE KIRKLAND LAKE AND PORCUPINE DISTRICTS, ONTARIO, AND THE ROUYN-NORANDA DISTRICT, QUEBEC

strontium should yield a mineral isochron of different age than that of the unaltered host rocks. These alteration minerals are extremely fine-grained, however, and it is not feasible to separate the various minerals out of the rocks. Therefore, these rocks were analyzed by the Rb-Sr whole rock method. Such whole rocks should contain components of two different ages, one age being the original age of the intrusive host rocks, and the other age being that of the alteration minerals. The examination of thin sections made from the alteration zone rocks shows that these rocks are composed predominantly of alteration products (greater than 75-80%) and that the remaining minerals show the effects of partial alteration and replacement. It would be expected that the whole rock analyses of these rocks would yield ages approaching that of the alteration minerals. If the time of host rock emplacement and that of the alteration were similar then little or no difference might be found between the age of the unaltered host rocks and that of the alteration zone. If, however, these two ages are significantly different this should be apparent in the age analyses.

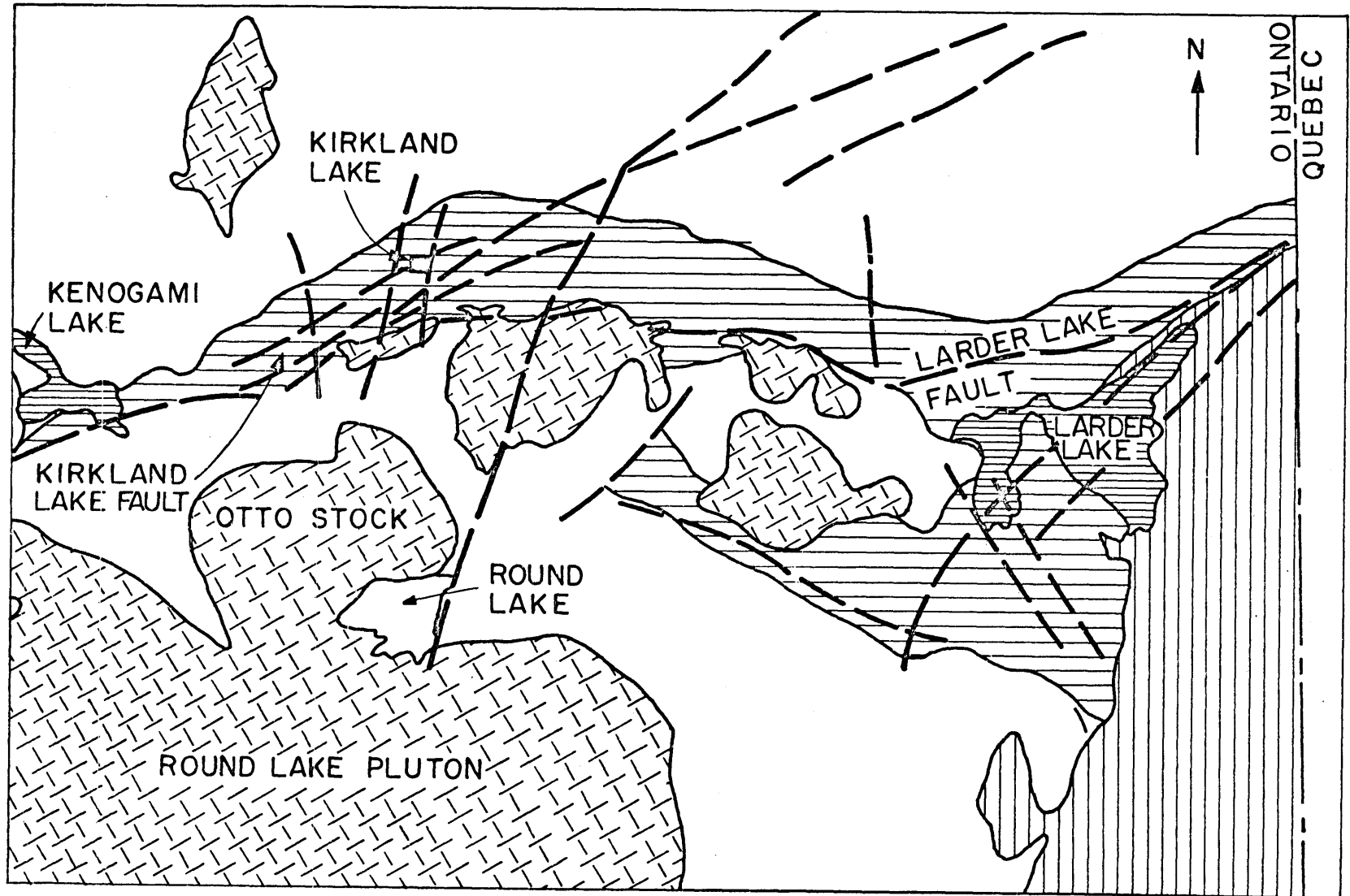
The linearity of the isochrons and the difference in the ages of the unaltered host rocks and the rocks of the alteration zone reported later in this section indicate that the assumptions made above are valid.

Geology

Geologic Setting. The Kirkland Lake district, which is located in the Superior province of North America, lies near the western end of a highly disturbed, east-west trending shear zone whose western termination lies near Kenogami Lake (see map, Figure III) and which extends eastward to the Ontario-Quebec boundary, and thence into Quebec. Major faults lie in and along this shear zone, and faults also transect the zone. A major break, the Larder Lake fault, forms the southern boundary of this zone. The Kirkland Lake fault is a major feature in the western part of the shear zone and has been the principal factor in the control and localization of the ores.

The country rocks of the region are all of Precambrian age and consist of volcanics, sediments, and intrusives. The sediments and volcanics have been severely folded and faulted. They have been subdivided into two age groups on the basis of field evidence, and are separated from one another by an angular and erosional unconformity. The older group is classified as Keewatin and the younger group is classified as Timiskaming. Fairbairn (1965, 1966) has dated volcanics from both groups in the Kirkland Lake area by the rubidium-strontium whole rock method and has found the isochrons obtained to be indistinguishable from one another; Fairbairn's age for the Keewatin is 2376 m.y. \pm 40 m.y. with an initial ratio of 0.7032, and his age for the Timiskaming is 2368 m.y. \pm 48 m.y. with an initial ratio of 0.7026. As pointed out by Fairbairn, the error

FIGURE III



GENERALIZED GEOLOGIC MAP OF THE KIRKLAND LAKE AREA
(LEGEND ON FOLLOWING SHEET)

FIGURE III, continued

LEGEND

PRECAMBRIAN
PROTEROZOIC



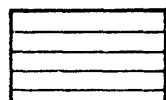
GOWGANDA FORMATION
CONGLOMERATE, ARKOSE, GREYWACKE, SLATE

ARCHEAN UNCONFORMITY



ACID INTRUSIVES
GRANITE, SYENITE AND ASSOCIATED PORPHYRIES

INTRUSIVE CONTACT



TIMISKAMING SERIES
CONGLOMERATE, GREYWACKE, VOLCANICS

UNCONFORMITY



KEEWATIN SERIES
CONGLOMERATE, GREYWACKE, TUFF, SCHIST

SCALE : 1 INCH TO 4 MILES

REFERENCE : ONTARIO DEPARTMENT OF MINES MAP 2046, TIMMINS -
KIRKLAND LAKE SHEET

limits on the isochrons would allow more than sufficient time for the unconformity to develop.

The Keewatin and lower Timiskaming series have been intruded by gabbro and diorite bodies, and all of these rocks have been intruded by rocks of acid to basic composition. These latter intrusives have been classified as Algomian age and it is in these rocks that most of the Kirkland Lake ores occur. Purdy and York (1967) have dated the Otto stock, a syenitic intrusive about 4 miles south of the Kirkland Lake district, and on the north edge of the Round Lake pluton, and have obtained a Rb-Sr age of 1730 m.y. with an initial ratio of 0.7046. However, Purdy and York used a Rb^{87} decay constant of $1.47 \times 10^{-10} \text{yr}^{-1}$; their age for the Otto stock recalculated with the decay constant used in this report ($1.39 \times 10^{-10} \text{yr}^{-1}$) is 1830 m.y. Purdy and York also obtained a Rb-Sr age for the Round Lake pluton of 2520 m.y. (when recalculated using a decay constant of $1.39 \times 10^{-10} \text{yr}^{-1}$) with a $\text{Sr}^{87}/\text{Sr}^{86}$ initial ratio of 0.7015; Fairbairn (1966) obtained a Rb-Sr age of 2530 m.y. and initial ratio of 0.7031 for this same body.

In the Kirkland Lake district the host rocks for the ore is an Algomian syenitic stock which has been described by Charlewood (1964) as follows:

"The intrusive rocks of the camp, with the exception of the diabase dikes, are host rocks for 95 percent of the ore. They form an elongate stock of which the long axis strikes easterly generally

parallel to the Timiskaming formations. The stock dips steeply south and widens with depth owing to the fact that the north limb dips more steeply than the south; it also pitches steeply to the west. Thus the intrusions were injected after the folding of the Timiskaming series and the older strata."

The intrusive body is made up of three major rock types. The oldest is an augite syenite; this was intruded by a syenite; and both of these rock types were intruded by a syenite porphyry.

Later diabase dikes intrude all of the above mentioned formations and the ores.

Descriptions of Host Rocks. The augite syenite is a dark rock with coarse, granitoid texture. The feldspar is predominantly oligoclase, and the chief mafic mineral is augite. Where the rock is altered it is brecciated and assumes the characteristic red coloration of the main ore zone; the altered rock is usually highly sheared, carbonatized and cemented with chlorite.

The syenite is a medium grained, pinkish rock of granitic texture. The feldspar is mainly orthoclase with some oligoclase. It also alters to give a characteristically red rock. It occurs as a westward-pitching pipe within the augite syenite. Contacts with the augite syenite may be sharp or gradational.

The syenite porphyry is the latest of the syenitic intrusives and cuts both of the older rocks. At the

western end of the ore zone it occurs as small irregular-shaped bodies and dikes. It is red to grey in color and has a porphyritic texture. The phenocrysts are orthoclase and oligoclase. Primary quartz is rare. The contacts of the syenite porphyry with the syenite and the augite syenite are sharp and distinct. The porphyry is the major host rock for the ore.

Kirkland Lake Fault. In the vicinity of Kirkland Lake the entire structure has been sliced in two by the Kirkland Lake fault, which is known in the mining camp as the Main Break. The ore zone is mostly localized in this fault zone. At the west end of the ore zone the fault is a single plane with local braided parallel slip zones. As the fault passes eastward it splits up into more and more branches, one of which however continues to be predominant. At the western end of the ore zone, in the vicinity of the Macassa mine, the south side of the fault has been thrust upwards about 1500 feet; at the eastern end of the zone the vertical displacement is about 350 feet. The horizontal displacement is negligible. The break is generally quite a clean one and where a gouge zone occurs it is only a few inches to a few feet in width.

In the ore zone the fault strike averages $N67^{\circ}E$ and the dip is about $75^{\circ}-80^{\circ} S$ (Thomson, 1948-2). The strike parallels the axis of the syenite intrusives and the strike of the Timiskaming series rocks. The fault has been followed in the underground workings to a depth of

over 8000 feet and is known, from drill cores, to extend to at least 8875 feet below the surface (Charlewood, 1964). In the lower levels of the Macassa mine the fault plane splits into North and South branches.

Numerous subsidiary fractures occur in the hanging wall of the fault and these are generally parallel to the Main Break but have flatter dips. Most of the ore occurs in the hanging wall side and it is generally associated with the Main Break and these subsidiary fractures. In the lower levels of the Macassa mine the ore is associated with the North branch of the Main Break and with another fracture, the '04 break, which is north of the North branch and which also has a steep southerly dip. Ore in the Macassa mine is also found in the fractured ground between the '04 break and the Main Break. The mine plans of four levels of the Macassa mine (Figures IV through VII) show the relationships among the various breaks, as does the cross section through this mine (Figure VIII).

Wallrock Alteration. The hydrothermal alteration of the syenitic wallrocks has produced a rock that is characteristically reddish in color, owing to the development of iron oxides. In some areas bleaching and/or silification of the rock has taken place. Chlorite, sericite, carbonates and secondary quartz have been extensively developed throughout the rocks of the alteration zone. The width of the alteration about a vein fracture is highly variable and may extend from one foot to several tens of feet away from

a fracture (Charlewood and Thomson, 1948).

According to Thomson (1948-2) the widespread carbonatization which occurred in the Kirkland Lake area probably preceeded the hydrothermal alteration of the rocks and the introduction of the ore minerals. Although both the carbonatizing fluids and the hydrothermal mineralizing fluids apparently utilized the same channelways in the rocks, they do not necessarily coincide in either occurrence or intensity. Also, the carbonatization affected much larger areas than did the hydrothermal alteration and mineralization. Some of the wallrock carbonate, however, is post alteration; the examination of thin sections made from some of the wallrock samples analyzed in this study reveals that a small part of the carbonate found in these samples occurs in quartz- and carbonate-filled fractures that are obviously post-alteration.

The rock analyses given by Todd (1928) suggest that the alteration of the wallrocks was not accompanied by any really marked changes in the chemical compositions of the rocks, although Bruce (1941) has pointed out that the amounts of some of the constituents in the fresh rocks show such a wide range of values that it would be difficult to prove whether or not any significant changes had occurred, this is particularly true for K_2O and Na_2O .

The texture of the altered rocks has been changed from granitoid to brecciated and streaky, largely because of rock movement.

Ores. The ores at Kirkland Lake have been termed mesothermal by Lindgren (1933). The principal ore mineral is native gold; gold and silver tellurides are of secondary importance. Sulfides, especially pyrite, are widespread in the ore zone but are of relatively minor occurrence. Some iron oxides occur and are the principal coloring agent in the alteration zone. The non-metallic gangue minerals are quartz, iron-bearing calcite and dolomite, tourmaline, leucoxene, chlorite, sericite, and some biotite. The veins are not zoned and the ores are quite uniform throughout the entire vertical range of 3000 feet that has been mined.

In the Macassa mine most of the ore is associated with the quartz vein filling, and is usually found along fractures in the quartz. The ore consists principally of altered country rock containing gold-bearing quartz stringers.

According to Hawley (1948) the mineralization occurred during the period of fracturing and faulting of the rock rather than afterward; progressive fracturing and mineralization led to the fracturing and replacement of early minerals by later ones. The general sequence of events in the main ore zone has been summarized by Hawley as follows:

1. Pre-ore alteration (deuteric or hydrothermal): relatively mild; carbonatization, chloritization and silicification of mafic minerals; slight sericitization and some iron-oxide staining of feldspars.

2. Hydrothermal alteration: more extensive alteration of wallrocks to ferruginous dolomite; more complete alteration of mafics to carbonates, quartz and chlorite; widespread dissemination of carbonates throughout the alteration zone.
3. Pyritization of wallrocks.
4. Main introduction of quartz.
5. Minor introduction of calcite into quartz veins and wallrocks.
6. Main deposition of metallic minerals, sulfides, tellurides and native gold, in that order; additional seritization of wallrocks.
7. Post-ore faulting, veining, and alteration: calcite, barite, quartz and minor sulfides introduced.

Controls of Ore Emplacement. The Kirkland Lake ores are structurally controlled. The faulting and fracturing of the rocks provided the fissures which were later filled by quartz. Subsequent fracturing of the quartz provided minute cracks and fractures in which most of the gold was deposited. The syenitic intrusives were more brittle than the surrounding country rocks and consequently were fractured to a greater extent than the surrounding rocks. The syenite porphyry was the most brittle of all the rocks, causing it to be fractured to a much greater extent than any of the other rocks. As a consequence, the syenite porphyry became the major host rock for the gold mineralization at Kirkland Lake.

Source of the Ore Mineralization. As in the case of nearly all ore deposits, the source of the economic mineralization at Kirkland Lake is not known. Dougherty (1939) believes that the successive intrusion of three syenitic rock types prior to the formation of the lode quartz indicates differentiation from a common magmatic source. Bateman (1950) has taken the intense silicification and carbonatization that has occurred in the ore zone to indicate that the intrusives and ore solutions were all derived from the differentiation of a granitic magma at depth. The fact that the alteration and ore mineralization are both uniform and unzoned throughout the great vertical range (over 8000 feet) in which they are known to occur indicates that there were probably no great thermal or chemical gradients in the ore zone at the time of mineralization; this would suggest that the (presumed) magmatic source of the ore mineralization was not close at hand.

Samples. Most of the samples examined from the Kirkland Lake district were collected from the Macassa mine. Permission to collect the samples underground was extended through the courtesy of Mr. M.R. MacPherson, Manager of the Macassa Gold Mine. Mr. W.G. Ward, Mine Geologist and Engineer, guided me through the underground workings and also assisted me in the collection of the samples. I would like to give special thanks to these men for both their interest in this study and their assistance to me in obtaining the samples.

The Macassa mine samples were collected from the 4625', 4750', 4900' and 5025' levels; the sample locations are shown on the plans of these levels (Figures IV through VII). The samples consisted of barren syenite country rock, and altered syenite and altered syenite porphyry from the ore zone. All of the samples were taken at least 100 feet from the one mappable diabase dike in the mine. The syenite country rock samples show a small amount of alteration, when examined in thin section, but it is believed that this alteration is of too small an extent to significantly affect the age analyses of these samples. Much of the alteration referred to in the syenite country rock samples is carbonatization, the effects of which are discussed later in this chapter. Thin stringers and veinlets of quartz and carbonate were visible in a few of the hand samples; in each instance these veinlets were excluded from the portion of the sample which was taken for analysis.

A group of six samples of rock from the alteration zone of the Kirkland Lake district were selected from among those available in the Lindgren Collection at M.I.T. These samples were from mines that are no longer open. No attention was paid to the original rock type, but rather samples were chosen which exhibited the prominent reddish coloration which is characteristic of the alteration around the main ore zone. The purpose of this test was to determine whether or not the same age would be obtained from a random

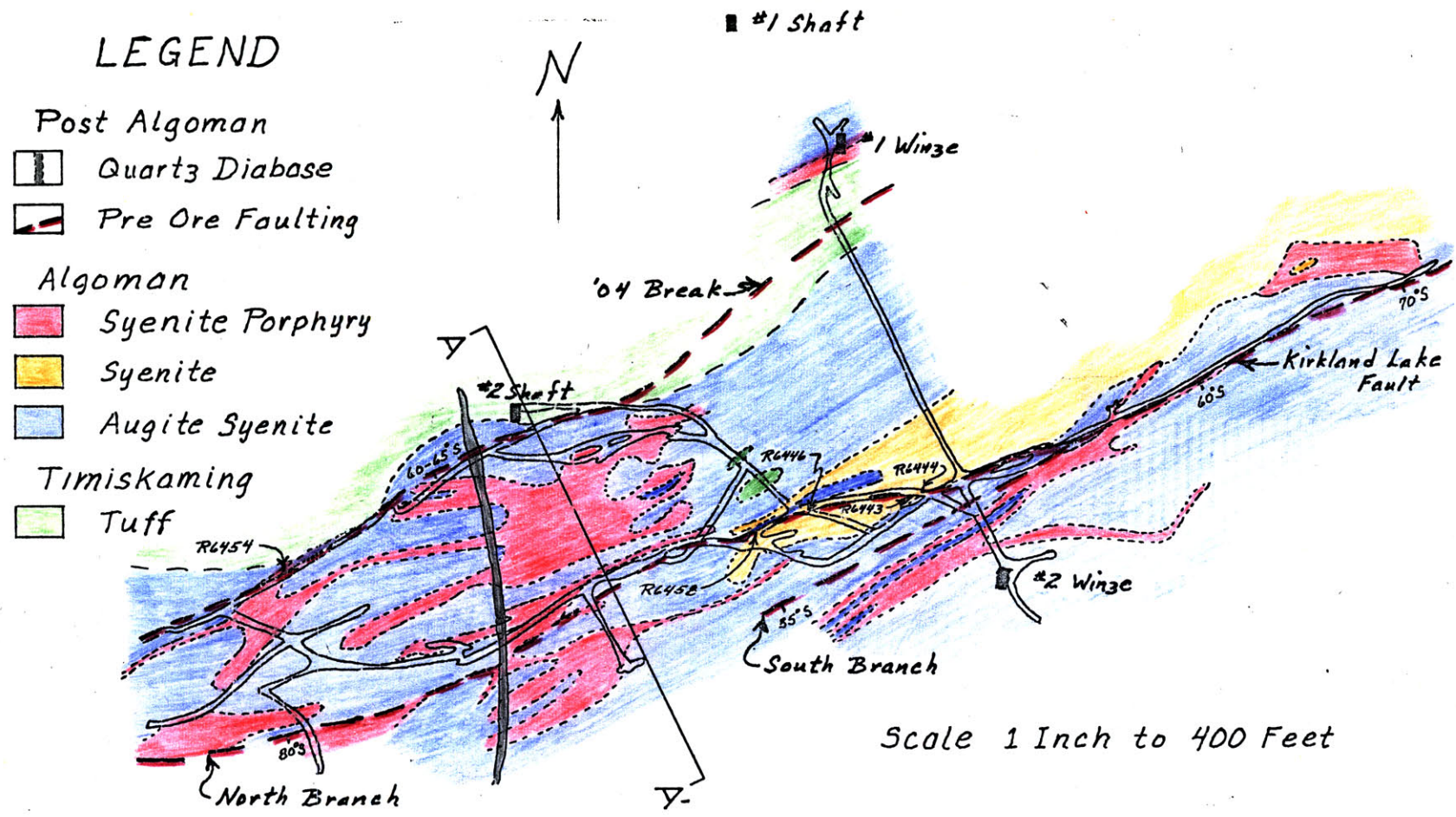


FIGURE IV

GEOLOGICAL PLAN OF THE 4625' LEVEL OF THE MACASSA MINE, KIRKLAND LAKE, ONTARIO.

(Mine plans supplied through the courtesy of the Macassa Gold Mines, Ltd.)

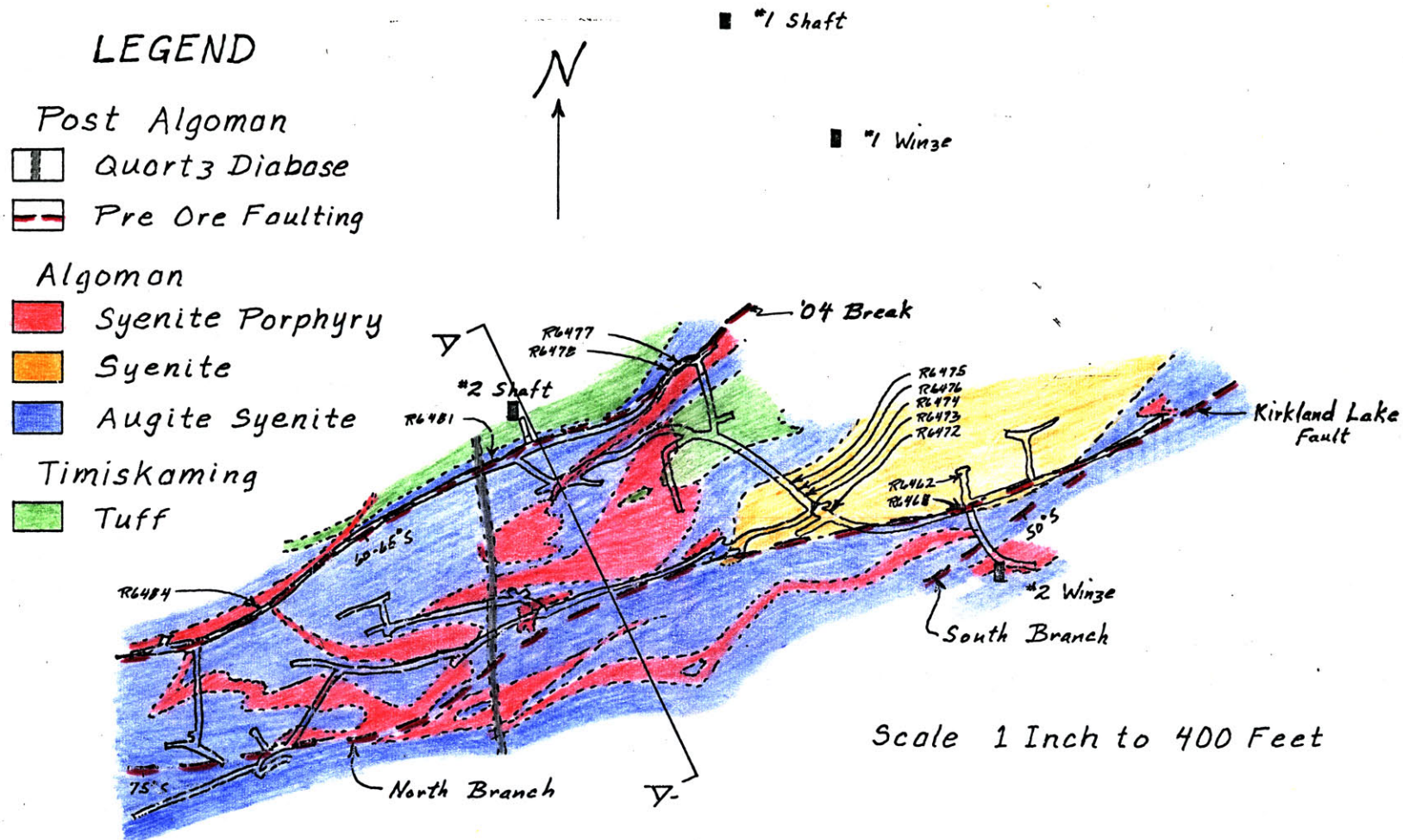


FIGURE V

GEOLOGICAL PLAN OF THE 4750' LEVEL OF THE MACASSA MINE, KIRKLAND LAKE, ONTARIO.

(Mine plans supplied through the courtesy of the Macassa Gold Mines, Ltd.)

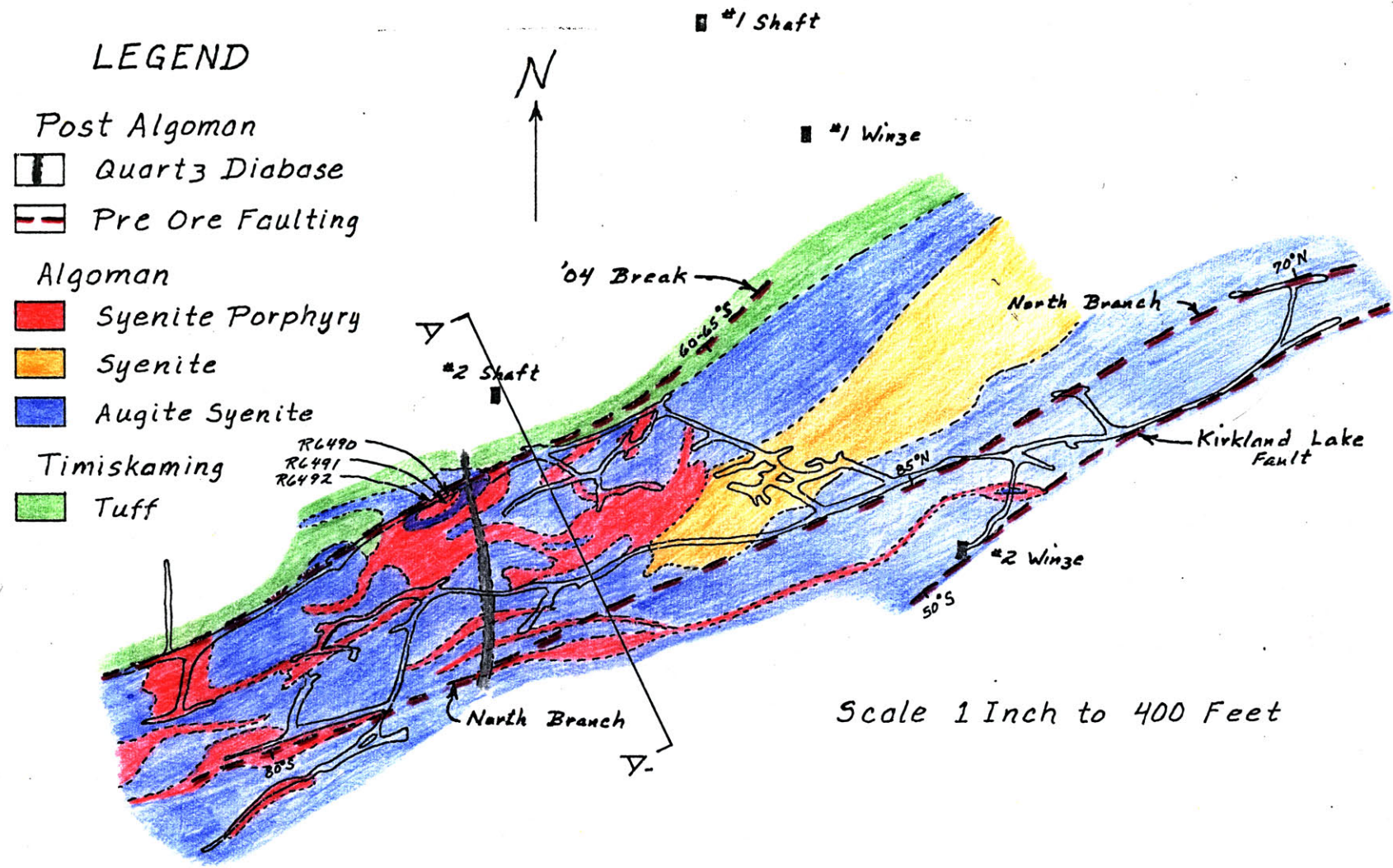


FIGURE VI

GEOLOGICAL PLAN OF THE 4900' LEVEL OF THE MACASSA MINE, KIRKLAND LAKE, ONTARIO.

(Mine plans supplied through the courtesy of the Macassa Gold Mines, Ltd.)

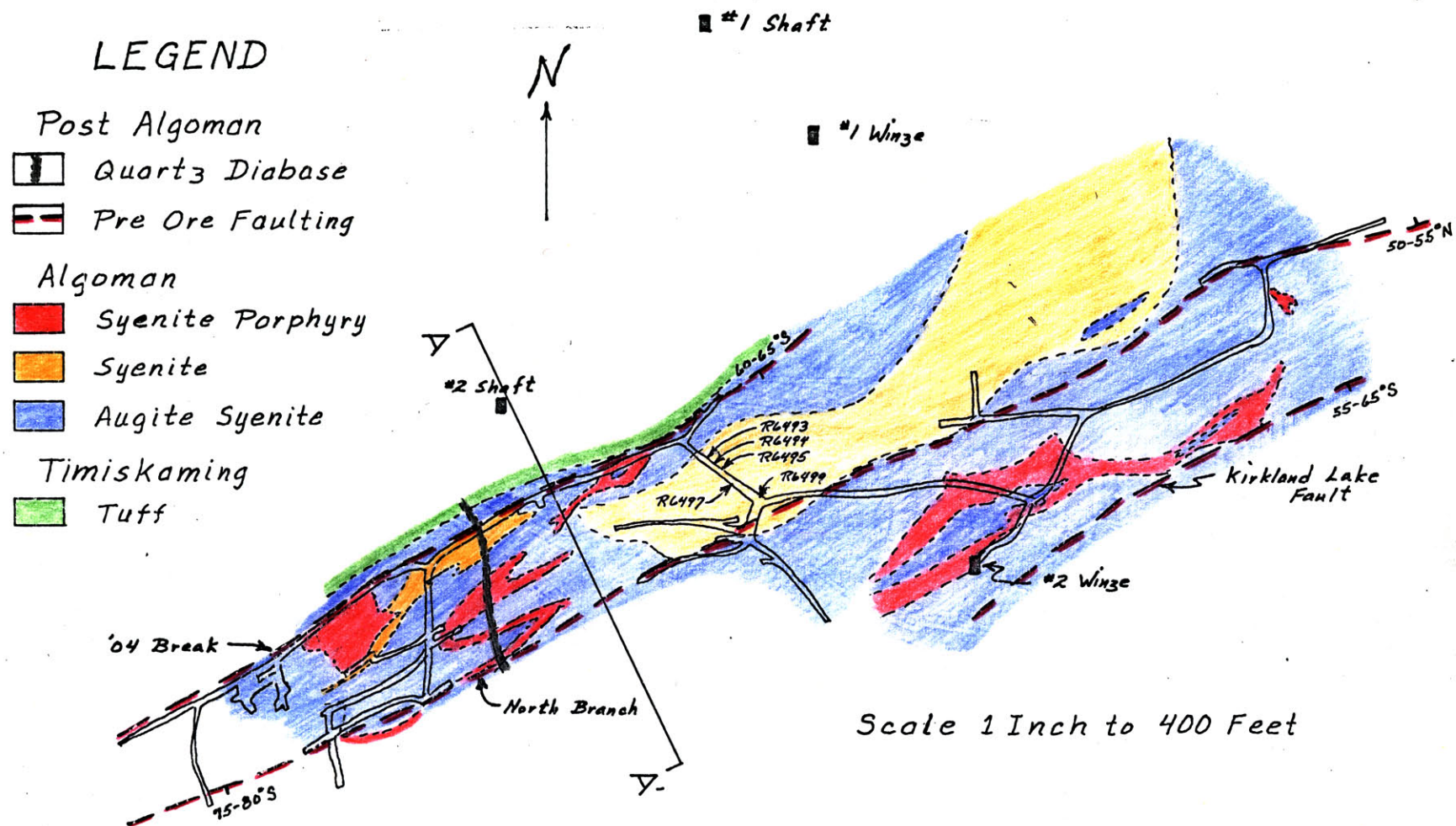


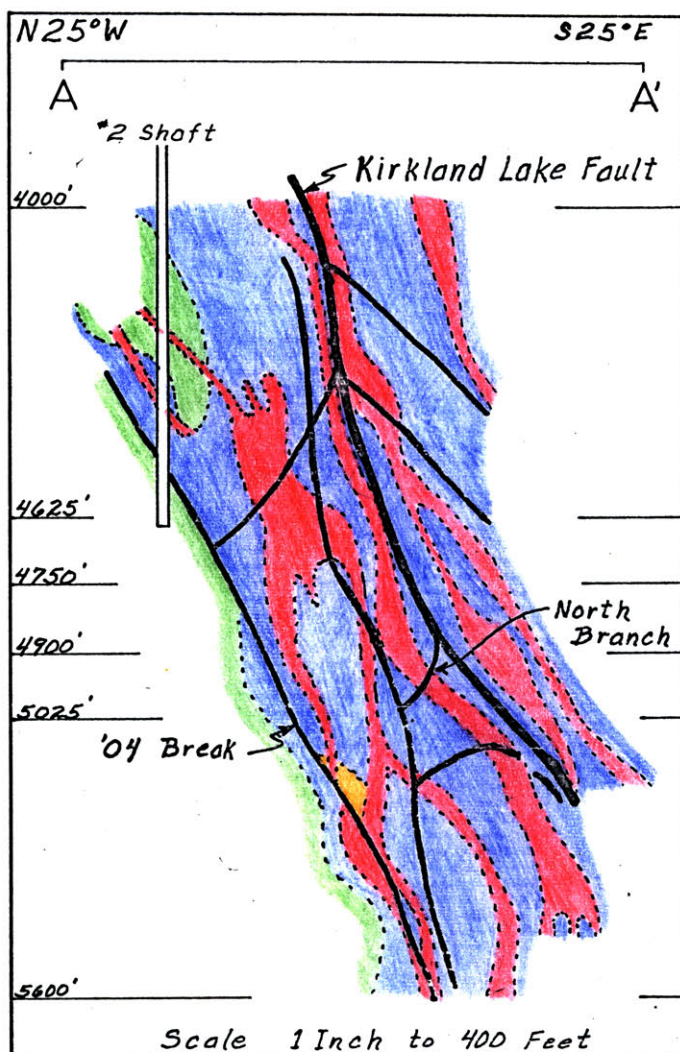
FIGURE VII

GEOLOGICAL PLAN OF THE 5025' LEVEL OF THE MACASSA MINE, KIRKLAND LAKE, ONTARIO.

(Mine plans supplied through the courtesy of the Macassa Gold Mines, Ltd.)

FIGURE VIII
 GEOLOGICAL CROSS SECTION THROUGH THE
 MACASSA MINE, KIRKLAND LAKE, ONTARIO.

(After Charlewood, G.H., 1964,
 Sheet A, Section No. 2 West.)



LEGEND

- Syenite Porphyry
- Syenite
- Augite Syenite
- Tuff

sampling of the Kirkland Lake ores as was obtained from the altered syenite samples from the Macassa mine.

RESULTS AND DISCUSSION

Whole Rock Analyses

Syenite. Eight of the best syenite samples that could be obtained from the Macassa mine were analyzed for Rb and Sr. The results of these analyses are listed in Table VI. Duplicate analyses were made on four of these samples, and as can be seen in the table these duplicates show good agreement with respect to both Rb and Sr concentrations and Sr isotopic compositions. Because the four samples which were not run in duplicate were prepared at the same time as the second set of the duplicates, the good agreement between the duplicates is taken as an indication that the quality of the analyses on all the samples is good.

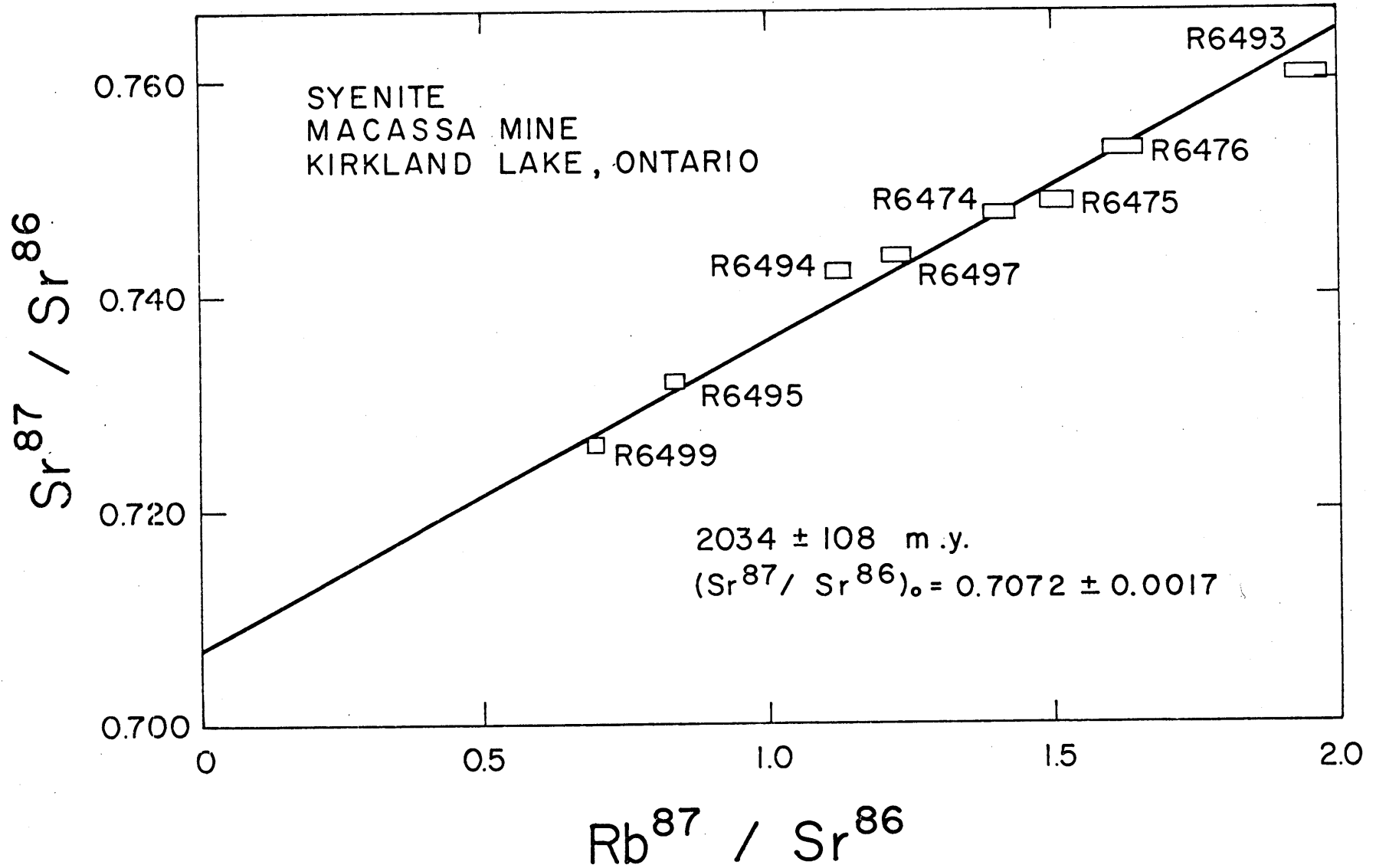
Shown in Figure IX is an isochron plot of these samples. The error limits for each analysis are shown by the size of the rectangle given for each sample point. On this plot the values shown for the samples on which duplicate analyses were made are the average of each set of duplicates. The samples show a large degree of scatter on the plot; this is most probably due to the masking effect of the strontium contained in the carbonate mineralization, as will be shown in a later section. The least squares isochron age for these points is 2034 ± 108 m.y. and the $\text{Sr}^{87}/\text{Sr}^{86}$ initial composition is 0.7072 ± 0.0017 .

TABLE VI

Syenite - Macassa Mine

<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6474	190	393	1.405	0.7477
R6475	207	400	1.504	0.7487
R6476	226	404	1.620	0.7535
R6493	236	351	1.955	0.7603
R6494	223	581	1.115	0.7424
	223	572	1.132	0.7422
R6495	209	725	0.836	0.7322
	210	723	0.843	0.7318
R6497	247	587	1.222	0.7440
	248	589	1.223	0.7435
R6499	196	817	0.696	0.7261
	193			

FIGURE IX



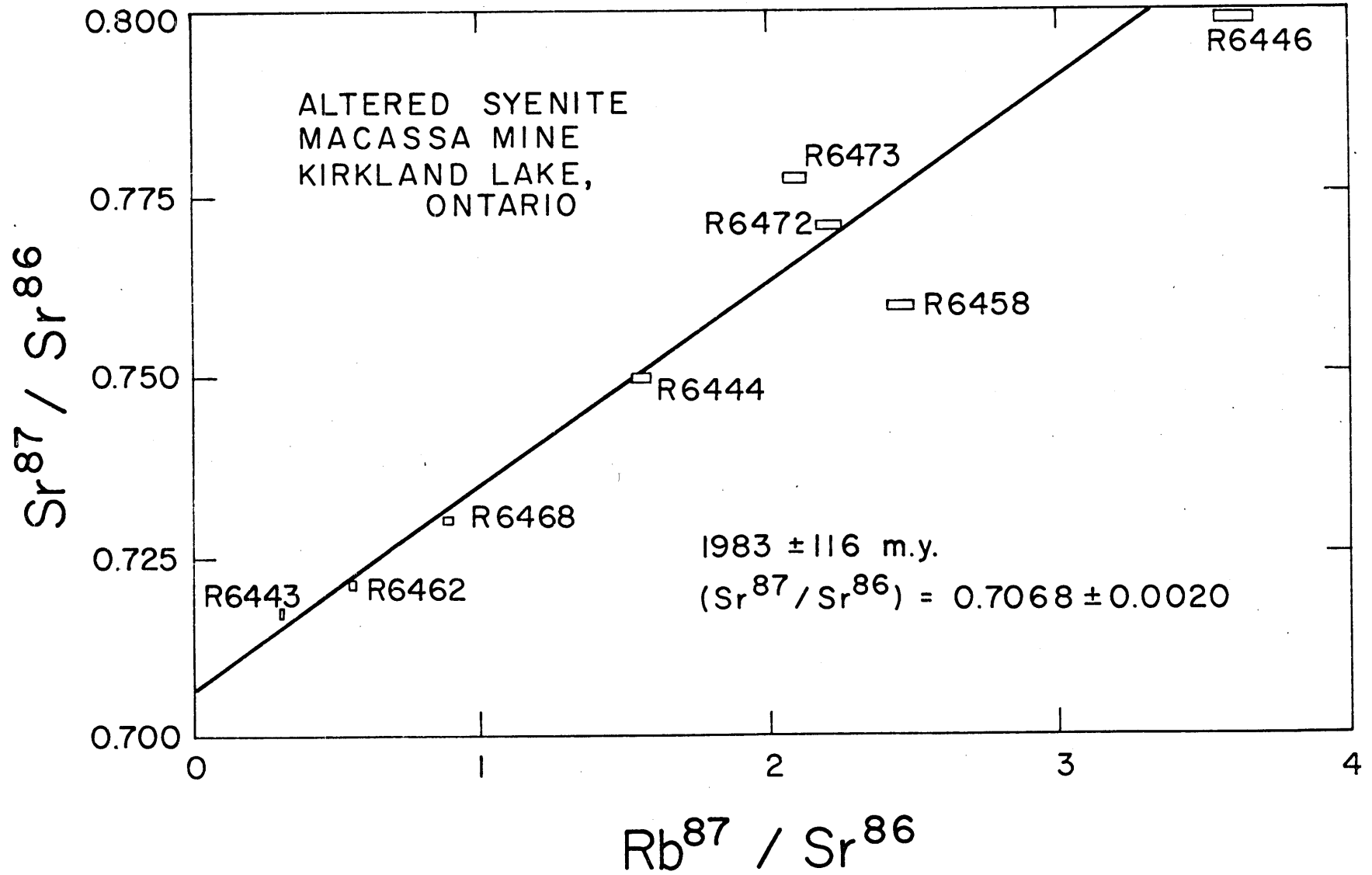
Altered Syenite. Eight samples of altered syenite from the Macassa mine were analyzed and the results are listed in Table VII. Figure X is an isochron plot for these samples. The least squares isochron for these samples, minus sample R6458, gives an age of 1983 ± 116 m.y. and an initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratio of 0.7068 ± 0.0020 . This age cannot be considered to be different from the preceding syenite age, within the limits of the errors on the isochrons. Sample R6458 was excluded from the age calculation in order to obtain the highest age value from these samples, since the purpose of this part of the study is to determine whether or not a younger age can be obtained from the rocks of the alteration zone than is obtained from the country rocks. Also, as will be shown later, this sample may not properly belong with the other samples on this plot. The inclusion of R6458 in the isochron age would lower it about 50 m.y.

TABLE VII

Altered Syenite - Macassa Mine

<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6443	72.3	807	0.309	0.7170
R6444	213	400	1.549	0.7496
R6446	264	213	3.620	0.7992
R6458	175	207	2.460	0.7597
R6462	175	913	0.554	0.7210
R6468	152	497	0.887	0.7300
R6472	292	387	2.199	0.7707
R6473	226	314	2.097	0.7724

FIGURE X



Altered Intrusive. Six samples of altered intrusive rock from the main ore zone were selected from among those available in the Lindgren Collection at M.I.T. These samples were selected at random and are from four different mines in the district that are no longer open. These samples were used to test the premise that all the altered rocks should yield approximately the same isochron age. The results of these analyses are listed in Table VIII, and they are shown diagrammatically in Figure XI. The least squares isochron age is 1917 ± 106 m.y. and the initial ratio is 0.7048 ± 0.0011 . Within the limits of the errors on the isochrons both this isochron and the altered syenite isochron are identical, and although both of these isochrons suggest a lower age than does the syenite isochron, all three of the isochrons are indistinguishable from one another, within the limits of the isochron errors.

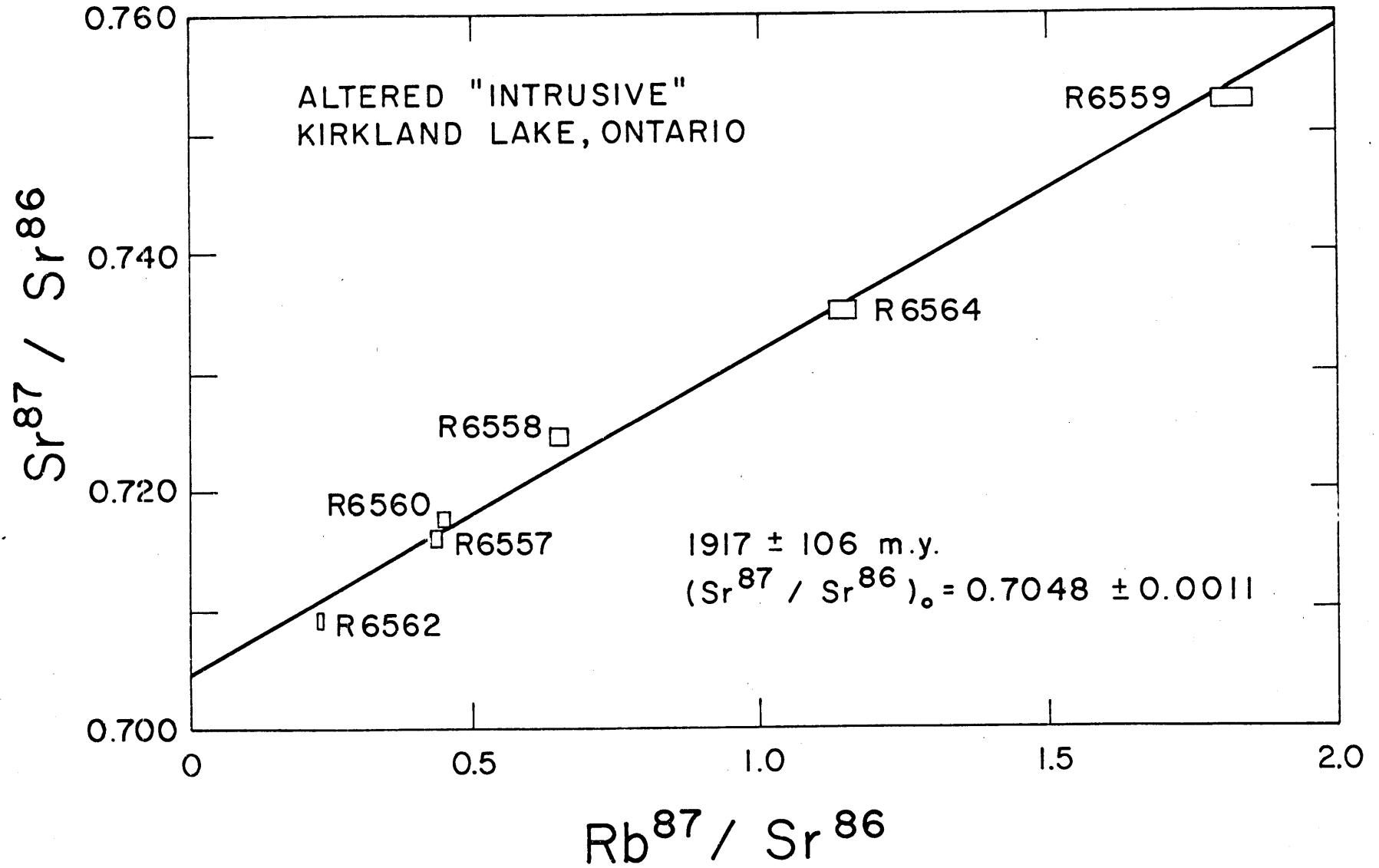
Conclusions of Whole Rock Analyses. Three suites of whole rock samples from the Kirkland Lake district have been analyzed for Rb and Sr. These suites consisted of samples of syenite and altered syenite from the Macassa mine and a suite of altered intrusive rocks selected at random from various places throughout the alteration zone in the district. All three isochrons are of rather poor quality and within the limits of the errors on the isochrons they are indistinguishable from one another. The two suites of altered samples may give isochron ages that

TABLE VIII

Altered Intrusive - Kirkland Lake, Ontario

<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6557	85.5	564	0.439	0.7162
R6558	119	531	0.650	0.7246
R6559	117	186	1.820	0.7527
R6560	108	697	0.449	0.7177
R6562	70.6	901	0.227	0.7095
R6564	52.0	132	1.143	0.7352

FIGURE XI



are slightly lower than that obtained from the suite of syenite samples, but there is no clear evidence to support this inference.

Two possibilities are suggested by the isochron analyses reported in this section. One possibility is that there was no large scale mixing and homogenization of the strontium in the alteration zone at the time of alteration, and the other possibility is that the alteration occurred only a relatively short time after the emplacement of the host rocks and thus the times of host rock emplacement and hydrothermal alteration are identical, or nearly so.

A third possibility not suggested by the foregoing analyses is suggested by the fact that all of these rock samples have been intensely carbonatized, leading to the development of calcite and dolomite in the rocks. This carbonate material would probably contain significant amounts of strontium which may be of a different age and of a different origin, and thus of a different composition than the strontium incorporated into the other alteration minerals, and thus might be masking the correct isochron analyses of these samples. This possibility will be investigated in the following section.

Investigation of Carbonate Strontium

Possible Effects of the Inclusion of Carbonate in the Whole Rock Analyses of Carbonatized Rocks. The syenitic host rocks of the Kirkland Lake district have been strongly carbonatized. Since this carbonate (calcite and dolomite) undoubtedly contains significant amounts of strontium

it was necessary to determine what effect this carbonate strontium had on the whole rock analyses.

One possibility is that no large scale homogenization of the strontium isotopic composition occurred at the time of wallrock alteration; local equilibrium may have been achieved between the carbonate and the other alteration minerals. In this case the carbonate Sr would act merely as a diluent and the removal of this strontium from the rock samples would not improve the isochron analyses.

A second possibility is that strontium isotopic homogenization was partially achieved at the time of alteration, but the carbonate strontium was not in equilibrium with the strontium in the other alteration minerals, possibly because the strontium is of a different generation or else is of more than one generation. In this case removing the carbonate Sr might improve the isochron analyses of the samples.

A third possibility is that strontium homogenization was largely achieved at the time of alteration, but that the carbonate strontium was not in equilibrium with this homogenized strontium. In this case the removal of the carbonate strontium should be expected to improve the isochron analyses of the samples.

Before a more thorough study was made of the Kirkland Lake samples, a preliminary leaching experiment was performed on four samples of the syenite country rock. Three different types of acids were used. The purpose of the

leaching experiment was to determine whether or not further useful information might be obtained from these samples, and to determine the relative leaching effects of the different acids. This experiment will now be discussed.

Leaching Experiment on Four Kirkland Lake Syenite Samples. One split of each of four samples of the syenite country rock was leached with 2N HCl and one split of each sample was leached with glacial acetic acid in order to determine the differences in amounts and compositions of Sr (and Rb) leached from the rocks by the two acids, and to determine the effects on the isochron analyses of the leached samples; a split of one sample was also leached with 6N HCl. The leaching procedure has previously been described in Chapter I. The filter papers used to filter two of the 2N HCl leached solutions were also examined for Rb to determine whether or not any insoluble Rb salts were being precipitated during the filtering step. These filter papers were boiled in 40 ml of demineralized water for 30 minutes, then the water was spiked with Rb spike and the solutions analyzed.

The results of all the analyses made in the leaching experiment are listed in Table IX, as are the whole rock sample analyses. These results show that the amount of Rb remaining in the filter papers was negligible. The 2N HCl leached more Sr and Rb from the rocks than did the acetic acid, and in general the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the 2N HCl leach were somewhat greater than were those of the

TABLE IX

Results of Leaching Experiment on Syenite Samples

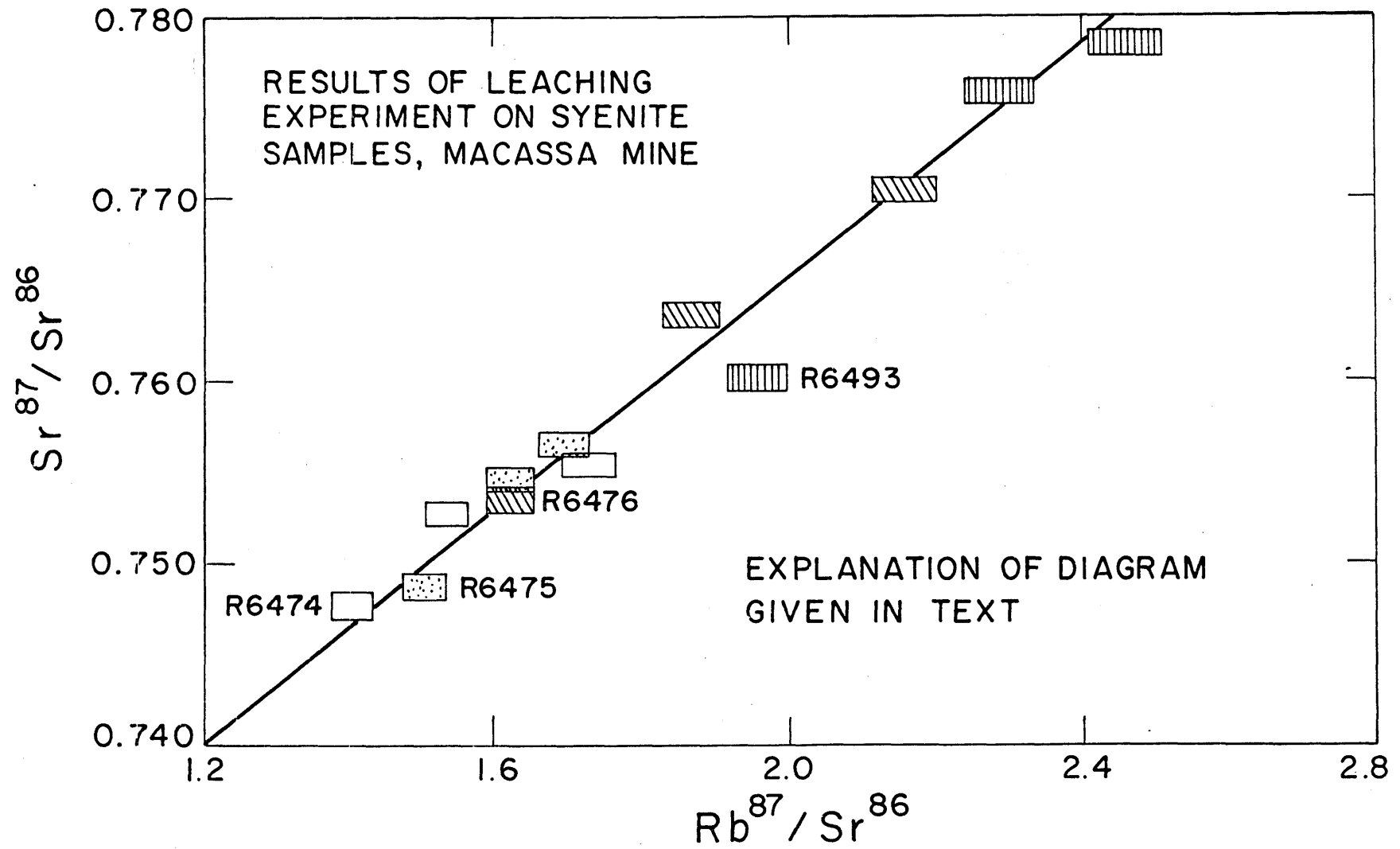
<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
Whole Rock Samples				
R6474	190	393	1.405	0.7477
R6475	207	400	1.504	0.7487
R6476	226	404	1.620	0.7535
R6493	236	351	1.955	0.7603
Samples Leached With Glacial Acetic Acid				
R6474a-1	187	354	1.535	0.7527
R6475a-1	196	352	1.619	0.7545
R6476a-1	214	334	1.866	0.7636
R6493a-1	238	304	2.281	0.7758
Solutions Leached by Glacial Acetic Acid				
R6474b-1	2.4	78.8		0.7132
R6475b-1	2.2	57.7		0.7199
R6476b-1	2.55	80		
R6493b-1	3.2	70.5		0.7129
Samples Leached With 2N HCl				
R6474a-2	198	333	1.729	0.7554
R6475a-2	198	340	1.693	0.7565
R6476a-2	233	314	2.161	0.7705
R6493a-2	232	275	2.460	0.7784
Solutions Leached by 2N HCl				
R6475b-2	1.9	75.6		0.7180
R6476b-2	7.0	113		0.7161
R6493b-2	6.6	112		0.7186
Filter Paper, 2N HCl Leach				
R6476b-2	0.3			
R6493b-2	0.02			
Sample Leached With 6N HCl				
R6475a-3	201	338	1.729	0.7556
Solution Leached by 6N HCl				
R6475b-3	5.3	76.0		0.7181

glacial acetic acid leach. The amount and composition of the Sr leached by the 6N HCl was identical with that leached by the 2N HCl, although the amount of Rb leached by the 6N HCl would appear to be somewhat greater than that leached by the 2N HCl.

The greater $\text{Sr}^{87}/\text{Sr}^{86}$ ratios of the materials leached by the 2N HCl and the 6N HCl when compared with that leached by the glacial acetic acid are probably due to small amounts of radiogenic Sr^{87} being leached by the HCl as evidenced by the greater amounts of Rb leached. This will be discussed more fully in a later section. The greater amounts of Sr leached by the HCl when compared with that leached by the glacial acetic acid are most probably accounted for by the fact that the HCl would tend to react to a greater extent with any dolomite present.

The results of the leached sample analyses are shown diagrammatically in Figure XII, along with the whole rock sample analyses. All three points corresponding to the three analyses of the same numbered sample are shown by the same symbol within the rectangles. The numbered point represents the whole rock sample; the point farthest up the isochron represents the sample after it was leached with 2N HCl; the intermediate point represents the sample after it was leached with glacial acetic acid. The size of each rectangle corresponds with the limits of the analytical errors for each point. Within the limits of these errors the three points for each sample fall on a straight

FIGURE XII



line; this would be expected since the analyses of the materials leached from each numbered sample by both acids are rather similar, they differ mainly in the amounts leached. There appears to be a tendency for the samples leached with glacial acetic acid to give slightly lower Rb^{87}/Sr^{86} ratios than would be expected, when compared with those of the unleached samples and the samples leached with 2N HCl, but it is not possible to say with certainty whether this slight effect is real or not. If this effect is real it could be due to a systematic error in the spiking of either the four samples leached with 2N HCl or the four samples leached with glacial acetic acid.

The quality of the leaching analyses can be determined in two ways. One method is to extend tie-lines between the whole rock and leached sample points and to extrapolate these lines back to the line $Rb^{87}/Sr^{86} = 0$, on the isochron plot. Within the limits of the analytical errors each tie-line should intersect the line $Rb^{87}/Sr^{86} = 0$ at the value of the Sr^{87}/Sr^{86} composition of the material leached from the sample. The other method is to calculate the material balance from the three sets of measurements made on each sample (i.e. whole rock, leached rock, and leached solution). This second method is quite sensitive to both the strontium concentrations and compositions in all three fractions of the sample.

In this study all three fractions of thirteen of the samples which were leached were analyzed. It will be

seen later that when the graphical test of the quality of the leaching analyses was applied to these samples three of them yielded poor tie-line linearity. When the arithmetic test was applied all of the samples gave excellent material balances. The reason for the three discrepant samples will be discussed when the sample analyses are discussed.

Conclusions of Leaching Experiment. The results of the leaching experiment show that the carbonate contains significant amounts of strontium; the removal of this carbonate might therefore be expected to lead to improved isochron results. Either 2N HCl or glacial acetic acid should yield satisfactory leaching results, although the 2N HCl might be expected to give somewhat better results due to the fact that it would more completely react with any dolomite present than would the glacial acetic acid.

2N HCl was used to leach two groups of samples in the following section, glacial acetic acid was used to leach one group.

Leached Rock Analyses

Leached Syenite. Splits of all eight of the syenite samples previously analyzed as whole rocks were leached with 2N HCl and re-analyzed, splits of seven of these samples were leached and analyzed in duplicate. The results of these analyses are listed in Table X and they are shown diagrammatically in Figure XIII. All fifteen of the leached rock analyses are shown on the isochron plot

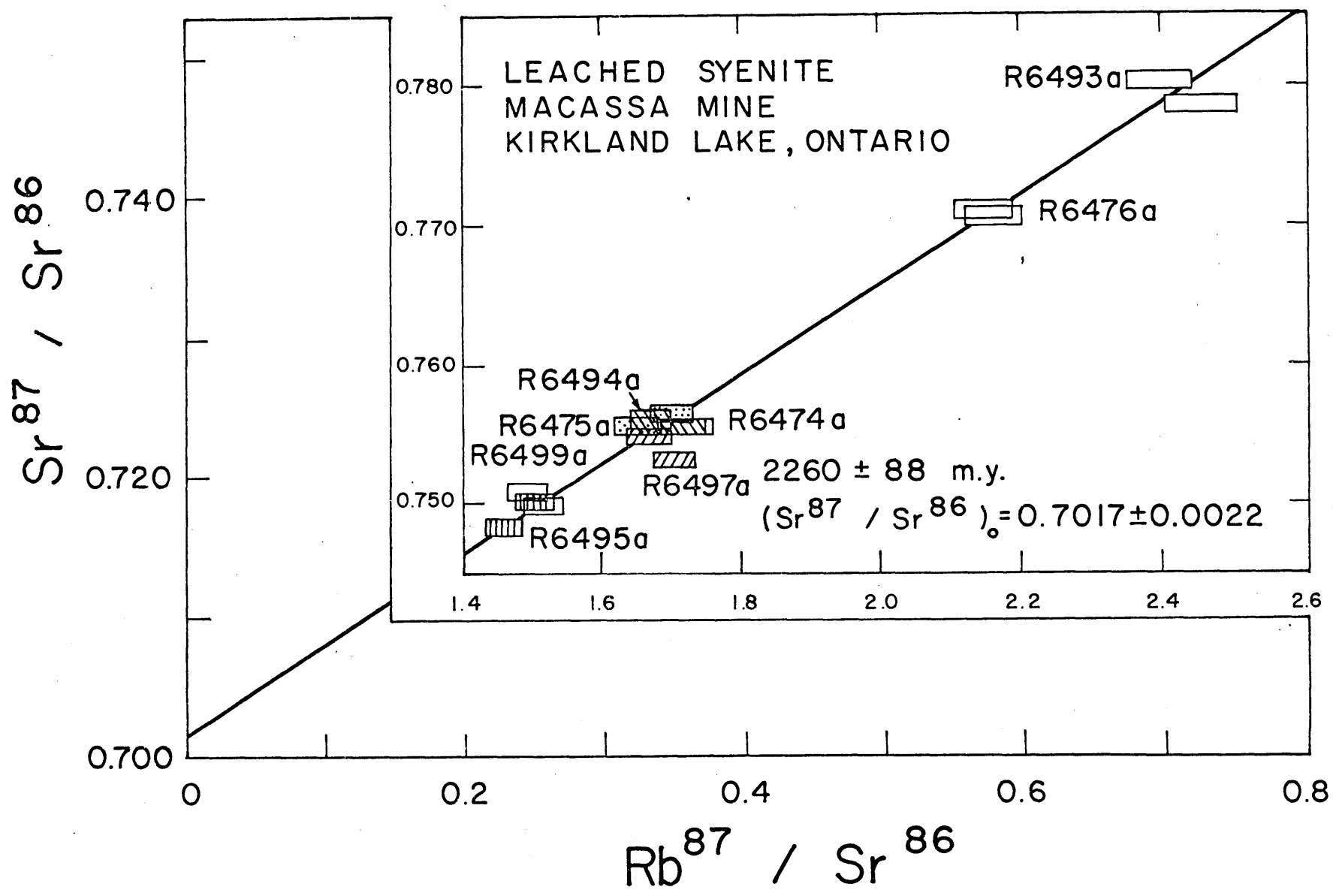
TABLE X

Leached Syenite* - Macassa Mine

<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6474a	198	354	1.729	0.7554
R6475a (1)	198	340	1.693	0.7565
" (2)	196	346	1.646	0.7556
R6476a (1)	230	312	2.147	0.7710
" (2)	233	314	2.161	0.7705
R6493a (1)	234	284	2.402	0.7802
" (2)	232	275	2.460	0.7784
R6494a (1)	244	414	1.716	0.7554
" (2)	241	421	1.665	0.7561
R6495a (1)	223	429	1.511	0.7501
" (2)	218	434	1.460	0.7485
R6497a (1)	259	444	1.696	0.7531
" (2)	255	445	1.666	0.7548
R6499a (1)	202	392	1.498	0.7509
" (2)	204	391	1.517	0.7500

*Samples leached with 2N HCl.

FIGURE XIII



so that a visual comparison can be made of the duplicate analyses. In the lower part of the diagram where the error rectangles for several samples overlap similar symbols have been used for each of the sets of duplicates to help in distinguishing among the various samples. The agreement between the seven sets of duplicates is considered to be good.

The least squares isochron age for these samples is 2260 ± 88 m.y. and the initial ratio is 0.7017 ± 0.0022 . The linearity of this isochron is markedly improved over that of the whole rock syenite isochron (Figure IX). In Figure XIII it can be seen that fourteen of the fifteen leached samples fall on the computed isochron, within the limits of the errors on the measurements. It is unfortunate that the spread in the $\text{Rb}^{87}/\text{Sr}^{86}$ ratios for these leached samples is not greater, but these samples are composed predominantly of feldspar, with only minor biotite, etc., therefore the rather restricted range of $\text{Rb}^{87}/\text{Sr}^{86}$ ratios is not surprising.

Listed in Table XI are the analyses of the solutions leached from these samples.

When the graphical test for the quality of the leaching analyses was applied to the eight syenite samples it was found that five of the samples gave excellent agreement. The tie-lines for samples R6475, R6476 and R6493 gave ordinate intercepts significantly below the $\text{Sr}^{87}/\text{Sr}^{86}$ ratios measured in the leached solutions; for all three

TABLE XI

Analyses of Solutions Leached from Syenite - Macassa Mine

<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6475b	1.9	75.6	0.7180
R6476b (2)	7.05	113	0.7161
R6476b (2) Filter paper	0.3		
R6493b (2)	6.6	112	0.7186
R6493b (2) Filter paper	0.02		
R6494b (1)		200	0.7146
R6494b (2)	3.5	208	0.7160
R6495b (1)		331	0.7113
R6495b (2)	5.0	337	0.7128
R6497b (1)		169	0.7132
R6497b (2)	7.0	173	0.7142
R6499b (2)		485	0.7086

samples these intercepts were close to 0.710. When the arithmetic test was applied all eight leached syenite samples gave excellent agreement, indicating that the quality of the leaching analyses was good. For both of these tests the average values of the seven sets of duplicate analyses were used for the leached rock values.

One possible reason for the non-linearity of the tie-line points for samples R6475, R6476 and R6493 could be due to errors in the Rb analyses for the leached samples. As can be seen in Table XI, from 1% to 3% of the Rb was leached from these samples. If a 1% to 3% correction is made in the Rb/Sr values for these three samples the linearity of the tie-line points is greatly increased. However, the radiogenic Sr^{87} occupies Rb lattice positions in the minerals, and because of the differences in the ionic sizes and charges of Rb and Sr, the radiogenic Sr^{87} is metastable in these Rb positions. It can therefore be logically assumed that if up to 3% of the Rb was leached from the samples then at least as much, if not more, Sr^{87} was also leached; the effect of this would be that the position of the leached rock point would not change relative to the position of the tie-line. However, the leaching of radiogenic Sr^{87} from the rock would also give greater than correct $\text{Sr}^{87}/\text{Sr}^{86}$ ratios in the material leached from the samples. An examination of Table XI will reveal that the $87/86$ ratios of the material leached from samples R6475, R6476 and R6493 is somewhat greater

than those of the other samples, And, although the analyses of the other samples indicate that approximately the same amount of Rb was leached from all the samples, considerably less Sr was leached from the three samples in question. Therefore, the effect of the addition of radiogenic Sr^{87} to these leached solutions would be expected to be more severe than with the other samples. Also, the Rb/Sr ratios of these three samples are the highest of all the syenite samples, thus relatively more Sr^{87} was available for leaching from the samples. Calculations show that the leaching of 2% to 3% of the radiogenic Sr^{87} would easily account for the non-linearities observed in two of the three samples. For sample R6493 the leaching of 4% to 5% of the radiogenic Sr^{87} would be necessary to account for the non-linearity observed.

It will also be seen in Table VII and in Table XII, to follow, that the altered syenite sample which gave the greatest $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in the leached material (sample R6446) also had the greatest Rb/Sr ratio of all the altered syenite samples and next to the lowest amount of Sr leached. This greater $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in the leached material is also probably due to the relative effects of leached radiogenic Sr^{87} .

It would appear, therefore, that the non-linearities in the tie-lines for samples R6475, R6476 and R6493 are due to the greater than correct $\text{Sr}^{87}/\text{Sr}^{86}$ ratios in the leached solutions and are not due to the incorrect relative positions of the leached sample points on the

isochron plot. The leaching of radiogenic Sr^{87} from the samples has probably had no more than a very minor effect on the leached sample isochrons, as is evidenced by the linearity of most of the tie-lines for both the leached syenite samples discussed here, and the leached altered syenite samples to be discussed in the following section. It would be fortuitous indeed if the effects of the Rb and the radiogenic Sr^{87} leached from the rocks and the excess Sr^{87} added to the leached solutions were to combine to give such good linearity for the majority of the tie-lines.

It is believed that the isochron plot obtained from the leached syenite samples gives the approximately correct age for this body. This age (2260 m.y.) must be considered to be close to the maximum age for this body, within the limits of error placed on the isochron, since it is known from field relations that this body intrudes the Timiskaming rocks which have previously been dated by Fairbairn as 2368 ± 48 m.y.

Leached Altered Syenite. Splits of four of the altered syenite samples showing approximate linearity in Figure X (samples R6444, R6446, R6462 and R6468) were leached with 2N HCl and re-analyzed, as was sample R6458. An isochron through the four best points, before leaching, gives an age of 1855 ± 79 m.y. and an initial ratio of 0.7071 ± 0.0014 .

The results of the leached rock analyses are listed in Table XII. The values for the leached rock analyses

TABLE XII

Leached Altered Syenite - Macassa Mine

Analyses of Leached Samples*

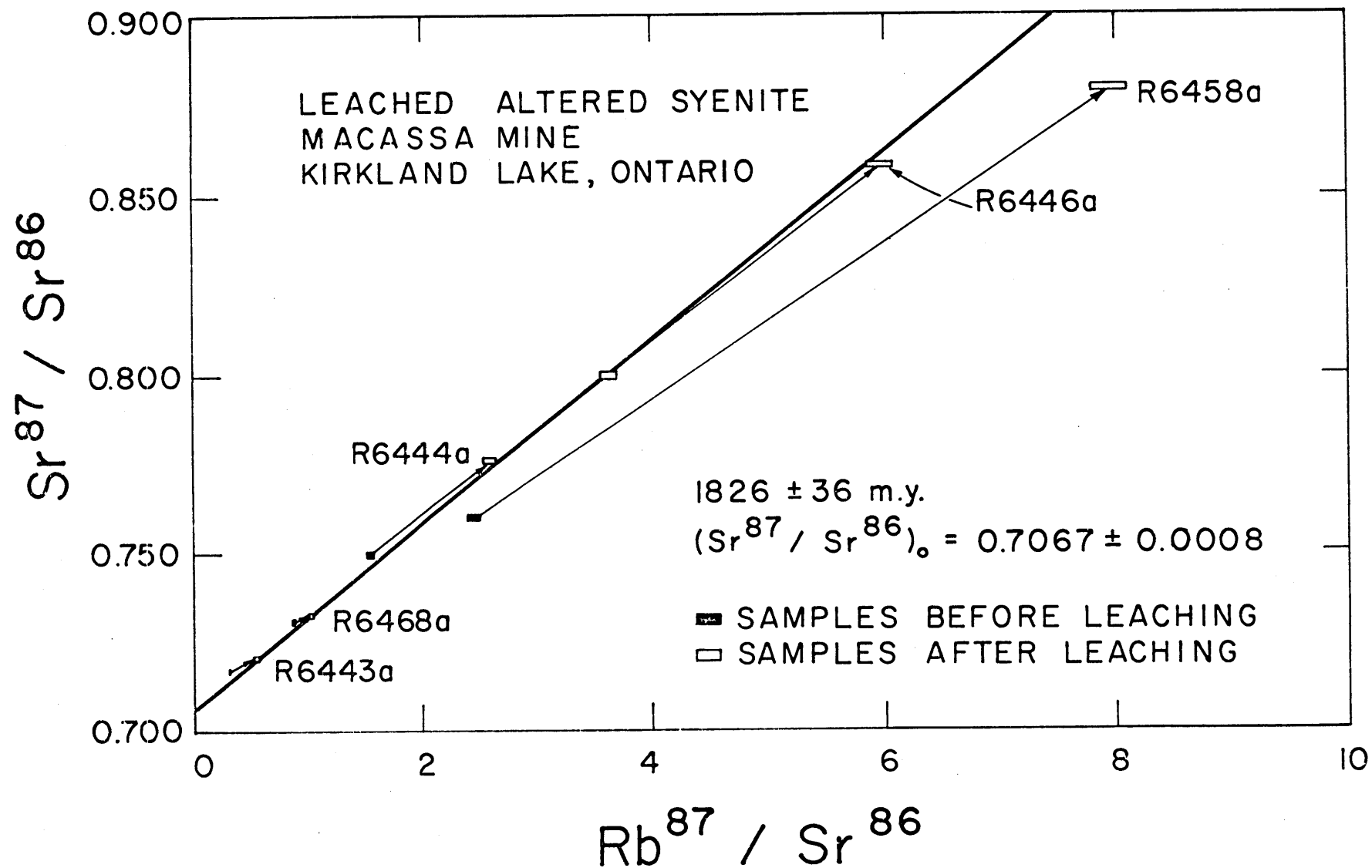
<u>Sample No.</u>	<u>Rb</u> _{ppm}	<u>Sr</u> _{ppm}	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6443a	78.5	415	0.548	0.7203
R6444a	221	246	2.618	0.7753
R6446a	254	125	5.974	0.8576
R6458a	164	60.6	7.965	0.8793
R6468a	149	438	0.987	0.7325

Analyses of Leached Solutions

R6443b	430	0.7135
R6444b	183	0.7156
R6446b	94.2	0.7192
R6458b	150	0.7135
R6468b	89.9	0.7152

*Samples leached with 2N HCl.

FIGURE XIV



are plotted in Figure XIV; also shown on this figure are the values for the whole rock samples and the tie-lines showing the shift of the points with leaching. The isochron age for the four linear samples is 1826 ± 36 m.y. with an initial ratio of 0.7067 ± 0.0008 . The linearity of the four best samples has been *increased* by the removal of the carbonate Sr while sample R6458 has been displaced further from the isochron, this may indicate that sample R6458 does not belong in the same group as the other samples.

When both the graphical and arithmetic tests for the quality of the leaching analyses were applied to these samples all five gave excellent agreement.

When compared with the leached syenite isochron (Figure XIII), the leached altered syenite isochron gives a significantly younger age than does that of the leached syenite.

Leached Altered Syenite Porphyry. Eight samples of altered syenite porphyry were leached with glacial acetic acid and then analyzed for Rb and Sr. Whole rock analyses were not made on any of these samples. The purpose of these leached rock analyses was to test the premise that any of the leached rocks of the alteration zone should yield approximately the same isochron age as that already obtained from the leached altered syenite samples, and that either 2N HCl or glacial acetic acid should yield about the same leaching results.

The results of these analyses are listed in Table XIII and they are shown diagrammatically in Figure XV. These samples show a fair degree of scatter on the isochron plot. The least squares isochron age given by these samples is 1734 ± 122 m.y. and the initial ratio is 0.7044 ± 0.0012 . Within the limits of error placed on this age, it is identical with the age calculated for the leached altered syenite samples (1826 ± 36 m.y.), and both of the leached altered rock isochrons give significantly younger ages than does the leached syenite isochron (2260 ± 88 m.y.).

Conclusions of Leached Rock Analyses. Three suites of carbonatized rocks from the Macassa mine have been leached and analyzed for Rb and Sr. These suites consisted of splits of the syenite and altered syenite samples which had previously been analyzed as whole rocks and a suite of altered syenite porphyry samples which have not been analyzed as whole rocks. The syenite and altered syenite samples were leached with 2N HCl; the altered syenite porphyry samples were leached with glacial acetic acid. The results of these analyses yield isochrons with greater linearity than those yielded by the unleached samples. When the two isochrons obtained from the suites of altered rocks are compared it is seen that they give identical ages within the limits of errors on the isochrons; when these two isochrons are compared with the isochron obtained from the leached syenite country rock it is seen that the rocks of the alteration zone yield significantly younger ages

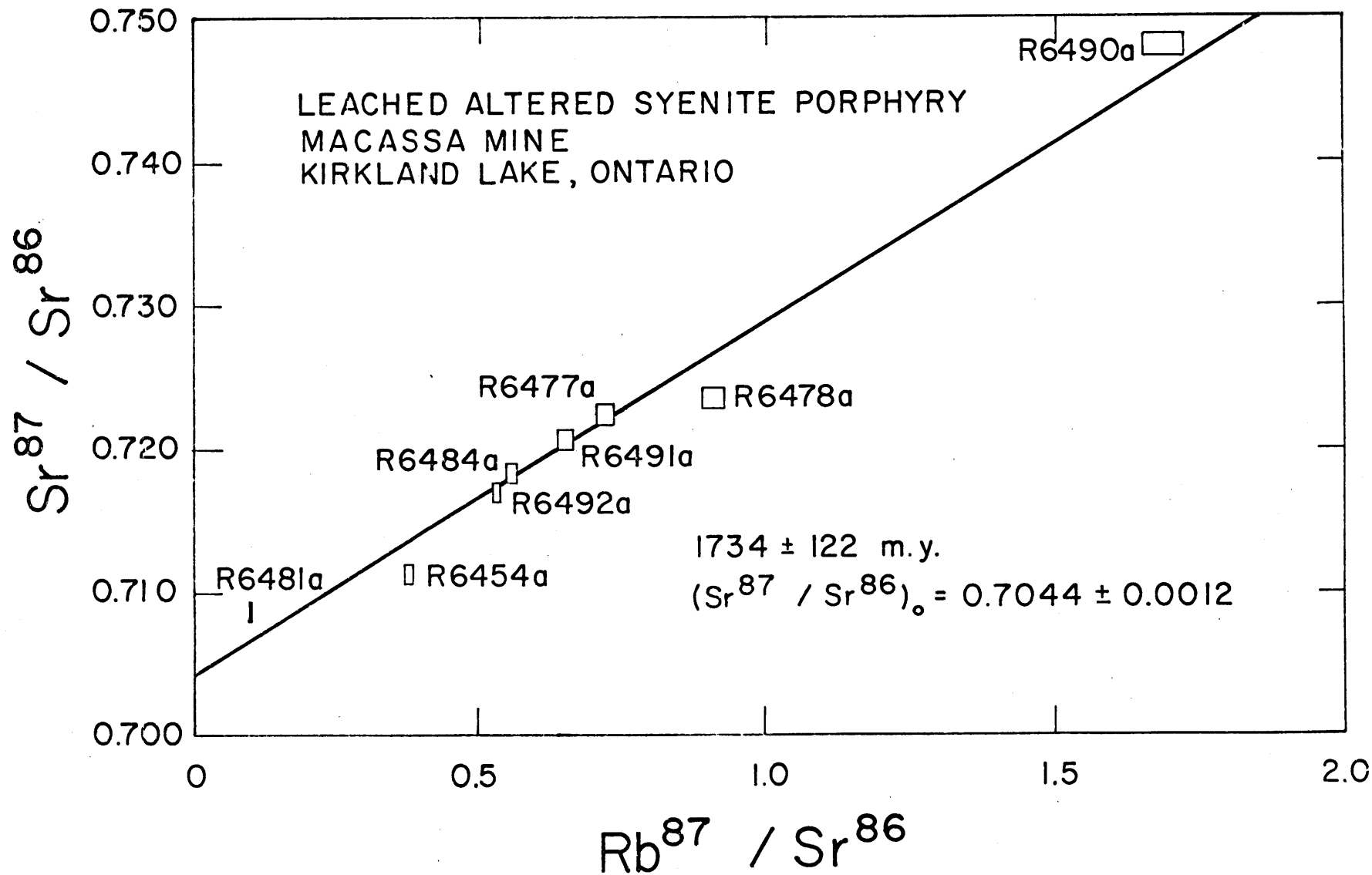
TABLE XIII

Leached Altered Syenite Porphyry - Macassa Mine*

<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6454a	92.7	718	0.374	0.7121
R6477a	138	569	0.704	0.7224
R6478a	137	437	0.909	0.7235
R6481a	61.1	1755	0.101	0.7087
R6484a	95.1	490	0.562	0.7185
R6490a	166	285	1.691	0.7480
R6491a	112	496	0.654	0.7207
R6492a	94.2	506	0.539	0.7170

*Samples leached with glacial acetic acid.

FIGURE XV



than do the country rock samples. The comparable results from both altered rock types using the two different types of acids are taken as assertions of the validity of the premises that any of the altered rock types should yield approximately the same isochron age, once the masking effect of the carbonate Sr has been removed, and that either 2N HCl or glacial acetic acid should yield comparable leaching results.

Conclusions of the Kirkland Lake Analyses

The analyses of a suite of syenite country rock samples and two suites of altered syenitic samples from the Kirkland Lake district have yielded Rb-Sr whole rock isochrons of rather poor quality and indistinguishable age (about 2000 m.y.), although it might be inferred that the altered rocks tended to give lower ages than did the country rocks. These rocks have all been intensely carbonatized and this carbonate material contains significant amounts of strontium; in a few cases the carbonate contains 50% or more of the whole rock strontium. When the syenite country rock samples and the altered syenite samples were leached with dilute acid and re-analyzed the linearities of the isochrons were improved and the isochrons for the two rock types yielded significantly different ages. The leached syenite samples yielded an age of about 2260 ± 88 m.y. and the leached altered syenite samples yielded an age of 1826 ± 36 m.y. A suite of altered syenite porphyry samples was leached with dilute acid and then analyzed

TABLE XIV

Comparison of Age Analyses from the Kirkland Lake Area

<u>Rock Unit</u>	<u>Age, m.y.</u>	<u>(Sr⁸⁷/Sr⁸⁶)_o</u>
Round Lake Pluton (Fairbairn)	2530	0.7031
" " " (Purdy & York)	2520	0.7015
Keewatin Series (Fairbairn)	2376	0.7026
Timiskaming Series (Fairbairn)	2368	0.7032
Syenite (leached)	2260	0.7017
Altered Syenite (leached)	1826	0.7067
Altered Syenite Porphyry (leached)	1734	0.7044
Otto Stock (Purdy & York)	1830	0.7046

for Rb and Sr. These samples yielded an isochron age of 1734 ± 122 m.y., an age which is identical with that measured for the leached altered syenite samples, within the limits of the errors in the isochrons.

It is believed that the leached syenite isochron age of 2260 ± 88 m.y. is the true age of this intrusive body. It cannot be older than this because it intrudes the Timiskaming rocks which have been dated by Fairbairn as 2368 m.y. It is also believed that the isochrons obtained from the leached altered syenite and the leached altered syenite porphyry samples approximate the time of hydrothermal alteration and, by inference, the time of mineralization. The younger ages in the altered rocks are due to the fact that these rocks are composed very largely of alteration products and that at the time of their formation these alteration products incorporated strontium whose isotopic composition had been largely homogenized throughout the alteration zone. The correspondence of the ages from the two different types of leached altered syenitic rocks lends support to the validity of the ages measured.

Listed in Table XIV are the ages measured in this study along with the ages of other rock units in the Kirkland Lake area that have been measured previously by other workers. The 2260 m.y. age for the syenite is geologically reasonable when compared with the age of the folded Timiskaming rocks which it intrudes. The 1830 m.y. age of the Otto stock indicates that there was igneous activity in the

area at about the same time that has been measured for the time of alteration, about 1800 m.y. ago.

Part B: The Rouyn-Noranda District, Quebec

Introduction. The Rouyn-Noranda district is located in western Quebec, near the Quebec-Ontario boundary (see map, Figure II). The Kirkland Lake district, Ontario, lies nearby to the west. The gold-copper ores of the district are massive replacements in sheared Keewatin rhyolites and tuffs; little veining occurs in the deposits. The ores consist of masses of chalcopyrite, pyrite, and pyrrhotite in widely varying proportions, with minor sphalerite and magnetite. The gangue minerals are quartz, chlorite and sericite. The country rocks have been intensely silicified and chloritized.

This district was chosen to test the possibility of obtaining "whole rock" ages from samples of the massive sulfide ores from trace amounts of Rb and Sr included in the sulfide minerals at the time of their formation; such ages should be the age of the mineralizing fluids, and thus, the age of the ores.

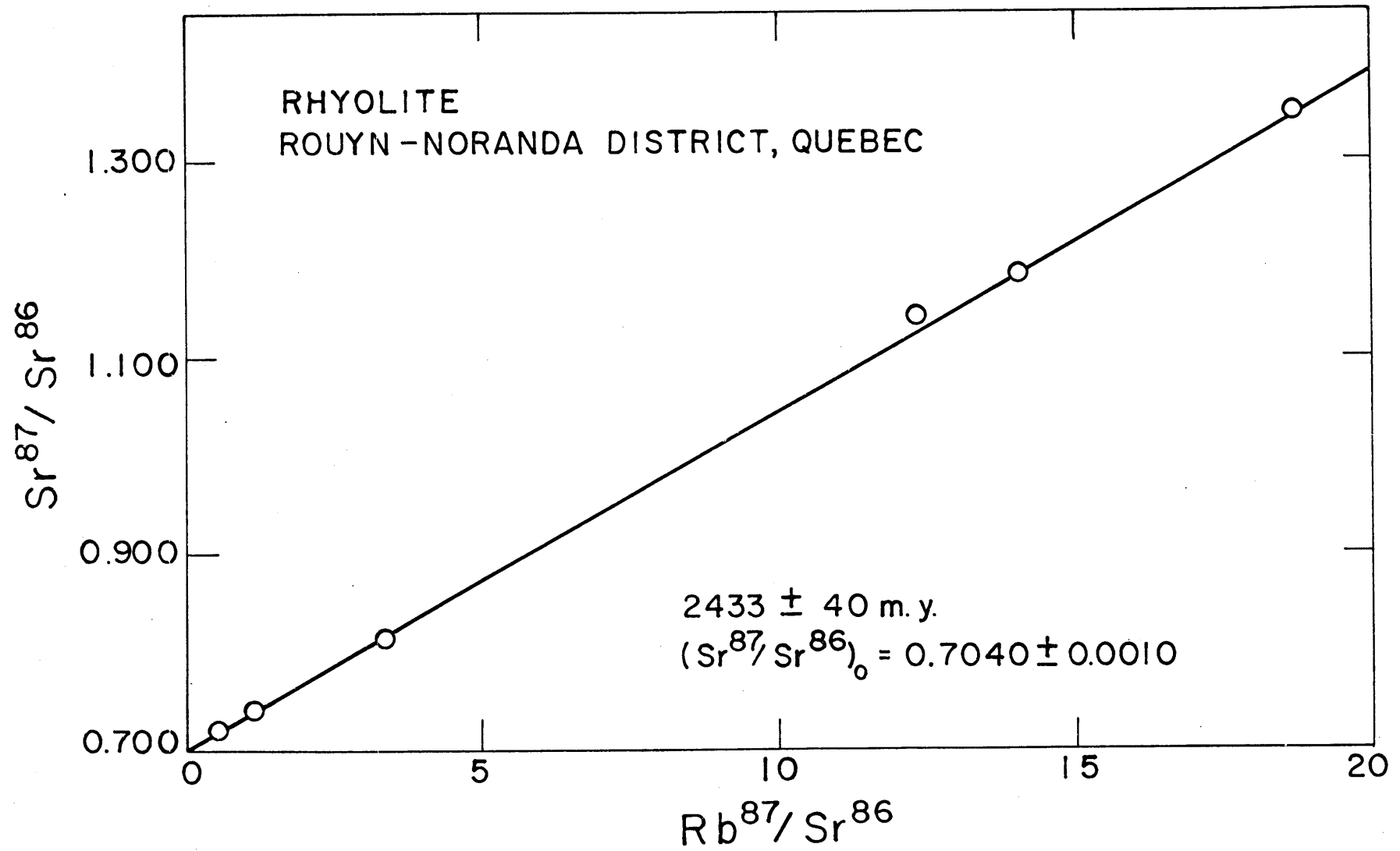
Results and Discussion. Seven samples of the rhyolite host rock have been analyzed by the Rb-Sr whole rock age method. The results of the sample analyses are listed in Table XV, and they are plotted in Figure XVI. The least squares isochron age for the rhyolite is 2433 ± 40 m.y. and the initial ratio is 0.7040 ± 0.0010 .

Eleven samples of sulfide ore have been analyzed for Rb and Sr, three of the samples were analyzed in duplicate. These samples consisted principally of intimate mixtures

TABLE XV

Rhyolite - Noranda, Quebec				
<u>Sample No.</u>	<u>Rb_{ppm}</u>	<u>Sr_{ppm}</u>	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6575	146	33.8	13.065	1.185
R6577	164	37.5	13.25	1.141
R6578	17.0	92.8	0.531	0.7229
R6579	31.6	83.2	1.103	0.7418
R6580	66.2	10.79	18.866	1.385
R6712	100	88.7	3.296	0.8123

FIGURE XVI



of chalcopyrite, pyrite, pyrrhotite and some sphalerite; two samples consisted almost entirely of massive sphalerite. No rock fragments were visible in the crushed sample materials when they were examined under a binocular microscope.

The analyses of the sulfide ores are listed in Table XVI along with two blank analyses that were made for the sample preparation procedure. The Sr blanks are particularly high, and the two blanks show widely different Sr and Rb concentrations. The blank contamination, then, is widely variable; it is probably also largely uncontrollable, in view of the several steps required to process these samples and the large volumes of reagents required to bring them into solution and to elute them through the ion exchange columns. The Rb and Sr contamination is not of significant proportions in the samples with the highest Rb and Sr concentrations since the average sample size was about 35 grams. The contamination would, however, become increasingly significant as the Rb and Sr concentrations in the samples become smaller and smaller. The effects of the Sr contamination on the $\text{Sr}^{87}/\text{Sr}^{86}$ compositions of the sample Sr cannot be estimated because the isotopic composition of the contaminating strontium is neither known nor known to be constant.

The three sets of duplicate analyses listed in Table XVI show very poor precision, varying from 9% to 22% for the Rb analyses and from 16% to 36% for the Sr analyses. This variability is not surprising in view of the low

TABLE XVI

Sulfide Ores - Noranda, Quebec

<u>Sample No.</u>	<u>Rb</u> ppm	<u>Sr</u> ppm	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6572	0.200 0.164	0.898 0.661	0.645 0.719	0.7265 0.7191
R6710	0.059 0.064	0.997 0.862	0.171 0.215	0.7133 0.7098
R6711	0.992 0.910	1.106 0.943	2.623 2.819	0.8116 0.8008
R6977	0.05	1.09	0.133	0.7126
R6978	0.05	0.154	0.943	0.7432
R6979	0.089	0.486	0.529	0.7346
R6981	0.025	0.135	0.536	0.7232
R6983	0.070	0.631	0.323	0.7138
R6985	0.066	0.288	0.664	0.7226
R6986	0.015	0.166	0.256	0.7204
R6988	0.012	0.334	0.104	0.7091
Blank	0.037*	0.339*		
"	0.023*	0.745*		

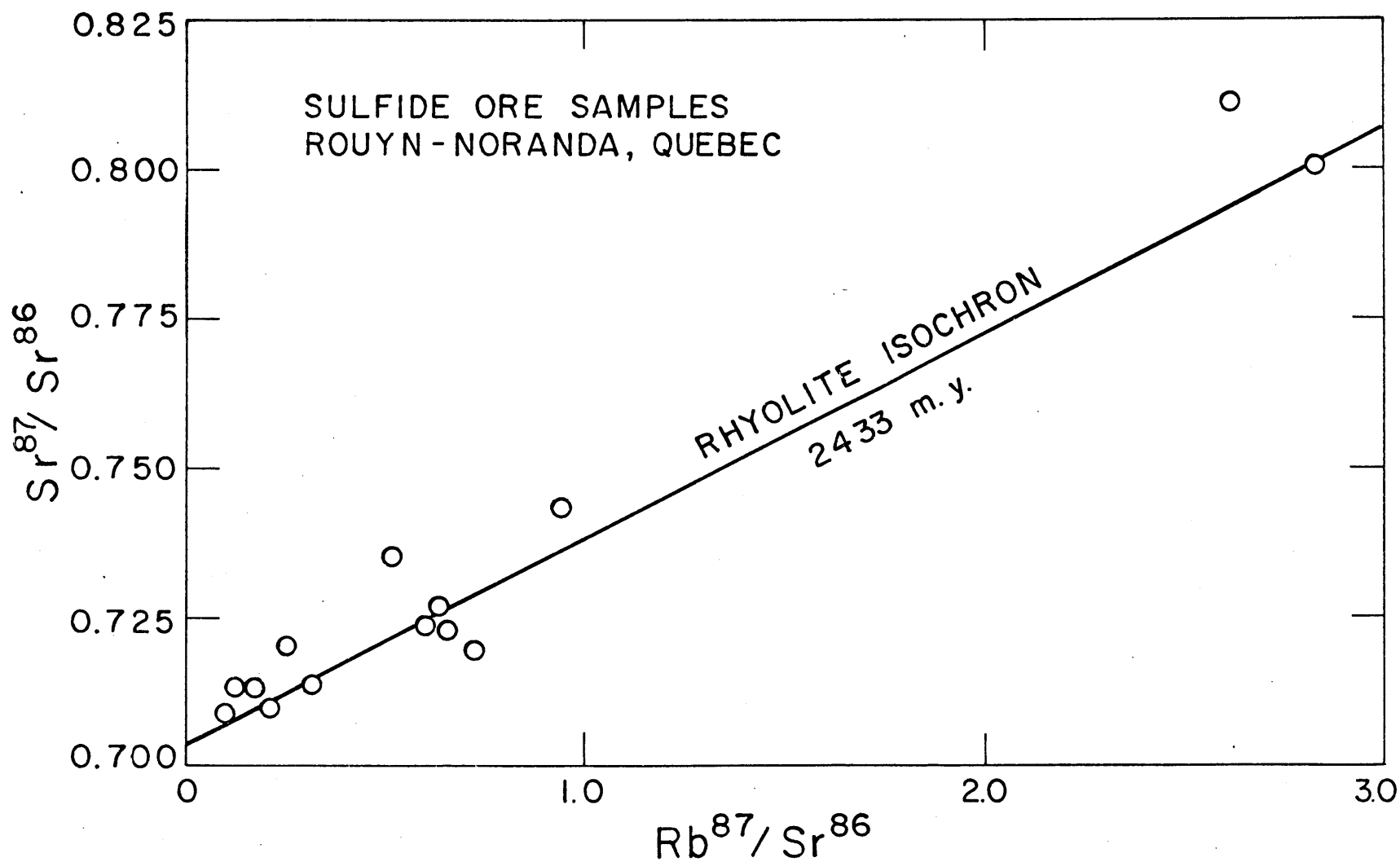
*Blank analyses given in micrograms per analysis.

concentrations of Rb and Sr. In a study of ultramafic rocks Roe (1964) measured differences of up to 25% between duplicate Rb analyses of rocks containing 0.07 to 0.35 ppm Rb and differences of up to 3.4% between duplicate Sr analyses of rocks containing 0.3 to 12 ppm Sr. Roe found that the percentage difference in the Rb analyses increased with decreasing Rb concentration, although the actual differences measured between the duplicates appeared to be independent of concentration; for samples with very low concentrations this might be due to the effects of sample contamination. Roe's duplicate Sr analyses showed much smaller differences than do those reported here, but only two of his samples were in the very low Sr concentration range found for the sulfide samples, consequently he had little data in this concentration range.

The wide variability between the duplicate Rb and Sr analyses is probably due mostly to the effects of uncontrollable contamination that occurred during the preparation of the samples. A part of this variability may also be due to instrumental errors since, for the most part, these samples had poor sample/spike ratios; they were spiked in excess to insure that there was adequate Rb and Sr for a mass spectrometer run.

The sulfide analyses are shown graphically in Figure XVII; also shown on this figure is the rhyolite isochron. The sulfide samples show a large degree of scatter on the plot and no attempt has been made to calculate an age from

FIGURE XVII



these analyses. The general correlation of the sulfide samples with the rhyolite isochron is, however, very interesting.

These analyses do indicate that the Rb and Sr concentrations and the Rb/Sr compositions of at least some of the sulfide minerals are sufficiently great to permit the isochron analyses of them, if the amounts of Rb and Sr contamination can be closely controlled. From the analyses made here it is not possible to determine which, if any, of the sulfide minerals has the greatest Rb/Sr compositions. If it can be ascertained that one particular mineral is more enriched in Rb, relative to Sr, than are the others it should be possible to obtain better isochron results by analyzing samples containing only this one mineral or by analyzing samples in which this mineral predominates.

Part C: The Porcupine District, Ontario

Introduction. The Porcupine district is located in eastern Ontario about 50 miles WNW of the Kirkland Lake district (see map, Figure II). Here Keewatin volcanics and sediments are unconformably overlain by sediments of the Timiskaming series. The rocks have been severely folded into a syncline. Algonian quartz porphyries and quartz-feldspar porphyries have intruded the rocks of the Keewatin series, but their relations with the Timiskaming series are not clear. The gold ores occur both as gold-quartz replacement masses in altered Keewatin schists and as mineralized veins and fracture fillings. Gold values in the porphyry are generally quite low.

This district was chosen to test the possibility of obtaining Rb-Sr ages of trace amounts of these elements included in the gold-quartz masses and, as in the case of the Noranda analyses, obtaining an age for the mineralizing solutions. The quartz porphyry was also dated to provide a basis of judging the reliability of quartz analyses.

Results and Discussion. Four samples of the quartz porphyry have been analyzed; these analyses are listed in Table XVII and they are plotted in Figure XVIII. The least squares isochron age of these samples is 2419 ± 26 m.y. with an initial ratio of 0.7039 ± 0.0005 .

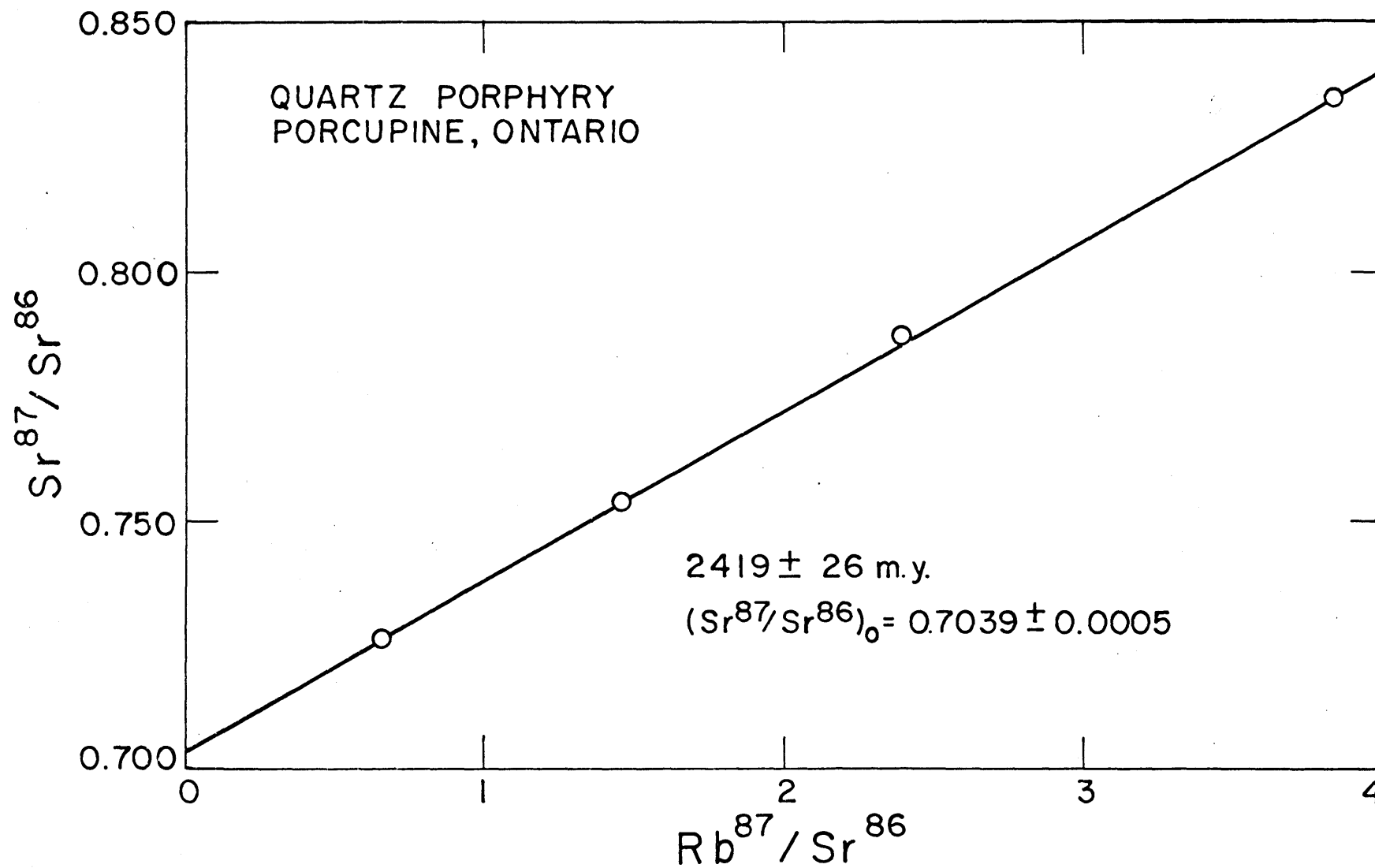
Five samples of the gold-quartz were analyzed. These samples were crushed in a clean steel mortar and then hand-picked in acetone under a binocular microscope to insure

TABLE XVII

Quartz Porphyry - Porcupine, Ontario

<u>Sample No.</u>	<u>Rb</u> _{ppm}	<u>Sr</u> _{ppm}	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6568	87.8	106.8	2.398	0.7868
R6569	66.6	133	1.452	0.7539
R6570	107	81.4	3.860	0.8348
R6571	53.3	235	0.658	0.7263

FIGURE XVIII



against the inclusion of visible rock fragments in the sample material. The results of the sample analyses and of one blank analysis are shown in Table XVIII.

The Sr blank analysis is particularly high; this may be due to contamination from the larger amounts of HF used to break down the silicate structure than are normally used in whole-rock analyses - the average sizes of the quartz samples were about 8 to 10 grams. This contamination is not significant in so far as the Sr concentration measurements are concerned, but its effect on the Sr isotopic measurements is not known.

The results of the gold-quartz analyses are shown diagrammatically in Figure XIX; also shown in this figure is the quartz porphyry isochron. The gold-quartz samples show a large degree of scatter on the isochron plot, especially at the lower end, although it might be inferred that there is a trend similar to the quartz porphyry isochron. Additional analyses of quartz samples from this district might lead to more definitive results, but there are two major problems with these samples. One problem is that most of the quartz is of the milky variety and thus it is very difficult to detect and eliminate all of the very small rock fragments which might be in the quartz; these rock fragments could significantly affect the analyses. The second problem is that the Rb/Sr ratios and the Rb concentrations in all five of the samples analyzed are rather low. Such samples would be very susceptible

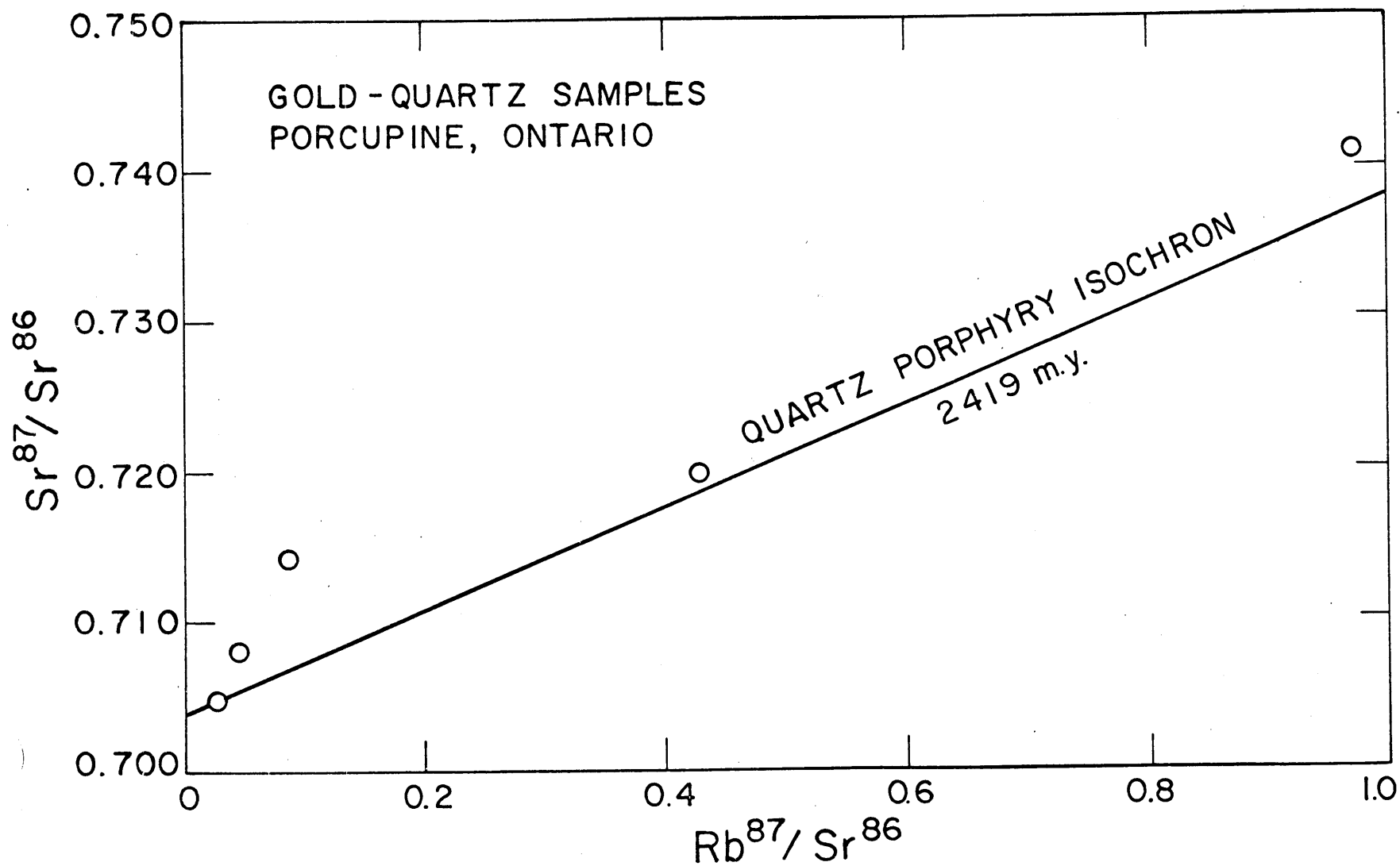
TABLE XVIII

Gold-Quartz Samples - Porcupine, Ontario

<u>Sample No.</u>	<u>Rb</u> ppm	<u>Sr</u> ppm	<u>Rb⁸⁷/Sr⁸⁶</u>	<u>Sr⁸⁷/Sr⁸⁶</u>
R6917	0.189	11.78	0.046	0.7081
R6918	0.141	13.47	0.030	0.7048
R6919	0.384	2.59	0.430	0.7197
R6920	1.86	5.53	0.977	0.7408
R6921	0.103	3.48	0.086	0.7140
Blank	0.039*	0.69*		

*Blank analyses given in micrograms per analysis.

FIGURE XIX



to the effects of contamination and to errors in the measurements of the isotopic compositions of the samples.

CHAPTER V

SUMMARY AND CONCLUSIONS

The strontium isotopic compositions of strontium-rich, rubidium-poor, gangue minerals from some vein-type hydrothermal mineral deposits have been measured. The gangue minerals were fluorite, calcite and barite and came from deposits in which 1) Tertiary mineralization lies within rocks of Tertiary age, 2) Tertiary mineralization lies within rocks of Precambrian age, and 3) the mineralization is Precambrian. The results of these analyses have shown that these minerals contain strontium that was derived from the host rocks or else had largely exchanged with the strontium in them. These minerals do not contain strontium that is representative of the original compositions of the mineralizing fluids or of their presumed primary subcrustal sources.

The analyses of carbonatized rocks from the Kirkland Lake gold district in eastern Ontario have yielded Rb-Sr whole rock isochron ages of about 2000 m.y. for both the syenite country rocks and the altered syenitic rocks of the ore zone. The isochrons are all of poor quality. Some of these samples were leached with dilute acid and the carbonate material removed from the rocks was analyzed for Sr; it was found that this carbonate material contains significant amounts of strontium and it was concluded that this carbonate strontium had a masking effect on the whole rock

isochron analyses. When this carbonate material was leached from the suite of syenite country rock samples and the samples were re-analyzed they yielded an isochron of improved linearity which gave an age of 2260 ± 88 m.y., and this age is believed to be the true age of the host rocks at Kirkland Lake. When the carbonate material was leached from suites of altered syenite samples and altered syenite porphyry samples from the ore zone and the rocks were analyzed for Rb and Sr they yielded isochron ages of 1826 ± 36 m.y. and 1734 ± 122 m.y., respectively, and it is concluded that the alteration and mineralization at Kirkland Lake occurred about 1800 m.y. ago. The 1830 m.y. age which Purdy and York obtained from the Otto stock, which is exposed about 4 miles south of the Kirkland Lake district, gives further evidence that there was igneous activity in this area about 1800 m.y. ago.

The analyses of massive sulfide ores from the Rouyn-Noranda district, Quebec, have shown that at least some sulfides contain large enough Rb and Sr concentrations and large enough Rb/Sr ratios to permit the isochron age analyses of them. The results which were obtained are of poor quality; this is believed to be due primarily to the contamination of the samples during their preparation and to the difficulties encountered in measuring very low concentrations of Rb and Sr.

The analyses of the gold-quartz samples from the Porcupine district, Ontario, have yielded less satisfactory

results than have the sulfide analyses. The Rb/Sr ratios and the Rb concentrations in the samples are all rather low. The isochron analyses of such samples would be particularly susceptible to errors due to sample contamination and instrumental errors in measuring the isotopic compositions of the samples.

One aspect of the Porcupine analyses may have some bearing on the geology of the Kirkland Lake area. The Timiskaming sediments at Kirkland Lake contain pebbles of a large variety of rock types. Hewitt (1962) has discussed the nature of these sediments and the rock pebbles which they contain. Because the pebbles are comprised of a large variety of rock types having a wide variety of hardnesses, Hewitt has deduced that the transport distances of these pebbles were short. In the area closely surrounding these Timiskaming sediments he was able to find suitable source rocks for all of the types of pebbles except the quartz porphyry ones. The 2420 m.y. old quartz porphyry at Porcupine would have been of sufficient age to have supplied the pebbles for the 50 m.y. younger Timiskaming sediments. The transport distance in this case would have been about 50 miles.

CHAPTER VI

SUGGESTIONS FOR FURTHER RESEARCH

More work needs to be done on the analyses of trace amounts of Rb and Sr in sulfide ores, as this method should yield the most reliable estimates of the ages of ore mineralizations. Because sulfide mineralization is common to such a wide variety of hydrothermal mineral deposits, this method should provide the most useful age tool for the majority of the deposits. The examination of separated sulfide minerals should lead to the possibility of determining which mineral, or minerals, contain the greatest amounts of Rb and the greatest Rb/Sr ratios and, thus, which minerals would be the most suitable for dating purposes. A major problem which must be solved in any such work is the difficulty of obtaining reliable and reproducible analyses from samples with very low concentrations of Rb and Sr. If a procedure could be devised for obtaining good quality mass spectrometer runs from samples with only a very few micrograms of Rb and Sr then sulfide samples of only a very few grams could be analyzed, and the likelihood of chemical contamination might be greatly reduced because of the smaller quantities of reagents needed to process the samples.

Some further work should be done on the analyses of trace amounts of Rb and Sr in vein quartz samples. The analytical difficulties that must be overcome in this

procedure are similar to those that must be overcome in the analyses of the sulfide samples. If good quality age determinations could be made on vein quartz samples they would provide a means of putting maximum age limits on the ore mineralization which occurs in them.

APPENDIX A

SAMPLE DESCRIPTIONS AND LOCATIONS

Kirkland Lake District, Ontario

- R6443 Altered syenite, with small inclusions of augite syenite (?). The rock has been highly carbonatized and silicified, and shows the characteristic red coloring of the alteration. The original rock texture has been largely destroyed.
W. drift, 4625' level.
Macassa mine.
- R6444 Altered syenite. The rock has been highly brecciated, sericitized carbonatized. Some feldspar structure still visible. Remnants of hornblende (?) laths make up about 2% of the sample.
Drift 46N1, 4625' level.
Macassa mine.
- R6446 Altered syenite. Highly brecciated and altered to quartz, carbonates and sericite. Magnetite, hornblende, leucoxene minor. Numerous quartz-carbonate veinlets cut the earlier alteration products.
Drift 46N1, 4635' level.
Macassa mine.
- R6454 Altered syenite porphyry. Groundmass and most phenocrysts highly brecciated and altered. A few phenocrysts still relatively fresh-looking, but all show strong staining by iron-oxide (?).
Minor pyrite.
Ore zone under 4604 stope.
Macassa mine.
- R6458 Altered syenite. Brecciated, sericitized, carbonatized and pyritized. Original texture largely destroyed.
50' N. of ventilation crisscut. 4625' level.
Macassa mine.
- R6462 Altered syenite. Similar to R6458, except minor magnetite and secondary amphibole(?) occur. About 50% of the rock is a mixture of quartz and carbonate.
100' N. of drift 47N, 4750' level.
Macassa mine.
- R6468 Altered syenite. Brecciated and highly altered. Iron-oxide staining strongly developed. Magnetite and pyrite minor.
East drift 47N, 4750' level.
Macassa mine.

- R6472 Altered syenite. Highly brecciated. Silicification and carbonitization prominent; minor pyritization. Iron staining less intense than in the previous samples.
Drift 47N W. 4750' level.
Macassa mine.
- R6473 Altered syenite. Very highly brecciated and altered. Sample is mostly an aggregate of microscopic crystals of quartz, sericite and carbonate. Numerous minute pyrite-filled fractures occur.
Drift 47N. W. 4750' level.
Macassa mine.
- R6474 Syenite. Granitic texture. Composed almost entirely of perthitic feldspar. Minor magnetite shows some alteration to leucoxene.
47N Crosscut. 4750' level.
Macassa mine.
- R6475 Syenite. Medium-grey colored rock of granitic texture. Feldspars largely perthitic. Carbonate filled fractures numerous. Minor pyrite and magnetite crystals and fracture fillings.
47N Crosscut. 4750' level.
Macassa mine.
- R6476 Syenite. Similar to R6475.
47N Crosscut. 4750' level.
Macassa mine.
- R6477 Altered syenite porphyry. Extremely brecciated; phenocrysts shattered. Groundmass completely altered to sericite, chlorite, quartz and carbonates. Minor magnetite and pyrite.
4704 W. drift.
Macassa mine.
- R6478 Altered syenite porphyry (?). Texture of original rock destroyed. Strongly iron stained. Minor magnetite and pyrite.
4704 W. drift.
Macassa mine.
- R6481 Altered syenite porphyry. Least altered of all the porphyry samples. Groundmass largely altered, but phenocrysts (30 to 40 % of rock) still relatively fresh. About 3-5% amphibole(?).
4701 Crosscut N.
Macassa mine.
- R6484 Altered syenite porphyry. Strongly brecciated and highly altered. Prominent iron staining.
4704 W. drift.
Macassa mine.

- R6490 Altered syenite porphyry. Highly brecciated and altered. About 5% disseminated magnetite and pyrite. Groundmass altered almost entirely to quartz, sericite and carbonates. Quartz and carbonate filled fractures are numerous and cut the earlier groundmass alteration. Ore zone. 4904 W. drift. Macassa mine.
- R6491 Altered syenite porphyry. Similar to R6490. Ore zone. 4904 W. drift. Macassa mine.
- R6492 Altered syenite porphyry. Very highly brecciated. Strong red-brown staining of groundmass. About 3% magnetite and pyrite, principally in fracture fillings. 4904 W. drift, near ore zone. Macassa mine.
- R6493 Syenite. Dark grey rock of granitic texture. Strongly carbonatized (in fractures). About 5% magnetite and pyrite. 50N2 Crosscut, 5025' level. Macassa mine.
- R6494 Syenite. Grey rock similar to R6493, but has been sheared to a greater extent. 50N2 Crosscut, 5025' level.
- R6495 Syenite. Grey rock of granitic texture. Has been sheared and fractured; fractures contain carbonate and quartz fillings. 50N2 Crosscut, 5025' level. Macassa mine.
- R6497 Syenite. Dark grey rock similar to R6493, but more strongly sheared and carbonatized. About 20% of the rock is carbonate. 50N2 Crosscut, 5025' level. Macassa mine.
- R6499 Syenite. Dark grey rock. Has been strongly sheared and fractured; carbonate and quartz are the major fracture fillings. About 5% magnetite and pyrite. About 5% amphibole(?). 50N2 Crosscut, 5025' level. Macassa mine.
- R6557 Altered syenitic wallrock. Shows strong iron staining of the alteration zone. 1025' level. Tough Oakes mine.

- R6558 Brecciated and altered syenitic wallrock; shows well developed iron staining.
2447' level.
Kirkland Lake mine
- R6559 Altered, brecciated and pyritized syenitic wallrock. Remnants of porphyritic texture still visible. Some free gold.
Sylvanite mine.
- R6560 Brecciated, altered and pyritized syenitic rock.
3200' level.
Kirkland Lake mine.
- R6562 Altered syenite porphyry. Original texture still visible.
1600' level.
Lake Shore mine.
- R6564 Quartz vein material containing large inclusions of altered syenitic wallrock.
Stope 422.
Lake Shore mine.

Rouyn-Noranda District, Quebec

- R6572 Massive pyrrhotite with pyrite and minor chalcopryrite.
500' level.
Waite mine.
- R6575 Rhyolite.
- R6577 Pyritized rhyolite.
110' level.
Nornada mines.
- R6578 Rhyolite
Huronian Belt Co.
- R6579 Rhyolite wallrock.
Huronian Belt Co.
- R6580 Brecciated rhyolite
No.1 level.
Horne mine.
- R6712 Rhyolite
700' level.
Horne mine.
- R6710 Massive chalcopryrite with some sphalerite and bornite.
150' level.
Amulet mine.

- R6711 Massive chalcopyrite with sphalerite and bornite.
150' level.
Amulet mine.
- R6977 Massive ore containing sphalerite, chalcopyrite
and pyrite.
150' level.
Amulet mine.
- R6978 Massive sulfide ore, containing fine-grained,
intermixed chalcopyrite, sphalerite, pyrite,
and pyrrhotite, with minor quartz.
75' level.
Amulet mine.
- R6979 Massive sphalerite.
75' level, NW of "C" shaft.
Amulet mine.
- R6981 Massive sphalerite with chalcopyrite, pyrite
and minor bornite.
75' level.
Amulet mine.
- R6983 Chalcopyrite and pyrrhotite, with minor pyrite.
Noranda Mines.
- R6985 Massive sulfide ore consisting of chalcopyrite
and pyrrhotite, with some bornite and pyrite.
700' level.
Waite mine.
- R6986 Chalcopyrite
Waite-Montgomery, at outcrop
- R6988 Pyrite and sphalerite, with some chalcopyrite.
Open pit.
Waite Ackerman - Montgomery.

Porcupine District, Ontario

- R6568 Sheared quartz porphyry.
425' level.
Hollinger mine.
- R6569 Sheared quartz porphyry. Pyrite prominent.
W. of Dome shaft.
- R6570 Sheared, pyritized quartz porphyry.
100' level.
Dome mine.
- R6571 Slightly sheared quartz porphyry.

- R6917 Gold-quartz ore, consisting of massive milky quartz and prominent free gold, with pyrite and some gold tellurides.
- R6918 Vein material, consisting of massive white quartz replacing pyritiferous schist; no ore minerals visible.
425' level.
Hollinger mine.
- R6919 Massive, vitreous white quartz; small inclusions of schist.
Dome mine.
- R6920 Gold-quartz replacing greenstone schist. The quartz is white and vitreous.
1750' level.
Dome mine.
- R6921 Massive, white vitreous quartz. Free gold visible.
Dome mine.

APPENDIX B

IBM/360 PROGRAM FOR THE LEAST SQUARES ANALYSIS
OF A STRAIGHT LINE
(After York, 1966)

```

$JCB          SPOONER, KP=26, TIME=3, PAGES=10
C          **** WAMSUTTA VOLCANICS / H. W. FAIRBAIRN ****
1          DIMENSION X(50),Y(50),U(50),V(50),P(50),Q(50),W(50),SQW(50),
          IRESX(50),RESY(50)
2          100 READ(5,1)B,N,(X(I),Y(I),P(I),Q(I),I=1,N)
3          1   FORMAT(F15.8, I10/(2F15.7,2E15.5))
4          SUMW=C.
5          SUMA=C.
6          SUME=C.
7          SUMC=C.
8          SUMD=C.
9          SUMF=C.
10         SUMS=C.
11         SUMT=C.
12         XBAR=C.
13         YBAR=C.
14         DO 2 I=1,N
15         W(I)=P(I)*Q(I)/(B*B*Q(I)+P(I))
16         SCW(I)=W(I)**2
17         2   SUMW=SUMW+W(I)
18         DO 3 I=1,N
19         XBAR=XBAR+W(I)*X(I)/SUMW
20         3   YBAR=YBAR+W(I)*Y(I)/SUMW
21         DO 4 I=1,N
22         U(I)=X(I)-XBAR
23         V(I)=Y(I)-YBAR
24         SUMA=SUMA+SQW(I)*(U(I)**2)/P(I)
25         SLMB=SUMB+SQW(I)*U(I)*V(I)/P(I)
26         SUMC=SUMC+SQW(I)*(V(I)**2)/P(I)
27         SUMD=SUMD+W(I)*(U(I)**2)
28         4   SUME=SUME+W(I)*U(I)*V(I)
29         CCA=C.6666667*SUMB/SLMA
30         COB=(SUMC-SUMD)/(3.0*SLMA)
31         COC=-SUME/SUMA
32         CPHI=(CCA**3-1.5*COA*COB+0.5*COC)/(CCA**2-COB)**1.5
33         IF(CPHI**2-1.0)6,6,10
34         6   ALPHA=(SQRT(1.0-CPHI**2))/CPHI
35         IF(-ALPHA)7,7,8
36         7   PHI=ATAN(ALPHA)
37         GO TO 9
38         8   PHI=3.1415927+ATAN(ALPHA)
39         9   SLOPEA=COA+2.0*SQRT(COA**2-COB)*COS(PHI/3.0)
40         SLOPEB=CCA+2.0*SQRT(COA**2-COB)*COS((PHI+6.283185)/3.0)
41         SLOPEC=COA+2.0*SQRT(COA**2-COB)*COS((PHI+12.56637)/3.0)
42         GO TO 30
43         10  A=3.0*(COB-COA**2)
44         C=-2.0*(COA**3)+3.0*COA*COB-COC
45         Z=(-C/2.0+SQRT((C**2)/4.0+(A**3)/27.0))**(1.0/3.0)
46         T=(-C/2.0-SQRT((C**2)/4.0+(A**3)/27.0))**(1.0/3.0)
47         SLOPEA=Z+T+CCA
48         SLOPEE=C.CCCCCC00
49         SLOPEC=C.CCCCCC00
50         30  AINT=YBAR-SLOPEA*XBAR
51         BINT=YBAR-SLOPEB*XBAR
52         CINT=YBAR-SLOPEC*XBAR

```



```

53      CC 31 I=1,N
54      SUMS=SUMS+W(I)*(SLOPEC*U(I)-V(I))**2
55      SUMT=SUMT+W(I)*(X(I)**2)
56      RESX(I)=- (SLOPEC)*W(I)*(CINT+SLOPEC*X(I)-Y(I))/(P(I)*X(I))
57      31  RESY(I)=W(I)*(CINT+SLOPEC*X(I)-Y(I))/(Q(I)*Y(I))
58      AN=N
59      SIGMAB=SQRT(SUMS/((AN-2.0)*SUMD))
60      SIGMAA=SIGMAB*SQRT(SUMT/SUMW)
61      WRITE(6,5)SLOPEA,AINT,SLOPEB,BINT,SLOPEC,CINT,XBAR,YBAR,SIGMAA,
        1SIGMAB,B
62      5  FORMAT(1CX,8HSLOPEA=,F15.8,5X,6HAINT=,F15.8//10X,8HSLOPER=,
        1F15.8,5X,6HBINT=,F15.8//10X,8HSLOPEC=,F15.8,5X,6HCINT=,F15.8//
        21CX,8H XBAR=,F15.8,5X,6HYBAR=,F15.8//10X,8HSIGMAA=,F15.8,
        33X,8HSIGMAB=,F15.8//10X,8H B=,F15.8)
63      WRITE(6,20)(RESX(I),RESY(I),I=1,N)
64      20  FORMAT(1CX,2PHRESX RESY//(9X,F11.8,13X,F11.8))
65      WRITE(6,21)(X(I),P(I),Y(I),Q(I),I=1,N)
66      21  FORMAT(56H X P Y Q
        1// (F15.7,2X,E15.5,2X,F15.7,2X,E15.5))
67      WRITE(6,99)
68      99  FORMAT(1H1)
69      GO TC 100
70      END

```

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BIOGRAPHICAL SKETCH

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