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Rb-sr isotopic studies relating to problems of geochronology on the Nelspruit and Mpageni granites

De Gasparis, Aurello Alfonso Amedio

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belts would have acted as a resistor protecting the Swaziland System from granitization.

Viljoen & Anhaeusser (1965) support this hypothesis and propose that the Nelspruit migmatite derives from a pre-Swaziland System assemblage: these rocks were granitized and the Nelspruit migmatite corresponds to the autochthonous granites of Read's granite series. The migmatite body started updoming causing deformation of the stratified rocks and the orogenic compression generated a granitic magma which "invaded the granitized material and the neighbouring rocks alike"(Anhaeusser, 1966). The magma formed an intrusive sheet of homogeneous granite along the contact between the migmatites and the Swaziland System rocks, and was responsible for the contact metamorphic aureole of the Nelspruit migmatite.

The Nelspruit migmatite is clearly intrusive into the Swaziland System rocks - this relationship has been described in detail by Visser et al (1956), Ramsay (1963), Anhaeusser (1964, 1966), Viljoen (1964), and Anhaeusser & Viljoen (1965). These authors describe a transfer of material across the contact in the form of conformable granitic sheets in the Fig Tree rocks like those found in the valley of the Dicey's Creek; and in the form of two generations of pegmatites that have intruded into the stratified rocks of the Swaziland System (Viljoen, 1964). In some places the migmatite grades into a sillimanite gneiss composed of quartz, sillimanite, sericite, felspar, ilmenite, rutile and cassiterite. Very course grained muscovite-bearing pegmatites occur as isolated, irregular masses of variable size in the stratified rocks. They resemble the pegmatites found at depth in the Consort Mine which are also purported to originate from the Nelspruit migmatite.

Highly metamorphosed rocks along the contact also confirm the intrusive nature of the migmatite. These consist of metamorphic schistose rocks. There are two major interpretations of the origin of these metamorphites:

A. Visser et al (1956) believe that the schist belt derives from a suite of intrusive basic and ultrabasic rocks, and

have recognized three types of these rocks, grouping them under the name of Jamestown. Associated with them and believed to have been derived from them, there is a large variety of basic schists. The authors quoted did not sub-divide these basic schists.

The Jamestown is composed of:

(1) Green serpentinite, which is the most widely distributed, consists mainly of serpentine which in places preserves olivine crystal outlines. It was deduced that this rock is derived from a highly magnesiferous peridotite.

(2) Blue serpentinite derives from rocks ranging from pyroxenite to olivine hypersthenite. Pyroxene and hypersthene are altered into fibrous tremolite or, less fraquently, actinolite and sometimes to basite - in this case the original texture of the rocks is destroyed. Chlorite also occurs, occasionally interstitial among the pyroxene crystals, suggesting the former presence of biotite or amphibole.

(3) Diabase, of which only six altered sheets have been found, is composed mainly of hornblende and interstitial felspar. The hornblende shows crystal outlines of original pyroxene in places, and is commonly replaced by antigorite and epidote accompanied by quartz, pyrite and calcite.

The basic schists are thought to have been formed by dynamic metamorphism from the intrusive rocks. They consist of chlorite magnetite schists accompanied by various quantities of quartz, sericite, carbonate and talc.

In the Kaap Muiden - Malelane area the contact between the serpentinites and the schists is transitional and at right angles to the strike.

Finally, quartz amphibolites occur right at the contact of the Nelspruit migmatite. These are of unknown origin and in places might derive from sandy shales.

B. A second, more detailed description of the metamorphic "aureole" is given by Anhaeusser (1964), Viljoen (1964) and Anhaeusser & Viljoen (1965). They have mapped an area stretching from the Consort Mine to Honeybird siding in detail. From this and later work they have concluded that most of

the rocks classified as Jamestown Igneous Complex and the schists can be ascribed to the Onverwacht Series, and that intrusive acid and basic rocks are present in minor quantities.

The stratified rocks show a decreasing degree of metamorphism away from the contact:

(a) hornblende-hornfels-facies along the contact zone;
(b) albitite-epidote-hornfels-facies covering most of the central part of the area, including the Consort Mine;
(c) green schist-facies along the Kaap river extending as far south as the Woodstock Mine and Noordkaap.

The schists underlie the Fig Tree Series as a stratified sequence while the serpentinites sometimes also intrude the top of the stratigraphic succession. An interesting phenomenon has been noticed: the grade of metamorphism is different on the two sides of the serpentinites. The side facing the Nelspruit migmatite has a much higher metamorphic grade, being at times near to the sillimanite-pyroxene-hornfels facies, while the side facing away from the migmatite is always of a lower grade and closer to the green schist facies. The basic intrusives might have acted as a barrier between the Swaziland rocks and the Nelspruit rocks attenuating the action of the metamorphism (Read, 1956).

The stratigraphic sequence that lies conformably under the Fig Tree shales and graywackes has been sub-divided as follows:

Contact amphibolites are composed predominantly of green pleochroic hornblende, plagioclase and variable amounts of quartz. South dipping foliation is present together with very marked mineralogical banding in more acid and more basic bands almost exclusively composed of hornblende. The banding, together with quartzite horizons that can be traced for several miles, point to sedimentary origin. Dolomitic rocks from which the contact amphibolites could have derived, exist at the base of the Onverwacht in the series that Gribnitz et al (1961) propose to call Oorschot.

Green amphibolite schists consist of light and dark green tremolite-actinolite schists that frequently grade to serpen-

tinites and antigorite is then abundant. Bodies of massive serpentinite with remnants of large olivine crystals and pyroxene are considered to be of magmatic origin (Jamestown).
Carbonate bearing talc and chlorite schists. These basic schists are of variable composition from talc schists to talc carbonate, to talc-chlorite-carbonate-quartz schists sometimes bearing tremolite. Because of banding, foliation and the presence of quartzites, a sedimentary origin from impure dolomites is inferred. The talc schists underlie the Fig Tree but in some places they have been found lying above the Moodies quartzites. This is ascribed to faulting and possibly to very strong folding.
Quartzites. This type of rock occurs in all the metamorphic zones and forms bands that can be followed for miles. Within the quartzites altered, shaly horizons are present. Those shales which are protected by the quartzites and have not been metamorphosed are probably part of the sediments from which the schists have derived.

The Mpageni Granite:

The Mpageni granite is intrusive in the Nelspruit migmatite. It forms a nearly circular body about six miles in diameter and contrasts with the grey coloration of the Nelspruit migmatite because of the presence of abundant pink felspar. This granite is massive and coarse grained - some of the felspar crystals are longer than half an inch. The main mineral constituents are: quartz, acid plagioclase, microcline and biotite and muscovite in minor quantities; iron ore minerals and sphene are common accessories; zircon, apatite, allanite and rutile are also present.

Along one of the central planes, running roughly east - west, the granite is cut by the Crocodile river valley. Along this valley outcrops a massive syenitic dyke of a fine - medium grained, grey facies. The contact with the Nelspruit migmatite is very sharp and well exposed; it is possible to see how the banding of the Nelspruit is sharply cut by the more homogeneous Mpageni and how apophyses of the latter extend into the migmatite.

The Mpageni is a rather high level pluton and possibly intruded the migmatite as a very hot and partly crystallized mass. Therefore, even though it did not metamorphose the migmatite to a noticeable extent, the increased heat gradient could have affected to some extent the isotopic composition of the Nelspruit minerals.

Van Zeden (Visser et al, 1956 p. 130) has expressed the opinion that this massive granite may represent a deep seated phase of the Nelspruit migmatite, and (op.cit. p.135) that the Mpageni granite and the migmatite are comagmatic being respectively the para-autochthonous and the autochthonous granite of the same granitization event. This hypothesis will be discussed later in the light of the results obtained in the present investigation.

CHAPTER III - THE EXPERIMENTAL TECHNIQUES

1. THE SAMPLING

Samples for total rock work must be representative of the average composition of the rock. They must therefore be large enough to include all the minerals present in the rock in their average proportions. Furthermore, one of the conditions to obtain an isochron is that the sample must have remained a closed chemical system since crystallization. As mineral to mineral diffusion of radiogenic Sr has been well documented (Allsopp, 1961; Fairbairn et al., 1961, Lanphere et al., 1963; and Hart, 1964), even in the case of a rock with a very homogeneous composition, a sample of small size might not yield the requirements of a closed chemical system. To overcome this, samples bigger than fifty times the size of the larger grains in the rock were collected as an empirical rule. The estimated weight of the samples varied roughly from 10 to 25 pounds.

A weathered rock might have undergone leaching in which case it would not have remained a closed system; for this reason only fresh samples were used and two inches or more of the surface subject to weathering were always discarded.

Crushing was performed successively with a hammer, a jaw crusher and a "Sieb-technic" machine, reducing a representative fraction of the sample to -200 mesh powder. Great care was taken to avoid contamination: the crushers were thoroughly cleaned before each sample was run and the first small quantity of sample run was discarded every time. Iron contamination from the crushers could not be avoided.

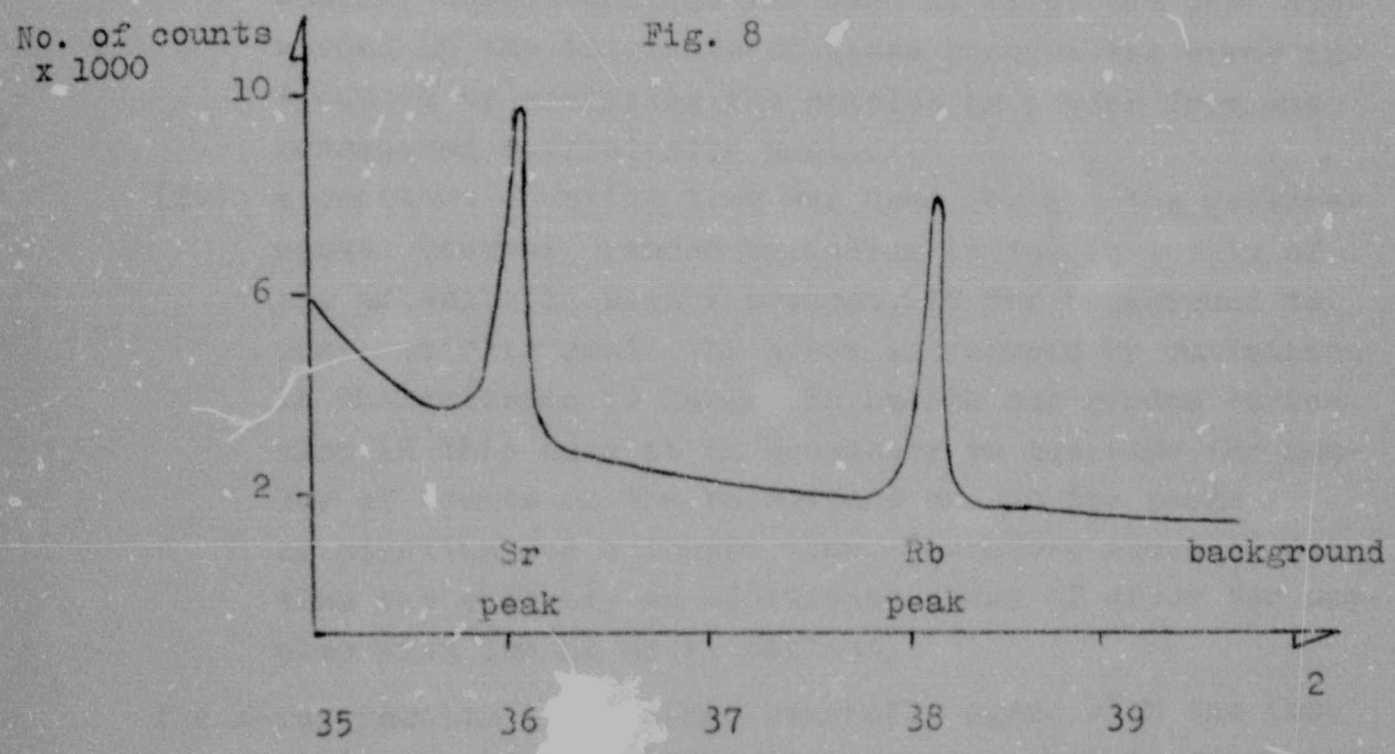
2. X-RAY FLUORESCENCE

The Rb and Sr concentrations in the samples were first measured roughly by X-ray fluorescence. The samples that gave the widest spread of Rb/Sr ratios were then chosen for mass spectrometer work (see Chapter II).

The instrument for X-ray work (Phillips) consists of a 1 kv. tungsten tube as a radiation source and a LiF analyzer crystal.

The radiation intensities were measured by a scintillation detector in connection with an electric timer. Intensities corresponding to the Rb and Sr peaks and the background were each measured in duplicate. Although not strictly correct the background was taken as the counts obtained in the intermediate position between the Sr and Rb peaks (see fig. 8), and was subtracted from the Sr and Rb readings.

Fig. 8



For each set of measurements the instrumental drift was checked in two ways: (a) the peak position was re-determined;

(b) the intensity, obtained by measurements on a standard sample taken before and after each set of measurements on unknown samples, was used to check small sensitivity changes.

The concentrations of Rb and Sr were obtained from the counts using a calibration diagram constructed by H.L. Allsopp by comparing results by X-ray and isotope dilution.

An accuracy of ± 5% is required in the X-ray results that are used mostly as a guide in the choice of samples for isotope dilution work, therefore some possible causes of error have been disregarded, such as:

(i) No matrix effect correction was applied but because the samples are of similar granitic composition, the

matrix effect will be nearly constant.

(ii) Inaccurate correction for background.

(iii) The samples were analyzed in the form of a fine powder layer approximately 2 mm. thick. More precision is given by pressed discs of a uniform dispersion of sample powder in a pure cellulose recipient so as to have smooth surfaces with uniform distribution of the sample. This technique was used at first but then discarded in the interests of speed because the error introduced by analyzing the samples in powder form was considered sufficiently small.

(iv) A constant counting time was used for all the measurements. However, random variation in the intensity of the emission is always present. If the background to peak ratio is small the error introduced by variations in the emission is large. To smooth out random variation in this case it is necessary to increase the number of counts on the background and on the peaks by counting for a longer time. Therefore short counting time was probably an additional cause of error for samples with low Rb or Sr content.

The X-ray results so obtained generally agree with the isotope dilution data to within five per cent, but in some cases the disagreement was as high as 10 to 20%.

3. ISOTOPE DILUTION TECHNIQUE

Isotope dilution techniques very similar to the one used at the B.P.I. have been described by Aldrich et al.(1956) and Compston et al.(1965). Nevertheless the technique used for the present investigation will be described in some detail.

A suitable amount of sample, generally not exceeding 0.5 gram and rarely as large as 1 gram, was weighed into a clean platinum dish, 10 ml. of Bakers AR 48% hydrofluoric acid was added and the solution slowly taken to dryness, generally overnight, on a water bath at approximately 45°C. Then 5 ml. of 70% Bakers AR perchloric acid and a further 5 ml. of hydrofluoric acid were added and the sample again

placed on a water bath at approximately 60°C to evaporate the surplus HF; the platinum dish was then placed on a hot plate at a temperature of about 150°C to evaporate the $HClO_4$ without splashing. The perchlorate was finally dissolved in 2.6 normal HCl and transferred without loss to a 50 ml. pyrex beaker. Sufficient acid (approx. 40 ml.) was used to prevent the solution, once cold, from precipitating.

With some samples a small residue of the original rock powder remained undissolved. It was rather difficult to identify the mineral components of the very fine powder of the residues, but they probably were mostly zircon, sphene and tourmaline. The sphene ($CaTiSiO_5$) may contain some Sr, tourmaline varies widely in composition and it may contain Ca and therefore Sr in the variety "uvite" ($H_4CaMg_4Al_5B_3Si_6O_{31}$) and sometimes K, and therefore Rb (Winchell, 1951 - p.465). Minute residues (less than 0.1% of the total sample) were ignored, but in one case (AA10), a residue of more than 0.2% of the total rock occurred. In this case the sample was identified by X-ray diffraction as tourmaline (see table 1); because of the black colour it was probably a schorlite ($NaFe_3B_3Al_3OH_4Al_3Si_6O_{27}$) and no attempt was made to dissolve it.

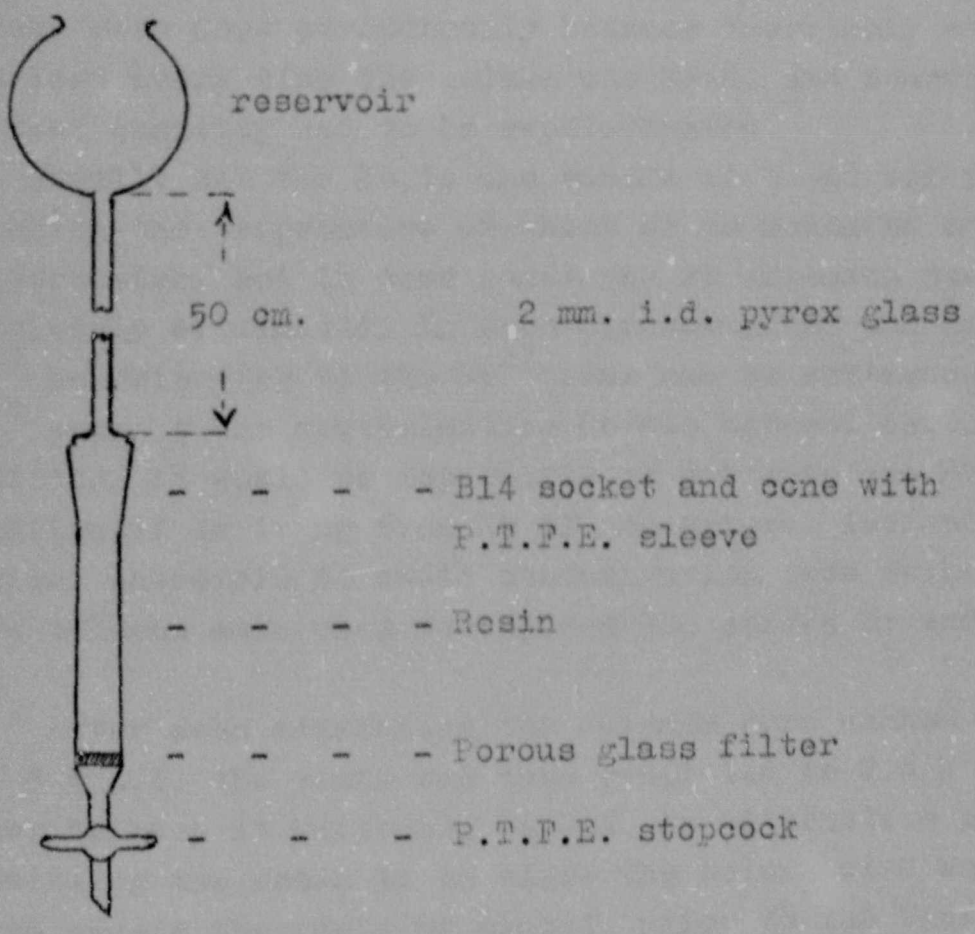
Table 1

Line No.	SAMPLE Intensity	d	TOURMALINE Intensity	d
1	100	2.56	100	2.58
2	80	3.99	85	3.99
3	70	4.21	70	4.24
4	70	3.46	70	3.51
5	70	2.95	85	2.96
6	60	6.34	40	6.41

When the solution was cool it was weighed and split into predetermined amounts in separate beakers for spiked Rb and Sr and unspiked Sr runs. At this stage a suitable amount of "spike" (see p.17) was added to the Rb and Sr

beakers. The aliquots were taken to dryness on a hot plate at about 150°C and when dry taken into solution again in about 5 ml. of 2.6 N HCl and loaded onto cation exchange columns (see fig. 9). The columns were then eluted with 2.6 N HCl and the required fraction collected. The Sr fractions were taken to dryness with a few drops of perchloric acid, and then heated to about 300°C for about 15 minutes to free them of any organic material, for example resin deriving from the columns or the water demineralizer. Two or three drops of sulphuric acid were added to the Rb fraction and a small amount was transferred to a pure silica beaker and heated to red heat on a Meaker burner to completely evaporate residual sulphuric acid. The Sr samples were loaded on the filament of the mass spectrometer with a pyrex glass micropipette in one or two drops of diluted hydrochloric acid; the Rb samples were loaded in the same way but using demineralized water.

Fig. 9



Cation exchange column

The ion exchange columns were of pyrex glass, approximately 250 - 300 mm. in length by approximately 12 mm. in diameter (see fig. 9). They were fitted with B14 sockets at the top with PTFE sleeves to prevent leakage between the socket and cone. Flow was controlled by PTFE stopcocks with 2 mm. openings. The columns were filled with a weighed amount of Dowex 50W-X8 200 to 400 mesh resin which rested on a porous glass filter. Above each column there was a 200 ml. reservoir connected to the column by a 50 cm. x 2 mm. i.d. pyrex glass tube and a B14 cone. The reservoir being 50 - 60 cm. higher than the level of the resin served to increase the flow rate.

The columns were calibrated by passing through them an artificial sample of a few mg. of a pure Sr or Rb salt (carbonate or acetate), fractions being collected in clean weighed beakers. The aliquots were taken to dryness and the beakers weighed again, and a histogram constructed by plotting weights of salt recovered against ml. of acid passed through the column (see fig. 9). As shown, the cut containing the bulk of the sample could be identified in this way. Calibration checks were done periodically because inevitably some resin was lost every time the column was used, and sometimes the initial quantity had to be repristinated.

Usually all the Rb in the sample is burnt off before reaching the temperature at which Sr is measured on the mass spectrometer, but in some cases the Rb emission cannot be completely eliminated. In such circumstances the amount of Rb^{87} contributing to the Sr^{87} peak can be estimated from the Rb^{85} peak if the contaminating Rb has natural isotopic composition. It would be impossible to estimate the Rb^{87} contamination if deriving from Rb of non-natural isotopic composition, therefore to avoid contamination from spiked Rb, separate columns were used for spiked Rb, spiked Sr and natural Sr.

After each separation the columns were washed with 100 ml. 6 N HCl, the resin was then resettled in 2.6 N HCl in order to keep it uniformly packed. An alternative method of resettling the resin is to elute the column with water, which causes the resin to expand, prior to the final elution

with 50 ml. of 2.6 N HCl. However, the expansion of the resin sometimes caused column breakage and this technique was abandoned in favour of shaking the column upside down and then letting the resin resettle.

4. THE LABORATORY

The chemical laboratory utilized filtered air to avoid possible contamination. The hot plates, the water bath and the water were still kept in fume cupboards.

Only purified water was used for the samples and the dilution of the acids. Ordinary tap water was first distilled through a single stage metal-glass still and then passed through an ionic resin demineralizer.

Separate beakers were used for Rb, spiked Sr and natural Sr; after use they were cleaned with 'magic', a mixture of 3% teepol, 5% HF, 20% HNO_3 and water. Then they were rinsed individually three times in distilled water and three times in demineralized water; finally they were left to dry on clean filter paper.

The platinum dishes could not be cleaned with 'magic' which would corrode the metal, they were boiled for one hour in 6 N HCl and one hour in demineralized water.

The pyrex glass for the micropipettes was first cleaned with 'magic' and then boiled for one hour in demineralized water.

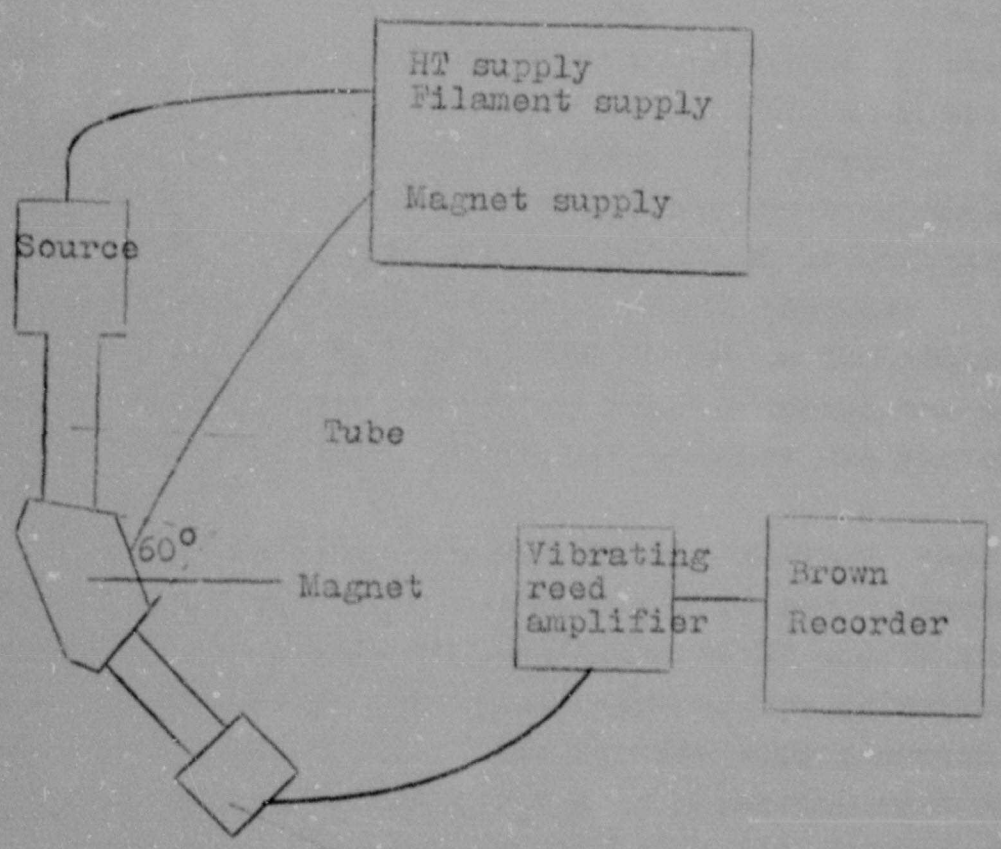
The contamination level for Rb and Sr was checked from time to time by preparing blanks, i.e. by spiking samples containing only the Rb-or Sr-contamination picked up during the various steps of the chemical treatment. It was found that the contaminating amount of Sr was, for all the blank runs, between 0.03 and 0.006 μg. and that of Rb between 0.02 and 0.003 μg., whereas the smallest concentration in the samples studied was more than 4 $\mu g/g$ for Sr, and more than 20 $\mu g/g$ for Rb. Therefore in the worst of the cases the contamination could have been for Sr of 3 parts in 400 and for Rb of 2 parts in 2000.

5. THE B.P.I. MASS SPECTROMETER

The instrument used to determine isotopic ratios was a modified Nier-type mass spectrometer. A schematic diagram is given in figure 10.

Fig. 10

The mass spectrometer



The main technical characteristics of the machine are:

(a) single-filament surface-emission ion source, with 2.5 kv accelerating voltage;
(b) all metal copper tube with a 6" radius of curvature;
(c) magnetic deflection of the beam by 60^{o};
(d) single collector with 10^{12} and 10^{11} resistances both adjusted for critical damping;
(e) vibrating reed electrometer amplifier.

The vacuum was generated by a mercury diffusion pump (30 liters/sec. capacity) with a liquid air cold trap,

backed by a rotary pump (112 liters/min. capacity). Because there was no vacuum lock the whole system was brought to atmospheric pressure every time a sample was loaded. To reduce oxidation of the tube and to keep the system free of impurities, the system was vented with pure nitrogen.

Heater tapes wrapped round the analyzer tube were used continually when the system was under vacuum; the vacuum is adversely affected by this procedure but better resolution is obtained. The relatively poor resolution obtained with the tube cold is considered to be generated by the influence on the beam of charged regions coinciding with poor conducting spots on the tube surface. The effect of increased temperature is to improve the conductivity of these spots (presumably resulting from oxidation or contamination) and to prevent local build-up of electric charges.

A Pirani vacuum gauge was fitted on the rotary pump and a Penning-type ionization gauge measured the pressure in the analyzer tube. Operating pressure was approximately 10^{-6} mm. of Hg.

Filaments were degassed in an auxiliary vacuum system at 4.5 and 2 amp. for respectively 10 and 5 minutes. This procedure also frees the filaments of Rb and Sr contamination because usual operating currents are approximately 1 amp. for Rb and 2.4 amp. for Sr. The effectiveness of this cleaning procedure was checked by inserting several unloaded filaments into the mass spectrometer and showing that no Rb or Sr emission could be obtained.

The source could be taken apart (see fig. 11) and its components ground with fine emery paper and swabbed with demineralized-water after every run.

The Rb samples were loaded in a central position on tantalum filaments; Sr samples were also loaded centrally but on rhenium filaments. Rhenium, although more costly, has a higher work function than tantalum and was preferred for Sr samples because of the increased efficiency of ionization.

From the equation (Hamilton, 1963 - p.20):

$$\frac{n^+}{no} \propto \exp\left[e(w - 1)/kt \right]$$

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