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THE
Rb^{87}-Sr^{87} AGE
OF
STONY METEORITES

by

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(1960)

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF
PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February, 1965

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Department of Geology and Geophysics, November 12, 1964

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ABSTRACT

The Rb^{87}-Sr^{87} Age of Stony Meteorites

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Submitted to the Department of Geology and Geophysics on November 12, 1964 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT - Refined Rb^{87}-Sr^{87} age measurements have been made on three stony meteorites: Pasamonte, a eucrite; Bath, an olivine-bronzite chondrite; and Bruderheim, an olivine-hypersthene chondrite. Each of these meteorites is a "fall" and was selected for its freshness of appearance and contamination free history. The analyses of these three meteorites have been combined with the analyses of three other fresh meteorites - Murray, a Type II carbonaceous chondrite analyzed by Beiser (1964), and Nakhla, a nakhlite, and Estherville, a mesosiderite, analyzed by Pinson et al., (1963) - for the construction of a highly precise meteorite isochron. These six specimens possess a wide spread of Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} ratios and yield a $4.45 \pm .03 \times 10^9$ years isochron (for $\lambda_{Rb^{87}} = 1.39 \times 10^{-11}$ years^{-1}) with an initial Sr^{87}/Sr^{86} ratio of .6982. If one assumes that the Pb-Pb and Rb-Sr techniques give the same age for meteorites, a decay constant of 1.36×10^{-11} years^{-1} can be calculated for Rb^{87} by comparing the Rb-Sr data with the Pb-Pb age of 4.55×10^9 years (Patterson, 1956). Insofar as the sampling has been carried out and within the precision of the measurements, all stony meteorites are of identical age. The major contribution of this work lies in the achievement of a high degree of analytical precision. Improvements in both the chemical and mass spectrometric techniques of analysis have made possible the precise measurement of exceedingly small quantities of Rb and Sr such as are found in meteorites and some ultramafic rocks.

Several phases were also separated from the Bjurböle chondrite for Rb-Sr analyses. The results, however, indicate that this chondrite is severely contaminated.

Thesis Supervisor: William H. Pinson
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ACKNOWLEDGEMENTS

The author is particularly grateful for the assistance of his thesis supervisor, Professor William H. Pinson. His time, effort, cooperation, helpful suggestions and persistence in seeing this investigation through to completion are deeply appreciated.

The author is also grateful to Professor P. M. Hurley for his assistance and for the use of a mass spectrometer under his supervision. The assistance of Professor H. W. Fairbairn is also appreciated. Helpful discussions were held with Mrs. U. B. Marvin, Dr. G. J. Wasserburg, Dr. Robert Dodd, Dr. H. L. Allsopp, and Dr. Gunther Faure for which the author is very grateful. The author also wishes to thank Mrs. U. B. Marvin for performing some X-ray analyses and Dr. W. H. Dennen for an optical spectrographic analysis.

This work was supported by grants from the National Aeronautics and Space Administration (DSR 9835) and the U. S. Atomic Energy Commission (DSR 7033). During part of this research the author held a National Science Foundation Fellowship.

The author is indebted to the following persons for meteorite samples: Dr. R. E. Folinsbee for the sample of Bruderheim; Dr. C. Frondel and Mrs. U. B. Marvin for the sample of Bath; Mr. E. P. Henderson for the

Bjurböle sample; and Dr. H. C. Urey for the Pasamonte sample. Also, the author wishes to thank Miss Erna Beiser for allowing him to use her analysis of the Murray carbonaceous chondrite and Professor W. H. Pinson for the use of the Nakhla and Estherville analyses.

Part of this work was done on the IBM 7094 digital computer at the M. I. T. Computation Center.

The author is indebted to Miss Lotte Schoop and Mr. Bonaventura Eggert for help with some German translations and to Miss Donna Tomasello and Mrs. Margaret Offenberger for typing this manuscript.

PART I

(Papers to be submitted for publication)

THE Rb^{87}-Sr^{87} AGE OF STONY METEORITES

ABSTRACT - Refined Rb^{87}-Sr^{87} age measurements have been made on six stony meteorites: Pasamonte, a eucrite; Estherville, a mesosiderite; Murray, a Type II carbonaceous chondrite; Nakhla, a nakhlite; Bath, an olivine-bronzite chondrite; and Bruderheim, an olivine-hypersthene chondrite. Each of these meteorites is a "fall" and was selected for its freshness of appearance and contamination-free history. These six specimens possess a wide spread of Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} ratios and yield a $4.45 \pm .03 \times 10^9$ years isochron (for $\lambda_{Rb^{87}} = 1.39 \times 10^{-11}$ years^{-1}) with an initial Sr^{87}/Sr^{86} ratio of .6982. If one assumes that the Pb-Pb and Rb-Sr techniques give the same age for meteorites, a decay constant of 1.36×10^{-11} years^{-1} can be calculated for Rb^{87} by comparing the Rb-Sr data with the Pb-Pb age of 4.55×10^9 years (Patterson, 1956). Insofar as the sampling has been carried out and within the precision of the measurements, all stony meteorites are of identical age. The major contribution of this work lies in the achievement of a high degree of analytical precision. Improvements in both the chemical and mass spectrometric techniques of analysis have made possible the precise measurement of exceedingly small quantities of Rb and Sr such as are found in meteorites and some ultramafic rocks.

Introduction

Rb-Sr age work on stony meteorites was initiated in 1956 with the publications of Herzog and Pinson (1956) and Schumacher (1956a,b,c, and d) and was followed a year later by the work of Webster et al., (1957). These early studies, however, encompassed few samples and frequently suffered from poor precision. The publications of Gast (1961 and 1962) were the first studies which included a sizeable number of different meteorites. Due perhaps to an unfortunate selection of samples, however, the achondrites all fall into one tight group and the chondrites into another (excepting, of course, the anomalous Beardsley sample). This gives the equivalent of a 2 point isochron. One, therefore, does not know whether these 2 groups are cogenetic and whether one of these groups represents the primordial parent material. Furthermore, it is difficult to say whether the individual age differences between the chondrites are real or just experimental error. In 1963 Gast also published some further Rb-Sr data on the Abee, Bruderheim and Hvittis meteorites.

The work of Pinson et al., (1963 and 1964) is a notable improvement over all previous studies in that for the first time a wide spread of Rb^{87}/Sr^{86} ratios were obtained from the chondrite data alone. This is important since it enables an isochron to be constructed without including achondrite data and without relying on a number of initial assumptions. Pinson et al., (1964) found that this isochron, indeed, projects through the achondrite points and yields the same age (4.52 b.y. with $\lambda = 1.39 \times 10^{-11}$ years $^{-1}$) as that which is obtained if the achondrite data is also included. Thus, it was demonstrated that chondrites and achondrites are in fact cogenetic and had the same initial Sr^{87}/Sr^{86} ratios; and thus, chondrites cannot be samples of the undifferentiated parent material. Although this work represents an important step forward, it was still plagued with moderately high blanks and poor analytical reproducibility. Therefore, it was not possible to investigate real age differences of the order of a few hundred million years.

In 1964 Murthy and Compston presented some further Rb-Sr age data for meteorites. They constructed a Rb-Sr isochron for carbonaceous chondrites and obtained a good spread in Rb^{87}/Sr^{86} ratios. They also presented a preliminary isochron constructed from individual chondrules separated from the Peace River meteorite.

Beiser and Pinson (1964) published an excellent analysis of the Murray carbonaceous chondrite.

The need for a meteorite isochron constructed from several highly precise Rb-Sr analyses, however, was still apparent. The first objective of this investigation, therefore, was to significantly lower the contamination level and to improve the reproducibility of replicate analyses. It was then hoped that a precise meteorite isochron could be constructed from a few selected high-quality analyses.

Experimental Techniques

The chemical procedure used for separating Rb and Sr in this investigation is a notable improvement over the work of Pinson et al., (1963 and 1964). Contamination has been significantly reduced and the reproducibility of replicate analyses greatly increased. Essentially, the following modifications in the procedure are responsible for this improvement:

First, purer reagents are now used. Five acids are employed in the chemical procedure - HF, HCl, $HClO_4$, HNO_3 and H_2SO_4. HCl and HNO_3 are prepared in the laboratory by distillation of reagent grade HCl and HNO_3 in vycor glass stills. $HClO_4$ and H_2SO_4 are now purchased from the G. Fredrick Smith Chemical Company, 867 McKinley Avenue, Columbus 22, Ohio. Both these acids are double vacuum distilled from vycor and shipped in vycor ampules (items #230 and #273, respectively, in the January, 1960 catalogue). A technique has also been developed for making our own hydrofluoric acid by bubbling HF gas (from a cylinder of liquid, anhydrous HF purchased from the Matheson Company, East Rutherford, New Jersey) into distilled, demineralized H_2O (see Shields, 1964 and 1965). H_2O used in the chemical procedure is purified by distillation in a Barnstead still, passage through a Barnstead Bantam demineralizer (standard cartridge) and then redistillation in a vycor glass still.

Second, all pyrex glassware was eliminated. It was felt that exchange phenomena might possibly exist between the glass and the ions in solution, especially at elevated temperatures and especially if any fluoride ions remained in solution after the sample was dissolved. An independent investigation was also being carried out at the same time on this problem by Wasserburg et al., (1964) at the California Institute of Technology. Their experiments indicated that significant amounts of contamination were introduced by both pyrex and kimax glassware and that this contamination might also be responsible for the poor reproducibility of replicate analyses. Our independent investigation did not involve actual analyses to determine the contribution of pyrex glassware; rather, our approach was to institute a number of changes in the procedure and then run a blank analysis on the entire procedure to see if there was any improvement.

All 100 ml pyrex beakers were replaced by 100 ml polypropylene beakers. The 5 ml pyrex beakers into which samples are transferred at the end of the chemical procedure were replaced by 5 ml vycor crucibles. Vycor ion exchange columns were also instituted and fused quartz wool (purchased from the Thermal American Fused Quartz Co., Route 202, Montville, New Jersey) was used to replace pyrex glass wool for holding back the ion exchange resin at the bottom of the column. Vycor capillary tips were also instituted instead of the pyrex tips for placing the final drop of sample on the mass spectrometer filament.

Third, it was decided that insoluble residues should be removed by centrifuging in vycor centrifuge tubes as opposed to passage through filter paper.

Finally, a policy of keeping all beakers, dishes and solutions covered as much as possible was instituted. A hot plate cover was made and lined on the inside with teflon tape (Temp-R-Tape, manufactured by the Connecticut Hard Rubber Company, New Haven 9, Connecticut). All beakers and dishes when not on the hot plate or steam bath are also covered with a sheet of laboratory parafilm.

The chemical procedure presently in use for separating Rb and Sr from meteorites and other materials with very low concentrations of Rb and Sr is as follows. Meteorite samples are first scraped and brushed clean on the surface to remove possible contamination from dust and human hands. Any remnants of the fusion crust are also chipped off. Samples are <u>not</u> washed or leached in acid prior to analysis since recent investigators have suggested that Rb and Sr contents may be altered in this manner (Gast, 1962; Pinson et al., 1963; Samles et al., 1964). All samples are stored in polyethylene bottles to eliminate the possibility of chipping or scraping the inside of a glass jar and thereby adding bits of soft, alkali-rich glass as contamination.

Samples are crushed by hand in a stainless steel mortar and pestle. A fresh surface is machined on the pestle and on the inside of the mortar before each new sample is crushed. Samples are crushed to pass through at least a 100 mesh sieve. Pieces of the Fe-Ni phase are also mixed in with the silicate material, although it might be preferable to separate the magnetic material by hand magnet, weigh it, and then apply a correction factor to the final answer. The sample is then coned and quartered to insure maximum homogeneity throughout.

The portion of sample to be dissolved for an analysis is then transferred into a platinum dish and set on a steam bath. HF and $HClO_4$ (or sometimes H_2SO_4) are then added. Samples are evaporated to perchloric acid fumes and then taken up in HCl at least twice after the last portion of HF has been added to insure removal of all fluoride ions. Finally, the dried sample is taken up in as small a volume of distilled H_2O as is necessary for dissolving the sample. Addition of a small amount of 2N HCl may sometimes be necessary here. The samples are then decanted into polypropylene beakers which are always kept soaking in concentrated HNO_3 when not in use.

After a meteorite has been dissolved in HF and $HClO_4$, a black insoluble residue often remains. Such a residue has also been observed by Gast (1962, 928), Schumacher (1956b), and Pinson et al., (1962, 19). X-ray analysis of some of this residue by Mrs. U. B. Marvin of the Smithsonian Astrophysical Observatory indicated a spinel structure with high concentrations of Fe and Cr. This is consistent with the findings of Gast (1962, 928); and thus, this residue should contain negligible Rb and Sr. This insoluble residue is removed by transferring the solution into vycor centrifuge tubes (which are always kept soaking in concentrated HNO_3) and centrifuging it for about five minutes. The liquid is then decanted back into a clean polypropylene beaker.

Rb and Sr are separated from the other elements in a sample by ion exchange. The resin used for this separation is Dowex 50 (8% cross-linked with DVB, 200-400 mesh, hydrogen form) cation exchange resin manufactured by the Dow Chemical Company, Midland, Michigan. This resin is put in a vycor glass column, as illustrated in Figure Ia, so that the resin bed is approximately 25 cm high. A 1000 ml polyethylene bottle is filled with the

Figure Ia

(see Figure 2.34 in Part II of this thesis) eluant, 2N HCl, and set on a shelf above the top of the column. This bottle is connected with tygon tubing to a ground glass 19/38 joint at the top of the column. A screw clamp is used on the tygon tubing to shut off the reservoir in the polyethylene bottle. This bottle of 2N HCl when connected to the column serves as a pressure head. It speeds up passage of a sample through the resin and can be left unattended for several hours.

The location of the Rb and Sr on the column is monitored with Rb and Sr radioactive tracers. The tracer must, therefore, be added prior to putting a sample on the column. These tracers are purchased from the Nuclear Science and Engineering Company, Box 10901, Pittsburgh 36, Pennsylvania. The Rb tracer is a mixture of Rb^{83} and Rb^{84} produced by proton bombardment of krypton. Sr^{85} tracer is produced by bombardment of Rb with protons and deuterons. Our numerous blank analyses demonstrate these tracers to be carrier free.

Columns are normally washed with 2000 ml of 2N HCl each time before applying a sample to insure removal of elements such as the rare earths. A level surface is then prepared on the top of the resin by adding about 10 ml of 2N HCl shaking the column by hand and allowing the resin to settle. The sample is then placed on the top of the resin bed.

Samples are eluted with 2N HCl. They are gently washed into the resin by adding 2 or 3 small portions of 2N HCl with a polyethylene squirt bottle and washing down the sides of the column. Finally, a 50 to 75 ml portion of 2N HCl is added gently onto the resin bed. The 1000 ml polyethylene bottle is then filled with 2N HCl and connected to the column via the glass joint. The clamp is then loosened and the column runs automatically.

Samples are collected off the columns in 15-20 ml portions with 100 ml polypropylene beakers. The activity in each beaker is monitored with a low level scintillation counter. Beakers are kept covered with parafilm, and only the 2 or 3 beakers which contain the maximum tracer activity are retained. The contents of these beakers are then combined and evaporated to 2 or 3 ml on a covered hot plate.

Frequently, Rb samples which have been run through the ion exchange columns only once are full of a white material. A sample of this material from the Bath chondrite was analyzed on the optical spectrograph by Dr. W. H. Dennen of M.I.T. and determined to be aluminum. Schumacher (1956b) mentions the presence of Al^{3+} but says that it is rapidly washed through the column and does not interfere with the Rb samples. Perhaps this is because he was eluting with stronger HCl than we are at present using, thereby complexing the aluminum as $AlCl_4^-$. The most effective procedure for removing aluminum from our Rb samples is still under investigation.

After the sample has been evaporated down to 2 or 3 ml in a polypropylene beaker, it is transferred into a 5 ml vycor glass beaker. These vycor glass beakers are kept soaking in concentrated HNO_3 acid and are leached with hot aqua regia before use. They are used only once. The sample is evaporated to dryness in this vycor beaker. A few drops of concentrated $HClO_4$ are then added to oxidize any resin which may have passed through the quartz wool. The sample is again evaporated to dryness and ignited over a Tyrell burner to eliminate perchlorates. One or two ml of HNO_3 are then added to the sample, and it is again evaporated to dryness. This last step is then repeated, and the sample is ready for mass spectrometer analysis.

To mount a sample on the filament of a mass spectrometer source one small drop of nitric acid is added to the sample. This is taken up in a vycor capillary syringe and dried on the center of a tantalum filament by passing a current of about one ampere through the filament.

The mass spectrometer used for making these Rb and Sr analyses is a 60° sector, six inch radius, solid source, single collector, Nier type instrument. The filament consists of a piece of .001" x .020" tantalum ribbon spot-welded to two posts in the source. A vibrating reed electrometer is used to amplify the ion current, and the signal is read out on a Brown strip chart recorder. A vacuum in the range of 10^{-7} mm. of mercury is obtained by coupling a Duo-Seal forepump with a mercury diffusion pump.

A sample of a typical mass spectrometer scan of a Sr spectrum is shown in Figure IIb.

Results

As a result of the changes incorporated into the chemical procedure the contamination level has been lowered significantly. For purposes of comparison, blank determinations before the changes were instituted are given in Pinson et al., (1963, 10) and reproduced in Table Ia. Blank determinations obtained with the new chemical procedure are listed in Table Ib. It can be readily seen that Sr contamination has been reduced by an order of magnitude and Rb contamination reduced by a factor of 2.

Figure Ib

(see Figure 2.4 in Part II of this thesis)

Table Ia

(see Table 6.1a in Part II of this thesis)

Table Ib

(see Table 6.1b in Part II of this thesis)

To insure that the mass spectrometer is operating reproducibly over the period of time during which a series of analyses are being made, it is standard procedure in the M.I.T. Geochronology Laboratory to run a Sr isotope ratio standard ($SrCO_3$, Eimer and Amend, Lot #492327) periodically. Table Ic lists the values obtained for the Sr^{87}/Sr^{86} ratio of this $SrCO_3$ standard. These runs overlapped the period during which the Pasamonte, Bath and Bruderheim meteorites were run on the mass spectrometer. The error is given as the standard deviation of a single analysis computed from the formula:

$$\sigma = \sqrt{\frac{\Sigma(\bar{x}-x)^2}{(n-1)}}$$

The Rb-Sr data from the analyses of the Bruderheim chondrite, the Bath chondrite and the Pasamonte achondrite are given in the following tables. The Rb analyses are listed in Table Id. Bath and Bruderheim were analyzed in duplicate, beginning with separate one gram samples and processing each one independently. The duplicate Rb sample of the Pasamonte meteorite was prepared but not analyzed. The Rb analysis of Pasamonte sample 7, however, was a long steady run of 106 sets; it was judged to be of the highest quality. Bruderheim sample 6 was run on two different mass spectrometers; this is

Table Ic

(see Table 6.2 in Part II of this thesis)

Table Id

(see Table 6.3a in Part II of this thesis)

indicated by the brackets in Table Id.

Sr isotope dilution analyses are listed in Table Ie. Each of these meteorites was analyzed in duplicate. The subscripts T and m refer to the corrected and measured values, respectively, since mass spectrometer discrimination can now be corrected for with our new Sr^{84}-Sr^{86} double spike. A Sr^{87}/Sr^{86} ratio for the original sample was calculated in the last column of Table Ie from the corrected Sr^{86}/Sr^{88} and Sr^{87}/Sr^{86} ratios. The (S) refers to the mass spectrometer on which the sample was run. Sample numbers correspond to those in Table Id since both Rb and Sr isotope dilution analyses are made from the same aliquot of sample. Bruderheim sample 6 was run twice on the same mass spectrometer. Note that Sr values in ppm are reported as Normal Sr. (Normal Sr is defined in this work as initial Sr or Sr with a Sr^{87}/Sr^{86} ratio of .698.)

The Sr isotope ratio results are listed in Table If. Likewise, duplicate measurements were made in each case. It should be remembered, however, that these are different samples and not the same ones that were used for the isotope dilution analyses. The calculated Sr^{87}/Sr^{86} ratios have been put in brackets, therefore, to indicate this. These calculated Sr^{87}/Sr^{86} ratios

Table Ie

(see Table 6.3b in Part II of this thesis)

Table If

(see Table 6.3c in Part II of this thesis) correspond instead to the samples in Table Ie. Note, however, that only the measured Sr^{87}/Sr^{86} ratios have been used in constructing the isochron. These measured Sr^{87}/Sr^{86} ratios have been normalized to a Sr^{86}/Sr^{88} ratio of .1194 (indicated in Table If by (87/86)*).

Each run normally consisted of between 54 to 72 sets of scans which were added up in groups of 6 sets each to facilitate the computations. Errors were calculated for each of the Sr isotope ratio analyses in Table If. These errors indicate the scatter of the normalized (87/86)* ratios in sets of six scans each. $\bar{\sigma}$ for an individual analysis is the standard deviation of the mean, or:

$$\bar{\sigma} = \sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}}$$

where n is the number of groups of 6 scans each. $\bar{E}$ is the percentage error:

$$\bar{E} = \frac{100(\bar{\sigma})}{\left(\frac{87}{86}\right)^*}$$

Table Ig is a summary of the Rb-Sr analyses on these three meteorites. The Rb^{87}/Sr^{86} values have been calculated with a computer program written by the author and described in Section 4.3, Part II of this thesis.

Table Ig

(see Table 6.3d in Part II of this thesis)

This program does not use the Rb and Sr concentrations in ppm, but instead starts with the Rb^{85}/Rb^{87} and Sr^{86}/Sr^{88} ratios measured on the mass spectrometer and calculates the Rb^{87}/Sr^{86} ratios directly.

The average Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^*$ ratios of Bruderheim, Bath and Pasamonte from Table Ig have been used in the construction of a meteorite isochron. Three other meteorites have also been used for this isochron: the Murray carbonaceous chondrite analyzed by Beiser (1964), the Nakhla achondrite analyzed by Pinson et al., (1963), and the Estherville mesosiderite analyzed by Pinson et al., (1963). The Murray carbonaceous chondrite was included on this isochron because it was analyzed in the same laboratory and with the same clean chemical techniques as Pasamonte, Bath and Bruderheim. Estherville and Nakhla were also included on this isochron because, even though they were analyzed before the clean chemical separation procedure was instituted, they contain such high concentrations of Sr and such low concentrations of Rb that errors in either of these measurements affect the Rb/Sr ratios to a very small degree. Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^*$ ratios which have been used for these meteorites are listed in Table Ih. The $(Sr^{87}/Sr^{86})^*$ ratios have been taken directly from Beiser (1964, 21) and Pinson et al.,

Table Ih

(see Table 6.3e in Part II of this thesis)

(1963, 9). Rb^{87}/Sr^{86} ratios for Nakhla and Estherville were taken from Pinson et al., (1963, 8) but were adjusted slightly so that a consistent value was used in all cases for the concentrations of the Rb and Sr spikes. Using the Rb^{85}/Rb^{87} and Sr^{86}/Sr^{88} ratios obtained by Miss Beiser in three separate isotope dilution analyses, the Rb^{87}/Sr^{86} ratio of Murray was determined using the computer program of Section 4.3 in Part II of this thesis.

A least squares isochron (following the methods set forth in Youden, 1951, 40-43) was constructed from the average Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^*$ ratios for the above 6 meteorites. A computer program described in Section 4.2 in Part II of this thesis was used for this calculation. The isochron is reproduced in Figure Ic. Figure Id shows the output data from the computer for this isochron. An explanation of the various quantities calculated by the computer and the errors associated with a least squares line is given in Section 4.22 in Part II of this thesis.

Using a decay constant for Rb^{87} of 1.39×10^{-11} years^{-1} (Aldrich et al., 1956), a slope of 0.06385 ± 0.0005 (or ± 0.7%) was calculated. This gives an age of $4.45 \pm .03 \times 10^{9}$ years as the solidification age of the stony meteorites. The initial ratio was determined

Figure Ic

(see Figure 7.1a in Part II of this thesis)

Figure Id

(see Figure 6.3b in Part II of this thesis) to be 0.6982 ± 0.0002. The errors quoted here are standard deviations and reflect only the scatter in the final points from a straight line.

In order to estimate whether or not there has been an improvement in the overall analytical reproducibility in relation to the work of Pinson <u>et</u> <u>al</u>., (1963), the author has calculated standard deviations from the various groups of duplicate (or replicate) analyses in both works using the following formula suggested in Dixon and Massey (1957, 143 ff.):

$$\text{S.D.} = \sqrt{\frac{\Sigma\Sigma(x_{ij}-\overline{x}_j)^2}{\Sigma_j n_j - k}}$$

where: x_{ij} = the value of the i^{th} replicate of the j^{th} sample

$\overline{x}_j$ = mean value of the j^{th} sample

k = total number of samples (<u>not</u> data points)

n_j = number of replicates of the j^{th} sample.

Standard deviations calculated in this way for both the Sr^{87}/Sr^{86} ratios and the Rb and Sr isotope dilution analyses are shown in Table Ii. It can be seen that the new chemical procedure has resulted in an improvement in the overall analytical reproducibility by factors of 7 and 3 for Rb and Sr isotope dilution analyses, respect-

Table Ii

(see Table 6.5a in Part II of this thesis)

ively. Note that in both cases the reproducibility is significantly better for Rb than for Sr. This is surprising especially since a new double Sr^{84}-Sr^{86} spike allows correction of Sr isotope dilution analyses for mass spectrometer discrimination. The reproducibility in $(Sr^{87}/Sr^{86})^*$ ratios has also been improved by a factor of 4.

The isochron of Pinson et al., (1963) has been reproduced in Figure Ie for comparison with the isochron in this thesis (Figure Ic). Note that a significant increase in analytical precision has been obtained; the standard deviation in the slope of the isochron has been improved from ± 0.0014 to 0.0005. The reduced scatter in the data is also readily noticeable by visual comparison of Figures Ic and Ie. The standard deviation of the Rb^{87}-Sr^{87} stony meteorite isochron has, therefore, been reduced from ± 90 million years to ± 32 million years.

Discussion

In conclusion, several points should be noted. First, a few years ago many investigators thought that meteorites did, in fact, exhibit real and significant age differences. This present work, however, has demonstrated that this is not the case (at least within the

Figure Ie

(see Figure 7.1b in Part II of this thesis) resolution of the present technique) and that previous scatter was due essentially to poor analytical precision.

Second, each of the six meteorites on the isochron of Figure Ic is from a different meteorite class. The following classes are represented:

1. Olivine-bronzite, or H-group, chondrite (Bath)
2. Olivine-hypersthene, or L-group, chondrite (Bruderheim)
3. Type II carbonaceous chondrite (Murray)
4. Nakhlite, or olivine-diopside achondrite (Nakhla)
5. Eucrite, or pyroxene-plagioclase achondrite (Pasamonte)
6. Mesosiderite (Estherville)

One can say, therefore, that probably at least 5 of these 6 different classes of meteorites underwent a chemical differentiation 4.5 billion years ago.

Third, Figure Ic includes analyses made not only at different times, but also by three different investigators. This indicates, therefore, that at least there are no significant differences between the analyses of these three workers in the M.I.T. Geochronology Laboratory.

Fourth, the biggest discrepancy in the isochron of

Figure Ic occurs between the Pasamonte and Estherville samples. Plans have been made to reanalyze these two meteorites in the near future. Several suggestions may be offered at present for the disagreement. First, the Estherville analysis was made by Pinson et al., (1963) before institution of the new, clean chemical separation procedure. Since Pasamonte lies practically within the limits of error of the Estherville analysis, it may be that a reanalysis of Estherville would eliminate the discrepancy. Second, Gast's average Rb^{87}/Sr^{86} value for Pasamonte is 0.008 and his average Sr^{87}/Sr^{86} ratio, when normalized to .1194, is .69875. This plots almost exactly on the least squares isochron of Figure Ic. This would tend to indicate that a reanalysis of Pasamonte might solve the problem. Finally, there is always the remote possibility that one (or both) of these two meteorites does have a different age. It seems, however, that the probability of some other differentiation event producing a Sr^{87}/Sr^{86} ratio nearly identical to the initial ratio of the meteorite isochron would be very small. The first two suggestions are considered most probable.

Finally, the remarkably close fit of these six meteorites to a straight line tends to indicate that initial assumptions, such as all meteorites have the same age and all were formed from the chemical differentiation of a homogeneous common parent material, have been satisfied. It also indicates that the precision of the measurements must be high. If any of these conditions were not met, the probability of all these meteorites falling along a single straight line would be small, indeed.

Patterson (1955 and 1956) presented an outstanding determination of the age of meteorites and the earth using the U^{238}-Pb^{206} and U^{235}-Pb^{207} decay schemes. His age was later substantiated by Hess and Marshall (1960). Further supplementary work has also been carried out by Starik <u>et</u> <u>al</u>., (1959 and 1960), Murthy and Patterson (1962) and Marshall (1962). It seems remarkable, indeed, that an entirely different decay scheme, such as Rb^{87}-Sr^{87}, should yield a solidification age for meteorites which agrees so closely with that determined by the Pb-Pb technique. After constructing a highly precise meteorite isochron using the Rb^{87}-Sr^{87} decay scheme, therefore, it is naturally of interest to see how it compares with the Pb-Pb age of meteorites. The question naturally arises as to which of these dating techniques now gives the most accurate solidification age.

Certainly one advantage in the Pb-Pb technique is that only the isotopic ratio of the Pb spectrum must be measured. In contrast, a Rb-Sr analysis for age measurement requires two separate isotope dilution analyses and also an isotope ratio analysis of the Sr spectrum. Isotope dilution analyses require considerably more work, since a series of spikes and shelf solutions must be prepared and periodically calibrated.

The Pb-Pb technique also has an advantage in that both the U^{238} and U^{235} half-lives are more accurately known than that of Rb^{87}.

On the other hand, there are also some disadvantages in the Pb-Pb method when compared with the Rb-Sr technique. Whereas Rb and Sr contamination in this present work is so low that it is considered insignificant, Pb workers suffer from a considerably more severe contamination problem. Typical lead blanks of 1.5 μgms Pb per analysis (Hess and Marshall, 1960, 285) and .68 μgms Pb per analysis (Marshall, 1962, 2006) have been reported recently. For ordinary chondrites with..05-.5 ppm Pb, carbonaceous chondrites with 1-5 ppm Pb and even troilites with 2-10 ppm Pb, it can be seen that this is a disturbingly high contamination level. Yet, contamination problems can be somewhat overcome by analyzing large samples. In spite of this, however, Hess and Marshall (1960, 285) report that in the case of chondrite analyses contamination may account for "... from 23 per cent to

82 per cent of the total amount of lead observed in the concentration determinations." They state, furthermore, that the "uncertainty in the blank is large, around 30 per cent". In the case of carbonaceous chondrites Marshall (1962, 2009) has estimated the contamination levels to be about 7-12%.

Recent investigations have further shown how few meteorites actually contain U and Pb concentrations which are consistent with the age measurements. Many of the meteorites analyzed contain far too little U to account for the observed increase in Pb^{206} and Pb^{207} over the past 4.5 billion years. Anders (1963, 438) has suggested that terrestrial weathering may be responsible for a large amount of this contamination, since meteorites exposed to ground water may soak up Pb preferentially to Fe in the sulfide phase.

Yet there is a large offsetting advantage to this contamination problem in that mean oceanic lead lies on the 4.5 billion year Pb-Pb isochron (see Figure 7.2, in Part II of this thesis). Thus, (assuming, of course, that all meteorites do lie on this same isochron) this contamination does not interfere with the Pb-Pb age of meteorites as much as might at first be expected. Hess and Marshall (1960, 289) estimated that despite the high contamination level the errors in the isotopic measurements were probably only about 3%.

Mass spectrometer discrimination is also an important problem to be considered. Since the per cent mass difference between the 2 Rb isotopes and between Sr^{86} and Sr^{88} is only slightly larger than that between Pb^{204} and Pb^{208}, one might expect that mass spectrometer discrimination would affect the Rb^{85}/Rb^{87}, Sr^{86}/Sr^{88} and Pb^{208}/Pb^{204} ratios to a roughly similar extent. In the case of Sr isotope ratio analyses and doubly spiked Sr isotope dilution analyses mass spectrometer discrimination can be corrected for. However, Rb and Pb analyses cannot at present be corrected for discrimination in this manner because natural Rb only contains 2 isotopes and Pb has only one non-radiogenic isotope. In the case of Pb a constant square root of mass correction is usually made, but this does not take into account the variations that occur from one run to the next. Rb and Pb, therefore, probably suffer from similar mass discrimination problems.

Everything considered, the author feels that the slope of the Rb-Sr meteorite isochron presented in this thesis is now as accurately determined as the slope of the Pb-Pb isochron. Certainly the scatter of the points about the least squares line is as good as in the case of the Pb-Pb isochron. In converting the slope into an age, however, the half-life and its associated errors are introduced. Here there is undoubtedly a greater uncertainty in the Rb^{87} half-life than in either the U^{238} or U^{235} half-lives. Thus, the final value for the age of meteorites may be more accurately determined by the Pb-Pb technique, but only because of the more accurately known half-lives of uranium.

One can, of course, make the assumption that the Rb-Sr and Pb-Pb techniques date the same event and should yield the same solidification age for meteorites. Present evidence indicates that this is certainly quite possible. Thus, a Rb^{87} decay constant can be calculated by combining the accurately measured slope of the Rb-Sr isochron in this thesis with the Pb-Pb age of 4.55×10^{9} years for meteorites (Patterson, 1956). Using a value of .06385 for the slope of this Rb-Sr isochron, a decay constant of 1.36×10^{-11} years^{-1} is obtained. This corresponds to a half-life of 5.1×10^{10} years for Rb^{87}. If one uses the Pb-Pb meteorite age of 4.6×10^{9} years proposed by Hess and Marshall (1960) then the decay constant for Rb^{87} becomes 1.345×10^{-11} years^{-1} and the half-life becomes 5.16×10^{10} years.

Acknowledgements

This work was supported by contracts from the National Aeronautics and Space Administration (DSR 9835) and the U. S. Atomic Energy Commission (DSR 7033). During part of this research the author held a National Science Foundation Fellowship.

Some of the calculations in this work were done on the IBM 7094 digital computer at the M.I.T. Computation Center.

The author is indebted to Dr. R. E. Folinsbee for the Bruderheim sample, Dr. C. Frondel and Mrs. U. B. Marvin for the Bath sample, and Dr. H. C. Urey for the Pasamonte sample.

The help of Professor W. H. Pinson, Professor P. M. Hurley and Professor H. W. Fairbairn is also gratefully acknowledged.

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Rb-Sr ANALYSES OF THE BJURBÖLE CHONDRITE

ABSTRACT - Several phases were separated from the Bjurböle chondrite for Rb-Sr age analysis. The results, however, indicate that this chondrite is severely contaminated.

Introduction

Rb-Sr age investigations of meteorites have so far been limited, except for the recent chondrule isochron of Murthy and Compston (1964), to analyses of whole meteorite samples (Herzog and Pinson, 1956; Schumacher, 1956; Webster, Morgan and Smales, 1957; Gast, 1960, 1961, 1962, and 1963; and Pinson *et al.*, 1962, 1963, and 1964). However, it would be of considerable interest to construct an isochron from the separated mineral phases of a single meteorite. The Bjurböle chondrite was chosen for this purpose since it is one of the few chondrites which is so friable that it can be crumbled between the fingers. The hard, strong chondrules, however, do not break with the groundmass and can be easily picked out of it with a pair of tweezers. It was planned, therefore, to make a Rb-Sr age study of the Bjurböle chondrite by analyzing not only the whole meteorite and the chondrules, but also some separated mineral phases.

Experimental Techniques

The chondrule separations were carried out first. Chondrules were picked out of the meteorite with a pair of new, clean, stainless steel tweezers. A total of 8.4 grams of chondrules were collected in this way. They were placed in a polyethylene vial, and after the separations were completed they were shaken at length to knock off any groundmass which might still be adhering. These chondrules were then stored in a clean polyethylene vial. Figure IIa shows a typical assortment of these chondrules. Figure IIb shows eight of the largest chondrules separated. The scale in both pictures is divided into millimeters.

A second phase consisting of the fine-grained groundmass, or "matrix" material, was then prepared from the fragments and rubble resulting from the chondrule separation. This material was passed through a 250 mesh stainless steel sieve to remove as many of the broken pieces of chondrule as possible. Admittedly, this is not a complete separation, but it was felt that at least a large percentage of the chondrule material was separated in this way.

The material which did not pass through the 250 mesh sieve was combined with another piece of the Bjurböle sample and crushed in a stainless steel mortar (with a freshly machined surface). A hand magnet was then used to remove metallic Fe-Ni. The material which was not attracted by the hand magnet was then sorted (using brand new stainless steel sieves) into the following different size fractions:

42 - 60 mesh
60 - 100 mesh
100 - 150 mesh
150 - 200 mesh

Figure IIa

(see Figure 6-4a in Part II of this thesis)

Figure IIb
(see Figure 6-4b in Part II of this thesis)

Each of these size fractions was then passed through a Franz Isodynamic separator. Eight to ten different magnetic portions were collected from each mesh size. Each of these magnetic fractions was passed through the separator twice.

Upon completion of these separations, 5 different phases of the Bjurbölė chondrite were prepared for Rb-Sr analysis:

1 - whole meteorite -- a large, unmolested chunk of the original sample still remained from which a piece was broken off for the whole meteorite analysis. A clean surface was scraped on this piece just before crushing for analysis.

2 - "matrix" or groundmass

3 - chondrules

4 - non-magnetic fraction -- that portion of the meteorite which was not attracted by the magnet at currents of less than 1 ampere.

5 - medium-magnetic fraction -- an olivine-pyroxene concentrate -- that fraction which was separated between currents of 0.2 and 0.7 amperes.

No attempt was made to use heavy liquids for phase separations. In view of recent evidence concerning the leaching of Rb and Sr from meteorites (Gast, 1962; Smales *et al.*, 1964; Pinson *et al.*, 1963) it was decided to analyze these 5 phases first.

The new chemical procedure for separating Rb and Sr from these Bjurböle samples has been discussed in Chapter II, Part II of this thesis. This new technique is a significant improvement over the procedure used in the analyses of Pinson et al., (1963). The essential modifications have included the elimination of pyrex glassware and the use of purer chemical reagents. The resulting blank analyses have been reduced by factors of 2 and 10 for Rb and Sr, respectively. The analytical reproducibility has also been improved markedly.

The mass spectrometer on which these Rb and Sr samples were analyzed is a 60^{o} sector, six-inch radius, solid source, single collector, Nier type instrument. The filament consists of a piece of .001" x .020" tantalum ribbon spot-welded to two posts in the source. A vibrating reed electrometer is used to amplify the ion current, and the signal is read out on a Brown strip chart recorder. A vacuum in the range of 10^{-7} mm. of Hg is obtained by coupling a Duo-seal forepump with a mercury diffusion pump.

Results

The results of the Rb-Sr analyses on these 5 Bjurböle samples are summarized in Table II. Both the Rb and Sr isotope dilution analyses were made from the same aliquot of sample, whereas the Sr isotope ratio analyses were made from a separate portion of sample. To be noted is the excellent reproducibility between the 3 sets of duplicate Sr isotope ratio analyses. These Sr^{87}/Sr^{86} ratios in Table II have been normalized to a

Table II

(see Table 6.4d in Part II of this thesis)

Sr^{86}/Sr^{88} ratio of .1194. The replicate Rb^{87}/Sr^{86} ratios also show good agreement and are a marked improvement over the work of Pinson et al., (1963). The Sr isotope dilution analyses on the chondrules, the medium-magnetic fraction and non-magnetic fraction were made with a new Sr^{84} - Sr^{86} double spike which allows a correction to be made for mass spectrometer discrimination. Blanks of .015 μgms Rb and .020 μgms Sr per gram of sample have been subtracted.

The Rb^{87}/Sr^{86} ratios listed in Table II have been calculated on the IBM 7094 computer at the M.I.T. Computation Center. A Fortran II computer program was written by the author for this calculation.

Discussion

The Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} ratios listed in Table II for these 5 Bjurböle samples are shown plotted in Figure IIc in relation to the author's recent meteorite isochron (Shields, 1964 and 1965). As can be seen from this Rb-Sr data, the Bjurböle chondrite is severely contaminated. Not one of the samples lies on the isochron. Even the whole meteorite sample, which escaped all of the phase separation procedures and was scraped down to a fresh surface just prior to crushing, lies way off the isochron. Since Bath, Bruderheim and Pasamonte received the same new, clean, chemical separation treatment as the Bjurböle whole meteorite sample, it seems highly unlikely that laboratory contamination is responsible for these anomalous results.

Two explanations may possibly be offered.

Figure IIc

(see Figure 6-4c in Part II of this thesis)

First, the description of the fall and recovery of the Bjurböle chondrite in Ramsay and Borgström (1902) allows us to estimate that the Bjurböle chondrite probably lay in sea water for anywhere from ½ a week to 2 or 3 weeks (or even more). Since this meteorite is especially friable, it is quite conceivable that the salt water percolated entirely through it. Indeed, the interior of the meteorite is full of heavily rusted areas. Ramsay and Borgström (1902, 9) mention that the meteorite (after salvage) dried out slowly and its surface became covered with a white salt.

Gast (1962, 937-939) has made some leaching experiments with H_2O. His results indicate that both Rb and Sr can be leached out of meteorites -- that Rb is preferentially soluble to Sr and radiogenic Sr is twice as soluble as normal Sr. Smales et al., (1964, 228) have also made some experiments to determine whether K, Rb and Cs can be dissolved out of meteorites with demineralized H_2O. Their results agree with those of Gast and indicate that even a few hours in H_2O at room temperature is sufficient to leach several percent of the Rb. Thus, it seems that sea water could have severely altered the Rb and Sr contents in the Bjurböle chondrite.

A second type of contamination might have been introduced from the clay and sand in which the meteorite landed. Bjurböle fell through 6-7 meters of mud and clay onto a layer of sand and gravel (Ramsay and Borgström, 1902, 6). As the meteorite is very friable, it broke into many pieces upon landing. No doubt, many small mineral grains in the sediment could have been shaken together in a polyethylene vial to remove loose adhering material. Perhaps, therefore, the chondrules were not only much more resistant to water seepage, but also the least contaminated with small detrital quartz and feldspar grains.

As a result of these Bjurböle chondrite analyses, the work of Pinson et al., (1962 and 1963), and the leaching experiments of Gast (1962) and Smales et al., (1964), it seems that terrestrial weathering is capable of altering certain of the trace element contents. In view of this we have decided to take the following precautions in selecting meteorites for future Rb-Sr investigations.

First, only meteorites which are classified as "falls" are suitable for Rb-Sr age analysis.

Second, the terrestrial history of the meteorite must be carefully examined. The environment in which it fell is of importance and also the probable length of time it spent on the ground before recovery. Only those meteorites which were recovered shortly after infall and had a minimal exposure to terrestrial weathering should be used.

Third, freshness of appearance should be considered. One should look both macroscopically and with the binocular microscope for signs of weathering, particularly limonite stains. Most meteorites contain some Fe-Ni metal which slowly rusts upon contact with H_2O. Meteorites also contain lawrencite ($FeCl_2$), a soft, green mineral which decomposes in air forming limonite (Mason, 1962, 60).

Some caution should be applied, however, driven into the matrix and also into any cracks in the surface of the meteorite. While separating out chondrules, the author discovered a number of clear to pink mineral grains which subsequent optical and x-ray analysis indicated to be quartz and feldspar. There was no fusion crust on the sample studied, and the grains appeared from macroscopic observation to belong to the meteorite. Quartz has been identified in iron meteorites, achondrites and enstatite chondrites (Mason, 1962, 63-64); therefore, it did not seem too unreasonable to find it in a hypersthene chondrite. The magnetic separations also produced many grains of this same description. It appears now, however, that these mineral grains, instead of being initially present in the meteorite, were probably driven into its friable matrix as it fell through the sediments.

Another investigator (Dodd, 1964) from the Air Force Cambridge Research Laboratory, recently arrived at the same conclusion from an independent study of petrographic thin sections of this meteorite. He observed in cracks broken up quartz and feldspar minerals that appeared to him to have been subsequently introduced into the groundmass. The author had one petrographic thin section made of Bjurböle, but it was of poor quality and this phenomenon was not observed.

It seems reasonable, therefore, that Bjurböle could have been beset with 2 types of contamination. It is noteworthy that of the five "phases" which were analyzed from Bjurböle, the chondrules fall closest to the isochron. The chondrules are hard and dense; and, unlike the matrix, they are not friable. Furthermore, each one was picked by hand from the meteorite, and then they were in using limonite stains as a positive identification of weathering and exposure to H_2O. There are some classes of meteorites which contain no metallic Fe-Ni (or only trace amounts of it), and probably no lawrencite as well -- for example, carbonaceous chondrites and some classes of achondrites. In these cases, a considerable amount of exposure to weathering might be required before rust began to appear. On the other hand, Mason (1962, 60) claims that some chondrites are so sensitive that they "become rust-brown or freckled with rust-colored spots" simply upon breaking off a fresh surface.

Most of the known meteorites are, therefore, unacceptable for Rb-Sr analysis if such stringent precautions are to be applied. Yet, if one uses samples of questionable freshness, an anomalous result leaves one facing the dilemma of whether or not terrestrial weathering was responsible.

Acknowledgements

This work was supported by contracts from the National Aeronautics and Space Administration (DSR 9835) and the U.S. Atomic Energy Commission (DSR 7033). During part of this research the author held a National Science Foundation Fellowship.

The author is indebted to Mr. E.P. Henderson of the U.S. National Museum in Washington, D.C. for providing a sample of the Bjurböle chondrite.

Some of the calculations in this work were performed on the IBM 7094 at the M.I.T. Computation Center.

The author gratefully acknowledges the help of

Professor W.H. Pinson, Professor P.M. Hurley and Professor H.W. Fairbairn.

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PART II

(Complete description of thesis investigation)

CHAPTER I

INTRODUCTION

1.1 - Introductory Meteoritics

Meteorites are complicated and puzzling phenomena. As they are practically our only known samples of extraterrestrial material*, they are understandably of considerable scientific interest. Without them, the only tangible part of the solar system available to the geochemist for analysis would be the earth's crust - a most unrepresentative portion not only of the solar system, but also of the earth as a whole. Despite the wealth of scientific data which has been gathered on meteorites in recent years, there is almost no agreement amongst scientists as to the origin and history of these strange objects.

Meteorites are generally divided into three classes: stones, irons, and stony-irons. Of the approximately 1700 recognized meteorites in the world

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*Tektites have been excluded from this discussion since it has not yet been conclusively demonstrated that they are of extraterrestrial origin.

today, 61% of them are stones, 35% irons, and 4% stony-irons. If one considers just those meteorites which have been observed to fall, however, the stones comprise an impressive 92%, while the irons account for only 6% and the stony-irons for 2% of the total number. The probable explanation for this discrepancy is that the irons are not only more resistant to weathering, but also more easily recognized on the ground. Scientists, therefore, tend to favor the figures for "witnessed falls" as being most representative of the absolute abundance of these three classes of meteorites.

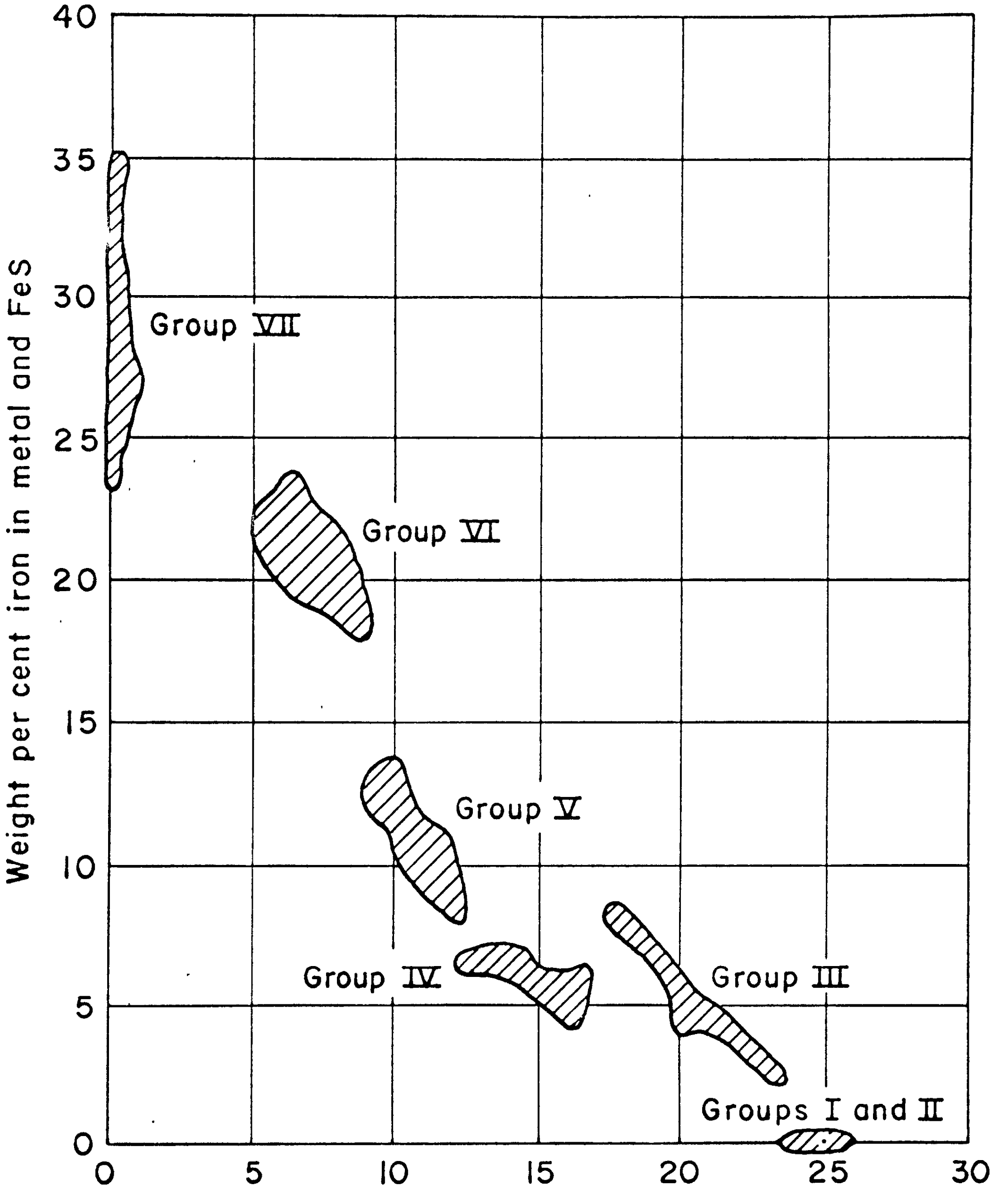
Further subdivisions also exist within each of the above meteorite classes. (A more complete discussion of the classification of meteorites is given in Mason, 1962a, 46-147.) For the stony meteorites a number of classification schemes have been proposed, but none has so far been entirely satisfactory. In many cases early classification schemes were long and often based on superficial characteristics. Some of the more recent ones have been hindered by the lack of high quality chemical and mineralogical analyses. In any event, stony meteorites are generally subdivided first into two major groups - the chondrites and the achondrites. This subdivision is based on the presence or absence of small rounded grains called chondrules.

Chondrites are by far the most abundant group of meteorites accounting for more than 85% of all observed falls. As a result of several investigations during the past ten years (notably Urey and Craig, 1953; Wiik, 1956; Ringwood, 1961; Mason, 1962b and 1963; and Keil and Fredriksson, 1964) and a gradual improvement in analytical techniques, it now appears that chondrites fall into 7 distinct groups. These are shown best when plotted on a diagram of weight per cent Fe in FeO versus weight per cent Fe in metallic iron and troilite, as shown in Figure 1.1a. Samples in this plot have been restricted to include only observed "falls" and only those chondrites for which high quality analyses exist. Chondrites in Groups I and II have also been recalculated on a volatile free basis. Unfortunately, Groups I and II are not resolved when diagrammed in this manner.

Almost all chondrites fall into Groups V and VI. It is interesting to note also that there are distinct chemical and mineralogical gaps between each of these groups. Yet despite the fact that each group is distinct, a most remarkable fact about chondrites is their extremely

Figure 1.1a

Relationship of Fe in FeO to Fe in FeS plus metallic Fe in Chondrites



Modified from a diagram in Mason (1962a, 78) uniform composition. The main distinction between each of these groups of chondrites is the per cent of iron in the oxidized state (FeO) and a small difference in total iron content. Groups I, II, III, VI, AND VII all have approximately the same total iron content, $\sim$ 28%, and Groups IV and V contain about 22% iron.

In the early 1900's, as a result of many poor chemical analyses and the inclusion of weathered finds amongst the data, these 7 groups could not be distinguished. Nevertheless, when all analyses were plotted as in Figure 1.1a, it was apparent that chondrites all had about the same total iron content, and that there was a definite trend from chondrites whose Fe was all in the form of metal and troilite to those whose iron was all FeO. As a result, Prior (1920) formulated the rule that the less the amount of metal phase, the richer the silicate is in FeO and the richer the metal is in Ni. There is also a corresponding increase in olivine content and decrease in pyroxene content with increasing FeO. It is now obvious, however, that this is not the whole story.

Groups I and II are not distinct in this diagram but are actually quite different in chemical and mineralogical composition; they make up the class of carbonaceous chondrites analyzed most throughly by Wiik (1956). Carbonaceous chondrites are a small group of chondrites which are very friable, disintegrate in H_2O and contain up to 5 per cent C. Furthermore, they are all observed "falls". Wiik (1956) divided carbonaceous chondrites into three groups which he called Types I, II and III. Type I carbonaceous chondrites have low densities (~ 2.2), considerable H_2O and are strongly magnetic. To make matters even more confusing, they contain no chondrules. Type II carbonaceous chondrites have densities in the range of 2.7 and are only weakly magnetic. Type III carbonaceous chondrites coincide with Group III of Figure 1.1a. Mason (1962a) has called this group the olivine-pigeonite chondrites, and Keil and Fredriksson (1964) have called them the HL, or high total iron - low metal, group. They have densities of ~ 3.5 and consist mainly of olivine and a small amount of pigeonite. Some of them contain up to 1/2 per cent of C, whereas others contain no carbon.

Group IV of Figure 1.1a has been referred to as the amphoterites or Soko-Banja group chondrites. Mason (1962a) lumped them together with those of Group V as the olivine-hypersthene chondrites. Keil and Fredriksson

(1964), however, have shown that they are, in fact, a distinct group and should be named separately. They prefer to call them the LL, or low total iron - low metal, group. Group IV chondrites contain olivine of 26-29 mole per cent Fe_2SiO_4.

Group V is the L-group of Urey and Craig (1953). Mason (1962a) has called them the olivine-hypersthene group of chondrites. Keil and Fredriksson (1964), however, point out that, according to the definitions of Poldervaart and Hess (1951), bronzite is strictly pyroxene of 10-30 mole per cent $FeSiO_3$ and hypersthene is pyroxene of 30-50 mole per cent $FeSiO_3$. Thus, none of the chondrites in any of the 7 groups of Figure 1.1a contain pyroxene of hypersthene composition. Keil and Fredriksson (1964), therefore, prefer to use the names HL, LL, L and H for Groups III, IV, V, and VI, respectively. In any event, the chondrites in Group V contain olivine of 21.6 - 24.4 mole per cent Fe_2SiO_4.

Group VI chondrites are the olivine-bronzite chondrites of Mason (1962a) and the H-group chondrites of Urey and Craig (1953). They contain olivine of 16.1 - 19.4 mole per cent Fe_2SiO_4. Group VII represents the enstatite chondrites, a relatively small group of chondrites comprising only eleven specimens. They contain almost no FeO and no olivine and consist essentially of enstatite and metallic Fe-Ni. Some of them contain up to 1/2 per cent of carbon.

The achondrites account for a very small per cent (~7%) of the total number of stones. They are usually subdivided into two further subgroups - the Ca-rich, or basaltic-type, achondrites and the Ca-poor, or chondritic type, achondrites. Mason (1962a, 105-106) classifies the achondrites as follows:

1. Calcium-poor achondrites
    - A. Enstatite achondrites or aubrites
    - B. Hypersthene achondrites or diogenites
    - C. Olivine achondrites or chassignites
    - D. Olivine-pigeonite achondrites or ureilites

2. Calcium-rich achondrites
    - A. Pyroxene-plagioclase achondrites (includes both eucrites and howardites)
    - B. Augite achondrites or angrites
    - C. Diopside-olivine achondrites or nakhlites.

The classification of achondrites is complicated by the fact that they are a much more diversified group of meteorites than the chondrites and several of them are unique specimens in themselves. Thus, the chassignites and angrites are represented by only one sample each, the nakhlites by two and the ureilites by three. Since achondrites are so much rarer than chondrites, they are much less available for scientific investigation and, therefore, have not been as throughly studied as the chondrites. As a group, however, they are much more coarsely crystalline than chondrites and almost devoid of metallic Fe-Ni. It is interesting to note that of the 64 recognized achondrites almost all of them are observed "falls".

The stony-iron meteorites comprise a relatively small group of specimens in comparison to the irons and the stones. They are subdivided into four classes: pallasites, mesosiderites, lodranites and siderophyres. The pallasites consist essentially of olivine and nickel-iron with the metal phase forming a more or less continuous network surrounding the olivine crystals. Of the 40 known pallasites only two have been observed to fall. Mesosiderites consist of approximately equal amount of metal and silicate, the silicate consisting mainly of plagioclase and pyroxene with minor amounts of olivine and other accessory minerals. In contrast to the pallasites, however, the iron-nickel in mesosiderites usually occurs in separate irregular grains. Mason (1962a) lists only 20 known mesosiderites of which 7 are "falls". The other two classes of stony-iron meteorites are represented by only one specimen each. The Steinbach siderophyre consists of orthopyroxene, tridymite and metallic Fe-Ni. The lodranite is made up of orthopyroxene, olivine and iron-nickel.

The iron meteorites are subdivided into three classes based on structure and Ni content. The hexahedrites contain from 4-6% Ni and exhibit characteristic "Neumann lines" upon etching a polished surface with acid. Octahedrites contain between 6 and 14% Ni and on etching show a characteristic Widmanstatten structure which is formed by exsolution intergrowths of α-iron (kamacite) and γ-iron (taenite). The octahedrites are further subdivided according to the width of the kamacite bands into coarse octahedrites, medium octahedrites and fine octahedrites. With increasing Ni content the kamacite bands become thinner and the Widmanstatten structure eventually disappears. Meteorites with greater than 12% Ni and no Widmanstatten structure are classified as Ni-rich ataxites. There is also another group of irons called Ni-poor ataxites which may show traces of Neumann lines. These have been grouped by Mason (1962a) with the hexahedrites since they are chemically similar. It is interesting to note that the octahedrites account for 81% of the iron meteorites. Furthermore, of the 36 recognized Ni-rich ataxites in the world, not one is an observed "fall".

Any theory pertaining to the origin of meteorites must, of course, give primary consideration to the chondrites since they are by far the most abundant class of meteorites. Their uniformity of composition must be weighted heavily and also the fact that they fall into different groups each separated from the other by chemical and mineralogical gaps. Furthermore, does any one of the chondrite groups represent the starting or parent material from which the others were formed? Numerous theories have been proposed for the origin of chondrites, but as can be readily seen this could not have been a simple process. Prior (1920) thought that the enstatite chondrites represented the starting material from which all other chondrites were formed by progressive oxidation. Urey and Craig (1953) thought that the high-iron and low-iron groups were formed by the break-up of 2 asteroid bodies of differing chemical composition. Mason (1960), Ringwood (1961) and Fish, Goles and Anders (1960) favored carbonaceous chondrites as the starting material. Carbonaceous chondrites have low densities, a high volatile element content and contain a number of phases which are in thermodynamic disequilibrium. Thus, carbonaceous chondrites, which could never have experienced high temperatures, might represent the parent material with the other chondrite groups being formed through the application of heat and pressure.

The formation of the iron meteorites can best be discussed by reference to the Fe-Ni phase diagram shown in Figure 1.1b. Lovering (1957) has determined that the average overall composition of the iron meteorites is approximately 11% Ni. If one starts with a melt of this composition and cools it slowly, taenite with approximately 5½% Ni will be the first solid phase to crystallize out. Assuming non-equilibrium and crystal fractionation, it is conceivable that solid phase varying in composition all the way up to the minimum of 68% Ni can occur. It is interesting that iron meteorites are known with compositions as low as 4% Ni and as high as 62% Ni.

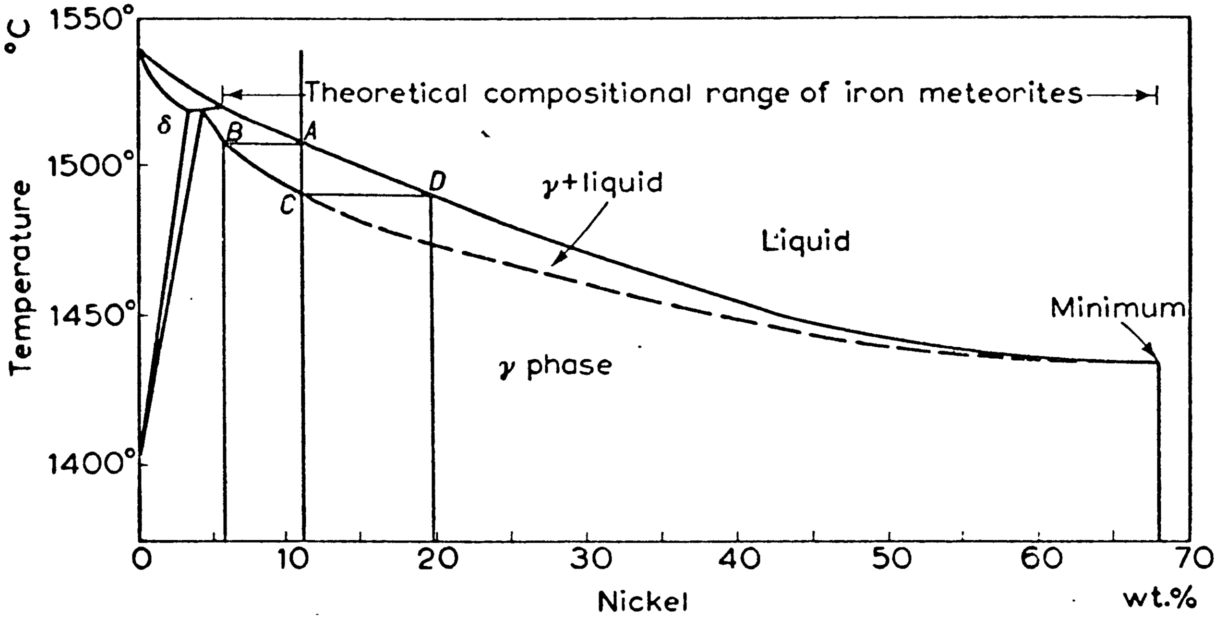


Figure 1.1b

PARTIAL PHASE DIAGRAM FOR Fe-Ni SYSTEM

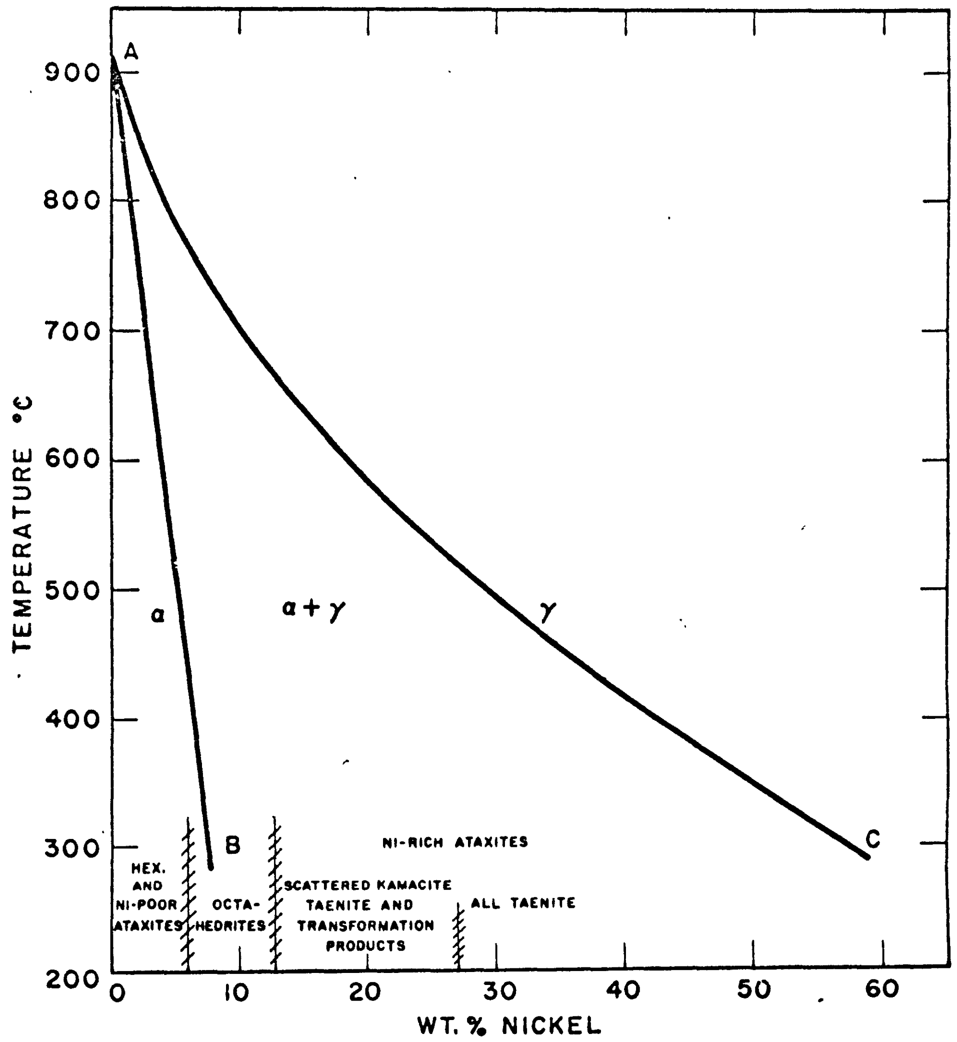
reproduced from Lovering (1957, 240)

The subsolidus relationships in the Fe-Ni system are shown in Figure 1.1c. As the solid cools further, kamacite begins to exsolve when the two phase boundary is intersected. With continued cooling the γ-phase becomes more Ni-rich and more α-phase continues to separate out. Only if the total composition is less than ~ 9% Ni will all the gamma phase be expected to convert to α-phase. The relationships between this phase diagram and the three classes of iron meteorites are obvious. There are a number of puzzling features, however. How can octahedrites occur with as little as 6% Ni, and why should not one expect to find Widmanstatten figures in meteorites with as high as 50 or 60% Ni? Uhlig (1954) suggests that pressure may be the answer, since application of the Clausius-Clapeyron equation predicts that the 2 phase region would be diminished and the phase boundaries lowered and moved to the left at higher pressures.

The many and varied theories which have been proposed to explain how and where all these different types of meteorites originated are far too lengthy and complicated to discuss in this short treatise. It seems that the more study one gives to the problem, the

Figure 1.1c

SUBSOLIDUS RELATIONSHIPS IN Fe-Ni PHASE DIAGRAM



reproduced from Uhlig (1954, 285)

more complicated it becomes. An excellent review of the subject is given in Anders (1964).

Many scientists today feel that the solar system coagulated from an originally cool cloud of gas and dust. As this cloud gradually contracted at the expense of gravitational potential energy, the sun, the planets and the meteoritic parent bodies (assuming meteorites come from the solar system) began to take form. It is possible that this original material was somewhat similar to carbonaceous chondrites in texture and composition. Wood (1963) has postulated that chondrules may be the original liquid condensations from the primordial solar nebula. Although there are many arguments and uncertainties about this early phase of formation, there are also conflicting views as to the size and characteristics of the meteorite parent bodies.

Briefly, three types of parent bodies have been proposed for meteorites (Anders and Goles, 1961). First, there are a number of investigators (for example, Ringwood, 1959 and 1961; Lovering, 1957 and 1958) who believe that meteorites began in large bodies of from lunar to planetary dimensions. This theory provides a source of heat for meteorite synthesis and a source of pressure for diamond formation and in certain ways helps to explain features observed in iron meteorites. However, it runs into difficulties when one tries to break up or construct a suitable cooling history for such a large body. Furthermore, if meteorites come from the asteroidal belt, Kuiper (1951) has estimated that the entire asteroidal belt at present only contains 0.03 lunar masses.

Urey (1956) has suggested that meteorites were formed in lunar sized parent bodies which were later broken up and regrouped into asteroidal sized objects. This theory has the advantage of being able to account for the production of most of the different kinds of meteorites that we observe; yet, Anders and Goles (1961) feel that many of the events in this theory have a low probability of occurrence. Again, it runs into the problem of mass loss from the asteroidal belt and the difficulty of breaking up a lunar sized object. The formation of the Cumberland Falls meteorite is also hard to explain by this theory (Anders and Goles, 1961, 61).

Anders and Goles (1961) have suggested that the meteorite parent bodies were of asteroidal size to start with. This theory has many attractive features especially since Goles and Anders (1961) have shown that extinct radioactive nuclides could have provided a suitable heat source for meteorite synthesis and diamonds could have been formed upon impact with the earth. The discontinuous groupings of Ga, Ge, and FeO contents are also nicely accounted for by this hypothesis. However, there has recently been some question (Carter and Kennedy, 1964) as to whether meteoritic diamonds could have been produced by shock transformations. The textures observed in iron meteorites are also harder to account for if formed in asteroidal sized parent bodies.

If we are to improve our theories about the origin of meteorites and the solar system (and the universe, for that matter) and eventually discover where these unusual objects come from and how they were formed, we must first obtain as much experimental and analytical data about them as possible. One important piece of information which interests us is the time scale over which these bodies existed. When were they formed? How long did they take to form? How long have they been traveling through space in their present state? Fortunately, among the many varied techniques available these days, the scientist can employ the use of radioactive nuclides to date different types of events. Meteorites and terrestrial materials contain a variety of isotopes which are unstable (or radioactive) and tend to decay to some other more stable nuclide. The half-lives (or length of time required for $\frac{1}{2}$ of the atoms present to decay) of these radionuclides can range anywhere from unmeasureable fractions of a second to many, many billions of years. In dating an object one must choose a nuclide with a half-life which is usually within one or two orders of magnitude of the time interval he is trying to measure. For the purpose of measuring the "solidification" age of meteorites, or the length of time over which meteorites have been solid objects, Rb^{87} is one of the most favorable radionuclides available.

1.2 - Fundamental Principles of the Rb^{87}-Sr^{87} Age Measurement Technique

The fundamental aspects of the Rb^{87}-Sr^{87} dating technique have been described in Annual Progress Reports of the M.I.T. Geochronology Laboratory and elsewhere in the literature (Faure, 1961; Brookins, 1963; Bottino, 1963). Briefly, 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^{87} is radioactive and decays to Sr^{87} with a half-life of approximately 5×10^{10} years. In closed systems containing Rb, therefore, the amount of Sr^{87} is continually increasing with time. It is convenient, for experimental reasons, to measure the abundance of Sr^{87} as the ratio of Sr^{87}/Sr^{86}. This ratio obviously increases with time in a closed system containing Rb since Sr^{86} is a stable isotope and is not known to be produced by the decay of any other naturally occurring nuclide.

The above quantities can be related by the familiar age equation which has been derived previously by Faure (1961, 73-78):

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p - \left(\frac{Sr^{87}}{Sr^{86}}\right)_o = \left(\frac{Rb^{87}}{Sr^{86}}\right)_p \left(e^{\lambda t} - 1\right) \qquad 1.2a$$

or:

$$t = \frac{1}{\lambda} \ln \left[1 + \frac{\left(\frac{Sr^{87}}{Sr^{86}}\right)_p - \left(\frac{Sr^{87}}{Sr^{86}}\right)_o}{\left(\frac{Rb^{87}}{Sr^{86}}\right)_p} \right] \qquad 1.2b$$

where t = age of system in years

λ = the decay constant, or the probability that an atom will decay in a given interval of time.

$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p$ = atomic ratio of Sr^{87} to Sr^{86} at present time.

$\left(\frac{Sr^{87}}{Sr^{86}}\right)_o$ = atomic ratio of Sr^{87} to Sr^{86} initially (at time t=0).

$\left(\frac{Rb^{87}}{Sr^{86}}\right)_p$ = atomic ratio of Rb^{87} to Sr^{86} at present time.

An age, t, can be calculated for a system from the above equation providing λ, $(Sr^{87}/Sr^{86})_p$, $(Sr^{87}/Sr^{86})_o$, and $(Rb^{87}/Sr^{86})_p$ can be determined. The value of the decay constant, λ , can be measured in an independent experiment which does not necessarily rely upon the Rb^{87}-Sr^{87} age equation. Flynn and Glendenin (1959) and Aldrich _et al._, (1956), for example, have made determinations of the decay constant for Rb^{87}, but this is a difficult experiment and at present the value is not accurately known. Both the $(Rb^{87}/Sr^{86})_p$ and $(Sr^{87}/Sr^{86})_p$ ratios can be measured in the laboratory (see Chapter 2). The $(Sr^{87}/Sr^{86})_o$, however, cannot be obtained from a single sample. This means that both t and $(Sr^{87}/Sr^{86})_o$ are not directly measureable, and thus one is dealing with a single equation in 2 unknowns.

To circumvent this difficulty a minimum of 2 subsystems (such as different mineral phases from the same rock sample, different whole rock samples from the same igneous body, or different metorite samples) which must be assumed to have the same age are usually analyzed. One can then solve for an age since there are now at least 2 equations in 2 unknowns.

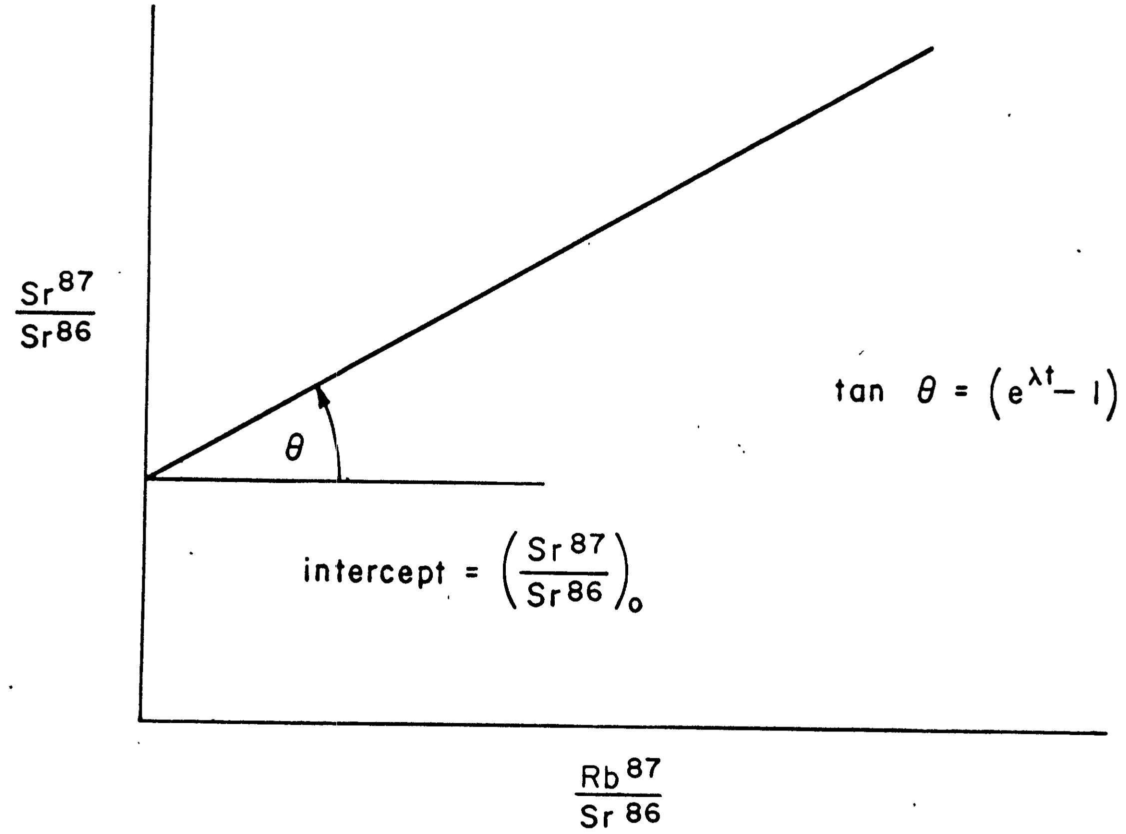
A standard approach for solving the Rb-Sr age equation is to construct an "isochron" diagram. Equation 1.2a can be rearranged as follows:

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_p = (e^{\lambda t}-1)\left(\frac{Rb^{87}}{Sr^{86}}\right)_p + \left(\frac{Sr^{87}}{Sr^{86}}\right)_o \qquad 1.2c$$

which is the equation of a straight line in the form $y = mx+b$. The quantity $(e^{\lambda t}-1)$ is, therefore, obtained from the slope of the line, tan θ, and the intercept of this line on the Sr^{87}/Sr^{86} axis gives the initial $(Sr^{87}/Sr^{86})_o$ ratio. These relationships are shown graphically in Figure 1.2a where $(Sr^{87}/Sr^{86})_p$ and $(Rb^{87}/Sr^{86})_p$ are plotted on the ordinate and abcissa, respectively.

When a series of subsystems (meteorites, for example) are plotted on a diagram as shown in Figure 1.2a, they should form a straight line - providing they all have the same age and a number of other initial assumptions (which will be discussed below) have been satisfied. Such a line is called an "isochron" meaning that all the samples on the line have the same age. It can be seen that a minimum of 2 points is required to determine a straight line (in this case, an isochron). A series of samples or points, however, not only gives

Figure 1.2a
Schematic Diagram of Isochron Plot



one a better fix on the line, but also allows the analyst a better estimate of the scatter in his data.

In the case of early Rb-Sr meteorite age investigations (see Section 1.3) essentially only 2 meteorite samples were employed to obtain an age. Furthermore, the samples which were used were not members of the same meteorite class - an achondrite was compared with a chondrite. Thus, a number of initial assumptions must be made if the ages are to be meaningful.

First, it must be assumed that the different Rb/Sr ratios of the various meteorites, or subsystems, originated during a single event - a chemical differentiation process in which chondrites and achondrites, for example, formed from some common parent material (possibly some homogeneous region of the early solar system). It follows, therefore, that they must be assumed to have the same age - an age which represents the end of the chemical differentiation process. (Anders, 1963, calls this a "solidification age" to distinguish it from other types of ages as will be mentioned later.) It is possible, however, that one of these types of meteorites is, in fact, a sample of the original, undifferentiated parent material. If so, the Rb-Sr age has no meaning for this undifferentiated material as Anders (1963, 426-427) points out, since it was obviously formed before the differentiation process occurred. The Rb-Sr age dates only the time at which the differentiation products were formed; it does not tell us anything about undifferentiated material. In a suite of n meteorite samples, therefore, a maximum of ($n-1$) can be safely considered as datable without further information.

Second, it must be assumed that the isotopic abundances of both Rb and Sr were initially homogeneous in the parent material at the time of differentiation.

Third, it must be assumed that isotopic fractionation of Rb and Sr isotopes has not occurred (or is insignificant) at least subsequent to this differentiation process.

Fourth, it is assumed that all meteorites have remained closed systems to the migration of Rb and Sr since this last chemical differentiation process ended.

Finally, it is assumed that any increase in Sr^{87} since this time has resulted solely from the decay of Rb^{87}.

Isochrons constructed from only 2 meteorite samples must lean heavily upon these assumptions and do not lend any evidence to either prove or disprove them. When one analyses a whole series of meteorites (as has been done in more recent Rb-Sr meteorite age studies), however, one is in a much stronger position to make statements about their history. In fact, considering the number of assumptions that must be satisfied and the complicated analytical procedure through which all samples must be processed, it seems remarkable, indeed, that a suite of meteorites should all fall onto a single straight line (as happens later on in this thesis). Therefore, this has usually been taken as strikingly good evidence that all of the initial assumptions have been satisfied. The probability of a whole series of meteorites falling on one straight line would be exceedingly small if one of the above assumptions had not been met or if the precision of the measurements were not extremely high.

A few remarks about isochron diagrams should be made at this point. Note that at time zero, when the chemical differentiation process is just ending, the various subsystems (meteorites, for example) are spread out along a horizontal straight line (see Figure 1.2b). The Sr^{87}/Sr^{86} ratio is identical in all samples (since isotopic fractionation is assumed insignificant), but each subsystem crystallizes with a different Rb/Sr ratio. In this case X might represent the total system. Such a situation (as shown in Figure 1.2b) might be analogous to the primary undifferentiated parent material (X) and a suite of individual meteorite samples (dots).

As time passes, all points move along straight line paths with slopes of -1 (Wasserburg, 1963); samples with high Rb^{87}/Sr^{86} ratios naturally "travel" at correspondingly faster rates. At some later time the age of the differentiation process can be measured from tan θ. It is seen, however, that this age does not tell anything about the history of X (the undifferentiated parent material or the total system)-the age dates only the differentiation process.

At some time after differentiation it is possible that a heating or melting event may have occurred in which Rb and Sr are remobilized but the total system is unaffected and still remains closed to Rb and Sr migration. Such a situation might be depicted in

Figure 1.2b
Schematic Diagram of a Chemical Differentiation

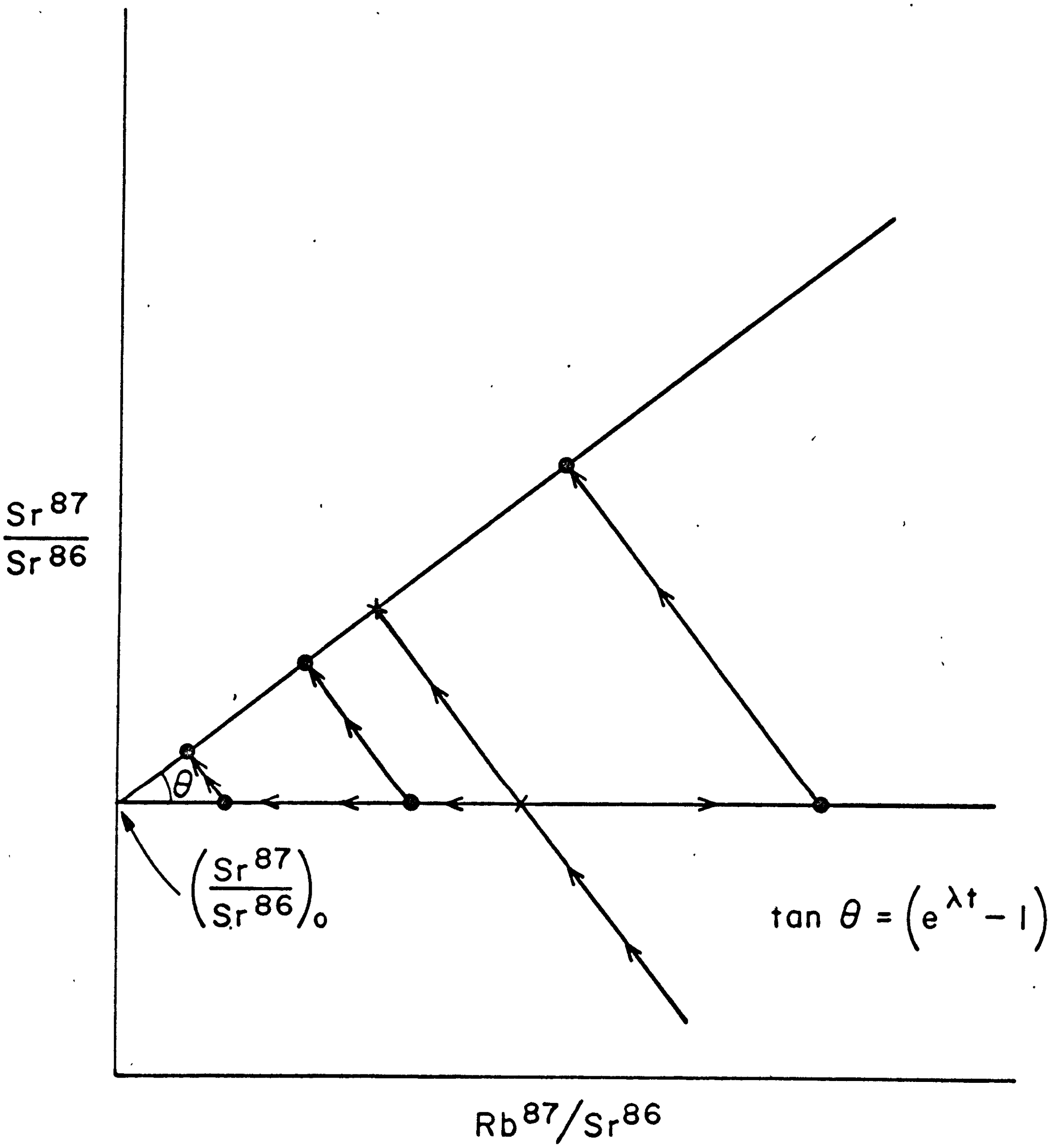
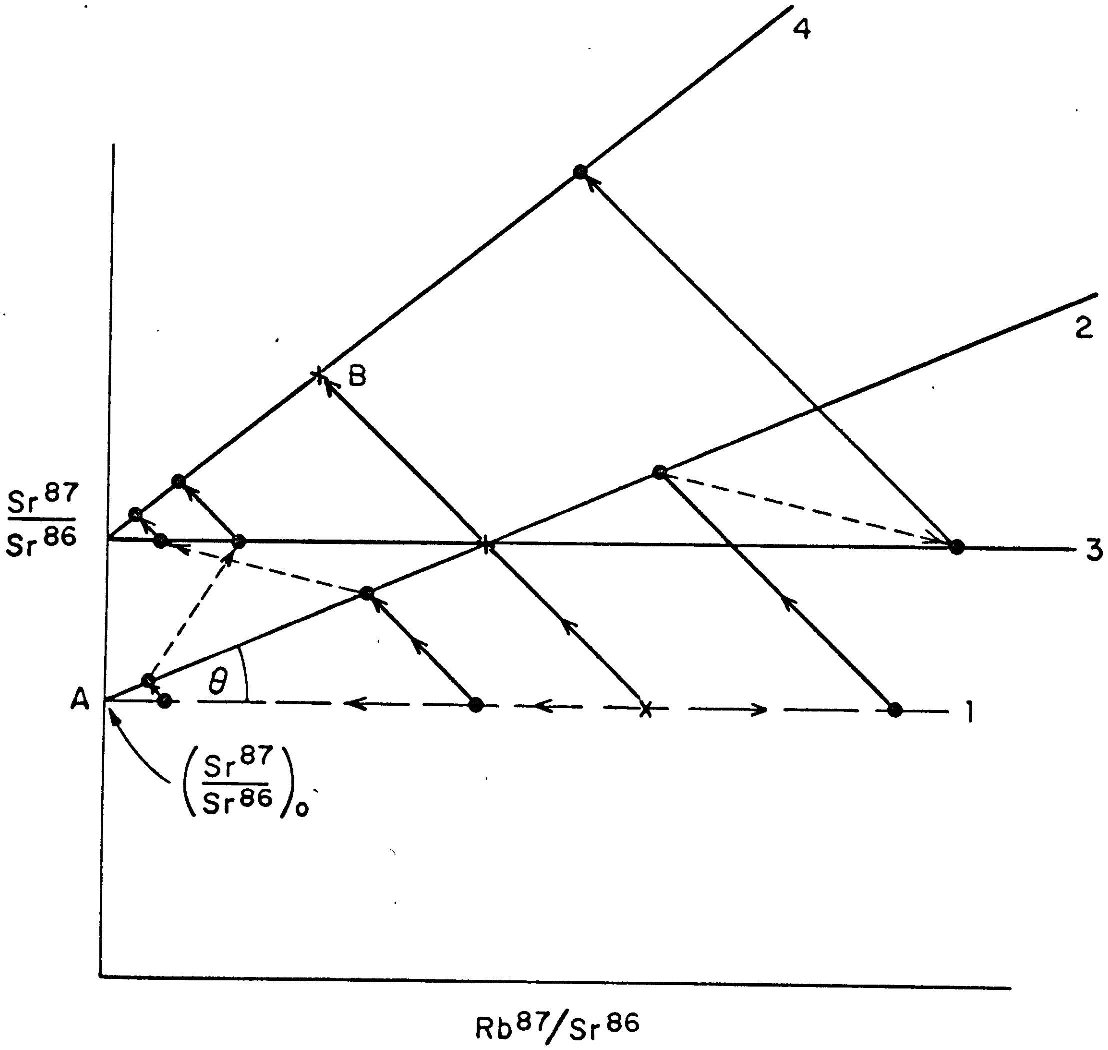


Figure 1.2c. In such a case the different subsystems are redistributed in some manner (dashed arrows) along a second horizontal line (line 3). All these subsystems now start "clocking time" again with a new and higher initial Sr^{87}/Sr^{86} ratio. Note, however, that the redistribution of Rb and Sr does not affect the position of the total system on the diagram. This type of situation could be represented by an individual meteorite and its different mineral phases, for example. If a sufficiently good spread in Rb/Sr ratios could be obtained from the separated minerals, it is possible that a metamorphic event might be identified subsequent to the time of chemical differentiation. Observe that the meteorite indicated by X could also represent primary undifferentiated parent material in which case it could have started from somewhere below line 1. In either situation, however, it is not possible in Figure 1.2c to "look through" the later heating event. An age for the original chemical differentiation can not be measured, therefore.

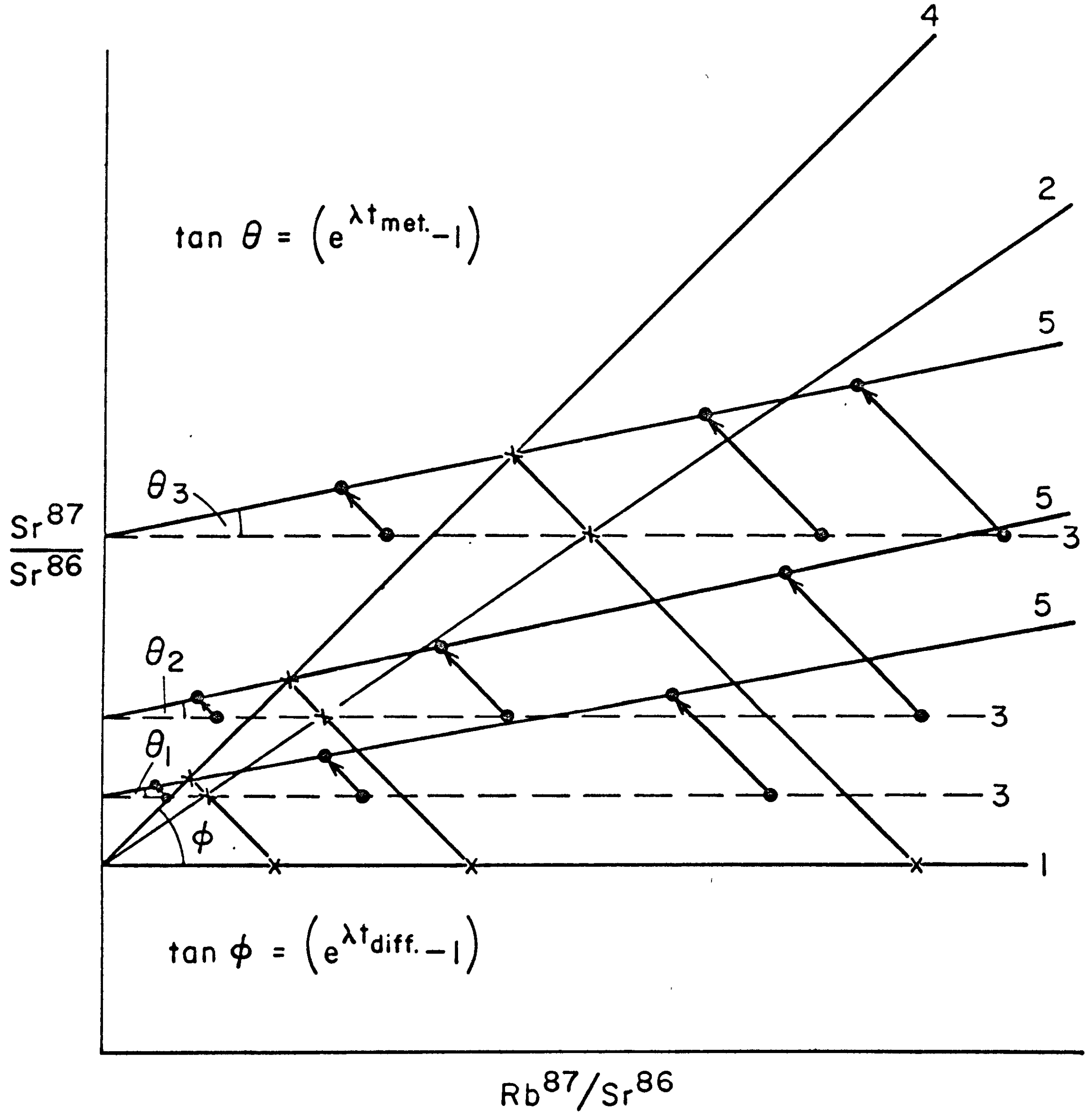
More complicated situations than this have been met with in the case of terrestrial rocks, however, where a subsequent heating event allows migration of

Figure 1.2c
Schematic Diagram of a Heating or Metamorphic Event



Rb and Sr to occur over small distances (Wasserburg, 1963). If, for example, the mineral grain size in an igneous rock were a millimeter or so and Rb and Sr were allowed to migrate only over a distance of about 1 cm, then a series of whole rock samples 30 cms on a side would not show the effect of a heating event when plotted on an isochron diagram. The mineral phases, however, might have undergone complete equilibration with respect to Rb and Sr. Thus, in Figure 1.2d, the mineral phases (dots) from a given whole rock sample (X) would spread out along a horizontal line passing through the undisturbed whole rock position. A series of parallel, horizontal straight lines would then be generated (lines 3), each passing through its respective whole rock position (X's which also correspond with line 2) and having a unique initial ratio. At some later time, therefore, the time of metamorphism can be obtained from the slope, tan θ, of any mineral isochron. The time of initial chemical differentiation can also be measured from an isochron through the whole rock samples. This is indicated in Figure 1.2d by line 4 which passes through all the whole rock samples,

Figure 1.2d
Schematic Diagram Relating a Metamorphic Event to the Time of Original Differentiation



marked X, and has a slope equal to tan ϕ. It can be seen that Figure 1.2c is in many ways similar to Figure 1.2d but only tells half the story. A line through points A and B in Figure 1.2c would, in fact, correspond to line 4 in Figure 1.2d.

In meteorite research situations such as depicted in Figure 1.2d have not yet been observed. We could, however, let the points marked X represent different individual meteorite samples. Then line 4 might give the age of differentiation of the meteorites (corresponding perhaps to the 4.45 billion year age obtained in this thesis). A subsequent heating event might also be observable and be measured with a mineral phase isochron (lines 5). In this case the dots could represent different mineral phases from the individual meteorites and would be expected to form a series of lines with smaller slopes than the whole meteorite isochron. However, if meteorites formed in a series of different parent bodies which were broken up at different times (as may be indicated by the gas retention ages) and these break-up episodes involved heating, it is possible that different meteorite samples would show different mineral phase ages, and thus in Figure 1.2d $\Theta_1 \neq \Theta_2 \neq \Theta_3$. It is, of course, again possible that one of the X's represents primary material unaffected by this chemical differentiation, and thus the age has no meaning for this sample.

Another more theoretical interpretation is also possible for Figure 1.2d. All meteorites which have been dated so far could be representatives of a single meteorite suite formed from a common parent material - perhaps in a certain region of the solar system such as the asteroid belt. It is also not inconceivable, although we do not as yet have any experimental evidence for such a situation, that there are other suites of meteorites formed from parent materials with different overall Rb/Sr ratios - perhaps in other regions of the solar system. Therefore, there might be an age (or ages) older than the 4.5 billion year whole meteorite isochron age which would indicate a time of initial homogenization for the entire solar system. The 4.5 billion year date might then refer merely to a later differentiation within some restricted region of the solar system, such as the asteroid belt.

In this case the X's in Figure 1.2d would represent the different parent materials or different regions of the solar system, and the dots would represent the individual meteorite samples. Thus, the 4.5 billion year whole meteorite isochron would be represented by one of the lines with a slope of tan θ. Although at present no Rb-Sr or U-Pb age data has been obtained to support this model, a fresh meteorite sample or series of samples which lay significantly off the present isochron in either direction would be suggestive that such a situation exists. The feasibility of dating this event, however, would rely upon the ability to recognize samples of the primary parent materials.

Finally, it should be pointed out that there are many other decay schemes which can be used for meteorite dating, depending upon the type of event to be dated. Anders (1963, 402) summarizes the 5 major kinds of events which can be dated with radionuclides as follows: a) nucleosynthesis, b) melting of meteorite parent bodies, c) cooling of meteorite parent bodies, d) break-up of meteorite parent bodies, and e) time of fall upon earth. Rb^{87}-Sr^{87}, as we have seen, is used for dating event b). Nucleosynthesis is dated with extinct radionuclides, and events d) and e) are dated with cosmic ray induced activities. We are not concerned with any of these last three types of events in this thesis.

Events b) and c) are quite similar in many respects and differ essentially in the characteristics of the daughter product nuclides. The cooling of meteorite parent bodies, event c), is dated with decay schemes such as $U^{238} \longrightarrow 8He^{4}$, $U^{235} \longrightarrow 7He^{4}$, and $K^{40} \longrightarrow Ar^{40}$ in which the daughter products are all noble gases. Noble gases have very high diffusion rates and escape from the parent material very easily at elevated temperatures. Thus, the meteorite parent bodies must have cooled to at least 300°K (Anders, 1963, 450) before the daughter products are retained and the decay schemes start keeping time.

In the case of the melting or differentiation of meteorite parent bodies, event b), besides Rb^{87}-Sr^{87}, there are also a number of other decay schemes which are commonly employed, such as $Re^{187} \longrightarrow Os^{187}$, $U^{238} \longrightarrow Pb^{206}$, and $U^{235} \longrightarrow Pb^{207}$. In contrast to He^{4} and Ar^{40}, these daughter products are retained at much higher temperatures. Thus, these decay schemes start keeping time much sooner - while the parent bodies are still at much higher temperatures.

It is important to remember that even within the group of decay schemes which date the same general event, however, each decay scheme dates a different process. The Rb-Sr method measures the time of separation of Rb from Sr. The U-Pb decay schemes date a U-Pb fractionation. Likewise, Re-Os dates still another type of separation. It may be that in all three of these cases fractionations occurred during the same event at exactly the same time. Yet, it is not inconceivable that this was not the case. It could be, for instance, that the U-Pb decay schemes date the separation of the iron meteorites from the silicate meteorites, whereas the Rb-Sr technique may date a slightly later fractionation in the various silicate meteorites. One should be somewhat cautious, therefore, in blindly comparing the two types of ages. It would not be surprising if someday it turned out that U-Pb ages were, in fact, slightly different from the Rb-Sr ages.

1.3 - Previous Rb-Sr Age Investigations of Meteorites

Rb-Sr age work on stony meteorites was begun in 1956 with the publications of Herzog and Pinson (1956) and Schumacher (1956a,b,c, and d). Herzog and Pinson (1956) analyzed the Homestead and Forest City chondrites and the Pasamonte achondrite. Unfortunately, however, they were plagued with poor analytical precision, poor mass spectrometry techniques, high blanks and insufficient data. Duplicate isotope dilution analyses for Rb and Sr on the Homestead chondrite show poor agreement, and in the case of Forest City only one isotope dilution analysis was performed. It is unfortunate that Homestead and Forest City turned out to have very similar Rb/Sr ratios. The Sr^{87}/Sr^{86} ratio of Homestead was obtained from only one mass spectrometer analysis, and that of Forest City was calculated from a poor Sr isotope dilution analysis. The Pasamonte achondrite analysis consisted of only one poor quality measurement of the Sr isotopic composition which set an upper limit on its Sr^{87}/Sr^{86} ratio. As a result of poor precision and few samples, Herzog and Pinson (1956) were only able to estimate upper and lower limits for the age of meteorites. Nevertheless, their analyses layed the groundwork for future investigations by showing that ages could be obtained for stony meteorites by the Rb-Sr method.

Also in 1956 Schumacher (1956a,b,c,d) published some Rb-Sr data on stony meteorites. He analyzed the Forest City chondrite, the Pasamonte achondrite and the Bustee achondrite. Unfortunately, his work suffered from many of the same difficulties as that of Herzog and Pinson. The reproducibility of replicate analyses does not compare with recent work, although his blanks would have been considered good up to a year or so ago. A big discrepancy which exists between his work and all other investigations is that the Sr^{87}/Sr^{86} ratios (corrected for mass spectrometer discrimination to $Sr^{86}/Sr^{88} = .1194$) obtained on Pasamonte and Bustee are far below any others that have ever been determined since. As the Sr^{86}, Sr^{87}, and Sr^{88} peaks were all measured on the same scale, a large reading error could have been introduced. As with previous work, this one encompassed only three meteorites. Since both Bustee and Pasamonte are achondrites and plot on almost exactly the same point, the isochron was drawn through essentially two points. Schumacher obtained an age of 4.7 billion years (b.y.) for the stony meteorites. Considering the error in his Sr^{87}/Sr^{86} ratio for Pasamonte, it seems that the agreement of this age with subsequent work may be coincidental.

In 1957 Webster, Morgan and Smales published some Rb-Sr data on meteorites. Their study encompassed two samples: the Forest City chondrite and the Johnstown achondrite. From these two meteorites they calculated an age of 4.6 b.y. This age agrees well with subsequent Rb-Sr age publications. Their quadruplicate isotope dilution analyses on Forest City show a spread of about 7.5%. The percent of Sr^{87} in both meteorites was calculated from the Sr isotope dilution analyses. This approach is frequently more subject to error than measuring the Sr^{87} abundance directly, especially if the analyses are not corrected for mass spectrometer discrimination.

All three of these investigations discussed so far also suffer from an additional important difficulty which makes them of limited value when compared with more recent studies. Each of them determines an age from essentially only 2 points so that no evidence is supplied to either prove or disprove any of the initial assumptions discussed in Section 1.2.

The publications of Gast (1960, 1961, 1962) were the first studies which encompassed a sizeable number of meteorite samples and thus for the first time opened up the possibility of testing some of these initial assumptions. Gast analyzed 4 achondrites (Pasamonte, Sioux County, Moore County, and Nuevo Laredo) and 5 chondrites (Holbrook, Richardton, Beardsley, Modoc, and Forest City). Due perhaps to an unfortunate selection of samples, however, his achondrites all fall into one tight group and his chondrites (except for Beardsley) into another. The Beardsley meteorite is an unusual chondrite from the point of view of Rb-Sr analyses and forms a separate third point on Gast's isochron. Beardsley is unusual not only because it has a unique Rb/Sr ratio, but also because different pieces of it have different Rb and Sr concentrations. Gast (1962) has made some experiments which indicate that some of this latter variation may, in fact, be due to terrestrial leaching of Rb and Sr, since part of Beardsley was not recovered until 2 years after infall. In any event, the "fresh" Beardsley II sample does appear to line up in general with the chondrite group and the achondrite group. A least squares isochron through all these points gives an age of 4.67 b.y. with $\lambda = 1.39\times10^{-11}$ years^{-1} (Gast's Model

I age).

One can take the initial ratio obtained from this isochron and calculate individual ages from the separate chondrites. These ages range from about 4.5 to 4.9 b.y. with $\lambda = 1.39\text{x}10^{-11}$ years^{-1} (Gast's Model II ages). If one assumes that chondrites are representative of parent material from which achondrites were differentiated, then the average of these ages (4.7 b.y.) gives the time of derivation of the achondrites. Unfortunately, Gast's reproducibility was not of good enough quality to tell whether these individual age differences are real or just experimental error. Gast states that disagreements between his replicate analyses are due to either sample inhomogeneities or a small amount of Rb and/or Sr absorbed on, or precipitated with, the insoluble residue. The results of this present investigation, however, indicate that the main source of disagreement between replicate analyses may be an interaction of pyrex glassware with the ions in solution as pointed out by Wasserburg et al., (1964).

If one includes the Beardsley chondrite, an isochron can be drawn from the 4 chondrite analyses alone (Gast's Model III age) yielding an age of 4.46 b.y. for $\lambda = 1.39 \times 10^{-11}$ years^{-1}. Assuming that Beardsley was originally a normal chondrite like the others, this age indicates the time when it became enriched in Rb. Thus, it appears that Beardsley is younger than the other chondrites. Beardsley is such an anomalous chondrite, however, that more experimental data should be obtained before weighing it too heavily in theories concerning the origin of meteorites.

The work of Gast (1960, 1961 and 1962) represents a considerable improvement over previous Rb-Sr analyses of meteorites. However, his blanks are higher than those which have been obtained more recently and his reproducibility is not of good quality (compare especially with results in Chapter VI of this work). Poor analytical precision makes it difficult to investigate real age differences between chondrites of the order of 10's or 100's of millions of years. His selection of chondrite samples, furthermore, do not present a sufficiently wide spread of Rb/Sr ratios so that one can obtain an accurate age from chondrite data alone.

In 1963 Gast extended his data further by publishing analyses on 3 more chondrites: Bruderheim, Hvittis and Abee. Abee and Hvittis are both enstatite chondrites. It is interesting to note that, whereas Bruderheim and Hvittis both give ages of 4.61 and 4.60 b.y., respectively, Abee gives an age of 4.24 b.y. with $\lambda = 1.39 \times 10^{-11}$ years^{-1}.

The work of Pinson et al., (1962, 1963, 1964) is a notable improvement over Gast's studies and all other previously mentioned investigations in that for the first time a wide spread of Rb^{87}/Sr^{86} ratios were obtained from the chondrite data alone. This is important since it enables an isochron to be constructed without including achondritic data and without relying on certain initial assumptions mentioned earlier. Pinson et al., (1964) found that this isochron, indeed, projects through the achondrite points and yields the same age (4.52 b.y. with $\lambda = 1.39 \times 10^{-11}$ years^{-1}) as that which is obtained if the achondrite data is also included. Thus, they showed that chondrites and achondrites are in fact cogenetic and had the same initial Sr^{87}/Sr^{86} ratios; and thus, chondrites cannot be samples of the undifferentiated parent material. These initial assumptions, therefore, are no longer necessary.

Pinson et al., (1962) began by analysing 17 meteorite samples. It soon became apparent, however, (Pinson _et al_., 1963) that meteorites which are classified as "finds" are unsuitable for Rb-Sr age analysis (a conclusion which was also supported by Gast, 1962). "Finds" when plotted on an isochron diagram, show considerable scatter, which is probably due to the alteration of Rb and Sr contents as a result of terrestrial erosion. The final isochron of Pinson _et al_., (1964) was constructed from only those meteorites which are classified as "falls" - Estherville, Nakhla, Farmington, Homestead, Forest City, Bath and Holbrook.

Although the work of Pinson _et al_., (1964) represents an important step forward, it was still plagued with some analytical difficulties. Blank analyses are again high when compared with those obtained in this work. (It should be pointed out, however, that the contamination levels of both Pinson _et al_., (1964) and Gast (1962) are sufficiently low so that errors resulting from this amount of contamination alone are insignificant when compared to the actual disagreement observed. The main reason for lowering contamination is so that samples with smaller concentrations of Rb and Sr may be analyzed.) As with previous investigators, poor analytical precision is still another problem. This is especially apparent in the isotope dilution analyses where, for example, after 5 replicate determinations on the New Concord chondrite, the standard deviation of a single Sr analysis amounted to 12.7%. As with Gast (1962), it was thought at first that sample inhomogeneity was responsible for this poor precision. 3-4 gram samples were thus taken for each analysis in an effort to improve the reproducibility. It was decided after the analytical work had been completed, however, that pyrex glassware could, indeed, have caused the poor precision (as pointed out by Wasserburg et al., 1964). Unfortunately, therefore, the isochron of Pinson et al., (1964) is not of sufficient precision to investigate real age differences of the order of 10's or 100's of millions of years.

In 1964, two further Rb-Sr age studies were published. Murthy and Compston (1964) presented some analytical data on several carbonaceous chondrites and on some individual chondrules separated from the Peace River chondrite. They succeeded in obtaining an isochron plot from three individual chondrules of Peace River, but since this isochron does not have an "anchor point" and yields an initial Sr^{87}/Sr^{86} ratio of .694, it is regarded by the author with some skepticism until more experimental data is available. All reliable Rb-Sr studies so far indicate that the initial Sr^{87}/Sr^{86} ratio for meteorites is not below .697. A plot of the carbonaceous chondrite analyses (Orgueil, Murray, Lancé, and Mokoia) shows a scatter not much better than that of Pinson et al., (1964). This carbonaceous chondrite isochron yields an age of 4.89 b.y. with $\lambda = 1.39 \times 10^{-11}$ years^{-1}. This age seems extremely high when compared with the other Rb-Sr meteorite ages.

The analysis by Beiser and Pinson (1964) of the Murray carbonaceous chondrite shows, for the first time, an increase in analytical precision over previous work. It was made with the new clean chemical separation procedures developed in this thesis investigation and discussed in Chapter II. It has been included on the isochron of Chapter VI since it was processed with the same chemical techniques and spike solutions and in the same laboratory as the other meteorites analyzed in this thesis. It is interesting to note that Beiser and Pinson (1964) obtained .725

and .421 whereas Murthy and Compston (1964) obtained .730 and .486 for the Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios of Murray, respectively. Both Sr^{87}/Sr^{86} ratios are "normalized" to a Sr^{86}/Sr^{88} ratio of .1194.

In summary, much of the previous Rb-Sr work on meteorites, except for the analysis of Beiser and Pinson (1964) has been hampered by poor analytical precision. In a number of cases the analytical data is also conflicting. Furthermore, many of these studies were limited to very few meteorite samples and, except in the case of Pinson _et al_., (1964) and Murthy and Compston (1964), had a poor spread, or no spread at all, in Rb^{87}/Sr^{86} ratios.

This present investigation was undertaken, therefore, with a number of objectives in mind. First, it was hoped that a clean chemical separation procedure could be developed for Rb and Sr which would result in not only lowering the contamination significantly, but also increasing the reproducibility of replicate analyses. Such a procedure would have wide applicability not only to meteorites, but also to all other Rb and Sr depleted materials such as ultramafic rocks and separated mineral phases from meteorites.

Second, it was decided to attempt the separation of some chondrules and mineral phases from a chondrite. This would permit the exploration of possible age differences between the chondrules, the separated minerals and the whole meteorite. A mineral isochron would also have a number of obvious advantages over a whole meteorite isochron.

Third, providing blanks and analytical reproducibility could be improved, it was decided to attempt the construction of a highly precise meteorite isochron employing the following ground rules: 1) as a result of the findings of Gast (1962) and Pinson et al., (1963) only "ultra-fresh" meteorite samples should be used, 2) several different classes of meteorites should be included on the isochron, 3) a suite of samples should be selected with a good spread in Rb^{87}/Sr^{86} ratios, and 4) all samples should be analyzed in the same consistent manner. If all the above conditions could be met and the resultant data, when plotted on an isochron diagram, showed the same amount of scatter as that of previous workers, then this would be a strong indication that meteorites, in fact, did exhibit age differences of the order of tens or hundreds of millions of years. If, however, they all fell on the same straight line, it would be strong evidence that all the meteorite classes included in the plot had been involved in the same sort of common chemical differentiation process and had remained chemical systems closed to the migration of Rb and Sr ever since.

CHAPTER II

EXPERIMENTAL TECHNIQUES

2.1 - Introduction

To obtain the Rb^{87}-Sr^{87} age of a sample, or series of samples, the $(Sr^{87}/Sr^{86})_p$ and $(Rb^{87}/Sr^{86})_p$ ratios must be measured (as discussed in Section 1.2). These quantities are both usually determined mass spectrometrically. The Rb^{87}/Sr^{86} ratio is obtained by isotope dilution analysis. The techniques of isotope dilution analysis have been previously discussed in Webster (1960), Pinson (1960), Faure (1961, 145-165), and Bottino (1963, 99-132). The Sr^{87}/Sr^{86} ratio is obtained by an isotope ratio measurement on the natural Sr in the sample. For a discussion of the techniques used in making isotope ratio measurements see Faure (1961, 166-184), Powell (1962, 115-139), and Krogh (1964).

If one plans to apply the Rb^{87}-Sr^{87} technique to materials which are highly depleted in Rb and Sr, a very clean chemical procedure for separating these elements must first be developed. At the start of this investigation the existing chemical procedure at the M.I.T. Geochronology Laboratory produced blanks of about 0.03 μgm Rb per gram of sample and 0.2 μgm Sr per gram of sample (Pinson <u>et</u> <u>al</u>., 1963, 10). Furthermore, disagreement between replicate isotope dilution analyses amounted to as much as 15% or more. It was decided, therefore, that if high quality work was to be performed on meteorites and meteorite phases the contamination level would have to be lowered significantly and the precision of replicate analyses increased. Such a procedure would, of course, be widely applicable to all other types of materials with low concentrations of Rb and Sr.

2.2 - Changes Instituted in the Existing Chemical Procedure

2.21 - Reagent Purification

Since it was felt that much of the contamination was being introduced via the chemical reagents, the first efforts were directed at obtaining pure water and acids.

Five acids are used in the chemical procedure - HF, HCl, $HClO_4$, HNO_3, and H_2SO_4. HCl and HNO_3 were already being prepared in the laboratory by distillation of reagent grade HCl and HNO_3 in vycor glass (a high purity, silica glass) stills. Blanks run on the HCl prepared in this way had indicated it to be of sufficient purity for our purposes: $\sim 4\times10^{-5}$ μgm Sr/ml (Pinson et al., 1963, 10). Blanks run on the $HClO_4$ and HF, however, indicated that these acids would have to be purified further. Fortunately, a chemical company (The G. Fredrick Smith Chemical Co., 867 McKinley Avenue, Columbus 22, Ohio) was located which produces an ultrapure grade of both

$HClO_4$ and H_2SO_4. Both acids are double vacuum distilled from vycor and shipped in vycor ampules (Items #230 and #273, respectively, in catalogue of January, 1960).

The procedure being used in the laboratory for the purification of H_2O involves distillation in a Barnstead still followed by passage through a Barnstead Bantam Demineralizer (standard cartridge). This water is then redistilled in a still of vycor glass.

Pure hydrofluoric acid was still a problem, however, since no company could be found which produced a purer grade of HF than the ordinary reagent grade. A process was therefore developed for making it in the laboratory. A cylinder of liquid, anhydrous HF was purchased from the Matheson Company, Inc. of East Rutherford, New Jersey. A special valve designed especially for HF cylinders also had to be purchased from the Matheson Company.

As shown in Figure 2.21a, the HF is directed through a piece of polyethylene tubing and a teflon bubbling mechanism into about 1000 ml of double vycor distilled H_2O. The polyethylene tubing can be formed into any desired shape by gently heating it in a bunsen flame. A good fit can be made over the outlet of the metal valve by heating the polyethylene tubing until it is clear, forcing it over the nozzle and allowing it to cool in place.

Figure 2.21 a

Diagram of Apparatus for Preparing HF Acid

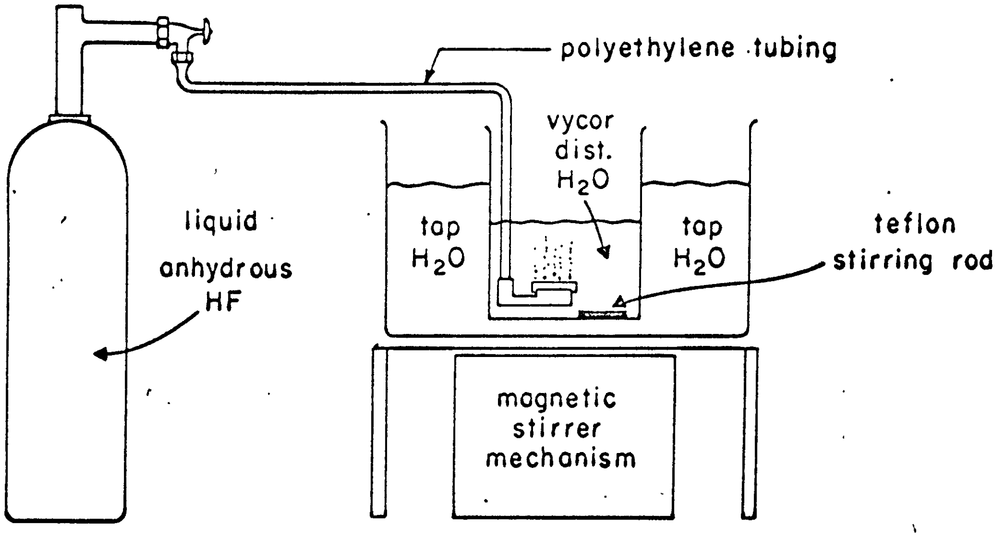


Figure 2.21 b

Cross-section of Bubbling Mechanism for HF Gas

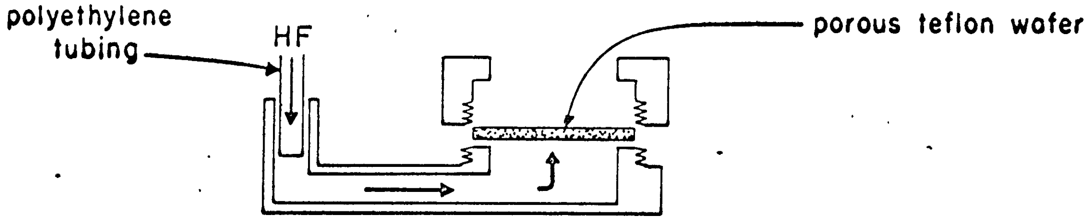
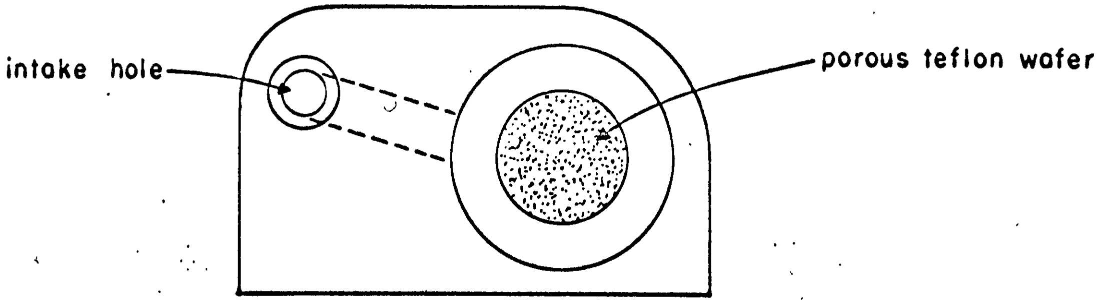


Figure 2.21 c

Plan View of Bubbling Mechanism



A bubbling mechanism was machined out of teflon to fit over the end of the polyethylene tubing as shown in Figure 2.21b. A wafer was cut out of porous teflon (obtained from the James R. Chisholm Corporation, Cambridge, Massachusetts) to fit over the outlet hole of the bubbler. A screw cap with a large central opening was machined to hold the wafer in place. A plan view of this bubbling apparatus is shown in Figure 2.21c.

The bubbler is set on the bottom of a 2000 ml polyethylene beaker with a flat bottom. The flat bottom is necessary so that a magnetic stirring device will operate in the beaker as shown in Figure 2.21a. The 2000 ml beaker should be wide enough so that both the stirring rod and the bubbler will sit on the bottom without interference. Actually, the apparatus will work just as well if the polyethylene tubing is cut a little short so that the bubbler is suspended off the bottom with the stirrer operating under it.

The 2000 ml beaker is then set inside a larger polyethylene tub (which also must have a flat bottom) that serves as a cooling bath. This tub is set on a 3 legged stand built so that it is just high enough to fit the magnetic stirring mechanism under it.

The 2000 ml beaker is filled with only about 1000 ml of distilled H_2O since a volume increase of approximately a factor of 2 will occur during the preparation of the HF. The outer tub is filled with tap water and serves as a cooling bath since the solubility of HF gas in water is highly exothermic. It is also suggested that a flat polyethylene lid be made for the 2000 ml beaker.

The above procedure will produce approximately 31 N HF acid. One can usually tell by visual observation whether or not the solution is nearing saturation with respect to HF gas, since white vapors begin to rise off the surface of the liquid at saturation. One should check to make sure that the solution is near room temperature, because if it is hot the white vapors will rise off the surface at a much lower HF concentration. The concentration of the first few batches should perhaps be checked by titration.

A few words of caution should be mentioned about preparing HF by the above technique. First, HF gas is <u>extremely</u> soluble in water. Before closing off the valve to the tank, the bubbling apparatus should be lifted out of the solution. If this is not done the HF acid will be sucked back through the porous teflon wafer into the polyethylene tubing and will corrode the metal valve on the tank. One should also take precautions to check that the main HF cylinder does not become exhausted while one is in the process of preparing a batch of HF. If this occurs, the entire 1000-2000 ml of solution will be rapidly sucked back into the main HF tank. This will corrode or destroy the tank and the metal valve and may also cause an explosion due to the rapid pressure change. Therefore, one should keep a record of how much HF still remains in the cylinder. Usually this can be done by weighing the cylinder and subtracting the given cylinder weight.

Second, so much heat is given off as the HF gas dissolves in water that if the solution is not closely watched it may begin to boil in a very short time. It is recommended, therefore, that either the regulator valve be opened only a small fraction of a turn, or the tank be shut off as described above several times with each batch to allow the solution sufficient cooling time.

Extreme caution should be exercised by anyone working with HF and especially by anyone preparing HF in the above manner. Hydrofluoric acid is an extremely toxic and corrosive acid causing severe, slowly healing burns. One should be very cautious about inhaling the vapors or spilling it on the skin. All work should be carried out in a well ventillated hood with rubber gloves and protective goggles.

2.22 - Elimination of Pyrex

A second line of attack on the contamination problem involved the elimination of pyrex glassware. It was felt that exchange phenomena might possibly exist between the glass and the ions in solution, especially at elevated temperatures and especially if any fluoride ions remained in solution after the sample was dissolved. An independent investigation was also being carried out at the same time on this problem by Wasserburg <u>et al</u>., (1964) at the California Institute of Technology. Their experiments indicated that significant amounts of contamination were introduced by both pyrex and kimax glassware and that this contamination might also be responsible for the poor reproducibility of replicate analyses. Our independent investigation did not involve actual analyses to determine the contribution of pyrex glassware; rather, our approach was to institute a number of changes in the procedure and then run a blank analysis on the entire procedure to see if there was any improvement.

All 100 ml pyrex beakers were replaced by 100 ml polypropylene beakers. Water and 2N HCl solutions do not wet the surface of these beakers and frequently they can be poured out dry. Furthermore, much smaller amounts of radioactive tracer can be detected through the walls of the polypropylene beakers. Unfortunately, however, the polypropylene beakers cannot be heated to as high a temperature on the hot plate or they will melt. Yet, this is not a serious handicap, since 100 ml of solution can be evaporated to dryness in a day if the hot plate is calibrated correctly. A steam bath with appropriate sized holes is much safer and faster.

The 5 ml pyrex beakers into which samples are transferred at the end of the chemical procedure were replaced by 5 ml vycor crucibles. These are made especially to order by Ryan, Velluto and Anderson Inc., 103 First Street, Cambridge, Massachusetts. Since samples are ignited in these crucibles, it was felt that this was a most important step in which to eliminate pyrex glassware.

Pyrex ion exchange columns had been used in the procedure with a wad of pyrex glass wool at the bottom to hold back the ion exchange resin. These columns were replaced by columns of vycor glassware. The pyrex wool was replaced by fused quartz wool purchased from the Thermal American Fused Quartz Co., Route 202, Montville, New Jersey.

Finally, the pyrex capillary tips used for placing a drop of sample on the mass spectrometer filament were replaced by vycor capillary tips.

2.23 - Miscellaneous Improvements

Samples, such as meteorites and ultrabasic rocks, frequently leave behind an insoluble residue when they are dissolved. This insoluble residue was normally removed by passing the solution through filter paper.

Since the contamination introduced by the filter paper is not known, it was decided that centrifuging the solutions might be a more satisfactory means of separating this insoluble residue. Therefore, vycor centrifuge tubes were purchased for this operation.

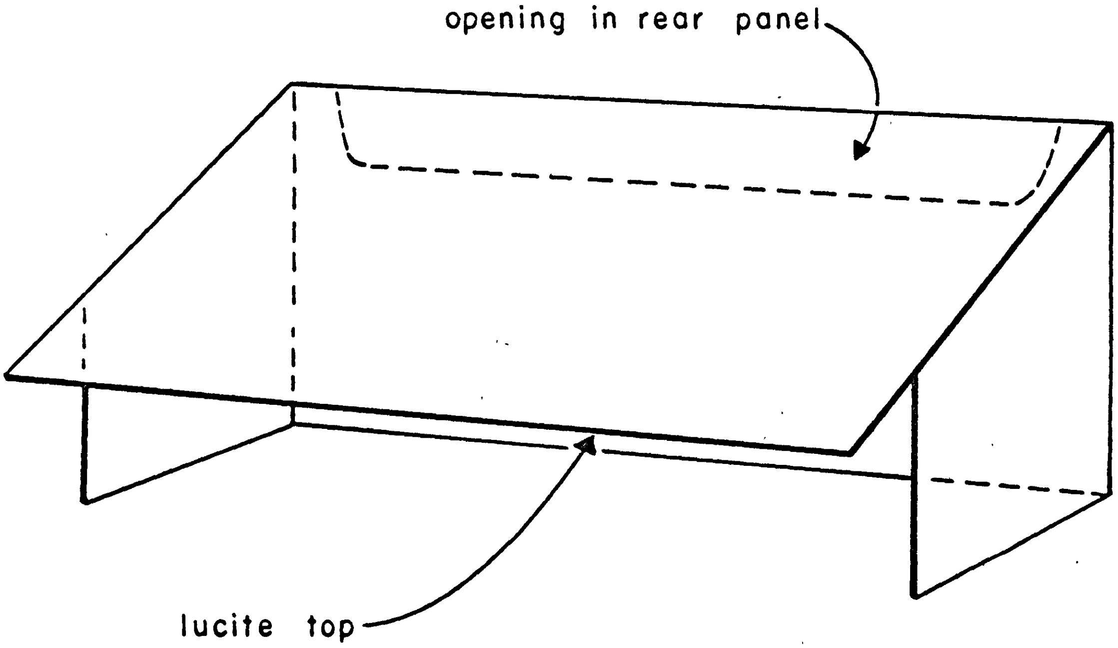
The contribution of laboratory fallout to the total contamination has not yet been determined. It seemed prudent, however, to institute the policy of keeping all beakers, dishes and solutions covered as much as possible. Accordingly, a sheet of parafilm is placed across the top of all beakers and dishes not on the hot plate or steam bath. Furthermore, a hot plate cover was made, as shown in Figure 2.23. The top is constructed out of plexiglas so that one can easily view the beakers inside. The three sides have been lined on the inside with a teflon tape (Temp-R-Tape, manufactured by the Connecticut Hard Rubber Co., New Haven 9, Connecticut) to prevent corrosive fumes from attacking them. There is an opening at the top of the back panel to permit the vapors to escape.

2.3 - Present Chemical Procedure

The chemical procedure presently used in the M.I.T. Geochronology Laboratory for the separation of rubidium and strontium from meteorites and other materials with very low concentrations of Rb and Sr is outlined below.

Figure 2.23

Hot Plate Cover



2.31 - Preparation of Samples

Extreme care should be taken at the start to insure that the sample has not been contaminated prior to analysis. Especially with meteorites and other Rb and Sr depleted materials, one should investigate the history of the sample. Great caution should be exercised with samples which have been exposed to terrestrial erosion, rained upon, immersed in sand, mud, or water, or handled incautiously in museum storage or elsewhere.

Meteorite samples are first scraped and brushed clean on the surface to remove possible contamination from dust and human hands. Any remnants of the fusion crust are also chipped off. Samples are not washed or leached in acid prior to analysis since recent investigators have suggested that Rb and Sr contents may be altered in this manner (Gast, 1962; Pinson *et al.*, 1963; Smales *et al.*, 1964). All samples are stored in polyethylene bottles to eliminate the possibility of chipping or scraping the inside of a glass jar and thereby adding bits of soft, alkali-rich glass as contamination.

Samples are crushed by hand in a stainless steel mortar and pestle. A fresh surface is machined on the pestle and on the inside of the mortar before each new sample is crushed. Samples are crushed to pass through at least a 100 mesh sieve. Pieces of the Fe-Ni phase are also mixed in with the silicate material, although it might be preferable to separate the magnetic material by hand magnet, weigh it, and then apply a correction factor to the final answer.

Next, the sample is coned and quartered to insure maximum homogeneity throughout. The amount of material desired for an analysis is then transferred with a spatula into a paper cup for accurate weighing. For strontium isotope ratio determinations the samples obviously need not be weighed except as a rough check on how much Sr will be present in the final sample.

2.32- Dissolving of Samples

The amount of sample to be dissolved for an analysis is dependent upon its Rb and Sr contents. Excellent long runs can be obtained routinely with one or two micrograms of Rb and a few micrograms of Sr. Often, high quality runs are made with much less Rb and Sr than this. Normally a gram of material is sufficient for a chondrite meteorite analysis. For samples with high concentrations of Rb and Sr much less than a gram of sample should be used. Samples containing a total of more than 100 micrograms of Rb and/or Sr should be discouraged as contributing to an unnecessary waste of spike.

The sample is transferred into a platinum dish and the appropriate amounts of Rb and Sr spikes (if any) are added. A Sr isotope ratio determination is not spiked since one is interested in obtaining the ratio of the Sr isotopes directly from the original sample. The amounts of Rb and Sr spikes to be added to an isotope dilution analysis are determined from the graphs of Rb^{85}/Rb^{87} or Sr^{86}/Sr^{88} versus Normal/Spike (see Brookins, 1963, 141-146). The optimum spiking range is where these curves have a slope of approximately -1. For the present Rb^{87} Dilute Spike (1.26 µgm Rb/ml) this means a N/S ratio of about 2.5. For the new Sr^{84}-Sr^{86} Double Spike (1.05 µgm Sr/ml) the N/S ratio should be about 1.25.

The platinum dishes are then set on a steam bath and HF and $HClO_4$ (or sometimes H_2SO_4) are added. Samples are evaporated to perchloric acid fumes and then taken up in HCl at least twice after the last portion of HF has been added to insure removal of all fluoride ions. Finally, the dried sample is taken up in as small a volume of distilled H_2O as is necessary for dissolving the sample. Addition of a small amount of 2N HCl may also be necessary here. The samples are then decanted into polypropylene beakers which are always kept soaking in concentrated HNO_3 when not in use.

2.33 - Removal of Insoluble Residue

After a meteorite has been dissolved in HF and $HClO_4$, a black insoluble residue often remains. A similar residue has been observed by Schumacher (1956b, 534), Pinson et al., (1962, 19), and Gast (1962, 928). Pinson et al., (1962, 19) determined that this residue amounts to no more than 0.5% by weight of the total Homestead meteorite, and Gast (1962, 928) determined that this residue "accounts for no more than 0.2 per cent of the original sample". Mrs. U. B. Marvin of the Smithsonian Astrophysical Observatory performed an x-ray fluorescence analysis on some of this insoluble residue (from the Bjurböle chondrite) and observed large Fe and Cr peaks. This is consistent with the findings of Gast (1962, 928) who identified Fe, Cr and Al in the residue. Mrs. Marvin also took an x-ray powder photograph of this insoluble residue. The x-ray powder photograph matched that of chromite but contained one extra unidentified line. Hoops (1964, 405) mentions that spinels are found in residues obtained from dissolving terrestrial rocks. Gast (1962, 928) mentions that Schumacher in 1956 also observed an x-ray diffraction pattern from this insoluble residue corresponding to a spinel structure but has omitted the reference to Dr. Schumacher's article in his bibliography. The author has been unable to locate any reference to a spinel structure in any of Dr. Schumacher's 1956 publications (Schumacher 1956a, 1956b, 1956c, and 1956d). Nevertheless, this insoluble residue is probably made up mostly of chromite and should contain negligible Rb and Sr.

This insoluble residue is removed by transferring the solution into vycor centrifuge tubes and centrifuging it for about five minutes. The liquid is then decanted back into a clean polypropylene beaker.

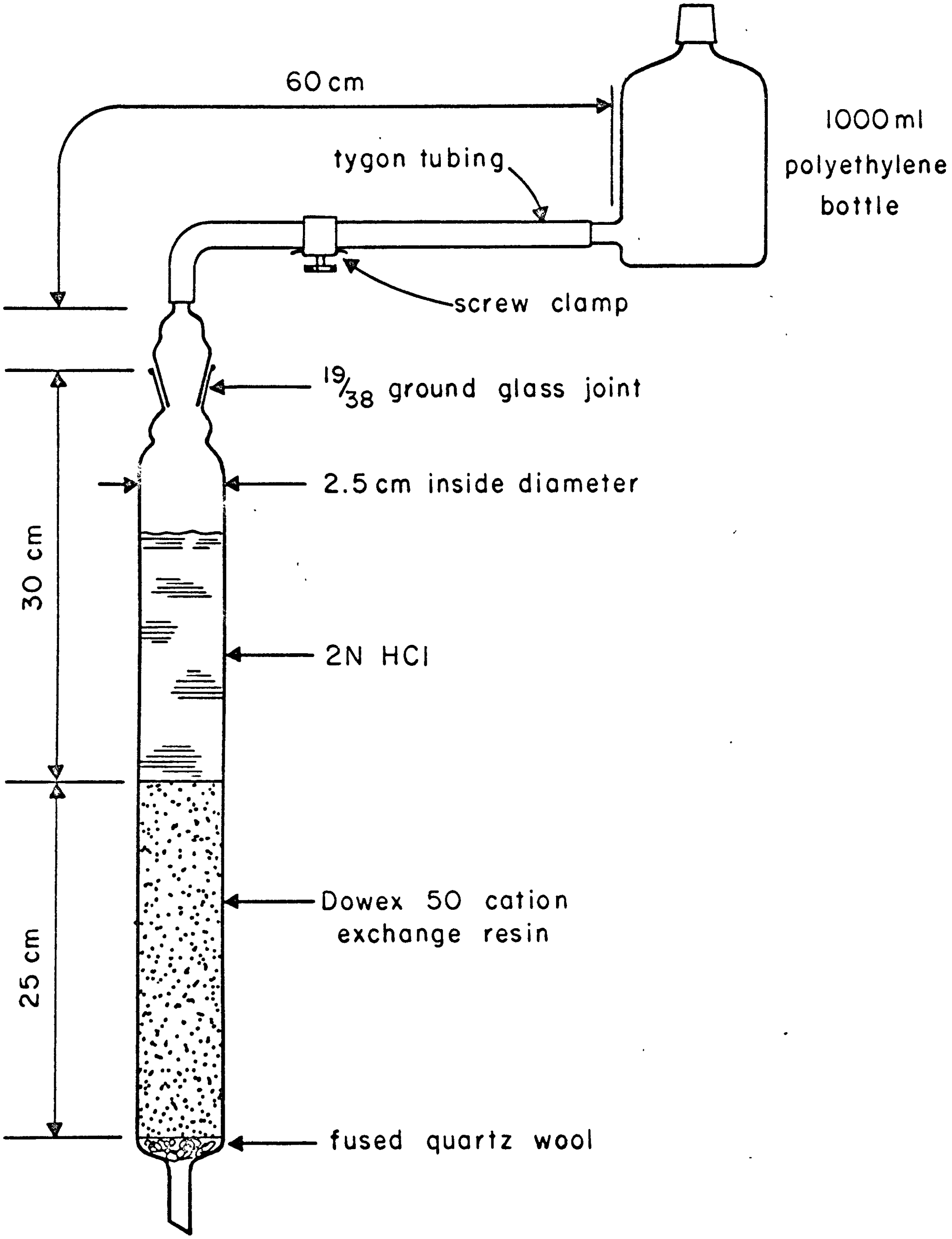
2.34 - Ion Exchange Techniques

Rb and Sr are separated from the other elements in a sample by ion exchange. The resin used for this separation is Dowex 50 (8% cross-linked with DVB, 200-400 mesh, hydrogen form) cation exchange resin manufactured by the Dow Chemical Company, Midland, Michigan. This resin is put in a vycor glass column, as illustrated in Figure 2.34, so that the resin bed is approximately 25 cm high. A 1000 ml polyethylene bottle is filled with the eluant, 2N HCl, and set on a shelf above the top of the column. This bottle is connected with tygon tubing to a ground glass 19/38 joint at the top of the column. A screw clamp is used on the tygon tubing to shut off the reservoir in the polyethylene bottle. This bottle of 2N HCl when connected to the column serves as a pressure head. It speeds up passage of a sample through the resin and can be left unattended for several hours.

The location of the Rb and Sr on the column is monitored with Rb and Sr radioactive tracers. The tracer must, therefore, be added prior to putting a sample on

Figure 2.34

Schematic Diagram of Ion Exchange Column



the column. These tracers are purchased from the Nuclear Science and Engineering Company, Box 10901, Pittsburgh 36, Pennsylvania. The Rb tracer is a mixture of Rb^{83} and Rb^{84} produced by proton bombardment of krypton. Sr^{85} tracer is produced by bombardment of Rb with protons and deuterons. Our numerous blank analyses demonstrate these tracers to be carrier free.

Columns are normally washed with 2000 ml of 2N HCl each time before applying a sample to insure removal of elements such as the rare earths. A level surface is then prepared on the top of the resin by adding about 10 ml of 2N HCl shaking the column by hand and allowing the resin to settle. The sample is then placed on the top of the resin bed.

Samples are eluted with 2N HCl. They are gently washed into the resin by adding 2 or 3 small portions of 2N HCl with a polyethylene squirt bottle and washing down the sides of the column. Finally, a 50 to 75 ml portion of 2N HCl is added gently onto the resin bed. The 1000 ml polyethylene bottle is then filled with 2N HCl and connected to the column via the glass joint. The clamp is then loosened and the column runs automatically.

Samples are collected off the columns in 15-20 ml portions with 100 ml polypropylene beakers. The activity in each beaker is monitored with a low level scintillation counter. Beakers are kept covered with parafilm, and only the 2 or 3 beakers which contain the maximum tracer activity are retained. The contents of these beakers are then combined and evaporated to 2 or 3 ml on a covered hot plate.

Frequently, Rb samples which have been run through the ion exchange columns only once are full of a white material. A sample of this material from the Bath chondrite was analyzed on the optical spectrograph by Dr. W. H. Dennen of M.I.T. and determined to be aluminum. Schumacher (1956b) mentions the presence of Al^{3+} but says that it is rapidly washed through the column and does not interfere with the Rb samples. Perhaps this is because he was eluting with stronger HCl than we are at present using, thereby complexing the aluminum as $AlCl_4^-$. The most effective procedure for removing aluminum from our Rb samples is still under investigation. At present, a second pass through the columns is suggested.

2.35 - Final Steps

After the sample has been evaporated down to 2 or 3 ml in a polypropylene beaker, it is transferred into a 5 ml vycor glass beaker. These vycor glass beakers are kept soaking in concentrated HNO_3 acid and are leached with hot aqua regia before use. They are used only once. The sample is evaporated to dryness in this vycor beaker. A few drops of concentrated $HClO_4$ are then added to oxidize any resin which may have passed through the quartz wool. The sample is again evaporated to dryness and ignited over a Tyrell burner to eliminate perchlorates. One or two ml of HNO_3 are then added to the sample, and it is again evaporated to dryness. This last step is then repeated, and the sample is ready for mass spectrometer analysis.

To mount a sample on the filament of a mass spectrometer source one small drop of nitric acid is added to the sample. This is taken up in a vycor capillary syringe and dried in the center of a tantalum filament by passing a current of about one ampere through the filament.

2.4 - Mass Spectrometry

The mass spectrometer used for making these analyses is a 60° sector, six inch radius, solid source, single collector, Nier type instrument. The filament consists of a piece of .001" x .020" tantalum ribbon spot-welded to two posts in the source. A vibrating reed electrometer is used to amplify the ion current, and the signal is read out on a Brown strip chart recorder. A vacuum in the range of 10^{-7} mm. of mercury is obtained by coupling a Duo-Seal forepump with a mercury diffusion pump.

The mass spectrometry techniques employed in this thesis investigation are essentially those used by previous investigators in the M.I.T. Geochronology Laboratory. They have been described in the Annual

Progress Reports of the Laboratory and in numerous Ph.D. theses (Faure, 1961, 170-184; Powell, 1962, 121-125; Bottino, 1963, 105-109). An up-to-date discussion of some recent improvements in the mass spectrometry technique which are partly responsible for the increased analytical precision obtained in this thesis investigation is given in Krogh (1964).

Below are listed a few supplementary suggestions for obtaining high precision in mass spectrometer analyses:

1. All analyses should be made under as nearly identical conditions as possible.
2. A Sr isotope ratio analysis should never be made unless the recorder pen returns unquestionably to zero between the 88 and 87 peaks and stops <u>at least</u> momentarily on the peak tops. A faithful tracing of a mass spectrometer scan is shown in Figure 2.4.
3. Each time the source is assembled the two collimating slits should be lined up with the alignment mechanism. It should be noted that they do not necessarily line themselves up automatically.
4. Baseline should be measured both before and after a run and several times during the course of a run, especially if the baseline has a tendency to drift. It is most accurately measured with a magnifying glass.
5. The author has found that placing a small slurry of a sugar, Ta and Tao mixture on the center of a filament increases the steadiness of the emission. It also seems to increase the life of the filament. It is put on with a new filament and then the new filament is cleaned in the normal way.

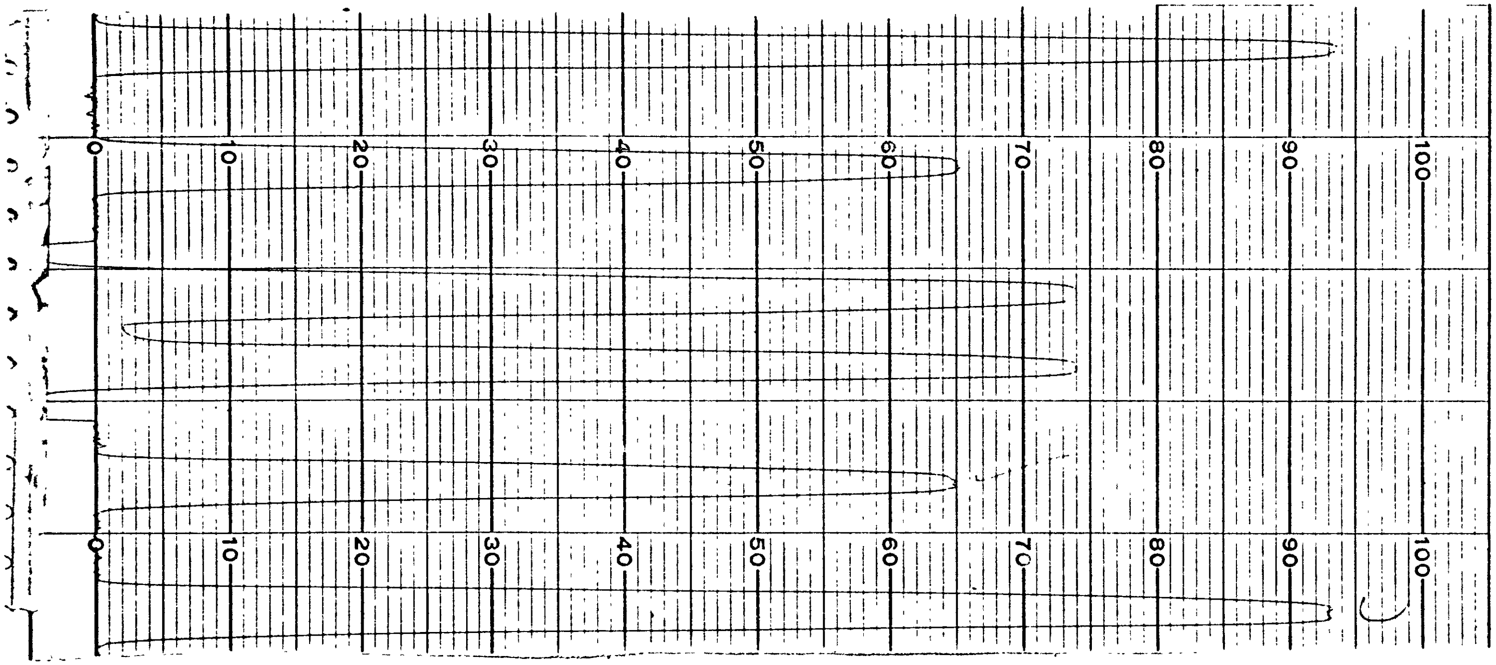


Figure 2.4

SAMPLE OF MASS SPECTROMETER SCAN OF Sr SPECTRUM

The normalization procedure has been discussed in previous Annual Reports and in Faure (1961, 177-180). (See also Section 6.3 of this thesis.)

CHAPTER III

SPIKES AND SHELF SOLUTIONS

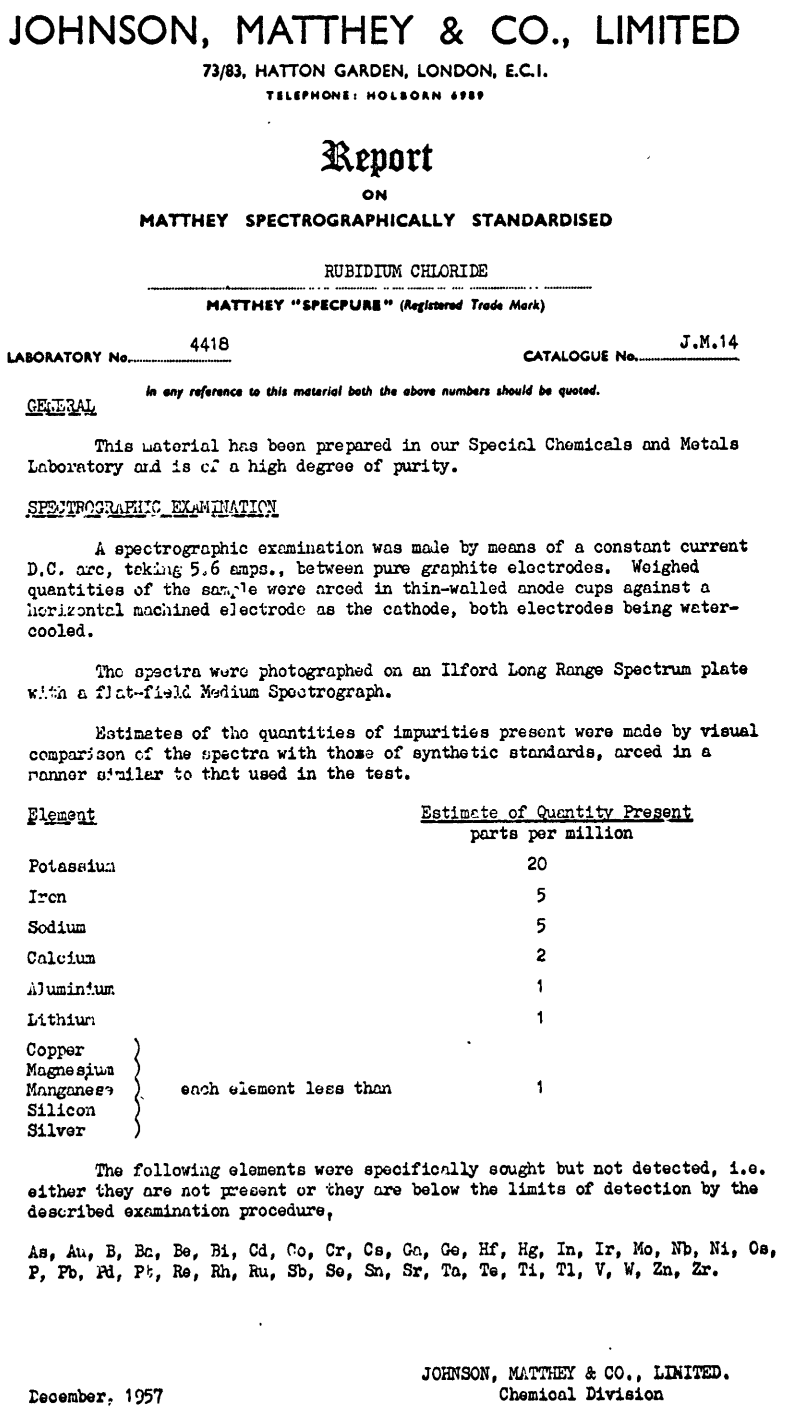
A discussion will be given in this section of the pertinent information concerning spikes and shelf solutions used or prepared during this thesis investigation. For a more complete description of the spiking procedures used in the M.I.T. Geochronology Laboratory see Pinson (1960), Pinson (1962), Brookins (1963, 141-147) and Faure (1961, 149-159). Errors quoted in the following tables are in Section 6.5.

3.1 - Preparation of Shields' Rb Shelf Solution

The preparation of Shields' Rb Shelf Solution is described in Shields' laboratory notebook #3 on pages 3, 10, and 11, and in Laboratory Record Book #12, p. 52. A "Specpure" grade of RbCl (Laboratory #4418, Catalogue #J. M. 14) was obtained from Johnson, Matthey and Co., Limited, 73/83, Hatton Garden, London, E.C.I. Pertinent information about this RbCl is given in Figure 3.1.

Assuming the Rb^{85}/Rb^{87} ratio in normal Rb is 2.59 ± .02 (Pinson, 1962, 91), the formula weight of this RbCl was calculated to be 121.01. The weight

Figure 3.1 - LABORATORY REPORT ON "SPECPURE" RbCl



JOHNSON, MATTHEY & CO., LIMITED

73/83, HATTON GARDEN, LONDON, E.C.1.
TELEPHONE: HOLBORN 6989

Report

ON

MATTHEY SPECTROGRAPHICALLY STANDARDISED

RUBIDIUM CHLORIDE

MATTHEY "SPECPURE" *(Registered Trade Mark)*

LABORATORY No. 4418 CATALOGUE No. J.M.14

In any reference to this material both the above numbers should be quoted.

GENERAL

This material has been prepared in our Special Chemicals and Metals Laboratory and is of a high degree of purity.

SPECTROGRAPHIC EXAMINATION

A spectrographic examination was made by means of a constant current D.C. arc, taking 5.6 amps., between pure graphite electrodes. Weighed quantities of the sample were arced in thin-walled anode cups against a horizontal machined electrode as the cathode, both electrodes being water-cooled.

The spectra were photographed on an Ilford Long Range Spectrum plate with a flat-field Medium Spectrograph.

Estimates of the quantities of impurities present were made by visual comparison of the spectra with those of synthetic standards, arced in a manner similar to that used in the test.

Element		Estimate of Quantity Present parts per million
Potassium		20
Iron		5
Sodium		5
Calcium		2
Aluminium		1
Lithium		1
Copper Magnesium Manganese Silicon Silver	each element less than	1

The following elements were specifically sought but not detected, i.e. either they are not present or they are below the limits of detection by the described examination procedure,

As, Au, B, Ba, Be, Bi, Cd, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, Mo, Nb, Ni, Os, P, Pb, Pd, Pt, Re, Rh, Ru, Sb, Se, Sn, Sr, Ta, Te, Ti, Tl, V, W, Zn, Zr.

December, 1957

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Chemical Division

percent of Rb in this salt is, therefore, 70.70%.

A small glass weighing bottle (7ml) was washed and dried in an oven over night. It was then placed in a dessicator for approximately one hour. The weight of the empty bottle was then determined to be 9.43533 gms. About 0.2 gms of RbCl were then added to the bottle and the weight of the dried weighing bottle plus the undried RbCl came to 9.63653 grams. This weighing bottle was placed in an oven for three hours and then in a dessicator to cool for approximately one more hour. The weight came to 9.63660 gms. The drying procedure was then repeated for two more hours followed by cooling in a dessicator for another hour and re-weighing. This time the weight was determined to be 9.63656 gms. Since the weighing bottle plus the RbCl did not seem to undergo any weight loss during this entire procedure, it was considered dry. (During this entire procedure the weighing bottle was never touched with the hands. It was maneuvered with a wire test tube holder.) Removing the top of the weighing bottle with a pair of tweezers, the contents were quickly dumped into a previously washed 2000 ml volumetric flask. The top was quickly placed back on the bottle and it was re-weighed. This time the empty weighing bottle weighed 9.43518 grams. The difference between this weight and the last full weight was 0.20138 gms., and this was the weight of RbCl transferred into the 2000 ml flask.

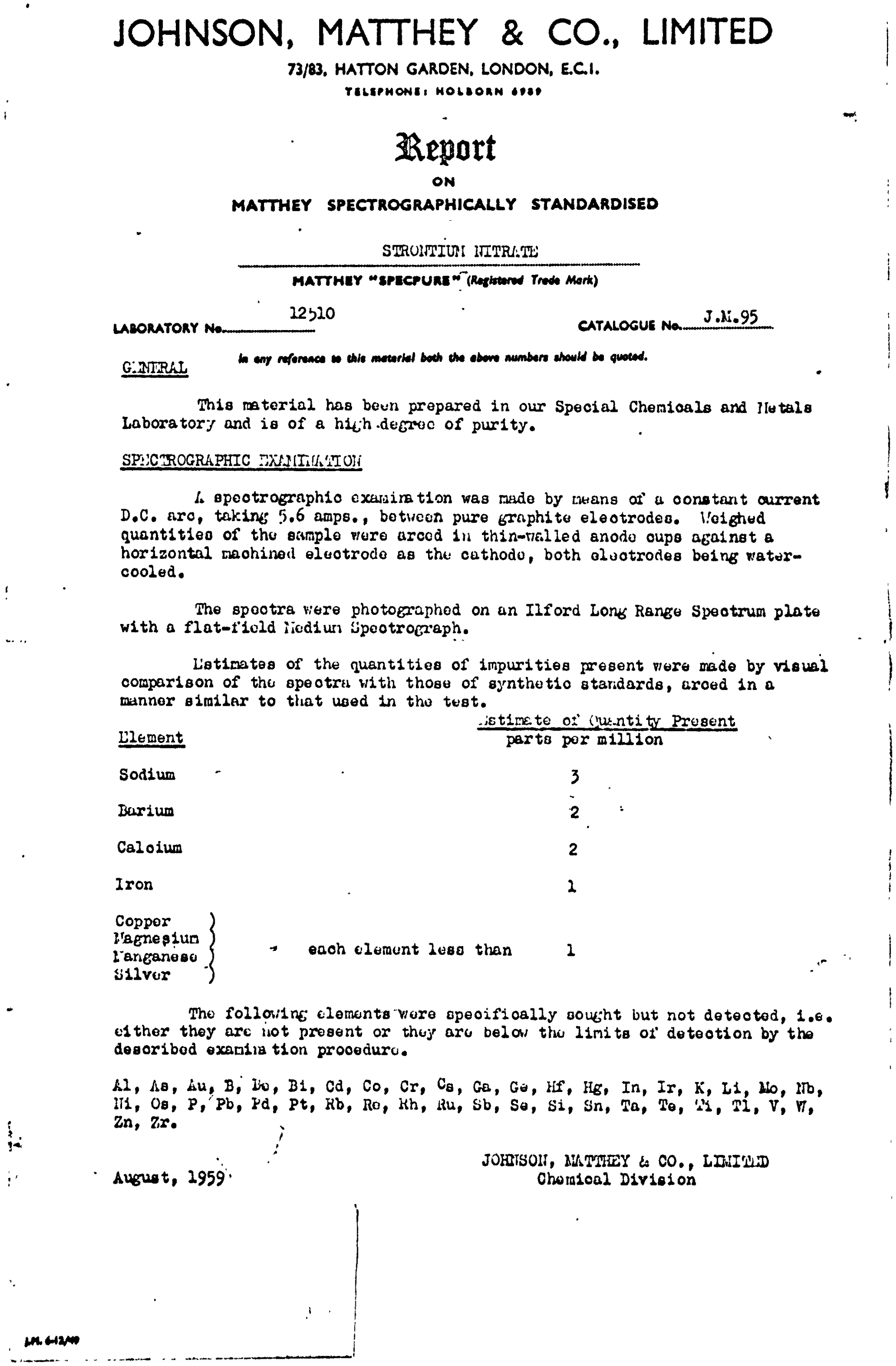
This flask (calibrated at 20°C) was diluted up to volume at 26½°C with vycor distilled 2N HCl. The temperature correction data were obtained from page 2192 of the Handbook of Chemistry and Physics (44th ed.). The volume corrected to 1997 ml. Since the RbCl was calculated to contain 70.70% Rb, this means that 0.14238 gms. of Rb were added to 1997 ml of 2N HCl. Shields' Rb Shelf Solution, therefore, contains 71.3 µgm Rb/ml.

3.2 - Preparation of Shields' Sr Shelf Solution

Shields' Sr Shelf Solution was prepared at the same time and in the same manner as Shields' Rb Shelf Solution (see Laboratory Record Book #12, p. 53). Johnson, Matthey "Specpure" $Sr(NO_3)_2$ (Laboratory #12510, Catalogue #J.M. 95) was used to make this solution. The optical spectrographic analysis and other pertinent data are reproduced in Figure 3.2.

Assuming that this $Sr(NO_3)_2$ has a Sr^{87}/Sr^{86} ratio of about .707, the formula weight of $Sr(NO_3)_2$

Figure 3.2 - LABORATORY REPORT ON "SPECPURE" $Sr(NO_3)_2$



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TELEPHONE: HOLBORN 6989

Report
ON
MATTHEY SPECTROGRAPHICALLY STANDARDISED

STRONTIUM NITRATE

MATTHEY "SPECPURE" *(Registered Trade Mark)*

LABORATORY No. 12510 CATALOGUE No. J.M.95

In any reference to this material both the above numbers should be quoted.

GENERAL

This material has been prepared in our Special Chemicals and Metals Laboratory and is of a high degree of purity.

SPECTROGRAPHIC EXAMINATION

A spectrographic examination was made by means of a constant current D.C. arc, taking 5.6 amps., between pure graphite electrodes. Weighed quantities of the sample were arced in thin-walled anode cups against a horizontal machined electrode as the cathode, both electrodes being water-cooled.

The spectra were photographed on an Ilford Long Range Spectrum plate with a flat-field Medium Spectrograph.

Estimates of the quantities of impurities present were made by visual comparison of the spectra with those of synthetic standards, arced in a manner similar to that used in the test.

Element		Estimate of Quantity Present parts per million
Sodium		3
Barium		2
Calcium		2
Iron		1
Copper Magnesium Manganese Silver	each element less than	1

The following elements were specifically sought but not detected, i.e. either they are not present or they are below the limits of detection by the described examination procedure.

Al, As, Au, B, Be, Bi, Cd, Co, Cr, Cs, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mo, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Si, Sn, Ta, Te, Ti, Tl, V, W, Zn, Zr.

August, 1959

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Chemical Division

J.M. 6-12/49

was calculated to be 211.72. 41.427% by weight of this is Sr. Strontium nitrate does form a hydrate, but this decomposes at 31.3°C.

A similar glass weighing bottle was washed, dried and cooled as described in the previous section. The weight of this empty bottle was then determined to be 9.63867 gms. About 0.21 grams of $Sr(NO_3)_2$ were then added to the dried bottle, and the weight was 9.85583 gms. This dried bottle plus undried salt was then put in an oven and dried for three hours. It was removed and cooled in a dessicator for another hour. The weight was again determined to be 9.85583. In view of such excellent agreement the salt was considered dried and was poured into a clean 1000 ml volumetric flask. The empty weighing bottle was quickly re-weighed again, and the weight determined to be 9.64121 gms. This weight is slightly higher than the original empty bottle weight since a few small grains of the salt were observed remaining in the bottle. This does not affect the determination, however, since it is the difference in the two weights that tells how much salt has actually been transferred into the 1000ml volumetric flask. The difference between the two above weights indicates that 0.21462 grams of $Sr(NO_3)_2$ were transferred into the flask.

This flask was calibrated at 20°C and diluted up to 1000 ml at 26½°C. The temperature correction (as described in the previous section) converted this to a volume of 998.6 ml. Thus 41.427% of .21462 gms. or .088911 grams of Sr in 998.6 ml of solution gives Shields' Sr Shelf Solution a concentration of 89.04 μgms Sr/ml.

3.3 - Rubidium Spikes

3.31 - Rb^{87} Dilute Spike (∼1.26 μgm Rb/ml)

This spike was used for all meteorite analyses in this thesis. The history of this spike is given in Pinson (1962, 96). Its isotopic composition was determined by four analyses which are listed in Pinson (1962, 95-96, Tables 9 and 15). The average of these four analyses yields a composition of 98.25% Rb^{87} and 1.75% Rb^{85}.

Numerous calibration runs have been made on this spike to determine its concentration. A listing of all these calibration runs is given in Table 3.31. The grand average of 1.232 μgms Rb/ml has been used as the best estimate of the concentration of this spike.

Table 3.31

Summary of Spike Calibration Runs on Rb^{87} Dilute Spike

Mass Spectrometer Record Number	Date of Mass Spectrometer Run	Laboratory Record Book Reference	Concentration of Spike in μgms Rb/ml	Analyst(s)*	Remarks
2943(I)	12/21/62	#10, p.39	1.236	CCS, WHP	Made with M.I.T. Rb Shelf Solution containing 12.23 μgms Rb/ml
2948(I)	12/21/62	#10, p.39	1.222	CCS, WHP, HWF	"
2954(L)	12/21/62	#10, p.39	1.204	CCS, WHP, HWF	"
2957(L)	1/8/63	#10, p.39	1.201	CCS, WHP, HWF	"
3191(S)	6/14/63	#11, p.36	1.249	WHP	"
3222(S)	6/27/63	#11, p.36	1.278	WHP	"
3314(L)	8/11/63	#11, p.46	1.255	CCS, WHP	"
3391(L).	11/18/63	#11, p.59	1.277	WHP	"
3393(L)	11/19/63	#11, p.59	1.269	WHP	"
3428(L)	12/16/63	#11, p.59	1.250	WHP	"
3626(L)	3/25/64	#12, p.30	1.212	WHP, TK	"
3627(I)	3/25/64	#12, p.30	1.209	WHP, TK	"

(continued)

Table 3.31 (continued)

Summary of Spike Calibration Runs on Rb^{87} Dilute Spike

Mass Spectrometer Record Number	Date of Mass Spectrometer Run	Laboratory Record Book Reference	Concentration of Spike in μgms Rb/ml	Analyst(s)*	Remarks
3663(L)	4/14/64	#12, p.39	1.238	WHP	($CaCO_3$+RbCl) standard (A)
3724(S)	5/13/64	#12, p.39	1.241	WHP, RMS	($CaCO_3$+RbCl) standard (C)
3639(L)	4/3/64	#12, p.39	1.221	RHM, RHR, WHP	(Dunite+RbCl) standard
3675(L)	4/20/64	#12, p.39	1.221	RHM, RHR, WHP	(Dunite+RbCl) standard
3676(S)	4/21/64	#12, p.39	1.238	RHM, RHR, WHP	(SiO_2+RbCl) standard
3653(L)	4/10/64	#12, p.39	1.224	RHM, RHR, WHP	(SiO_2+RbCl) standard
3804(L)	6/22/64	#12, p.68	--	WHP, RMS	calibration of Bruderheim chondrite with New Rb^{87} Spike
3814(L)	6/30/64	#12, p.68	--	WHP, RMS	
3714(S)	5/9/64	#12, p.31	1.212	WHP, RMS	calibration of Rb^{87} Dilute Spike with Bruderheim chondrite
3753(S)	5/27/64	#12, p.31	1.208	WHP, RMS	
3784(L)	6/10/64	#12, p.31	1.210	WHP, RMs	

Average = 1.232 μgms Rb/ml
σ = .005
$\bar{E}$ = .4%   Total Spread = 6.3%

* WHP = W. H. Pinson
CCS = C. C. Schnetzler
HWF = H. W. Fairbairn
TK = T. Krogh
RMS = R. M. Shields
RHM = R. H. McNutt
RHR = R. H. Reeseman

This number has been used in the Rb calculations in this thesis.

3.32 - New Rb^{87} Spike ($\sim$2.7 μgm Rb/ml)

This spike was used just at the end of this thesis investigation to help calibrate the *Rb^{87} Dilute Spike* ($\sim$1.26 μgm Rb/ml). The *Rb^{87} Dilute Spike* became exhausted in June 1964; all subsequent Rb determinations are thus being made with this *New Rb^{87} Spike* ($\sim$2.7 μgm Rb/ml). The preparation and history of this *New Rb^{87} Spike* are discussed in Laboratory Record Book #12, p. 41 and in Pinson (1962, 96). It was prepared from the *Rb^{87} Waste Spike Solution* containing 26.94 μgm Rb/ml. 200 ml of the 26.94 μgm Rb/ml *Rb^{87} Waste Spike* were diluted up to 2000 ml (R.B. #12, p. 41) on April 3, 1964 to produce this *New Rb^{87} Spike* with $\sim$2.7 μgm Rb/ml.

The isotopic composition of the *New Rb^{87} Spike* has been determined in four mass spectrometer analyses. The first three analyses were made on the *Rb^{87} Waste Spike* (Pinson, 1962, 96, Table 17), and the fourth was made by Roe on the *New Rb^{87} Spike* after dilution. The results are listed in Table 3.32a.

The concentration of this spike has been determined

TABLE 3.32a

ISOTOPE RATIO ANALYSES OF NEW Rb^{87} SPIKE

Date	Mass Spectrometer Record Number	Atomic % Rb^{85}	Atomic % Rb^{87}	Analyst
8/12/62	2635(L)	3.02	96.98	Bottino
9/13/62	2725(S)	3.05	96.95	Bottino
7/28/62	2773(S)	2.89	97.11	Bottino
5/9/64	2716(L)	2.964	97.036	Roe
	Average =	2.98	97.02	

in a series of spike calibration runs. All calibrations on this spike as of 7/25/64 are listed in Table 3.32b.

3.33 - Rb^{85}/Rb^{87} Ratio

An article (Shields *et al.*, 1963) was recently published in the *Journal of Geophysical Research* recommending a new Rb^{85}/Rb^{87} ratio of 2.5991 for natural Rb. The results in this thesis have been calculated using the commonly accepted value of 2.590 for the Rb^{85}/Rb^{87} ratio. Interestingly enough, changing the Rb^{85}/Rb^{87} ratio from 2.590 to 2.5991 does not affect the calculations of Rb concentration, since the changes are compensatory and essentially cancel each other out.

To start with, one calculates the Rb concentration of the shelf solution using the new Rb^{85}/Rb^{87} ratio. The following formula can easily be derived for calculating the atomic weight of Rb from the Rb^{85}/Rb^{87} ratio:

$$\text{Atomic weight} = \frac{85A+87}{A+1} \qquad 3.33a$$

where $A = Rb^{85}/Rb^{87}$ ratio. Changing A from 2.59 to 2.5991 results in changing the atomic weight from 85.5571 to 85.5556 or only .002%. The calculation of the concentration of the shelf solution is, therefore,

Table 3.32b

Spike Calibration Runs on New Rb^{87} Spike

Date of Mass Spectrometer Run	Mass Spectrometer Record Number	Laboratory Record Book Reference	Conc. in μgms Rb/ml	Analysts	Remarks
5/1/64	3697(L)	#12, p.41	2.773	Pinson, Roe	M.I.T. Rb Shelf Solution with 12.23 μgms Rb/ml
5/18/64	3733(L)	#12, p.41	2.767	Pinson, Roe	"
5/2/64	3701(L)	#12, p.41	2.719	Pinson, Roe	"
5/3/64	3704(L)	#12, p.41	2.764	Pinson, Roe	"
5/21/64	3742(L)	#12, p.41	2.777		
6/14/64	3798(L)	#12, p.65	2.665	Pinson, Shields	"
6/12/64	3791(L)	#12, p.65	2.658	Pinson, Shields	"
6/12/64	3789(L)	#12, p.65	2.754	Pinson, Shields	Shields' Rb Shelf Solution with 71.3 μgms Rb/ml
6/14/64	3796(L)	#12, p.65	2.686	Pinson, Shields	"
7/10/64	3834(L)	#12, p.74	2.678	Pinson, Shields	"
7/15/64	3848(L)	#12, p.74	2.710	Pinson, Shields	"

Average = 2.723 μgms Rb/ml
σ = .014
E = .5% Total Spread = 4.4%

effectively unchanged.

Next, this shelf solution is used to determine the concentration of a spike solution. The familiar equation used to calculate the N/S ratio in a sample consisting of a mixture of spike and shelf solutions is:

$$\left(\frac{85}{87}\right)_m = \frac{.7215N + .0175S}{.2785N + .9825S} \qquad 3.33b$$

where:

$\left(\frac{85}{87}\right)_m$ = resultant $\frac{Rb^{85}}{Rb^{87}}$ ratio measured on the mass spectrometer,

N = number of atoms of normal Rb in sample,

S = number of atoms of spike Rb in sample.

Rewriting this equation in terms of A gives:

$$\left(\frac{85}{87}\right)_m = \frac{\left(\frac{A}{A+1}\right)N + .0175S}{\left(\frac{1}{A+1}\right)N + .9825S}$$

Solving this equation for N/S we get:

$$\frac{N}{S} = \frac{.0175 - .9825\left(\frac{85}{87}\right)_m}{\left[\dfrac{\left(\frac{85}{87}\right)_m - A}{(A+1)}\right]} \qquad 3.33c$$

Multiplying the right-hand side of this equation by the weight factor and solving for S gives:

$$S = \frac{N_{shelf}}{\left[\dfrac{.0175 - .9825\left(\frac{85}{87}\right)_m}{\left(\dfrac{\left(\frac{85}{87}\right)_m - A}{(A+1)}\right)}\right](\text{weight factor})}$$

where S is the number of μgms of Rb spike added to the sample and N_{shelf} is the Rb concentration in the shelf solution. S, of course, equals the concentration of the spike times the number of ml of spike added to the sample:

$$S = (S_{conc.})(\text{ml. of spike added}).$$

Therefore,

$$S_{conc.} = \frac{N_{shelf}}{\left[\dfrac{.0175 - .9825\left(\frac{85}{87}\right)_m}{\left(\dfrac{\left(\frac{85}{87}\right)_m - A}{(A+1)}\right)}\right](\text{weight factor})(\text{ml. spike added})}, \qquad 3.33d$$

To determine the concentration of normal Rb in a sample, equation 3.33c is also used, but this time it is solved for N.

$$N_{sample} = \left[\frac{.0175 - .9825\left(\frac{85}{87}\right)_n}{\left(\frac{\left(\frac{85}{87}\right)_n - A}{(A+1)}\right)} \right] (\text{weight factor})(\text{ml spike added})_2(S_{conc.}) \qquad 3.33e$$

where $(85/87)_n$ is another Rb^{85}/Rb^{87} ratio measured on the mass spectrometer and N_{sample} is the number of μgms of normal Rb in the sample. It can be seen from equations 3.33d and e that the concentration of Rb in a sample (N_{sample}) is effectively related to the concentration of Rb in the shelf solution (N_{shelf}) via the spike solution.

We are interested in observing the effect on isotope dilution analyses of changing the Rb^{85}/Rb^{87} ratio from 2.590 to 2.5991. We have already shown that this change does not significantly affect the atomic weight of Rb or the shelf solution concentratiion, N_{shelf}. Let us substitute equation 3.33d into equation 3.33e. The weight factor terms and the (A+1) terms cancel out immediately. The only term left in the equation that is affected by such a change, therefore, is A which occurs in the factor:

$$\frac{\left(\frac{85}{87}\right)_m - A}{\left(\frac{85}{87}\right)_n - A}$$

In isotope dilution analyses errors are minimized by spiking samples so that the resultant N/S ratio occurs where the slope of equation 3.33b equals -1, plotting $\frac{85}{87}$ versus N/S. This means that all Rb analyses should have approximately the same N/S ratio and, therefore, similar $(85/87)_{\text{measured}}$ ratios. Thus, the factor:

$$\frac{\left(\frac{85}{87}\right)_m - A}{\left(\frac{85}{87}\right)_n - A}$$

reduces essentially to one. It can be seen, therefore, that switching to the new value of 2.5991 for the Rb^{85}/Rb^{87} ratio does not significantly affect the Rb concentrations calculated from the Rb isotope dilution analyses.

In using this Rb concentration to calculate the Rb^{87}/Sr^{86} ratio, however, the difference between these two Rb^{85}/Rb^{87} values does introduce a change in the final Rb^{87}/Sr^{86} ratio. Yet, this change amounts to only .34%. The commonly accepted value of 2.590 has been used in this thesis pending further substantiation of the new 2.5991 ratio.

3.4 - Strontium Spikes

3.41 - Sr^{86} Dilute Spike (∼2.2 μgm Sr/ml)

The Bjurböle whole meteorite analyses and the Bjurböle matrix analyses were made with the Sr^{86} Dilute Spike. The history of this spike solution is given in Pinson (1962, 92-95) and in Laboratory Record Book #11, p. 44. The isotopic composition of this spike was determined from four mass spectrometer analyses which are listed in Pinson (1962, 94, Table 6). The average of these four analyses yields an isotopic composition as follows:

0.05%	84
83.73%	86
9.48%	87
6.74%	88

The concentration of this Sr^{86} Dilute Spike has been determined from an average of seven spike calibration runs listed in Table 3.41.

3.42 - Sr^{84}-Sr^{86} Double Spike (∿1.05 µgm Sr/ml)

In the fall of 1963, a new strontium spike enriched in both Sr^{84} and Sr^{86} was introduced to replace the Sr^{86} Dilute Spike (∿2.2 µgm Sr/ml). This new double spike has an added advantage in that mass spectrometer discrimination can be corrected for in a Sr isotope dilution analysis. The techniques and equations which have recently been developed to correct for mass spectrometer discrimination are discussed in Krogh (1964). The preparation of this spike is discussed in Laboratory Record Book #11, p. 64. With the introduction of this new Sr spike, a truly remarkable precision has been achieved in Sr isotope dilution analyses.

Two calibration runs have so far been made on this spike to determine its concentration. Table 3.42a lists the data from these two runs.

The isotopic composition of this spike has been determined from three mass spectrometer analyses as given in Table 3.42b.

TABLE 3.41

SPIKE CALIBRATION RUNS ON Sr^{86} DILUTE SPIKE

(All made with MIT Sr Shelf Solution containing 7.42 μgms Sr per ml)

Mass Spectrometer Record Number	Date of Mass Spectrometer Run	Lab Record Book Reference	Conc. in μgms Sr/ml	Analysts
2935(I)	12/13/62	#10, p.39	2.176	Pinson, Schnetzler
2939(I)	12/16/62	#10, p.39	2.182	Pinson, Schnetzler
2940(I)	12/18/62	#10, p.39	2.179	Pinson, Schnetzler
3189(S)	6/13/63	#11, p.36	2.168	Pinson, Shields
3215(S)	6/25/63	#11, p.36	2.174	Pinson, Shields
3379(S)	11/8/63	#11, p.56	2.173	Pinson, McNutt, Krogh
3383(L)	11/12/63	#11, p.56	2.199	Pinson, McNutt, Krogh

Average = 2.176 μgms Sr/ml

$\overline{\sigma}$ = .004

$\overline{E}$ = .18%

Total Spread = 1.4%

TABLE 3.42a

SPIKE CALIBRATION RUNS ON Sr^{84}-Sr^{86} DOUBLE SPIKE

Mass Spectrometer Record Number	Date of Mass Spectrometer Run	Sr^{86}/Sr^{88} Measured	Sr^{86}/Sr^{88} Corrected	Sr^{84}/Sr^{88} Measured	Sr^{84}/Sr^{88} Corrected	Concentration in μgms Sr/ml
3414(S)	12/9/63	.3748	.37595	.1418	.1427	1.0505
3415(L)	12/9/63	.3769	.3756	.1435	.1425	1.0495
					Average =	1.050 μgms Sr/ml

TABLE 3.42b

ISOTOPE RATIO ANALYSES ON Sr^{84}-Sr^{86} DOUBLE SPIKE

Mass Spectrometer Record Number	Date of Mass Spectrometer Run	84 atom %	86 atom %	87 atom %	88 atom %
3424(S)	12/13/63	25.53	50.36	6.95	17.16
3427(L)	12/14/63	25.78	50.41	6.91	16.90
3488(S)	1/30/64	25.68	50.33	6.92	17.06
	Averages =	25.66	50.37	6.93	17.04

These percentage abundances have subsequently been slightly adjusted by Krogh (1964) in the following manner. A plot of 84/88 versus 86/88 was constructed. Normal Sr (with Sr^{84}/Sr^{88} = .0068 and Sr^{86}/Sr^{88} = .1194) was then plotted. Each of the three spike analyses above and two blank analyses (3499(L), 2/6/64; 3528(S), 2/19/64) made at approximately the same time were also plotted. A series of 5 lines were then drawn from normal strontium to each of the 5 spike and blank analyses. The average slope of these 5 lines was then calculated and drawn. Each of the three isotope ratio analyses of the spike was then adjusted back to this line of average slope. The average of these three corrected spike analyses was then determined as:

25.71	atom	%	84
50.36	"	%	86
6.906	"	%	87
17.021	"	%	88

3.43 - Calculation of Sr^{87}/Sr^{86} Ratio in Original Sample from Sr Isotope Dilution Analysis

Since Sr isotope dilution analyses can now be corrected for mass spectrometer discrimination one has another means of obtaining an accurate value for the

Sr^{87}/Sr^{86} ratio of a sample. This approach of calculating the Sr^{87}/Sr^{86} ratio from the corrected isotope dilution analysis is especially important for samples which are strongly depleted in Sr. The derivation of the equation to calculate the Sr^{87}/Sr^{86} ratio in a spiked sample is given below.

The number of Sr^{87} atoms in a spiked sample is equal to the number of Sr^{87} atoms contributed by spike Sr plus the number contributed by normal Sr plus the number of radiogenic Sr^{87} atoms. It should be clearly stated at the start that normal strontium is initial Sr or non-radiogenic Sr. Thus:

$$(87) = AN + BS + Sr^{87*} \qquad 3.43a$$

where: (87) = total number of 87 atoms in the spiked sample

Sr^{87*} = number of radiogenic Sr^{87} atoms

N = number of atoms of normal Sr in the spiked sample

S = number of atoms of spike Sr in the spiked sample

A = fraction of Sr^{87} atoms in normal Sr

B = fraction of Sr^{87} atoms in spike Sr

Substituting fractional abundances of Sr^{87} in spike and normal meteorite Sr into equation 3.43a, we get:

$$(87) = .0689N + .06906S + Sr^{87*} \tag{3.43b}$$

Similarly for Sr^{86} atoms in the spiked sample:

$$(86) = CN + DS \tag{3.43c}$$

where

(86) = total number of Sr^{86} atoms in the spiked sample

C = fraction of Sr^{86} atoms in normal Sr

D = fraction of Sr^{86} atoms in spike Sr

Substituting in values for C and D, equation 3.43c becomes:

$$(86) = .09872N + .5036S \tag{3.43d}$$

Dividing equation 3.43b by equation 3.43d gives:

$$\left(\frac{87}{86}\right)_T = \frac{.0698N + .06906S + Sr^{87*}}{.09872N + .5036S} \tag{3.43e}$$

The subscript, T, indicates that this is the "true" or corrected 87/86 ratio. The ratio measured on the mass spectrometer, $(87/86)_m$, must be corrected first for fractionation to obtain the $(87/86)_T$ ratio.

An equation can also be similarly derived for the Sr^{87}/Sr^{86} ratio in the original unspiked sample:

$$(87) = .0689N + Sr^{87*} \qquad 3.43f$$

$$(86) = .09872N \qquad 3.43g$$

since there is no contribution from the spike in this case. Again, dividing equation 3.43f by equation 3.43g we get:

$$\left(\frac{87}{86}\right)_{sample} = \frac{.0689N + Sr^{87*}}{.09872N} \qquad 3.43h$$

Since one is interested in calculating the $(87/86)_{sample}$, equation 3.43e is solved for Sr^{87*} and substituted into equation 3.43h. After simplifying, the following equation is obtained for calculating the Sr^{87}/Sr^{86} ratio in a sample from the Sr isotope dilution analysis:

$$\left(\frac{Sr^{87}}{Sr^{86}}\right)_{sample} = \frac{\left(\frac{87}{86}\right)_T(.09872)\left(\frac{N}{S}\right)_T + (.5036)\left(\frac{87}{86}\right)_T - .06906}{(.09872)\left(\frac{N}{S}\right)_T} \qquad 3.43i$$

where the subscript T refers to the corrected or "true" value of the quantity (i.e., after correction for mass spectrometer discrimination).

Briefly, the $(87/86)_T$ and $(N/S)_T$ ratios are obtained as follows: The measured Sr^{86}/Sr^{88} and Sr^{84}/Sr^{88} ratios are first corrected for machine discrimination (as described in Krogh, 1964). The $(Sr^{86}/Sr^{88})_T$ ratio is then divided into the $(Sr^{86}/Sr^{88})_m$ ratio to obtain the percentage fractionation. One takes ½ of this percentage fractionation (since Sr^{87} is only half-way between Sr^{86} and Sr^{88}) and applies it to the $(Sr^{87}/Sr^{86})_{measured}$ ratio IN THE OPPOSITE DIRECTION to obtain the $(Sr^{87}/Sr^{86})_{true}$ ratio. The $(Sr^{86}/Sr^{88})_{true}$ ratio is then also used in the following familiar equation to calculate the $(N/S)_T$ ratio:

$$\left(\frac{N}{S}\right)_T = \frac{.5036 - .17021\left(\frac{86}{88}\right)_T}{\left(\frac{86}{88}\right)_T(.82676) - .09872}$$

Sr^{87}/Sr^{86} ratios were calculated in the above manner for a number of the meteorites analyzed in this thesis. A comparison between calculated Sr^{87}/Sr^{86} and measured Sr^{87}/Sr^{86} ratios for Pasamonte, Bruderheim and Bath is shown in Table 3.43. Everything considered, the agreement is surprisingly good. It should be emphasized, however, that only the measured Sr^{87}/Sr^{86} ratios were used for the isochron.

TABLE 3.43

COMPARISON OF MEASURED Sr^{87}/Sr^{86} WITH CALCULATED Sr^{87}/Sr^{86}

Meteorite	$\left(\frac{Sr^{87}}{Sr^{86}}\right)^*$ Measured	$\left(\frac{Sr^{87}}{Sr^{86}}\right)$ Calculated
Pasamonte	.69956 .69929	.69950 (S) .69910 (S)
Bath	.74360 .74332	.7471 (L) .7428 (S)
Bruderheim	.74641 .74624	.7457 (S) (.7449)† (S) (.7470) (S)

* normalized to Sr^{86}/Sr^{88} = .1194

† same sample run twice

(S) = Mass Spectrometer named Sally

(L) = Mass Spectrometer named Lulu

CHAPTER IV

COMPUTER PROGRAMS

4.1 - Introduction

Arithmetical calculations made by hand are frequently error-prone and often quite time consuming. Accordingly, two computer programs have been written to aid in certain of the routine calculations made at the M.I.T. Geochronology Laboratory. The first program computes a least squares isochron from the Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios following the method set forth in Youden (1951). The second program computes the Rb^{87}/Sr^{86} ratios for a series of samples from the measured Rb^{85}/Rb^{87} and $(Sr^{86}/Sr^{88})_T$ ratios obtained in the Rb and Sr isotope dilution analyses.

These programs have been written in Fortran II for the IBM 7094 digital computer at the M.I.T. Computation Center. It should be emphasized at the start that M.I.T. personnel who wish to use these programs must file an application for computer time at the Computation Center. The Computation Center makes no charge for the use of any of its facilities, but all publications which include work done on the computer must contain an acknowledgement to the Computation Center. The Computation Center should also receive a reprint or abstract of any such publication.

4.2 - A Computer Program to Calculate a Least Squares Isochron and Associated Errors

4.21 - Introduction

The essential features of this program have already been discussed in Shields (1963a), but the program has been somewhat modified since then. Instead of using the Rb/Sr weight ratios as input, the program now uses the Rb^{87}/Sr^{86} ratios as input. This makes the program simpler, more widely applicable, and not subject to changes each time new values for the isotopic ratios of Rb and Sr are introduced.

A copy of the program is shown in Figure 4.21a. A sample copy of the output from this program is shown in Figure 4.21b. The only information which is submitted as data to the program is the value of the decay constant, the number of samples, the normalized Sr^{87}/Sr^{86} ratios and the Rb^{87}/Sr^{86} ratios. All slopes, intercepts, ages and errors are computed by the program.

4.22 - What the Program Computes

This section summarizes the various quantities calculated in the program. First, the following summations are computed:

$$\sum\left(\frac{Sr^{87}}{Sr^{86}}\right), \sum\left(\frac{Rb^{87}}{Sr^{86}}\right), \sum\left(\frac{Sr^{87}}{Sr^{86}}\right)^2, \sum\left(\frac{Rb^{87}}{Sr^{86}}\right)^2, \sum\left(\frac{Rb^{87}}{Sr^{86}}\right)\left(\frac{Sr^{87}}{Sr^{86}}\right)$$

Figure 4.21a

FORTRAN II LEAST SQUARES ISOCHRON PROGRAM

```
*M3226-1585,FMS,RESULT,1,1,500,250                  ROBERT M. SHIELDS
*     XEQ
*     LABEL
CISOCH
C     PROGRAM TO COMPUTE ISOCHRON BY LEAST SQUARES FROM RB87/SR86 RATIOS
      DIMENSION SRIR(500), RB7SR6(500), DUMMY(8), SNAME(500,7)
    8 READ 10, DLAMDA, N, (DUMMY(I), I=1,7), (SRIR(I), RB7SR6(I), (SNAME
     1(I,J), J=1,7), I=1,N)
   10 FORMAT (E10.4,7X,I3,9X,7A6/(2F15.7,7A6))
      AN=N
      SRIRT=0.
      RBSRT=0.
      PRODT=0.
      ASQSUM=0.
      BSQSUM=0.
      DO 40 I=1,N
      SRIRT=SRIRT+SRIR(I)
      RBSRT=RBSRT+RB7SR6(I)
      PRODT=PRODT+(SRIR(I)*RB7SR6(I))
      ASQSUM=ASQSUM+(RB7SR6(I)**2)
      BSQSUM=BSQSUM+(SRIR(I)**2)
   40 CONTINUE
      ASLOPE=((AN*PRODT)-(RBSRT*SRIRT))/((AN*ASQSUM)-(RBSRT**2))
      AINTCT=(SRIRT/AN)-(ASLOPE*RBSRT/AN)
      AGE=(LOGF(ASLOPE+1.))/DLAMDA
      SSQRD=(BSQSUM-(SRIRT**2/AN)-(ASLOPE*((AN*PRODT)-(SRIRT*RBSRT))/AN)
     1)/(AN-2.)
      AS=SQRTF(SSQRD)
      DEVSLP=SQRTF(SSQRD/(ASQSUM-(RBSRT**2/AN)))
      DEVINT=SQRTF((DEVSLP**2)*ASQSUM/AN)
      DLTAGE=(DEVSLP)/(DLAMDA*(ASLOPE+1.))
      AEBARS=(100.*DEVSLP/ASLOPE)
      AEBARI=(100.*DEVINT/AINTCT)
C     COMPUTE SLOPE AND INTERCEPT WITH AXES REVERSED - INDICATED BY PREFIX B
      BSLOPE=((AN*PRODT)-(RBSRT*SRIRT))/((AN*BSQSUM)-(SRIRT**2))
      BCOTAN=(1./BSLOPE)
      BINTCT=(RBSRT/AN)-(BSLOPE*SRIRT/AN)
      BSRIRO=-BINTCT/BSLOPE
      BAGE=LOGF((1./BSLOPE)+1.)/DLAMDA
      BSSQRD=(ASQSUM-(RBSRT**2/AN)-(BSLOPE*((AN*PRODT)-(RBSRT*SRIRT))/AN
     1))/(AN-2.)
      BS=SQRTF(BSSQRD)
      BDVSLP=SQRTF(BSSQRD/(BSQSUM-(SRIRT**2/AN)))
      BDVCOT=(BDVSLP/(BSLOPE**2))
      DTBAGE=BDVSLP/(BSLOPE*DLAMDA*(1.+BSLOPE))
      BEBARS=(100.*BDVSLP/BSLOPE)
      PRINT 70, (DUMMY(I), I=1,7), DLAMDA, N, ASLOPE, DEVSLP, AEBARS, AI
     1NTCT, DEVINT, AEBARI, AS, AGE, DLTAGE
   70 FORMAT (14H1FINAL RESULTS,30X,7A6///18H DECAY CONSTANT = ,E11.5//
     121H NUMBER OF SAMPLES = ,I3///37H REGRESSION OF SR87/SR86 ON RB87/
     2SR86//9H SLOPE = ,F11.8,8X,31H STANDARD DEVIATION OF SLOPE = ,F9.7
     3,12X,16HPERCENT ERROR = ,F8.4//13H INTERCEPT = ,F11.7,4X,35H STAND
     4ARD DEVIATION OF INTERCEPT = ,F10.8,7X,16HPERCENT ERROR = ,F8.4//4
     54H STANDARD DEVIATION OF SINGLE MEASUREMENT = ,F10.8//7H AGE = ,E1
     61.5,12H YEARS +OR- ,E11.4,32H YEARS AT ONE STANDARD DEVIATION)
      PRINT 72, BCOTAN, BDVCOT, BEBARS, BSRIRO, BS, BAGE, DTBAGE
   72 FORMAT (37H-REGRESSION OF RB87/SR86 ON SR87/SR86//9H SLOPE = ,F11.
     18,8X,31H STANDARD DEVIATION OF SLOPE = ,F12.7,9X,16HPERCENT ERROR
     2= ,F8.4//13H INTERCEPT = ,F11.7//44H STANDARD DEVIATION OF SINGLE
     3MEASUREMENT = ,F11.7//7H AGE = ,E11.5,12H YEARS +OR- ,E11.4,32H YE
     4ARS AT ONE STANDARD DEVIATION)
      PRINT 75, (SRIR(I), RB7SR6(I), (SNAME(I,J), J=1,7), I=1,N)
   75 FORMAT (30H-     SRIR           RB87/SR86//(1H0F12.7,2X,F15.7,8X,7
     1A6))
      GO TO 8
      END
*     DATA
```

```
FINAL RESULTS                                    SHIELDS THESIS ISOCHRON

DECAY CONSTANT =  .13900E-10

NUMBER OF SAMPLES =   6

REGRESSION OF SR87/SR86 ON RB87/SR86

SLOPE =   .06383663          STANDARD DEVIATION OF SLOPE =  .0004742          PERCENT ERROR =    .7428

INTERCEPT =    .6982289      STANDARD DEVIATION OF INTERCEPT =  .00021755     PERCENT ERROR =    .0312

STANDARD DEVIATION OF SINGLE MEASUREMENT =  .00035607

AGE =  .44519E 10 YEARS +OR-   .3207E 08 YEARS AT ONE STANDARD DEVIATION

REGRESSION OF RB87/SR86 ON SR87/SR86

SLOPE =   .06385016          STANDARD DEVIATION OF SLOPE =     .0004649       PERCENT ERROR =    .7281

INTERCEPT =    .6982243

STANDARD DEVIATION OF SINGLE MEASUREMENT =    .0054672

AGE =  .44528E 10 YEARS +OR-   .3144E 08 YEARS AT ONE STANDARD DEVIATION

     SRIR           RB87/SR86

    .7463300        .7491000        BRUDERHEIM
    .7434600        .7116000        BATH
    .7250000        .4210700        MURRAY
    .7065000        .1325700        NAKHLA
    .6994000        .0225000        ESTHERVILLE
    .6994300        .0113000        PASAMONTE
```

Figure 4.21b

OUTPUT DATA FROM ISOCHRON PROGRAM

Using these quantities the least squares slope of the isochron is computed from the formula,

$$\text{Slope} = \frac{n\sum(xy) - \sum x \sum y}{n\sum x^2 - (\sum x)^2}$$

in which y equals Sr^{87}/Sr^{86}, x equals Rb^{87}/Sr^{86}, and n equals the number of samples. The intercept of this line, $(Sr^{87}/Sr^{86})_o$, can be found from the equation:

$$\text{Intercept} = \frac{\sum y}{n} - (\text{Slope}) \frac{\sum x}{n}$$

The age in years is then easily calculated:

$$t = \frac{1}{\lambda} \ln (\text{Slope} + 1)$$

The standard deviations, or 67% confidence limits, are also computed for the above quantities. The standard deviation of a single measurement is calculated first. The quantity of importance here is the sum of the squares of the deviations of the individual points from the least squares line. This single measurement standard deviation can be evaluated from the following equation:

$$\sigma_i = \sqrt{\frac{\dfrac{n\sum y^2 - (\sum y)^2}{n} - \dfrac{(n\sum xy - \sum x \sum y)}{n\sum x^2 - (\sum x)^2}}{(n-2)}}$$

σ_i can then be used to calculate the standard deviations of the slope and intercept as follows:

$$\sigma_{slope} = \frac{\sigma_i}{\sqrt{\sum x^2 - n\bar{x}^2}} \quad , \quad \sigma_{intercept} = \sigma_i \sqrt{\frac{\sum x^2}{n\sum x^2 - (\sum x)^2}}$$

The percentage errors at one standard deviation, E, are also of interest. These errors are calculated as follows:

$$E_{slope} = \frac{100\,(\sigma_{slope})}{slope} \quad , \quad E_{intercept} = \frac{100\,(\sigma_{intercept})}{Intercept}$$

Finally, the error in the age (expressed in years) is computed from the derivative of the age equation:

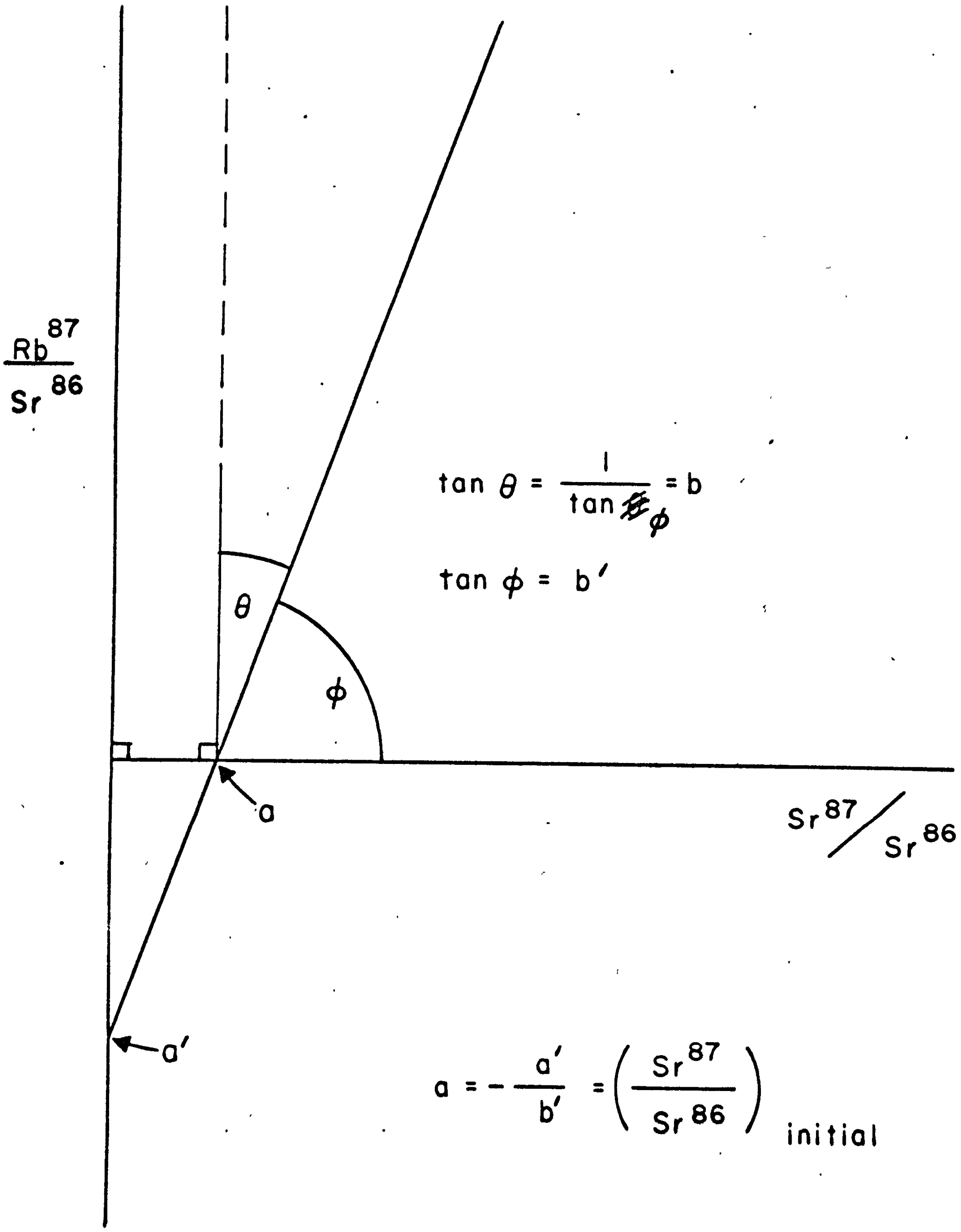
$$\frac{dt}{d(slope)} = \frac{1}{\lambda(slope+1)}$$

All calculations discussed above are then repeated with the Rb^{87}/Sr^{86} ratio plotted on the y-axis (see Figure 4.22a). A variation which occurs in this case is that the slope of interest, b, is the reciprocal of the slope, b', which is calculated. Also, the intercept of the line occurs on the Rb^{87}/Sr^{86} axis. Thus, the following conversion formula is used to obtain the Sr^{87}/Sr^{86} initial ratio (refer to Figure 4.22a):

$$a = -\frac{a'}{b'}$$

Figure 4.22a

Regression of Rb^{87}/Sr^{86} on Sr^{87}/Sr^{86}



No errors have been calculated for the intercept in this second case because the error on the Rb^{87}/Sr^{86} axis is not truly representative of the error on the Sr^{87}/Sr^{86} axis. The age is obtained from the reciprocal of the slope; and thus, the age equation takes the form:

$$t = \frac{1}{\lambda} \ln \left(\frac{1}{\text{slope}} + 1 \right)$$

The error in the age can be determined from:

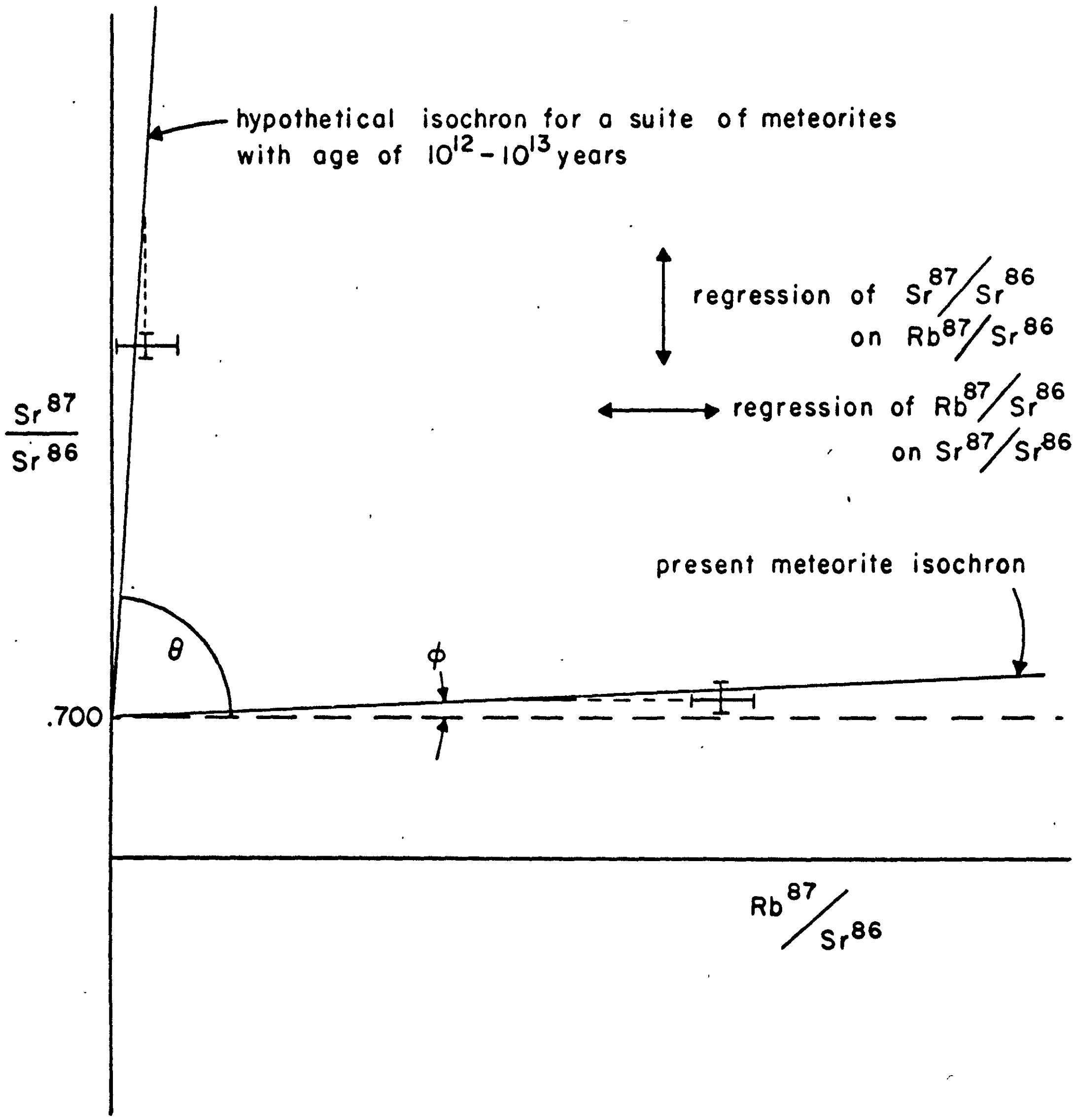
$$\frac{dt}{d(\text{slope})} = \frac{-\frac{1}{(\text{slope})^2}}{\lambda \left(\frac{1}{\text{slope}} + 1 \right)}$$

Two final points should be mentioned before concluding this section. First, the errors calculated for a least squares line by the methods outlined in Youden (1951, 41-43) should be taken lightly when applied to an isochron such as the one in this thesis. A meteorite isochron has the steepest slope of any suite of samples which will probably be dated (at least in the forseeable future); and yet, when plotted to true scale the isochron is nearly horizontal. The standard deviation of both the slope, σ_{slope}, and the intercept, $\sigma_{\text{intercept}}$, of this isochron are calculated from the standard deviation of a single measurement, σ_i .

This σ_i is in turn calculated from the squares of the distances of the individual points from the least squares isochron line, and does not take into account the analyst's estimate of individual analytical precision errors (error bars in Figure 6.3a). In the case of the regression of Sr^{87}/Sr^{86} on Rb^{87}/Sr^{86} (the first case discussed), these distances are measured almost perpendicular to the isochron (see Figure 4.22b). In the second case, the distances of the individual points from the least squares isochron line are measured in a direction almost parallel to the isochron and thus are considerably larger. Thus, σ_i will have a tendency to be larger in the case of the regression of Rb^{87}/Sr^{86} on Sr^{87}/Sr^{86} (which fortunately is the case for us). However, if one was to obtain a second suite of meteorites identical to this present set, analyzed with the same analytical precision, and differing only in having an age of 10^{12}-10^{13} years so that the slope of the isochron approached 90°, (see Figure 4.22b), then σ_i in the first case (regression of Sr^{87}/Sr^{86} on Rb^{87}/Sr^{86}) would be larger and σ_i in the second case would be smaller; the major error would then be credited to the Sr^{87}/Sr^{86} measurements. What this means, therefore, is that these errors are to some extent merely a function of the age of the sample!

Figure 4.22 b

Schematic Diagram of the Effect of Age on Error



Second, the question naturally arises as to which of these 2 lines is more appropriate. The answer to this question is left to the judgement of the individual reader and, of course, depends upon the problem at hand. It is important that the analyst decide which quantity contains the most error. In Rb-Sr work at the M.I.T. Geochronology Laboratory the Rb^{87}/Sr^{86} ratios usually have considerably more error associated with them than the Sr^{87}/Sr^{86} ratios. Thus, instead of averaging these two lines, it may be more appropriate in this case to use the second isochron - the regression of Rb^{87}/Sr^{86} on Sr^{87}/Sr^{86}. In this thesis, however, the difference is insignificant.

4.23 - How to Use the Program

The FORTRAN II program in Figure 4.21a should be punched out on standard IBM cards - one line to a card. Utmost care should be taken that each letter, number, and special character is in the proper column. Addition or omission of even a blank space could result in failure of the program to translate.

This FORTRAN II source deck is then submitted to the computer, and a second deck containing a translation of the source program into binary machine language is obtained. This binary deck should then be run through the IBM 557 Alphabetic Interpreter with the "73-80" board installed. This will label and number each card to avoid scrambling the deck. Each time thereafter that a run is submitted to the computer this binary deck is used - <u>without alteration</u> - together with the data cards pertaining to the specific problem at hand. The amount of time required to execute an average run with this binary deck is about 2 seconds.

The order of the cards in the deck when submitting a run with the binary deck must be as follows:

* I.D. card
* XEQ card
Binary deck
* DATA card
Data cards

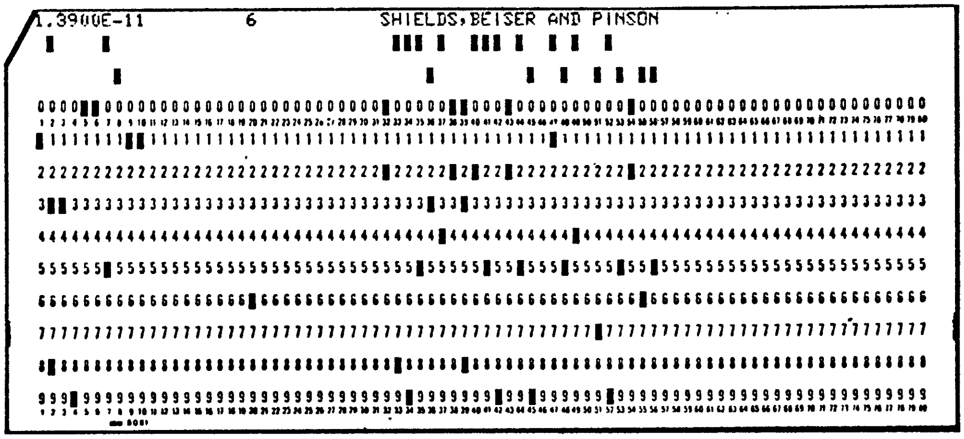
The *I.D. card is an identification card whose format varies depending upon the specific institution and computer to be used. At the M.I.T. Computation Center the format for the IBM 7094 is as shown in the first line of the FORTRAN II program in Figure 4.21a. A * must be placed in column 1, followed by the problem number (in this case M3226). A minus sign is punched next, followed by the programmer's number (in this case 1585). The rest of the data on this card can be copied without alteration. No blank spaces should be left between any of this information. In the I.D. card the computer disregards all information to the right of the first blank space. Thus, the user may fill out the rest of the I.D. card (after at least one blank space has been left) with other labeling information of his own choosing, as shown in Figure 4.21a.

The * XEQ card follows the * I.D. card and must contain a * in column 1 and the letters XEQ in columns 7 through 9. Nothing else should appear on this card. The binary deck follows the * XEQ card. At the end of the binary deck a * DATA card must be placed. This card must contain a * in column 1 and the letters DATA in columns 7 through 10. Nothing else may be punched on this card.

The data cards follow the * DATA card. These are the only cards that are changed from one run to the next. Thus, once the deck is assembled as described in the preceding paragraphs it will never need to be altered.

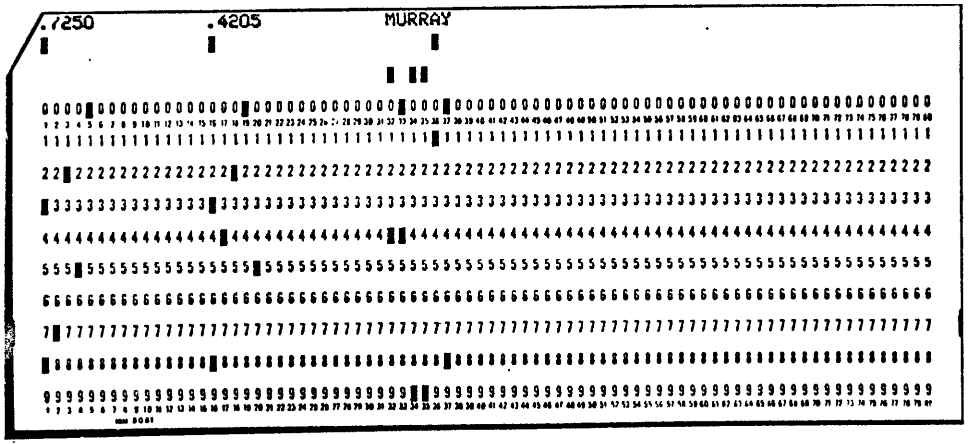
The first data card is different from all the rest. It should have the form shown in Figure 4.23a. The decay constant is punched in columns 1 through 10 as shown. The number of samples is punched next in columns 18 through 20. This number must be right adjusted so that the units digit always appears in column 20. It must not have a decimal point. If

Figure 4.23a - EXAMPLE OF FIRST DATA CARD



1.3900E-11 6 SHIELDS,BEISER AND PINSON

Figure 4.23b - EXAMPLE OF SUBSEQUENT DATA CARDS



.7250 .4205 MURRAY

there are more than 9 samples, then the tens digit appears in column 19. Columns 30 through 72 are reserved for identifying information of any kind as shown in Figure 4.23a. (and printed in line 1, Figure 4.21b).

All subsequent data cards are alike and have the form shown in Figure 4.23b. Each of these data cards represents an individual sample. The normalized Sr^{87}/Sr^{86} ratio is punched in columns 1 through 15. The Rb^{87}/Sr^{86} ratio is punched in columns 16 through 30. Each number punched in data cards 2 through n must have a decimal point in it. It is <u>not</u> necessary to fill unused columns with zeros; the computer does this automatically. In all but the first data card it is <u>not</u> necessary to place the decimal point in any special column. It <u>is</u> important, however, not to exceed the specified number of columns allowed for any given quantity. If a number should happen to exceed the specified field width, the computer will send back an error diagnostic and will not compute an answer. Columns 31 - 72 of data cards 2 through n may be filled with identifying information of any sort, such as the sample name. This will simply be stored and printed on the output page (as shown in Figure 4.21b).

An added feature of this revised isochron program is that it will calculate any desired number of isochrons in the same run. To do this the first data card is punched, as described above, in columns 18 - 20 with a number indicating how many of the samples are to be included in the first isochron plot. Another data card of the same form as the first data card is then placed after the data card which represents the last sample for the first isochron. The appropriate number of samples to be included in this second isochron is again punched in columns 18 - 20 and is then followed by the data cards representing the individual samples of this second isochron. This routine may be continued indefinitely to produce n isochrons. In a recent run, the total time required to process 10 separate isochrons each containing from 3 to 28 samples a piece was 27 seconds.

Finally, the size limitations of this program should be mentioned. As presently written this program can compute an isochron for anywhere from 3 to 500 samples. It has been written in "single precision arithmetic" so that no number should contain more than 8 significant digits. Numbers larger than 8 digits will be truncated so that only the eight most significant digits are stored in the computer. Sr^{87}/Sr^{86} and Rb^{87}/Sr^{86} ratios must be less than 10,000 and 1,000,000, respectively, or the computer will send back an error diagnostic and refuse to complete the program. These ratios, furthermore, should not contain more than 7 digits to the right of the decimal point. If a number should happen to have more than seven decimal digits, the extra digits will be dropped but the program in this case will continue to operate successfully.

4.24 - Notation Used in the Program

In case it is desired to examine more closely the FORTRAN II source program in Figure 4.21a, a list of the quantities used in the program together with their FORTRAN name is given below. The FORTRAN II language sets up a series of rules which must be strictly adhered to in the naming of constants and variables. Thus, the symbols used to represent quantities in this program are different from those normally used. Every effort has been taken, however, to choose names for their mnemonic value. All names beginning with the letter A refer to the least squares line computed assuming all error occurs in the Sr^{87}/Sr^{86} ratios (regression of Sr^{87}/Sr^{86} on Rb^{87}/Sr^{86}). All variable names beginning with the letter B refer to analogous quantities computed with all error assigned to the Rb^{87}/Sr^{86} atomic ratios.

DLAMDA	Decay constant
N AN	Number of samples
SRIR	$\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ for an individual sample
SRIRT	$\sum(\mathrm{Sr}^{87}/\mathrm{Sr}^{86})$
RB7SR6	$\mathrm{Rb}^{87}/\mathrm{Sr}^{86}$ atomic ratio for an individual sample
RBSRT	$\sum(\mathrm{Rb}^{87}/\mathrm{Sr}^{86})$
PRODT	$\sum(\mathrm{Rb}^{87}/\mathrm{Sr}^{86})\ (\mathrm{Sr}^{87}/\mathrm{Sr}^{86})$
ASQSUM	$(\mathrm{Rb}^{87}/\mathrm{Sr}^{86})^2$
BSQSUM	$(\mathrm{Sr}^{87}/\mathrm{Sr}^{86})^2$
ASLOPE BSLOPE	slope of isochron
AINTCT	$(\mathrm{Sr}^{87}/\mathrm{Sr}^{86})_o$ or initial $\mathrm{Sr}^{87}/\mathrm{Sr}^{86}$ ratio
BINTCT	intercept of isochron on $\mathrm{Rb}^{87}/\mathrm{Sr}^{86}$ axis
BSRIRO	$(\mathrm{Sr}^{87}/\mathrm{Sr}^{86})_o$ with $\mathrm{Rb}^{87}/\mathrm{Sr}^{86}$ plotted on y-axis

AGE BAGE	Age of system in years
SSQRD BSSQRD	variance of single measurement
BDVCOT	standard deviation of b (see Figure 4.22a)
AS BS	standard deviation of single measurement
DEVSLP BDVSLP	standard deviation of slope
DEVINT BDVINT	standard deviation of intercept
DLTAGE DTBAGE	error in age in years computed at one standard deviation
AEBARS BEBARS	E, or error in slope computed at one standard deviation
AEBARI BEBARI	E, or error in intercept computed at one standard deviation

4.3 - A Computer Program to Calculate Rb^{87}/Sr^{86} Ratios

4.31 - Introduction

In computing an isochron it is important that all Rb^{87}/Sr^{86} ratios be calculated consistently. This program takes the isotopic ratios measured in the isotope dilution analyses (the Rb^{85}/Rb^{87} and the corrected Sr^{86}/Sr^{88} ratios) and calculates directly the Rb^{87}/Sr^{86} ratios without first calculating the elemental concentrations of Rb and Sr in ppm. This approach has some advantages in that it eliminates possible arithmetical errors and reduces round-off errors. Furthermore, it is unnecessary to know the Sr^{87}/Sr^{86} ratios, the K factors, or the Sr atomic weights for the samples to make this calculation. Only if it is desired to use the blank correction term (see equation 4.33s, Section 4.33) is a Sr^{87}/Sr^{86} ratio involved. In this case, however, it is the Sr^{87}/Sr^{86} ratio of the contaminating Sr that is used. Since this is usually not determined, a value of .709 has been incorporated into the program for the Sr^{87}/Sr^{86} ratio of the contaminating Sr. The sample weights must be included in this program only because of the presence of the blank correction term which is expressed as μgms of Rb or Sr per gram of sample. If this term were not present the weights of the samples would also be unnecessary.

A copy of this Fortran II program is shown in Figure 4.31a. The printed output from the computer appears as shown in Figure 4.31b. Essentially all that this program does is to solve equations 4.33u and 4.33v of Section 4.33 for each sample. Input data for this program consists of the average Rb and Sr blanks, the number of samples, the Sr^{87}/Sr^{86} ratios, the measured Rb^{85}/Rb^{87} ratios, the corrected Sr^{86}/Sr^{88} ratios, the number of μgms of Rb and Sr spikes added to each sample and the weights of the samples. The Sr^{87}/Sr^{86} ratios are included in this program only for completeness in the output data tabulation and as a means of identification. They are not used in the program and may be left blank on the data cards.

This program as presently compiled can be used only with the <u>Rb^{87} Dilute Spike</u> ($\sim$1.26 μgm Rb/ml) and the <u>Sr^{84}-Sr^{86} Double Spike</u> ($\sim$1.05 μgm Sr/ml). As will be shown in Section 4.33, however, it is readily converted for use with any spike desired.

For natural Rb and Sr the following isotopic ratios have been used in this program:

$$Sr^{84}/Sr^{88} = .0068$$

Figure 4.31a

FORTRAN II PROGRAM TO CALCULATE Rb^{87}/Sr^{86} RATIOS

```
*M3226-1585,FMS,RESULT,1,1,500,250              ROBERT M. SHIELDS
*      XEQ
*      LABEL
CRB590
C      PROGRAM TO COMPUTE RB87/SR86 RATIOS
       DIMENSION SRIR(500), RB7SR6(500), DUMMY(8), R8587(500), S8688T(500
     1), SRB(500), SSR(500), RUBJ(500), STRN(500), WGHT(500)
    8 READ 10, RBLNK, SBLNK, N, (DUMMY(I), I=1,7), (SRIR(I), R8587(I), S
     18688T(I), SRB(I), SSR(I), WGHT(I), I=1,N)
   10 FORMAT (2F5.4,6X,I4,10X,7A6/(3F15.7,3F10.6))
      DO 40 I=1,N
      RUBJ(I)=((.00320302*SRB(I)*(.01748-.98252*R8587(I)))/((.278551*R85
     187(I)-.721448)*WGHT(I)))-(RBLNK*.0032557)
      STRN(I)=((.0013901*SSR(I)*(.5036-S8688T(I)*.17021))/(WGHT(I)*(S868
     18T(I)-.1194)))-(SBLNK*.0011244)
      RB7SR6(I) = RUBJ(I)/STRN(I)
   40 CONTINUE
      PRINT 70, (DUMMY(I), I=1,7), RBLNK, SBLNK
   70 FORMAT (40X,7A6///61H RB85/RB87 = 2.5900    SR86/SR88 = .1194    S
     1R84/SR88 = .0068//80H-RB87 DILUTE SPIKE (1.26 UGMS/ML)          SR8
     24-SR86 DOUBLE SPIKE (1.05 UGMS/ML) //17H-RUBIDIUM BLANK  F9.6//18H
     3-STRONTIUM BLANK  F9.6//)
      PRINT 75, (SRIR(I), RB7SR6(I), R8587(I), S8688T(I), SRB(I), SSR(I)
     1, WGHT(I), I=1,N)
   75 FORMAT (96H-     SRIR        RB87/SR86     RB85/RB87    (SR86/SR88
     1)T  UGMS RB SPIKE  UGMS SR SPIKE   WEIGHT //(1H0F12.7,F15.7,5F14.7
     1))
      CALL EXIT
      END
*     DATA
```

Figure 4.31b

OUTPUT DATA FORMAT FROM Rb^{87}/Sr^{86} PROGRAM

```
                              FINAL METEORITE ISOCHRON DATA

RB85/RB87 = 2.5900    SR86/SR88 = .1194    SR84/SR88 = .0068

RB87 DILUTE SPIKE (1.26 UGMS/ML)          SR84-SR86 DOUBLE SPIKE (1.05 UGMS/ML)

RUBIDIUM BLANK    .015000

STRONTIUM BLANK    .020000

     SRIR        RB87/SR86     RB85/RB87    (SR86/SR88)T  UGMS RB SPIKE  UGMS SR SPIKE    WEIGHT

   .6994300      .0113153     1.4963800      .5169800      .0295600     26.2500000      .4097600
   .7434600      .7072705      .9937300      .5233500     1.2320000      8.4000000     1.0647500
   .7434600      .7158973     1.0508700      .4959970     1.2320000      8.4000000     1.1596800
   .7463300      .7566071     1.0953500      .4905550     1.2320000      8.4000000     1.0958600
   .7463300      .7443859     1.0375000      .5160800     1.2320000      8.4000000      .9997200
   .7463300      .7388557     1.0364000      .5141560     1.2320000      8.4000000      .9997200
   .7452800      .7499519     1.8323000      .5664200      .3696000     10.5000000      .8987800
   .7452800      .7617562     1.9180000      .5125700      .3696000     10.5000000     1.0473000
   .7421100      .7873704     1.1613700      .5036700     1.1088000      8.4000000      .9520500
   .7421100      .7968650     1.1179700      .5312200     1.1088000      8.4000000      .8719500
   .7352300     1.2850382     1.8447200      .9158800      .1478400      5.2500000      .0129000
   .7352300     1.2823578     1.9365300      .8155500      .1478400      5.2500000      .0154500
```

$$Sr^{86}/Sr^{88} = .1194$$

$$Rb^{85}/Rb^{87} = 2.59$$

Again, the size limits of this program should be mentioned. Rb^{87}/Sr^{86} ratios for anywhere from 1 to 500 samples can be computed at one time with this program. The Rb and Sr blank terms must either be zero or lie between the following limits:

$$.0001 < \mu gms/gm < .9999$$

The limitations already discussed in Section 4.23 also hold for the Sr^{87}/Sr^{86}, Rb^{85}/Rb^{87}, and Sr^{86}/Sr^{88} ratios with the added restrictions that the Rb^{85}/Rb^{87} and Sr^{86}/Sr^{88} ratios must be less than 10^5. The number of μgms of Rb and Sr spikes added and the sample weights must be expressed in numbers smaller than 1,000 and not have more than 6 digits to the right of the decimal point. Again, this program can also be easily altered.

4.32 - How to Use the Program

The use of this program is practically the same as that described for the isochron program in Section 4.23. The only difference occurs in the format of the data cards. The format for the first data card is shown in Figure 4.32a. The Rb contamination in units of μgms per gram of sample is punched in columns 1-5. The Sr contamination is punched in columns 6-10. If either or both of these quantities is zero or insignificant,

Figure 4.32a - EXAMPLE OF FIRST DATA CARD

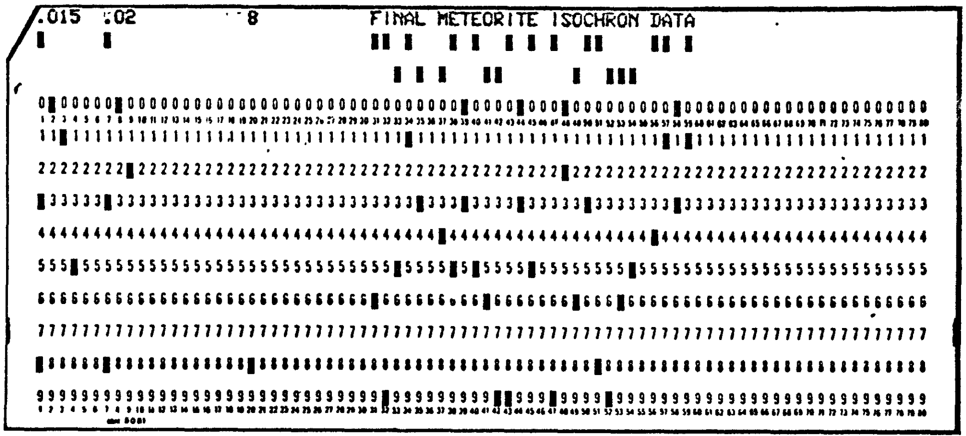
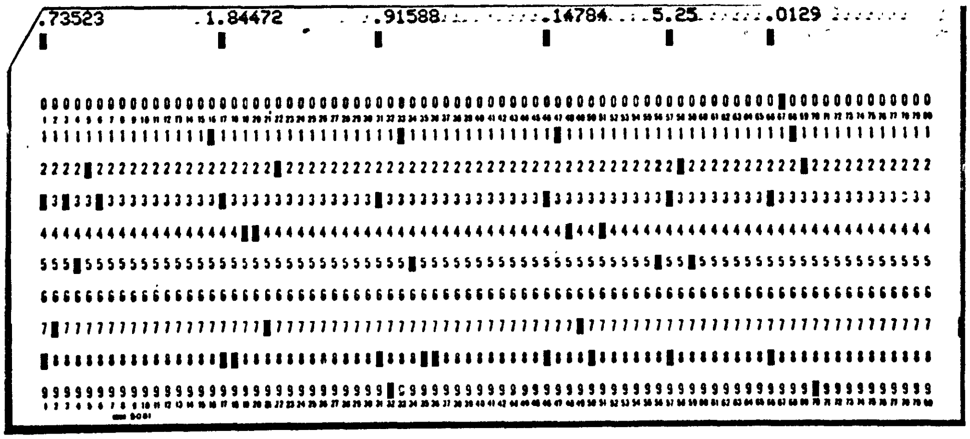


Figure 4.32b - EXAMPLE OF SUBSEQUENT DATA CARDS



these two fields may be left blank. Each of these numbers must, however, contain a decimal point. The number of samples to be computed is punched in columns 17-20. This number must be right adjusted so that the units digit always appears in column 20. This is the only number which must not have a decimal point associated with it. Columns 31-72 are reserved for identifying information of any sort.

All subsequent data cards have the form shown in Figure 4.32b. The columns of the data cards are arranged as follows:

Columns	1 -15	contain	Sr^{87}/Sr^{86} ratio
"	16-30	"	measured Rb^{85}/Rb^{87} ratio
"	31-45	"	corrected Sr^{86}/Sr^{88} ratio
"	46-55	"	number of μgms of Rb spike added
"	56-65	"	number of μgms of Sr spike added
"	66-75	"	weight of sample in grams.

These numbers must all have decimal points but may be punched anywhere within the specified field. An empty field will again be interpreted by the computer as zero.

4.33 - Derivation of Equations Used to Calculate Rb^{87}/Sr^{86} Ratios

The equations used in this program to calculate the Rb^{87}/Sr^{86} ratios are derived as follows. One gram-atomic weight of an element contains 6.023×10^{23} atoms (Avogadro's number). Therefore, the number of atoms present in an unknown quantity of an element (Rb, for example) is equal to:

$$Rb_a = \frac{(Av.\ No.)(N)}{(Rb_{at.\,wt.})} \qquad 4.33a$$

where Rb_a = the number of Rb atoms

(Av.No.) = Avogadro's number

$(Rb_{at.\,wt.})$ = atomic weight of Rb

N = number of grams of Rb

The number of Rb^{87} atoms present is equal to the product of the atomic fraction of Rb^{87} in normal Rb times the number of Rb atoms or:

$$Rb_a^{87} = \frac{(Av.\ No.)(N)(f)}{(Rb_{at.\,wt.})} \qquad 4.33b$$

where f = the atomic fraction of Rb^{87} in normal Rb. Since we are interested in expressing Rb_a^{87} in terms of the Rb^{85}/Rb^{87} ratio measured on the mass spectrometer, we must obtain an expression for N. We use the familiar equation:

$$\left(\frac{85}{87}\right) = \frac{AN + BS}{CN + DS} \qquad 4.33c$$

where A and C are the atomic fractions of Rb^{85} and Rb^{87} in normal Rb, respectively, B and D are the atomic fractions of Rb^{85} and Rb^{87} in spike Rb, respectively, N and S are the total number of Rb atoms in normal Rb and spike Rb, respectively, and $\left(\frac{85}{87}\right)$ is the Rb^{85}/Rb^{87} ratio measured on the mass spectrometer. Solving this equation for N/S we get:

$$\left(\frac{N}{S}\right)_a = \frac{B-\left(\frac{85}{87}\right)D}{C\left(\frac{85}{87}\right)-A} \qquad 4.33d$$

To convert this (N/S)a ratio to a weight ratio we multiply by a weight factor - the ratio of the atomic weight of normal Rb to the atomic weight of spike Rb:

$$\left(\frac{N}{S}\right)_w = \left[\frac{B-\left(\frac{85}{87}\right)D}{C\left(\frac{85}{87}\right)-A}\right]\frac{(Rb_{at.wt.})}{(Rb_{sat.})} \qquad 4.33e$$

where $Rb_{sat.}$= Rb spike atomic weight.

Solving this equation for N and expressing N in grams per gram of sample gives:

$$N = \frac{\left[B-\left(\frac{85}{87}\right)D\right](Rb_{at.wt.})(S_{Rb})}{\left[C\left(\frac{85}{87}\right)-A\right](Rb_{sat.})(W)} \qquad 4.33f$$

where S_{Rb} is the number of grams of Rb spike added to the sample and W is the weight of the sample. Finally, substituting N back into equation 4.33b gives:

$$Rb^{87}_{a} = \frac{(\text{Av. No.})(f)\left[B - \left(\frac{85}{87}\right)D\right](Rb_{at.wt.})(S_{Rb})}{(Rb_{at.wt.})(Rb_{sat.})\left[C\left(\frac{85}{87}\right) - A\right](W)} \qquad 4.33g$$

To include a blank correction term in equation 4.33g we make use of equation 4.33b letting N stand for the blank contamination. The blank is often taken as the average of a number of individual determinations and is expressed as µgms of Rb per gram of sample. Thus, it is convenient to subtract the average blank expressed in grams per gram from equation 4.33g:

$$Rb^{87}_{a} = \frac{(\text{Av. No.})(f)\left[B - \left(\frac{85}{87}\right)D\right](Rb_{at.wt.})(S_{Rb})}{(Rb_{at.wt.})(Rb_{sat.})\left[C\left(\frac{85}{87}\right) - A\right](W)} - \frac{(\text{Av. No.})(f)(J)}{(Rb_{at.wt.})} \qquad 4.33h$$

where J = average number of µgms of Rb contamination per gram of sample. Note that the expression for the number of Rb^{87} atoms in the sample must be divided by the weight of the sample to be consistent with the blank which is expressed in grams per gram of sample. If we were not interested in correcting for blank contamination the W term would be unnecessary since both Rb and Sr are determined from the same sample.

The following currently used values may be substituted into equation 4.33h:

f = .278551

B = .01748 (for the $\underline{Rb^{87}}$ Dilute Spike)

$D = .98252$

$Rb_{at.wt.} = 85.5571$

$Rb_{sat.} = 86.9650$

$A = .721448$

$C = .278551$

The Rb atomic weight used here has been calculated using $Rb^{85}/Rb^{87} = 2.590$. Substituting the above values into equation 4.33h gives:

$$Rb_a^{87} = (Av.No.)(.278551)\left[\frac{(.01748 - \left(\frac{85}{87}\right).98252)(S_{Rb})}{86.965\left[.278551\left(\frac{85}{87}\right) - .721448\right](W)} - \frac{(J)}{85.5571}\right] \qquad 4.33i$$

The equation for the number of Sr^{86} atoms in a sample is derived in the same manner as for Rb^{87}. An important advantage here is that the Sr^{87}/Sr^{86} ratio and the initial Sr^{87}/Sr^{86} ratio are unimportant and enter into the equation only in the blank term.

Equation 4.33b also holds for Sr, and a blank term of the same form can be subtracted:

$$Sr_a^{86} = \frac{(Av.No.)(N)(f)}{(Sr_{at.wt.})} - \frac{(Av.No.)(f)(I)}{(Sr_{at.wt.})} \qquad 4.33j$$

where I is the Sr blank in μgms of Sr per gram of sample. The fraction of Sr^{86}, f, in a natural strontium sample is determined from the following four ratios:

$$\frac{84}{88} = .0068 \qquad \left(\frac{86}{88}\right) = .1194$$

$$\frac{87}{88} = \left(\frac{87}{86}\right)(.1194) \qquad \left(\frac{88}{88}\right) = 1$$

Therefore, the fraction of Sr^{86} equals:

$$f = \frac{.1194}{1.1262 + .1194\left(\frac{87}{86}\right)} \tag{4.33k}$$

The atomic weight of natural Sr is determined by multiplying the atomic fraction of each isotope by its weight and adding:

$$Sr_{at.wt.} = \frac{.0068(84) + .1194(86) + 88 + .1194(87)\left(\frac{87}{86}\right)}{1.1262 + .1194\left(\frac{87}{86}\right)} \tag{4.33l}$$

or:

$$Sr_{at.wt.} = \frac{98.8312 + 10.3878\left(\frac{87}{86}\right)}{1.1262 + .1194\left(\frac{87}{86}\right)} \tag{4.33m}$$

Therefore, substituting equations 4.33k and 4.33m into equation 4.33j and cancelling we get:

$$Sr_a^{86} = \frac{(Av.No.)(N)(.1194)}{98.8312 + 10.3878\left(\frac{87}{86}\right)} - \frac{(Av.No.)(I)(.1194)}{98.8312 + 10.3878\left(\frac{87}{86}\right)} \tag{4.33n}$$

To derive an expression for N, the number of grams of Sr, we begin in the same manner as with Rb:

$$\left(\frac{86}{88}\right)_T = \frac{RN+XS}{YN+ZS} \tag{4.33o}$$

In the case of Sr, however, the new Sr^{84}-Sr^{86} Double Spike affords the means of correcting for mass spectrometer discrimination. Thus, the 86/88 ratio used in equation 4.33_o should be the corrected or "true" Sr^{86}/Sr^{88} ratio, $(86/88)_T$, (See Krogh, 1964). Solving equation 4.33_o for N/S, multiplying by the appropriate weight factor and then solving for N (in grams per gram of sample) we get:

$$N = \frac{(S_{Sr})(Sr_{at.wt.})\left[X - Z\left(\frac{86}{88}\right)_T\right]}{(Sr_{sat.})\left[Y\left(\frac{86}{88}\right)_T - R\right](W)} \qquad 4.33_p$$

where S_{Sr} is the number of µgms of spike Sr that have been added, W is the sample weight in grams and $Sr_{sat.}$ is the atomic weight of spike Sr. Since R is the fraction of Sr^{86} in natural Sr and Y is the fraction of Sr^{88} in natural Sr, and the $Sr_{at.wt.}$ is expressed in equation 4.33m, equation 4.33p becomes:

$$N = \frac{(S_{Sr})\left[X - Z\left(\frac{86}{88}\right)_T\right]\left[98.8312 + 10.3878\left(\frac{87}{86}\right)\right]}{(Sr_{sat.})(W)\left[1.1262 + .1194\left(\frac{87}{86}\right)\right]\left[\frac{(86/88)_T}{\left[1.1262 + .1194\left(\frac{87}{86}\right)\right]} - \frac{.1194}{\left[1.1262 + .1194\left(\frac{87}{86}\right)\right]}\right]} \qquad 4.33q$$

and upon simplifying gives:

$$N = \frac{(S_{Sr})\left[X - Z\left(\frac{86}{88}\right)_T\right]\left[98.8312 + 10.3878\left(\frac{87}{86}\right)\right]}{(Sr_{sat.})\left[\left(86/88\right)_T - .1194\right](W)} \qquad 4.33r$$

Substituting equation 4.33r back into equation 4.33n gives:

$$Sr^{86}_{a} = \frac{(Av.No.)(.1194)(S_{Sr})\left[X - Z\left(\frac{86}{88}\right)_{\mathrm{II}}\right]}{(Sr_{Sat.})(W)\left[\left(\frac{86}{88}\right)_T - .1194\right]} - \frac{(Av.No.)(I)(.1194)}{\left[98.8312 + 10.3878\left(\frac{87}{86}\right)\right]} \qquad 4.33s$$

It can be seen, therefore, that the only place where the Sr^{87}/Sr^{86} ratio of natural Sr occurs is in the blank correction term. Since this blank term is small or insignificant unless one is analyzing in the range of less than 1 ppm Sr and since one does not analyze for the Sr^{87}/Sr^{86} ratio of the contaminating Sr anyway, a value of .709 has been substituted for this term in the computer program. If one also substitutes the following currently accepted values for the <u>Sr^{84}-Sr^{86} Double Spike</u>:

$$X = .5036$$
$$Z = .17021$$
$$Sr_{sat.} = 85.8927$$

equation 4.33s simplifies to the following:

$$Sr_a^{86} = (Av.No.)\left[\frac{(S_{Sr})\left[.5036 - .17021\left(\frac{86}{88}\right)_T\right](.1194)}{(W)\left[\left(\frac{86}{88}\right)_T - .1194\right]85.8927} - (I)(.001124)\right] \qquad 4.33t$$

Since Avogadro's number occurs in both equations 4.33i and 4.33t, it will cancel out when the final Rb^{87}/Sr^{86} ratios are calculated. Therefore, in the equations used in the computer program the (Av.No.) term has been dropped. The final form of equations 4.33i and 4.33t used in the program are as follows:

$$Rb_a^{87} = \frac{\left[.01748 - \left(\frac{85}{87}\right).98252\right](S_{Rb})(.003203)}{\left[.278551\left(\frac{85}{87}\right) - .721448\right](W)} - (.003256)(J) \qquad 4.33u$$

$$Sr_a^{86} = \frac{(S_{Sr})\left[.5036 - .17021\left(\frac{86}{88}\right)_T\right](.0013901)}{(W)\left[\left(\frac{86}{88}\right)_T - .1194\right]} - (.001124)(I) \qquad 4.33v$$

The Rb^{87}/Sr^{86} ratios are then easily calculated by dividing equation 4.33v into equation 4.33u.

In this thesis investigation the Bjurböle whole meteorite and Bjurböle matrix analyses were made using the <u>Sr^{86} Dilute Spike</u> (~2.18 ugms Sr/ml). The <u>Sr^{86}</u> Dilute Spike was also used in the Murray carbonaceous chondrite analysis by Beiser (1964). With this spike the mass spectrometer discrimination cannot be corrected for, and thus the measured Sr^{86}/Sr^{88} ratios were used. A computer program similar to the one just described was also written to calculate these Rb^{87}/Sr^{86} ratios. In this case only the Sr^{86}_{a} equation was revised. The following parameters were instead substituted into equation 4.33s:

$$X = .8373$$
$$Z = .0674$$
$$Sr_{sat.} = 86.2286$$

Thus, the following equation results for the <u>Sr^{86} Dilute Spike</u>:

$$Sr^{86}_{a} = \frac{(S_{Sr})\left[.8373 - .0674\left(\frac{86}{88}\right)_M\right](.0013847)}{(W)\left[\left(\frac{86}{88}\right)_M - .1194\right]} - (.001124)(I) \qquad 4.33w$$

4.34 -Notation Used in the Program

A list of the quantities used in this program together with their Fortran name is given below:

SRIR	The Sr^{87}/Sr^{86} ratio of an individual sample
RB7SR6	The Rb^{87}/Sr^{86} " " " " "
R8587	The Rb^{85}/Rb^{87} ratio measured on the mass spectrometer
S8688T	The Sr^{86}/Sr^{88} ratio corrected for mass spectrometer discrimination
SRB	The number of μgms of Rb Spike added to the sample
SSR	" " " " " Sr " " " " "

RUBJ	The quantity Rb_a^{87} calculated in equation 4.33 u, Section 4.33
STRN	The quantity Sr_a^{86} calculated in equation 4.33 v Section 4.33
WGHT	The sample weight
N	The number of samples
RBLNK	The Rb contamination per gram of sample
SBLNK	" Sr " " " " "

CHAPTER V

DESCRIPTION OF SAMPLES

5.1 - Introduction

Four meteorites were analyzed during the course of this thesis investigation: the Bjurböle chondrite, the Bath chondrite, the Bruderheim chondrite, and the Pasamonte achondrite. The analyses of three other meteorites, made previously by other workers in the M.I.T. Geochronology Laboratory, have also been included here for purposes of comparison. A summary of pertinent data concerning these seven meteorites is given in Table 5.1a.

Table 5.1b lists a chemical analysis for each of these stony meteorites. The analyst and a reference to the article in which the analysis appeared is given at the bottom of the table. Urey and Craig (1953) reviewed a large number of stony meteorite analyses including the Bjurböle, Pasamonte and Nakhla analyses. Accordingly, these analyses were taken from their article rather than from the original reference. Unfortunately, a chemical analysis of the Bath chondrite has never been performed.

Below is a short description of each of these seven meteorites. Special emphasis has been placed on available data concerning the infall and the probable length of time that elapsed before recovery. The importance of the terrestrial history of meteorites used

Table 5.1a

Reference Data for Meteorite Samples

Meteorite	M.I.T. sample number	Previous sample number, if any	Donor	No. of gms.	Analyst(s)
Bruderheim chondrite	M 5441	U. of Alberta #B89	Dr. R. E. Folinsbee U. of Alberta	44	this work
Bath chondrite	M 5465	Harvard Museum #445	Dr. C. Frondel and Mrs. U. B. Marvin Harvard Museum Collection	15	this work
Pasamonte achondrite	M 5439	--	Dr. H. C. Urey	--	this work
Bjurböle chondrite	M 5333	--	Dr. E. P. Henderson U.S. National Museum Washington, D.C.	118	this work
Murray carbonaceous chondrite	M 5160	U.S. National Museum #1769	Dr. E. P. Henderson U.S. National Museum Washington, D.C.	35	Beiser (1964)
Nakhla achondrite	M 4870	Harvard Museum #489b	Dr. C. Frondel and Mrs. U. B. Marvin Harvard Museum Collection	16	Pinson et al. (1962, 1963)
Estherville mesosiderite	M 4868	Harvard Museum #390	Dr. C. Frondel and Mrs. U. B. Marvin Harvard Museum Collection	38.5	Pinson et al. (1962, 1963)

Table 5.1b

Chemical Analyses of Meteorite Samples

	Bruderheim(1)	Bjurböle(2)	Murray(3)	Nakhla(4)	Pasamonte(5)
SiO_2	39.94	41.06	28.69	48.96	48.20
MgO	24.95	25.75	19.77	12.01	6.47
FeO	12.94	13.17	21.08	20.66	17.04
Al_2O_3	1.86	2.55	2.19	1.74	13.91
CaO	1.74	1.82	1.92	15.17	10.24
Na_2O	1.01	1.24	0.22	0.41	0.31
K_2O	0.13	0.32	0.04	0.14	0.06
Cr_2O_3	0.60	0.59	0.44	0.33	0.30
MnO	0.33	0.12	0.21	0.09	0.42
P_2O_5	0.29	0.32	0.32	--	--
TiO_2	0.12	--	0.09	0.33	0.07
FeS	6.38	5.44	7.67	0.16	0.19
Fe^o	8.59	6.87	0.00	--	--
Ni^o	1.30	0.78	0.00	--	--
CO^o	0.05	0.04	0.00	--	--
total metal	9.94	7.69	0.00	--	2.64
H_2O^+	0.10	--	9.98	0.17	--
H_2O^-	0.01	--	2.44	0.07	--
NiO	--	--	1.50	--	--
CoO	--	--	0.08	--	--

(continued)

Table 5.1b (continued)

Chemical Analyses of Meteorite Samples

	Bruderheim(1)	Bjurböle(2)	Murray(3)	Nakhla(4)	Pasamonte(5)
C	0.04	--	2.78	--	--
total Fe	22.69	20.55	21.24	16.15	16.00
Total	100.38	100.07	100.04	100.29	99.85

(1) Baadsgaard *et al.* (1961)
(2) Ramsay and Borgström (1902)
(3) Wiik (1956)
(4) Prior (1912)
(5) Foshag (1938)

for Rb-Sr studies will be seen later. Some of the information and many of the references in this section were obtained through Prior and Hey (1953) and Mason (1962a).

5.2 - The Bruderheim Chondrite

The Bruderheim meteorite is a very fresh-looking, grey chondrite. The circumstances of its fall have been described by Folinsbee and Bayrock (1961) as follows:

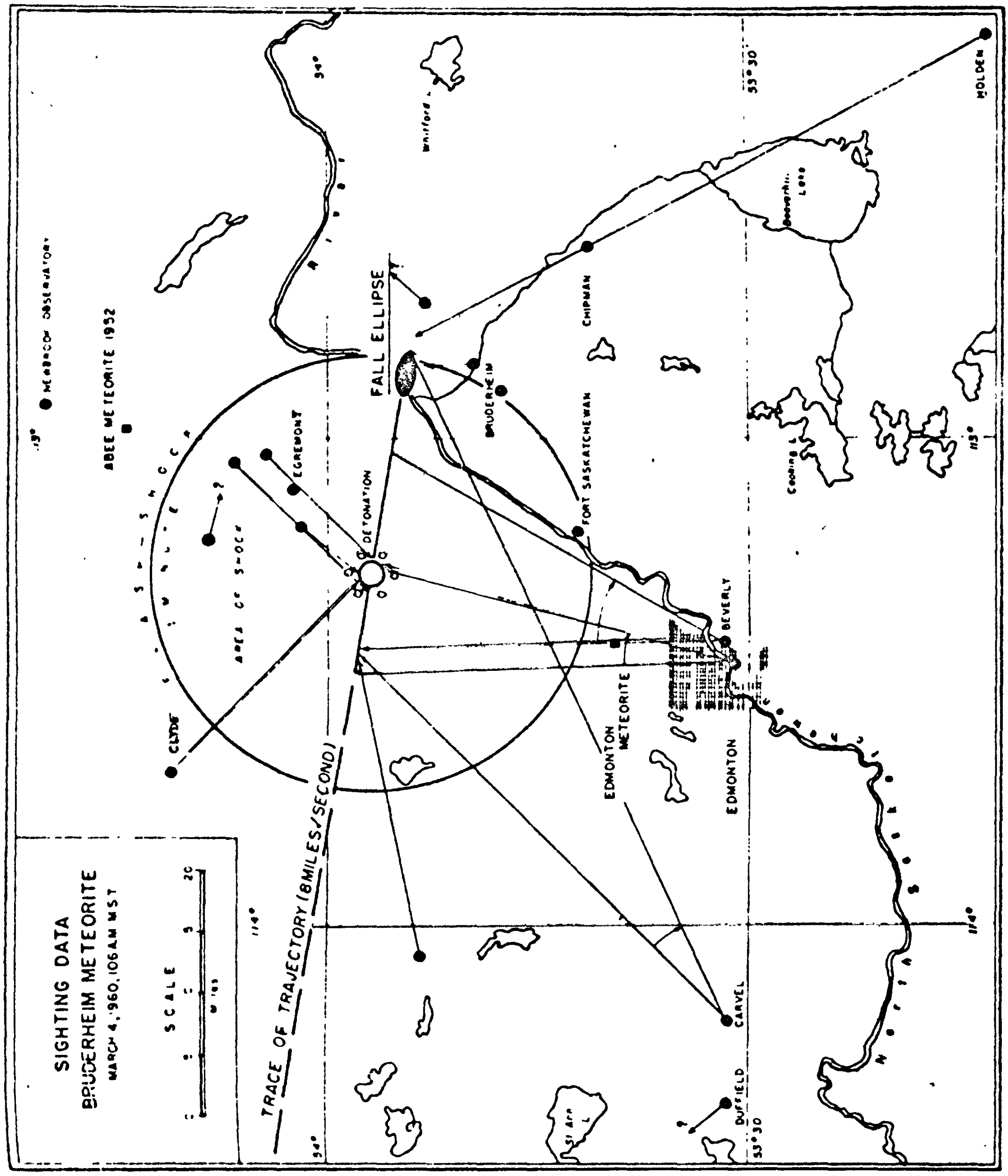
> "Bruderheim, a detonating bolide, entered the earth's atmosphere at 1:06 a.m., M.S.T., March 4, 1960, creating a flash visible for 200 miles, followed by detonations resembling a sonic boom audible over an area of 2,000 square miles.....The fireball, travelling on an azimuth of N.100°, slope 40°, in the direction of the earth's revolutionary path, had an initial atmospheric velocity of about 8-10 miles per second, facilitating entry....Falling vertically onto frozen ground at terminal velocity, most individuals rebounded onto the snow surface, facilitating recovery. Mapping and recovery were continued during the spring break-up period, yielding the university a total of 188 sizable gray chondritic meteorites weighing 303 kilograms. The largest individual weighed 31 kilograms; 500 recovered individuals, each smaller than 100 grams, are uncatalogued."

Further information concerning the fall and recovery of the Brüderheim chondrite can be obtained in Folinsbee and Bayrock (1961) and Baadsgaard et al., (1961). Figure 5.2 shows the flight path and fall area of the Bruderheim meteorite.

The piece which has been analyzed in this

Figure 5.2

LOCATION OF BRUDERHEIM CHONDRITE



reproduced from Folinsbee and Bayrock
(1961, 219)

investigation is part of a fragment labeled "B89" by the University of Alberta. It was picked up the day of infall. In a letter which accompanied the sample Dr. Folinshee wrote:

> "The sample of Bruderheim is part of B89, a piece picked up the day of infall by one of the local farmers and it is the freshest of all our samples."

As can be seen from the chemical analysis in Table 5.1b, Bruderheim is a member of the low-iron, or L, group of chondrites in the Urey and Craig (1953) classification. Mason (1963) determined that the olivine contains 24 mole per cent Fe_2SiO_4 (Fa). Bruderheim, therefore, is an olivine-hypersthene chondrite.

In view of its accurately known history, its lack of exposure to terrestrial weathering, and its fresh, unrusted appearance, Bruderheim was considered an excellent candidate for Rb^{87}-Sr^{87} age analysis.

A further advantage in selecting the Bruderheim chondrite is that it has been widely distributed to scientists for many different types of investigations. A partial list of those working on the Bruderheim chondrite is given in Baadsgaard *et al.*, (1961). Already a number of "gas retention" and "cosmic ray exposure" ages have been reported. Gast (1963) has also reported a Rb^{87}-Sr^{87} age for this meteorite. It would make an interesting comparison, therefore, to obtain a Rb-Sr "solidification age" with our new clean chemical procedure and improved mass spectrometry techniques. An anomalous Rb-Sr age in this case could not be attributed to leaching of Rb or Sr by exposure to terrestrial weathering.

5.3 - The Bath Chondrite

Bath is another very fresh-looking grey chondrite which fell in Brown county, South Dakota. Foote (1893) describes the circumstances of its fall as follows:

> "On the 29th day of August, 1892, about four o'clock in the afternoon, while Mr. Lawrence Freeman and his son were stacking upon his farm two miles south of Bath, they were alarmed by a series of heavy explosions. On looking up they saw a meteoric stone flying through the air followed by a cloud of smoke. Its course was easily traced to the point where it fell within about twenty rods from where they were standing. The stone penetrated the hardened prairie to a depth of about sixteen inches and when reached it was found to be so warm that gloves had to be used in handling it. Three small pieces of an ounce or two each had apparently been blown off by explosions, but the stone still weighed 46 3/4 lbs. One of these small pieces was found by some men not far distant and was broken up and distributed among them. The explosions were plainly heard by a large number of people at Bath, two miles away, and at Aberdeen, nine miles away, it sounded like distant cannonading. The exterior of the stone presents the usual smooth black crust. The interior is quite close-grained

> resembling in texture the stones from Mócs. The iron is abundantly disseminated through the mass, and although the grains are small they are easily distinguished and separated on pulverizing."

Prior and Hey (1953) also state that the fall of the Bath chondrite consisted of only one 46 3/4 lb. stone. It seems reasonable to assume, therefore, that the various samples of Bath in different museums were all obtained from this one stone which was picked up immediately after infall.

An interesting contradiction occurs in the literature, however, over the freshness of the Bath meteorite. Foote (1893) stated above that the meteorite was picked up so soon after infall that it was still warm. Merrill (1919), however, writes the following:

> "Macroscopically the stone is gray, but, owing to oxidation, so filled with rust spots as to give it a brownish cast....".

As already stated, the sample of Bath in the Harvard Museum Collection has a fresh, light-grey color, similar to that of Bruderheim. Furthermore, Professor W. H. Pinson of M.I.T., Mrs. U. B. Marvin of the Smithsonian Astrophysical Observatory and the author all agree that there is no evidence of rust or weathering on this sample. To what, then, was Merrill (1919) referring when he described an oxidized, rusty stone? Perhaps Dr. Merrill's sample of Bath had a different history than Harvard's sample subsequent to infall. In any event, the sample studied in this investigation looks extremely fresh and was selected as an excellent candidate for Rb-Sr analysis.

Unfortunately, the Bath chondrite has never been subjected to a chemical analysis. Mason (1963), however, has studied the olivine composition of Bath using a petrographic microscope and X-ray techniques. He has determined that the olivine contains 19 mole per cent fayalite (Fe_2SiO_4) and, therefore, that Bath should be classified as an olivine-bronzite, or H-group, chondrite.

It should be remarked that the sample of Bath analyzed in this thesis is different from the one analyzed by Pinson et al., (1962 and 1963). Although both samples were obtained from the same specimen at Harvard University (HM #445), the one studied in this work was obtained at a much later date, was given a different M.I.T. sample number, and has been stored in a different bottle. It was decided to reanalyze the Bath chondrite in this investigation using a different sample from that of Pinson et al., (1962 and 1963) for several reasons: (a) as a check on the analytical reproducibility of different workers over a period of time, (b) as a check on the possibility of sample inhomogeneity, and (c) as a check on whether the new clean chemical procedure and improved mass spectrometry would yield different results.

5.4 - The Pasamonte Achondrite

The fall of the Pasamonte achondrite was probably one of the greatest meteoric displays ever recorded. It was especially important in that a number of photographs of the bolide and its luminous trail were obtained. Figure 5.4a shows a picture of the meteor in flight taken by Mr. Charles M. Brown as it was about to pass over his house. The diameter of the fireball in this picture was about 6 miles (Nininger, 1936a, 384).

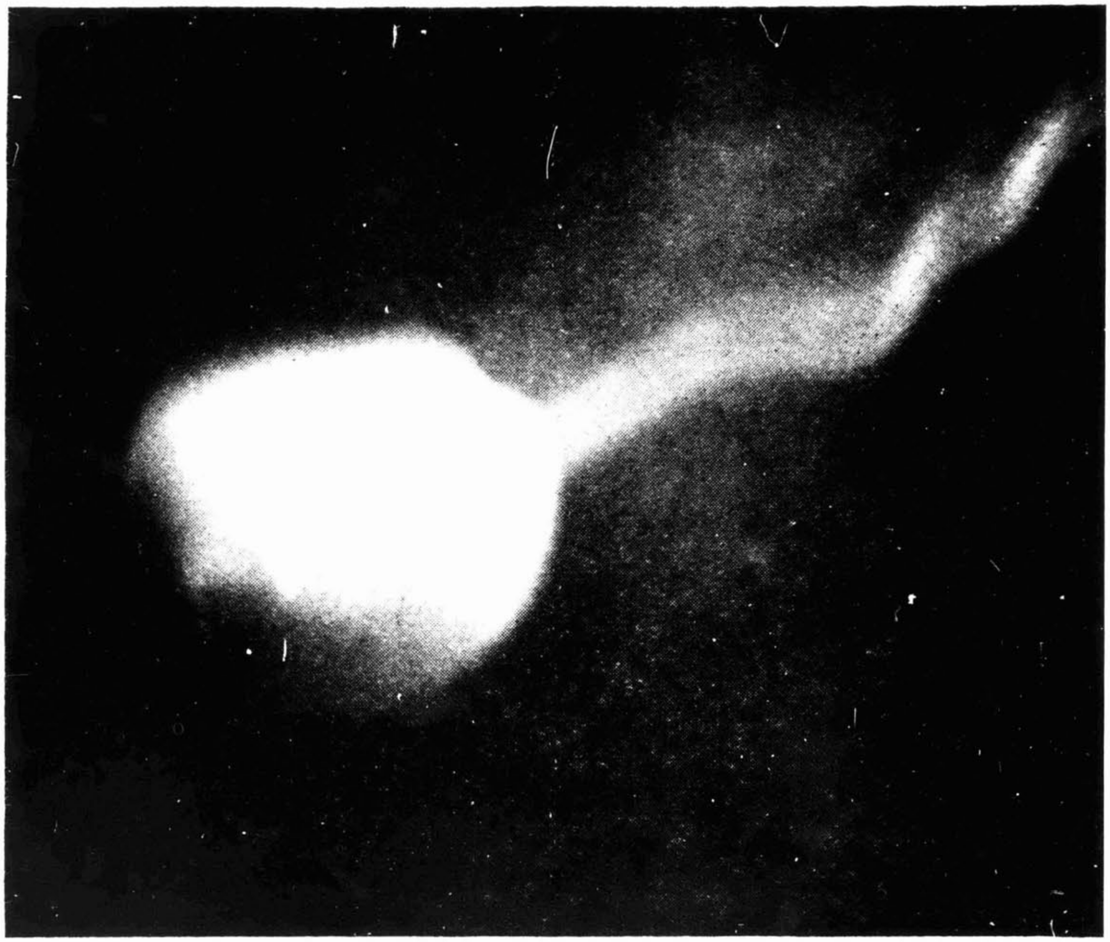
The circumstances of the Pasamonte fall have been described by Nininger (1934a, 1936a, and 1936b) and discussed at length in Nininger (1934b). The flight path of the meteor is shown in Figure 5.4b. The meteorite arrived at 5:04 a.m., M.S.T. on March 24, 1933. The trajectory of its flight path made an angle of about 8 1/2° with the horizontal. The meteor approached from 12 1/2° N. of E. and first became visible at a height of about 78 miles. It disappeared from sight at an altitude of about 17 miles (Nininger, 1934a, 106). Its entry velocity was estimated by Nininger (1934b, 304) at about 40 miles per second.

The light and accoustical phenomena which accompanied this fall must have been very impressive. Nininger (1936a, 385) states the following:

> "Seasoned cattlemen who were accustomed to facing the vicissitudes

Figure 5.4a

PHOTOGRAPH OF PASAMONTE FIREBALL



Reproduced from Nininger (1936a, 387)

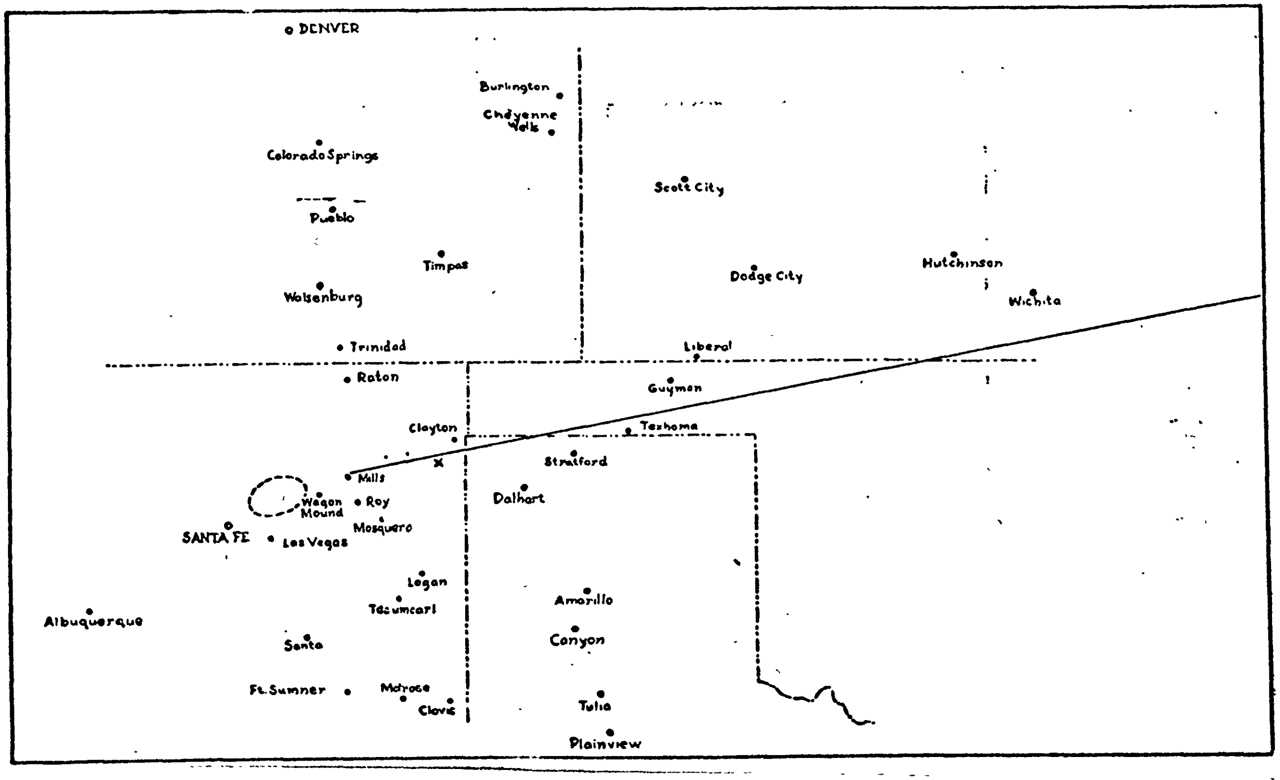


Figure 5.4b TRAJECTORY OF PASAMONTE ACHONDRITE

Reproduced from Nininger (1934b, 300)

> of frontier life and who ordinarily knew no fear, told me that they despaired of life during the terrible moment of the meteor's passage; yet they were 75 miles from its nearest approach!"

According to Nininger (1936b, 332) the fireball was described as:

> "'terrifying' from distances as great as 300 miles on either side of its course......Letters arrived from seven states and it was learned that searching parties had actually gone out to explore various parts of Texas, Kansas, Oklahoma, Colorado, Nebraska, and Arizona - all looking for the meteorite which I knew had landed; if at all, in northeastern New Mexico."

The search for, and location of, the individual stones from the Pasamonte fall are discussed in Nininger (1936b). He describes his recovery of the first Pasamonte specimens on December 23 as follows:

> "...one of the herdsmen had brought to the ranch house just such a fragment as I was seeking. The stone had been very friable and the various men of the force had each 'whittled at it with his knife' until it had been destroyed..."

In all, about 75 individual stones (amounting to about 4 kg.) were recovered over a two year period. The stones were scattered for a distance of about 28 miles parallel to, and 4 miles north of, the path of the bolide (as shown in Figure 5.4c). Surprisingly enough, all recovered stones were found at least 10 miles behind the point where the bolide disappeared.

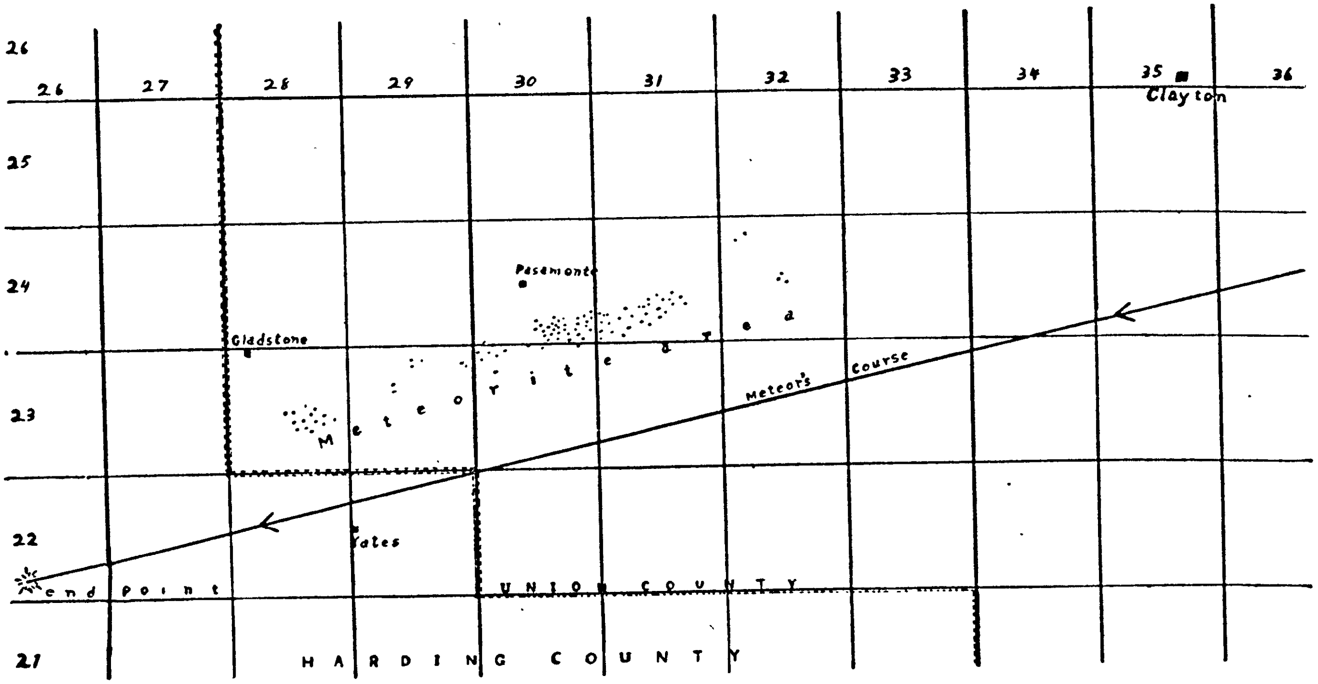


Figure 5.4c LOCATION OF PASAMONTE STONES

Reproduced from Nininger (1936b, 338).

Most of the stones were found lying on top of the dry soil and were completely covered with fusion crust.

Fortunately, for many meteorite investigators. the region of Union county, New Mexico is arid and receives little rainfall. Nininger (1936b, 334) describes it as follows:

> "The topography of the Pasamonte region may be described as a rolling plain, a grazing land for the most part; however, quite a few fields have been broken up and are used for dry land farming....To the east the land becomes more sandy and rather hilly..."

Probably, therefore, these stones were not subjected to much rain or weathering. The specimen analyzed in this investigation was donated by Dr. H. C. Urey, who obtained his sample from H. H. Nininger. Although it does seem possible that this sample could have lain upon the ground for up to 2 years after infall, macroscopic examination indicates it to be quite fresh and free of rust or brownish coloration.

Pasamonte is a highly brecciated meteorite. Nininger (1936b, 337) describes it as follows:

> "The meteorite consists of a tuffaceous material much of which is so finely divided that, when a piece of the stone is broken or rubbed, it emits a cloud of dust so fine that it rises like smoke from a cigarette."

It is made up of dark grey fragments imbedded in a light grey matrix. Dr. Urey supplied samples of both the light and the dark phases. Only the light phase has been analyzed in this investigation.

A chemical analysis of Pasamonte is given in Table 5.1b. Foshag (1938) also studied the minerology of the Pasamonte meteorite. He determined the major mineral constituents to be anorthite and pigeonite with minor amounts of tridymite, metallic iron, and magnetite-chromite. Pasamonte is, therefore, a calcium-rich, or basaltic-type, achondrite. More specifically, it is a eucrite (Mason, 1962a, 106).

A Rb-Sr analysis of the Pasamonte meteorite is important because Pasamonte strontium has an isotopic composition very close to the initial isotopic composition of meteoritic Sr. It, therefore, serves as an anchor point for the meteorite isochron. Gast (1962) and Schumacher (1956a and c) have already made Rb-Sr analyses on Pasamonte which show considerable disagreement. The results of this investigation will, therefore, serve also as a check on the analyses of these other workers.

5.5 - The Bjurböle Chondrite

The fall and recovery of the Bjurböle chondrite have been described by Ramsay and Borgström (1902). Below is a loose translation of parts of this description:

> "The meteorite appeared on March 12, 1899 at about 10 hrs. 29 min. and 30 secs. P.M. local time and at its closest approach

to Helsingfors showed an apparent radius similar to that of the full moon but with a remarkably greater brightness. Behind it, and according to some observers in front of it also, a tail of bluish-white colored light was seen which suddenly flared up several times. Around the meteorite the color gradually changed into red, yellow and also green.

"This appearance was followed by a strong and lengthy boom. Many observers, including myself, first heard a sharp bang, and then the noise gradually changed into a rumble which lasted for several minutes ...

"At first the meteorite was seen in Riga and Stockholm. Then it passed over the Baltic Sea south of Aland and west of Dago, but appeared only as an unusually bright shooting star. Apparently it reached its greatest light intensity while passing between Hango and Dago right above the Bay of Finland. After that the bolide gradually approached the Finnish coast and went south from Helsingfors towards the place where it fell by the farm Bjurböle, about 7 1/2 km SSE of the town of Borga.

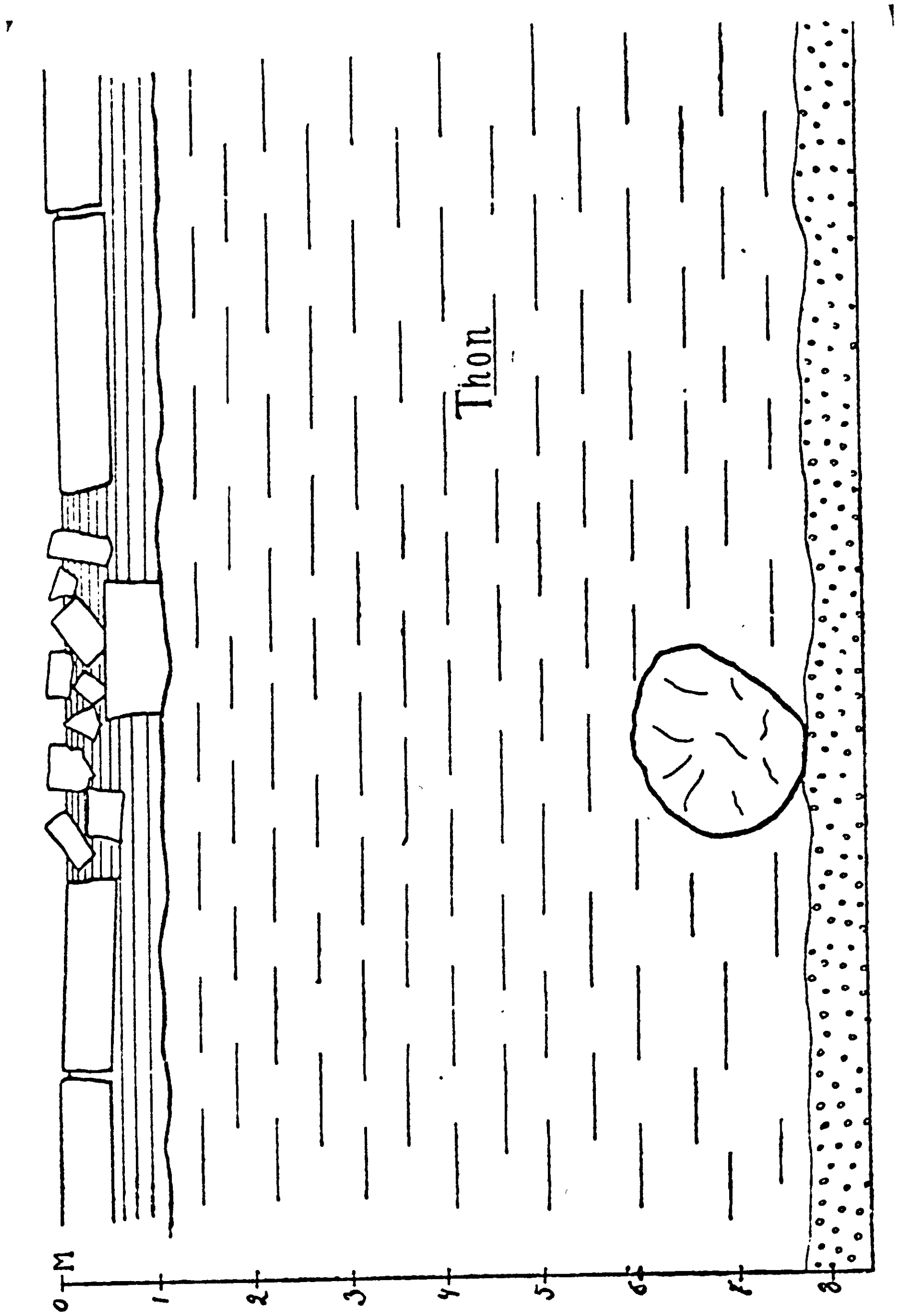
- - - - - - - -

"The next day we were informed that near the coast by the farm Bjurböle there was a big hole in the ice from the previous night. One of us immediately went to see the place and made the following observations.

"In the ice, which was about 40 cm thick, we saw a big hole with almost vertical sides. It had an irregularly ellipsoidal shape. The maximum radius was 4.25 meters, and the minimum radius was 3.50 meters - with uneven edges. The hole was filled with large and small pieces of sharp edged ice

Figure 5.5

LOCATION OF BJURBOLE CHONDRITE STONES



Reproduced from Ramsay and Borgstrom (1902, 6) piled on top of each other. The hole was situated approximately in the middle of an ellipsoidal area of broken ice which was separated by fractures from the surrounding solid ice and lowered by a few cms. The radii of this larger ellipse were about 9.5 and 8 meters. From the edge of the small hole there were radiating fractures towards the periphery of the larger ellipse.

"The depth of water in the hole was 90 cms. The bottom consisted of soft mud which was made up mostly of organic debris. Below this there was pure grey clay down to a depth of 8 meters, where one could feel hard sand and gravel with long sticks.

"Around the hole to a distance of 20-25 meters the ice was covered with innumerable pieces of greyish-black mud....By the shape and appearance of these pieces of mud one could easily see that they had splashed out of the hole. Microscopic analysis of this mud showed the same diatoms and other plant and animal remains which also occurred in the mud.

"Attempts to locate the supposed meteorite by probing with sticks were at first unsuccessful. Nevertheless, the probability of having located the right place was so great that the Geological Commission in Helsingfors made plans to salvage the meteorite in this place. They built a waterproof well out of wooden planks which was lowered through the ice and water into the soft mud. By pumping they tried to empty the well from water, mud and clay, but as this was not completely successful, the meteorite was finally lifted out by divers. It lay 6 meters below the surface of the water in the clay."

Unfortunately, impact with the earth broke the meteorite up into many pieces, the biggest of which weighed 80.2 kg. The total recovered weight of meteorite material was 328 kg; Ramsay and Borgström (1902, 8) estimated that the total mass of meteorite which hit the earth must have been at least 400 kg.

The chemistry, mineralogy and structure of the Bjurböle chondrite have also been discussed by Ramsay and Borgström (1902). A chemical analysis of Bjurböle is given in Table 5.1b. This indicates it to be a member of the low-iron (L) group of Urey and Craig (1953). Mason (1963) determined the olivine composition of Bjurböle to be 26 mole % fayalite. Bjurböle is, therefore, an olivine-hypersthene chondrite.

One can estimate from the above article that the Bjurböle meteorite probably lay submerged in sea water and sediment for at least a week or so after its infall. No doubt spending this length of time in the salt water is partly responsible for its rusted appearance. The meteorite is so friable that it is not unreasonable to suppose that it became thoroughly saturated with salt water. Metallic iron, and lawrencite ($FeCl_2$) if it is present, will react with salt water to form limonite. The Bjurböle chondrite will be discussed further in section 6.4.

5.6 - The Murray Carbonaceous Chondrite

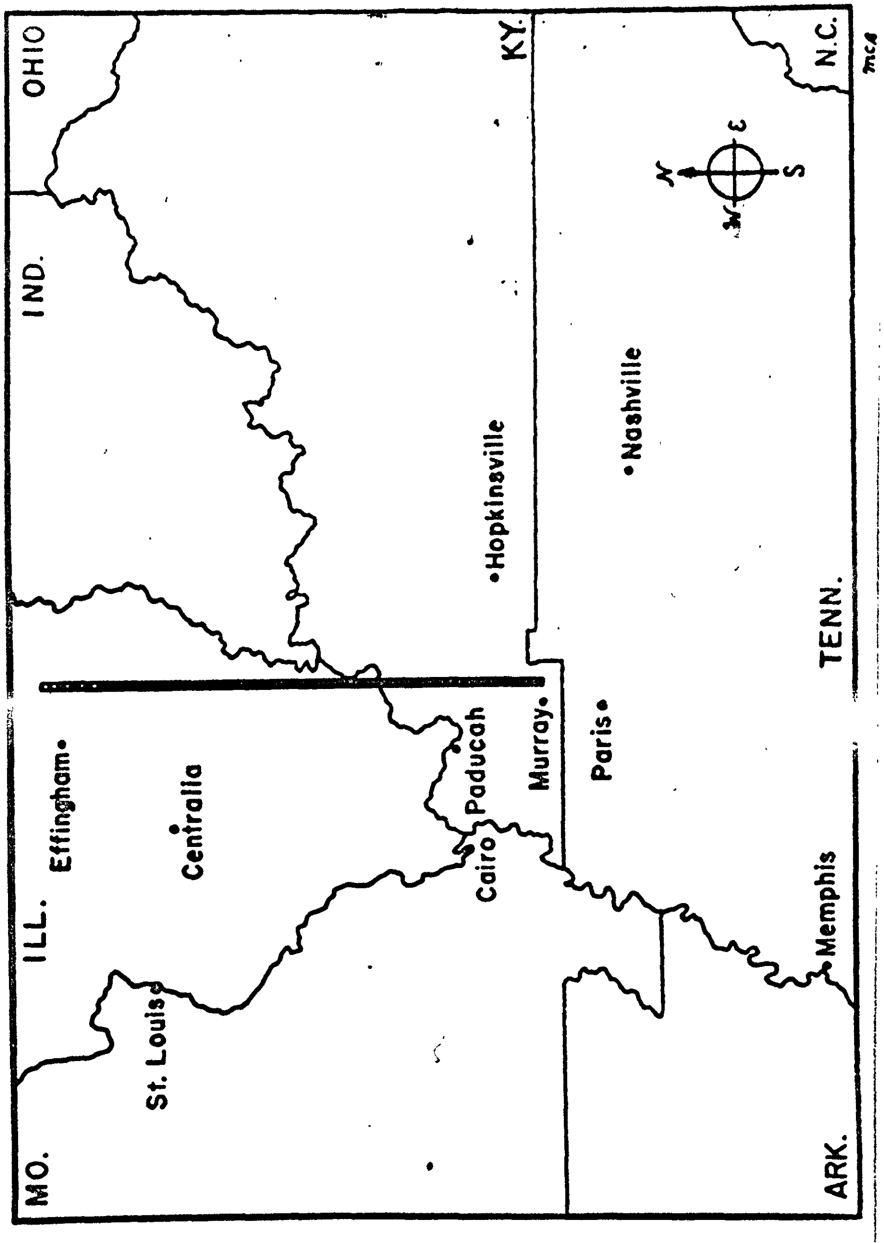
The Murray carbonaceous chondrite fell at 1:45 a.m., C.S.T. on September 20, 1950 in Calloway county, Kentucky. Horan (1953, 114-115) describes the fall as follows:

> "...The red-orange ball of flame traveled along a path that extended approximately north to south.... leaving a luminous train visible in 5 states. The brilliant light was described by eyewitnesses as having been of such intensity that the sky was illuminated "as bright as day". About 5 seconds later, the bolide exploded with a blinding flash over western Kentucky at an altitude greater than 45 km. The force of the explosion and succeeding thundering sounds jarred windows over a thousand-square-mile area.... These optical and acoustical displays were followed by a shower of meteoritic fragments that fell to Earth in Calloway County, Kentucky, at a place 9 miles east of Murray, near Wildcat Creek, on Kentucky Lake.... Several observers reported hearing masses thudding into the ground approximately 30 seconds after the explosion."

Olivier (1954) has worked out the atmospheric path and orbital elements for this meteorite from the reports of about 40 witnesses. Figure 5.6 shows the projected path of the fireball and the location of the fall. It is interesting that he calculated a parabolic orbit and a geocentric velocity of 71 km/sec for this meteorite. Horan (1953, 115) claims that Murray was

Figure 5.6

PROJECTED PATH OF THE MURRAY CARBONACEOUS CHONDRITE



Reproduced from Horan (1953, 114)

travelling in an hyperbolic orbit with respect to the sun. Regardless of this discrepancy, this is a remarkably high entry velocity when compared to the entry velocities of most meteorites.

A number of observers of the Murray fall heard stones hit the ground, and several pieces were picked up shortly thereafter by local farmers. One stone even pierced the roof of a house. Unfortunately, however, the first official attempts to recover stones from the Murray fall were not made until October 22 (a month after the infall). Horan (1953, 116) writes as follows:

> "...Intermittent rain hindered the search...Altho many masses had been heard to fall in the nearby woods, only a few small pieces were found, while other fragments were given to the party by farmers..."

The largest piece collected by this search party weighed 3.4 kg.

Horan's paper, published in 1953, was read at the 15th annual meeting of the American Meteoritical Society on September 2-4, 1952. At that time a total of 7 kg. of meteoritic fragments had been recovered. This was almost 2 years after infall. Mason (1962a, 96), however, claims that 12.6 kg. of material were picked up from the fall. This means that 5.6 kg. were not located until at least 2 years after infall.

In response to a letter concerning the history of the fragments analyzed by Beiser (1964), Dr. Roy Clarke of the Smithsonian Institution, U. S. National Museum in Washington D. C. replied as follows (his reply was dated August 19, 1964):

> "The Murray meteorite material that Miss Beiser received from us was from a collection we purchased from a private collector in 1959. This collector had undertaken a field investigation in 1955, five years after the date of fall. It was during this 1955-1958 period that he obtained most, if not all, of his specimens.
>
> "Unfortunately, there is no way for us to tell now when the pieces that were sent to M.I.T. were collected. Some of the Murray specimens were recovered immediately, but many of them were recovered much later. It is possible that your material spent several months on the ground. However, Henderson knows the type of work you people do, and I am sure he would have selected fresh appearing material."

One can only guess, therefore, whether the sample analyzed by Beiser (1964) lay on the ground for several months, or even years, after infall or whether it was picked up immediately by a local inhabitant. It does seem remarkable, however, that a person could recover carbonaceous chondrite fragments 5 years after the date of infall in a climate which has significant rainfall.

An analysis of the Murray carbonaceous chondrite is given in Table 5.1b. Murray is a Type II carbonaceous chondrite. It is immediately obvious that Murray differs from the other meteorites in this table since it contains considerable amounts of H_2O, several per cent of C, but no metal phase. If, however, these analyses are all recalculated on an atom % basis with the elimination of H_2O,. C, O, and S, Murray agrees very closely with the other groups of chondrites. It is, in fact, a member of the (H), or high-iron, chondrite group of Urey and Craig (1953). A point that should be made concerning Wiik's (1956) analysis is that he calculated all S as FeS. Mason (1962a, 98) points out, however, that the Type II carbonaceous chondrites "contain little or no FeS". They are made up essentially of serpentine with most of their sulfur in the elemental state. The Fe should, therefore, be recalculated and added to the FeO, and the sulfur should be recalculated as S^0 or sulfate.

Excellent Rb-Sr analyses of the Murray carbonaceous chondrite were made by Beiser (1964). The results of her analyses have been included for comparison with the other meteorites discussed in this thesis. Murthy (1964) has also recently analyzed the Murray carbonaceous chondrite.

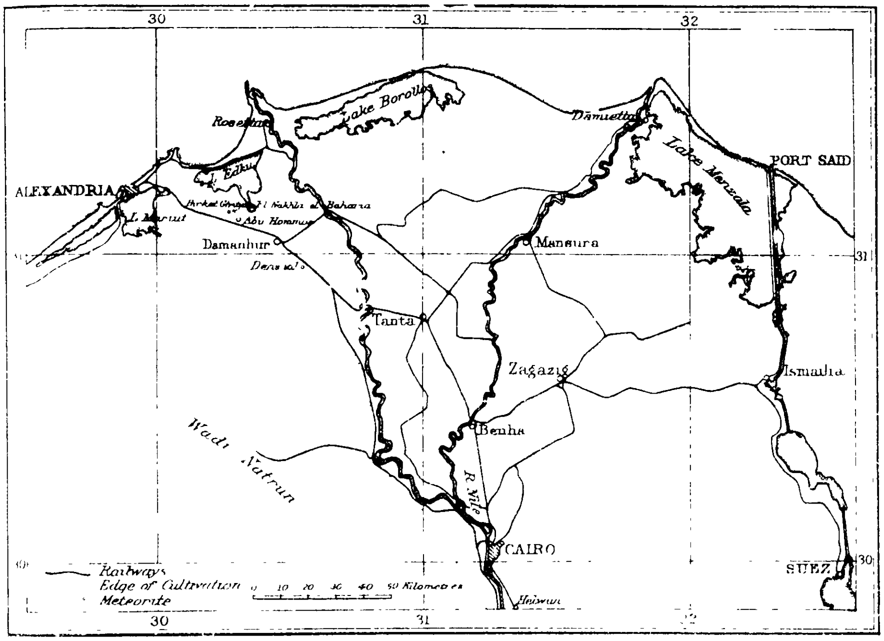
5.7 - The Nakhla Achondrite

The Nakhla achondrite arrived at 9 A. M. on June 28, 1911. The stones fell around the village of El Nakhla el Baharia in the district of Abu Hommos which is east of Alexandria, Egypt. The region of fall is shown in Figure 5.7. Accounts of the fall and recovery of the Nakhla meteorite are given by Ball (1912) and Hume (1911). Ball has determined that an early newspaper account stating the date of fall as June 29th and the place of fall as Denshal are incorrect; furthermore, he states that a report "that one of the stones fell on a dog at Denshal, 'leaving it like ashes in a moment' is doubtless the product of a lively imagination". Ball (1912) summarizes the fall of the Nakhla achondrite as follows:

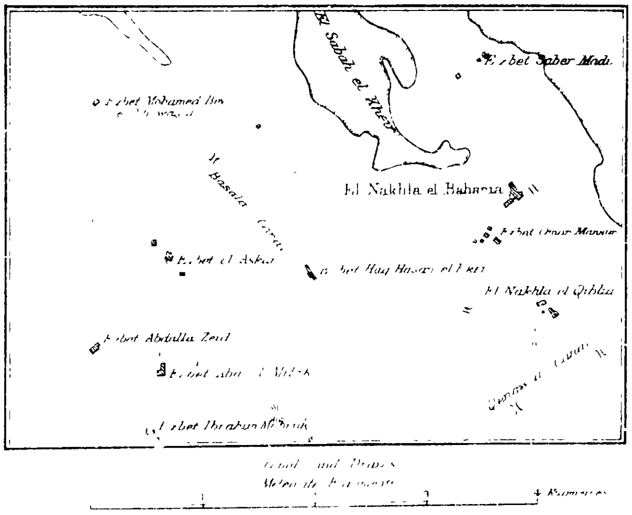
> "....it appears that the stones fell over an area about 4 1/2 kilometres in diameter, and were derived from the explosion of a single large meteorite at a considerable altitude in the air. The direction of approach of the object was from the northwest, and its track, marked by a column of white smoke, is said to have been inclined only some 30° to the horizontal. The explosion appears not to have been a single one, but to have been several times repeated, with a loud noise variously likened to the firing of a gun and to the pulling-up of a railway train at a station. The column of smoke is said to have been seen, and the sound of the explosion heard, near the

Figure 5.7 - LOCATION OF NAKHLA STONES

SKETCH-MAP OF LOWER EGYPT
SHOWING THE POSITION OF EL NAKHLA EL BAHARIA



LARGE SCALE MAP OF EL NAKHLA EL BAHARIA DISTRICT,
SHOWING THE PLACES WHERE THE PRINCIPAL METEORITE-FRAGMENTS WERE FOUND



Reproduced from Ball (1912)

> village of Birket Ghetas, which is some seven kilometres from the centre of the area where the stones fell. Curiously enough, a peasant who saw a stone fall about fifty metres from him near Ezbet Saber, on the opposite side of the centre of the fall to Birket Ghetas, did not remark any sound of the explosion, but only noticed a cloud of dust where the stone struck the earth. The stones buried themselves to depths of from ten to thirty centimetres in the ground, and are stated to have been cool when dug out. The holes showed an inclined course, not a vertical one."

According to Ball (1912) and Prior (1912), 40 stones were recovered amounting to a total weight of 10 kg. Prior and Hey (1953, 255), however, claim that the 40 stones amounted to a total weight of 40 kg. The author has been unable to resolve this discrepancy. All the stones are at least partially covered with a shiny, black fusion crust and are extremely friable, being easily crushed with the fingers. The largest fragment recovered weighs 1,813 grams and the smallest weighs 20 grams.

Almost all of these stones were recovered within 4 months after infall. Since the average annual rainfall for Cairo is about 1" per year and summer is the dry season, it seems reasonable to suppose that these samples were never rained upon. Furthermore, as was seen from the above quotation, the stones only penetrated from 10 to 30 centimeters into the earth. Therefore, we can probably assume that the Nakhla fragment analyzed for Rb and Sr, by Pinson et al., (1963) was never wet.

A chemical analysis of Nakhla is given in Table 5.1b. It has the highest CaO content of any known meteorite except for Angra dos Reis. Mineralogically, Nakhla consists of about 75% green diopside and about 15% reddish-brown olivine with traces of feldspar and magnetite (Prior, 1912, 275-276). The unusual color of the olivine is no doubt a result of its high iron content amounting to 66 mole % Fe_2SiO_4 (Mason, 1962a, 116).

Nakhla is practically a unique meteorite. It instituted a new class of achondrites called "Nakhlites" (Ball, 1912, 13). Mason (1962a, 106) also refers to this class as the diopside - olivine achondrites. Nakhlites are a subgroup of the Ca-rich, or basaltic type, achondrites. The Lafayette achondrite, a 600 gram individual stone found in 1931, is the only other known Nakhlite.

5.8 - The Estherville Mesosiderite

The Estherville mesosiderite fell at 5 p.m. on May 10, 1879 in Emmet county, Iowa. Its dazzling white bolide left a long trail of white smoke as it passed through the atmosphere. The fall was accompanied by loud explosions heard throughout the area. Descriptions of the fall and recovery of the Estherville meteorite are given in Shepard (1879), Peckham (1879), Smith (1880) and Wilson (1928).

The Estherville fall was a gigantic meteorite shower from which over 750 lbs. of meteorite material were recovered. The location and shape of the fall area are shown in Figure 5.8. The main part of the fall consisted of three large fragments which weighed 431, 151 and 92 1/2 lbs.

The 437 pound mass was seen to hit the ground by a Mr. Charles Ega who was standing "one hundred rods" from where it fell. Fortunately, the fall occurred during daylight or this largest mass might never have been found. It landed in a hole which had already been dug and was about 6 feet deep and 12 feet in diameter. The hole was filled with water. The meteorite had penetrated another 8 feet below the bottom of the hole (or 14' below the surface of the ground) into blue clay. It was three days before this piece was finally recovered. The fate of this 437 lb. mass during the next few months is described in Wilson (1928, 327) as follows:

> "The large meteorite was taken to town for exhibition. For several days the big, black stone lay on a dry-goods box in front of the Emmet House facing the public square in Estherville. There it attracted much attention and scores of people came from far and near to see it. Noticing the popular interest in the

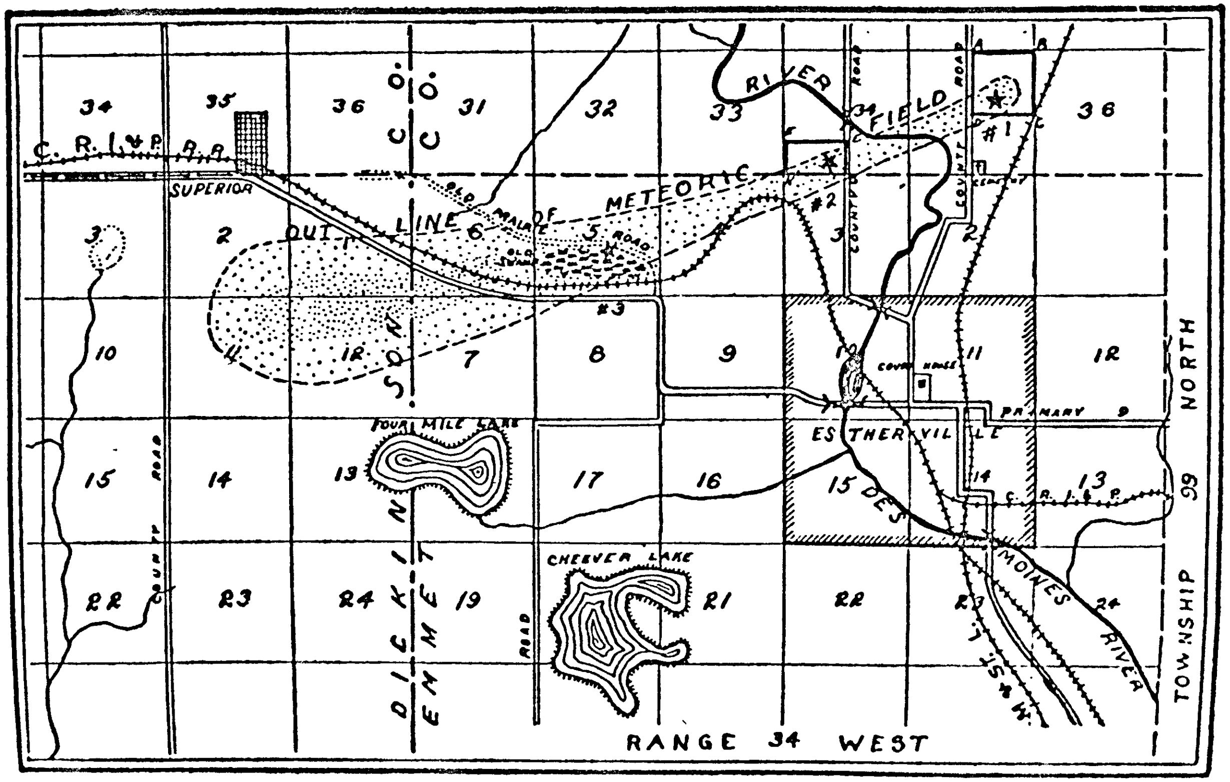


Figure 5.8

LOCATION OF STONES FROM ESTHERVILLE SHOWER
reproduced from Wilson (1928, 322)

> meteorite, some of the boys who found it conceived the idea of exhibiting it for money. Accordingly they put it in a strong box, loaded it in a wagon, and started out across Minnesota,...
>
> "The boys had not proceeded far, however, until disquieting rumors reached their ears concerning the legality of their ownership. Hastily returning, they stopped at George Osborn's place where they wrapped their prize in an old quilt and buried it in a cornfield, marking the spot by means of two pairs of stakes whose lines intersected over the place of burial. There the meteorite remained during part of the summer..."

This mass has subsequently been divided between the London, Vienna and Paris museums.

The 151 pound mass was also observed to fall. It landed two miles from the 431 pound mass but was not recovered until four days after the infall. It had penetrated 4 1/2 feet below the surface of the ground. Unlike the larger mass, this piece landed in "dry, gravelly soil". It is now at the University of Minnesota in Minneapolis.

The recovery of the third largest piece of the Estherville fall is described in Wilson (1928, 329) as follows:

> "The third of the three largest pieces was not discovered until the twenty-third of February, 1880, more than nine months after the "fall". As witnesses of the meteor, the Pietz

> brothers, who spent the winter trapping in the sloughs then so common on the prairies of northwest Iowa, had decided upon the approximate location of the spot where another piece was supposed to have fallen. One day late in February as they were going along the old prairie road beside a swamp about four miles to the southwest of the largest fall and two miles from the second one, almost in a direct line, they observed a hole in the edge of the slough. Upon sounding it with their rat spear, they detected a hard body at the bottom. Surmising what it was, they began digging and secured the stone at a depth of five feet. Smaller pieces were likewise discovered near-by...."

As to the whereabouts of this 92 1/2 pound mass of Estherville, Wilson (1928, 332) states the following:

> "...The one hundred pound piece, found by the Pietz boys, as well as the thirty-two pound fragment found with the largest meteorite, seem to have disappeared, though they, too, may repose in some museum."

Many smaller pieces from the Estherville shower were picked up during the summer and fall of 1879. A list of the whereabouts of many of the Estherville specimens is given in Dillé (1928). This article also contains a list of all the individual fragments in the Harvard Museum Collection. Unfortunately, there is no information in any of the aforementioned references about the location and date of recovery of any but the three largest fragments. The history of the sample analyzed by Pinson et al., (1962 and 1963), therefore, can only be guessed at from information available in these accounts. It seems that many of the smaller fragments lay on the ground for several months to even a year before recovery. This means that they were probably rained on many times. Indeed, the Estherville sample does have some rust spots, but it is not nearly as rusty as the Bjurböle chondrite.

The only chemical analysis available for Estherville was performed by Smith (1880, 462). He analyzed the meteorite in three separate portions: (1) insoluble silicate, or that silicate which could not be dissolved in HCl; (2) soluble silicate, or that portion of the silicate which was soluble in HCl; and (3) metallic nickel-iron. The analysis of the insoluble silicate is given as follows:

SiO_2	54.12
FeO	21.05
MgO	24.50
Cr_2O_3	trace
$Na_2O+K_2O+Li_2O$	.09
Al_2O_3	.03
	99.29

This analysis indicates that the insoluble silicate portion corresponds essentially to pyroxene. The soluble silicate has the following composition:

SiO_2	41.50
FeO	14.21
MgO	44.64
	100.35

The soluble silicate consists, therefore, of olivine. Finally, the metallic fraction of Estherville has the following composition:

Fe	92.001
Ni	7.100
Co	.690
Cu	trace
P	.112
	99.903

Unfortunately, Smith did not give any figures as to the relative proportions of these three components of the meteorite.

There are only 20 known mesosiderites in the world today, and only 7 of these are falls. Estherville, therefore, is a comparatively rare variety of meteorite. Since it has a low Rb/Sr ratio, it also falls near the zero point on the meteorite isochron and, therefore, should make an interesting comparison with the Pasamonte achondrite.

CHAPTER VI

RESULTS

6.1 - Blanks

As a result of the changes incorporated into the chemical procedure (see Section 2.2) the contamination level has been lowered significantly. For purposes of comparison, blank determinations before the changes were instituted are given in Pinson *et al.*, (1963, 10) and reproduced in Table 6.1a.

Blank determinations obtained with the new chemical procedure are listed in Table 6.1b. It can be seen that Sr contamination has been reduced by an order of magnitude and Rb contamination reduced by a factor of 2. Since the M.I.T. Geochronology Laboratory has now been moved into a new air-conditioned building, it is expected that contamination levels may improve even further in the future.

6.2 - $SrCO_3$ Isotope Ratio Standard

To insure that the mass spectrometer is operating reproducibly over the period of time during which a series of analyses are being made, it is standard procedure in the M.I.T. Geochronology Laboratory to run

TABLE 6.1a

Rb AND Sr BLANK DETERMINATIONS (Pinson *et al.*, 1963, 10)

Rb Contamination (µgms Rb/gm of sample)	Sr Contamination (µgms Sr/gm of sample)
.034	.187
.045	.210
.025	.156
.020	.274
.017	.107
--	.225
.043	.204
.035	.213
Ave. = .031	Ave. = .197

TABLE 6.1b

Rb AND Sr BLANK DETERMINATIONS (this work)

Rb Contamination (μgms Rb/gm of sample)	Sr Contamination (μgms Sr/gm of sample)
--	.016
--	.021
.015	.022
.013	.023
.013	.035
.022	.016
.0097	.012
Ave. =.015	Ave. =.020

a Sr isotope ratio standard ($SrCO_3$, Eimer and Amend, Lot #492327) periodically. Table 6.2 lists the values obtained for the Sr^{87}/Sr^{86} ratio of this $SrCO_3$ standard. These runs overlapped the period during which the Pasamonte, Bath and Bruderheim meteorites were run on Snagtooth. The error is given as the standard deviation of a single analysis computed from the formula:

$$\sigma = \sqrt{\frac{\Sigma(\bar{x}-x)^2}{(n-1)}}$$

6.3 - Rb-Sr Analyses of Bruderheim, Bath, and Pasamonte and the Meteorite Isochron

Rb-Sr data from the analyses of the Bruderheim chondrite, the Bath chondrite and the Pasamonte achondrite are given in this section. These analyses plus the analysis of Beiser (1964) on the Murray carbonaceous chondrite and those of Pinson et al., (1963) on the Estherville mesosiderite and Nakhla achondrite have been used to calculate a meteorite isochron and hence a "solidification" age for meteorites. The results of the Bjurböle chondrite analyses are listed separately in Section 6.4

Table 6.2

Reproducibility of SrCO$_3$ Isotope Ratio Standard

Date	Mass Spectrometer Record Number	Sr^{86}/Sr^{88}	(Sr^{87}/Sr^{86})meas.	(Sr^{87}/Sr^{86})*	Analyst
12/28/63	3443(S)	.1179	.7119	.7074	Beiser
1/20/64	3468(S)	.11824	.71076	.70730	Krogh
2/28/64	3549(S)	.11861	.70977	.70743	Krogh
5/26/64	3743(S)	.11959	.70697	.70753	Shields
6/4/64	3772(S)	.11987	.70613	.70751	Shields
	Mass Spectrometer moved to new building on 6/15/64				
6/28/64	3808(S)	.11826	.71117	.70776	Roe
			Average =	.70748	
			σ =	.00016	

* normalized to Sr^{86}/Sr^{88} = .1194

The Rb analyses for Bruderheim, Bath and Pasamonte are listed in Table 6.3a. The Bath and Bruderheim analyses were done in duplicate, beginning with separate one gram samples and processing each one independently. The duplicate Rb sample of the Pasamonte meteorite was prepared but not analysed. The Rb analysis of Pasamonte sample 7, however, was a long steady run of 106 sets; it was judged to be of the highest quality. These samples were all spiked with the $\underline{Rb^{87}}$ Dilute Spike ($\sim$1.26 μgms Rb/ml). A value of 1.232 μgms Rb/ml was used for the concentration of this spike. The measured Rb concentrations were each corrected by subtracting a blank of .015 μgms Rb per gram of meteorite (see Section 6.1). Bruderheim sample 6 was run on two different mass spectrometers; this is indicated by brackets in Table 6.3a.

The Sr isotope dilution analyses are listed in Table 6.3b. Each of these meteorites was analysed in duplicate with the $\underline{Sr^{84}-Sr^{86}}$ Double Spike ($\sim$1.05 μgms Sr/ml). A value of 1.050 μgms Sr/ml was used for the concentration of this spike. The subscripts T and m refer to the corrected and measured values, respectively, since mass spectrometer discrimination can be

Table 6.3a

Rubidium Analyses

Meteorite	Mass Spectrometer Record Number	Sample Weight	Measured Rb^{85}/Rb^{87}	µgms Rb Spike added	Rb ppm measured	Rb ppm* corrected for blank
Pasamonte Achondrite						
7	3768(S)	.40976	1.49638	.02956	.3393	.324
8	--	.41717	--	.02956	--	--
Bath Chondrite						
3	3699(S)	1.06475	.99373	1.232	2.454	2.44
4	3691(S)	1.15968	1.05087	1.232	2.474	2.46
Bruderheim Chondrite						
5	3753(S)	1.09586	1.09535	1.232	2.812	2.80
6	3384(L)	.99972	1.0375	1.232	2.809	2.79
	3714(S)		1.0364	1.232	2.803	2.79

* a blank of .015 µgms Rb/gram of meteorite was subtracted

Table 6.3b

Strontium Isotope Dilution Analyses

Meteorite	Mass Spectrometer Record Number	Sample Weight	$\left(\frac{84}{88}\right)_m$	$\left(\frac{86}{88}\right)_m$	$\left(\frac{87}{86}\right)_m$	$\left(\frac{87}{88}\right)_m$	$\left(\frac{86}{88}\right)_T$	$\left(\frac{N}{S}\right)_T$	µgms Sr spike added	Normal Sr Measurd.	Normal* Sr Corrected for blank and fractiona.	Calc. $\frac{87}{86}$
Pasamonte Achondrite												
7	3762(S)	.40976	.21878	.51869	.248415	.12885	.51698	1.26439	25.25	82.176	82.69	.69950(S)
8	3720(S)	.41717	.21788	.51609	.24906	.12853	.51286	1.27979	25.25	81.227	82.21	.69910(S)
Bath Chondrite												
3	3633(S)	1.06475	.22208	.52495	.25608	.13445	.52335	1.24121	8.40	9.939	9.98	.7471(S)
4	3722(S)	1.15968	.20905	.49937	.26272	.13119	.495997	1.34635	8.40	9.827	9.94	.7428(S)
Bruderheim Chondrite												
5	3702(S)	1.09586	.20405	.49139	.26567	.13055	.40956	1.36908	8.40	10.680	10.70	.7457(S)
6	3778(S)	.99972	.21641	.51552	.25825	.13313	.51608	1.26771	8.40	10.90	10.86	.7449(S)
	3710(S)		.21810	.51683	.25836	.13357	.51416	1.27490	8.40	10.829	10.92	.7470(S)

* a blank of .020 µgms Sr/gram of meteorite was subtracted

corrected for with the Sr^{84}-Sr^{86} Double Spike. A Sr^{87}/Sr^{86} ratio for the original sample was calculated from the corrected Sr^{86}/Sr^{88} and Sr^{87}/Sr^{86} ratios for each sample (see Section 3.43). The (S) refers to the mass spectrometer on which the sample was run. Sample numbers correspond to those in Table 6.3a since both Rb and Sr isotope dilution analyses are made from the same aliquot of sample. Bruderheim sample 6 was run twice on the same mass spectrometer. An average blank of .020 μgms Sr/gram of meteorite (Section 6.1) was subtracted from each analysis. Note that Sr values in ppm are reported as Normal Sr, i.e., non-radiogenic Sr.

The Sr isotope ratio results are listed in Table 6.3c. Likewise, duplicate measurements were made in each case. It should be remembered, however, that these are different samples and not the same ones that were used for the isotope dilution analyses. The calculated Sr^{87}/Sr^{86} ratios have been put in brackets, therefore, to indicate this. These calculated Sr^{87}/Sr^{86} ratios correspond instead to the samples in Table 6.3b. Note, however, that only the measured Sr^{87}/Sr^{86} ratios have been used in constructing the isochron.

The measured ratios have been corrected for

Table 6.3c

Strontium Isotope Ratio Analyses

Meteorite	Mass Spectrometer Record Number	(87/86) measured	(86/88) measured	(87/86)* corrected	$\bar{\sigma}$ (87/86)*	E (87/86)*	(87/86) calculated from I.D.
Pasamonte Achondrite							
5	3569(S)	.69710	.12024	.69956	2.5×10^{-4}	.04%	.69950(S)
6	3575(S)	.69776	.11992	.69929	2.6×10^{-4}	.04%	.69910(S)
Bath Chondrite							
1	3706(S)	.74477	.11903	.74360	1.6×10^{-4}	.02%	.7471(L)
2	3703(S)	.74146	.12000	.74332	2.2×10^{-4}	.03%	.7428(S)
Bruderheim Chondrite							
2	3717(S)	.74819	.11883	.74641	2.4×10^{-4}	.03%	.7457(S)
8	3775(S)	.74584	.11953	.74624	2.1×10^{-4}	.03%	.7449(S) .7470(S)

* Normalized to Sr^{86}/Sr^{88} = .1194

mass spectrometer discrimination in the usual way - called "normalization" and indicated by (87/86)* (see Faure, 1961, 177-180). The average Sr^{86}/Sr^{88} ratio obtained in the M.I.T. Geochronology Laboratory over a long period of time has been .1194. If the 86/88 ratio of a run differs from this number it is assumed that the difference is due to machine discrimination. In correcting for this it must be remembered that the mass difference between Sr^{87} and Sr^{86} is only ½ that between Sr^{86} and Sr^{88}. Thus, it is assumed that the 87/86 ratio is fractionated only ½ as much. The formula used for correcting the 87/86 ratios is:

$$\left(\frac{87}{86}\right)^{*} = \left(\frac{87}{86}\right)_{m} \left[\frac{\frac{\left(\frac{86}{88}\right)_{m} - .1194}{2} + .1194}{.1194}\right]$$

or:

$$\left(\frac{87}{86}\right)^{*} = \left(\frac{87}{86}\right)_{m} \left[\frac{\left(\frac{86}{88}\right)_{m} + .1194}{2(.1194)}\right]$$

Each run normally consisted of between 54 to 72 sets of scans which were added up in groups of 6 sets each. Errors in Table 6.3c were calculated for each of these isotope ratio analyses. These errors indicate the scatter of the normalized $(87/86)^*$ ratios in sets of six scans each. $\bar{\sigma}$ for an individual analysis is the standard deviation of the mean, or:

$$\bar{\sigma} = \sqrt{\frac{\sum(\bar{x}-x)^2}{n(n-1)}}$$

where n is the number of groups of 6 scans each. $\bar{E}$ is the percentage error:

$$\bar{E} = \frac{100(\bar{\sigma})}{\left(\frac{87}{86}\right)^*}$$

Table 6.3d is a summary of the Rb-Sr analyses on these three meteorites. The Rb^{87}/Sr^{86} values have been calculated with the computer program described in Section 4.3. This program does not use the Rb and Sr concentrations in ppm, but instead starts with the Rb^{85}/Rb^{87} and Sr^{86}/Sr^{88} ratios measured on the mass spectrometer and calculates the Rb^{87}/Sr^{86} ratios directly (see Section 4.33).

The average Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^*$ ratios

Table 6.3d

Summary of Rb-Sr Analyses

Meteorite	Rb ppm	Sr ppm	$\frac{Rb^{87}}{Sr^{86}}$	Average Rb^{87}/Sr^{86}	$\left(\frac{Sr^{87}}{Sr^{86}}\right)^*$	Average $\left(\frac{Sr^{87}}{Sr^{86}}\right)^*$
Pasamonte	.324	82.69	.01132	.01132	.69956	.69943
Achondrite	--	82.21	--		.69929	
Bath	2.44	9.98	.7073	.7116	.74360	.74346
Chondrite	2.46	9.94	.7159		.74332	
Bruderheim	2.80	10.70	.7566	.7491	.74641	.74633
Chondrite	2.79	10.86	.7444			
	2.79	10.92	.7389		.74624	

* normalized to $Sr^{86}/Sr^{88} = .1194$

of Bruderheim, Bath and Pasamonte from Table 6.3d have been used in the construction of a meteorite isochron. Three other meteorites have also been used in the calculation of this isochron; the Murray carbonaceous chondrite analyzed by Beiser (1964), the Nakhla achondrite analyzed by Pinson et al., (1963), and the Estherville mesosiderite analyzed by Pinson et al., (1963). The Murray carbonaceous chondrite was included on this isochron because it was analyzed in the same laboratory with the same clean chemical techniques (outlined in Chapter 2).as Pasamonte, Bath and Bruderheim. Estherville and Nakhla were also included on this isochron because, even though they were analyzed before the clean chemical separation procedure was instituted, they contain such high concentrations of Sr and such low concentrations of Rb that errors in either of these measurements affect the Rb/Sr ratios to a very small degree. Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^*$ ratios which have been used for these meteorites are listed in Table 6.3e. The $(Sr^{87}/Sr^{86})^*$ ratios have been taken directly from Beiser (1964, 21) and Pinson et al., (1963, 9). Rb^{87}/Sr^{86} ratios for Nakhla and Estherville were taken from Pinson et al., (1963, 8) but were adjusted slightly so that a consistent value was used in all cases for the

Table 6.3e

$\left(\frac{Rb^{87}}{Sr^{86}}\right)$ and $\left(\frac{Sr^{87}}{Sr^{86}}\right)^*$ Ratios for Murray, Nakhla, and Estherville

	Rb^{87}/Sr^{86}	Sr^{87}/Sr^{86*}
Murray		
Carbonaceous Chondrite(1)	.4211	.7250
Nakhla		
Achondrite(2)	.1326	.7065
Estherville		
Mesosiderite(3)	.0225	.6994

* Normalized to Sr^{86}/Sr^{88} = .1194

(1) Beiser (1964)

(2) Pinson *et al.*, (1963)

(3) Pinson *et al.*, (1963)

concentrations of Rb and Sr spikes. The Rb^{87}/Sr^{86} ratio of Murray was calculated using the computer program of Section 4.3 from the measured Rb^{85}/Rb^{87} and Sr^{86}/Sr^{88} ratios obtained by Miss Beiser in three separate isotope dilution analyses.

A least squares isochron (following the methods set forth in Youden, 1951, 40-43) was constructed from the average Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^{*}$ ratios for the above 6 meteorites. The computer program of Section 4.2 was used for this calculation. The isochron is reproduced in Figure 6.3a. Figure 6.3b shows the output data from the computer for this isochron. An explanation of the various quantities calculated by the computer and the errors associated with a least squares line is given in Section 4.22. The isochron is computed twice - the line of regression of Sr^{87}/Sr^{86} on Rb^{87}/Sr^{86} is computed first followed by the line of regression of Rb^{87}/Sr^{86} on Sr^{87}/Sr^{86}. Using the following parameters:

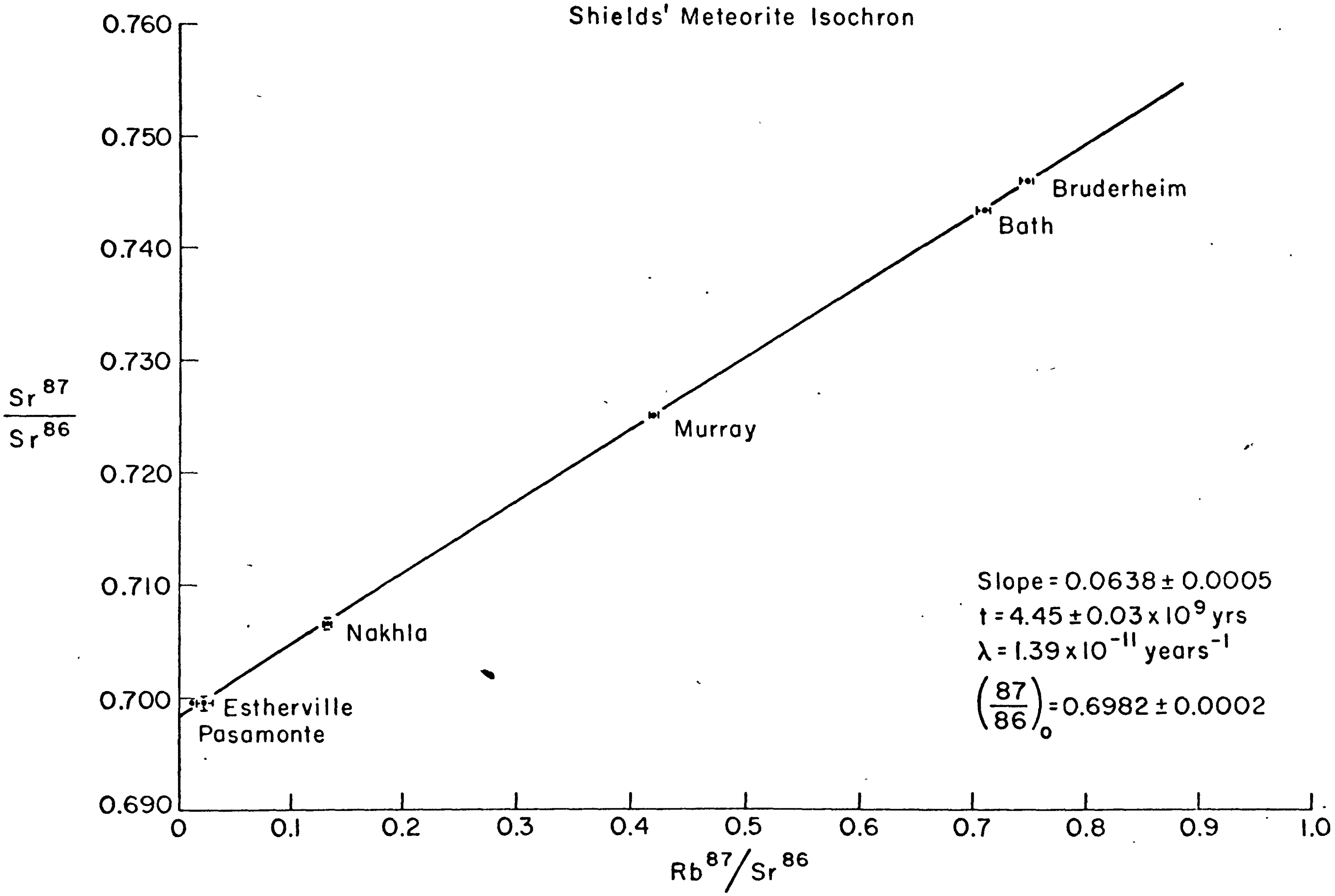
λ = 1.39×10^{-11} yrs.$^{-1}$
(Aldrich et al, 1956)

Rb^{87} Dilute Spike = 1.232 μgms Rb/ml

Sr^{84}-Sr^{86} Double Spike = 1.050 μgms Sr/ml

Figure 6.3a

Shields' Meteorite Isochron



```
FINAL RESULTS                                    SHIELDS THESIS ISOCHRON

DECAY CONSTANT =  .13900E-10

NUMBER OF SAMPLES =   6

REGRESSION OF SR87/SR86 ON RB87/SR86

SLOPE =    .06383663         STANDARD DEVIATION OF SLOPE =  .0004742           PERCENT ERROR =    .7428

INTERCEPT =     .6982289     STANDARD DEVIATION OF INTERCEPT =  .00021755      PERCENT ERROR =    .0312

STANDARD DEVIATION OF SINGLE MEASUREMENT =  .00035607

AGE =  .44519E 10 YEARS +OR-   .3207E 08 YEARS AT ONE STANDARD DEVIATION

REGRESSION OF RB87/SR86 ON SR87/SR86

SLOPE =    .06385016         STANDARD DEVIATION OF SLOPE =     .0004649        PERCENT ERROR =    .7281

INTERCEPT =     .6982243

STANDARD DEVIATION OF SINGLE MEASUREMENT =    .0054672

AGE =  .44528E 10 YEARS +OR-   .3144E 08 YEARS AT ONE STANDARD DEVIATION


     SRIR            RB87/SR86

    .7463300        .7491000         BRUDERHEIM

    .7434600        .7116000         BATH

    .7250000        .4210700         MURRAY

    .7065000        .1325700         NAKHLA

    .6994000        .0225000         ESTHERVILLE

    .6994300        .0113000         PASAMONTE
```

Figure 6.3b

COMPUTER OUTPUT DATA FOR SHIELDS' METEORITE ISOCHRON

<u>Sr^{86} Dilute Spike</u> = 2.176 μgms Sr/ml

a slope of 0.06385 ± 0.0005 (or ± .7%) was calculated. This gives an age of 4.45 ± .03 x 10^9 years as the "solidification" age of the stony meteorites. The initial ratio was determined to be .6982 ± .0002. The errors quoted here are standard deviations (or 67% confidence limits). A discussion of errors and of the calculation of the individual error bars on the meteorite isochron is given in Section 6.5. This meteorite isochron is discussed and compared with other Rb-Sr meteorite work in Chapter 7.

6.4 - The Bjurböle Chondrite Analyses

The Bjurböle chondrite was the first meteorite studied in this investigation. It was chosen for the purpose of making Rb-Sr analyses on chondrules and separated mineral phases (see Shields, 1963b). Bjurböle is one of the few chondrites which is so friable that it can be crumbled between the fingers. The hard, strong chondrules, however, do not break with the groundmass and can be easily picked out of it with a pair of tweezers. Bjurböle was available in sufficient quantity so that 100 gms could be spared for this study.

Chondrules were separated first. They were picked out of the meteorite with a pair of new, clean, stainless-steel tweezers. A total of 8.4 gms of chondrules were collected in this way for analysis. They were placed in a polyethylene vial, and after the separations were completed they were shaken at length to knock off any groundmass which might still be adhering. These chondrules were then stored in a clean polyethylene vial. Figure 6.4a shows a typical assortment of some of these chondrules. Figure 6.4b shows 8 of the largest chondrules separated. The scale in both pictures is divided into millimeters.

A second phase consisting of the fine-grained groundmass, or "matrix" material, was then prepared from the fragments and rubble resulting from the chondrule separation. This material was passed through a 250 mesh sieve to remove as many of the broken pieces of chondrule as possible. Admittedly this is not a complete separation, but it was felt that at least a large percentage of the chondrule material was separated in this way.

The material which did not pass through the 250 mesh sieve was combined with another chunk of the

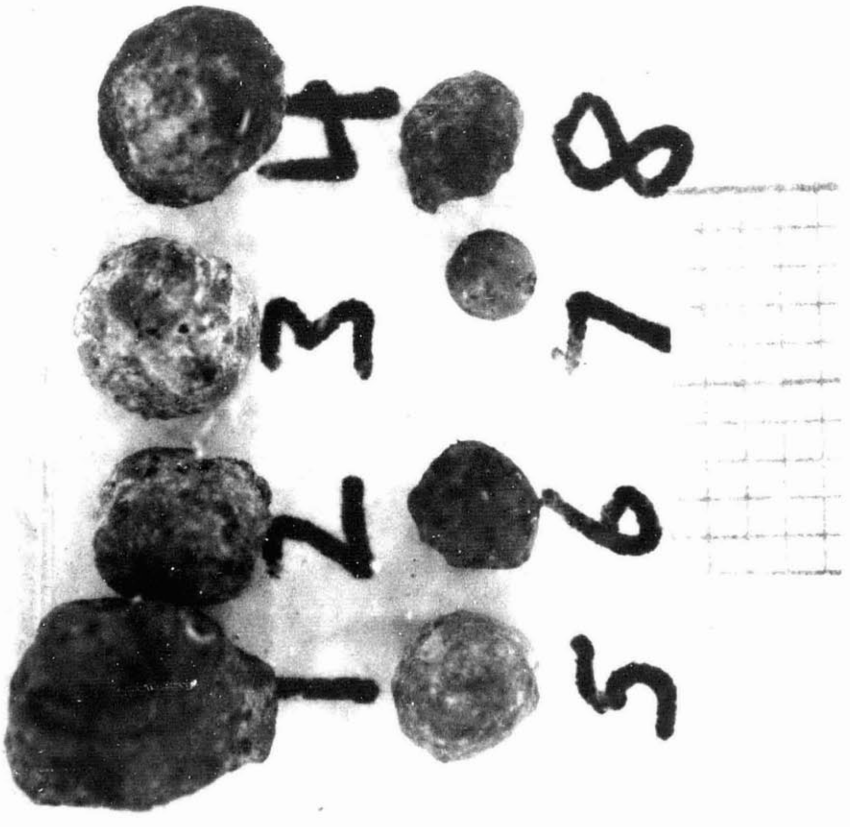
Figure 6.4a

CHONDRULES SEPARATED FROM BJURBÖLE

scale is in millimeters

Figure 6.4b

PHOTOGRAPH OF EIGHT LARGEST BJURBÖLE CHONDRULES



scale is in millimeters

Bjurböle sample and crushed in a stainless steel mortar (with a freshly machined surface). This material was then sorted (using brand new stainless steel sieves) into the following different size fractions:

42- 60 mesh
60-100 "
100-150 "
150-200 "

A hand magnet was then used to remove metallic (Fe,Ni). Each of these size fractions was then passed through a Franz Isodynamic Separator. Eight to 10 different magnetic portions were collected for each mesh size. Each of these magnetic fractions was passed through the separator twice.

Upon completion of these separations, 5 different phases of the Bjurböle chondrite were prepared for Rb-Sr analysis:

1) whole meteorite (a large, unmolested chunk of the original sample still remained from which a piece was broken off for the whole meteorite analysis. A clean surface was scraped on this piece just before crushing.)

2) "matrix" or groundmass
3) chondrules
4) non-magnetic fraction, or that portion of the meteorite which was not attracted by the magnet at currents of less than 1 ampere.
5) medium-magnetic fraction, an olivine - pyroxene concentrate - that fraction which was separated between currents of .2 and .7 amperes..

No attempt was made to use heavy liquids for phase separations. In view of recent evidence concerning the leaching of Rb and Sr from meteorites (Gast, 1962; Smales et al., 1964; Pinson et al., 1963) it was decided to analyze these 5 phases first.

The results of the Rb-Sr analyses on these 5 phases are listed in the following tables. Data on the Rb isotope dilution analyses are given in Table 6.4a. The whole meteorite was analyzed in triplicate - starting with 3 individual 1 gram samples and processing each one independently. The other 4 phases were analyzed in duplicate. The Rb^{87} Dilute Spike (~1.26 μgm Rb/ml) was used in the spiking of each of these

Table 6.4a

Bjurböle Chondrite Rubidium Analyses

Sample	Mass Spectrometer Record Number	Sample Weight	Rb^{85}/Rb^{87} Measured	μgms Rb Spike added	Rb ppm Measured	Rb ppm* Corrected for blank
Whole Meteorite						
3	3453(L)	3.00835	1.0497	3.696	2.855	2.84
4	3450(L)	3.13119	1.0724	3.696	2.846	2.83
5	3451(L)	3.07562	1.0678	3.696	2.876	2.86
Matrix						
1	3389(L)	.82287	1.13936	2.464	8.034	8.02
4	3341(L)	.86988	1.17372	2.464	8.023	8.01
Chondrules						
1	3545(L)	.89878	1.8323	3.696	3.418	3.40
2	3634(L)	1.0473	1.9180	3.696	3.463	3.45
Medium Magnetic Fraction						
3	3533(L)	.95205	1.16137	1.1088	3.235	3.22
4	3539(L)	.87195	1.11797	1.1088	3.299	3.28
Non-Magnetic Fraction						
7	3530(L)	.0129	1.84472	.14784	97.49	97.48
8	3542(L)	.01545	1.93653	.14784	97.50	97.49

* Rb blank correction of .015 μgms Rb/gm of meteorite has been subtracted

samples (see Section 3.31). A value of 1.232 μgms Rb/ml was used as the concentration of this spike. A blank correction of .015 μgms Rb per gram of meteorite has been subtracted from each of the measured Rb concentration values (see Section 6.1).

The Sr isotope dilution analyses are listed in Table 6.4b. The sample numbers correspond to those in Table 6.4a. Both Rb and Sr isotope dilution analyses are made from the same aliquot of sample. The whole meteorite and the matrix analyses were made before the $\underline{Sr^{84}-Sr^{86}}$ Double Spike ($\sim$1.05 μgms Sr/ml) was instituted. They were spiked with the $\underline{Sr^{86}}$ Dilute Spike ($\sim$2.18 μgms Sr/ml); thus fractionation was not corrected for and the Sr^{87}/Sr^{86} values were not calculated. Values of 1.050 and 2.176 μgms Sr/ml were used for the concentrations of the $\underline{Sr^{84}-Sr^{86}}$ Double Spike and $\underline{Sr^{86}}$ Dilute Spike, respectively. The subscripts T and m refer to the "true" or corrected value and the measured value, respectively. An average Sr blank of .020 μgms Sr per gram of meteorite (see Section 6.1) has been subtracted from each of these analyses. Again, these values are reported as normal or non-radiogenic Sr.

The Sr isotope ratio measurements on these

Table 6.4b

Bjurböle Chondrite Strontium Analyses

Sample	Mass Spectrometer Record Number	Weight	$\left(\frac{84}{88}\right)_m$	$\left(\frac{86}{88}\right)_m$	$\left(\frac{87}{86}\right)_m$	$\left(\frac{87}{88}\right)_m$	$\left(\frac{86}{88}\right)_T$	$\left(\frac{N}{S}\right)_T$	µgms Sr spike added	Normal Sr ppm measurd.	Normal Sr** ppm, corrected for fractionatn. and blank	Calc. $\frac{87}{86}$
Whole Meteorite*												
3	3420(L)	3.00835	--	.43413	--	--	--	3.1100	10.895	11.44	11.42	--
4	3419(L)	3.13119	--	.41769	--	--	--	3.2860	10.895	11.61	11.59	--
5	3426(L)	3.07562	--	.42696	--	--	--	3.1844	10.895	11.46	11.44	--
Matrix*												
1	3327(L)	.82287	--	.39515	--	--	--	3.5612	4.358	19.10	19.08	--
4	3322(L)	.86988	--	.38990	--	--	--	3.6352	4.358	18.50	18.48	--
Chondrules												
1	3517(L)	.89878	.23743	.55931	.24826	.13886	.56642	1.10179	10.50	13.476	13.12	.7541(L)
2	3511(L)	1.0473	.21459	.51206	.26017	.13048	.51257	1.28090	10.50	13.139	13.09	.7487(L)
Medium Magnetic Fraction												
3	3527(L)	.95205	.21611	.51062	.26012	.13282	.50367	1.31534	8.40	11.538	11.83	.7459(L)
4	3526(L)	.87195	.23158	.53919	.25261	.13625	.53122	1.21310	8.40	11.597	11.91	.7482(L)

(continued)

Table 6.4b (continued)

Sample	Mass Spectrometer Record Number	Weight	$\left(\frac{84}{88}\right)_m$	$\left(\frac{86}{88}\right)_m$	$\left(\frac{87}{86}\right)_m$	$\left(\frac{87}{88}\right)_m$	$\left(\frac{86}{88}\right)_T$	$\left(\frac{N}{S}\right)_T$	µgms Sr spike added	Normal Sr ppm measurd.	Normal Sr** ppm, corrected for fractionatn. and blank	Calc. $\frac{87}{86}$
Non-Magnetic Fraction												
7	3520(L)	.0129	.43280	.92037	.19286	.17787	.91588	.52804	5.25	217.057	219.39	.7384(L)
8	3523(L)	.01545	.37696	.81717	.20313	.16514	.81555	.63380	5.25	218.944	219.89	.731(L)

* analyses made with Sr^{86} Dilute Spike

** A blank correction of .020 µgms Sr/gram of meteorite has been subtracted.

Bjurböle chondrite phases are given in Table 6.4c. These analyses were made on different one gram samples from those used for the isotope dilution analyses. Note the excellent agreement in the $(Sr^{87}/Sr^{86})^{*}$ values between duplicate analyses on the whole meteorite, matrix and chondrules. Only single isotope ratio analyses were run on the medium-magnetic and non-magnetic fractions. The errors and normalization procedure are discussed in Sections 6.5 and 6.3 respectively. The last column in Table 6.4c lists the 87/86 ratios calculated from the isotope dilution analyses of Table 6.4b. These ratios have been put in brackets to indicate that they do not correspond to the samples of Table 6.4c. These calculated values were among the first attempts with the <u>Sr^{84}-Sr^{86}</u> <u>Double Spike</u> (~1.05 μgms Sr/ml) to calculate 87/86 ratios in the original sample. They are not nearly as precise as the later calculated 87/86 ratios in Table 6.3c.

Table 6.4d summarizes the Rb-Sr data for the Bjurböle chondrite. Note the excellent agreement between duplicate analyses. The greatest disagreement (3%) occurs between the duplicate Sr analyses on the matrix material. The matrix was the first sample

TABLE 6.4c

BJURBÖLE CHONDRITE STRONTIUM ISOTOPE RATIO ANALYSES

Sample	Mass Spectrometer Record Number	$(\frac{87}{86})_m$	$(\frac{86}{88})_m$	$(\frac{87}{86})^*$	$\bar{\sigma}^{***}(87/86)^*$	$\bar{E}^{****}(87/86)^*$	$(\frac{87}{86})^{**}$ Calculated
Whole Meteorite							
1.	3461(L)	.75016	.11924	.74946	2.7×10^{-4}	.036%	
2.	3571(S)	.74945	.11940	.74945	1.8×10^{-4}	.02%	
Matrix							
2.	3329(L)	.75172	.11938	.75169	2.2×10^{-4}	.03%	
3.	3324(L)	.74787	.12061	.75166	2.9×10^{-4}	.04%	
Chondrules							
1.	3760(S)	.74519	.11939	.74516	1.5×10^{-4}	.02%	.7541(L)
2.	3756(S)	.74479	.11958	.74539	2.4×10^{-4}	.03%	.7487(L)
Medium-Magnetic Fraction							
4.	3694(S)	.74184	.11949	.74211	1.5×10^{-4}	.02%	.7459(L) .7482(L)
Non-Magnetic Fraction							
5.	3689(S)	.73398	.11981	.73523	2.4×10^{-4}	.03%	.7384(L) .731 (L)

* normalized to $Sr^{86}/Sr^{88} = .1194$

** Sr^{87}/Sr^{86} ratio calculated from Sr isotope dilution analysis in Table 3.5b. These values are not from the same sample.

*** $\bar{\sigma} = \sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}}$ **** $\bar{E} = \frac{\bar{\sigma}}{(87/86)^*}(100)$

TABLE 6.4d

SUMMARY OF BJURBÖLE CHONDRITE Rb-Sr ANALYSES

Sample	Rb ppm	Sr ppm	Rb^{87}/Sr^{86}	Average Rb^{87}/Sr^{86}	$(Sr^{87}/Sr^{86})^*$	Average $(Sr^{87}/Sr^{86})^*$
Whole Meteorite						
	2.840	11.42	.72071		.74946	
	2.831	11.59	.70753	.71766		.74946
	2.861	11.44	.72475		.74945	
Matrix						
	8.019	19.08	1.21387	1.2352	.75169	.75168
	8.008	18.48	1.25651		.75166	
Chondrules						
	3.403	13.123	.74995	.75585	.74516	.74528
	3.448	13.093	.76176		.74539	
Medium-Magnetic Fraction						
	3.220	11.831	.78737	.79212	.74211	.74211
	3.284	11.913	.79687			
Non-Magnetic Fraction						
	97.48	219.39	1.28504	1.2837	.73523	.73523
	97.49	219.89	1.28236			

*normalized to $Sr^{86}/Sr^{88} = .1194$

analysed in this entire thesis and fractionation could not be corrected for with the Sr^{86} Dilute Spike. The majority of the duplicate analyses agree to better than 1%. Rb^{87}/Sr^{86} ratios have been calculated using the computer program described in Section 4.3.

The average Rb^{87}/Sr^{86} and $(Sr^{87}/Sr^{86})^{*}$ values in Table 6.4d have been plotted in Figure 6.4c along with the meteorites and the meteorite isochron of Section 4.3. A discussion of these Bjurböle analyses is given in Chapter 7.

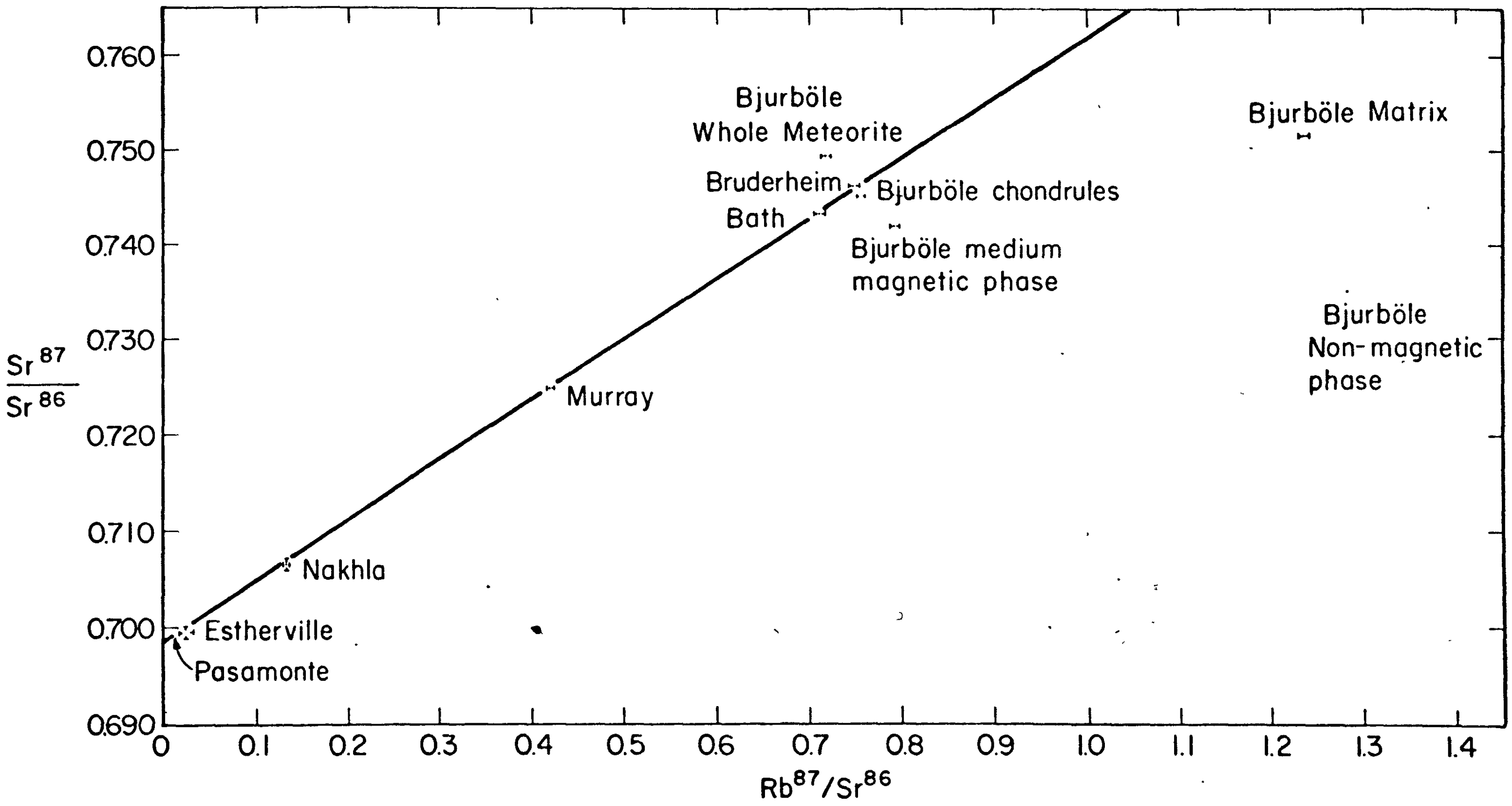
6.5 - Errors and Improvements in Analytical Precision

The precision and accuracy of Sr isotope ratio measurements have been previously discussed by Faure (1961, 174-184), Powell (1962, 125-138), Bottino (1963, 121-131) and Krogh (1964). Briefly, the following quantities are used in estimating errors in Sr isotope ratio analyses:

1. Standard deviation of a single analysis:

$$\sigma = \sqrt{\frac{\Sigma(\bar{x} - x_i)^2}{(n-1)}}$$

Figure 6.4c
Shields' Meteorite Isochron Including Bjurböle Analyses



2. Standard deviation of the mean:

$$\bar{\sigma} = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n(n-1)}}$$

3. Percent error of a single analysis:

$$E = \frac{100\,(\sigma)}{\bar{x}}$$

4. Percent error of the mean:

$$\bar{E} = \frac{100\,(\bar{\sigma})}{\bar{x}}$$

These formulas have also been used in calculating reproducibility errors for groups of replicate spike calibrations (in Chapter 3).

The calculation of errors associated with a least squares line is described in Youden (1951, 41-43) and has been discussed in Section 4.22.

The calculation of the individual error bars on the isochrons (in Figures 6.3a, 6.4c, and 6.5), however, should be discussed further. Those which represent the reproducibility of replicate Sr isotope ratio analyses can be calculated easily, since the total spread between the highest and lowest Sr^{87}/Sr^{86} values is small. Thus, the analytical precision can be assumed to be roughly constant over the entire range of values. A series of duplicate analyses are available here from which an estimate of the standard deviation is desired. Two different formulas which are essentially similar have been used for this calculation.

Youden (1951, 16) gives the following formula for calculating a standard deviation from duplicates:

$$S.D. = \sqrt{\frac{\sum d^2}{2n}}$$

where d is the <u>difference</u> between an individual set of duplicate analyses and n is the number of duplicates. Note that 2n is, therefore, the number of individual analyses. A formula suggested in Dixon and Massey (1957, 143ff.) is as follows:

$$S.D. = \sqrt{\frac{\sum_i \sum_j (x_{ij} - \bar{x}_j)^2}{\sum_j n_j - k}}$$

where: X_{ij} = the value of the ith replicate of the jth sample

$\bar{x}_j$ = mean value of the j^{th} sample

k = total number of samples (<u>not</u> data points)

n_j = number of replicates of the j^{th} sample.

Both of these formulas give the same answer.

The calculation of the individual error bars for Rb^{87}/Sr^{86} ratios, however, has been the cause for much deliberation by the author. Frequently in the past, it has been customary to simply guess at a reasonable overall error from a glance at the scatter of data points and a backlog of experience and knowledge as to the long-term general reproducibility in the laboratory. The author, however, does not consider this a very rigorous approach, especially since he is interested in arriving at some more or less objective method for comparing his analyses with those of Pinson <u>et</u> <u>al</u>., (1963). Furthermore, as a result of the new, clean chemical separation procedure, it is of interest to determine whether or not the precision of replicate Rb and Sr isotope dilution analyses has been improved and by how much.

The calculation of these Rb^{87}/Sr^{86} error bars, however, requires some thought. The Rb^{87}/Sr^{86} ratios in this investigation range over more than 2 orders of magnitude. Does either the absolute error or the percentage error between duplicate Rb/Sr ratios remain constant over this range? Perhaps the error gets smaller as the Rb/Sr ratio decreases, since the ratio becomes more insensitive to absolute errors of the same size. Also, the Sr content often increases as the Rb/Sr ratio decreases and, therefore, should be determined just as accurately (if not more accurately) with a corresponding decrease in Rb/Sr error. Yet, what happens in the case of an achondrite like Johnstown which has only 2 ppm Sr and 0.1 ppm Rb? Should it have the same error bars as Nakhla with 60 ppm Sr and 3 ppm Rb? And finally, in all these analyses the sample size and the amount of spike added was controlled so that each sample ended up with the same N/S ratio and roughly the same amount of Sr in the beaker. One might conclude from this, therefore, that larger concentrations of Rb and Sr might even be determined with less absolute accuracy.

At first, it was decided to leave out the error bars altogether and let the reader judge the precision from the agreement between replicate analyses and the scatter of points along the isochron. Yet, an objective approach for comparing the present errors with those of Pinson <u>et al</u>., (1963) seemed very desirable. Thus, the following method has been used.

Although it is difficult to say whether the Rb/Sr ratio errors vary in some consistent manner, it does seem reasonable that, to a first approximation, the absolute errors between replicate determinations of Rb (and Sr) concentration remain constant, i.e., independent of absolute concentration over the range measured. Thus, the above formula of Dixon and Massey can be applied, since in this case there are a series of duplicate or triplicate sets of concentration values. An overall standard deviation is calculated for the Rb analyses and also for the Sr analyses. The standard deviation for the Rb/Sr ratios is then obtained from the following formula (Harvey, 1962, 261):

$$\sigma = N\sqrt{\left(\frac{\sigma_1}{N_1}\right)^2+\left(\frac{\sigma_2}{N_2}\right)^2}$$

where: $N = \frac{N_1}{N_2}$,

N_1 and N_2 are the average Rb and Sr analyses, respectively, for a given sample, and

σ_1 and σ_2 are the overall standard deviations for the Rb and Sr analyses, respectively.

Using this formula one can calculate a $\sigma_{Rb/Sr}$ for each sample.

One important factor which this approach fails to consider, however, is possible sample inhomogeneities. It is conceivable that one of the samples in a duplicate set might contain a chunk of metallic Fe-Ni. This would tend to lower both the Rb and Sr contents of that sample. If one dealt only with Rb/Sr ratios, this error would be cancelled out. However, since Tables 6.3d and 6.4d indicate that corresponding Rb and Sr values do not vary systematically in many cases and since great pains were taken to homogenize samples before analysis, this source of error is not considered very significant. (It should be emphasized that this source of error was taken into consideration when plotting the positions of each sample on the isochron. The Rb^{87}/Sr^{86} ratios for each analysis were calculated first and then averaged.)

The resulting error bars are shown in Figures 6.3a, 6.4c, and 6.5. Figure 6.5 shows the isochron of Pinson et al., (1963) with error bars calculated by Shields in the same manner as described above. The reader can easily see the improvement in precision. For Nakhla and Estherville the error bars are the same in both figures. Nakhla and Estherville were not included in the error calculations of Figures 6.3a and 6.4c. Error bars for Figures 6.3a and 6.4c were calculated from the following analyses: Pasamonte, Murray, Bath, Bruderheim, and the 5 different Bjurböle samples listed in Table 6.4d.

A more quantitative comparison of these errors is shown in Table 6.5a. In the case of Pinson et al., (1963) the absolute reproducibility was better for Rb than for Sr by a factor of 3. However, considering that chondrites contain about 3 ppm Rb and 10 ppm Sr, this amounts to about 6% in both cases. In the present investigation it can be seen that the overall precision has been improved by factors of about 7 and 3 for Rb and Sr, respectively. In the case of chondrites this amounts to about 1% for Rb and 2% for Sr. It is surprising that the Sr errors are not smaller than the

Figure 6.5

Pinson et al. (1963) Isochron

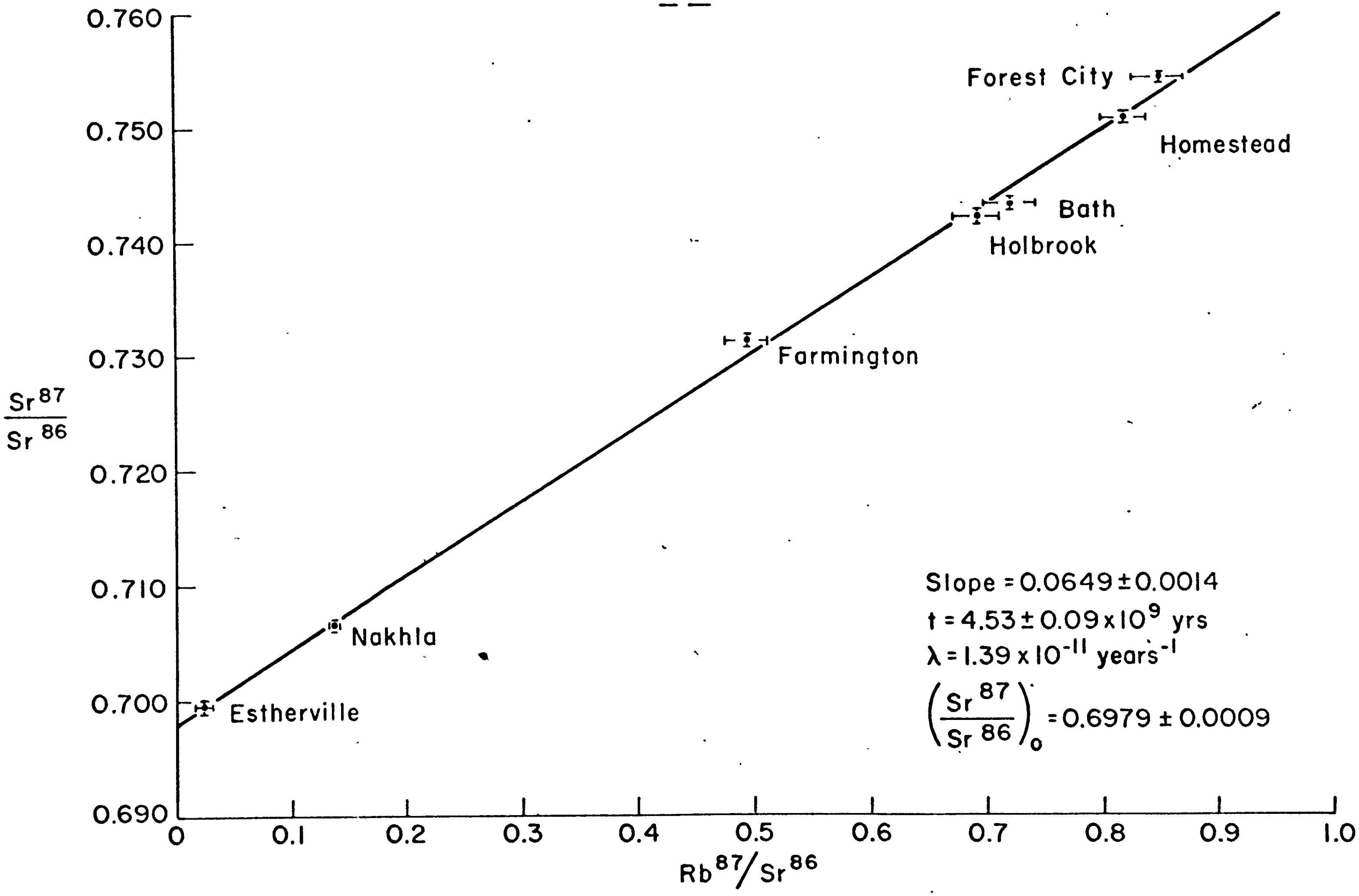


TABLE 6.5a

COMPARISON OF OVERALL STANDARD DEVIATIONS

	Pinson *et al.* (1963)	Shields (1964)
σ_{Rb}	.184	.0285
σ_{Sr}	.560	.206
σ_{SrIR}	.0006	.00014

Rb errors since the new Sr^{84}-Sr^{86} Double Spike allows a correction to be made for mass spectrometer discrimination in Sr analyses.

Note also that the precision in Sr isotope ratio analyses has been significantly improved. This is probably due not only to the new chemical procedure, but also to improved mass spectrometry techniques. The vertical bars in Figure 6.3a have not been drawn, since they amount only to the width of the pencil point.

Tables 6.5b and 6.5c give the individual Rb/Sr standard deviations which have been plotted in Figures. 6.3a, 6.4c and 6.5. Note that there is a tendency for the error to decrease as the Rb/Sr ratio decreases. This is not always true, however, as can be seen in the cases of Estherville and the Bjurböle non-magnetic phase. The Bjurböle non-magnetic phase has such large Rb and Sr concentrations that in both cases they swamp the overall σ_{Rb} and σ_{Sr} . The Rb content of Estherville, however, is almost as low as σ_{Rb} ; thus, the error contribution from $\left(\frac{\sigma_{Rb}}{Rb}\right)^2$ becomes very large.

A few concluding remarks should be made here about the present state of the meteorite isochron. As has just been shown, a significant increase in analytical

TABLE 6.5b

STANDARD DEVIATIONS OF Rb/Sr RATIOS[*]

Pinson *et al.* (1963)

	$\sigma_{Rb/Sr}$
Homestead	.021
Bath	.024
Holbrook	.021
Forest City	.023
Farmington	.018
Nakhla	.003
Estherville	.008

[*] plotted in Figure 6.5

TABLE 6.5c

STANDARD DEVIATIONS OF Rb/Sr RATIOS*

(this work)

	$\sigma_{Rb/Sr}$
Pasamonte	.0004
Bath	.0058
Bruderheim	.0056
Bjurböle Whole Meteorite	.0051
Bjurböle Chondrules	.0046
Bjurböle Matrix	.0049
Bjurböle Medium-Magnetic Phase	.0053
Bjurböle Non-Magnetic Phase	.0004
Murray	.0038

* plotted in Figures 6.3a and 6.4c

precision has been obtained in this thesis investigation. As a result, the standard deviation of the slope of the isochron has been reduced from .0014 to .0005. Contamination has also been reduced by factors of 2 and 10 in the cases of Rb and Sr, respectively. This means that not only can one extend the Rb-Sr technique to samples with smaller concentrations of Rb and Sr, but also it is now possible to resolve smaller age differences between samples. In the case of the present meteorite isochron a standard deviation of ± 32 million years was calculated for the slope by the methods of Youden (1951, 42-43). This corresponds to a 95% chance that the age of 4.45 b.y. is good to ± 89 million years and a 99% chance (or almost a sure bet) that the age is not off by more than 146 million years either way. Thus, another suite of meteorites with an age, about 100 million years different from the present suite could probably be resolved in the M.I.T. Geochronology Laboratory.

These statements are made from the standpoint of precision errors only, however. Statistics does not tell us anything about accuracy errors. Fortunately, most accuracy errors can be circumvented by analyzing two suites of samples in the same laboratory. If a second series of meteorites with a slightly different age were to be investigated in the M.I.T. Geochronology Laboratory, accuracy errors would not interfere with the age resolution, since they would tend to cancel out. It is when one compares 2 isochrons which were each obtained in separate laboratories by independent workers, however, that accuracy errors become important and age resolution deteriorates. In this case different sets of spike solutions, different chemical separation procedures, and different mass spectrometer techniques are used - all of which can lead to small, consistent differences between the two laboratories.

The determination of an accurate absolute age for meteorites (or any other sample) by the Rb-Sr technique is still another problem, however. In this case accuracy errors become important. The present age of 4.45 b.y. obtained for the meteorite isochron could be affected by a number of such errors. No doubt, the largest uncertainty in the entire Rb-Sr age technique is the inaccurately known Rb^{87} half-life. A glance at the age equation (Section 2.1) is sufficient to show that the age of a system is inversely proportional to the decay constant. A half-life of 50 b.y. (Aldrich et al., 1956) has been used in this thesis; this value is roughly in the middle of the recently determined values which range from 43 to 65 b.y. Another error which could change the age slightly (though not nearly as much as in the case of the Rb^{87} half-life) would be an incorrect determination of the concentration of either of the spike solutions. A spike concentration error would move all the points on the isochron horizontally (some more than others, of course) resulting in a slightly different slope and age. There is also the possibility of a small consistent error being introduced by mass spectrometer bias. It is not inconceivable that mass spectrometers frationate Rb quite differently from Sr, since these 2 elements are ionized at very different temperatures. Someday the extent of mass spectrometer bias for both Rb and Sr may be determined which could result in a slight adjustment of both the Rb^{87}/Sr^{86} and Sr^{87}/Sr^{86} ratios. The contribution of contamination to the error in this meteorite isochron is considered to be insignificant.

It is important, however, to realize how these errors affect various quantities in the age equation.

The initial Sr^{87}/Sr^{86} ratio, for example, is not affected at all by errors in either the Rb^{87} half-life or the calibration of spike solution concentrations. If either of the spike solutions were calibrated erroneously, the points on the isochron would move horizontally; hence, the isochron would be rotated with the $(87/86)_o$ acting as a pivot. If the mass spectrometer were giving a constant bias, however, the $(87/86)_o$ and all the other 87/86 ratios would be affected. Finally, it should be remembered that the isochron line and its slope are determined from experimental data without recourse to the Rb^{87} half-life. A change in the value of the half-life, therefore, does not affect the slope or initial ratio of the isochron.

CHAPTER VII

DISCUSSION

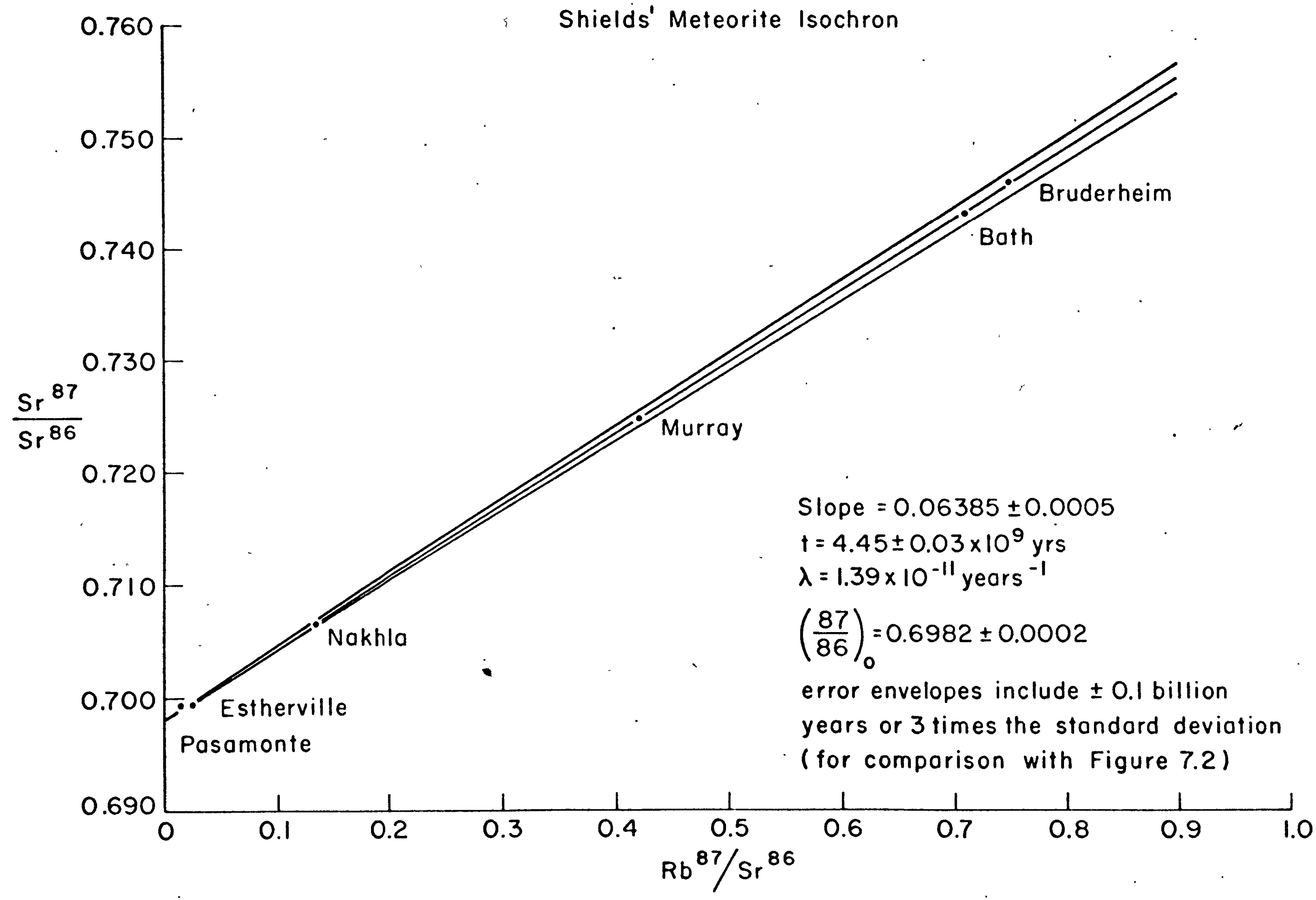
7.1 - The Meteorite Isochron and Other Recent Rb-Sr Meteorite Age Investigations

The meteorite isochron described in Section 6.3 has been reproduced in Figure 7.1a without error bars (a discussion of the errors has already been given in Sections 6.5 and 4.22). Error envelopes of ± 0.1 billion years (or 3 times the standard deviation) have been drawn for comparison with the Pb-Pb isochron in Figure 7.2. The isochron of Pinson _et_ _al_., (1963) has been reproduced in Figure 7.1b also without error bars for purposes of comparison with Figure 7.1a.

First, as can be seen from Figures 7.1a and 7.1b a significant increase in analytical precision has been obtained over the work of Pinson _et_ _al_., (1963). The standard deviation in the slope of the isochron has been improved from ± 0.0014 to ± 0.0005; this is readily noticeable even by visual observation. Thus, the standard deviation in the Rb^{87}-Sr^{87} age of meteorites has been reduced from ± 90 million years to ± 32 million years. (For a further discussion of errors and improvements in analytical precision see Sections 6.5,

Figure 7.1a

Shields' Meteorite Isochron



Slope = 0.06385 ± 0.0005

$t = 4.45 \pm 0.03 \times 10^9$ yrs

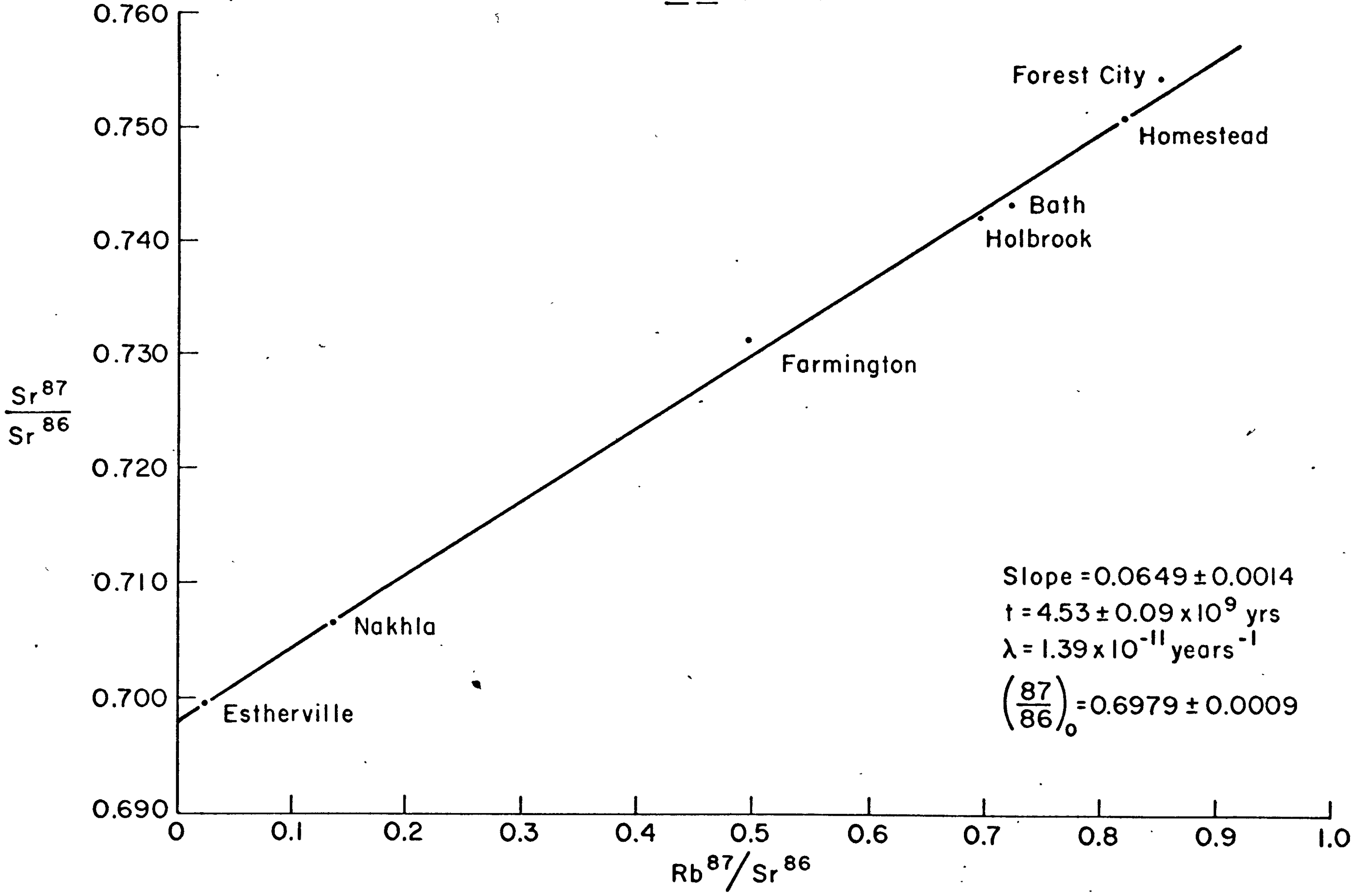
$\lambda = 1.39 \times 10^{-11}$ years^{-1}

$\left(\frac{87}{86}\right)_0 = 0.6982 \pm 0.0002$

error envelopes include ± 0.1 billion years or 3 times the standard deviation (for comparison with Figure 7.2)

Figure 7.1b

Pinson *et al.* (1963) Isochron



6.1 and 6.2) It is interesting to note that several years ago many investigators thought that meteorites did, in fact, exhibit real and significant age differences. The present work, however, has demonstrated that this is not the case (at least within the resolution of the present technique) and that previous scatter was due essentially to poor analytical precision.

Second, much of the error in the isochron of Figure 7.1a is contributed from the Pasamonte and Estherville discrepancy. Plans have been made to reanalyze these two meteorites in the near future. Several suggestions may be offered at present for the disagreement. First, the Estherville analysis was made by Pinson et al., (1963) before institution of the new, clean chemical separation procedure. Since Pasamonte lies practically within the limits of error of the Estherville analysis, it may be that a reanalysis of Estherville would eliminate the discrepancy. Second, Gast's average Rb^{87}/Sr^{86} value for Pasamonte is 0.008 and his average Sr^{87}/Sr^{86} ratio, when normalized to .1194, is .69875. This plots on the present isochron of Figure 7.1a within the width of the pen line. This would tend to indicate that a reanalysis of Pasamonte might solve the problem. Finally, there is always the remote possibility that one (or both) of these two meteorites does have a different age. It seems, however, that the probability of such an event producing a Sr^{87}/Sr^{86} ratio nearly identical to the initial ratio of the meteorite isochron would be very small. The first two suggestions are considered most reasonable.

Third, each of the six meteorites on the isochron of Figure 7.1a is from a different meteorite class. The following classes are represented:

1. Olivine-bronzite, or H-group, chondrite (Bath)
2. Olivine-hypersthene, or L-group, chondrite (Bruderheim)
3. Type II carbonaceous chondrite (Murray)
4. Nakhlite, or olivine-diopside achondrite (Nakhla)
5. Eucrite, or pyroxene-plagioclase achondrite (Pasamonte)

6. Mesosiderite (Estherville)

One can say, therefore, (from the discussion in Section 1.2) that probably at least 5 of these 6 classes of meteorites underwent a chemical differentiation 4.5 billion years ago.

Fourth, Figure 7.1a includes analyses made not only at different times, but also by three different investigators. This indicates, therefore, that at least there are no significant differences between the analyses of these three workers in the M.I.T. Geochronology Laboratory.

Finally, the remarkably close fit of these six meteorites to a straight line tends to indicate that the initial assumptions discussed in Section 1.2 have been satisfied.

In view of the extreme difficulty involved in obtaining an accurate Rb-Sr age for meteorites, it is often advisable to have some means of comparison with work done in other laboratories. This provides a partial check on the accuracy of the analyses. Thus, it is not uncommon for several independent workers to analyze the same meteorite.

Pasamonte has been analyzed by Schumacher

(1956a,b,c, and d), Herzog and Pinson (1956) and Gast (1962). The early works of Schumacher and Herzog and Pinson are of poor quality. Schumacher's Sr^{87}/Sr^{86} ratio for Pasamonte is much lower than that obtained by any other investigator. Gast (1962) made 5 replicate Sr^{87}/Sr^{86} analyses on Pasamonte. When normalized to a Sr^{86}/Sr^{88} ratio of .1194, his average of .69875 is in good agreement with the value of .69943 obtained in this work. The Sr isotope dilution analyses are also in excellent agreement. The Rb analysis of Gast is .1 ppm lower than that obtained in this present work.

Gast (1963) has also measured a Rb-Sr age of 4.62 billion years on the Bruderheim chondrite (with $\lambda = 1.39\text{x}10^{-11}$ years^{-1}). Unfortunately, only the final age value was available to the author so that the individual analyses cannot be compared. Gast's age is .17 billion years older than the one measured in this work.

The Bath chondrite has been analyzed by Pinson <u>et</u> <u>al</u>., (1963). The agreement with this present work is very good. The primary difference is between the 2 Rb^{87}/Sr^{86} analyses and arises from numerous subsequent spike calibrations on the Rb^{87} Dilute Spike ($\sim$ 1.26 μgms Rb/ml). This spike was used in both analyses, but subsequent extra spike calibrations resulted in using a 2% lower value for the concentration of the spike in this thesis.

The Murray carbonaceous chondrite was analyzed by Beiser (1964) and Murthy and Compston (1964). These analyses do not show as good agreement as might be expected. The Sr^{87}/Sr^{86} ratios disagree by 0.005 and the Rb^{87}/Sr^{86} ratios disagree by 0.064.

It is also of interest to compare this thesis isochron with other recent Rb-Sr meteorite isochrons. An age of 4.45×10^{9} years (with $\lambda = 1.39 \times 10^{-11}$ years^{-1}) was obtained in this present work for the Rb-Sr age of stony meteorites. This is slightly younger than the isochron age of 4.52 billion years determined by Pinson *et al.*, (1963) using the same decay constant. Closer examination shows that this age difference cannot be ascribed to a change in the value of the Rb^{87} Dilute Spike, since the age of this present isochron has already been made older by lowering this spike concentration 2%.

Gast (1962) has calculated three types of isochron ages (see Section 1.3). He obtains an age of 4.67×10^9 years ($\lambda = 1.39 \times 10^{-11}$ years^{-1}) for the time of differentiation of the chondrites from the achondrites, assuming this took place in one single event (Model I age). If one assumes, however, that differentiation took place at a different time for each meteorite, then a series of ages ranging from 4.5 to 4.9×10^9 years (with an average value of 4.7×10^9 years) are calculated from the individual chondrites (Model II ages). Finally, one can determine the time when the Beardsley chondrite became enriched in Rb by constructing an isochron through the four chondrite points giving an age of 4.46×10^9 years. Gast's Model I and II ages are both older than the age obtained in this present investigation. The Model III age, however, is younger than both Gast's Model I and Model II ages. Although it agrees with this present work, this Model III isochron does not contain an "anchor point" - or point close to the initial Sr^{87}/Sr^{86} ratio. Furthermore, Beardsley is a very anomalous chondrite, and thus this Model III age should be treated cautiously until further experimental data are available.

Murthy and Compston (1964) constructed an isochron from the analyses of four carbonaceous chondrites and the Peace River chondrite. They obtained a good spread in Rb/Sr ratios and an age of 4.9×10^9 years (with $\lambda = 1.39 \times 10^{-11}$ years^{-1}). It is interesting that the Peace River chondrite falls in line with the four carbonaceous chondrites and that omitting it does not significantly lower the age. The age of 4.9×10^9 years, however, is older than any other isochrons that have been determined so far. Murthy and Compston (1964) also constructed an isochron from three individual chondrules separated from the Peace River meteorite, but since a least squares analysis of these points yields an initial Sr^{87}/Sr^{86} ratio of .694 it seems hazardous to compare it at present to the other meteorite isochrons.

Finally, the Rb-Sr data can be used to make some observations on the nature of the primordial material. The question is often raised as to which, if any, of the observed groups of meteorites represents the primary undifferentiated material. Ordinary chondrites, carbonaceous chondrites, and chondrules have all been suggested as possible representatives of this primitive material. This present thesis isochron has been constructed from 6 different types of meteorites; therefore, at least 5 of these types must have been differentiated about 4.5×10^9 years ago. The work of Pinson et al., (1963), however, showed that an isochron of 4.5×10^9 years can be drawn from the ordinary chondrite data alone, thus indicating that the ordinary chondrites, themselves, underwent a differentiation at that time. Furthermore, Murthy and Compston (1964) have shown that isochrons yielding a similar age can be constructed not only from the carbonaceous chondrite data alone, but also from a series of individual chondrules. Thus, it seems that (at least within a resolution of $\pm \frac{1}{2}$ billion years) neither the ordinary chondrites nor the chondrules from an ordinary chondrite can represent the undifferentiated material. The three groups of carbonaceous chondrites also underwent differentiation with respect to one another at about this same time, but the possibility is still open that the Type I or Type II carbonaceous chondrites may be samples of the primitive material.

7.2 - Rb-Sr versus the Pb-Pb Age for Meteorites

Patterson (1955 and 1956) presented an outstanding determination of the age of meteorites and the earth using the U^{238}-Pb^{206} and U^{235}-Pb^{207} decay schemes. His age was later substantiated by Hess and Marshall (1960). Further supplementary work has also been carried out by Starik et al., (1959 and 1960), Murthy and Patterson (1962) and Marshall (1962). It seems remarkable, indeed, that an entirely different decay scheme, such as Rb^{87}-Sr^{87}, should yield a solidification age for meteorites which agrees so closely with that determined by the Pb-Pb technique. After constructing a highly precise meteorite isochron using the Rb^{87}-Sr^{87} decay scheme, therefore, it is naturally of interest to see how it compares with the Pb-Pb age of meteorites. The question naturally arises as to which of these dating techniques now gives the most accurate solidification age.

The Pb-Pb age technique takes advantage of the fact that there are two uranium isotopes, U^{238} and U^{235} both of which decay to different stable isotopes of lead. Thus the equations:

$$\left(\frac{Pb^{206}}{Pb^{204}}\right)_P - \left(\frac{Pb^{206}}{Pb^{204}}\right)_0 = \left(\frac{U^{238}}{Pb^{204}}\right)_P \left(e^{\lambda t}-1\right) \qquad 7.2a$$

and

$$\left(\frac{Pb^{207}}{Pb^{204}}\right)_P - \left(\frac{Pb^{207}}{Pb^{204}}\right)_o = \left(\frac{U^{235}}{Pb^{204}}\right)_P \left(e^{\lambda_5 t} - 1\right) \qquad 7.2b$$

can be combined by division to yield the following age equation.

$$\frac{\left(\frac{Pb^{206}}{Pb^{204}}\right)_P - \left(\frac{Pb^{206}}{Pb^{204}}\right)_o}{\left(\frac{Pb^{207}}{Pb^{204}}\right)_P - \left(\frac{Pb^{207}}{Pb^{204}}\right)_o} = \left(\frac{U^{238}}{U^{235}}\right)_P \frac{\left(e^{\lambda_8 t} - 1\right)}{\left(e^{\lambda_5 t} - 1\right)} \qquad 7.2c$$

where λ_8 and λ_5 are the decay constants of U^{238} and U^{235}, respectively. Pb^{204} is a stable nuclide which is not known to be produced by the decay of any natural radionuclide; it serves an analogous purpose to that of Sr^{86} in the Rb-Sr technique.

As in the case of Rb-Sr, equation 7.2c can also be arranged in the form of $y = mx + b$:

$$\left(\frac{Pb^{207}}{Pb^{204}}\right)_P = \left(\frac{U^{235}}{U^{238}}\right)\frac{\left(e^{\lambda_5 t}-1\right)}{\left(e^{\lambda_8 t}-1\right)}\left(\frac{Pb^{206}}{Pb^{204}}\right)_P - \frac{\left(e^{\lambda_5 t}-1\right)}{\left(e^{\lambda_8 t}-1\right)}\left(\frac{U^{235}}{U^{238}}\right)\left(\frac{Pb^{206}}{Pb^{204}}\right)_o + \left(\frac{Pb^{207}}{Pb^{204}}\right)_o \qquad 7.2d$$

This is the equation of a straight line when plotted with $(Pb^{207}/Pb^{204})_p$ and $(Pb^{206}/Pb^{204})_p$ on the ordinate and abcissa, respectively. A difference between the 2 methods, however, occurs in the determination of the initial ratios of the daughter element(s). In Rb-Sr work, the initial ratio occurs as the intercept on the Sr^{87}/Sr^{86} axis; in Pb-Pb ages it is considered to be the lead with the lowest Pb^{207}/Pb^{204} and Pb^{206}/Pb^{204} ratios, i.e., that found in certain unaltered iron meteorites where the Pb/U ratio is so large that no significant contribution from U decay would have occurred in the last 4.5 billion years. It is obvious, of course, that in the Pb-Pb method the initial ratio is not required for the determination of an age; only the slope of the line between any 2 points is necessary. Figure 7.2 shows the composite Pb-Pb isochron for meteorites reproduced from Anders (1963, 437).

It is immediately obvious that the first big advantage in the Pb-Pb technique is that only isotopic ratios need be measured. The Atomic Energy Commission has been extremely interested in the U^{238}/U^{235} ratio of natural uranium today, and thus this number has been accurately measured. The analysis of a sample

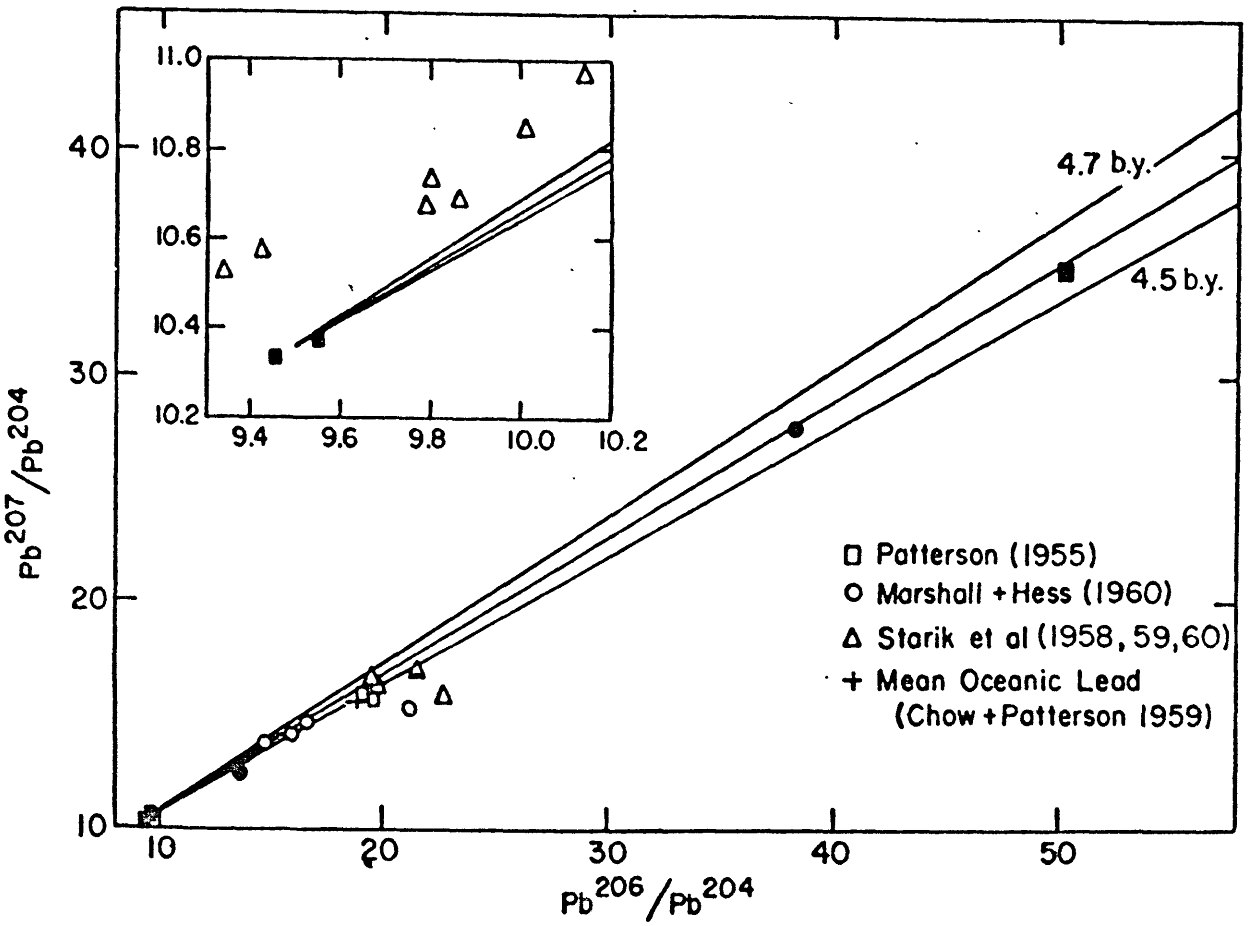


Figure 7.2 COMPOSITE Pb^{207}-Pb^{206} METEORITE ISOCHRON

Reproduced from Anders (1963, 437)

for the determination of a Pb-Pb age, therefore, requires only one isotope ratio analysis of the Pb spectrum. In contrast, a Rb-Sr analysis for age measurement requires two separate isotope dilution analyses and also an isotope ratio analysis of the Sr spectrum. Isotope dilution analyses require considerably more work, since a series of spikes and shelf solutions must be prepared and periodically calibrated.

Second, the Pb-Pb technique has an advantage in that both the U^{238} and U^{235} half-lives are more accurately known than that of Rb^{87}. Over 25 independent measurements have been made of the Rb^{87} half-life; these range all the way from 43 to 65 billion years. Independent measurements on both the U^{238} and U^{235} half-lives, however, show spreads of $<\frac{1}{2}\%$ and 12%, respectively (Aldrich and Wetherill, 1958, 259). The U^{235} half-life is not as easily measured as that of U^{238}, since even in highly enriched U^{235} samples 1/3 or more of the activity comes from U^{234} (a daughter of U^{238}) whose alpha peaks are not easily resolved from those of U^{235}.

On the other hand there are also some

disadvantages in the Pb-Pb method when compared to the Rb-Sr technique. Whereas Rb and Sr contamination in this present work is so low that it is considered insignificant, Pb workers suffer from a considerably more severe contamination problem. Typical lead blanks of 1.5 μgms Pb per analysis (Hess and Marshall, 1960, 285) and .68 μgms Pb per analysis (Marshall, 1962, 2006) have been reported recently. For ordinary chondrites with .05-.5 ppm Pb, carbonaceous chondrites with 1-5 ppm Pb and even troilites with 2-10 ppm Pb, it can be seen that this is a disturbingly high contamination level. Yet, contamination problems can be somewhat overcome by analyzing large samples. In spite of this, however, Hess and Marshall (1960, 285) report that in the case of chondrite analyses contamination may account for "...from 23 per cent to 82 per cent of the total amount of lead observed in the concentration determinations." They state, furthermore, that the "uncertainty in the blank is large, around 30 per cent". In the case of carbonaceous chondrites Marshall (1962, 2009) has estimated the contamination levels to be about 7-12%.

Recent investigations have further shown how few meteorites actually contain U and Pb concentrations which are consistent with the age measurements. Many of the meteorites analyzed contain far too little U to account for the observed increase in Pb^{206} and Pb^{207} over the past 4.5 billion years. As is discussed in Section 7.5, terrestrial weathering may be responsible for a large amount of this contamination, since meteorites exposed to ground water may soak up Pb preferentially to Fe in the sulfide phase (Anders, 1963, 438). In Figure 7.2 only the solid points represent meteorites with consistent U and Pb concentrations.

Yet there is a large offsetting advantage to this contamination problem in that mean oceanic lead lies on the 4.5 billion year Pb-Pb isochron (see Figure 7.2). Thus, (assuming, of course, that all meteorites do lie on this same isochron) this contamination does not interfere with the Pb-Pb age of meteorites as much as might at first be expected. Hess and Marshall (1960, 289) estimated that despite the high contamination level the errors in the isotopic measurements were probably only about 3%.

Mass spectrometer discrimination is also an important problem to be considered. Since the per cent mass difference between the 2 Rb isotopes and between Sr^{86} and Sr^{88} is only slightly larger than that between Pb^{204} and Pb^{208}, one might expect that mass spectrometer discrimination would affect the Rb^{85}/Rb^{87}, Sr^{86}/Sr^{88} and Pb^{208}/Pb^{204} ratios to a roughly similar extent. In the case of Sr isotope ratio analyses and doubly spiked Sr isotope dilution analyses mass spectrometer discrimination can be corrected for by adjusting measured ratios to agree with commonly accepted values for the ratios of the stable non-radiogenic isotopes (as discussed in Section 6.3 and in Krogh, 1964). However, Rb and Pb analyses cannot at present be corrected for discrimination in this manner because natural Rb only contains 2 isotopes and Pb has only one non-radiogenic isotope. In the case of Pb a constant square root of mass correction is usually made, but this does not take into account the variations that occur from one run to the next. Rb and Pb, therefore, probably suffer from similar mass discrimination problems.

It is interesting to speculate for a moment on the extent of this fractionation. It is an observed fact that not only do different workers in different laboratories tend to get different values for the average of a large number of Sr^{86}/Sr^{88} ratios measured over an extended period of time, but also there is a significant variation in the Sr^{86}/Sr^{88} ratios measured from one run to the next. At the M.I.T. Geochronology Laboratory the Sr^{86}/Sr^{88} ratios commonly range anywhere from .1180 to .1210, which is a spread of 2½% (as a conservative estimate). The per cent mass difference in the case of Sr^{86} and Sr^{88} is also about 2½%. It is probably a reasonable assumption, therefore, that Rb also fractionates to this extent.

The Pb^{207}/Pb^{204} ratio represents a mass difference of about 1½%. Assuming a similar type of fractionation, the Pb^{207}/Pb^{204} ratios might, therefore, be expected to fractionate over a range of about 1½%. Thus, Pb ratios measured in different laboratories could show not only consistent differences of a per cent or so, but also disagreements between individual replicate analyses of the same amount. Referring back to Figure 7.2, for Pb^{207}/Pb^{204} ratios in the range of 10 to 20 this would represent a variation of from .15 to .3, respectively. A glance at the insert in Figure 7.2 shows that this might indeed explain the discrepancy between the results of Starik et al., (1958, 1959 and 1960) and Patterson (1955) and also account for small age differences.

Everything considered, the author feels that the slope of the Rb-Sr meteorite isochron presented in this thesis is now as accurately determined as the slope of the Pb-Pb isochron. Certainly the scatter of the points about the least squares line is as good or better than in the case of the Pb-Pb isochron. (Compare Figures 7.1a and 7.2, but remember that Figure 7.2 includes the data of three different workers. Error envelopes in both Figures represent 10^8 years.) In converting the slope into an age, however, the half-life and its associated errors are introduced. Here there is undoubtedly a greater uncertainty in the Rb^{87} half-life than in either the U^{238} or U^{235} half-lives. Thus, the final value for the age of meteorites may be more accurately determined by the Pb-Pb technique, but only because of the more accurately known half-lives of uranium.

One can, of course, make the assumption that the Rb-Sr and Pb-Pb techniques date the same event and should yield the same solidification age for meteorites. Present evidence indicates that this is certainly quite possible. Thus, a Rb^{87} decay constant can be calculated by combining the accurately measured slope of the Rb-Sr isochron in this thesis with the Pb-Pb age of $4.55x10^{9}$ years for meteorites (Patterson, 1956). Using a value of .06385 for the slope of this Rb-Sr isochron, a decay constant of $1.36x10^{-11}$ $years^{-1}$ is obtained. This corresponds to a half-life of $5.1x10^{10}$ years for Rb^{87}. If one uses the Pb-Pb meteorite age of $4.6x10^{9}$ years proposed by Hess and Marshall (1960) then the decay constant for Rb^{87} becomes $1.345x10^{-11}$ $years^{-1}$ and the half-life becomes $5.16x10^{10}$ years.

It should be pointed out, however, that it is dangerous to assume that both the Pb-Pb and Rb-Sr techniques give the exact same age. In the case of terrestrial rocks, the Pb ages are usually determined from different minerals than those used for the Rb-Sr age determinations. Yet, these minerals used for Pb ages may all have crystallized at an earlier time and higher temperature, for example, than the minerals from which the Rb-Sr ages are measured. Furthermore, it is not unreasonable to suppose that igneous bodies such as batholiths and pegmatites, may take many millions of years to crystallize. Thus, a consistent interval may exist between the time when the Pb age minerals and the Rb-Sr age minerals become closed systems.

The frequently used Rb^{87} half-life of Aldrich et al., (1956) has been determined by comparing in this way the Pb ages on uraninites and a monazite with the Rb-Sr data from lepidolites, biotites, muscovites and microclines - minerals which could easily be expected to crystallize at different temperatures. In making the Rb-Sr data agree with the Pb ages, therefore, possible small age differences may be covered up. Thus, it may turn out that these two techniques do, in fact, give slightly different solidification ages for meteorites. Furthermore, it is entirely possible that, if the U^{235} and Rb^{87} half-lives were ever accurately measured by laboratory counting experiments, a comparison of the Pb-Pb and Rb-Sr ages might turn out to be a powerful method for studying the cooling rates of igneous bodies.

7.3 - Rb-Sr Versus Gas Retention Ages of Meteorites

It is also of interest to compare briefly some gas retention ages with this Rb-Sr age of 4.45 billion years. Gas retention ages have been measured for all the meteorites discussed in this thesis except Estherville. Table 7.3 lists both the K-Ar and the U-He ages which have been determined so far. These ages were taken from Anders (1963, 441-444), and references to the analyst(s) in each individual case are given at the bottom of the table.

It is immediately obvious that not only are these ages all younger than the Rb-Sr age, but also there are large age differences between these meteorites. Some meteorites, such as Bjurböle and Pasamonte, show ages close to the Rb-Sr age, whereas others, such as Bath, have considerably younger gas retention ages. Furthermore, the U-He ages are usually younger than the K-Ar ages.

The first point which must be remembered is that the daughter product in these decay schemes is a noble gas. Since noble gases tend to diffuse much more rapidly than Rb or Sr at any given temperature, they are lost from the parent mineral structures at temperatures below which Rb-Sr starts keeping time. Therefore, U-He and K-Ar ages date a more recent event - the time at which the meteorites were cool enough to retain noble gases (at least below 300°K

TABLE 7.3

GAS RETENTION AGES

Meteorite	K-Ar Age (b.y.)	U-He Age (b.y.)
Bath	1.17(A)	.47(A)
Bjurböle	4.32(B) 4.34(A)	4.2(C) 4.3(A) 4.0(D)
Bruderheim	1.85(A) 1.9 (E) 1.6 (F) 1.8 (G)	1.1(A) 1.5(F)
Murray	1.9 (H) 2.51(I) <2.77(F) 1.58(A)	
Nakhla	1.50(G)	
Pasamonte	3.80(B) 4.25(J) 3.80(G)	3.6(C) 3.6(K)

References for Table 7.

(A) Kirsten, Krankowsky and Zäringer (1963)
(B) Geiss and Hess (1958)
(C) Eberhardt and Hess (1960)
(D) Reed and Turkevich (1957)
(E) Baadsgaard, Campbell and Folinsbee (1961)
(F) Signer (1961)
(G) Stauffer (1962)
(H) Stauffer (1961)
(I) Reynolds (1960)
(J) Wanke and König (1959)
(K) Hintenberger, König and Wänke (1962)

according to Anders, 1963, 450). An explanation for the lower U-He age is probably the fact that He diffuses even more rapidly than Ar. A lower U-He age, therefore, might indicate slow cooling whereas agreement between the K-Ar and U-He ages might indicate a rapid drop in temperature.

It is interesting to speculate on the cause of these large age differences and the possible events which these gas retention ages date (a discussion of gas retention ages is given by Anders, 1963, 439-456). First, it is conceivable that these different ages represent different break-up times for the meteorite parent bodies. Large collisions could be expected to produce heating, and thus previously acquired Ar and He might be expelled at the time of break-up (thus resetting the "clocks"). Second, these gas retention ages may represent the time at which the various parent bodies cooled down past a certain temperature. Since all these meteorites have the same Rb-Sr age, the different K-Ar and U-He ages might then reflect different cooling rates and hence different sized parent bodies. Third, each of these meteorites was probably travelling in a different orbit and hence the perihelia were different in each case. Those meteorites with smaller perihelia might, therefore, be expected to loose more Ar and He, since they would undergo more intense solar heating. Finally, it is possible that these low gas retention ages are the result of continuous diffusion losses of Ar and He over long periods of time (Goles, Fish and Anders, 1960). These losses could have occurred either in the parent bodies or after the breakup and during exposure to cosmic rays.

In summary, it is interesting that a suite of meteorites representing several different meteorite classes and having a good spread in Rb/Sr ratios all give a consistent Rb-Sr age, whereas they each give different and younger gas retention ages.

7.4 - The Bjurböle Chondrite

Unfortunately, the Bjurböle chondrite appears to be thoroughly contaminated from the point of view of Rb-Sr studies (refer to Figure 6.4c). Even the whole meteorite sample, which escaped all of the phase separation procedures and was scraped down to an ultrafresh surface just prior to crushing, lies way off the isochron. Since Bath, Bruderheim and Pasamonte received the same new, clean, chemical separation treatment as the Bjurböle whole meteorite sample, it seems highly unlikely that laboratory contamination is responsible for these anomalous results.

Two explanations may possibly be offered. First, the description in Section 5.5 allows us to estimate that probably the Bjurböle chondrite lay in sea water for anywhere from ½ a week to 2 or 3 weeks (or even more). Since this meteorite is especially friable, it is quite conceivable that the salt water percolated entirely through it. Indeed, the interior of the meteorite is full of heavily rusted areas. Ramsay and Borgström (1902, 9) mention that the meteorite (after salvage) dried out slowly and its surface became covered with a white salt. Gast (1962, 937-939) has made some leaching experiments with H_2O. His results indicate that both Rb and Sr can be leached out of meteorites - that Rb is preferentially soluble to Sr and radiogenic Sr is twice as soluble as normal Sr. Smales _et al._, (1964, 228) have also made some experiments to determine whether K, Rb and Cs can be dissolved out of meteorites with demineralized H_2O. Their results agree with those of Gast and indicate that even a few hours in H_2O at room temperature is sufficient to leach several percent of the Rb. Thus, it seems that sea water, with its high concentration of ions in solution, could not only differentially leach Rb and Sr from the meteorite, but also mix sea water Rb and Sr with meteoritic Rb and Sr.

A second type of contamination might have been introduced from the clay and sand in which the meteorite landed. Bjurböle fell through 6-7 meters of mud and clay onto a layer of sand and gravel. As the meteorite is very friable, it broke into many pieces upon landing. No doubt, grains of sand could have been embedded into the matrix and also into any cracks in the surface. While separating out chondrules, the author discovered a number of clear to pink mineral grains which subsequent optical and x-ray analysis indicated to be quartz and feldspar. There was no fusion crust on the sample studied, and the grains appeared from macroscopic observation to belong to the meteorite. Quartz has been identified in iron meteorites, achondrites and enstatite chondrites; therefore, it did not seem unreasonable to find it in a hypersthene chondrite. The magnetic separations also produced many grains of this same description. It appears now, however, that these mineral grains, instead of being initially present in the meteorite, were probably driven into its friable matrix as it fell through the sediments.

Another investigator (Dodd, 1964) from the Air Force Cambridge Research Laboratory, recently arrived at the same conclusion from an independent study of petrographic thin sections. He observed veins of broken up quartz and feldspar minerals that appeared to him to have been subsequently introduced into the groundmass. The author had one petrographic thin section made of Bjurböle, but it was of poor quality and this phenomenon was not observed.

Bjurböle, therefore, could have been beset with 2 types of contamination. It is noteworthy that of the five "phases" which were analyzed from Bjurböle, the chondrules fall closest to the isochron. The chondrules are hard and dense, and unlike the matrix they are not friable. Each one was picked by hand from the meteorite, and then they were shaken together to remove loose adhering material. Perhaps, therefore, the chondrules were not only much more resistant to water seepage, but also the least contaminated with quartz and feldspar grains.

7.5 - Leaching and the Use of Weathered Meteorites for Rb-Sr Analysis

As a result of these analyses on the Bjurböle chondrite and the work of Pinson et al., (1962) on a number of meteorites classified as "finds", the problem has arisen as to how one judges whether or not a meteorite is suitable for Rb-Sr analysis. Pinson et al., (1962) started out by making Rb-Sr analyses on 17 meteorite samples including several "finds". When plotted on an isochron diagram, however, these "finds" showed a considerable scatter. Pinson et al., (1963) discarded all the analyses on meteorites classified as "finds", observing that the resultant data refined into a much better straight line. They, therefore, recommended that all work be restricted to include only fresh samples.

Chapter 5 was included in this thesis in an attempt to arrive at some conclusion on just how much weathering each of the samples studied here had been exposed to. Extreme freshness was the most important criterion used in selecting Bath and Bruderheim. Pasamonte, Nakhla, Estherville and Murray were also considered fresh specimens, yet it is now apparent that these samples could have lain upon the ground for an appreciable period of time before recovery. Nevertheless, all 6 meteorites taken together form a very good isochron. The Bjurböle sample looks rusted and gave anomalous results although it was probably salvaged within a week or so after infall. It is interesting to note some results of other investigators who have studied "finds" and leaching phenomena.

Gast (1962, 937-939) studied the anomalous Beardsley chondrite, an olivine-bronzite chondrite. He analyzed two samples of Beardsley, one of which was picked up the day of infall, and the other of which was not recovered until two years later. Although both Beardsley samples are highly enriched in Rb compared to all other known ordinary chondrites, the Beardsley sample picked up the day of infall gives an age of 4.5 billion years, and the one recovered 2 years later gives an age of 5.7 billion years. (Pinson _et_ _al_., 1962, obtained an age of 5.1 billion years for Beardsley.) Both samples show the same Sr contents, but the sample picked up the day of infall contains 14.2 ppm Rb whereas the one recovered 2 years later has only 4.8 ppm Rb. The Sr^{87}/Sr^{86} ratios are also quite different in the 2 samples.

In order to explore these unusual results further, Gast (1962) performed some leaching experiments on the unweathered sample. After 12 hours in warm distilled H_2O, 24 hours in room temperature H_2O, 3 hours in boiling H_2O and another 24 hours in boiling 1% acetic acid solution, he succeeded in leaching 27% of the Rb, 25% of the radiogenic Sr and 12% of the normal Sr out of the meteorite. Although the laboratory treatment was probably more severe than natural weathering, it would not require nearly as much leaching as this to result in an anomalous age.

One final point which is perhaps noteworthy in Gast's (1962) article concerns the 4 achondrites which he analyzed. Nuevo Laredo has a slightly higher Sr^{87}/Sr^{86} ratio than the other three (Gast, 1962, 941). Could this be due to the fact that Nuevo Laredo is a "find" recovered in 1950?

Smales et al., (1964, 227-232) have also performed some leaching experiments on several meteorites. They employed three types of treatments: a) immersion in demineralized H_2O at room temperature for ½ hour, b) immersion in room temperature demineralized H_2O for 8-10 days, and c) immersion in 60-70°C H_2O for 4 hours. For Ivuna, a Type I carbonaceous chondrite, 53% of the total Rb was leached out in step a) alone! The combination of all three types of treatments leached 79% of its Rb. Mighei, a Type II carbonaceous chondrite, lost 16% of its Rb in the first step and 31% after all three treatments had been administered. For the ordinary chondrites Homestead and Crumlin, 2-3% of the Rb was leached out in step a) and a total of about 10% in all 3 steps.

Especially in the case of carbonaceous chondrites, this is an impressive amount of Rb which is removable with pure demineralized H_2O alone. Considering the description of the fall and recovery of the Murray carbonaceous chondrite (Section 5.6) it does seem surprising that it falls on the isochron. The Rb-Sr age data would seem to indicate, therefore, that it couldn't have been wet, and yet we are informed that it could easily have lain upon the ground for 5 years or so! The amount of Rb leachable from Homestead and Crumlin, though not as much as that in the case of Mighei or Ivuna, would be sufficient to cause an anomalous age.

Rb-Sr workers are not the only ones who have encountered difficulty in working with weathered meteorites. U-Pb investigations have also been affected by rain and weathering. Anders (1963, 438) states that of all the iron meteorites analyzed so far which contain highly radiogenic lead only one, Sikhote-Alin, is not a "find". His explanation for this is that the solubility product of PbS is 8 orders of magnitude smaller than that of FeS (10^{-20} vs. 10^{-28}). Troilite, therefore, soaks up lead preferentially from groundwaters. It is interesting that in the several samples of Toluca troilite which have been analyzed the samples which contain radiogenic lead (Marshall and Hess, 1961; Murthy, 1962) showed ten times as large a concentration of Pb as the sample which contained lead of primordial isotopic composition (Starik _et_ _al_., 1960). Furthermore, Starik and co-workers discovered that in the cases of Santa Catharina, Sikhote-Alin, and Chinge there is a decrease in Pb concentration from the surface of the meterorite to the center by a factor of 5.

In the case of chondrites, Hess and Marshall (1960, 291) have reported that the Pb leached from the surface regions of Plainview and Holbrook was principally terrestrial Pb. Furthermore, a second sample of Holbrook picked up 25 years after infall contained Pb of more radiogenic isotopic composition than the piece picked up immediately after infall. In summary, Anders (1963, 435) states that there are only three (3) cases, Beardsley, Nuevo Laredo, and Richardton, where the stony meteorite "lead and uranium data are in tolerable agreement" (and Nuevo Laredo is not a "fresh" sample).

It seems fairly certain, therefore, that exposure to terrestrial weathering can alter certain of the trace element contents. Yet, it is difficult to judge just how much H_2O a meteorite can withstand before its Rb and Sr contents are upset. No doubt, this will depend to a large degree on how friable the meteorite is. It is suggested, therefore, that the following criteria be weighted heavily in the selection of samples for Rb-Sr analysis.

First, freshness of appearance should be considered. One should look both macroscopically and with the binocular microscope for signs of weathering and particularly limonite stains. Most meteorites contain at least 5% Fe-Ni metal which slowly rusts upon contact with H_2O. Meteorites also contain lawrencite ($FeCl_2$), a soft, green mineral, which "is deliquescent and decomposes in air to give ...(limonite) and hydrochloric acid which immediately attacks the meteoritic iron,..." (Mason, 1962, 60). Lawrencite, according to Mason, has been identified in a number of iron meteorites, but no positive identifications have yet been reported for stone meteorites. However, it seems that it must occur as an accessory mineral in many chondrites since they often rust very easily.

Some caution should be applied, however, in using limonite stains as a positive identification of weathering and exposure to H_2O. There are some classes of meteorites which contain no metallic Fe-Ni (or only trace amounts of it), and probably no lawrencite as well - for example, carbonaceous chondrites and some classes of achondrites. In these cases, a considerable amount of exposure to weathering might be required before rust began to appear. On the other hand, Mason (1962, 60) claims that some chondrites are so sensitive that they "become rust-brown or freckled with rust-colored spots" simply upon breaking off a fresh surface.

Second, the terrestrial history of the meteorite is important. An account of the fall and recovery of the sample should be studied. The environment in which it fell is of importance. Did it land in a swamp or lake? Did it fall in a wet climate? How long did it lay upon the ground before it was recovered? The information supplied in Chapter 5 indicates how difficult it is to obtain a really fresh sample of a meteorite - one which was unquestionably picked up the day of infall. Only in the case of Bath and Bruderheim can one say with assurance that they were recovered immediately. No doubt, however, meteorites like Nakhla and Pasamonte which fell in arid regions can remain unaltered a lot longer than those which land in more humid climates.

It is recommended, therefore, that all future Rb-Sr work on meteorite samples be restricted to the freshest possible "falls" keeping the above criteria in mind. No doubt, many acceptable Rb-Sr ages can be obtained from samples which have undergone significant weathering; yet, in the event that an anomalous age should be obtained, one then faces the dilemma of whether or not terrestrial weathering was responsible for the results.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

1. The chemical procedure for separating Rb and Sr has been significantly improved.

2. The contamination level for Sr has been lowered by an order of magnitude and for Rb has been reduced by a factor of 2.

3. The reproducibility of replicate analyses has also been greatly increased.

4. Two computer programs have been written in Fortran II to aid in certain routine arithmetical calculations.

5. High-precision Rb-Sr analyses have been made on the Bruderheim chondrite, the Bath chondrite and the Pasamonte achondrite.

6. These three analyses have been combined with the Murray carbonaceous chondrite analysis of Beiser (1964) and the Estherville mesosiderite and Nakhla achondrite analyses of Pinson et al., (1963) in the construction of a highly precise

meteorite isochron.

7. An age of 4.45 ± .03 billion years has been calculated for the stony meteorites from the slope of this isochron using a decay constant of 1.39×10^{-11} years $^{-1}$ (Aldrich et al., 1956).

8. The initial ratio of Sr^{87}/Sr^{86} has been determined for meteorites as 0.6982 ± 0.0002.

9. The precision in the slope at this isochron has been improved by a factor of 7 over that of Pinson et al., (1963).

10. If one makes the assumption that the Pb-Pb and Rb-Sr techniques should give the same age for meteorites, then the half-life of Rb^{87} can be determined using the Pb-Pb age of 4.55×10^{9} years (Patterson, 1956). The half-life of Rb^{87} so determined is 5.1×10^{10} years which is equivalent to a decay constant of 1.36×10^{-11} years^{-1}.

11. It is reasonable to assume that 5 of the 6 classes of stony meteorites represented on this Rb-Sr isochron underwent a chemical

differentiation 4.5 x 10^9 years ago.

12. The results of the Rb-Sr analyses on the Bjurböle chondrite show that this meteorite is hopelessly contaminated.

13. From the results of this Bjurböle chondrite analysis (and other evidence presented in Section 7.5) it is concluded that only the freshest possible meteorite samples should be used in Rb-Sr age investigations.

CHAPTER IX

SUGGESTIONS FOR FUTURE WORK

Most thesis investigations raise more questions than they can answer. At their conclusion, therefore, one can easily think of many interesting experiments for exploring the subject still further. In the case of the present work, a few topics are suggested below for future study:

1. Brecciated stony meteorites frequently consist of two types of components. Pasamonte, for instance, contains both light and dark phases, and Cumberland Falls (a unique meteorite) contains fragments of black enstatite chondrite imbedded in a matrix of white enstatite achondrite. It would be interesting to measure the Rb^{87}-Sr^{87} ages of each of the 2 different types of components of such a meteorite. Gerling and Rik (1955) and Reed and Turkevich (1957) have measured both K-Ar and U-He ages on the polymict breccias Kunashak and Pervomaiskii. Their results indicate that, in fact, there are large gas retention age differences between the two

portions of a brecciated meteorite.

2. As a result of the reduced contamination level and increased analytical precision in the M.I.T. Geochronology Laboratory, it would be of interest to make some mineral phase separations on a carefully selected, very "fresh" stony meteorite. Rb^{87}-Sr^{87} ages on a series of separated mineral phases from one single meteorite might indicate a possible heating event subsequent to the 4.45×10^9 years "whole meteorite" solidification age. Fresh meteorites such as Bath and Bruderheim would be excellent candidates for such a study, since a whole meteorite Rb^{87}-Sr^{87} age has already been obtained for them.

3. Again as a result of improved analytical techniques, it would be of great interest to make exploratory Rb-Sr age measurements on some other meteorite classes. The olivine from a pallasite and the troilite from an iron meteorite might make short, fruitful investigations. Although they probably contain very little Sr, one could make a reasonably accurate isotope dilution analysis

providing there was at least .01 ppm Sr present. One could determine both the Sr content and the Sr^{87}/Sr^{86} ratio from a single Sr isotope dilution analysis with the <u>Sr^{84}-Sr^{86}</u> <u>Double Spike</u>.

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The solubility of corundum in basic hydrothermal solvents. J. Phys. Chem. 67, 835-839.

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