

MASS SPECTROMETRIC DETERMINATION OF THE RELATIVE ISOTOPE ABUNDANCES
OF CALCIUM AND THE DETERMINATION OF GEOLOGIC AGE

by

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ABSTRACT

Title: Mass Spectrometric Determination of the Relative Isotope Abundances of Calcium and the Determination of Geologic Age.

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Techniques of mass spectrometric determination of the relative isotope abundances of calcium were investigated, in order that the $K^{40} \rightarrow Ca^{40}$ decay scheme might be utilized as a check on other methods of geologic age determination, and for the purpose of investigating natural variations in the isotopic composition of calcium. Using $Ca(NO_3)_2$ on a platinum-plated tantalum filament as a primary ion source, and measuring ion currents with a vibrating reed electrometer, complete isotopic assays (except Ca^{46}) were made with a precision of $\pm 1\%$ and an absolute accuracy known to within $\pm 3\%$ or better, on samples as small as one microgram.

Isotope abundance results obtained for "common" calcium (Devonian limestone) were, in atom percent:

40	96.88 ± 0.05	43	0.138 ± 0.002
42	0.655 ± 0.006	44	2.12 ± 0.04
48	0.200 ± 0.006		

Calcium extracted from the Homestead meteorite was isotopically identical to "common" calcium to within $\pm 1\%$, and the Ca^{46}/Ca^{40} ratio was measured as $0.000033 \pm 3\%$. Original calcium in lepidolites is fractionated relative to "common" calcium by no more than $\pm 2\%$ in the Ca^{48}/Ca^{40} ratio.

Techniques for the separation and purification of microgram quantities of calcium from lepidolites without excessive contamination were developed. The method of isotope dilution was applied to the determination of total potassium, total calcium and radiogenic calcium in lepidolites.

The $K^{40}-Ca^{40}$ "ages" for five different lepidolites were determined as:

Bikita Quarry, Southern Rhodesia	1980 ± 100 m.y.
Bob Ingersoll Mine, Black Hills, South Dakota	1180 ± 90 m.y.
Skuleboda, Sweden	1190 ± 150 m.y.
Brown Derby Mine, Colorado	1) 1370 ± 150 m.y.
	2) 1570 ± 130 m.y.

These "ages" are lower than "ages" obtained on the same samples, or closely associated samples, by the Rb-Sr method and the Pb-U method.

The extent of disagreement is variable, indicating that post-formational geochemical alteration of some of these lepidolites may have occurred.

A determination of the radiogenic argon content of a specimen of the Bob Ingersoll lepidolite by L. Strickland, when compared to the radiogenic calcium determination for the same sample in this research, gave a branching ratio for K^{40} decay, $\lambda_K / \lambda_B = 0.15 \pm 0.02$. This determination is not consistent with the recent published determinations of λ_K / λ_B suggested by comparisons of K^{40}/A^{40} ages and Pb/U ages.

Certain aspects of thermal ion production were studied and the literature on this subject reviewed. It is suggested that the mechanism of positive ion production in the system mentioned above is extremely complex, and is more intimately connected with the properties of the salt than of the filament. The measured calcium isotope ratios were observed to vary by as much as 17% during evaporation of a single sample, and the form of this fractionation as a function of percent sample emitted was not entirely reproducible. Abnormal emission of Ca^+ , Mg^+ , and Al^+ ions was observed at temperatures as low as 900-1000°K.

Isotopic assay of alkalis is not an entirely straight forward procedure, and incorrect results may be easily obtained due to isotopic fractionation during analysis. By consistently observing only the first portion of emission, results with a reproducibility of better than $\pm 0.5\%$ may be obtained.

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INTRODUCTION

The primary objective of this research was the development and application of methods which would allow the utilization of the $K^{40} \rightarrow Ca^{40}$ decay scheme for geologic age determination. It was desired at the same time to begin a program of investigation of the natural variations of the relative isotopic abundances of calcium. The material following in this introduction consists of a brief review of the recent results which have motivated this research, followed by a sequential account of the research program.

In the decade before the Second World War a new branch of geology and geophysics was opened up, primarily by A. O. Nier and his co-workers. Although the mass spectrometer had been in use for some time, Nier (1940) designed a simple and dependable instrument which was well adapted for abundance studies, and he was among the first to apply it to geological problems. His classical paper (Nier, 1939) presenting the isotopic abundances of a number of leads from radioactive minerals introduced a great advance in the accuracy and confidence in uranium-lead age determination work. The existence of variations in stable isotope abundances was also demonstrated, and their potential as a geologic tool discussed.

After the war, concentration on isotope research, now called "isotope geology," or "nuclear geology," expanded at a rapid pace both in the direction of age determination, and in studies of stable isotope variations in nature. Geologists, physicists, geophysicists, chemists, electrical engineers, and other scientific specialists have entered

the field and contributed to its rapid rise. Data has been produced so rapidly that numerous excellent review articles, conferences, and books on isotope geology, e.g., Ingerson (1953), Kohman and Saito (1955), National Research Council (1953), Kulp (1955), Rankama (1954), and Faul (1954), have been published in recent years.

Methods of Age Determination

The recent application of mass spectrometry, in addition to other techniques, to age determination of rocks and minerals, has resulted in the utilization of nearly every natural radioactive decay scheme known. The rapid development of these age techniques has begun to answer a number of questions for geologists, but, as is generally true, as many problems have been posed as answered. Among the most important are the discrepancies which have shown up when attempts to date the same material by different methods have been made. These discrepancies may have physical, geological, or analytical causes, and their understanding may provide information even more useful than the pure dating of rock units.

Excellent discussions of age methods are available in the reviews by Faul (1954), Kohman (1955) and Kulp (1955). Since one of the major purposes of this research was to provide additional data to help clarify present discrepancies in age results, a brief examination of some developments in this field is presented.

Uranium-Lead Methods

The decays, $U^{238} \rightarrow Pb^{206} + 8 He^4$, and $U^{235} \rightarrow Pb^{207} + 7 He^4$, are the bases of several age methods. Since the decay constants for U^{238} and U^{235} are well known, a knowledge of either of the ratios U^{238}/Pb^{206} ,

or U^{235}/Pb^{207} , should provide an "age," if original lead is either absent or corrected for. Since the ratio U^{238}/U^{235} has exhibited no natural variations, and the decay rates of U^{235} and U^{238} differ considerably, the ratio Pb^{207}/Pb^{206} also yields an age. U/He methods, total lead methods, radiation damage methods, and others based on this decay series are discussed in the above references. The ratios 206/238, 207/235, and 207/206, provide the primary ages, the other methods being more or less calibrated and checked against them.

In practice, the "ages" determined for a particular mineral from the three different ratios 206/238, 207/235, 207/206, are generally in considerable disagreement. This is apparently true not only for uranium rich minerals with strongly metamict structures (Faul, 1954) but also for zircons (Aldrich, 1954). In general the 206/238 and 207/235 "ages" are lower than the 207/206 age. There has been some controversy over the major causes of these discrepancies, with radon leakage (Kulp, et al., 1954) and lead-leaching (Collins, et al., 1954) considered as two important factors. Recent results presented at the 1955 American Geophysical Union meeting in Washington were consistent with the concept of lead-leaching, and indicated that the 207/206 age is generally probably closest to the true mineral age.

In the case of minerals in which all three ratios yield identical ages, there is good reason to believe that the age has been well determined. At the present time, in fact, this is about the only case in which the absolute age can be considered well-determined. There is a justified tendency, then, to use such a uranium-lead age as a basis for the establishment of other age methods.

Rubidium-Strontium Method

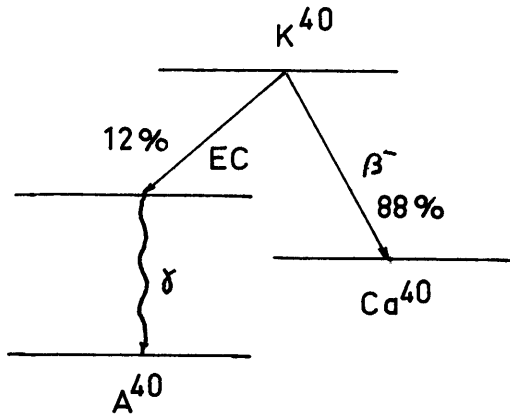
The use of the simple beta decay of Rb^{87} , $\text{Rb}^{87} \rightarrow \text{Sr}^{87} + \beta^-$, for the determination of geologic age was developed by Professor Louis H. Ahrens (1949). Ahrens used optical spectrographic techniques to determine the ratios of total rubidium to total strontium in a number of lepidolites, assuming the strontium was purely radiogenic. This assumption had been investigated by Mattauch (1937) and found to be true in many cases. Ahren's results were in fair agreement with the best ages known at the time for his specimens, and the Rb/Sr method appeared to be established. Aldrich and his co-workers (Davis and Aldrich, 1953) then began investigations of this method using the potentially more accurate (and more time-consuming) tools of mass spectrometry and isotope dilution. The application of the Rb/Sr method was later extended to granitic materials, such as biotites and feldspars, by Tomlinson and Das Gupta (1953), and Aldrich and Herzog, et al. (1955). However, a variable discrepancy ranging from about zero to one hundred percent appeared between the optical spectrographic results and the isotope dilution results. Although some of the major disagreements have been corrected by later work (Aldrich, 1954), the general tendency of the isotope dilution results to be significantly higher than the optical spectrographic results has not yet been satisfactorily explained. In addition, ratios ranging from 0.9 to 1.6 between Rb/Sr ages and U/Pb ages obtained for the same pegmatites have been observed (see Part IV). In some cases the lead ages are at least as doubtful as the Rb/Sr ages, but a significant tendency for Rb/Sr ages to be "too high" has been established (Aldrich, et al., 1955). The possibilities of rubidium leaching, and an incorrect physical determination of the Rb^{87} half-life

or a physically undetectable bound beta decay (Kohman, 1953), have been suggested to account for some of these discrepancies.

Potassium-Argon Method

From the standpoint of breadth of application, the potassium-argon method appears to be the most promising age method now under investigation. However, until the decay constants for K^{40} have been established, and the possible leakage of argon thoroughly studied, the results obtained will remain in doubt.

K^{40} , a very rare (0.0119%) isotope of potassium, disintegrates by beta emission to Ca^{40} with a decay constant, $\lambda_{\beta} = 0.48 \times 10^{-9} \text{ yr.}^{-1}$, and by K-electron capture accompanied by a gamma ray, to A^{40} , with $\lambda_{\kappa} = 0.065 \times 10^{-9} \text{ yr.}^{-1}$ (Birch, 1951). The branching ratio, $\lambda_{\kappa}/\lambda_{\beta}$, which gives the ratio of the number of argon atoms produced to the num-



ber of calcium atoms produced is thus about 0.135. The decay constants given are by no means well established. The half-life of K^{40} has been studied extensively in recent years, with over one-hundred papers published on the subject (see, e.g., Birch, 1951).

Due to the importance of K^{40} in the thermal history of the earth, the changes in the measured constants have been accompanied by many attempts to re-examine thermal history in the light of new data. The branching ratio, and the constants for A^{40} production have been the major subject of recent uncertainty. Recent physical measurements, utilizing X-rays, γ -rays, and Auger electrons, are in fair agreement, and indi-

cate a value $R = 0.10 - 0.13$ (Faul, 1954, Kohman, 1955, Wasserburg and Hayden, 1955). A measurement of the actual content of A^{40} and radiogenic Ca^{40} in the Stassfurt sylvite (Inghram, et al., 1950) gave $R = 0.126$. However, Wasserburg and Hayden (1954, 1955), Shillibeer (1954), and others who have been measuring the argon content of ancient minerals, have found that a branching ratio of about $0.085 - 0.09$ provides the best fit of their data to the best uranium-lead age data available. A large amount of this "calibration" work was, however, carried out on feldspars, and Aldrich, et al. (1955), have recently found that many feldspars give ages which are erratically lower than other ages determined for the same rock unit. They found, surprisingly, that argon may be better retained in micas than in feldspars.

The Application of $K^{40} \rightarrow Ca^{40}$ Decay to Geologic Age Determination

The present uncertainties and discrepancies in geologic age results due to uncertainties in half-lives, branching ratios, and geological effects, indicate that work of a calibrating and confirming nature must be performed for a considerable period before widespread age measurements may be made with confidence. One of the major purposes of this research was to utilize the $K^{40} \rightarrow Ca^{40}$ decay to provide information which may be useful in the attempt to interpret some of the present discrepancies in age work.

Attention was brought to focus on the geologic importance of radiogenic Ca^{40} by Ahrens and Evans (1948), who used optical spectrographic total calcium measurements in lepidolites to estimate limits for the decay constants of K^{40} . Inghram, et al. (1950) made an actual measurement by isotope dilution techniques, of the amount of radiogenic

Ca^{40} in the Stassfurt sylvite. Ahrens (1952) and Holyk (1952) measured by optical spectrograph the total calcium contents of a large number of lepidolites, and combining these values with the best ages known for those minerals, deduced that the radiogenic Ca^{40} content ranged from 1% to 40% of the total calcium, demonstrating that $\text{K}^{40}/\text{Ca}^{40}$ age measurements were feasible, at least for the more favorable lepidolites.

The reasons for the lack of extensive recent research on the determination of radiogenic Ca^{40} in minerals is clear. While the parent isotope, K^{40} , is a rare isotope, the daughter, Ca^{40} , is the most abundant calcium isotope, comprising ninety-seven percent of total normal calcium. Even in potassium-rich ancient pre-Cambrian minerals, the content of radiogenic Ca^{40} should only be of the order of ten to forty parts per million. In most minerals, the increase in Ca^{40} due to K^{40} decay is expected to be insignificant relative to the original calcium in the mineral at the time of formation. Determination of radiogenic calcium is therefore only possible in those rare minerals which are rich in potassium, and which have excluded original calcium from their structure nearly completely, such as lepidolites, rose muscovites, and a few other relatively rare minerals. Also, in such cases, the minerals are very favorable for Rb/Sr age measurements, and are suitable for K/A age determinations. The development in this research of methods of determining radiogenic Ca^{40} does not, therefore, mean the development of a new age technique for general geologic use. The usefulness of the method lies purely in its ability to aid in the understanding and interpretation of other, more generally useful methods. As such it has a number of definite advantages.

One of the major drawbacks of the K/A method is uncertainty in the branching ratio. Determination of radiogenic argon and of radio-

genic calcium on the same mineral provides a geologic minimum value for the branching ratio. L. Strickland at this laboratory has made or will make argon measurements on several lepidolites for which radiogenic Ca^{40} has been determined. The results of this work are given in Part IV.

The geochemical similarities between calcium and strontium, and between rubidium and potassium, and the unusually large Rb/K ratios in lepidolites, allow simultaneous age determinations by Rb/Sr, K/Ca, and K/A on the same mineral specimen, and should make possible a fairly definitive interpretation of the results thus obtained.

It was hoped, therefore, that by developing the K/Ca age method for application to lepidolites, that valuable information might be obtained for the interpretation of other age results.

Natural Fractionation of Calcium Isotopes

In the accelerated research in isotope geology, natural isotopic abundance variations have been extensively studied for hydrogen, boron, carbon, nitrogen, oxygen, silicon, sulphur, argon, potassium, iron, and other elements (Rankama, 1954) with extremely valuable results. Calcium, which is one of the most common and widespread elements found in rocks and minerals, and which has the largest relative mass spread between natural isotopes of all elements except hydrogen, has not yet been investigated. In this research a beginning was made on such an investigation, but no measurable natural variations have yet been found. The techniques developed in this work for mass spectrometric investigations of calcium should be helpful to an extensive study of natural fractionation in calcium.

Experimental Problems

The determination of radiogenic calcium in minerals required the development of chemical and mass spectrometric techniques. First it was necessary to separate fairly pure microgram quantities of calcium from silicate minerals without excessive contamination by common calcium. Second, it was necessary to develop a method of accurate measurement of the isotope abundances of microgram quantities of calcium. Isotope dilution techniques (see Faul, 1954, pp. 70-73) could then be utilized to determine the absolute content of radiogenic Ca^{40} .

The major chemical problem was that of laboratory contamination. By careful procedures, and the use of Vycor glassware throughout, the degree of contamination was brought to an acceptable level of about ten to twenty micrograms for a one-gram sample. The techniques utilized are discussed in Part II.

The major difficulties were in mass spectrometric technique, and consisted first of a critical sensitivity problem and second, of the fact that the measured isotopic ratios for a particular calcium sample changed by as much as twenty percent during the course of a determination. Because of these problems, considerable work was done on the production of positive calcium ions, and is discussed in Part I, Sections 2 and 3, which include a brief survey of literature on the subject. The sensitivity was successfully increased by a ten-fold increase in ionization efficiency, combined with a six-fold increase in collection sensitivity. Attempts to eliminate the isotopic fractionation were unsuccessful, but it was determined that a precision of about one percent could be attained despite fractionation effects.

After calibrations were made (Part I, Section 6), the method was applied to geologically interesting samples. It was originally hoped that a large suite of samples could thus be examined, but the time consumption of the method, the necessity for experiments of a checking nature, and maintenance and improvement of equipment and methods, limited the output to K/Ca ages of four different localities. These results are discussed in Part IV.

The separate and real problem of isotopic examination of alkalis is discussed in Part III.

PART I. TECHNIQUES OF MEASUREMENT OF THE RELATIVE
ISOTOPIC ABUNDANCES OF CALCIUM

1. GENERAL DESCRIPTION OF MASS SPECTROMETER

The mass spectrometer, which had its birth in the early "positive ray" apparatus of J. J. Thomson and others, is simply a device which separates atoms according to mass, and subsequently determines the relative abundances of the different isotopes. The instrument used in this research, shown in Fig. 1 and Fig. 2, was a Nier type (Nier, 1947), 60° sector, six-inch radius, direction focusing mass spectrometer, which was built in the M.I.T. Department of Geology and Geophysics under the supervision of L. F. Herzog (Herzog, et al., 1954). For use in this research program some new components were constructed, and a number of alterations of existing components were made.

The essential components of the mass spectrometer are shown in a block diagram in Fig. 3. The sample to be analyzed is deposited in an aqueous solution on a thin metal filament in the ion source, and dried. During operation the filament is heated by an A.C. filament supply, producing positive ions in the region surrounding the filament. The ions are drawn out of this region, accelerated to about 2000 volts, and collimated to a narrow sheet beam by a series of slitted plates in the source. When the rapidly travelling ions enter the 60° sector magnetic field of about 3000 gauss, they assume a circular motion with curvature depending on mass, and the different isotopes form a diverging set of ion beams as they leave the magnetic field. The particular ion beam which leaves perpendicular to the magnetic field hits a

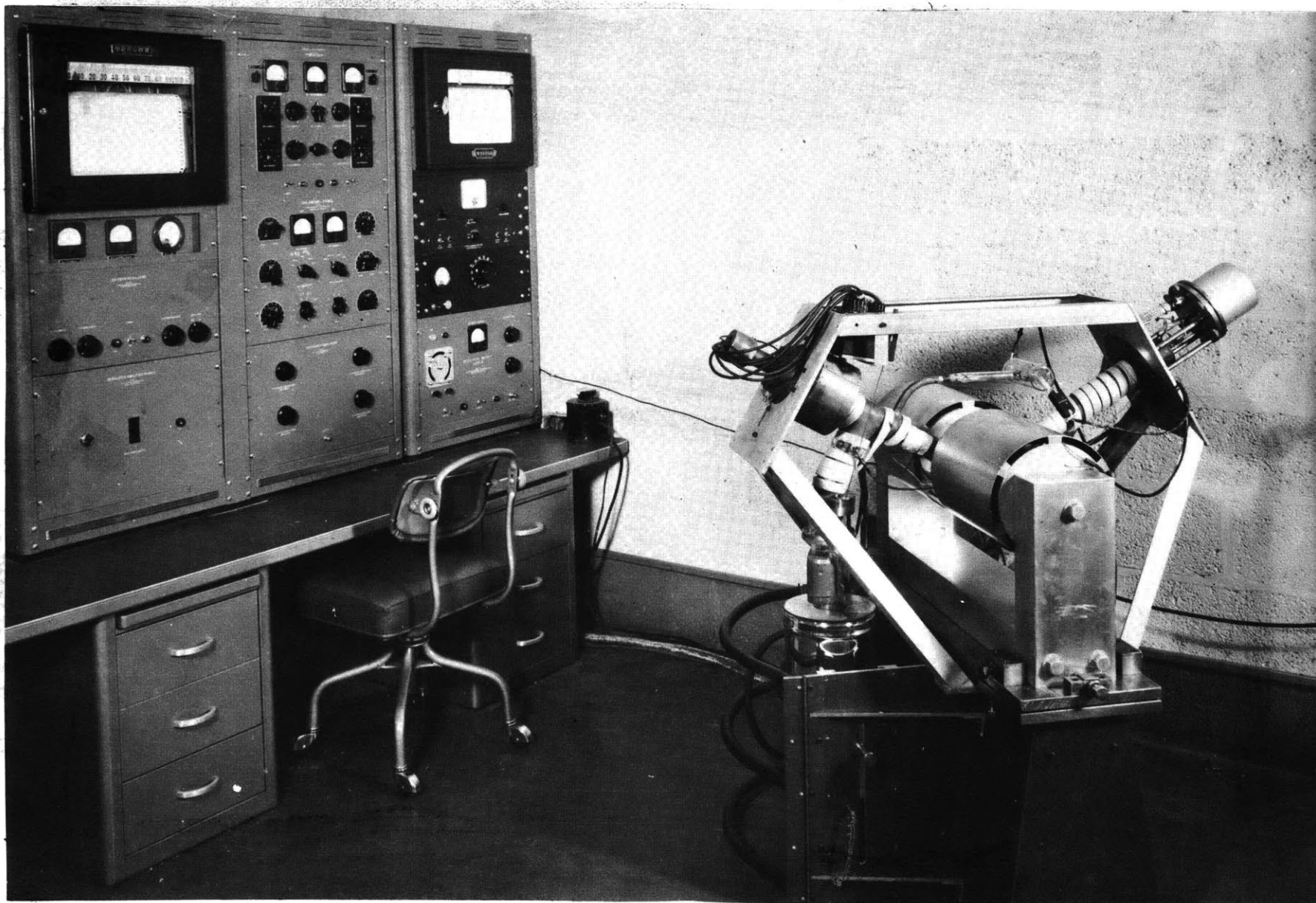


Figure 1. Mass Spectrometer and Control Panel.

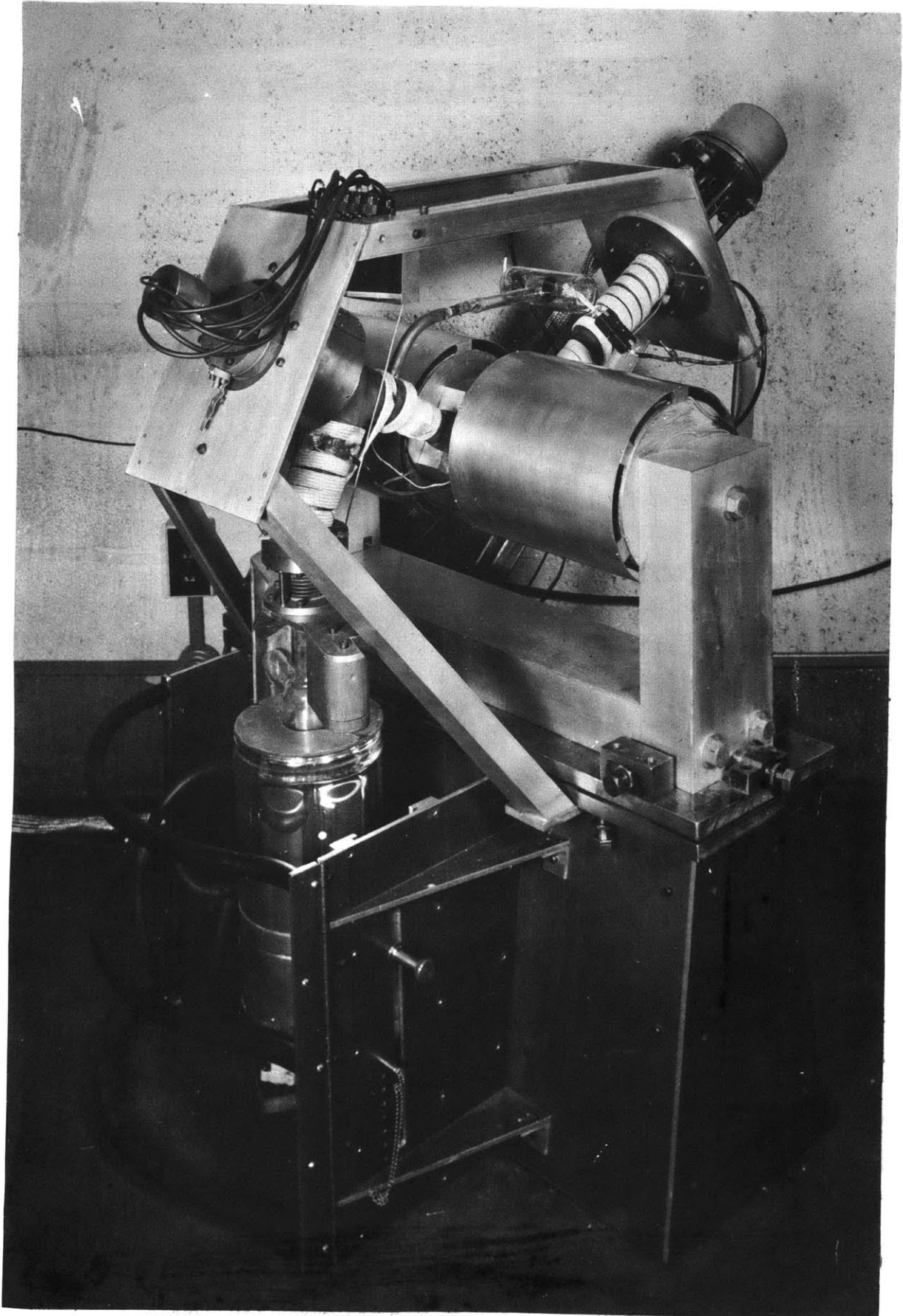


Figure 2. Mass Spectrometer, Showing Details of Mounting.

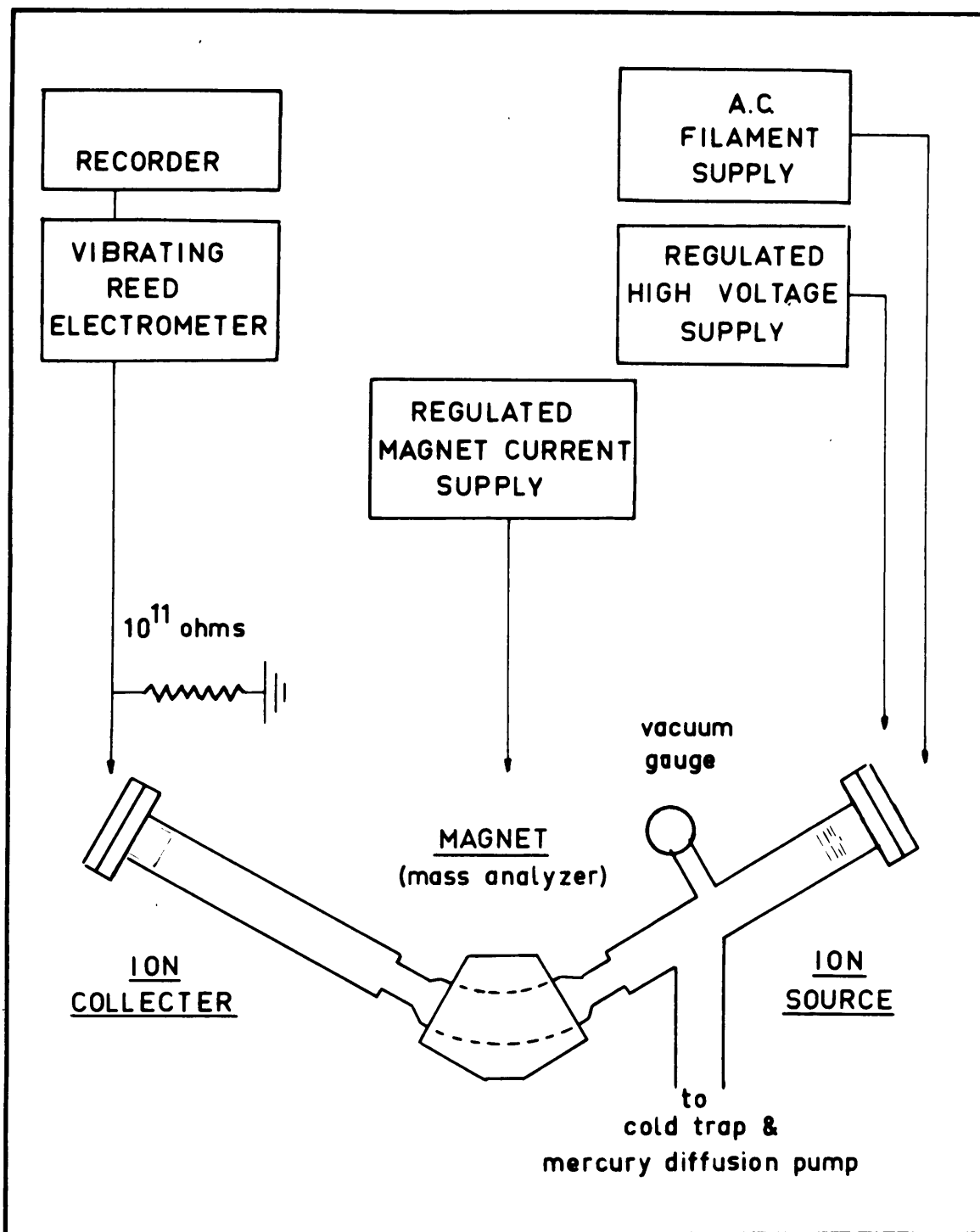


Figure 3. Block Diagram of the Essential Components of the Mass Spectrometer.

nichrome box in the ion collector. The current thus produced is put across a 10.11 ohm Victoreen resistor, amplified by a vibrating reed electrometer, and recorded on a Brown potentiometer strip chart recorder. In a routine relative abundance determination the magnetic field is varied continuously, and the ion beams corresponding to different isotopes are collected successively. This results in a series of peaks on the recorder, which are proportional in height to the relative atomic abundances of the different isotopes. Detailed discussions of all aspects of mass spectrometry may be found in the works by Inghram and Hayden (1954), Barnard (1953), and Ewald and Hintenberger (1953).

The Ion Source

The accelerating system in the ion source is similar to that fully described by Nier (1947) and by Herzog (1952). It consists of a filament, surrounded by a tantalum shield box (1) (see Fig. 3) with a wide slit; split plates (2) for "drawing out" ions and focusing, and two collimating slits (3, 4). The positive ions formed at the filament are accelerated out of the shield box by an electrostatic field which originates in a voltage difference of from -45 volts to -260 volts between the split plates (2) and the filament, and which penetrates through the slit in (1) to the filament. The box (1) is kept at $+4\frac{1}{2}$ volts relative to the filament for focusing purposes. The two halves of the split plate (2) may be given a voltage difference of from zero to ninety volts, thus correcting for any slight misalignment of the slit system and filament. The remainder of the 2000 volts acceleration is provided between plate (2) and plate (3), which is grounded.

One disadvantage of this system is that the voltage between (1) and (2) must perform the function of providing the "drawing out" potential as well as focusing the divergent ion beam on the collimating system. Provision for independent performance of these two functions would probably provide some increase in sensitivity. The maximum collection efficiency (ratio of ions produced to ions collected) for this source was about four percent, compared to other published values of "less than one percent" (Barnard, 1954), and two percent (Hayden, 1948). Since resolution at mass 40 was better than was required, the collection efficiency could be increased somewhat.

The Vacuum System

For good resolution of adjacent mass currents, and for accurate results, a high vacuum must be maintained. In this instrument a Welch mechanical backing pump, a mercury diffusion pump designed by Homer Priest of M.I.T., and a cold trap were used. In general liquid air was used in the cold trap, and pressures of from 5×10^{-7} to 5×10^{-6} millimeters of mercury were maintained for alkaline earth runs. In rare cases, alkali determinations were made in pressures as high as 2×10^{-5} millimeters of mercury, though this practice is not generally recommended. The system was generally baked out for two to four hours after inserting each alkaline earth sample, but for alkali determinations this procedure could not be followed since re-evaporated alkalis were deposited on the filament during the process of baking out.

Other Aspects

The production of positive ions is fully discussed in the following sections. Possible mass discrimination in the source, and other

possible sources of error are discussed in Section 7. L. Strickland (1955) gives details of the regulated high voltage supply and the magnet supply. The ion current collection and measurement system is discussed in Section 5.

2. METHODS OF POSITIVE ION PRODUCTION

There are many ways to obtain positive ions, but for this research there were two major limitations. First, since the mass spectrometer used was a single focusing device with no velocity selector, a source of ions with a minimum energy spread was required. Second, there is no calcium compound (to my knowledge) that is a gas at room temperature, or at a temperature that can be maintained throughout the volume of the source. Therefore the calcium must be introduced as a solid and subsequently vaporized. This latter limitation is especially important, for the best precision obtainable today in solids analysis is of the order of $\pm 0.5\%$, whereas by the use of a comparison method, gas analyses with a precision of $\pm 0.02\%$ (Urey, 1948) or better may be obtained.

The ion sources fulfilling the above requirements are surface ionization sources, and a source involving electron bombardment of calcium vapor driven from a hot filament. The former method appeared more promising and was already in use in this laboratory in the measurement of strontium, and was therefore tentatively chosen for the calcium work.

The generally accepted basis of the surface emission ion source is the fact that when an element with a low ionization potential is evaporated from a hot surface made of a material with a high work function, a certain portion of the element is evaporated in ionic form. In simple cases (see Section 3) the ratio of ions evaporated to atoms evaporated is,

$$\frac{n^+}{n_0} = \exp \left(\frac{\phi^- - I}{kT} \right) \quad (1)$$

where ϕ^- = thermionic electron work function of the filament material,
 I = 1st ionization potential of the sample element,
 T = absolute temperature,
 k = Boltzmann's constant.

For alkalis, which have very low ionization potentials, it is simple to obtain a filament with $\phi^- > I_{\text{alkali}}$, so the surface emission source provides great sensitivity. However, the ionization potentials for the alkaline earths are moderately high, $I_{\text{Mg}} = 7.61$ e.v., $I_{\text{Ca}} = 6.09$ e.v., $I_{\text{Sr}} = 5.67$ e.v., so that a practical filament material with $\phi^- > I_{\text{alkaline earth}}$ has not yet been found. Wolfram and tantalum oxide surfaces have reported work functions of the order of 8 - 9 electron volts, but such work functions are apparently no longer effective when the surface is coated. For alkaline earths then the ionization efficiency increases with increasing temperature. A refractory compound of the element is therefore desirable. Of course, the equation (1) does not strictly apply when a compound is used, but it has been found to be qualitatively useful in many cases to which it should not apply.

Despite the relatively low work function of clean tantalum ($\phi^- = 4.1$ e.v.), slightly oxidized tantalum was found to be a very satisfactory filament material for use with strontium (Herzog, 1954). For the initial calcium runs, therefore, calcium compounds such as CaC_2O_4 , CaCO_3 , or $\text{Ca}(\text{NO}_3)_2$, all of which transform to the refractory CaO at elevated temperatures, were applied to slightly oxidized tantalum filaments. Two major problems were soon apparent, however. The source was not sensitive enough for practical consistent application in the measurement of microgram quantities of calcium, and it was found that

the measured isotopic ratios changed progressively by as much as twenty percent during a single run.

The measured collection efficiency (ions collected/atoms applied) in these early runs was about 0.4×10^{-6} or less, compared to about 40×10^{-6} for strontium measurements. Many attempted measurements failed due to lack of sufficient ion current. This difference may have been due to the difference in the ionization potentials of calcium and strontium, and is in qualitative agreement with the dependence of n^+/n on ionization potential in simplified thermionic emission theory. Taking $I_{Sr} = 5.67$, $I_{Ca} = 6.09$, $\phi_{Ta} = 4.1$ e.v., running temperature for SrO, $T = 1500^\circ K$ and for CaO, $T = 1600^\circ K$, we obtain from (1) a ratio of strontium ionization efficiency/calcium ionization efficiency equal to 58. The experimental ratio was $40 \times 10^{-6} / 0.4 \times 10^{-6} = 100$. The sensitivity problem for calcium was intensified by the fact that larger ion currents were necessary because of the greater differences in the abundances of the calcium isotopes.

Due to these problems, considerable work was done in an attempt to find an adequate ion source for calcium determinations. By intensely oxidizing the tantalum filaments, a ten-fold increase in calcium ionization efficiency was achieved, but this technique caused frequent filament burn-outs, and is therefore unsatisfactory. An attempt was made to produce a variation of the Kunsman anode (Riemann, 1934); very fine nickel filings were deposited along with a $CaCl_2$ sample on a tantalum filament, and the filament was heated in a nitrogen atmosphere to produce a nickel melt with the calcium sample suspended therein. Burn-out occurred in this melting process, however. An attempt to use a wolfram filament was also frustrated by burn-out.

Some tests (now considered inadequate) were made on double filament type sources and electron bombardment sources (discussed later in this section) but these showed no advantage.

Platinum-Plated Tantalum Filaments

A consistent efficiency increase by a factor of ten was finally achieved by using "platinum plated" filaments. These filaments are made by a standard platinum plating procedure. Tantalum is not well suited for platinum-plating, and the resulting filaments have a very "spotty" finish. After plating, the filament is heated in air (to about 700°C) until occluded gases cause the platinum coating to "bubble," producing a very rough surface. It was thought that a higher degree of contact between sample and filament material would thus be achieved. The sample is then applied in aqueous solution as the nitrate. The operating characteristics of this filament are discussed in the following section.

The platinum plating solution (Blum and Hogaboom, 1949) is made from equal portions of the following solutions:

- (1) Chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) 10.5 g/l.
- (2) Ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) 45 g/l.
- (3) Boric acid (H_3BO_3) 15 g/l.

The ammonium phosphate was added to the chloroplatinic acid and the precipitate allowed to settle. The boric acid was then added and the mixture was boiled gently for several hours until the odor of ammonia could no longer be detected and the solution acquired a pale lemon-yellow color. The solution was then put in a beaker, and an anode consisting of twelve inches of 0.010 inches diameter platinum wire was

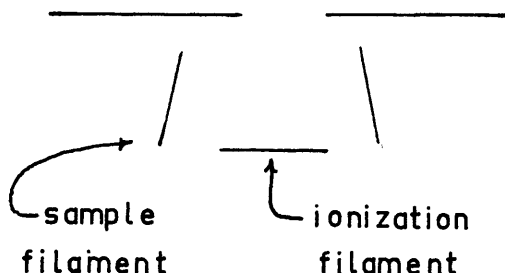
inserted. Four (2" x 0.030" x 0.001") lengths of tantalum ribbon, spot-welded to a thick nichrome wire, were then inserted in the solution surrounding and equidistant from the anode. A three milliamperere current was generated for about one hour, and the plated filaments were removed from the solution and washed with 3.0N HCl and distilled water. Since each filament may be used for several runs, the supply thus obtained lasts for several months.

Double Filament Source

Inghram and Chupka (1953) described a double-filament surface ionization source, in which one filament was used to evaporate the sample, and a separate filament was used for ionization of the impinging atoms. They reported a large increase in sensitivity and ionization efficiency for several elements with high ionization potentials. The major reason for this advantage is that in a single filament source the operating temperature is limited by the evaporation rate of the sample. In the double filament source the vaporization temperature and the ionization temperature may be independently varied, thus allowing higher ionization temperatures, limited only by the melting point of the ionization filament material. In addition, the effective θ (thickness of sample atoms) on the ionizing surface is much smaller. Counteracting these advantages are the facts that the geometrical design of the source should be such that primary ions from the sample filament are excluded from the ion beam and that only a fraction of the evaporated atoms impinge upon the ionization filament.

A simple double filament source was built and tested with CaCl_2 (a less refractory form is desirable in this case to minimize

ionization at the sample filament). The geometrical arrangement is



shown to the left. An oxidized tantalum filament was used for ionization in the hope that in this application its apparent high work function might be more effective. A clean tantalum filament was used for evaporation of the

sample. Separate filament supplies were constructed for heating the two filaments.

In operation, ionization occurred predominantly at the ionization filament, as was predicted, and a fair calcium current was obtained. From five peak sets the measured $44/40$ ratio was 0.0222, in good agreement with results obtained using single filament sources. However, there was no observed sensitivity improvement over the slightly oxidized tantalum single filament source.

It is now my consideration that this type of source was not given an adequate trial for calcium investigations. It is now believed that the limiting factors to the precision of the single filament primary ion source are mainly due to the complexity of the mechanism of ion production, non-reproducibility of fractionation form, and an apparent increase in the effective positive ion work function during operation. It is thought that these factors might be minimized with a double filament arrangement, though fractionation during a run would still probably occur. If a sensitivity improvement could be achieved, this type of source would be capable of giving more reproducible results than a single filament source.

Improvements in the sensitivity and general operation could be made in the following manner. First the sample should, if possible, be applied to a clean tantalum filament in elemental form, because CaCl_2 molecules may not be as effectively broken up and ionized as atoms of calcium, and because there would only be a single evaporation product. This might be achieved by applying $\text{Ca}(\text{NO}_3)_2$, converting to the oxide in a vacuum, and then heating in a hydrogen atmosphere. Evidence mentioned in Section 3 suggests that a "platinum-plated" tantalum filament might be very effective as an ionizing filament. Platinum and wolfram filaments, which are impractical for single filament application, should also be investigated.

Electron Bombardment Sources

The possibility of using an electron bombardment source for this work was seriously considered. For solids analysis such a source consists of a small furnace from which the element or a compound thereof is evaporated, plus an electron gun to produce a constant flow of monoenergetic electrons. The major drawbacks to this type of source are the presence of background peaks, and again, sensitivity. When electron bombardment is used for ionization some of the residual gas in the mass spectrometer is ionized, as well as the sample vapor. The presence of a large CO_2^+ peak (the observed CO_2^+ current using a standard Nier type source was about 10^{-11} amperes) at mass 44 precluded the use of Ca^+ ions. The measured appearance potential of this peak was of the order of fourteen volts, so it definitely would be present in maximum efficiency calcium ionization operation. Smaller background peaks were also present at masses 40, 41, 42, 43, and 48.

The possibility of evaporating CaI_2 and measuring the CaI_2^+ current does have some promise, especially for work in which large calcium samples are available. Although this method is recommended by Inghram and Hayden (1954), and is used by the Atomic Energy Commission Stable Isotopes Division (Baldock, 1954), no data has yet been published on its sensitivity or reproducibility. In using a compound of this type there is sometimes mass discrimination due to isotope exchange reactions and the evaporation of molecules other than CaI_2 (Baldock, 1954). The necessary presence of a magnetic field would also introduce a constant mass discrimination effect. However, the addition of two heavy iodine atoms to each calcium atom would make relative molecular mass differences between different isotope carriers small, and thus the mass fractionation effects due to vaporization should be insignificant. The background in this mass range has not, however, been investigated at this laboratory.

Barnard (1954) states that for a conventional electron bombardment ion source of maximum sensitivity a gas flow of 2×10^{-3} liters per second yields an ion current of 10^{-10} amperes. This corresponds to a "collection efficiency" of approximately 10×10^{-6} . In this laboratory Strickland (1955) was able to obtain a collection efficiency of 6×10^{-6} on a similar source. To my knowledge there is no published data on the ionization efficiency of a furnace type electron bombardment source for solids, but it is expected that it would be considerably lower than in the case of gases, because of relative atomic velocities, the production of different molecular fragments in the processes of vaporization and ionization, and the fact that the CaI_2 vapor would condense upon the walls of the ionization chamber in its first collision

(in an ordinary gas source each atom passes through the ionizing electron beam three to four times).

A Source with Cylindrical Symmetry

A small source arrangement with cylindrical symmetry was built for testing purposes. The unit consisted of a small, thin-walled stain-

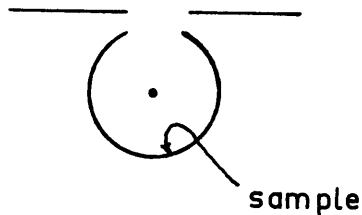
less steel cylinder 0.14 inches in diameter, with an ion exit slit parallel to the axis. It was enclosed at both ends with lavite

discs. A wolfram wire filament 0.007 inches in diameter along

the axis of the cylinder was connected to a filament supply. An

unsuccessful attempt was made to fabricate the outer cylinder from thin tantalum so that it could be heated simply by passing a current through it. Preliminary tests were made in which the outer cylinder was heated by radiation from the axial filament, and it was thought that if such tests were promising, provision for heating the cylinder externally by filaments or by high voltage electron bombardment could be made.

This arrangement was tested first as an electron bombardment source. The expected advantages in such an application were that with the flow of a large ion current from the cylinder it would tend to act as a pump to keep the ionization region relatively free of residual gases, and that since the evaporated atoms should remain in the cylinder for a relatively long period of time, the ionization efficiency should be high.



In order to accelerate electrons from the inner filament to the walls of the cylinder without collecting positive ions on the center filament, a high frequency voltage supply was connected between the center wire and the outer cylinder. The frequency was adjusted so that the light electrons were accelerated to the cylinder walls during one period, while the heavy positive ions merely had a radial oscillatory motion superimposed on their drift. An electrostatic field was leaked into the cylinder through the ion exit slit to remove positive ions.

A test was made with a coating of CaCl_2 on the inner walls of the cylinder. The electron current at twenty volts R.M.S. electron accelerating voltage was a maximum of several milliamperes at a frequency of 3.2 megacycles per second. Small calcium ion currents were observed and were proved to be due to electron bombardment by using a space charge limited electron current and observing no change in Ca^{40} ion current with a change in filament temperature. However, at R.M.S. R.F. voltages of greater than about 6.0 volts, the peak shape deteriorated. In addition, excessive residual background gas peaks were also observed.

The source was also tested using the intensely heated wolfram filament for thermionic ionization, with the outer cylinder held at a small, constant positive voltage relative to the filament. Monoenergetic, stable, calcium currents up to 2×10^{-11} amperes were observed, and the source arrangement showed some promise in this respect. Further investigation of this source with an added accessory "external" cylinder heating unit is recommended.

3. THE THERMAL EMISSION OF POSITIVE IONS

The simplified account of positive ion emission from heated filaments which was presented in Section 2 is useful in a qualitative sense, but the process is actually not always so simply explained. An account of some of the literature on this complex subject, along with some of the observations made in this research is therefore presented in this section.

Following its discovery in the late nineteenth century, the emission of positive ions from heated substances was intensively investigated up until about the mid-thirties (for a review of this early work see Riemann (1934); most of the later work may be found by referring to Nottingham (1954)). As electron emission became relatively more important through its application to electronics, research turned away from the investigation of positive ion emission. Recently, interest in this phenomenon has been renewed, partially due to its increased application in mass spectrometry.

As a result, perhaps, of the economic values involved, thermionic electron emission is rather well understood, though the properties and mechanisms of oxide coated cathodes are still under dispute. A theory for simple cases of positive ion emission has proved fairly compatible with experimental results, but positive ion emission from complex systems is very poorly understood.

The thermal emission of positive ions may be grouped into the following categories:

- 1) Simple thermionic emission, including

- a) ionization of metallic vapors in the presence of heated filaments,
 - b) emission from a heated filament coated with an element,
 - c) impurity emission from heated filaments, and
 - d) "characteristic emission," or the slight emission that occurs from all pure metals when heated to a very high temperature.
- 2) Emission from heated electrolytes.
 - 3) Ion emission from the complex systems of refractory compounds on heated filaments which are commonly used in mass spectrometry.

Theory of Simple Thermionic Emission

The case of ionization of a metallic vapor in the presence of a heated filament has been treated from a purely thermodynamic point of view. Riemann (1938) demonstrates that the Saha-Langmuir-Kingdon theory of equilibrium between neutral atoms, positive ions, and electrons in an elemental gaseous mixture at absolute temperature T, leads to the relationship:

$$\ln \left(\frac{n^+ n^-}{n} \right) = - \frac{I}{kT} + \frac{3}{2} \ln T + \ln \frac{2 \sigma_p (2\pi m k)^{3/2}}{\sigma_a h^3} \quad (2)$$

- where n^+ , n^- , n = molecular concentrations of ions, electrons, and atoms, respectively,
 σ_p and σ_a = ionic and atomic statistical weights,
 I = work to ionize atom, or 1st ionization potential,
 m = electron mass,
 K = Boltzmann's constant,
 h = Planck's constant.

This relationship thus provides an "equilibrium constant" for the reaction $\text{Ca} \rightleftharpoons \text{Ca}^+ + e^-$ in a free system. It represents an equilibrium between the rate of ionization due to high energy collisions and the rate of recombination of positive ions with electrons. If now the system is in equilibrium with a metallic surface at the same tempera-

ture, the electron concentration will be fixed by the metal according to thermionic electron theory:

$$\ln (n^-) = - \frac{\phi^-}{KT} + \frac{3}{2} \ln T + \ln \frac{2(2\pi mK)^{3/2}}{h^3} \quad (3)$$

where ϕ^- is the thermionic electron work function of the metal. Substituting (3) in (2) Riemann obtains

$$\frac{n^+}{n} = \frac{\sigma_p}{\sigma_a} \exp \frac{\phi^- - I}{KT} \quad (1)$$

a formula for the "ionization efficiency," or ratio of positive ions to atoms.

The assumptions upon which this derivation is based are seldom met in practice, but this formula has been applied with some degree of success to observations of heated filaments in the presence of metallic vapors (Riemann, 1934) and by Morosov (1947) for the surface ionization of barium on wolfram, and by other workers. Many complications have, however, been observed, possibly due to the presence of contaminants. In general experimental results have agreed fairly well with theory in the case of temperature dependence, but actual currents obtained have been less by a factor of 100-1000 than those predicted by theory.

Smith (1930) developed a formula equivalent to (1) for the case of characteristic ion emission (i.e., emission of positive ions from a pure metal), also by thermodynamical reasoning. Grover (1937) arrived at the same formula by physical reasoning, specifically examining the potential barrier to electron escape from the metallic surface.

We thus have two approaches: the first considers an equilibrium constant for the reaction $\text{Ca} \rightleftharpoons \text{Ca}^+ + e^-$ with a hot metal surface acting as a buffer and supplying a given concentration of electrons; the second considers the problem of an atom coming out of the interior of a metal and breaking through the surface, with a certain probability that one of its electrons will not break through the barrier. Both approaches reach the same formula for ionization efficiency, and indeed, this formula has been applied to other types of positive ion emission with some success.

Consider formula (1) again. The critical values are the electron work function of the metal filament and the ionization potential of the sample element. If $\phi^- > I$ the metal has a greater affinity for electrons than the evaporating atom. In this case (e.g., alkalis on Pt) (n^+/n) is greater than one, and decreases with increasing temperature. If $I > \phi^-$, (n^+/n) is less than one, and increases with increasing temperature. It is apparent then (on the basis of this simple theory) that for any element with a moderately high ionization potential, such as alkaline earths, it is desirable to 1) use a filament with a maximum electron work function; 2) deposit the material on the filament in a refractory form; 3) since we are rapidly removing positive ions it is also desirable to remove emitted electrons as rapidly as possible by setting up a proper potential.

If we also take into account the temperature dependence of evaporation, we should have (at least for the case of a layer of calcium with $\theta < 0.1$ on a clean metal surface) a relationship of the sort

$$n^+ = A e^{-\phi^+/KT} \quad \text{ions/second} \quad (4)$$

$$A \propto (T/m)^{\frac{1}{2}}, \quad m = \text{atomic weight},$$

where ϕ^+ is the "positive ion work function," given (Grover, 1937) by $\phi^+ = L_0 + I - \phi^-$, where L_0 is the latent heat of evaporation per atom, I is the work to ionize an atom or the ionization potential, and ϕ^- is the electron work function. An approximation to the positive ion work function may also be obtained by calculating the image potential for a positive ion leaving the surface.

Emission from Heated Electrolytes

A case to which the above sort of "simple" theory does not seem to apply is that of positive ion emission from a thick coating of an electrolyte, for example an alkali halide, on a hot wire. Ionization efficiencies and other observations suggest that most of the ions are emitted from the surface of the electrolyte, rather than from the salt-filament interface, suggesting that any control of ionization exerted by the filament surface is of a different nature from that discussed above. This emission may be thought of as somewhat analogous to thermionic electron emission, with the positive ions merely attaining a high enough energy to break out of the lattice.

This phenomenon is discussed extensively by Riemann (1934). Positive ion emission is typically observed from Cd, Zn, Fe, Al, Mg (!), NH_4 , Cu, Tl, and alkali halides, Al and Ca flourides, PbCrO_4 , and negative ion emission from lead halides. Early workers observed that in many cases ionization was related to the mobility of ions in electrolysis. In the case of water soluble salts, a definite enhancement of ion emission was observed when water was present as an impurity, suggesting that hydration of positive ions by water molecules makes their

escape from the lattice somewhat easier. This resulted in an initial decrease in positive ion current as water was driven out of the salt. AgCl, which is not soluble in water, did not show this effect. Many other types of impurities were also found to enhance emission. It was also found that an electrostatic "drawing-out" field enhanced emission in most cases. All of these findings suggest a simple thermal escape of ions from the electrolyte, with the filament surface acting possibly as a reducing agent or remote electron acceptor.

Riemann (1934), Blewett and Jones (1936) and Bondy and Vanicek (1936), among others, found that complex glasses, such as $1 \text{ LiO}_2 \cdot 1 \text{ Al}_2\text{O}_3 \cdot 2 \text{ SiO}_2$, often gave more copious emission than simple salts. Blewett suggests that this is due to the loose binding (coordination of six to eight) of the lithium. Kunsman (see Reimann, 1934), Koch (1936) and others have obtained copious alkali emission from anodes formed by a mixture of a fine powder of iron oxide or tungsten with alkali halides. The function of the metallic powder in these sources is not entirely understood.

Positive Ion Emission from Alkali Salts

In the alkali work in this research, a tantalum or platinum plated tantalum filament thinly coated with an alkali salt (usually chloride, sometimes phosphate) was used. Bradt (1947) found that "salt or ash deposits on the platinum (filament) result not only in a non-uniform work function over the surface, but become charged in operation, and consequently, introduce an appreciable background between isotope peaks." Bondy, et al. (1935), found that they could not use alkali halides because of excessive vapor pressures at low emitting

temperatures. However, such effects were never observed in this laboratory.

The variation of alkali current with temperature for a solution of the anions of a lepidolite (except silicon) deposited as chloride on an unoxidized tantalum filament, is shown in Fig. 4. Since the filaments were not calibrated throughout the temperature range represented, an extrapolation was necessary. The method of temperature calibration is given in Appendix I. The positive ion currents follow the law $I = A \exp(-\phi^+/KT)$, and the values of ϕ^+ obtained, along with other pertinent properties are given in Table I.

TABLE I

<u>Isotope</u>	<u>Slope</u>	ϕ^+ (e.v./atom)	Ioniza- tion Po- tential (e.v./atom)	Latent Heat of Vaporiza- tion for the Chloride* (e.v./atom)	Dissociation Energy of the Chloride ** (e.v./atom)	$L_o + I - \phi^+$ *** (e.v./atom)
Rb ⁸⁵	10,500	2.07	4.16	1.60	4.38	3.69
K ⁴¹	10,800	2.15	4.32	1.69	4.40	3.86
Na ²³	14,000	2.77	5.12	1.77	4.24	4.12
Li ⁷	16,800	3.34	5.36	1.57	5.14	3.59

* National Bureau of Standards (1952).

** Gaydon (1947).

*** The electron work function for Ta is 4.1 e.v.

Since in this case the alkali chloride must be evaporated, dissociated, and an electron removed from the alkali, one might expect higher positive ion work functions. It may be seen from the last column in Table I, however, that there is a suggestion of agreement with the work function for Ta (4.1 volts) if the dissociation energies are neglected. This suggests that one might use a "latent heat of vapori-

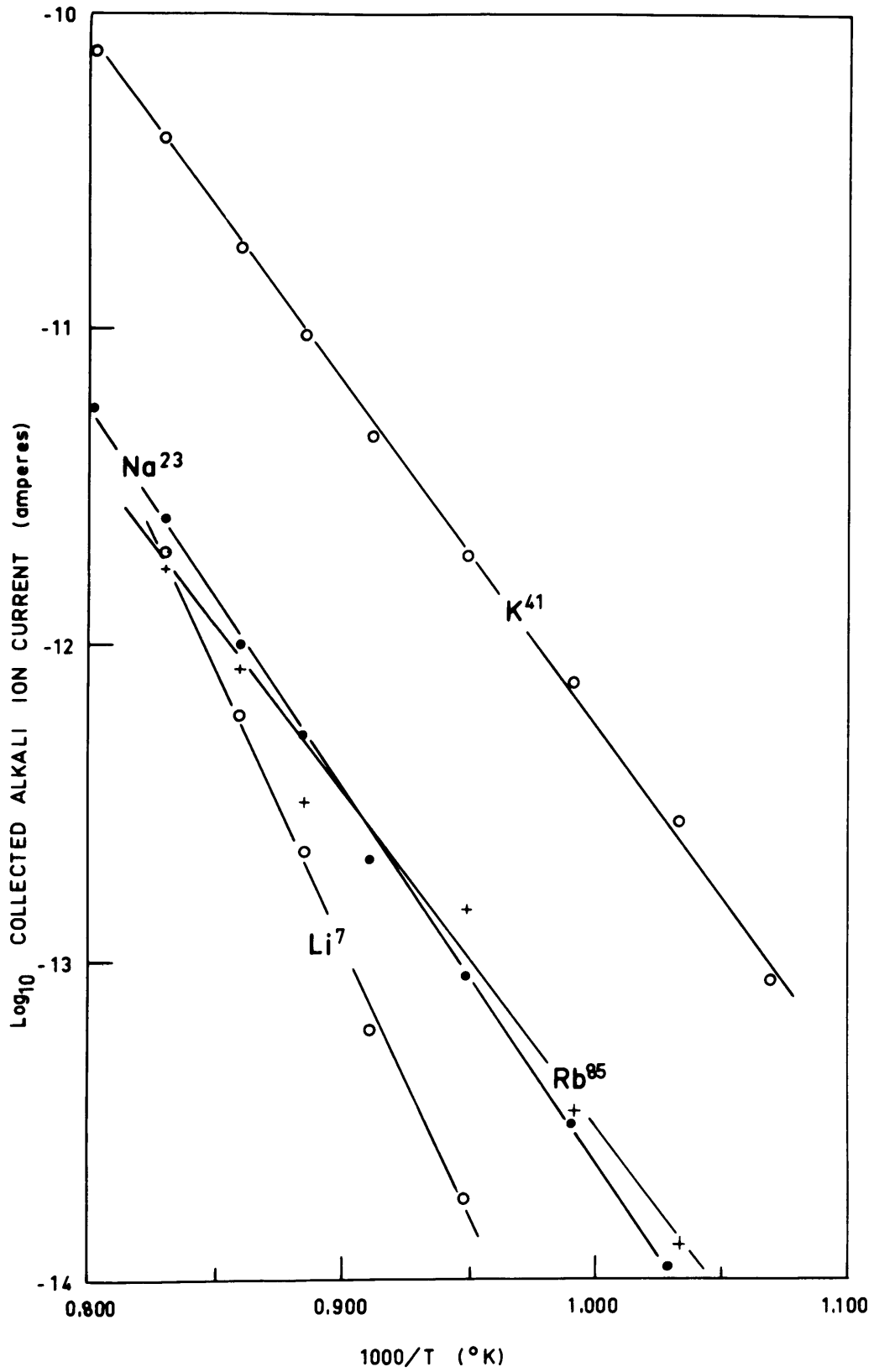


Figure 4. Alkali Ion Current as a Function of Temperature.

zation" of the alkali atom from the alkali salt and obtain some agreement with simple theory. Such a parameter has not, to my knowledge, been measured.

For comparison with Table I, Grover (1937) obtained a positive ion work function of 0.5 volts for K^+ emission from an uncoated molybdenum filament. Bull and Marshall (1951) obtained $\phi^+ = 2.4$ volts for K^+ emission from a wolfram filament in the presence of K vapor, $\phi^+ = 2.1$ e.v. for Rb, and $\phi^+ = 1.8$ e.v. for Cs.

The Oxide-Coated Cathode

Because of their wide application in the electronics industry, oxide coated cathodes have been extensively studied in an effort to understand their electron emission characteristics. Some of the more general observations which have resulted from this work are presented in the review articles by Blewett (1939), Eisenstein (1948) and Nergaard (1952), and are briefly reviewed below.

Commercial cathodes are generally made up of a nickel base with some reducing agent impurities, coated with a mixture of barium and strontium carbonates, with a small amount of calcium occasionally added. The carbonates are converted to oxides under vacuum, and it is then necessary to activate the filament in order to obtain copious electron emission at the normal operating temperatures of about 900 to 1000°K.

The primary activation mechanism is thought to be the production of free barium metal, though the recent results of Moore, et al. (1955), indicate that other factors may be of equal importance. Activation may be achieved by heating the filament for a period of time, causing the filament core (which may be considered a reducing agent)

to react with the oxide, or by drawing electron current, causing electrolysis with the evolution of oxygen at the oxide surface. It is nearly impossible to thermally activate a filament with a clean platinum core, and an activated filament may be deactivated by heating it in the presence of oxygen.

The currently popular theory (Eisenstein, 1948) on the oxide cathode is that barium oxide is an excess impurity (N-type) semiconductor, with the impurity centers (i.e., free barium) near the surface of the oxide. The free barium atoms provide electron energy levels in the forbidden region and thus provide a supply of electrons which can more easily move into the conduction band, and which can be more easily emitted from the oxide. The presence of SrO or certain other impurities may distort the lattice and thus decrease the difference between some of the impurity levels and the conduction band, thereby enhancing electron emission. The excess barium may be located at normal lattice sites, in which case electrons are trapped in surrounding empty electronegative atom sites, or the barium may be distributed interstitially throughout the lattice, with electrons trapped in the fields of the interstitial atoms.

The electrical conductivity of the activated oxides is of the order of $10^{-2} \Omega^{-1} \text{cm}^{-1}$ for activated cathodes at about 1000°K , and increases slightly with temperature. For unactivated cathodes the conductivity is less by about a factor of 100.

Oxide-coated cathodes do not saturate easily; that is, the electron current continues to increase with increasing voltage drop when the current should no longer be space-charge limited. This may be due in part to the Schottky effect, and in part to the fact that the oxide

coatings generally have a very rough surface, causing local effects on the electric field. This non-saturation was also observed in this work for Ca^+ ion emission from CaO , and may contribute to isotopic mass discrimination effects.

Some of the typical values (Blewett, 1939) obtained for the thermionic electron work function for oxide-coated cathodes are given below and should be compared with a value of about four to four and one-half electron volts for most metals.

<u>Compound</u>	<u>Thermionic Electron Work Function (Volts)</u>	<u>Electron Emission A/cm^2 at 1000°K</u>
BaO	1.1	10^{-5} to 10^{-3}
SrO	1.4	10^{-4} to 10^{-2}
CaO	1.9	10^{-3} to 10^{-1}

Although the importance of free barium metal near the surface of the relatively thick oxide coating has been demonstrated by experiments in which the outer layers of the oxide were removed, or the oxide coating mechanically knocked off, causing a large decrease in emission, some other results throw some doubt on the importance of the thick oxide coating. Moore (see Eisenstein) found that very thin oxide films, down to a monomolecular layer, deposited on filaments were capable of producing electron emission on a par with the conventional thick coatings. Some of his results are given below:

Emission Characteristics of Thin Oxide Films (Moore, from Eisenstein (1948))

	<u>Work Function (Volts)</u>	<u>Emission, A/cm^2 at 1000°K</u>
CaO on W	2.1	10^{-5}
SrO on W	1.3	0.3

BaO on W	1.2	0.9
SrO on Ni	2.0	10^{-5}

A more definite dependence on the base metal is indicated for thin oxide films than for thick coatings. In addition to the above data, it was found that W and Mo cores yield nearly identical emissions which are somewhat higher than for nickel and much higher than for platinum and gold. The copious electron emission from thin oxide films requires an explanation different from that offered for thick oxide coatings.

The recent results by Moore, et al. (1955), provide further doubt. At their level of sensitivity, they found no correlation between concentration of free barium metal in BaO cathodes with thermionic electron emission, and concluded that "if excess Ba (or Sr) is important, the significant amounts are probably less than one atom of Ba in 10^6 molecules of (BaSr)O." They found the concentration of free barium in the oxides to be of the order of six atoms of barium in 10^5 oxide molecules. At least in the case of carbonized nickel cathodes, $3.2 \pm 0.3\%$ of the barium in (BaSr)O "evaporated" from the oxide when the cathodes were aged for one-half hour to 56,000 hours after initial activation. This surprising result may be related in some way to the low-temperature positive ion emission observed in this research.

The Evaporation Products of Alkaline Earth Oxides

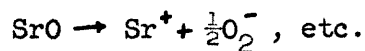
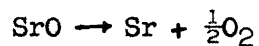
The rate of evaporation of CaO and SrO was studied by Claassen and Veenemans (1933) by evaporating the oxide at known temperatures for known periods of time in a high vacuum and directly measuring the total weight of the product. Their results are given below:

$$\text{SrO } \log (m \sqrt{T}) = - 3.07 \frac{10^4}{T} + 13.35 \quad L_0 = 140 \text{ Kcal/mol.} \quad (5a)$$

$$\text{CaO } \log (m \sqrt{T}) = - 2.74 \frac{10^4}{T} + 9.77 \quad L_0 = 121 \text{ Kcal/mol.} \quad (5b)$$

where m = rate of evaporation of oxide, in grams /cm² - sec., T = absolute temperature, and L_0 = latent heat of vaporization. For our own work, these results are translated into rate of sample loss as a function of temperature in Figure 5.

Aldrich (1951) studied the evaporation products of barium and strontium oxides deposited on various base metals, and verified the value of L_0 obtained by Claassen and Veenemans for BaO. He also observed considerable evaporation of free barium from BaO on all materials except a platinum base, with the largest Ba/BaO ratio obtained for tantalum, the best reducing agent among the metals tested. He initially obtained a Ba/BaO ratio of about 100 for tantalum, and after the filament was thermally aged the ratio decreased to ten. For SrO on platinum he found the evaporation of Sr to exceed that of SrO by at least an order of magnitude and he found that a significant amount of Sr⁺ ions were also evaporated. The temperature dependence of the SrO, Sr, and Sr⁺ evaporation products was the same, and corresponded to that obtained by Claassen and Veenemans (1933) for the evaporation of SrO. Aldrich suggests that these results may be due to the thermal dissociation of the vaporized SrO by the reactions



If this were the case, however, one would expect the dissociation energy to influence the temperature dependence of Sr and Sr⁺ production. In addition, since the dissociation energies of BaO and SrO, 4.7

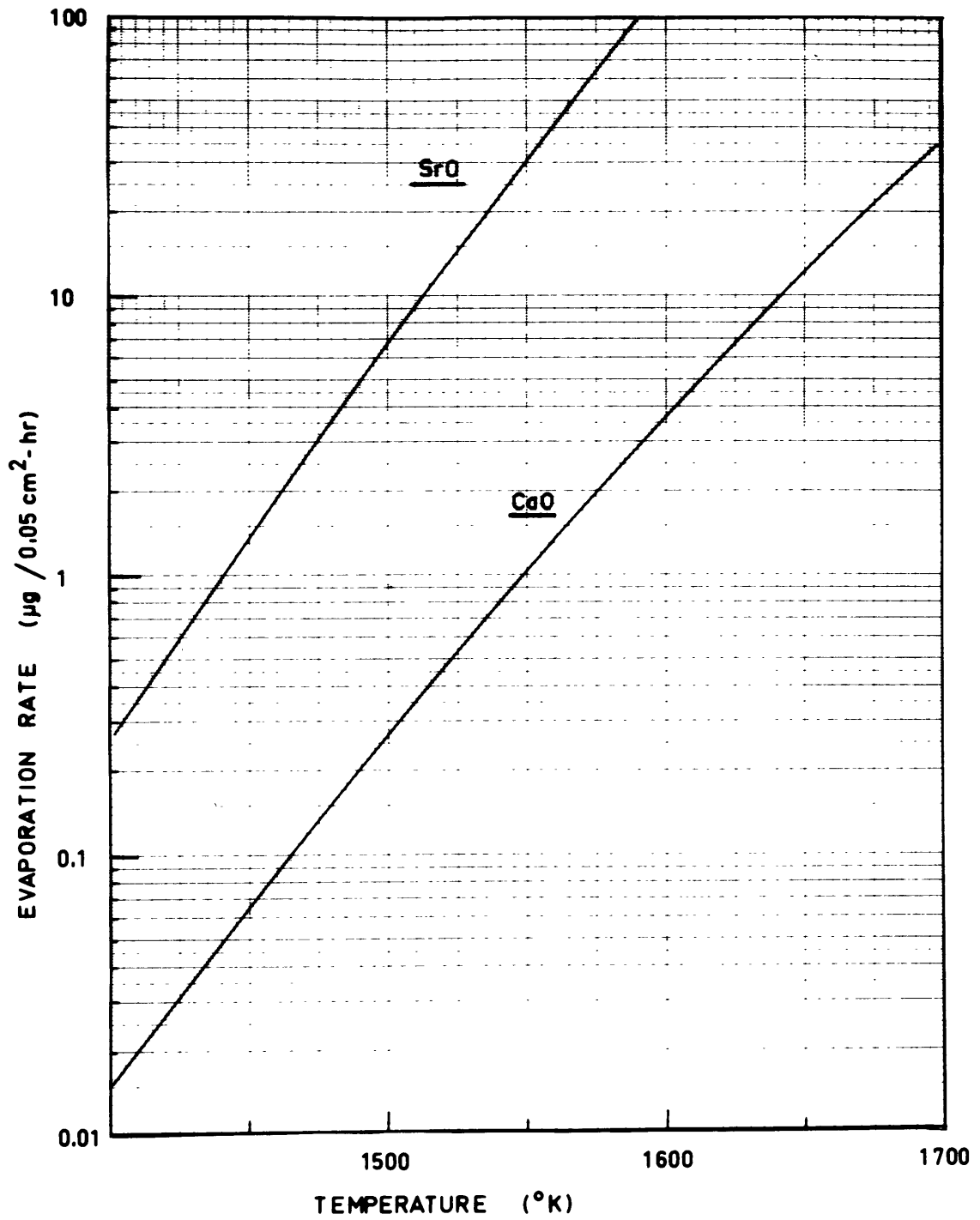


Figure 5. Minimum Rate of Sample Loss Versus Temperature for CaO and SrO.

and 4.5 electron-volts/molecule respectively (Gaydon, 1947), are similar, the same effects should have been observed for barium, which was not the case.

Bickel and Holroyd (1954) studied the evaporation products of SrO on platinum by the same method as Aldrich. They confirmed Aldrich's results for Sr evaporation from an aged system in the temperature range up to about 1640°K, but above this temperature the rate of increase of Sr evaporation with increasing temperature was less, corresponding to a latent heat of evaporation of about 60 Kcal/mol. For the initial heating the temperature dependence was linear over the entire temperature range studied and corresponded to $L = 164$ Kcal/mol. They suggest that the source of the evaporated Sr atoms and ions is free strontium occurring as impurities in the SrO, and that the decrease in the slope of their curve at high temperatures may be due to a "diffusion limited" process whereby free strontium becomes locally depleted at the surface of the oxide.

Hayden (1948) studied the positive ion emission from a number of oxides. He found that a tungsten filament generally gave the most efficient ionization for elements with which it could be used, although it could not be used for all elements.

"In general, the emission from nitrates or oxides of elements of normal valence one or two was, when emission occurred, of the form R^+ . Emission from elements of valence 3 or 4 was of the form RO^+ ."

Hayden gave a table of observed ionization efficiencies for a number of oxides. The observed values are not consistent with equation (1) if it is imagined that emission was from elements, rather than from oxides. Hayden gave a value of 0.08% for SrO on Ta, compared with

Herzog's (1954) value of 0.10%. He also found that with use, a given filament became more efficient in ion formation (up to a factor of 2) and that heating the filament rapidly so as to obtain a short, intense burst of ions was, by as much as a factor of four, less efficient than slowly raising the filament temperature. These observations have been confirmed in this laboratory for SrO and CaO on oxidized tantalum (Herzog, 1954) but were not observed in the case of CaO on a platinum-plated tantalum filament. Another important observation by Hayden was that "the ionization efficiency seemed independent of the size of the sample so long as the amount of material on the filament was small (roughly less than 100 micrograms)." Since a 100 microgram sample would constitute a layer several thousand atomic radii thick, this observation supports the idea that the positive ions are evaporated from the bulk oxide rather than from the oxide-filament interface.

Herzog (1952) studied a number of filament-compound systems for Sr⁺ ion production, including nickel-plated wolfram filaments. He observed better emission from refractory compounds, and also found pure platinum and wolfram filaments impractical due to burn-out.

Observations on the Production of Positive Ions from the Alkaline Earths

Nature of the System

In the adopted procedure, a sample of calcium nitrate was applied to a platinum plated tantalum filament (see Section 2) in aqueous solution, the water being evaporated away by heating the filament. The filament was then heated to about 800 to 900^oK in a helium atmosphere to dry it out and firmly bind the sample to the filament. Some conversion from nitrate to oxide also probably occurred at this point. After evacuation, the filament is heated for a considerable period under vacuum at 900 to

1200°K to evaporate off the alkalis. At this point "activation" may occur, with the production of some free calcium metal as impurity in the oxide, and the results of Moore (1955) suggest that a small quantity of the calcium may be lost. The sample which is run is thus believed to be a CaO layer with some free calcium, and small amounts of alkali impurities. Interface compounds such as Ca platinate, Ca tantalate, etc., undoubtedly are formed at the filament oxide boundary. In the case of the lepidolite runs there may also be traces of magnesium present. Other systems which were tested but were found to be unsatisfactory due to insufficient positive ion production were calcium carbonate on clean tantalum and on oxidized tantalum, and calcium oxalate on oxidized tantalum. Calcium oxalate on wolfram was also tested, but the filament burnt out at temperatures at which Ca⁺ ion emission began.

Ionization Efficiency

In most of the calcium runs the amount of calcium applied to the filament was known, at least approximately. Since the samples were run to completion, i.e., completely evaporated, the total number of ions produced was known. Therefore the ion collection efficiency (ions collected/atoms evaporated) could be calculated.

In order to convert these values to ionization efficiencies ((n^+/n_0) = the number of ions produced per evaporating atom), the efficiency of the mass spectrometer was measured. This measurement was made on an alkali chloride sample, but would presumably apply to any other sample used. The entire mass spectrum was swept at optimum focus and the only appreciable ion currents were K and Rb, which totaled 2.1×10^{-10} amperes. The high-voltage supply was then turned off, and a

variable voltage was applied between the filament and the shield box. Positive ion current was collected on the shield box and measured. In order to reproduce normal emitting conditions, a positive plate was maintained nearby to draw off electrons, though it was found that this had no effect on the measured ion current! The total measured positive ion current is shown as a function of plate voltage in Figure 6. Up to a "plate voltage" of a few volts the current is space charge limited, according to the Langmuir-Child law, but it can be seen that the current does not saturate. The point at twenty-two volts was considered representative of the gradient in normal operation, giving the total observed ion current as 50×10^{-10} amperes. The efficiency of the mass spectrometer (ratio of ions collected to ions produced) was therefore 2.1/50, or about 4%. The ionization efficiency may therefore be obtained by multiplying the collection efficiency by 25.

The ionization efficiencies obtained for a number of runs are given in Table 2. A number of unsuccessful runs using CaCO_3 on Ta or TaO, and CaC_2O_4 on TaO are not included, but gave ionization efficiencies of less than 0.0005. With $\text{Ca}(\text{NO}_3)_2$ samples on platinum-plated filaments ionization efficiencies of from 0.005 to 0.01 could be fairly dependably obtained. This represents an improvement by about a factor of ten relative to other methods. The results are in rough agreement with Hayden's (1943) finding that (n^+/n) is not strongly dependent on sample size.

A very important question is whether the Ca^+ ions come from the bulk oxide, or whether they originate at the oxide-core interface, as was postulated by Backus (Herzog, et al., (1954)). If the latter were the case, one would not expect that the Ca^+ ions so formed could

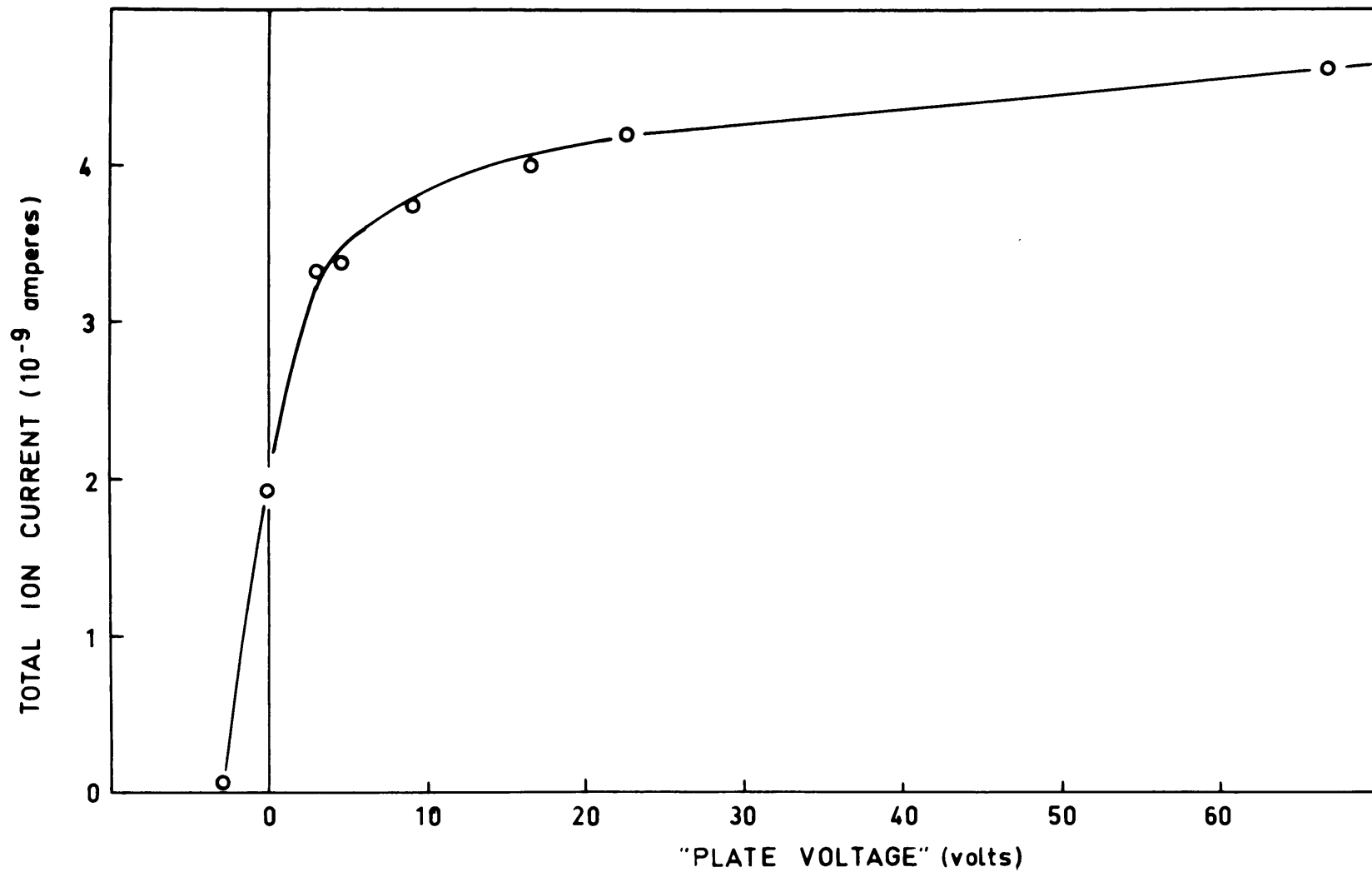


Figure 6. Non-saturation of Positive Ion Current.

diffuse back out through the CaO lattice as ions and therefore most of the emission would come from the vacuum-core-oxide interface. At the same time the CaO coating would be evaporating from its entire surface. One would thus expect the ionization efficiency to be considerably lower than that predicted by the equation $n^+/n_o = e^{(\phi^- - I/KT)}$. The predicted efficiency for Ca atoms on a Ta surface ($\phi^- = 4.1$ e.v.) would be at (at 1600°K) $n^+/n_o = e^{-1.9(11,600)/1600} = 10^{-6}$ compared with the observed value of about 10^{-5} . For Ca atoms on a platinum-plated Ta filament (assuming $\phi^- = 4.6$), $n^+/n_o = e^{-1.5(11,600)/1600} = 10^{-5}$, compared with the observed value of about 10^{-4} . Thus the actual ionization efficiency was an order of magnitude greater than that predicted for the elemental calcium evaporating from a hot wire. This suggests that the "seat of positive ion emission" is in the bulk oxide, rather than at the core-oxide interface.

Temperature Dependence of Ca⁺ Ion Current

The temperature dependence of Ca⁺ ion current is shown in Fig. 7. These measurements were made on the Bob Ingersoll calcium sample which was run as Ca(NO₃)₂ on a used, platinum-plated tantalum filament. The different curves represent measurements made during different parts of the run. The temperature dependence was definitely linear, and followed the formula $I = A e^{-\phi^+/KT}$. The effective positive ion work function could thus be calculated from the observed slopes:

$$\phi^+ = \frac{\ln I}{(1/T)} \frac{1}{11,600} \text{ electron volts/ion.} \quad (6)$$

TABLE 2. Observed Ionization Efficiencies

Sample	Sample Form	Amount Sample (μ g)	Total Collected (coulombs)	Collection Efficiency ppm.	Ionization Efficiency (-%)
I. TaO filaments					
Pasamonte Meteorite	CaC_2O_4	> 100	7	< 0.3	< .0008
Ca Standard	$\text{Ca}(\text{NO}_3)_2$ + Borax	50	17	1.4	.004
Ca ⁴⁸	CaC_2O_4	40	4	0.4	.001
Bikita id I	$\text{Ca}(\text{NO}_3)_2$ + Borax	4-8	0.4	0.2-0.4	.0005-.001
Very Strongly Oxidized Ta Ca ⁴⁸	$\text{Ca}(\text{NO}_3)_2$	40	35	3.6	.009
II. Pt-plated filaments					
A. New filaments					
Ca ⁴⁸ + Ca ⁴²	$\text{Ca}(\text{NO}_3)_2$	80	16	0.8	.002
Ca ⁴⁸ + Ca ⁴²	$\text{Ca}(\text{NO}_3)_2$	60	60	4	.010
CaStd.	$\text{Ca}(\text{NO}_3)_2$	40	17.4	1.8	.005
Ca ⁴² + Ca ⁴⁰	$\text{Ca}(\text{NO}_3)_2$	12	15	5.2	.01
Bik id II-A	$\text{Ca}(\text{NO}_3)_2$	~ 5	4	~ 3	~ .01
Bik id II-B	$\text{Ca}(\text{NO}_3)_2$	~ 5	6	~ 5	~ .01
B. Used filaments					
Homestead Meteorite	$\text{Ca}(\text{NO}_3)_2$	> 100	175	< 10
Ca Std.	$\text{Ca}(\text{NO}_3)_2$	90	45.0	2.1	.005
Ca ⁴²	$\text{Ca}(\text{NO}_3)_2$	60	40	2.8	.007
Bikita Unspiked "	"	~ 40	16	~ 1.0	~ .002
Brown Derby id "	"	~ 30	35	~ 5	~ .01
Bob Ingersoll id "	"	~ 15	~ 37	10	~ .02

Note: To this table should be added a number of runs of CaCO_3 and CaC_2O_4 on tantalum and tantalum oxide filaments, which had $n^+/n < 0.001$ and were therefore failures.

The values obtained were:

<u>Measurement Conditions</u>	<u>ϕ^+ (volts)</u>
1) Initial heating	4.5
2) Decreasing temperature after 40 minutes at 1600°K	4.3
3) Increasing temperature after 40 minutes at 1600°K	4.5
4) Decreasing temperature after 5 hours at 1600°K	4.6
5) Increasing temperature after 5 hours at 1600°K	4.6

Similar measurements were made on two other samples, obtaining values of $\phi^+ = 4.8$ in one case, and $\phi^+ = 5.7$ in the second case. The reason for the one high value is not known, though in this case the sample was spread out more than usual over the filament and less than normal emission was obtained. The values given are slightly less than the latent heat of evaporation of CaO, $L_0 = 5.3$ e.v./atom (Claassen and Veenemans, 1933). It is difficult to account for the values obtained by any sort of extrapolation of the formula (1) for simple cases. For comparison, the ionization potential of Ca = 6.09 volts, the dissociation energy of CaO = 5.9 e.v./molecule (Gaydon, 1947) and the approximate value for the electron work function for the filaments was 4.6 e.v.

The fact that the calcium was primarily evaporated from CaO is semiquantitatively confirmed by observing that at about 1600°K the current was from 10^{-12} to 10^{-11} amperes. The rate of CaO evaporation, from Figure 5, should have been about 1.5 micrograms per hour, or 10^{-6} ampere equivalents. This implies a collection efficiency ranging

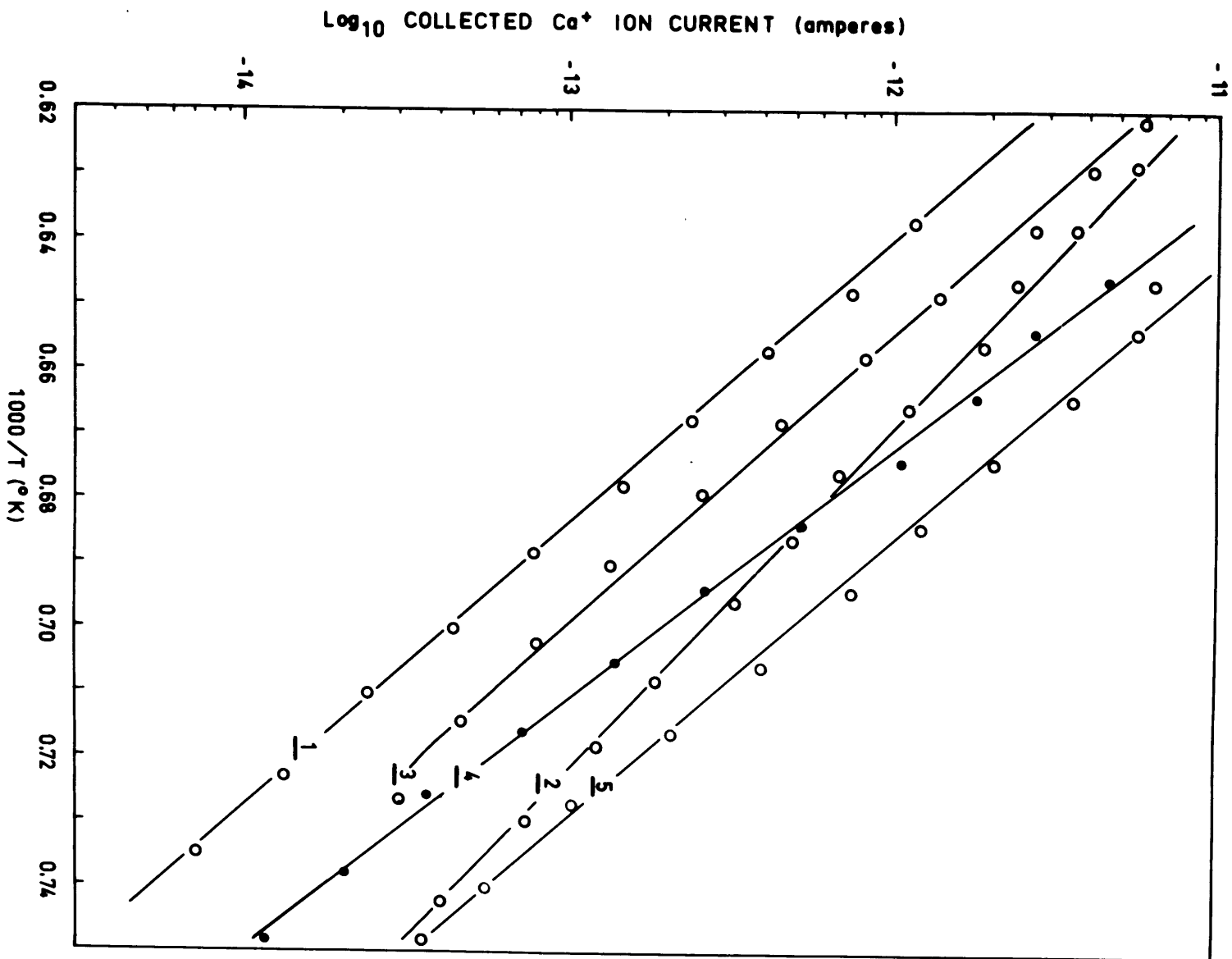


Figure 7. Calcium Ion Current as a Function of Temperature.

during the run from 1 to 10 ppm., which is in fair agreement with the value obtained for the average efficiency by an independent method (Table 2).

Time Variation of Positive Ion Current

In general the positive ion current was observed to increase (over a period of several hours) by a factor of ten or more after initially raising the temperature, level off and remain constant for a variable period, and decrease as the last (layers) of the sample were removed. It is believed that this increase may have been due to an increase of ionization efficiency with time, which correlated with a decrease in electron emission. Since a decrease of the positive ion work function of less than 10% would result in an ionization efficiency increase by a factor of ten, such a variation would not be evident over experimental error in the sort of experiment illustrated in Fig. 7.

The initial variations of Ca^{40} current with time as well as the electron current variation are shown for the first two hours in Fig. 8. An increase in Ca^{40} current correlates with a decrease in electron current, though their product also decreases somewhat, possibly due to sample depletion at the hot spots of the filament.

Low Temperature Calcium Emission

In the case of lepidolite calcium samples, and in that case only, it was possible to obtain Ca^+ ion currents at extremely low temperatures, of the order of 800 to 900°K. (Somewhat similar effects have recently been observed for lepidolite strontium samples.) This was observed for calcium oxalate on TaO, as well as for calcium nitrate on platinum-plated filaments. Evidence suggests that these ion currents were only

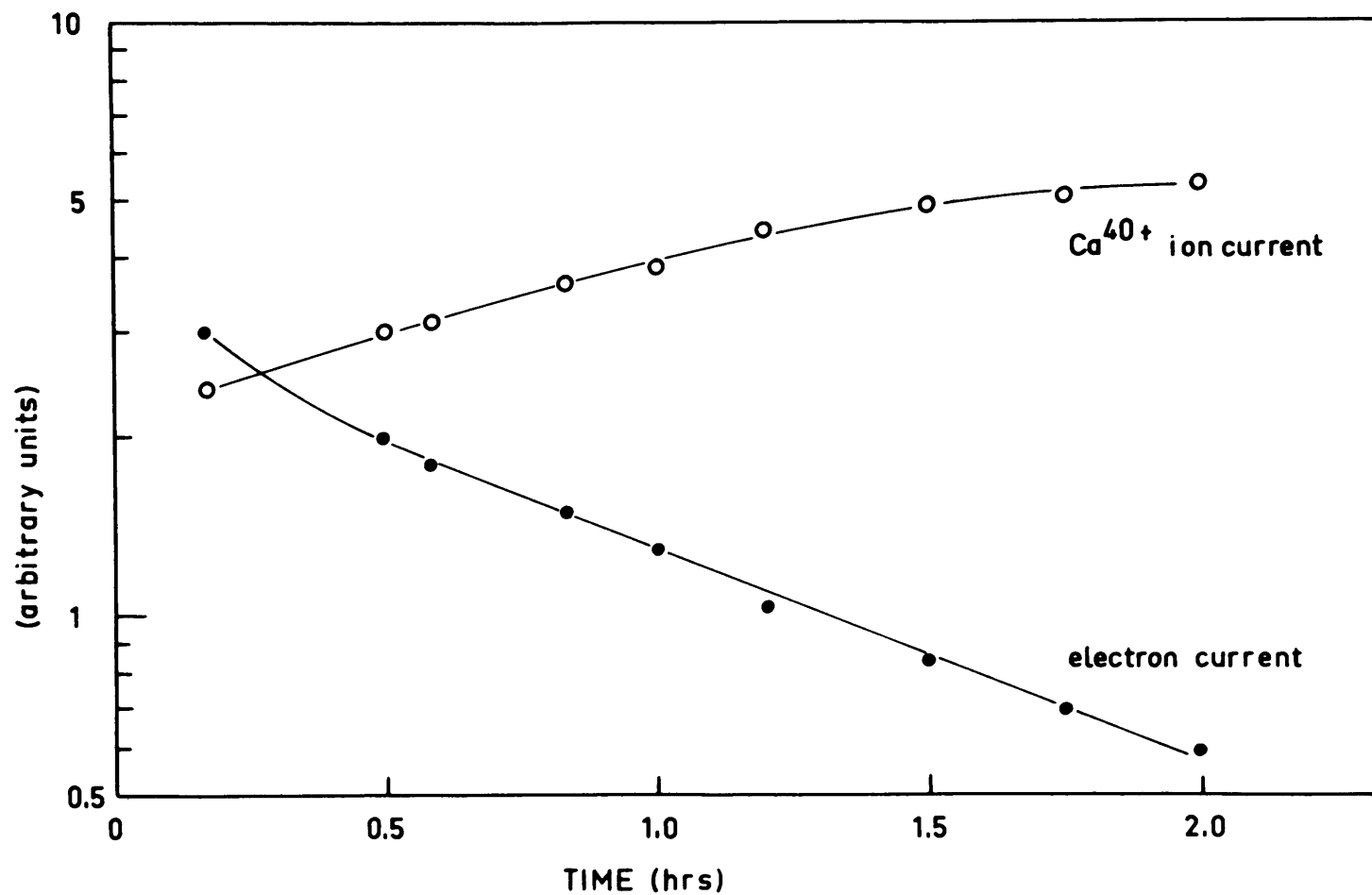


Figure 8. Initial Time Variation of Positive Ion Current and Electron Current. At $t = 0.2$, the Ca^{40+} ion current was 7×10^{-13} amperes, and the electron current was 3×10^{-6} amperes.

present when a drawing out voltage gradient was maintained, and that they were not accompanied by significant evaporation of the sample.

A complete mass spectrum was taken at about 900°K, with a drawing out potential between the filament and split plates in the source of about 310 volts. The sample had been heated for a considerable period with no electrostatic field applied and the nitrate had presumably been converted. The observed masses and ion current intensities are given in Table 3.

The alkalis were all represented as impurities, with the heavier elements concentrated due to the ion exchange separation. Magnesium, aluminum and calcium are ordinarily not detectable at this temperature, but for this low temperature emission, their appearance was typical. Optical spectrographic examination of the purified sample had revealed no detectable aluminum. Magnesium may have been present in the sample in trace amounts. Since magnesium has a high ionization potential (7.61 volts) its presence in ionized form was most surprising. It may be added that Mg^+ ions were never observed at normal operating temperatures (the sample was always pre-conditioned at a lower temperature).

The abnormally emitted ions also had abnormal peak shapes, shown for Ca^{40} in Fig. 9, compared with the normal alkali peak shapes. This shape appears to be due to an excessive energy spread in the emitted ions, with a high energy "tail." At a given temperature this sort of emission lasted for a variable length of time, generally decreasing with time, as if the supply of calcium which could be withdrawn in this manner was being depleted.

The abnormal emission was found to definitely decrease with decreasing drawing out field more rapidly than the normal alkali emission,

TABLE 3. Low Temperature Positive Ion Emission

<u>Ion</u>	<u>Approximate Intensity (amperes x 10⁻¹⁵)</u>	<u>Peak Shape</u>
Li ⁶	small	} normal
Li ⁷	14.0	
Na ²³	86.0	normal
Mg ²⁴	22.0	} distorted
Mg ²⁵	2.7	
Mg ²⁶	2.8	
Al ²⁷	43.0	distorted
(?)Si ²⁸	2.6	
K ³⁹	370	normal
Ca ⁴⁰	496	distorted
K ⁴¹	30.9	normal
Ca ⁴²	2.6	} distorted
Ca ⁴³	small	
Ca ⁴¹	8.2	
Ca ⁴⁸	small	
(?)Fe ⁵⁶	4.4	distorted
67	1.8	
83	2.2	
Rb ⁸⁵	2660	} normal
Rb ⁸⁷	1040	
Cs ¹³³	9200	normal

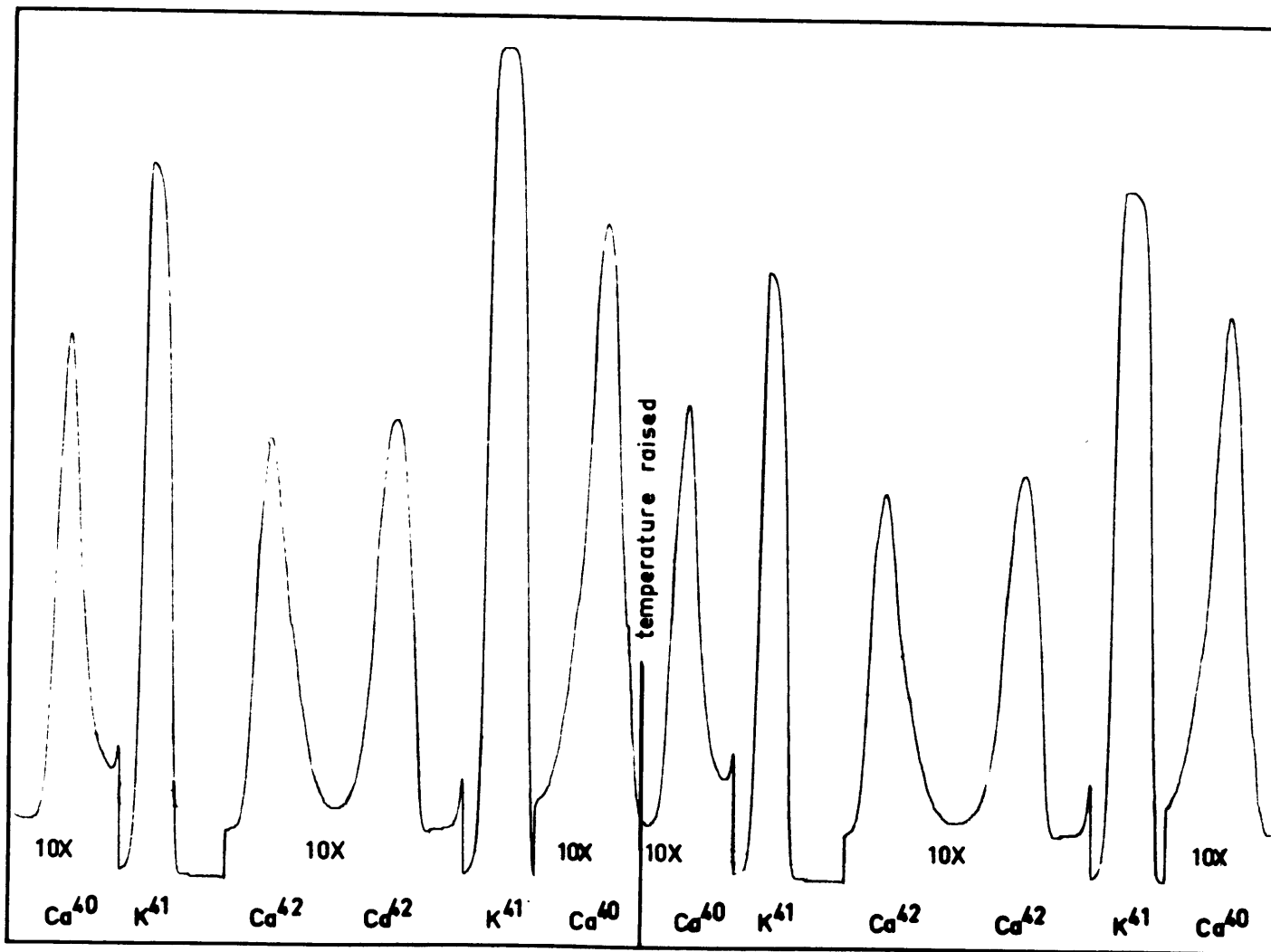


FIGURE 9. LOW TEMPERATURE CALCIUM.

which served as a comparator. For example, by decreasing the accelerating potential from 2200 volts to 900 volts, and thereby decreasing the drawing out field proportionately, the K^{41} peak decreased by a factor of 2.7 while the Ca^{40} current decreased by a factor of 14. It was inferred that with no drawing out field, none of the abnormal emission took place.

Brief and rough isotope measurements taken during the low temperature emission were abnormal, but a definite relationship was not established.

The low temperature calcium emission had a temperature dependence essentially identical to that of normal calcium emission, with $\phi^+ = 4.6$ e.v. in the temperature range 900 to 1100°K. However, it is not likely that the emission was due to efficient ionization of small amounts of evaporated CaO. If all of the CaO evaporating were ionized at 1000°K the maximum ion current obtainable would be 6×10^{-19} amperes, while currents of 10^{-12} amperes were actually observed at that temperature.

It is suggested that this abnormal calcium ion current may have been due to the electrical drawing out of a small portion of calcium ions which were very loosely bound near the surface of the oxide. The additional impurities contained in the lepidolite samples were probably the reason that this low temperature emission was confined to lepidolite samples. The rough surfaces of the oxide possibly caused fairly high electrical gradients locally, aiding the process.

Due to the large energy spread in this type of emission, and because of the abnormal isotope ratios obtained, it is considered unlikely that this abnormal emission could be developed into a useful source

of positive ions for isotope abundance measurements. This low temperature emission was excluded from all calculations involving ionization efficiency, isotope ratio calculations, and so forth.

Ion Currents Due to Re-evaporated Calcium

As in the case of the alkalis, when the filament reaches a sufficiently high temperature, calcium may be re-evaporated from parts of the shield box adjacent to the filament. The system is then operating like a double filament source, with the evaporated atoms or molecules being ionized on the hot filament. Care must be taken that the filament is far enough from the shield box so that this type of emission is not significant at normal operating temperatures. Since the filaments are never located in precisely the same positions, this phenomenon has been observed to a variable extent.

In one run in particular (the Ca^{48} spike calibration), after normal emission had subsided, and as the temperature of the filament was increased for cleaning purposes, a particularly large amount of this sort of emission was observed. In fact, the total charge collected was ten times that collected in normal emission, demonstrating that with a platinum-plated tantalum filament of the proper geometry a highly efficient double filament source might be constructed. This was also the only time that CaO^+ was observed, the Ca^+/CaO^+ ratio equalling 500.

Since one of my colleagues disagrees with the supposition that this high temperature calcium emission is due to an evaporation of calcium compounds from the source shield box, it should be noted that my interpretation is indirectly based on two facts: 1) the high temperature emission is generally initiated at a temperature several hundred

degrees Kelvin above the temperature at which normal emission has nearly completely decayed; 2) runs in which such emission was observed differ from those in which it was not in that in the former case the interior of the source shield box exhibits a smudgy darkening around the exit slit, while in the latter case it exhibits a neat pattern of Newton's rings.

Conclusions

The emission of positive ions from oxide coatings is a complex phenomenon which requires much further study. The evidence of Aldrich, Bickel and Holroyd, Hayden, Herzog, and this research suggests that the mechanism of positive ion production is quite different from that in the case of an element on a hot filament, with the "seat of ion emission probably in the bulk oxide," and that the ionization efficiency is more dependent on the properties of the compound and activation process than on the thermionic electron work function of the base metal.

4. ISOTOPIC FRACTIONATION DURING ANALYSIS

Although Brewer (1936) reported isotopic fractionation during mass spectrometric analysis of the lighter alkalis, no reports of similar effects for other elements have been published until very recently. Sherwin and Dempster (1941), however, did report that by using electrodes of varying composition in a spark ion source they obtained large variations in the measured calcium isotopic ratios.

L. F. Herzog (1954), working in this laboratory, found a definite change with time of the measured strontium isotope ratios during evaporation of Sr^+ ions from a SrO tantalum system. Since that time, fractionation during strontium analysis has been observed in this laboratory to a varying degree, often not appearing at all (Herzog in personal communication), and this effect has been verified by other workers (P. Gast, L. T. Aldrich in personal communications (1955)).

A Controlled Fractionation Experiment

Following the first fractionation observation by Herzog, a controlled experiment on a CaO on tantalum system was carried out. An A.E.C. enriched Ca^{48} spike was chosen for the experiment because its comparable contents of Ca^{48} and Ca^{40} allowed examination of the end points of emission. One hundred micrograms of the sample, in carbonate form, were applied to the preoxidized surface of a tantalum filament as uniformly as possible. Ca^{48} and Ca^{40} current peaks were continuously recorded on a Weston strip chart recorder from the time the ion current was large enough to measure, until the sample was exhausted to the extent that measurable ion current could no longer be obtained. Since the Ca^{40} and Ca^{48} ion currents were comparable in in-

tensity, this experiment could be carried out at a filament temperature lower than that maintained in normal calcium runs. Emission thus lasted for a longer period than usual. The sample emitted at a level of about one to 5×10^{-13} amperes for 65 hours over a period of ten days (the filament current was maintained at a level at which calcium vaporization was negligible when work was discontinued at night). During this period a total of 580 peak sets of Ca^{40} and Ca^{48} were recorded and measured.

The results of this experiment are shown in Fig. 10. The measured ratio of $\text{Ca}^{48}/\text{Ca}^{40}$ is plotted against $\int_0^t a' dt$, where $a' = \text{Ca}^{48}$ current and $t =$ time. The abscissa thus represents the fraction of a sample emitted before a measurement was made. Each point represents the average of about ten peak sets. The general spread of the data was mainly due to the fact that in automatic sweeping about eight minutes elapsed between recording of a Ca^{40} peak and an adjacent Ca^{48} peak.

An attempt was made to keep the filament temperature reasonably constant for the first three days of the run. Filament current was raised at intervals after that point, in accordance with the requirements for measurable emission. An estimate of the filament temperature is included in Fig. 10.

The measured $\text{Ca}^{48}/\text{Ca}^{40}$ ratio of the ion stream varied over a 17% range during the run. The variations through the twenty-sixth were initially thought to be caused purely by the mass dependence of the vapor pressure, and a reasonable model based on this assumption and the assumption that the "seat of ionization" was at oxide-core-vacuum interface, was proposed (see Herzog, et al., 1954). It was considered that an extrapolation to zero of the "plateau" of March 24 and 25 in

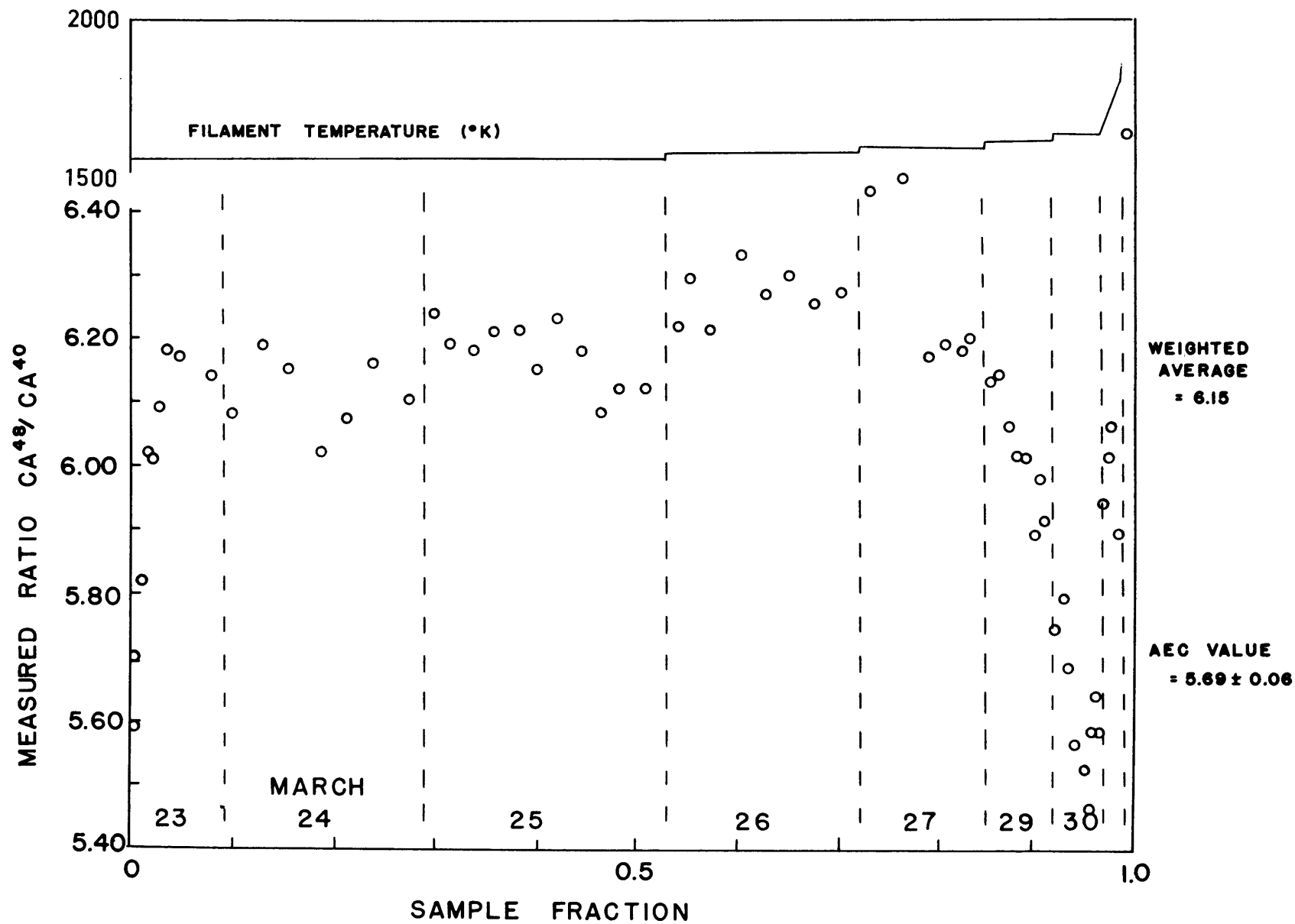


FIG. 10. FRACTIONATION OF CALCIUM IN SOLID SOURCE EMISSION

Fig. 10 would be representative of the true isotopic ratio, and that a calcium analysis procedure might be set up on that basis.

However, subsequent analyses demonstrated that the nature of the fractionation was not entirely reproducible, and a different interpretation was required. In addition, independent indications (see Section 3) that the seat of emission is actually in the bulk oxide or at its surface suggest a somewhat different interpretation. The strange behavior of the ratio beyond March 29 is now believed to be due to re-evaporated calcium.

Later Results on Calcium Fractionation

In the course of calcium analysis a number of different forms of isotopic fractionation have been observed. Some typical examples of the forms of fractionation observed are shown in Fig. 11. Except in the middle portion of the "Bikita I.D. 1" curve, each point represents the average of five or more peak sets. It may be seen that a plateau of varying duration was observed, and in some cases the duration of the "plateau" was too short to be observed, resulting in a continuous variation of the ratio. In a large number of runs no measurable fractionation was apparent, i.e., fractionation effects were less than three percent during the observed emission. In most such runs the $\text{Ca}^{48}/\text{Ca}^{40}$ ratio was not recorded during the first and last ten percent of emission, and the apparent lack of fractionation was probably due to a "plateau" of long duration, as in the case of Fig. 1.

It was predicted on the basis of the earlier model that the relative duration of the plateau would be directly dependent upon the ratio of the size of the oxide-core-vacuum interface to the size of the

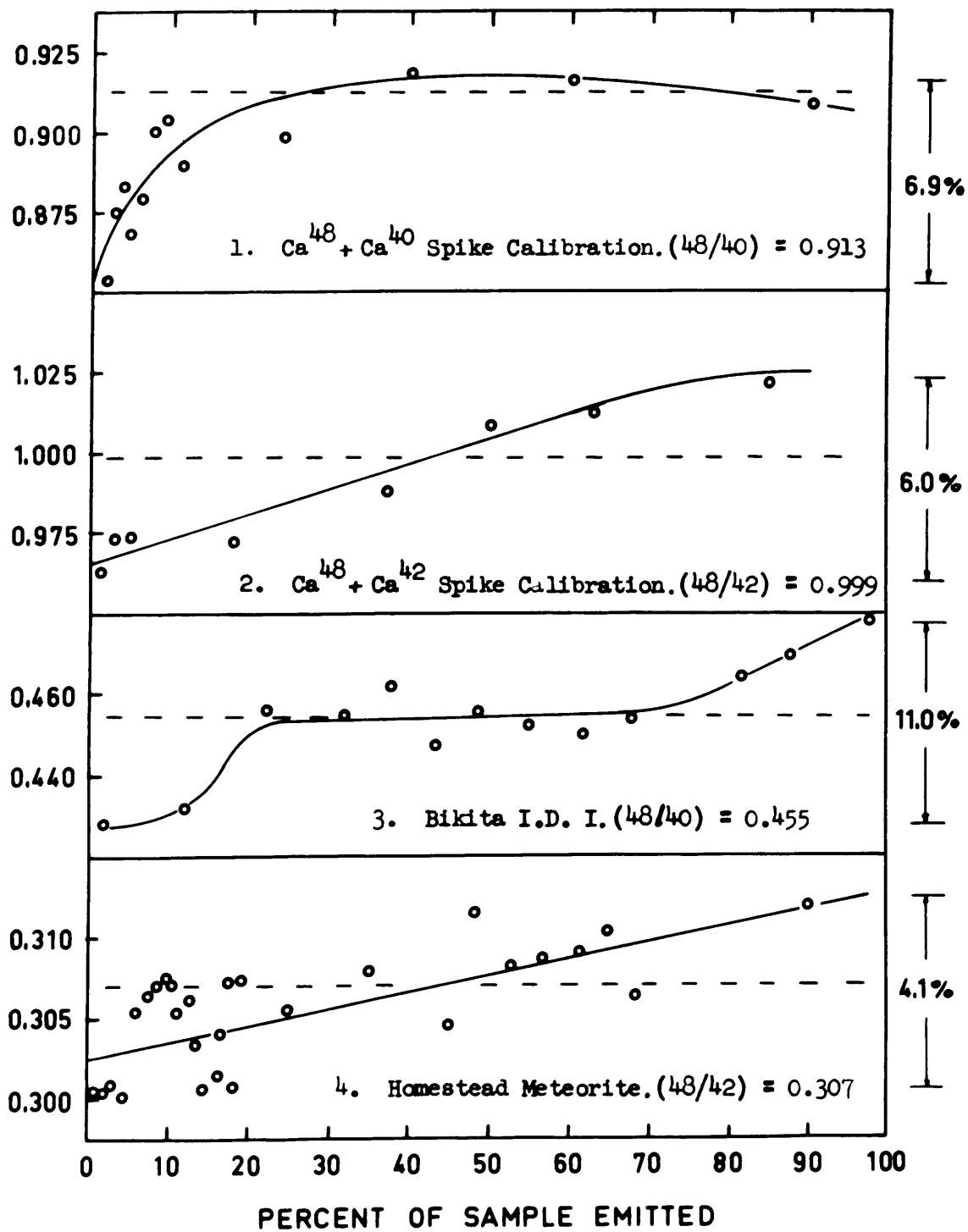


Figure 11. Typical Fractionation Curves for Calcium Analyses.

sample. However, no correlation between sample size or distribution and the relative duration of the plateau was observed.

Relationship between Different Ratios

The fractionation effects were definitely due to mass differences, as was demonstrated by the fact that the extent of fractionation was dependent on the mass difference of the two isotopes. To illustrate this point, typical fractionation curves for three different isotope ratios are shown in Fig. 12. A greater spread of values in these curves is due to the fact that each point represents a single peak set. Filament temperature and Ca^+ ion current as a function of percent of sample emitted are also indicated.

Where a sufficient number of peak sets were available in the runs showing large fractionation effects, groups of ratios taken in the early and late parts of the emission were compared. The percent difference between early and late average isotope ratios was computed and normalized to a ten percent difference for the $(48/40)$ ratio. In Fig. 13 the resulting values are plotted as a function of the square root of mass ratio, e.g., $48/40 = 1.095$. Standard deviations are indicated for each point and are based on the peak to peak precision discussed in Section 6, combined with the number of peak sets used in the determination of each point. The dependence on mass is evident, but the data is not good enough to demonstrate the power of the mass difference upon which fractionation effects depend. It is assumed that they are dependent on the square root of the mass ratio.

Discussion

In the calcium runs in which mass fractionation occurred the measured isotope ratios showed an enrichment in the heavier isotopes

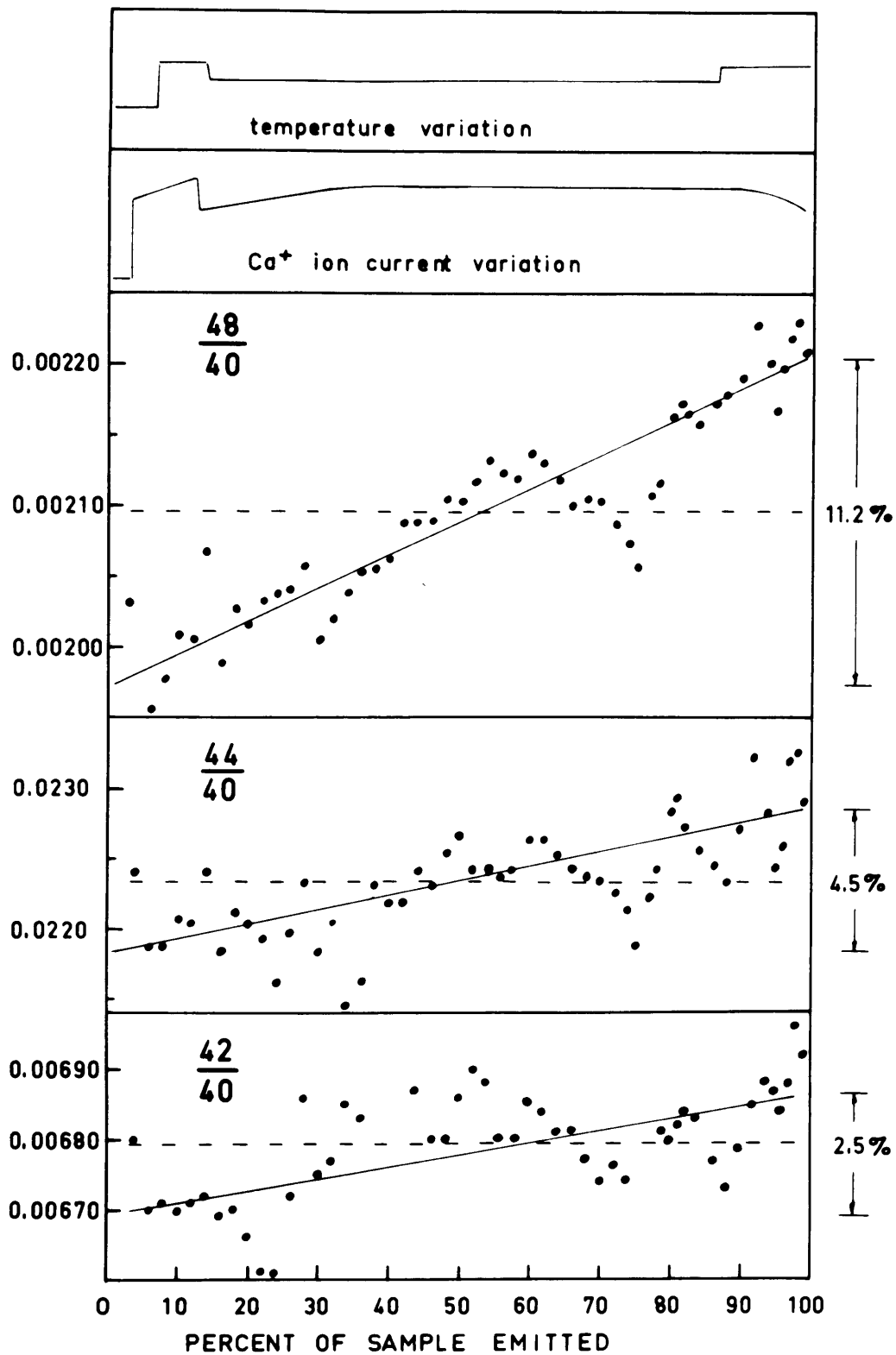


Figure 12. Fractionation Curves for the Different Isotope Ratios. The data are from the fourth calcium standard run. Each point represents an individual determination (peak set).

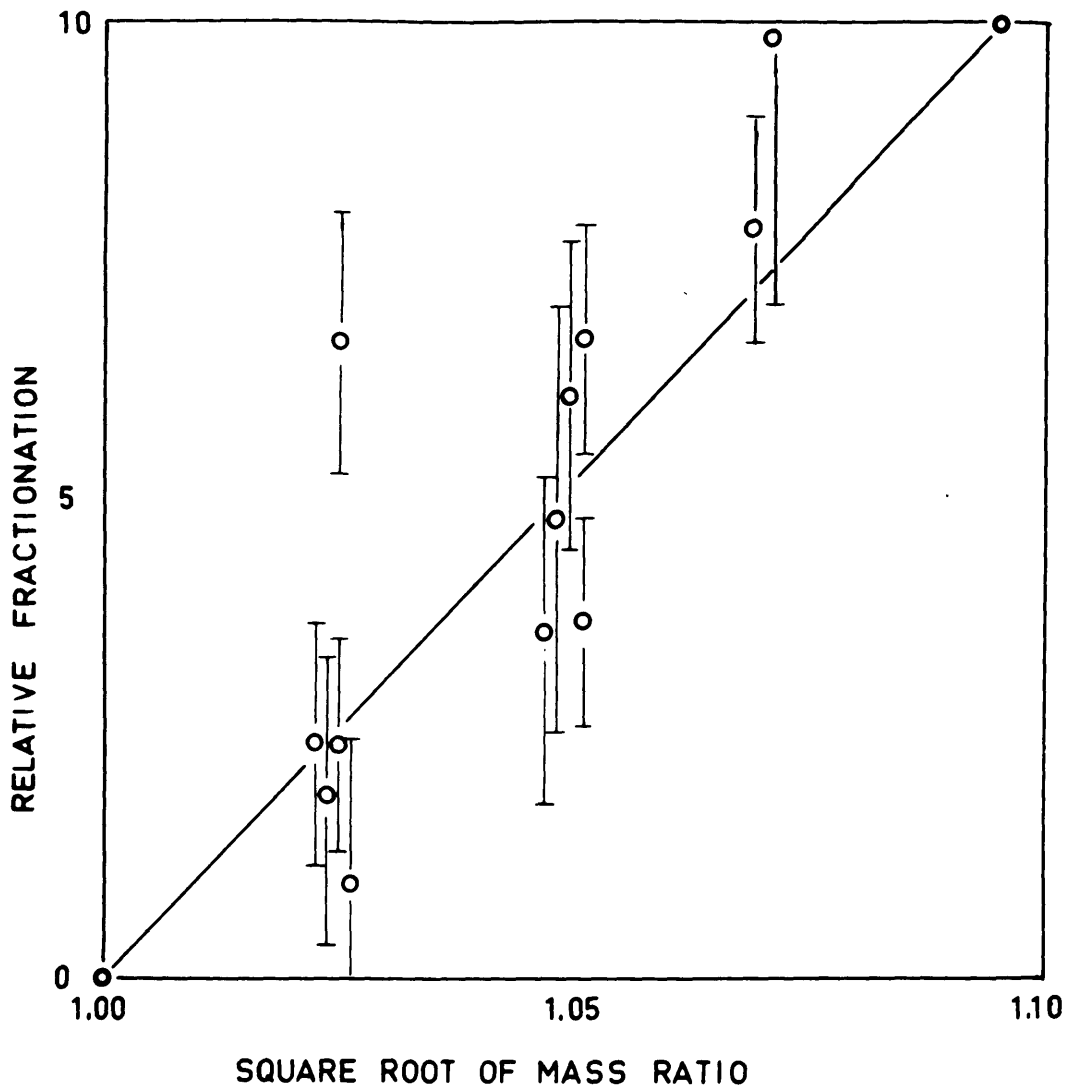


Figure 13. Dependence of Fractionation Effects
On the Square-Root of Mass Ratio.

with time, which varied in form from a sharp increase followed by a plateau with variable end effects, to a continuous enrichment.

The rate of evaporation of an atom or molecule is inversely dependent on the square root of mass. In the case of ideal evaporation from a liquid this dependence would lead to a continuous exponential enrichment of the heavier isotopes with time. In the case of ideal sublimation from a solid without diffusion, one would expect no significant fractionation effects, since complete removal of the successive layers of the solid would occur. The typical sample is about ten to 100 micrograms of calcium, applied to an area of approximately 0.05 cm^2 . Assuming the ionic radii of Ca^{++} and O^{--} to be one angstrom, the thickness of the sample is of the order of:

$$T \sim (2)(10 \text{ to } 100)\left(\frac{10^{-6}}{40}\right)(6 \times 10^{23}) \frac{0.05}{4 \times 10^{-16}} = \underline{2400 - 24,000 \text{ atoms}}$$

The presence of impurities would increase this figure. Thus for ideal sublimation from a solid without diffusion one would expect no fractionation effects, except possibly within less than one percent of the end points of emission. It is doubtful that the fact that the effective surface area of the oxide is somewhat greater than 0.05 cm^2 would affect this conclusion.

Since the sample is generally run at a temperature of about 1600°K , and the melting point of CaO is 2845°K (Handbook of Chemistry & Physics, 33rd Edition), it is definitely believed that the sample is in the solid state during examination. It is doubtful that the presence of traces of impurities can lower the melting point sufficiently to alter this conclusion. Nearly all of the alkali impurities have been removed by the time observation of the calcium is begun.

It is suggested that the fractionation effects are due primarily to the dependence of evaporation rate on mass, and that the emitted ions must have a varying degree of mobility through the CaO lattice, either as atoms or ions, prior to their emission. Whether the source of emitted ions is in the calcium ions located at normal lattice sites, or in interstitial free calcium is not known. It is thought that the degree of mobility of the source atoms or ions may determine the relative duration of the isotope ratio plateau observed in fractionating calcium runs. The solid sample may thus emit like a solid, if the calcium atoms or ions are relatively immobile, or in a manner approaching that of a liquid, if rapid mixing processes are possible.

The relative mobility, in turn, may be determined by the presence of impurities, the exact "activation" history of the oxide, spatial relationships of the filament and oxide, chemical properties of the core, and characteristics of the interface compounds. The difficulties in controlling such factors are apparent in the large number of apparently conflicting results which have been published on oxide-coated cathodes. The non-reproducibility of these factors may thus account for the variations observed in the form of the calcium fractionation curves.

Effect of Fractionation on Isotope Analysis

Since efforts to develop a non-fractionating sensitive ion-production method were unsuccessful, the reproducibility of the emission-weighted average of fractionating sources was examined and found to be satisfactory. It is significant that such an average actually nearly represents the true isotope abundances of the calcium originally deposited. This aspect is discussed in Sections 6 and 7.

5. THE COLLECTION AND MEASUREMENT OF POSITIVE ION CURRENTS

There are a number of different schemes for measuring positive ion currents in isotope abundance determinations. Sensitivity, dependability, and convenience are the requirements for any such system, though great sensitivity is not required when working with the alkalis. Because of the sensitivity problem involved in working with very small calcium samples, however, sensitivity became the primary requirement for the measurement system in this work. In this chapter, the methods employed in this research and the reasons for their choice will be discussed.

Multiple Collection versus Single Collection

There are two fundamentally different methods employed in abundance determinations; single collection, in which the different isotope currents are scanned, measured and compared, and multiple collection, in which the ratios between isotopes or groups of isotopes are directly obtained by an electrical null method.

In a dual collection system (Nier, 1947) small fluctuations in the ion current do not affect the results, since the different ion beams are compared simultaneously. This method is more convenient than single collection because less operator time is required for a given precision. Dual collection was rejected in this work because 1) it is, in practice, less sensitive than single collection; 2) potassium ion currents, which fluctuate considerably and independently of calcium ion currents, are extremely difficult to eliminate; 3) many difficulties were encountered in an unsuccessful attempt to use dual collection for strontium measure-

ments (Herzog, 1954) for which it is much more suitable; 4) because of the wide mass spread of the calcium isotopes, design of a dual collector involves a number of difficulties.

Multiple collection (Hunter, et al., 1949), in which a separate receptacle is used for each isotope, eliminates only the second objection above, and also introduces mass discrimination (Barnard, 1954), so it too was rejected.

Despite its greater inconvenience and time consumption, single collection eliminates all of the difficulties mentioned above, so this method of collection was employed in this work. A single defining slit is used, and as the magnet current varies linearly with time, the different isotopically pure ion beams pass through the slit. Since the currents corresponding to different isotopes are measured at different times, and the ion emission is not strictly constant over time (generally the ion current is either increasing or decreasing in a manner approximating linearity during a single scan) a single scan gives a slightly distorted isotopic ratio. If the scan is repeated a number of times, however, such variations are statistically neutralized and the true ratio may be determined.

Design of the Single Collector

A slightly altered Nier type double collector (Nier, 1947) which was in use as a single collector for strontium measurements, was employed in the early calcium work (see Herzog, 1952, 1954). This collector had several disadvantages for calcium work:

- 1) Its sensitivity was limited by the use of lavite insulation, and by an unintentional spring mounting of the final collector element which caused a seismic response;

2) A transient capacitative response was obtained when a peak left the second collector element, causing odd secondary peaks and other effect (see Fig. 15);

3) It was permanently set up for use of a D.C. feedback amplifier and conversion to vibrating reed electrometer amplification was desired. A single collector for calcium measurements was therefore designed and built.

The collector is shown diagrammatically in Fig. 14a. The outer tantalum cover box serves as a shield to prevent all ions except those of a particular mass from reaching the collection system, as a ground shield, and also as the attachment mechanism. Its base is screwed into a circular ring attached to the flange, and the circular shield box holds the collector parts in a stable position through four-point contact. Small phosphor bronze springs are used to eliminate strain on the fused silica spacers, which also serve as insulators. Plate (2) contains the defining slit. Plate (3) is the "electron repeller" plate and is held at -90 volts relative to ground. Due to the geometric design the escape of secondary electrons from the final collection unit (4) is negligible. An electron repeller plate is still necessary in order to keep secondary electrons produced at the edges of the defining slit from hitting the final collection unit. An example of peaks obtained with the electron repeller and without is shown in Fig. 15. The troughs on both sides of the latter peaks are due to the electrons produced at the slit edges. The final collection unit is designed to prevent the escape of secondary electrons and reflected positive ions. The Faraday cup is a common device to reduce the angle of access for escaping particles. The sloping collection plate (Inghram and Hayden,

1954) tends to cause reflected ions and electrons to bounce into the trap on the left hand side of the collection box. The final collection unit is connected to a 10^{11} ohm Victoreen resistor which is across the input to a vibrating reed electrometer.

A rough sketch of some typical ion beams in relation to the collection system is given in Fig. 14b. This sketch is based on an experimental determination of the ion beam width at the defining slit, which gave a result of 0.006 inches. The source collimating slits used with this collector in the examples given were two 0.008 inch slits which were separated by 0.4 inches.

This collector unit has given consistently good results, with no vibration response, and no measurable noise contribution.

Measurement of Small Currents

In the early part of this work a Nier-type (Nier, 1947) D.C. feedback amplifier was used. Sensitivity problems in Ca^+ ion production, however, made a change to a more sensitive amplifier desirable. An electron multiplier was briefly considered, but due to the numerous mass discrimination problems involved (Ingrahm and Hayden, 1954), an increase achieved in ionization efficiency, and immediate availability, an Applied Physics Corporation Model 30 vibrating reed electrometer was chosen. This unit showed a six-fold sensitivity advantage relative to the D.C. amplifier. It also had the definite advantage of long period stability of the zero point. The major disadvantage of this unit was a one second time constant. Since more than 99% of maximum current was maintained for about eight to ten seconds, however, the time constant caused no trouble. Faster instruments are available. The sensitivity limit (signal which is ten times the noise) for this set-up

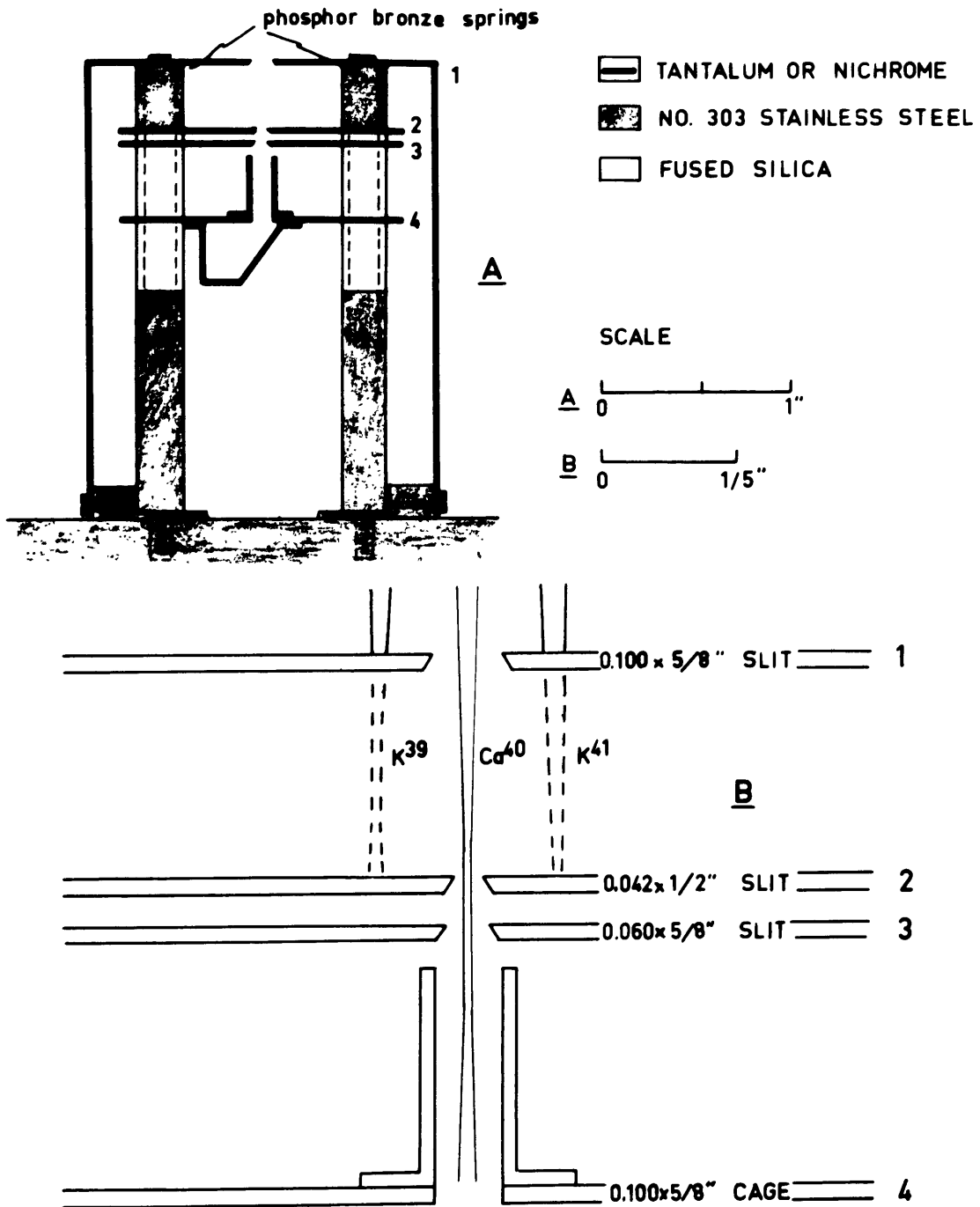


FIGURE 14. SINGLE COLLECTOR UNIT

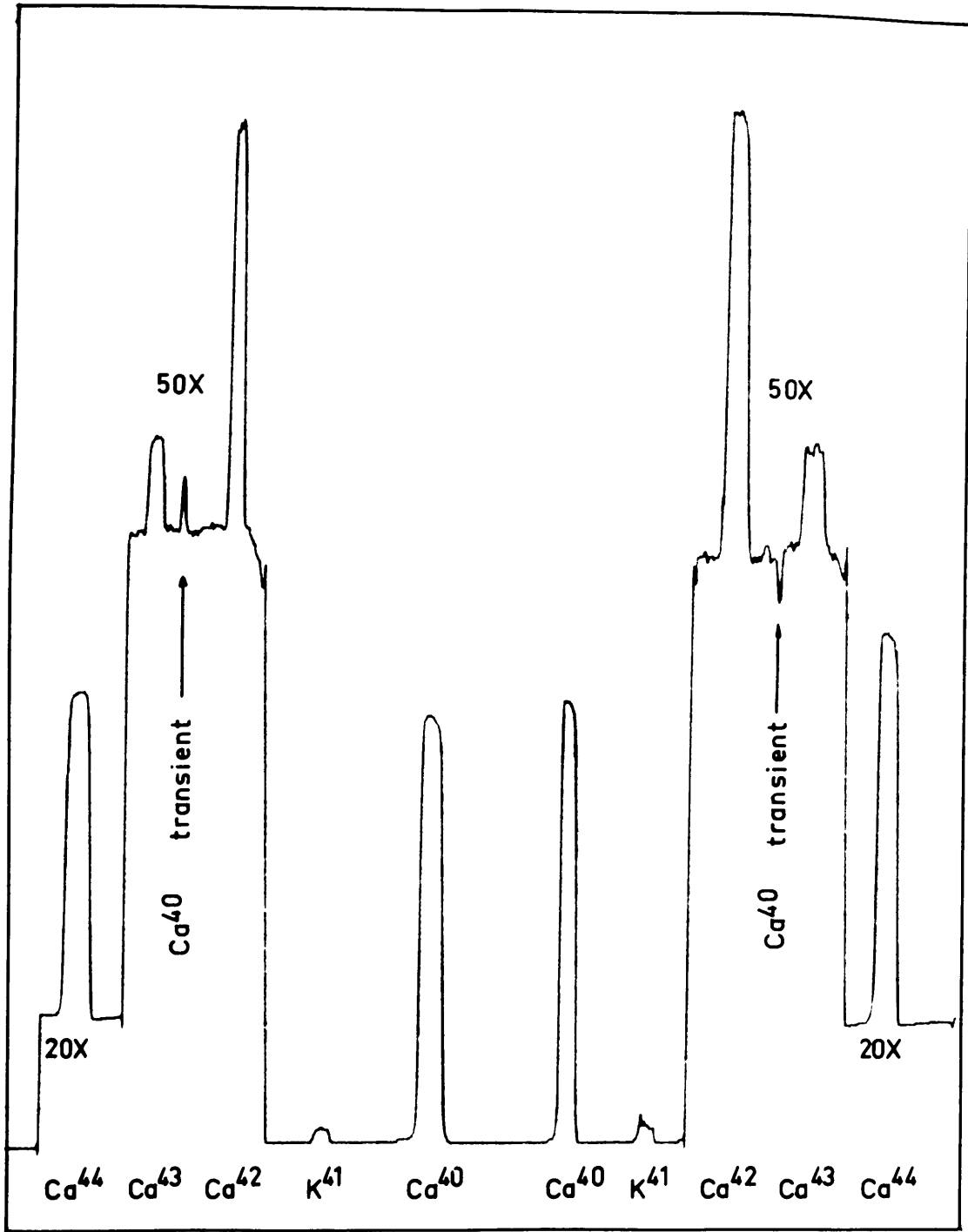


FIG. 15A. PERFORMANCE OF EARLY COLLECTION SYSTEM (Ca^{48} spike)

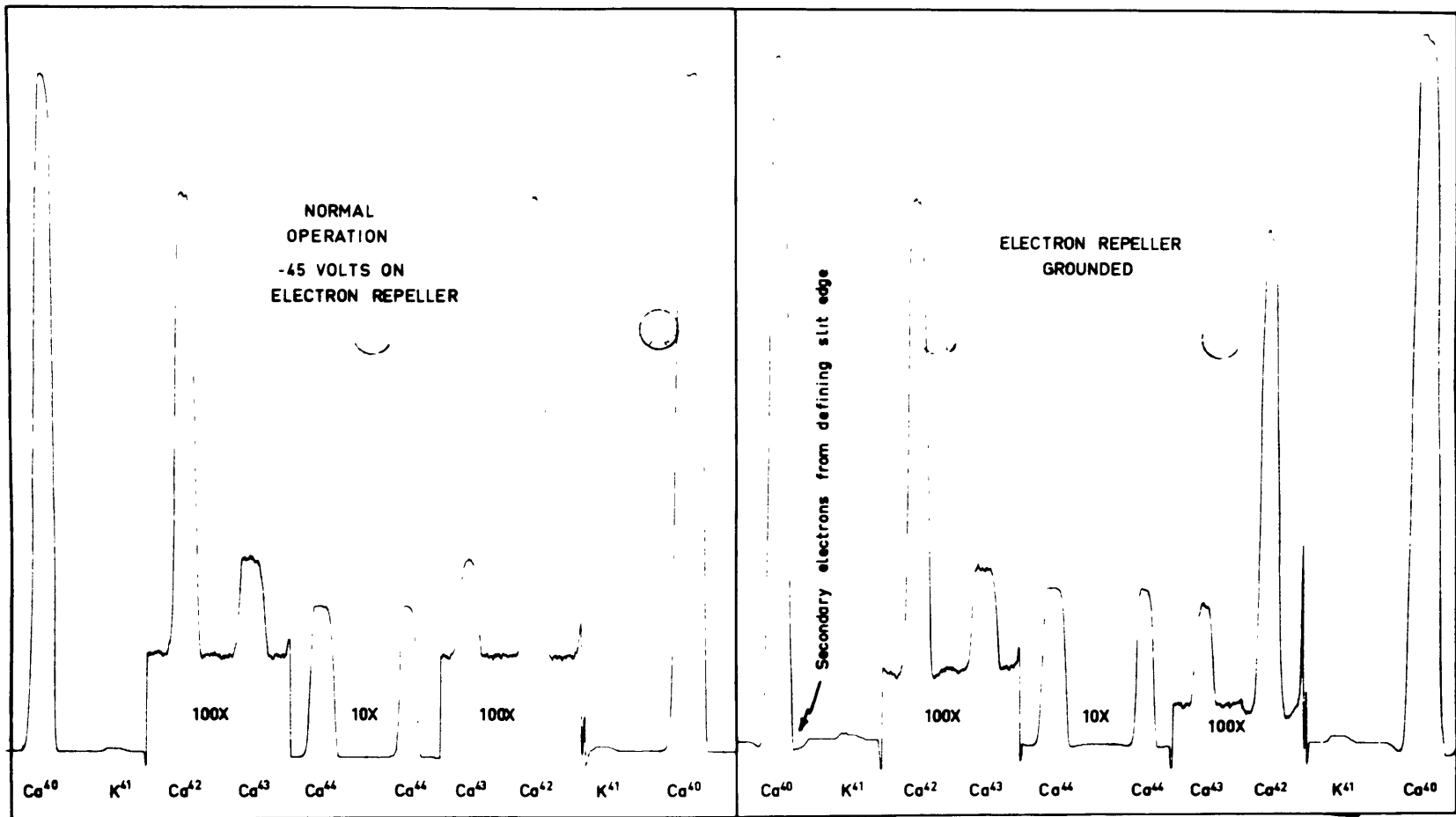


Fig. 15B. Homestead Meteorite Calcium- Typical peak sets (left) -size reduced.

is about 0.3×10^{-15} amperes. The theory of the vibrating reed electrometer is discussed by Palevsky, et al. (1947).

Because of the large differences in abundances of the different calcium isotopes, scale changing was employed (i.e., the output of the amplifier was put across one of a set of different resistors). Appropriate calibrations and corrections for the true resistor ratios were made primarily on the D.C. amplifier. Samples which were measured on both collection systems gave results which were identical to within one percent.

6. OPERATIONAL PROCEDURES

The standard procedures followed in a calcium run are described in this section. These procedures were not always followed in the early work but were ultimately found to be most successful in producing a stable intense ion beam.

Nature of the Sample

The preparation of the sample and filament are discussed in Section 2 and Part II, Section 1.

Application of the Sample

In earlier techniques of sample application, considerable trouble was experienced with the solutions erratically spreading out and adhering to the filament posts. For that reason the highly satisfactory method which was finally developed is discussed in detail below.

The sample is taken up in a clean section of small diameter pyrex tubing with a constricted tip. The tubing is attached to a small syringe mounted above the source assembly, which has the attached filament exposed. The constricted tip of the glass tubing is moved to a position about a millimeter above the center of the filament, and a drop of the solution is extended. The drop is confined to the center of the filament by the presence of the glass tip, and the relative spreading of the sample over the filament may be closely controlled by varying the size of the drop. A current is passed through the filament, and as the water evaporates, additional solution is added to the drop. When the solution is exhausted from the sample tube, the filament temperature is lowered and the sample is allowed to dry rather slowly. By this method a sample may be quickly and easily applied to the filament.

Conditioning the Sample

The mass spectrometer vacuum system must be opened up in the process of sample changing. When this is done, helium is streamed through the system. After the source is reattached to the mass spectrometer, the filament is heated to about 800°K for about five minutes in a helium atmosphere, in order to remove water and thoroughly bind the sample to the filament. The filament current is turned off and the mass spectrometer evacuated. When a vacuum of the order of 10^{-4} mm of mercury is reached, the filament current is slowly raised until a temperature of about 900 to 1000°K is reached and is left at this temperature overnight (resulting in the removal of most of the alkalis). The mass spectrometer tube is also baked out for a period of several hours overnight. The accelerating voltage is then slowly raised to about 1600°K, the normal operating temperature for calcium observation. During this process the last stages of alkali removal are completed.

Isotope Ratio Observation

The source voltages are then adjusted to optimum focus, the collected calcium ion current adjusted (by means of filament current) to a level of about 7×10^{-11} amperes, and automatic magnetic sweeping is begun, recording intensities of the calcium isotopes from Ca^{40} to Ca^{48} . Occasionally, if the sample was particularly small or precious, measurements of Ca^{40} , Ca^{42} , and Ca^{44} were taken at a lower temperature before the temperature was raised to the normal operating level. Continuous observation of the isotope ratios was maintained until the sample was completely depleted. The calcium ion current was the largest ion current present during measurement, generally at least by a factor of

ten. Small alkali ion currents due to re-evaporation effects persisted throughout observation.

By observing peak shape, filament temperature, and focusing properties during emission, care must be taken to exclude low temperature calcium emission and re-evaporated calcium from the final data.

Data Handling

The record consisted of a series of peaks corresponding to the various isotopes of calcium. In order to cancel out linear variations with time of the ion current, similar peaks from adjacent sweeps were averaged and recorded. Assuming a smooth linear variation of ion current, this averaging process gives the relative intensities of the different isotope currents at effectively the same time.

In the final process of averaging the calculated ratios, isotope ratios were weighted according to ion current intensity; that is, more weight was given to ratios which were obtained from higher calcium ion current. Since ion currents were varying most rapidly at the beginning and end of emission, the first and last ten to fifteen percent of emission was rejected from the average. The relationship between the emission-weighted average thus obtained and the fractionation curves may be seen in Section 4.

This method of obtaining an average was necessitated by the lack of a plateau on many runs, and the desire for a standardized method of obtaining an answer. Its validity is dependent in part on a homogeneous isotope distribution in the activated sample, and upon the maintenance of a constant ionization efficiency throughout the run. The

fact that these conditions were not upheld is reflected in the fact that the degree of reproducibility (about $\pm 1\%$) obtained is not as good as that possible on the basis of "peak-to-peak" precision (± 0.1 to 0.2%).

Cleaning the Filament

After exhaustion of the sample the filament was maintained at about $2000-2200^{\circ}\text{K}$ for an hour to flash off all traces of impurities in preparation for another sample.

7. THE SENSITIVITY, PRECISION, AND ABSOLUTE ACCURACY OF ISOTOPE ABUNDANCE MEASUREMENTS

Sensitivity

The following statements are based on observations of fractionation effects, peak-to-peak reproducibility, measured ionization and collection efficiencies, and related data which is discussed elsewhere. In order to obtain calcium isotopic ratios including those involving Ca^{43} and Ca^{48} with a precision of the order of one percent, using the method outlined in the previous sections, it is a minimum requirement to obtain a current of 5×10^{-12} amperes for a period of one hour. Since overall sensitivity is 0.02 coulombs per gram, a minimum sample of one microgram of calcium is required for complete isotopic analysis. For a radiogenic Ca^{40} analysis using Ca^{42} spike a minimum of 0.1 μg of calcium is required, and for a pure isotope dilution analysis for total common calcium content 0.01 micrograms are required.

Due to some variability in the ionization efficiency for Ca, for consistent success all of these figures should be increased by a factor of ten. The sensitivity might be increased by the use of an electron multiplier, but it is doubtful that there will be any investigations requiring a greater sensitivity.

Possible Sources of Error - Discrimination Effects

If the ion current is space-charge limited at the ion source, mass discrimination occurs (Bainbridge, 1931). Also, mass discrimination effects may be introduced by the geometry of the source. Data, such as that presented in Fig. 6, suggest that due to the roughness of the oxide surface local small-scale space-charge effects might be ex-

pected. In order to roughly check this possibility, Ca^{40} and Ca^{48} ion currents were varied by altering the electrostatic drawing-out field and the deflecting voltage. The relative variations in Ca^{40} and Ca^{48} current at relative stages of poor focusing were determined. The ion currents were varied by a factor of four, but the relative variations of Ca^{40} and Ca^{48} corresponded throughout to within $\pm 0.2\%$. Thus it appears that space-charge and focusing effects in the source do **not** introduce significant mass discrimination. It is also evident that it is not necessary to maintain optimum focus for accurate abundance determinations, and that none of the fractionation effects can be attributed to focusing variations.

Becker and Walcher (1953) have calculated and experimentally verified that mass discrimination errors are introduced in the process of analyzing the ion beam if currents greater than 10^{-9} amperes are used. In normal operation the total ion current was of the order of 5×10^{-12} amperes, while in the most extreme case (determination of Ca^{46} abundance in the Homestead meteorite) the current was 2.5×10^{-10} amperes. The results have thus not been influenced by this effect.

It is believed that most of the measured mass discrimination and the limit of reproducibility are related to isotope fractionation effects and the non-reproducibility of the form thereof. A somewhat variable increase with time in the effective ionization efficiency would account for many of the observations. It is suggested that such a phenomenon is the limiting factor in precision in solid source isotope abundance studies of other elements, such as strontium. It is further suggested that the use of a less complex type of primary ion source, such as the double filament source mentioned in Section 2, might provide an increase in precision in solid source isotopic abundance studies.

Possible Sources of Error - Contamination Tests

The possibility of contamination of the measured ratios by calcium originally in the clean filaments was checked. For a new, clean platinum-plated filament the maximum observed current at mass 40 was 1×10^{-14} amperes, and this current decreased by a factor of five in about three minutes. This should be compared with a normal operating Ca^+ ion current of 5×10^{-12} amperes. Similar results were obtained in the case of a clean tantalum filament. However, in both cases excessive and persistent alkali currents of the order of 10^{-12} amperes were obtained. Therefore, new filaments could not be used for alkali determinations. Instead, used filaments which had been flashed and mass spectrometrically checked were employed in all alkali determinations.

The possibility of contamination during the conversion to nitrate and subsequent sample handling and loading was effectively checked by the $\text{Ca}^{42} + \text{Ca}^{48}$ run discussed later in this section, and was demonstrated to be less than 0.1 micrograms and thus completely insignificant.

Precision and Reproducibility

In stating errors for mass spectrometric abundance determinations, three entirely different parameters are often referred to without clarification. These are: 1) the peak-to-peak precision of a single mass spectrometric determination, often divided by the square root of the number of peak sets or individual null determinations made during the run to give an estimate of the standard deviation of the mean; 2) the sample-to-sample precision, obtained by making a number of entirely separate abundance determinations on the same sample; 3) the absolute error, or the probable difference between the true value and the measured value expressed as a standard deviation. This parameter may be estimated by the experimenter or may be determined experimentally.

The peak-to-peak precision is primarily an expression of the regularity of the ion current, and is of the order of one percent standard deviation for calcium and potassium determinations. Since about fifty or more peak sets are generally taken during either type of run, the computed standard deviation of the mean is generally of the order of ± 0.1 to 0.2 percent, and is thus generally entirely unrelated to the actual sample-to-sample precision.

In the case of calcium, fractionation effects increase the apparent peak-to-peak error if the variations are incorrectly regarded as random. The spread of measured ratios in a calcium run in which appreciable fractionation did not occur is shown in Fig. 16, for the Brown Derby No. 503 isotope dilution run. Ratios involving Ca^{43} and Ca^{48} show a slightly larger spread because they are the smallest peaks measured.

In contrast, the spread of measured values in a calcium standard run in which appreciable fractionation occurred is shown in Fig. 17, and the standard deviations based on the assumption that the variations are random are given. The largest spread occurs in the (48/40) ratio, which exhibited the greatest fractionation. If fractionation effects were entirely reproducible, the limiting error would be less than the stated average deviation of the mean (0.5%), which is not the case.

In order to estimate the sample-to-sample precision, which is the most important parameter in the determination of the absolute error in the radiogenic calcium determinations, a number of entirely separate isotope determinations were carried out on the standard calcium. A few early runs, in which the entire emission was not observed, were rejected and are discussed in Appendix II. It is apparent that poor results would be obtained if only a part of the fractionating emission is observed, and for this

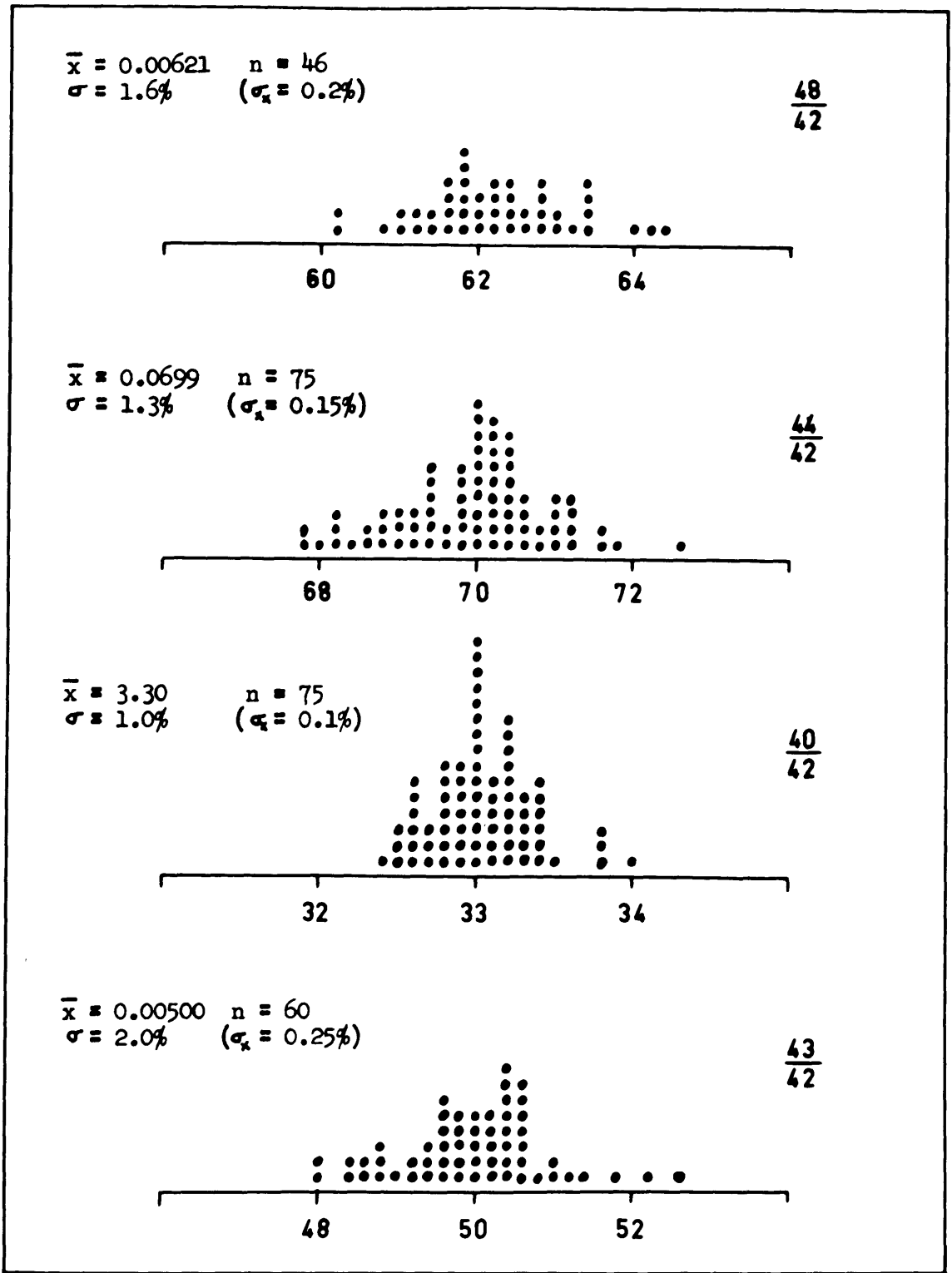


Figure 16. Variations in Measured Isotope Ratios in a "Non-fractionating" Calcium Run. The data are from the Brown Derby #503 Isotope Dilution Run. Each point represents an individual determination (peak set) of an isotope ratio.

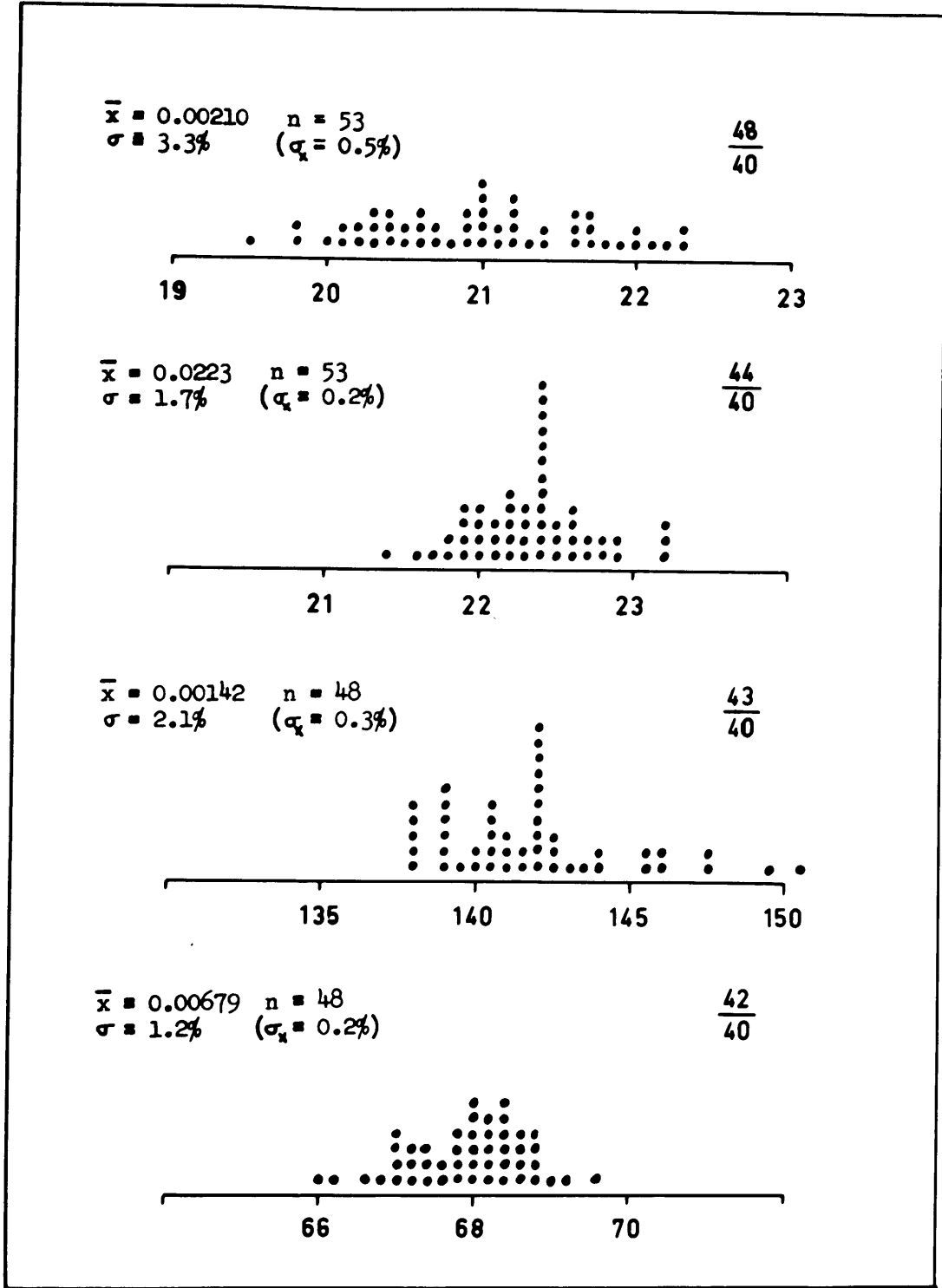


Figure 17. Variations in Measured Isotope Ratios in a Fractionating Calcium Run. The data are from the fourth calcium standard determination. Each point represents an individual determination (peak set) of an isotope ratio. Standard deviations were computed on the basis of the incorrect assumption that the variations were random.

reason the calcium samples must be run to completion. The results on common calcium are given in Part IV, and indicate a precision of about $\pm 1\%$. Data obtained in isotope dilution runs may also be used for an estimate of precision, and are consistent with the above estimate.

CALIBRATION OF SPIKES AND SPIKE SOLUTIONS AND THE ABSOLUTE
ACCURACY OF MASS SPECTROMETER MEASUREMENTS

Two calcium "spikes," enriched in the comparatively rare isotopes Ca^{48} and Ca^{42} were obtained from the Atomic Energy Commission (see Keim, 1953). This section is concerned with measurements made on these stable isotope tracers, and implications concerning the absolute accuracy of the method of measuring Ca isotope abundances which has been outlined in previous sections.

Isotope Composition of the Calcium Spikes

Table 4 shows the isotope abundances of the two spikes and of "normal" calcium as measured by the A.E.C. and at M.I.T. There are definite disagreements between the measurements made at M.I.T. and those made by the A.E.C.

TABLE 4. Isotope Composition of Spikes and Common Calcium

<u>Atom Percentage</u>	<u>40</u>	<u>42</u>	<u>43</u>	<u>44</u>	<u>48</u>	<u>A.W.</u>
Common* M.I.T. avg.	96.84	0.658	0.1385	2.155	0.2036	40.12
Ca^{42} * M.I.T.	17.64	81.75	0.0793	0.5023	0.0245	41.66
Ca^{42} A.E.C.	16.92	82.52	0.081	0.457	0.022
Ca^{48} M.I.T. I	13.8	85.5
Ca^{48} * M.I.T. II	14.55	0.1597	0.0349	0.6154	84.75	46.79
Ca^{48} A.E.C. I	14.82	0.155	0.129	0.625	84.28
Ca^{48} A.E.C. II	22.90	0.20	0.04	0.74	76.12

*Values used in isotope dilution computations.

If in the case of Ca^{42} spike it is assumed that there is a slight contamination of the M.I.T. sample relative to the A.E.C. sample, the following

results are obtained. The amount of normal calcium contamination is expressed in micrograms per milliliter of the M.I.T. solution as calculated from the various ratios:

$$\frac{40}{42} + 0.18, \quad \frac{43}{42} - 0.14, \quad \frac{44}{42} + 0.46, \quad \frac{48}{42} + 0.26.$$

The results for different ratios vary considerably, but taking the average, we obtain a contamination of +0.19 g/ml, which is certainly conceivable. The difference does not appear to be due to isotope fractionation.

The differences between the various measurements on the Ca⁴⁸ spike can be accounted for in the following manner:

1) The A.E.C. measurements are different from M.I.T. measurements due to a relative mass discrimination, the M.I.T. measurements being relatively enriched in the heavier isotopes.

2) The second M.I.T. measurement was contaminated in the process of preparation of the spike solution by less than 0.5 μ g/ml (the first measurement was made on the sample as obtained from the A.E.C. and was primarily designed as a study of calcium isotope fractionation during measurement).

3) The second A.E.C. sample was contaminated by about 0.106 atoms of Nier common calcium to one atom of A.E.C. I spike. If this is assumed, the abundances for A.E.C. II agree with the A.E.C. I measurements to within the stated errors.

4) The A.E.C. I, Ca⁴³ measurement may have been a typographical error, since it is in disagreement with all other measurements.

Solutions of Spikes and Common Calcium Standard Solutions

For isotope dilution work, very dilute solutions of the spikes are necessary, and their concentrations must be accurately known. It is difficult to weigh out accurately the small quantities used (10 to 20 mg) on the scales used throughout this work. For this reason, and as a rough check on the fractionation of the mass spectrometer measurements, standard solutions of common calcium were made up for calibration purposes. The weights of the solutions are given in Table 5.

The errors quoted are only based on rough estimates of the accuracy of the scales and on the relative care taken in the weighings. The standard I and the two spike weight errors may be too optimistic.

Isotope Dilution Measurements

Table 6 gives the results of the three isotope dilution (see Part II) experiments performed, including the mixtures prepared, the isotope ratios obtained, the computed result for each ratio, and the average, which is taken as the final result. In the case of all ratios involving Ca^{43} in the Ca^{48} spike, the results are in sharp disagreement with other results. This is not true, however, for the Ca^{43} in Ca^{42} spike. It is therefore concluded that the Ca^{43} abundance measurement in Ca^{48} spike was erroneous, and those results have not been included in the average.

Consider the concentration ratios in the last column of Table 6. If common calcium were present as a slight contaminant, it would not alter the value obtained (1.083) from the (48/42) ratio, but would decrease all other values obtained from ratios involving Ca^{48} , and increase all values obtained from ratios involving Ca^{42} . It may be safely said that to within one percent no such effect is present, and therefore that less than 0.1 micrograms of contamination calcium were introduced.

TABLE 5. Weighing of Standard and Spike Solutions

<u>Solution</u>	<u>Sub- stance</u>	<u>Percent Impurity (maker's estimate)</u>	<u>Weight (mg)</u>	<u>Effective Volume (ml)</u>	<u>CaCO₃ Concentration I Impurities ($\mu\text{g/ml}$)</u>	<u>Multiple Gravimetric Factor*</u>	<u>Ca Concentration ($\mu\text{g/ml}$)</u>
Ca.Std. I	CaCO ₃	0.5	55.9 ± 0.9	500	114	0.3987	45.5 ± 0.7
Ca.Std. II	CaCO ₃	0.5	636.4 ± 2.0	12500	50.9	0.3987	20.30 ± .10
Ca ⁴⁸ Spike	CaCO ₃	0.2	21.8 ± 0.3	150	145	0.4369	63.5 ± 0.9
Ca ⁴² Spike	CaCO ₃	0	12.8 ± 0.2	250	51.2	0.4097	20.98 ± 0.40

* Includes compensation for impurities.

TABLE 6. Measured Isotope Ratios and Computed Concentrations of Spike Solutions

3.00 ml. Ca ⁴² Solution + 3.00 ml. Ca Std.Soln. II		1.00 ml. Ca ⁴⁸ Solution + 1.00 ml. Ca Std.Soln. I		1.00 ml. Ca ⁴⁸ Solution +3.00 ml. Ca ⁴² Soln.	
Ratio	Concentration ($\mu\text{g}/\text{ml}$)	Ratio	Concentration ($\mu\text{g}/\text{ml}$)	Ratio	Concentration Ca ⁴⁸ (3)Concentration Ca ⁴²
$\frac{40}{42}$ 1.411	20.69 \pm 1%	$\frac{40}{48}$ 1.095	65.08 \pm 1%	$\frac{40}{48}$ 0.3864	1.087 \pm 1%
$\frac{43}{42}$ 0.00267	20.73 \pm 1.4%	$\frac{42}{48}$ 0.00807	64.68 \pm 1.4%	$\frac{43}{48}$ 0.001283	(1.201)
$\frac{44}{42}$ 0.03313	20.39 \pm 1.4%	$\frac{43}{48}$ (0.00162)	(61)	$\frac{44}{48}$ 0.01338	1.086 \pm 1%
$\frac{48}{42}$ 0.002886	20.12 \pm 1.4%	$\frac{44}{48}$ 0.02788	65.36 \pm 1.4%	$\frac{40}{42}$ 0.3861	1.078 \pm 1%
				$\frac{43}{42}$ 0.04282	(0.824)
				$\frac{44}{42}$ 0.1337	1.081 \pm 1%
				$\frac{48}{42}$ 0.999	1.083 \pm 1%
Average (Weighing error in- cluded)	20.52 \pm 0.20		65.04 \pm 1.0		1.083 \pm 0.009

The isotope dilution results are compared in Table 7 with the results of weighing. All of the discrepancies are of the order of two percent, which is reasonable when one considers the weighing errors involved.

TABLE 7. Comparison of Results

	<u>Ca⁴⁸ Spike</u>	<u>Ca⁴² Spike</u>
Concentration by weighing	63.5 ± 0.9	21.0 ± 0.4
Concentration by I.D.	65.0 ± 1.0	20.5 ± 0.2
Difference	+1.5 ± 1.4	-0.5 ± 0.5
Percentage Difference	+2.3 ± 2.2	-2.4 ± 2.4
	<u>⁴⁸Spike Concentration/⁴²Spike Concentration</u>	
Ratio from Sep. I.D.	1.057 ± 0.019	
Ratio from M.S. Run	1.083 ± 0.009	
Difference	+0.026 ± 0.021	
Percentage Difference	+2.4 ± 1.8	

Accuracy of Mass Spectrometer Measurements

Although the calcium isotope measurements have a reproducibility of about one percent, there was some reason to believe that the final values may all have been somewhat enriched in the heavier isotopes to a constant degree. The reasons for this suspicion were 1) the apparent increase of ionization efficiency during a run, and 2) disagreement with other workers in that direction.

The results of these calibration runs were recomputed after fractionating all isotope ratios involved, on the supposition that if the agreement could thus be improved, discrimination would definitely be indicated, and could be corrected for.

The assumed mass discrimination was based roughly on the differences of the square roots of the atomic weight ratios. Thus for a 10% increase in the $^{48}/^{40}$ ratio, the other ratios would be increased as follows:

$$\frac{^{44}}{^{40}} \quad 6.0\%, \quad \frac{^{43}}{^{40}} \quad 4.1\%, \quad \frac{^{42}}{^{40}} \quad 2.8\%$$

The results of these computations are depicted in Fig. 18. The abscissa represents the percentage difference between the spike solution concentration as measured by weighing and by isotope dilution, i.e., the values in the last row of Table 7. The ordinate represents the percentage fractionation applied to the $^{48}/^{40}$ ratio. The dotted lines represent an approximation of one standard deviation.

The $Ca^{42} + Ca^{48}$ run disagreement is apparently independent of such an effect. The error represented, of the order of two percent, therefore must be attributed to weighing errors and random mass spectrometric errors involved in the numerous measurements giving this value. The Ca^{42} run indicates an actual measurement discrimination of $-11\% \pm 1\%$, while the Ca^{48} run indicates $+3\% \pm 3\%$. The average of these is $+2\% \pm 3\%$. Thus a small positive mass discrimination is indicated, as was suspected. The poor definition and the magnitude of this value, combined with the considerations in the next paragraph, make it appropriate to assume zero fractionation for all isotope dilution runs.

Effect of Fractionation on Isotope Dilution Determinations
in Ca^{40} Age Determinations

Isotope dilution methods have been employed (see Part II) to determine radiogenic Ca^{40} present in lepidolites. This method basically is dependent upon the comparison of the different results obtained when com-

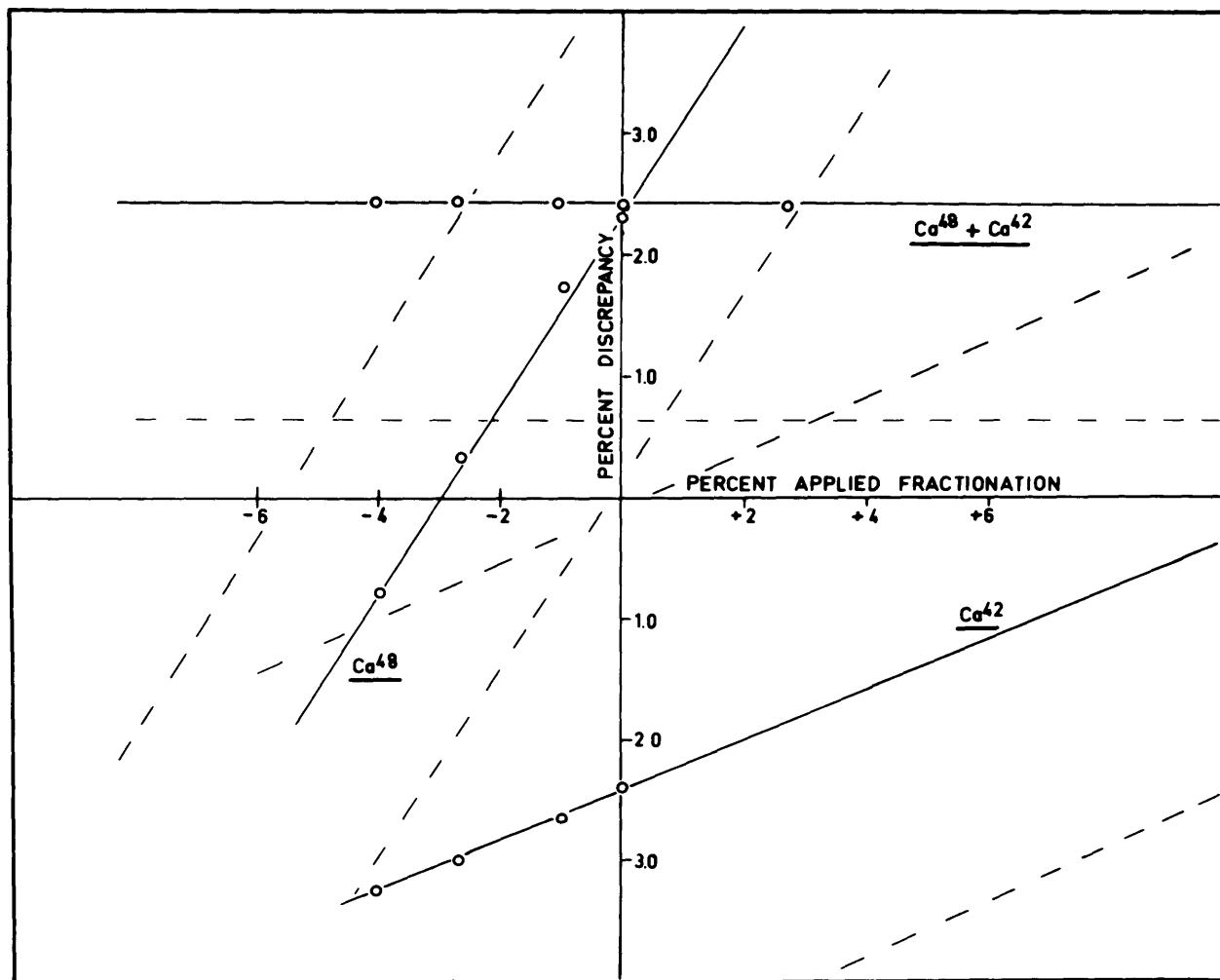


Figure 18. Discrepancy between values of tracer solution concentrations obtained by direct weighing and values obtained by mass spectrometric calibration as a function of degree of mass discrimination assumed for all isotope abundance measurements. The dashed lines represent estimates of the standard deviation.

puting Ca^{40} content from isotope ratios involving Ca^{40} , and from those "independent" of Ca^{40} . Since calcium in the samples in general has a low percentage of radiogenic Ca^{40} (~10%), the internal consistency of a particular run is of primary importance, producing the largest error by about an order of magnitude.

Neglecting the "constant" mass discrimination, as indicated in Fig. 18, may cause a discrepancy of about 2 - 3% in the isotope dilution answer. In Fig. 19 the percentage standard deviation (computed on the basis of the differences between calculated concentration) of the sum of all concentrations obtained for a particular run at a particular degree of fractionation is plotted versus assumed fractionation. It is seen that in all cases the deviation is nearly independent of consistent discrimination. Therefore, neglecting the small discrimination indicated does not introduce any additional error in the value of radiogenic Ca^{40} .

It is important to point out that, unlike a consistent discrimination throughout all runs, for a particular run which contains an irregular discrimination, or an irregular result of any kind, the deviation parameter discussed above is a sensitive detector (e.g., see the Ca^{43} result for Ca^{48} spike). This method of detecting discrepancies will be further discussed in Parts II and IV.

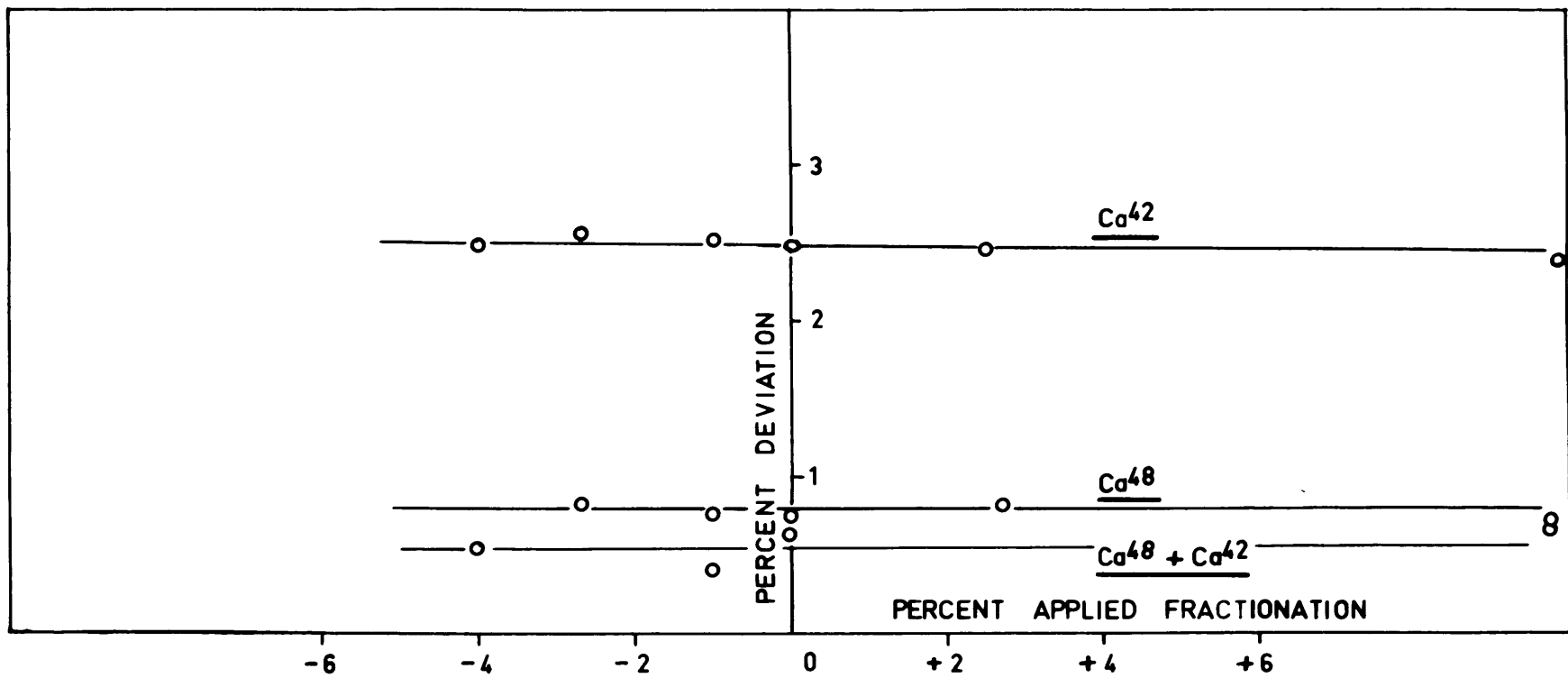


Figure 19. Total deviation of (w_c/w_s) values computed from different measured isotope ratios, as a function of degree of mass discrimination assumed for all isotope abundance measurements.

PART II. THE SEPARATION, PURIFICATION AND DETERMINATION
OF THE CALCIUM CONTENT IN MINERALS

1. THE SEPARATION OF SMALL QUANTITIES OF CALCIUM FROM LEPIDOLITES

In order to utilize the decay of K^{40} to Ca^{40} for geologic age measurements, it was necessary to separate microgram quantities of calcium from silicate materials, without introducing an overwhelming amount of contamination. The various steps of this procedure are discussed in this section.

Mineralogical Purification of Lepidolites

A number of the samples used in this investigation were received in the prepared or partially prepared state. It was desired, however, for purposes of this thesis, and for purposes of preparing a large suite of samples for this work, to adopt or develop a relatively simple method of separating lepidolites from accompanying minerals, mostly quartz and feldspars. A good separation is required by the fact that a small amount of impurity minerals can introduce a large quantity of common calcium.

The samples were first crushed in a steel percussion mortar. The first few yields were discarded and considered as a cleaner for the mortar and pestle. The sample was then sized by sieve shaking, the coarser fractions being subjected to further crushing. This process in itself provides some degree of separation, for micaceous materials tend to retain their original grain size parallel to the cleavage planes. The fractions enriched in micas are then collected for further purification.

At this stage several methods were tried or considered. The use of a magnetic separator, described by Holyk (1952), was attempted on sev-

eral samples, but with little success. Apparently inclusions in much of non-micaceous material gave it magnetic properties similar to those of the lepidolite. This method was therefore abandoned. Heavy liquids, a fairly standard method of lepidolite separation, were then considered. The pertinent heavy liquids were checked for alkali and alkaline earth content by optical spectrograph and were found to be sufficiently clean. However, prolonged soaking of the lepidolites was considered undesirable if it could possibly be avoided. In addition the tendency of the micaceous material to float in liquid with a lower density caused some trouble. A more satisfactory method was sought.

The method finally adopted was an air flow separation. In this procedure, the partially purified material is carefully sized and put in the bottom of a gently tapered funnel. Air is blown up through the material, carrying many of the mica flakes up and over the edges where they are collected. The rounder grains, with a lower ratio of surface area to weight, tend to remain in the funnel. This method is simple, and produces a fair concentration of mica. This partially purified material is then placed on an inclined sheet of paper and gently shaken. The rounded grains roll off the paper more easily than the flaky lepidolite. A final examination of the concentrate of lepidolite is made, and the non-lepidolite grains are discarded. The final sample (with the exception of the Bikita Quarry sample) appeared to be better than 99% pure lepidolite.

Chemical Processing - The Contamination Problem

Attempts to find Ca^{40} in lepidolites had been made at other laboratories prior to the beginning of this research program without success.

The failure was believed to be due to laboratory contamination by common calcium. A check of the purity of the reagents to be used was therefore made before attempting a separation. A large volume of each of the reagents was evaporated to dryness in a Pyrex evaporating dish, the residue taken up in a drop of water, placed in a pure carbon electrode, and dried. The electrodes were then arced, along with some electrodes containing known quantities of calcium, on a diffraction grating optical spectrograph. The results of this rough measurement are given in Table 8. The approximate amounts used in digestion and separation procedures for one gram of lepidolite are given, and the estimated contamination contribution from each reagent is computed.

It was suspected that the large calcium content of the HCl might be due to leaching from the Pyrex glassware used. Optical spectrographic estimates of calcium contents of several glasses made in this laboratory and the resistance of glasses to acid leaching are compared in Table 9. From the results above it appears probable that a significant amount of calcium contamination was introduced through the leaching action of hot HCl on the Pyrex glassware used. Table 9 indicated that this problem could be eliminated by the use of Vycor brand glassware. An all-Vycor still was constructed, and Vycor glassware was obtained for use throughout the entire chemical procedure. A test similar to those shown in Table 8 was made for 3.0N HCl, using Vycor glass throughout, and the calcium concentration was found to be less than 10^{-2} ppm. After making this change a sample of 26 micrograms of Ca^{48} spike was put through a procedure similar to that described below, and examined on the mass spectrometer. A total contamination of about 12 micrograms of common calcium was observed. From the work with lepidolites it appears that calcium contamination

TABLE 8. Purity of Reagents Used

<u>Reagent</u>	<u>Volume Evaporated (ml)</u>	<u>Approximate Calcium Concentration (ppm)</u>	<u>Amount Used For One Gram of Lepidolite (ml)</u>	<u>Approximate Contribution to Contamination (μg)</u>
1. 48% HF (reagent grade)	30	10^{-3}	10-30	0.1
2. 70% HClO ₄ (reagent grade)	30	10^{-3}	10-20	0.1
3. 3.0 N HCl (reagent, redistilled in Pyrex system)	30	0.5	50-100	25-50

TABLE 9. Properties of Various Glasses

<u>Glass</u>	<u>Approximate Calcium Content (ppm)</u>	<u>Weight Loss after Boiling in 5% HCl for 24 hours (mg/cm²)(Nordberg, 1947)</u>
Pyrex brand	300	4.5×10^{-3}
Vycor brand	10	5×10^{-4}
Fused Silica	10

varies somewhat from run to run, and is generally probably of the order of 10-30 micrograms of calcium per one gram sample. It is thought that a large portion of this was due to airborne dust deposited during ion exchange collection. Special apparatus could be built to avoid this source of contamination by operating the columns in an enclosed, filtered-air atmosphere.

The Analytical Procedure

The analytical procedure followed for separation of calcium from lepidolites is adapted from that described by Aldrich, Doak and Davis

(1953) and by Pinson (1955) for the separation of small quantities of strontium from lepidolites. A single sample was used for determination of Rb, K, and radiogenic Ca^{40} and Sr^{87} content. Two portions of a purified lepidolite sample, each weighing about one gram, were weighed carefully on an analytical balance. They were then separately washed with very dilute ($< 0.01N$) HCl followed by several rinsings with redistilled water (the water used throughout these procedures was M.I.T. tap distilled water, which had been put through an ion exchange demineralizer, and then redistilled in the Vycor glass still). The samples were then placed in large platinum dishes, and a known volume of one of the A.E.C. enriched calcium spike solutions, plus a known volume of the Sr^{84} spike solution, was added to one of the dishes. The spiked sample was used for an actual determination of the concentration of Ca^{40} , and Sr^{87} , and the unspiked sample was used in some cases for a determination of the isotopic ratios of the non-radiogenic calcium in the lepidolite, and provided a check on the answer obtained (see also Part IV).

The two samples were run side by side on the same hot plate to ensure equal contamination. It was thought that spattering of the solutions could be eliminated by the use of relatively low temperatures throughout. Spattering in a dish is very easy to observe, because small deposits of the solutes appear on the sides of the dish, and observations indicated no spattering. However, it was found that the unspiked solution often became contaminated with a very small amount (about 0.01 micrograms) of the Ca^{42} spike. This level of cross-contamination was insignificant except in the case of isotopic ratios involving Ca^{42} in the unspiked sample. Such ratios could not be used in the estimates of original lepidolite calcium fractiona-

tion, and it is therefore recommended that spiked and unspiked solutions should not be processed in the same vicinity.

About ten to twenty milliliters of 48% HF (reagent grade) plus about ten milliliters of 70% HClO₄ (reagent grade) were added to each platinum dish, and digested smoothly on a warm hot-plate. It was sometimes necessary to add more acid. Two to five hours are required for complete digestion, and at that time the lepidolite should be entirely in solution (an insoluble residue observed in the case of the Bikita lepidolite was found to be mostly topaz, and is discussed fully in Part IV).

After digestion, the solutions are taken to dryness. The perchlorates are then dissolved in about eighty milliliters of very dilute HCl, and the spiked solution is diluted to 100 milliliters in a volumetric flask. A five milliliter aliquot of this solution is taken for potassium and rubidium determinations, and the remainder of the solution is returned to its platinum dish. From this point on, loss of part of the solution or part of the calcium does not affect the final result. In order to indicate the elements present in the solution at this point, the average composition of lepidolites is given in Table 10.

A partial removal of K, Rb, and Cs in the Ca aliquot is necessary at this point. The high ratio of potassium to calcium in lepidolites (about 2000) makes effectively complete separation of K and Ca on the ion exchange column difficult, although the separation is excellent when more nearly comparable amounts of K and Ca are put through the column. Rubidium and cesium also overlap with Ca in the separation, and are undesirable in the mass spectrometric work because of their copious ion emission. The partial removal is made simply by evaporating the solution down to 5-10 ml (with the formation of a precipitate) and decanting off the solution. Due to their

solubility, K, Rb, and Cs perchlorates are thus depleted in the solution by about a factor of ten, while only a small amount of calcium is lost by coprecipitation. Na and Li perchlorates remain in solution. The relative solubilities are given by Sidgwick (1953, p. 1233). The procedure was monitored by optical spectrograph. A more complete separation of the alkalis could be achieved by the use of ethyl alcohol, in which the solubilities of K, Rb, and Cs are very poor, but it was found by Herzog (1952) that a very large portion of the strontium was lost in that procedure. The enriched solution, containing Fe, Al, Mn, Li, K, Rb, Cs, Mg, Ca, and Sr, is diluted to ten to fifteen milliliters and is put on the ion exchange column. The dilution is a necessary step, for if a saturated solution is added to the column it may cause "plugging," and significantly decrease the flow rate of the column.

The final "isolation" of calcium is achieved by the use of an ion exchange column (Nachod, 1949). The procedure used is described by Pinson (1954). The column consists of graded layers (about a half inch thick) of Dowex 50, 200-400 mesh, 8% cross-linked resin in a Vycor glass tube. The resin is kept in the tube by a piece of Vycor glass wool placed at the constricted exit of the tube. Dimensions of the column are about 25 x 2.5 cm, and the flow rate is about nine ml/hour, and is held constant during a separation. The elutriant used is 3.0N HCl, and the eluate is collected in small polystyrene bottles, using an automatic fraction collector (Pinson, 1954).

The separation achieved for a solution containing approximately equal concentrations of alkalis and alkaline earths is shown in Fig. 20. These data were obtained by monitoring the column by means of optical spectrograph, using the methods described by Pinson (1954). Unfortunately, even with chemical enrichment of the Ca/alkali ratio there is a tendency for the alkalis to tail out a bit, with the result that the calcium fraction is

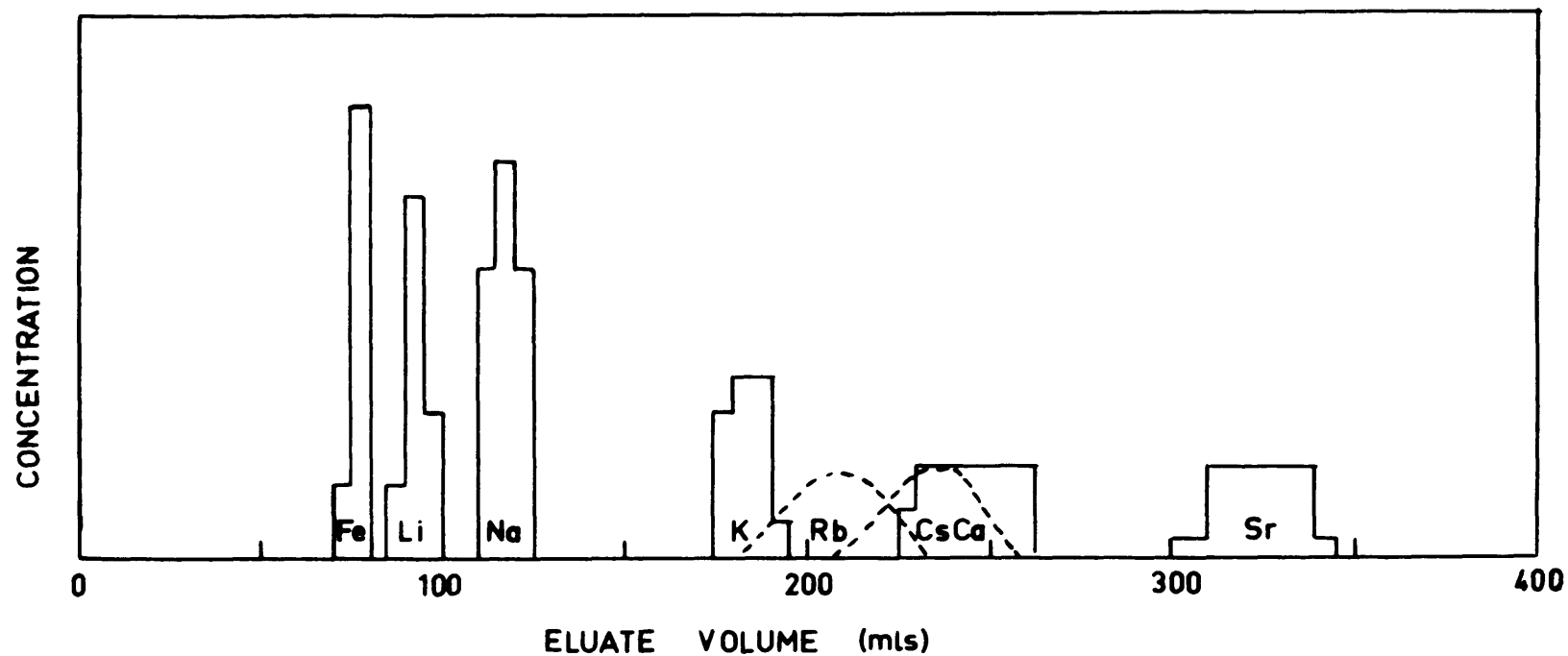


Figure 20. Separation of Alkalis and Alkaline Earths by Ion Exchange Techniques. The applied sample contained 0.06 grams each of Fe, Li, Na, K, Ca, Sr, and Ba in 3 mls. of 3.0N HCl. The column and standard techniques used are described in the text.

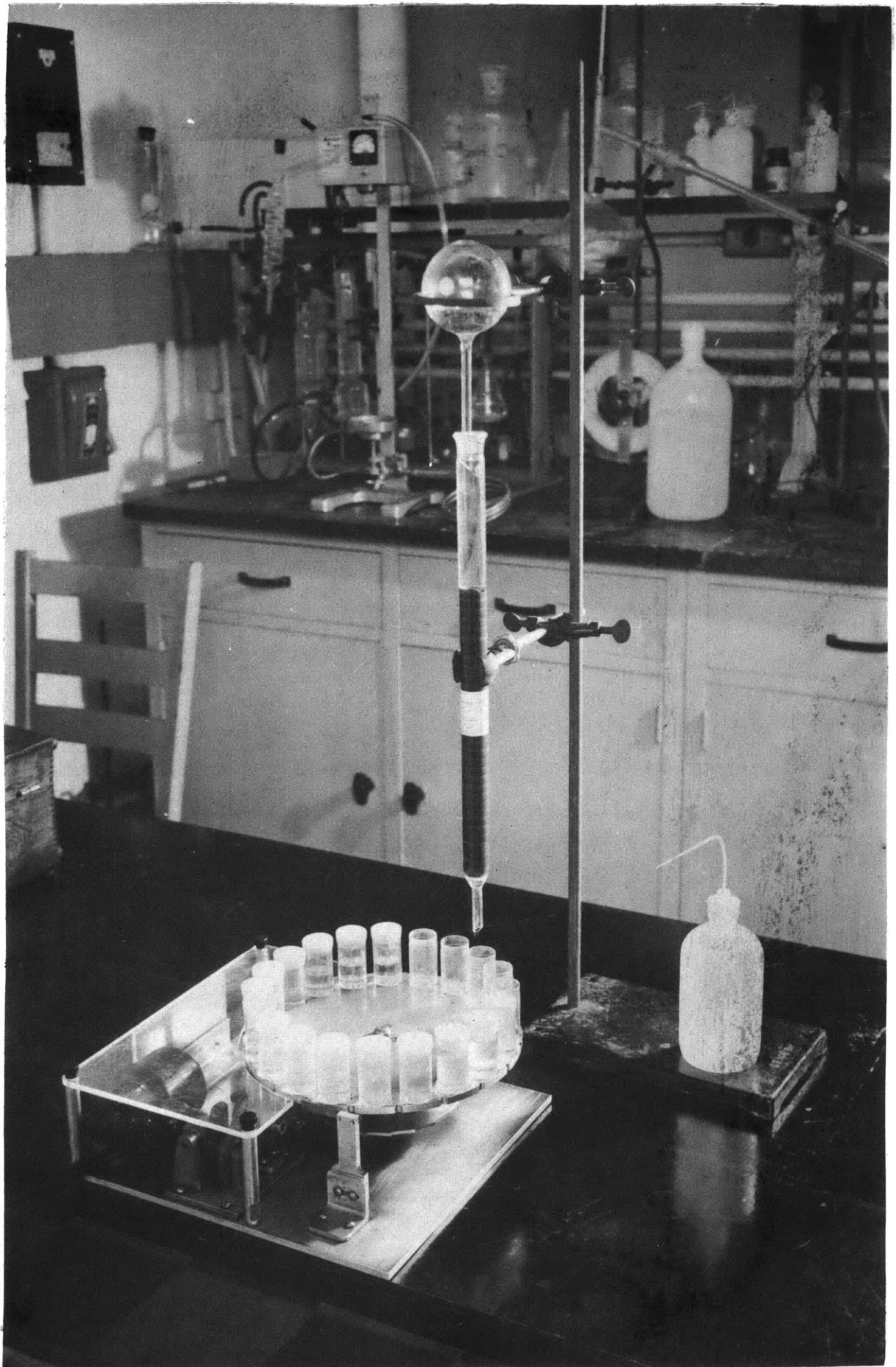


Figure 20b. Ion Exchange Column and Collection System (dust-protective shield removed).

slightly contaminated by alkalis. These alkali elements must be evaporated from the filament in the mass spectrometer before calcium measurements may begin.

TABLE 10. Average Composition of Lepidolites

(Adapted from Heinrich, 1953)

	<u>Percentage</u>
SiO ₂	50
Al ₂ O ₃	29
Li ₂ O	3.8
K ₂ O	10
Na ₂ O	0.4
Rb ₂ O	0.5
Cs ₂ O	0.08*
MgO	0.04
CaO	0.007
SrO	0.006
MnO	1.16
TiO ₂	0.014
F	5.4

On early runs, each individual sample was monitored by optical spectrograph, but it was found that the performance of the column was consistent enough to eliminate that procedure, and the position of the calcium fractions and strontium fractions were estimated. The fraction containing the calcium is then evaporated to dryness, about one to two milliliters of reagent grade HNO₃ are added (it has been established that no

contamination is introduced in this step), and the sample is converted to CaNO_3 by taking to dryness. Boiling in nitric acid also serves to decompose any resin that may be present. The nitrate is then dissolved in a small volume of distilled water, and is ready for application to the filament for mass spectrometric examination.

Particular care must be taken throughout the procedure to avoid contamination. Throughout digestion, and during all evaporation procedures, a polyethylene shield was used to protect the sample from airborne dust. All non-volumetric glassware was thoroughly cleaned with a detergent such as Alconox, and thoroughly rinsed with tap water, demineralized water, hydrochloric acid, and distilled water. Volumetric glassware, such as pipettes, were cleaned by a five minute soaking in a sulphuric acid plus sodium dichromate cleaning solution, thoroughly rinsed with tap water and distilled water, and dried in an oven.

The washing of the lepidolites prior to digestion is a critical procedure. The contaminant calcium acquired in handling of the lepidolite must be washed off, but the washing solution must not be so strong as to leach out any of the Ca^{40} from the lepidolite. When strong hot acid washes were used, optical spectrographic examination indicated that some alkali and alkaline earth leaching may have taken place, though such an effect was not observed by Tomlinson and Das Gupta (1953), even for boiling aqua regia. Therefore very weak acid was used for washing. The reproducibility of the measured amount of Ca^{40} , discussed in Part IV, when different workers in this laboratory perform somewhat different chemical techniques throughout the separation process, is good evidence for the validity of the procedures. However, the critical acid strength and solution contact time for significant lepidolite leaching should be further studied in subsequent work.

Early in this program the question of isotopic fractionation by the ion exchange separation process was considered, and preliminary results (Herzog, et al., 1954) supported the possibility of fractionation. Later mass spectrometric work, however, has indicated that the results indicating fractionation were actually due to source fractionation in the mass spectrometer. In any case an attempt was made to take nearly the entire calcium fraction as a unit for mass spectrometric analysis.

2. THE METHOD OF ISOTOPE DILUTION

The recent availability (Keim, 1953) of artificially enriched stable isotopes from the Atomic Energy Commission has introduced a powerful tool for chemical analysis. Tilton (Faul, 1954) gives an excellent discussion of isotope dilution techniques. An idealized picture of the analytical application of isotope dilution is the following. An analyst wishes to determine the concentration of a monoisotopic element with atomic number A and atomic weight M_1 in a given sample. He obtains an enriched stable isotope of atomic number A and atomic weight M_2 . At any time during the solution of a known amount of his sample, he adds a known amount of the enriched spike. After complete solution and mixing, the unknown A and the spike A are chemically identical, so their ratio remains constant throughout further chemical processing despite incomplete recovery of the sample at any stage. The mixture may be analyzed mass spectrometrically either immediately after solution, as in the case of alkali determination in lepidolites, or after extraction and purification of the element being analyzed, as in the case of calcium and strontium. If the amount of contamination is insignificant or well-determined, the ratio of unknown to spike can be directly determined with an accuracy limited only by the precision of isotopic analysis, the accuracy with which small mass discrimination effects are known, and the accuracy with which the original weighings and calibrations were made.

Since its first application to a geological problem by Inghram, et al. (1950), this method has become widely used, especially by researchers in the field of age determination. It has been demonstrated that agreement within 3 to 5% can be obtained between two entirely different laboratories at least in the case of rubidium and strontium analyses (Herzog, et al., 1955).

For the measurement of radiogenic calcium content of lepidolites, mass spectrometric analysis is necessary in any case because the Ca^{40} contained in lepidolites is made of both originally deposited calcium and radiogenic calcium. The amount of original Ca^{40} may be inferred from the quantity of any of the other calcium isotopes (if the original Ca is assumed to be of normal isotopic composition), and may be subtracted from the total amount of Ca^{40} present. Since the Ca^{40} in most lepidolites is predominantly original calcium, the error in the determination of radiogenic calcium is large, and the only significant contribution to this error is due to the precision of the mass spectrometric isotopic analysis of calcium.

Formulae and Computations

In the following formulae and discussion, this notation will be used for convenience.

w_s = weight of spike calcium added to the lepidolite solution

w_c = weight of original calcium in the lepidolite, assumed to have the isotopic abundances of the calcium standard (see Table 16)

w_r = weight of radiogenic calcium in the lepidolite

$\left(\frac{44}{48}\right)_{id}$, $\left(\frac{42}{48}\right)_{id}$, $\left(\frac{43}{48}\right)_{id}$ = isotope ratios measured in an isotope dilution experiment using Ca^{48} spike

$\left(\frac{48}{42}\right)_{id}$, $\left(\frac{44}{42}\right)_{id}$, $\left(\frac{43}{42}\right)_{id}$ = isotope ratios measured in an isotope dilution experiment using Ca^{42} spike

$(48)_{48s}$, $(44)_{48s}$, etc. = relative isotopic abundances of Ca^{48} spike in atom percent

$(48)_{42s}$, etc. = relative isotopic abundances of Ca^{42} spike

$(48)_c$, etc. = relative isotopic abundances of original calcium

m_{48s} , m_{42s} , m_c = atomic weights of spike and original calcium

Any isotope ratio in a mixture of two isotopically different components is given by considering the total number of atoms (or a proportional expression) of each isotope present. For a mixture of ^{48}Ca spike and lepidolite calcium for example,

$$\left(\frac{^{40}}{^{48}}\right)_{\text{id}} = \frac{\frac{w_c}{m_c} (^{40})_c + \frac{w_s}{m_{^{48}\text{S}}} (^{40})_{^{48}\text{S}} + \frac{w_r}{40} (100)}{\frac{w_c}{m_c} (^{48})_c + \frac{w_s}{m_{^{48}\text{S}}} (^{48})_{^{48}\text{S}}} \quad (8)$$

By simple algebraic manipulation of such expressions, the desired w_c/w_s and w_r/w_s may be expressed in terms of the measured isotope ratios. Using the values given in Table 4 for the isotopic abundances of spike calcium and common calcium, the following formulae are obtained for isotope dilution using Ca^{48} spike:

$$\frac{w_c}{w_s} = 0.859 \left[\frac{\left(\frac{^{44}}{^{48}}\right)_{\text{id}} (84.75) - 0.6154}{2.155 - \left(\frac{^{44}}{^{48}}\right)_{\text{id}} (0.2036)} \right] \quad (9a)$$

$$\frac{w_c}{w_s} = 0.859 \left[\frac{\left(\frac{^{42}}{^{48}}\right)_{\text{id}} (84.75) - 0.1597}{0.658 - \left(\frac{^{42}}{^{48}}\right)_{\text{id}} (0.2036)} \right] \quad (9b)$$

$$\frac{w_r}{w_s} = \left(\frac{^{40}}{^{48}}\right)_{\text{id}} \left[0.7261 + 0.00203 \left(\frac{w_c}{w_s}\right) \right] - 0.9655 \left(\frac{w_c}{w_s}\right) - 0.1246 \quad (9c)$$

Since $(^{43}/^{48})_{^{48}\text{S}}$ was not well determined, the values for $(^{43}/^{48})_{\text{id}}$ were not used.

For isotope dilution determinations with Ca^{42} spike:

$$\frac{w_c}{w_s} = 0.963 \left[\frac{\left(\frac{44}{42}\right)_{id} (81.75) - 0.5023}{2.155 - \left(\frac{44}{42}\right)_{id} (0.658)} \right] \quad (10a)$$

$$\frac{w_c}{w_s} = 0.963 \left[\frac{\left(\frac{43}{42}\right)_{id} (81.75) - 0.0793}{0.1385 - \left(\frac{43}{42}\right)_{id} (0.658)} \right] \quad (10b)$$

$$\frac{w_c}{w_s} = 0.963 \left[\frac{\left(\frac{48}{42}\right)_{id} (81.75) - 0.0245}{0.2036 - \left(\frac{48}{42}\right)_{id} (0.658)} \right] \quad (10c)$$

$$\frac{w_r}{w_s} = \left(\frac{40}{42}\right)_{id} \left[0.7849 + 0.00656 \left(\frac{w_c}{w_s}\right) \right] - 0.9655 \left(\frac{w_c}{w_s}\right) - 0.1694 \quad (10d)$$

Formulae for (w_c/w_s) in terms of all other isotope ratios not involving Ca^{40} could also be used, but are of little value, since they are dependent on the formulae given and are also more subject to error.

The fact that (w_c/w_s) can be computed from several different "independent" measured ratios provides an internal check on each isotope dilution run. By comparing the different values of (w_c/w_s) , the accuracy of the run may be ascertained, and any excessive fractionation effects in the isotope dilution mass spectrometer run, or in the lepidolite's original calcium, may be detected.

Propagation of Errors

The partial relative error in the computed values of (w_c/w_s) due to a relative error in the measured ratios $(48/42)_{id}$, etc., of one percent, is shown in Fig. 21. For any other assumed error in the ratios the ordinate must be expanded directly. For a comparison of values of (w_c/w_s) obtained

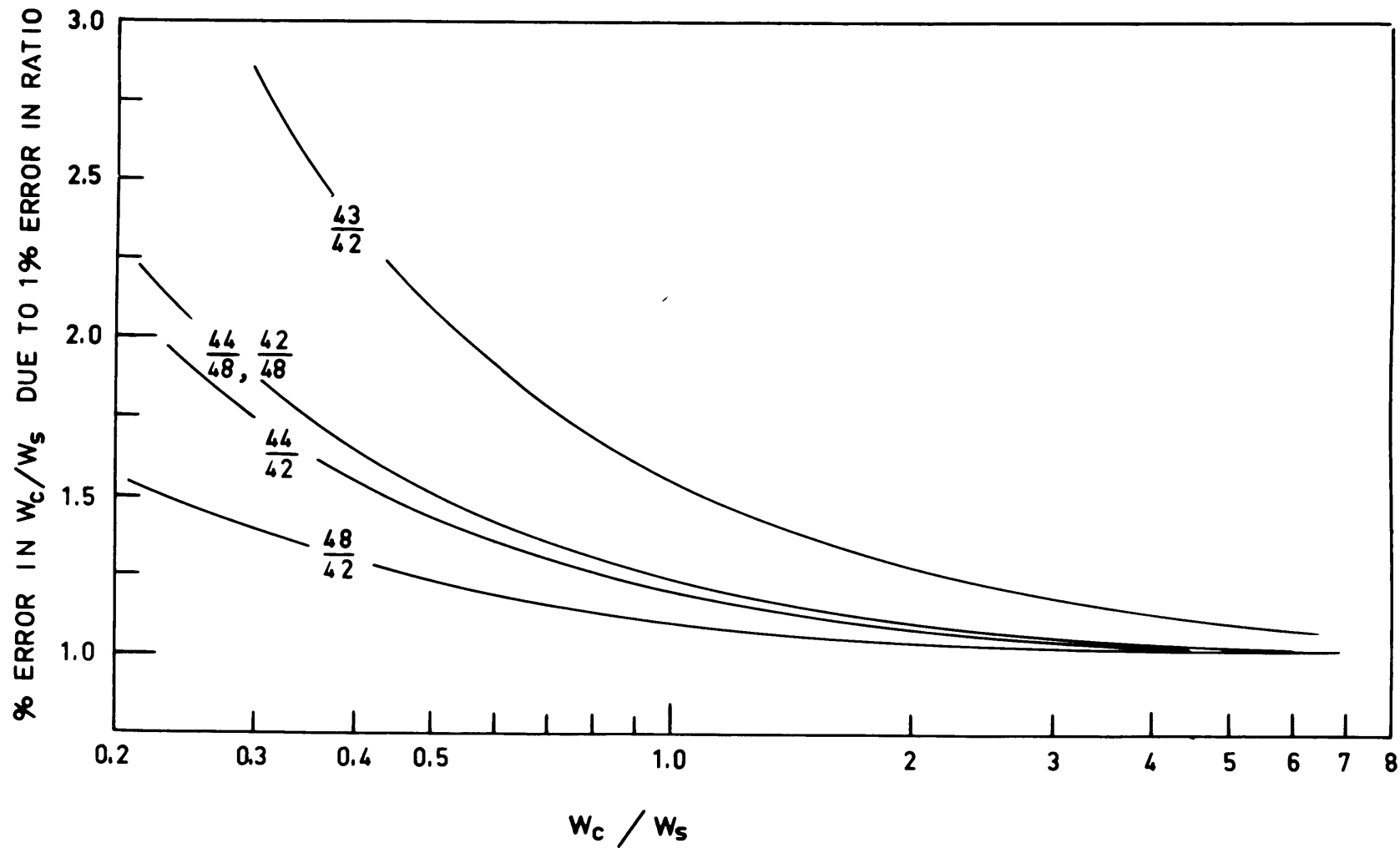


Figure 21. Error in Isotope Dilution Results Due to Mass Spectrometric Error in Isotope Dilution Runs.

from different ratios, and for an estimate of the accuracy of the final value of w_r , the precision of isotope ratios, rather than their absolute accuracy, should be considered. For such uses, then, the errors given in Fig. 21 may be used directly.

The relative error (precision) in the values of spike isotope abundances is of the order of $\pm 0.2\%$ for the enriched isotopes and $\pm 1\%$ for the others, and does not contribute significantly to the error in (w_c/w_s) . The relative error in $(42)_c$, $(43)_c$, $(44)_c$, and $(48)_c$, where the isotope in question appears in the numerator of the measured isotope ratio is inversely propagated into the value of (w_c/w_s) without change in magnitude, and should be considered random relative to the error shown in Fig. 21 when computing the total error in (w_c/w_s) .

If we assume that any differences between "common" calcium, and the original calcium in the lepidolites is due purely to a relative mass fractionation, the different values of (w_c/w_s) obtained in an isotope dilution may be used to check the assumption that the original calcium was normal. The relative error introduced in (w_c/w_s) is shown as a function of degree of fractionation of lepidolite calcium in Fig. 22. The separations between the curves may be compared with actual results.

Error in Radiogenic Calcium Determination

Errors in weighing and spike calibration, absolute errors in isotope determinations, etc., are all of the order of one to three percent, and are therefore insignificant compared to the error due to the precision of isotope determinations. The two major contributions to the absolute error in w_r are the uncertainty (used in the sense of reproducibility) in (w_c/w_s) , and uncertainty in the measured value $(40/48)_{id}$ or $(40/42)_{id}$.

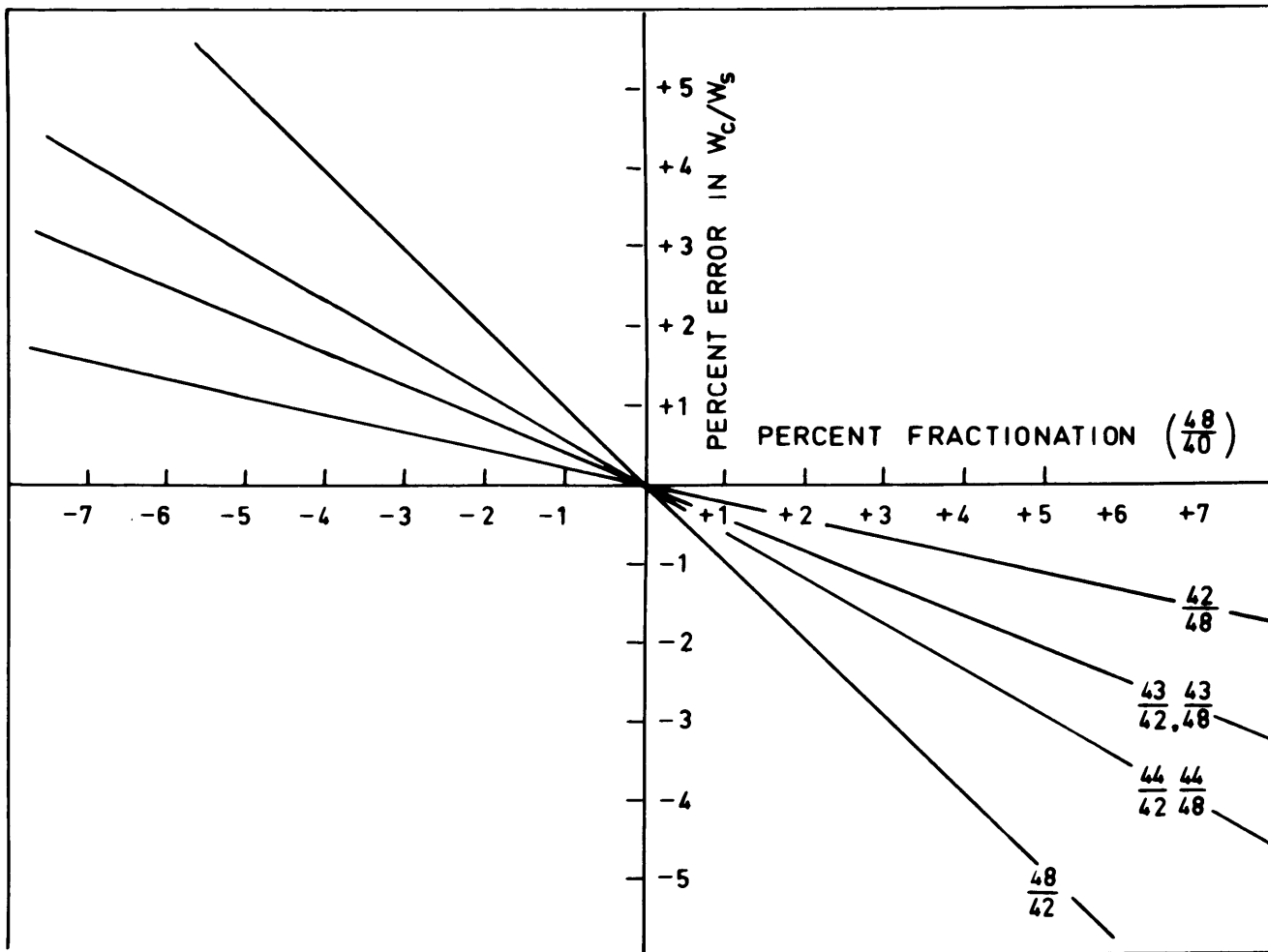


Figure 12. Error in Isotope Dilution Results Due to Uncertainty
 in the Isotope Abundances of Original Calcium in Lepidolites.

For both calcium spikes, the relative error in w_p due to uncertainty in (w_c/w_s) is:

$$\frac{\partial (w_r)}{w_r} \approx \left(\frac{w_c}{w_r}\right) \frac{\partial w_c}{w_c} \quad (11)$$

For the Ca^{48} spike:

$$\frac{\partial (w_r)}{w_r} \approx 0.73 \left(\frac{40}{48}\right)_{id} \left(\frac{w_s}{w_r}\right) \frac{\partial \left(\frac{40}{48}\right)_{id}}{\left(\frac{40}{48}\right)_{id}} \quad (12a)$$

For the Ca^{42} spike:

$$\frac{\partial (w_r)}{w_r} \approx 0.78 \left(\frac{40}{42}\right) \left(\frac{w_s}{w_r}\right) \frac{\partial \left(\frac{40}{42}\right)_{id}}{\left(\frac{40}{42}\right)_{id}} \quad (12b)$$

In both (11) and (12) precisions should be used rather than absolute errors. The relative error in $(40/48)_{id}$ and $(40/42)_{id}$ was taken as $\pm 1\%$ unless otherwise indicated. The two contributions to the error should be regarded as random relative to one another in computing total error.

Choice of Enriched Tracer

The Ca^{48} spike was originally chosen for this work mainly because an excellent Ca^{48} spike was available, and because Ca^{48} makes up a very small part of normal calcium. However, the Ca^{42} spike used in later determinations has a number of definite advantages. First, in the comparison of values of (w_c/w_s) computed from different measured ratios, the ratios available when using Ca^{42} spike provide a more sensitive check on the presence

of fractionation effects. Second, the most critical ratios, $(^{40}/^{42})_{id}$ and $(^{44}/^{42})_{id}$ in the case of the Ca^{42} spike may be measured more precisely than those in the case of Ca^{48} spike [$(^{40}/^{48})_{id}$ and $(^{44}/^{48})_{id}$]. This is because of smaller fractionation effects, and less time lapse between adjacent peaks in the former case.

PART III. ANALYTICAL METHODS FOR THE ALKALIS AND RELATED PROBLEMS

1. MASS SPECTROMETRIC DETERMINATION OF THE RELATIVE ISOTOPIC ABUNDANCES OF ALKALIS, AND THE ISOTOPIC COMPOSITION OF POTASSIUM AND RUBIDIUM

In order to determine K and Rb concentrations by the isotope dilution method, it is necessary to measure the relative isotopic abundances of K and Rb samples with accuracy, and it is necessary to know accurately the isotopic composition of common Rb and K. In order to make age calculations the relative abundances of the radioactive isotopes must be accurately known.

Fractionation Effects

The use of the surface ionization source provides copious ion currents for the alkalis. For this reason most abundance determinations made on the alkalis have been made with such an ion source. Brewer (1936a), using a platinum filament impregnated with the appropriate alkali salt, found that the $\frac{\text{Rb}^{85}}{\text{Rb}^{87}}$ ratio remained constant throughout the evaporation process. The $\frac{\text{K}^{39}}{\text{K}^{41}}$ ratio remained constant at 14.22 throughout most of the run, but had dropped slightly to 14.1 after 90% of the sample had been emitted, and was as low as 13.8 for the very last traces of emission. The $\frac{\text{Li}^6}{\text{Li}^7}$ ratio decreased considerably over a run. He attributed these effects to the dependence of diffusion rate on mass, the lighter isotopes diffusing more rapidly out of the filaments.

Bradt, Parham, and Brewer (1947) confirmed Brewer's earlier observations for potassium isotopes, again using a platinum disc impregnated with a potassium salt. They found that the positive ion emission from im-

pregnated sources "always passes through a definite cycle with respect to time. The ion current at first increases with temperature until a fairly flat plateau is reached. Thereafter, the emissivity decreases, approaching zero when all the alkali is removed." They found that the K^{39}/K^{41} ratio was essentially constant for the increasing part of the emission, and for the plateau, but decreased during the decrease in emission, again suggesting a diffusion effect.

Published Potassium Measurements

The measurements of the relative abundances of the potassium isotopes which have been published since 1935 are given in Table 11. Large variations which far surpass the reported standard deviations are apparent. Of course, the stated errors in general are not meant to be statements of absolute accuracy, but rather of precision. However, Nier (1950) and Greenewalt, et al. (1955), gave estimates of absolute accuracy. There are three possible explanations of these discrepancies. The first is that the differences shown are true differences in isotope ratios between the different samples analyzed. Unfortunately the source of the potassium analyzed is frequently not mentioned by the analyst. This explanation is supported by Brewer's (1936b, c) results, indicating natural K^{39}/K^{41} ratios ranging from 12.63 to 14.6. However, Cook (1943) analyzed a very large suite of samples, including types in which Brewer had found large variations. Although Cook had many troubles with variations in the raw data, he concluded that all of the samples he analyzed had K^{39}/K^{41} ratios of 14.12 ± 0.28 .

The diametrically opposed results of Brewer and Cook are difficult to explain. Brewer's investigations of his reproducibility of the K^{39}/K^{41} ratio were extensive and conclusive (exemplified by his sea water determi-

TABLE 11. Published Measurements of the Relative Abundances
Of the Potassium Isotopes (1935 - 1955)*

<u>Reference</u>	<u>Comments</u>	$\frac{K^{39}}{K^{41}}$	$\frac{K^{39}}{K^{40}}$
Nier (1935)	Electron bombardment of K vapor	13.96 ± 0.10	8600 ± 860
Bondy, et al. (1935)	Thermionic emission	16.2
Brewer (1935)	Thermionic emission	14.25 ± 0.04	8300 ± 100
Sampson & Bleakney (1936)	8600
Manley (1936)	Magnetic moment	13.4 ± 0.5
Bondy & Vanicek (1936)	Thermionic emission	14.0
Brewer (1936b, c)	Thermionic emission - plant ash	12.63 - 14.32
	sea water (14 determinations)	14.20 ± 0.0035
	mineral	14.11 - 14.6
Cook (1943)	Thermionic emission - constant value obtained from a large number of mineral and plant sources	14.2 ± 0.28
Paul & Pahl (1944)	13.96 ± 0.10
White & Cameron (1948)	Thermionic emission	13.66 ± 0.10
Nier (1950)	Electron bombardment of K vapor - sylvite	13.48 ± 0.07	7800 ± 80
Reutersward (1952)	Thermionic emission - raw value**	14.32 ± 0.05	8140 ± 40

Greenewalt (1955)	Thermionic emission	13.70 ± 0.07	8140 ± 240
Straight weighted average	13.96	8100

The straight weighted average gives percentage abundances:	K ³⁹	K ⁴⁰	K ⁴¹
Atom percentage:	93.31	6.68	0.0115

* Values through 1948 are from the table published by White and Cameron (1948).

** Reutersward corrected his ratios to Nier's 39/41 (1950) value on the assumption that the difference was due to mass discrimination, and obtained a K⁴⁰ abundance of 0.0118%, compared to Nier's value of 0.0119%.

nations). He even measured the ratios using different types of primary ion sources and obtained good reproducibility. Most of the samples on which he obtained anomalous values were remeasured with the same result. In later work Brewer repeatedly confirmed the existence of natural variations in the K^{39}/K^{41} ratio (see Rankama, 1945, for a discussion of Brewer's later results and also for a discussion of this entire problem). Brewer did observe that mineral variations were not commonly large. In his 1936b paper he gave analyses of potassium from twelve different mineral sources and all measured K^{39}/K^{41} ratios were within the range 14.23 to 14.32 except a Hawaiian basalt (14.11) and a wyomingite (14.6)

Cook used a multiple filament source which allowed the examination of eight different samples without opening his vacuum system. On each such group of samples he found no evidence of variation greater than $\pm 1\%$. From group to group, he did observe differences which he attributed to evaporation effects in the thermionic emission sources. The only possible error in his work might be an overwhelming contamination problem, though this is very unlikely in view of the fact that he was not dealing with trace amounts of potassium. In short, a conclusion about the existence of extensive natural variations in the isotope abundances of potassium can not be drawn at this time.

The second possibility is that the differences are due to varying mass discrimination effects (excluding fractionation effects due to diffusion, evaporation, etc., at the primary ion source) in the instruments of the different workers. If we assume that there are no large natural variations in the K^{39}/K^{41} ratio, this explanation is supported by the observations of Brewer and Bradt, that fractionation effects only occur at the very end of emission. Presumably, the wide acceptance of Nier's value (1950) as the

"correct" value for the K^{39}/K^{41} ratio is based on this view. Nier calibrated his instrument for mass discrimination effects by the use of mixtures of abnormal argon "spikes" with common argon. He was thus able to correct for any mass discrimination effects apart from those introduced in the process of subliming the solid potassium sample.

The third possible interpretation (supported by the observations of Cook (1943)) is that most of the observed variation may be due to variable fractionation effects occurring in the process of vaporizing the sample, and depending on a large number of factors. Measurements made at M.I.T. indicate that unless care is taken to reproduce emitting conditions, large variations in measured alkali isotope ratios may occur.

Common Potassium Measurements Made at M.I.T.

Incidental potassium isotope measurements made during mass spectrometric runs on various samples are given in Table 12. The primary source of ions was a tantalum or platinum-plated filament coated with a salt, primarily of the element to be analyzed. Potassium is so easily ionized that enough potassium ion current for isotopic measurement is present in nearly all samples. Most of these determinations were made without carefully reproducing emitting conditions, and large variations are apparent. Some of the values may represent the later phases of K evaporation, through none of the samples were depleted by as much as 90%. Mass fractionation in the impurity K in the Bikita lepidolite definitely occurred; the average value of the first nineteen determinations was 12.85, and of the last nineteen, 13.75. The differences between ratios shown in the table are thus not considered to represent real differences. It should also be stated that some of the alkalis were the last traces to get through the ion exchange columns,

TABLE 12. Incidental Potassium Measurements Made on
M.I.T. Mass Spectrometer

<u>Sample</u>	<u>Number of Sets</u>	$\frac{K^{39}}{K^{41}}$
Impurity K in CaCO ₃ reagent	24	13.90
Impurity K in RbCl reagent*	26	13.95
Impurity K in Sr fraction - Jakkalswater lepidolite*	56	14.27
Impurity K in Sr fraction - Homestead meteorite	17	13.42
Impurity K in Ca fraction - Bikita lepidolite	38	13.30
Bureau of Standards K ₂ CO ₃ (Greenewalt, <u>et al.</u> , 1955)		13.70

*Herzog, et al. (1954).

though it is not thought that this contributed to the observed variations. The determination by Greenewalt, et al. (1955) was a carefully monitored run in which a very large number of measurements were made, and no apparent fractionation took place. The potassium sample was not run to completion, and this result, along with others taken during isotope dilution experiments with alkalis, indicate that a stable reproducible ratio may be obtained.

Rubidium Determinations

Although Brewer found no significant fractionation effects for rubidium impregnated platinum discs, such effects have been found at this laboratory for the alkali salt coated filaments used. In Table 13 some of the published values of the Rb⁸⁵/Rb⁸⁷ ratio are given, along with some incidental measurements made at M.I.T. The M.I.T. measurements are also shown graphically in Fig. 23.

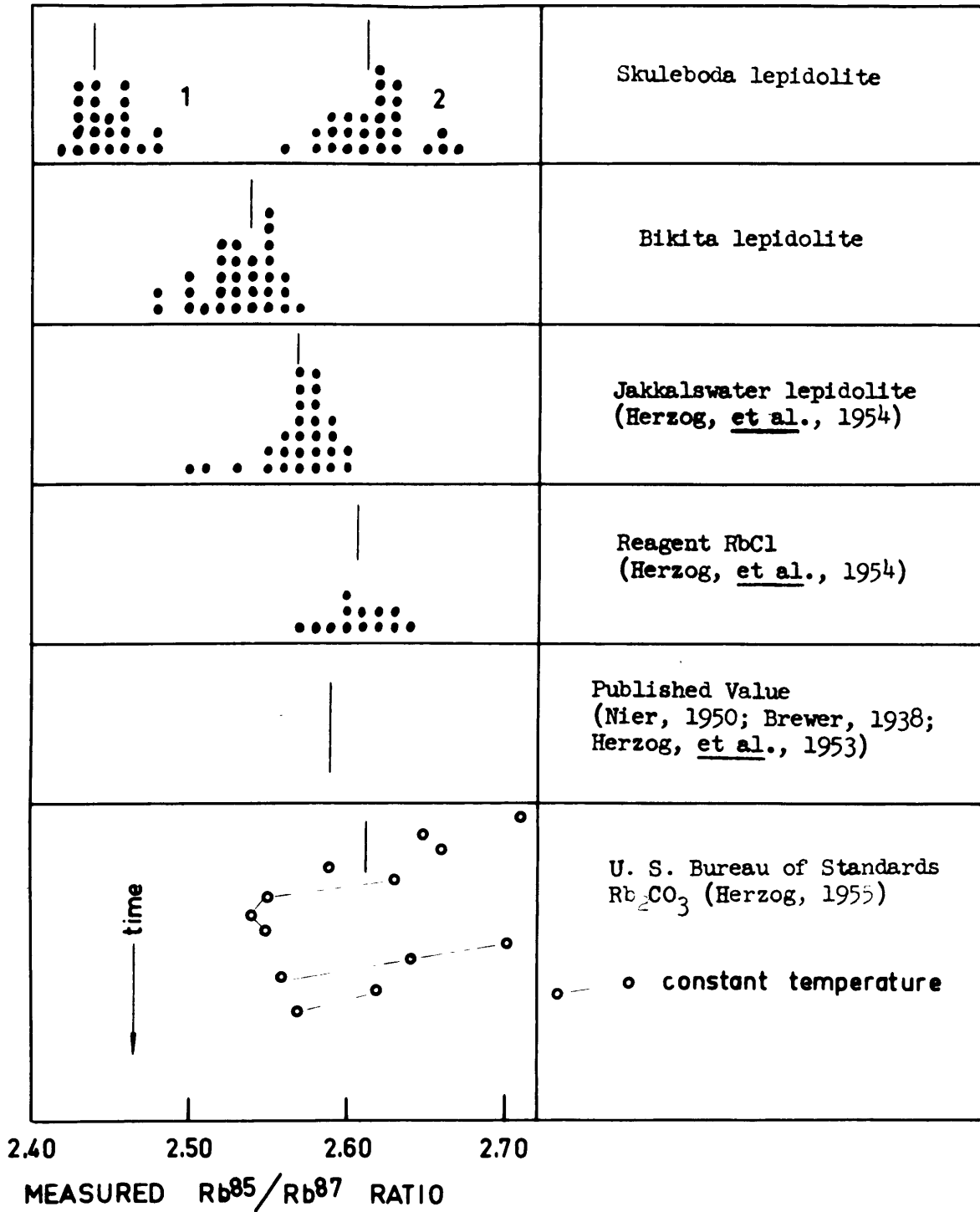


Figure 23. Incidental Rubidium Isotope Abundance Determinations.

TABLE 13. Published Measurements of the Relative Abundances
of the Rubidium Isotopes and Incidental Rubidium
Measurements Made on M.I.T. Mass Spectrometer

	$\frac{\text{Rb}^{85}}{\text{Rb}^{87}}$
Brewer (1938)	2.60 (2.59 - 2.61)
Nier (1950)	2.591 ± 0.006
Herzog, <u>et al.</u> (1953)	2.591 ± 0.003
M.I.T. (1952 - 1955)	
U.S. Bureau of Standards RbCl*	2.63
RbCl reagent**	2.605
Impurity Rb in Sr fraction - Jakkalswater lepidolite**	2.57
Rb in Bikita lepidolite	2.54
Rb in Skuleboda lepidolite	2.44
Impurity Rb in Ca fraction - Skuleboda lepidolite	2.62

*Herzog, personal communication (1955).

**Herzog, et al. (1954).

Again Brewer found some "natural" variations, reporting that the $\text{Rb}^{85}/\text{Rb}^{87}$ varied from 2.59 to 2.61. The precisions reported by Nier (1950) and Herzog (1953) are not statements of absolute accuracy, but rather of something like peak-to-peak precision. However, from the data available, it appears that the $\text{Rb}^{85}/\text{Rb}^{87}$ ratio may be stated as 2.60 ± 0.02 .

Some of the early incidental measurements were made on lepidolite rubidium, and indicated an enrichment of Rb^{87} which would have a significant effect on the reported Rb/Sr ages for lepidolites. The sample with the most abnormal $^{85}/^{87}$ ratio, the Skuleboda lepidolite, was redetermined, taking care that all measurements were made in the early part of rubidium emission, and a normal $\text{Rb}^{87}/\text{Rb}^{85}$ ratio was observed.

An extensive measurement of the Bureau of Standards RbCl was made by Herzog (1955, personal communication), and the results are shown in the bottom of Fig. 23. Each point represents the average of a number of peak sets; a total of 124 peak sets were taken. It is apparent that widely divergent, self-consistent results could be obtained, depending on the part of the emission observed. At constant temperatures a definite fractionation effect may be seen, the $\text{Rb}^{85}/\text{Rb}^{87}$ decreasing with time. This is similar to the effects observed by Brewer and Bradt for K and those observed for Sr and Ca by Herzog, et al. (1954). Since the sample is spread out over the filament, as the temperature is increased, the fractionation cycle may begin again, as is indicated in this experiment.

Conclusions

It is apparent that the accurate determination of the relative abundances of alkali isotopes is not a straightforward problem. Isotope dilution measurements for potassium and rubidium content (see Section 2) and other data, however, indicate that it is possible to obtain results with a reproducibility better than one percent.

The question of the possible existence of natural isotopic variations in K and Rb has not yet been satisfactorily answered. It is my opinion that much of the apparent variation in Table 11 is due to instrumental discrimination and fractionation effects. If no variations are found, as was indicated by Cook, the absolute isotope abundances can be established only if all possible discriminatory effects are corrected for. This may be done for potassium, for example, by an isotope dilution experiment similar to that performed by Nier (1950), using accurately weighed mixtures of normal and abnormal potassium instead of argon.

From the available data, values must be chosen for the computation of isotope dilution results and of geologic ages. I have chosen the value of $K^{39}/K^{41} = 13.70$ for isotope dilution because it was determined by the same method and on the same instrument that was used for isotope dilution measurements.

Because most workers have accepted Nier's value of 0.0119% for the atomic abundance of K^{40} , I have adopted this value for age computations. However, it appears from Table 1 that this value may actually be too high, and may contribute to the observed discrepancies between K/A ages and other ages.

For rubidium calculations it appears that the value $Rb^{85}/Rb^{87} = 2.60 \pm 0.02$ may be used with confidence.

2. ANALYSIS FOR POTASSIUM CONCENTRATION

In order to obtain K/Ca ages and Rb/Sr ages, it was necessary to measure the potassium and rubidium content of each lepidolite. Although significant inhomogeneities in the lepidolite samples were considered unlikely, alkali and alkaline earth determinations were made on the same solution. After the lepidolite was completely in solution, it was diluted to 100 ml, and a five milliliter aliquot taken for alkali analysis. The solution thus contained all of the original constituents of the lepidolite (see Part II), except for silicon and fluorine, which are liberated in the process of solution. Flame photometric analysis using a Perkin-Elmer Model 52 instrument was attempted, but interference effects (especially by rubidium) caused large discrepancies, and the resolution of the instrument was rather poor. It is probable that good results could have been obtained by the use of standard solutions with alkali content in lepidolite proportions, and internal standards (Edwards and Urey, 1955). However, isotope dilution measurement was adopted for both potassium and rubidium since the number of analyses required was small.

Techniques

The alkali analysis aliquot was further diluted, and a portion of this solution containing about 600 micrograms of lepidolite was measured into a Vycor dish. Known quantities of the A.E.C. enriched potassium and rubidium spikes were added. After mixing the solutions thoroughly, the entire solution was taken to dryness and carefully stored. The residue was later dissolved in water, and about one to two percent of the sample applied to a pre-cleaned filament. Platinum-plated tantalum filaments which

had been used for an alkaline earth run and cleaned by intense heating were generally used. The primary ion source thus consisted of a mixture of various cations, in lepidolite proportions, combined in the form of chlorides and perchlorates.

Because of the low temperature at which re-evaporation of alkalis from all parts of the mass spectrometer takes place, the mass spectrometer tube was not baked out. The filament was kept below 400°K until measurements were made. The pressure was generally from 0.5 to 1×10^{-5} mm of mercury during alkali measurements. The filament temperature was raised to the point where the collected K^+ ion current was about 10^{-11} amperes, the Rb^+ ion current 10^{-12} amperes, and the other alkali currents approximately in the proportions shown in Fig. 4. Automatic magnetic sweep sets of potassium isotope currents were taken for two hours, rubidium sets were taken for two hours, and additional potassium peaks were taken for an additional hour. The filament current was kept constant throughout this period, and the alkali current either remained constant, or decreased very slightly (never by more than about 50%). This is in contrast to the reported behavior of impregnated platinum filaments (Bradt, et al., 1947), and is in contrast to some of the incidental alkali measurements, in which a smaller quantity of the alkalis were present, and a larger current decrease was noted.

Reproducibility

In order to check the reproducibility of this method, the Bob Ingersoll lepidolite isotope dilution sample was mass spectrometrically examined twice by the standard procedures. The results are shown in Fig. 24; the $41/39$ ratio was determined as $1.183 \pm 0.15\%$ and $1.187 \pm 0.2\%$ respectively. The stated standard deviations are expressions of the peak-

to-peak reproducibility in each run, and are due primarily to random fluctuations in the potassium ion current. The two values are in excellent agreement, and there is no apparent evidence of any contribution to the error due to fractionation effects. The two results for the $\text{Rb}^{85}/\text{Rb}^{87}$ ratio were, respectively, 0.9420 and 0.9377. There is some indication that if one were to try to achieve better reproducibility by emitting for a longer period, and thus obtaining more peak sets, fractionation effects would become the limiting factor to attainable precision.

No significant differences were observed in any of the alkali runs between the potassium isotope ratios measured during the first two hours, and those measured during the fifth hour, verifying the unimportance of fractionation effects. This is believed to be due to the fact that only a small portion of the sample was used up during measurement.

On the basis of work done by Greenewalt, et al. (1955), and on the basis of the determined accuracy of the measurement of the $\text{Ca}^{42}/\text{Ca}^{40}$ ratio, the accuracy of the alkali isotope abundance measurements is believed to be within two percent, and probably somewhat better.

Isotope Dilution Calculations

The abnormal potassium tracer was obtained from the A.E.C., and its isotopic composition, reported by the A.E.C., and verified by Greenewalt, et al. (1955) to within one percent, is shown in Table 14. The spike solution was made up by Greenewalt and W. H. Pinson, and was determined by weighing and by an isotope dilution calibration to contain 49.5 micrograms of potassium per milliliter.

Using the values in Table 14, the weight ratio of normal potassium to spike potassium, w_c/w_s , is given by:

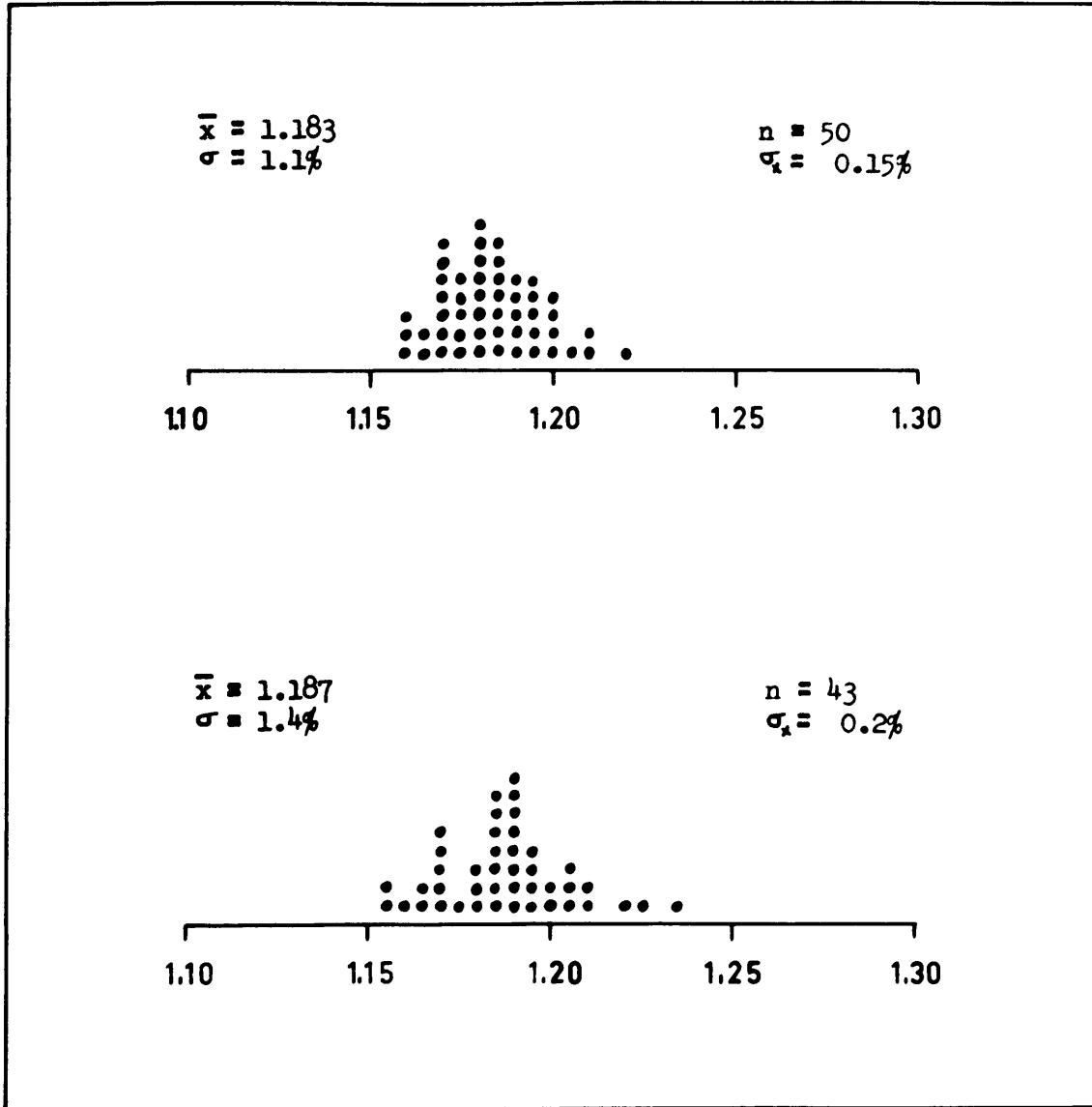


Figure 24 Duplicate Analyses of K^{41}/K^{39} Ratio of the Bob Ingersoll Potassium Isotope Dilution Sample. Each point represents an individual determination (peak set) of the K^{41}/K^{39} ratio.

TABLE 14. Isotopic Composition of A.E.C. K⁴¹ Spike and Normal K Used in Isotope Dilution Calculations

	Abundance (atom percent)		Atomic Weight
	<u>K⁴¹</u>	<u>K³⁹</u>	
A.E.C. K ⁴¹ Spike	99.2	0.8	41.0
Normal K	6.80	93.2	39.2

* * * * *

$$\frac{w_c}{w_s} = 0.956 \left[\frac{.992 - .008 \left(\frac{41}{39}\right)_m}{.932 \left(\frac{41}{39}\right)_m - .068} \right] \quad (7)$$

where $(41/39)_m$ is the measured K^{41}/K^{39} ratio of the mixture of spike potassium and lepidolite.

Results

The results of the potassium analyses are given in Table 15. As indicated by Herzog (1955) and Greenewalt, et al. (1955), the stated potassium contents are believed to have an accuracy of at least $\pm 3\%$. The differences between the values obtained by isotope dilution and those obtained by Harvey by optical spectrographic determinations are not surprising. It is believed that Harvey's analyses were routine analyses for all constituents. Comparable differences between optical spectrographic results and isotope dilution analyses have been found by Pinson and Herzog (1955). When errors are quoted for optical spectrographic total analyses, they are generally of the order of ten to twenty percent.

TABLE 15. Results of Potassium Isotope Dilution Runs

<u>Sample</u>	<u>Weight of Sample (μg)</u>	<u>Weight of K⁴¹ Spike (μg)</u>	<u>No. of Peak Sets</u>	<u>Measured K⁴¹/K³⁹ Ratio</u>	<u>$\frac{w_c}{w_s}$</u>	<u>%K</u>	<u>Optical Spectrographic Results C.E. Harvey %K</u>
Bikita I.D. II	695	49.5	60	1.184	0.908	6.47
Brown Derby No. 499	527	49.5	55	1.218	0.880	8.25	7.54
Brown Derby No. 503	619	49.5	50	1.038	1.046	8.36	7.50
Bob Ingersoll	512	49.5	1) 50 2) 45	1.183 1.187	0.908 0.905	8.77 8.74
Skuleboda	975	99.0	53	1.400	0.758	7.70	9.25

PART IV. PROBLEMS AND RESULTS OF GEOLOGICAL SIGNIFICANCE

1. THE ISOTOPE ABUNDANCES OF COMMON CALCIUM

Since the discovery of natural variations in isotopic abundances, the definition of the "common" or "normal" isotopic composition of any element has been difficult. There are two major causes of natural isotope abundance variations; natural nuclear reactions such as radioactive decay and those reactions which are caused by cosmic ray bombardment, and isotopic mass fractionation, which may cause the different isotope ratios to vary in a very regular manner, usually according to the square root of mass.

The only major source of the first type of variation which is known in the case of calcium isotopes is the decay of K^{40} . Taking the crustal weight percent abundance of $K = 2.6\%$, $Ca = 3.6\%$ (Rankama and Sahama, 1950), the K^{40} content of the crust is $(0.00012)(2.6) = 0.00029\%$ by weight, while the Ca^{40} content is $(0.97)(3.6) = 3.5\%$ by weight. The present ratio of K^{40}/Ca^{40} in the crust is thus 83×10^{-6} . Using a decay constant for K^{40} , $\lambda = 0.55 \times 10^{-9} \text{yr.}^{-1}$, and a branching ratio of 0.125, the total amount of Ca^{40} produced through the decay of K^{40} in the crust for a period of five billion years would be, in weight percent of the crust,

$$(0.00029)(0.88) [1 + \exp(5 \times 10^9 \times 0.55 \times 10^{-9})] = 0.0037\%.$$

The percent increase in Ca^{40} would thus be $0.0037/3.5 \times 100 = 0.1\%$. The total change in the isotope abundances of crustal calcium during the history of the earth is thus not measurable. There should be no variations in calcium isotope abundances due to this cause except in those very rare potassium minerals which are extremely depleted in calcium.

Variations due to natural fractionation may be expected, but definite proof of such variations has not yet been demonstrated. This possibility should, however, prompt research workers in this field to give the geologic source of their material when isotope abundances are measured.

Modern measurements of the isotope abundances of calcium have been published by Nier (1938), Sherwin and Dempster (1941), and White and Cameron (1948), and their results are given in Table 18.

Limestone Calcium

A bottle of Mallinckrodt "Calcium Carbonate A.R., Low Alkali" was chosen as a standard for the work done in this laboratory. According to the Mallinckrodt laboratories (J.C. Perry, personal communication, 1955):

The calcium in this item originates in limestone from quarries near Jamesville, New York. This is a Devonian age limestone and comes from principally two strata: (1) Onondaga limestone, immediately above Oriskany sandstone, and (2) Helderbergian or Stromatopora limestone, immediately below the Oriskany sandstone.

Four different measurements were made on this sample, using somewhat different sources, and the results are given in Table 16. The first three determinations were made using a D.C. feedback amplifier, while the last measurement was made using a vibrating reed electrometer. The $^{46}/^{40}$ ratio was determined in a separate run as $^{46}/^{40} = 0.000047 \pm 0.000010$. The precision of the measurements expressed as standard deviation appears to be of the order of one percent, and is best for the $^{42}/^{40}$ and $^{44}/^{40}$ ratios (see also Part I). However, in Part I, Section 7, it was demonstrated that the ratios obtained are not absolute ratios but must be slightly corrected for mass discrimination effects. Applying the appropriate corrections, the following values are obtained (see Table 17).

TABLE 16. Composition of Calcium from a Devonian Limestone (Raw Data)

<u>Primary Ion Source</u>	<u>Total No. of Peak Sets</u>	<u>$\frac{42}{40}$</u>	<u>$\frac{43}{40}$</u>	<u>$\frac{44}{40}$</u>	<u>$\frac{48}{40}$</u>	<u>$\frac{48}{42}$</u>
CaC ₂ O ₄ on TaO	20	.00678	.00144	.0223	.00212	.312
Ca(NO ₃) ₂ *Borax on TaO	23	.00696*	.00144	.0222	.00208	.298*
Ca(NO ₃) ₂ on used Pt. plated filament	57	.00682	.00142	.0222	.00212	.310
Ca(NO ₃) ₂ on new Pt. plated filament	53	.00697	.00142	.0223	.00210	.308
Average*		.00680	.00143 ₀	.0222 ₅	.00210 ₂	.310 ₂

*Ratios involving Ca⁴² in the second run appear to be anomalous and were not included in the average. This run was the poorest in the group from the standpoint of emission stability.

TABLE 17. Composition of Calcium from a Devonian Limestone (Corrected)

<u>Isotope Ratios</u>		<u>Isotope Abundances (atom percent)</u>	
$\frac{48}{42}$.306 ± .007	40	96.88 ± .05
$\frac{42}{40}$.00676 ± .00006	42	0.655 ± .006
$\frac{43}{40}$.00142 ± .00002	43	0.138 ± .002
$\frac{44}{40}$.0219 ± .0004	44	2.12 ± .04
$\frac{46}{40}$.000047 ± .000010	46	0.0046 ± .0010
$\frac{48}{40}$.00206 ± .00006	48	0.200 ± .006

The stated standard deviations may be considered a measure of the absolute accuracy of the stated values, except, perhaps, in the case of Ca⁴⁶.

Comparison with Published Data

The results obtained by previous workers for "common" calcium are compared with the results of this research in Table 18. Herzog (1952) stated that he obtained values in agreement with White and Cameron, but not with Nier. The observed differences (with the exception of Nier's value for $^{43}/^{40}$) are consistent with the hypothesis that the values of Nier and of White and Cameron show a slight depletion in the heavier isotopes due to mass discrimination. This may be attributed to the fact that most workers did not completely evaporate the samples, and thus may have obtained values during the early part of the fractionation process discussed in Part I, Section 5. This possibility was in fact suggested by Nier (1938). It is also possible that the differences are real, though the sources of calcium measured were not given in the literature.

Isotope Abundances of Two Meteorites

In order to verify the calculations that no significant changes in the relative abundance of Ca^{40} have occurred during geologic time, and to further investigate the possibility of natural calcium fractionation, portions of the calcium from two meteorites were examined mass spectrometrically. The calcium was extracted by W.H. Pinson of this laboratory.

The samples analyzed were from the Homestead meteorite, a typical chondritic stony meteorite, which was determined by Herzog and Pinson to have a minimum age of 2800 million years (Herzog, et al., 1955), and the Pasamonte meteorite, an achondrite originally selected for strontium analysis because the literature indicated that it had a particularly low K/Ca ratio (Urey and Craig, 1953).

TABLE 18. Published Measurements of the Isotope Ratios of "Common" Calcium

	$\frac{42}{40}$	$\frac{43}{40}$	$\frac{44}{40}$	$\frac{46}{40}$	$\frac{48}{40}$	$\frac{48}{42}$
Sherwin and Dempster (1941)						
1. Calcium metal, vaporization from iron furnace, ionization by electron bombardment.00217
2. Spark between two calcium rods.00227
3. Spark between copper electrodes and a silver-calcium alloy.01920
4. Nier (1938) calcium metal, vaporization from furnace, ionization by electron bombardment.	.0066 ±.0002	.00150 ±.00004	.0213 ±.0007	.000034 ±.000005	.00191 ±.00006	.289 ±.009
5. White and Cameron (1948) - solid source - thermionic emission.	.0066 ±.0001	.00136 ±.00004	.0220 ±.000200185 ±.00002	.280 ±.003
6. Present work - solid source - thermionic emission.	.00676 ±.00006	.00142 ±.00002	.0219 ±.0004	.000047* ±.000010	.00206 ±.00006	.306 ±.007
% Difference between (4) and (6).	- 2.4 ± 3	+5.6 ± 3	- 2.7 ± 3	- 7.3 ± 4.5	- 9.7 ± 4.5
% Difference between (5) and (6).	- 2.4 ± 1.4	- 4.2 ± 3	+0.5 ± 1.5	-10.2 ± 3	-12.6 ± 3

* $\left(\frac{46}{40}\right)$ in Homestead meteorite, a better measurement, was in agreement with Nier.

TABLE 19. Comparison of Calcium from a Limestone with
That from Two Meteorites

	$\frac{42}{40}$	$\frac{43}{40}$	$\frac{44}{40}$	$\frac{46}{40}$	$\frac{48}{40}$	$\frac{48}{42}$
Calcium Standard (Devonian Limestone)	.00680	.00143 ₀	.00222 ₅	(.00004 ₇)	.00210 ₂	.310 ₂
Homestead Meteorite	.00677	.00142	.0224	.000033	.00208	.307
Pasamonte Meteorite	.0070	.00153	.022900217	.312

The results are given in Table 19. The Homestead meteorite run was an excellent run, with a total of 122 determinations for all ratios except $46/40$, which is based on seventeen determinations. The $46/40$ ratio was in fact better measured for the Homestead meteorite than for the limestone Ca, and may be considered to lie within three percent of the correct value. It is in better agreement with Nier's (1938) determination. All other ratios agree with those found for limestone calcium within one percent, which is considered to be the precision of the measurement.

The Pasamonte meteorite was an early, and rather poor, run, made before final development of techniques. The values are based on fourteen peak sets. Isotope ratios not involving Ca^{40} are in good agreement with the limestone calcium values. However, a relative depletion in Ca^{40} of about three percent is indicated. In view of the Homestead meteorite results, and the calculations made in the first part of this section, the validity of this apparent depletion should remain in doubt until further work can be done. Because of the wide implications of this result the Pasamonte calcium should be remeasured.

Original calcium in lepidolites is discussed in the section following.

2. THE DETECTION AND MEASUREMENT OF RADIOGENIC CALCIUM

The lepidolites chosen for analysis were selected because of their extreme age and because other analytical work had already been carried out on samples from the same geologic source. In this section the samples are briefly discussed from an analytical viewpoint and in the next section from a geologic age viewpoint.

Analytical Results

The isotope ratios obtained in isotope dilution measurements on lepidolites are given in Table 20. Errors are assigned on the basis of a normal reproducibility of $\pm 1\%$. In particularly good runs, the error in the measured ratios ($^{40}/^{42}$) and ($^{44}/^{42}$), is thought to be slightly less, since fractionation effects are less important than for other ratios. When the measurement was not optimum, slightly larger errors were assigned on the basis of the peak-to-peak precision.

The application of the formulae and error estimates in Part II, Section 2, to the data in Table 20 results in the values given in Table 21.

Where the stated values may be compared, as in the case of the different values of (w_C/w_S) computed on the basis of different isotope ratios, the observed differences are fairly consistent with the stated errors. In these runs, and in measurements of lepidolite calcium without isotope dilution, some of the small differences between (w_C/w_S) as computed from different ratios could be interpreted as a slight heavy fractionation of lepidolite calcium relative to the calcium standard and others could be interpreted as a slight light fractionation, but such differences are generally within the indicated experimental error. Assuming that the

TABLE 20. Calcium Isotope Dilution Measurements on Lepidolites

Isotope Dilutions with Ca⁴² Spike

<u>Sample</u>	<u>(⁴⁰/₄₂) I.D.</u>		<u>(⁴³/₄₂) I.D.</u>		<u>(⁴⁴/₄₂) I.D.</u>		<u>(⁴⁸/₄₂) I.D.</u>		<u>Weight of Lepidolite (grams)</u>	<u>Weight of Spike Calcium (micrograms)</u>
Bob Ingersoll	0.8189	0.8	0.001664	1	0.01712	0.8	0.001355	1	1.025	102.5
Brown Derby #503	3.303	0.8	0.004996	1	0.06993	0.8	0.006211	1	1.238	61.5
Brown Derby #499	1.208	1	(0.0021)		0.02468	1	(0.0019)		1.055	102.5
Bikita I.D. III	1.272	1.2		0.0264	1		0.841	102.5

Isotope Dilutions with Ca⁴⁸ Spike

	<u>(⁴⁰/₄₈) I.D.</u>		<u>(⁴²/₄₈) I.D.</u>		<u>(⁴³/₄₈) I.D.</u>		<u>(⁴⁴/₄₈) I.D.</u>			
Skuleboda	7.525	1	0.04802	1	0.00990	1	0.1573	1	1.000	17.6
Bikita I.D. I	2.198	1	0.0141	2		0.463	1	1.000	65.0
Bikita I.D. II-A	1.56	1	0.0103	1		0.0341	1	0.869	97.5
Bikita I.D. II-B	1.58	1.4	0.0099	2		0.0350	1	0.869	97.5

Estimates of per-cent standard deviation are given to the right of the measured values.

TABLE 21. Results of Calcium Isotope Dilution Measurements

Isotope Dilutions with Ca⁴² Spike

Sample	$\left(\frac{w_c}{w_s}\right)$						$\left(\frac{w_r}{w_s}\right)$	w_c	w_r	Per Cent Radiogenic Calcium
	$\left(\frac{44}{42}\right)$ I.D.	$\left(\frac{43}{42}\right)$ I.D.	$\left(\frac{48}{42}\right)$ I.D.	Adopted						
Bob Ingersoll	0.403 .005	0.397 .010	0.410 .007	0.403 .005	0.086 .009	40.3	8.65 .9	17.6 1.8		
Brown Derby #503	2.38 .03	2.34 .04	2.33 .04	2.35 .02	0.203 .030	117.0	10.1 1.5	8.0 1.2		
Brown Derby #499	0.682 .014	0.682 .014	0.126 .014	66.3	12.2 1.4	15.5 1.8		
Bikita I.D. III	0.746 .014	0.746 .014	0.115 .016	90.9	14.0 1.9	13.3 1.8		

Isotope Dilutions with Ca⁴⁸ Spike

Sample	$\left(\frac{44}{48}\right)$ I.D.		$\left(\frac{42}{48}\right)$ I.D.		Adopted	$\left(\frac{w_r}{w_s}\right)$	w_c	w_r	Per Cent Radiogenic Calcium
Skuleboda	5.14 .05	5.18 .05	5.16 .04	0.432 .062	90.8	7.6 1.1	7.7 1.1
Bikita I.D. I	1.33 .014	1.35 .027	1.33 .013	0.200 .020	86.0	13.0 1.3	15.1 1.5
Bikita I.D. II-A	0.910 .014	0.934 .014	0.922 .010	0.121 .013	103.0	13.6 1.4	11.6 1.2
Bikita I.D. II-B	0.940 .021	0.890 .020	0.915 .015	0.142 .024	104.0	15.9 2.7	13.4 2.2

For all quantities except w_c , estimates of standard deviation are given to the right of the calculated values.

common calcium observed is dominantly original lepidolite calcium, as was indicated by a blank run (see Part II, Section 1), it can be safely stated that lepidolite calcium is not fractionated relative to the standard calcium by more than $\pm 2\%$ in the (48/40) ratio.

The Bikita Quarry Lepidolite

The Bikita Quarry lepidolite sample was obtained from Prof. Louis H. Ahrens, who collected it in Southern Rhodesia. It was a portion of the M.I.T. sample N45 which was sent out to seven different laboratories throughout the world as an intercalibration standard (Herzog, et al., 1955). The fine-grained lepidolite sample was used in the form in which it was sent out as a standard, and contained about one to two percent quartz plus a very small amount of topaz as impurities. Under microscopic examination no evidence of weathering was observed, but minor twinning, and the presence of a few small inclusions was noted.

The Bikita lepidolite was completely analyzed three times, as a control experiment, with the complete chemistry carried out by two different workers. One of the portions was also analyzed twice by mass spectrometer. The results are repeated for comparison in Table 22. Variations in w_c are due mainly to variations in laboratory contamination. The chemistry for the Bikita I.D. I was performed by W.H. Pinson, and that on the other two runs by the author. In the Bikita I.D. II run the lepidolite was washed with 1.0 N HCl and then in boiling water for about ten minutes. No measureable loss of radiogenic calcium resulted, and the quantity of common calcium was certainly not decreased. In the other two runs very dilute HCl and cold distilled water were employed for washing.

TABLE 22. Results on Bikita Calcium

Sample	$\frac{w_c}{w_s}$			Adopted	w_c	w_r	Per Cent Radiogenic Calcium
	$\left(\frac{44}{48}\right)$ I.D.	$\left(\frac{44}{42}\right)$ I.D.	$\left(\frac{42}{48}\right)$ I.D.				
Bikita I.D. I	1.33 ± .014	1.35 ± .021	1.33 ± .013	86.0	13.0 ± 1.3	15.1 ± 1.5
Bikita I.D. II-A	0.910 ± .014	0.934 ± .014	0.922 ± .010	103.0	13.6 ± 1.4	11.6 ± 1.2
Bikita I.D. II-B	0.940 ± .021	0.890 ± .020	0.915 ± .015	104.0	15.9 ± 2.7	13.4 ± 2.2
Bikita I.D. II avg.	0.920 ± .010	103	14.2 ± 1.3	12.1 ± 1.2
Bikita I.D. III	0.746 ± .014	0.746 ± .014	90.9	14.0 ± 1.9	13.3 ± 1.8
Average Value	13.9 ± 1.0

Insoluble Residue

In all three analyses there was a small insoluble residue, which was saved for analysis. Optical spectrographic examination revealed dominant silicon and aluminum content, but a trace of calcium in a concentration of about 0.5 ppm (of original lepidolite sample) was indicated. The insoluble residue was studied under the microscope by the immersion method and was positively identified as topaz on the basis of the following observations. The residue consisted of irregular, colorless grains with good cleavage, and contained numerous inclusions. It was anisotropic, non-pleochroic, exhibited parallel extinction in longitudinal section, a positive biaxial interference figure, and very weak birefringence. All of the grains had an index of refraction very close to 1.620.

A portion of the residue was mounted directly on a filament with a borax binder, and examined mass spectrometrically. A small amount of calcium emission was observed, roughly yielding the isotope ratios $^{42}/^{40} = 0.0067$, $^{44}/^{40} = 0.0220$. Therefore, no significant amount of radiogenic calcium was contained in the insoluble residue.

Isotope Ratios of Bikita Calcium

A sample of Bikita calcium with no added spike was run along with the third isotope dilution run. The results are given in Table 23. It was at first thought that a definite enrichment in the lighter isotope was indicated, based mainly on the relative values of the ($^{42}/^{40}$) and ($^{44}/^{40}$) ratios. On later runs, it was established that a very minor amount of ^{42}Ca spike was introduced into the unspiked solutions, probably by unobservable spattering of the spiked solution, causing the ($^{42}/^{40}$) ratio to be too high. In the case of this sample, about 0.01 micrograms of

TABLE 23. Comparison of Unspiked Bikita Calcium with "Common" Calcium

<u>Isotope Ratio</u>	<u>$\frac{48}{40}$</u>	<u>$\frac{44}{40}$</u>	<u>$\frac{43}{40}$</u>	<u>$\frac{42}{40}$</u>	<u>Average</u>
Bikita Ca (unspiked)	0.00176	0.0192	0.00122	0.00612*
Common Ca	0.00210 ₂	0.0222 ₅	0.00143 ₀	0.00680
% Radiogenic Ca ⁴⁰ in Bikita Ca	15.9 ± 1.4	13.4 ± 1.4	14.3 ± 1.4	*	14.5

*Discarded due to contamination by Ca⁴² spike.

Ca⁴² spike were apparently introduced as contamination, and in the worst case 0.05 micrograms were introduced. Thus, only the ratios involving Ca⁴² were affected, and no significant introduction of the unspiked solution into the spiked solution occurred.

Excluding the (40/42) ratio, the agreement between the excess Ca⁴⁰ content computed from the different isotope ratios is good. If anything, a very slight enrichment in the lighter isotopes is indicated as was the case in Bikita I.D. II-B. However, in Bikita I.D. II-A and I.D. I, a slight enrichment in the opposite direction was indicated (compare Table 22 and Fig. 22). It was therefore concluded that the slight variations were not due to an abnormal original calcium composition in the lepidolite, but were merely random errors attributable to the mass spectrometric technique. The degree to which the original composition may not be normal is included in the final estimates of error.

In view of the fact that the percent radiogenic calcium is dependent upon the amount of laboratory contamination, which varied, the results in Tables 22 and 23 are in good agreement, and support the observation that contamination was in the range of ten to twenty micrograms per sample.

The Brown Derby Lepidolites

The Brown Derby (Colorado) lepidolite specimens, #499 and #503, were obtained from Prof. E.W. Heinrich. They are two paragenetically different lepidolites (Heinrich, 1953). Details of their geological environment had not yet been obtained from Professor Heinrich at the time of this writing. Spectrochemical analyses by C.E. Harvey of both samples, however, have been reported by Heinrich (1953).

Both of the specimens were medium-grain (1 to 3 mm diameter flakes), and were very fresh and clean. After final purification, several hundred grains were examined under the microscope and no impurities were detected. Many of the grains had long thin liquid or air bubbles as inclusions.

The Bob Ingersoll Lepidolite

The Bob Ingersoll lepidolite (Black Hills, South Dakota) was obtained from L.H. Ahrens, and was also an international interlaboratory calibration standard (M.I.T. no. A106). The purified specimen appeared to contain less than 0.5% impurities, was medium grain-size, and the grains were relatively free of inclusions and showed no evidence of alteration. The lepidolite grains were complex intergrowths, and had a peculiar feature which may be due to a combination of twinning and strain. This was a pattern of similarly oriented tetragonal pyramids which had the appearance of an aggregate of quartz crystals. The angles of extinction under crossed-Nicols of the two adjacent sides of the pyramids differed by about 30°.

Skuleboda Lepidolite

The Skuleboda (Sweden) lepidolite was also obtained from Prof. E.W. Heinrich. A complete spectrochemical analyses and x-ray study was

published by Heinrich (1953). The specimen contained large books of lepidolite. A fresh book was chosen for analysis and the chemistry on this sample was performed by W.H. Pinson.

Comparison of Isotope Dilution Results for Total Calcium with Previous Optical Spectrographic Analyses

The total calcium content for each of the lepidolites determined by isotope dilution is listed in Table 24 along with published spectrochemical analyses of the same samples. The measurements by Holyk (1952) and Ahrens (1951) were careful determinations specifically aimed at calcium determination. The measurements by Harvey (Heinrich, 1953) were a part of a routine spectrochemical analysis for all elements. The isotope dilution results are corrected for 10 to 20 micrograms of contamination by common calcium, as was indicated by a blank run (Part II, Section 1), and corroborated by the Bikita Ca results.

It is suggested that Harvey's estimates were consistently low. The measurement by Holyk was made on the same sample of Bikita quarry lepidolite as that used in this research. Since the specific samples of the Bob Ingersoll measured by Holyk and Ahrens are not known, little can be concluded from a comparison of results on this locality.

Summary

The percent of total calcium which was radiogenic ranged from eight to eighteen percent in the five Pre-Cambrian lepidolites from four different localities which were examined. This result is in general agreement with Holyk (1952), who estimated that a group of Pre-Cambrian lepidolites contained from three to forty percent radiogenic calcium. The quantity of radiogenic calcium could thus be determined with an error of from ten to twenty percent in the analyzed samples. It appears that

TABLE 24. Comparison of Calcium Analyses by Different Methods

<u>Sample</u>	<u>Total Calcium by Isotope Dilution (ppm)</u>	<u>Corrected For 10 to 20 Micrograms Contamination</u>	<u>Total Calcium by Optical Spectrograph Analyst Result(ppm)</u>	
Bikita Quarry	1) 99
	2) 117	90 - 100	Holyk	60
	3) 105
Bob Ingersoll	49	30 - 40	Holyk	93
			Ahrens	50
				35
Brown Derby #503	127	110 - 120	Harvey	14
Brown Derby #499	88	70 - 80	Harvey	35
Skuleboda	99	80 - 90	Harvey	14

radiogenic calcium determinations can be made on most old lepidolites. Until further development work is done on the measurements of relative calcium isotope abundances, it appears that the determination of K/Ca ages will be confined to lepidolites, sylvites, and a few other rare minerals.

3. A COMPARISON OF AGES OBTAINED BY DIFFERENT METHODS

The Calculation of K/Ca Ages

K^{40} decays by β^- emission to Ca^{40} , with a decay constant λ_{β} , and by electron-capture to A^{40} with a decay constant λ_{κ} . The total rate of K^{40} decay is then $\lambda = \lambda_{\beta} + \lambda_{\kappa}$ disintegrations/year. The branching ratio of K^{40} is defined as $R = \lambda_{\kappa} / \lambda_{\beta}$, and is therefore equivalent to the ratio of radiogenic argon to radiogenic calcium.

The concentration of K^{40} at any time t after formation of a closed system with an original K^{40} content of K_0^{40} is:

$$K^{40} = K_0^{40} e^{-\lambda t} \quad (13)$$

The excess concentration of Ca^{40} after time t is:

$$Ca_{\text{radiogenic}}^{40} = \frac{1}{R+1} K^{40} (e^{\lambda t} - 1) \quad (14)$$

If either the Ca^{40}/K^{40} ratio or the A^{40}/K^{40} ratio is known, the "age" of the rock may be calculated:

$$\text{Calcium:} \quad t = \frac{1}{\lambda} \ln \left(1 + \frac{(R+1) Ca^{40}}{K^{40}} \right) \quad (15a)$$

$$\text{Argon:} \quad t = \frac{1}{\lambda} \ln \left(1 + \frac{(R+1) A^{40}}{(R)K^{40}} \right) \quad (15b)$$

The accepted value of λ has undergone remarkable fluctuations in recent years, with corresponding fluctuations in the ideas concerning the nature of the earth's crust, though the physical determinations of λ_{β} have been fairly consistent. The extensive literature through 1950 has been summarized by Birch (1951) and the data through 1953 by Endt

Kluyver (1954). The "preferred value" of λ has been given by Sawyer and Wiedenbeck (1950) as $(0.55 \pm 0.02) \times 10^{-9} \text{ yr}^{-1}$, by Endt and Kluyver as $0.53 \times 10^{-9} \text{ yr}^{-1}$, and Birch (1951) prefers a value slightly higher than $0.55 \times 10^{-9} \text{ yr}^{-1}$. Since the value $\lambda = 0.55 \times 10^{-9} \text{ yr}^{-1}$ has been used for most of the $\text{K}^{40}/\text{A}^{40}$ age calculations in the literature, this value will be used in this work.

On the basis of the recent data, it is probably safe to say ~~that~~ the true value of R lies in the range 0.085 - 0.150. It should be pointed out that this uncertainty in R causes a large uncertainty in $\text{K}^{40}/\text{A}^{40}$ ages, but is unimportant in $\text{K}^{40}/\text{Ca}^{40}$ ages, introducing an uncertainty of less than 4%, which is small relative to the error in the determination of Ca^{40} .

If the concentrations of $\text{Ca}^{40}_{\text{radiogenic}}$ and of total potassium in a mineral are known, and the constants $\lambda = 0.55 \times 10^{-9} \text{ yr}^{-1}$, $R = 0.125$, $\text{K}^{40} = 0.00119\%$ of total potassium are used, the "age" of the mineral is given by:

$$t = 1.82 \times 10^9 \ln \left(1 + 9300 \frac{\text{Ca}^{40}}{\text{K}} \right) \quad (16)$$

K - Ca Ages

The total K content, radiogenic calcium content, and calculated age of each of the samples measured is summarized in Table 25. In Table 26 these results are compared with results obtained by different age methods.

Discussion

It is apparent from Table 26 that the determination of geologic age is not a straightforward problem. In addition to the comparisons

TABLE 25. K - Ca Ages

<u>Sample</u>	<u>K (%)</u>	<u>Ca⁴⁰ radiogenic (ppm)</u>	<u>"Age" (m.y.)</u>
Bikita Quarry I.D. I	(6.47)	13.0 ± 1.3	1920 ± 120
Bikita I.D. II	6.47	14.2 ± 1.3	2020 ± 110
Bikita I.D. III	(6.47)	14.0 ± 1.9	2000 ± 160
Brown Derby #503	8.36	10.1 ± 1.5	1370 ± 150
Brown Derby #499	8.25	12.2 ± 1.4	1570 ± 130
Bob Ingersoll	8.77	8.65 ± .90	1180 ± 90
Skuleboda	7.70	7.6 ± 1.1	1190 ± 150

listed here, the literature contains a large number of less complete comparisons (geochronological identity of specimens used in different methods not well-established, or fewer or rougher methods of age determination applied) which may be found in the articles by Holmes (1954), Ahrens (1955), Faul (1954), Kulp (1955), and in a number of abstracts published by the group at the Carnegie Institution (Aldrich, Davis, Tilton, Wetherill, Nicolaysen). The relationships between different age methods are being extensively investigated by a number of laboratories, and a great deal of additional data will become available within the next five years. It is premature to attempt to draw many definite conclusions at the present time, but a discussion of the possible implications of the few data which are now available may prove useful in designing future research.

Lead - Ages

The uranium-lead age of 1600 ± 50 m.y. for the Bob Ingersoll Mine may be considered a true age. Although the published Brown Derby Mine

TABLE 26. Comparison of Ages Obtained by Different Methods

Locality	Uranium-Lead Age			"Best Value"
	$\frac{206}{238}$	$\frac{207}{238}$	$\frac{207}{206}$	
1. Black Hills, South Dakota (Bob Ingersoll)	(uraninite) (206/238 and 207/238 agree within 2%.)			1600 ± 50 ^a
2. Brown Derby Mine, Colorado	935 (zircon)	1100	1425 ^h	(1425)
3. Bikita Quarry, Southern Rhodesia	In this general area the average lead age is about 2650. ^j			
4. Skuleboda, Sweden				
Capetown, South Africa ⁱ	350	375	550 ± 50	(zircon)
Uncompaghre, Colorado ⁱ	1050	1380	{ 1810 1650	{ (apatite) (biotite)
Bagdad, Arizona ⁱ	630	750	1190	(zircon)
Fission Mine, Wilberforce, Ontario ^h	1077		1035 ^h	(uraninite)
Pope Tantalum Mine, Southern Rhodesia ^j			2510	(microlite)

- a. Wetherill, et al. (1955).
- b. Ahrens (1955).
- c. M.I.T. - unpublished.
- d. Tomlinson and Das Gupta (1955).
- e. Strickland (1955).
- f. This research.
- g. Presented orally by Wetherill at 1955 American Geophysical Union meeting in Washington.
- h. Paul (1954).
- i. Aldrich, et al. (1954). The 1980 age was obtained on a particularly fine-grained lepidolite.
- j.

TABLE 26. (continued)

Optical Spec.	Rubidium-Strontium Age			Potassium-Argon Ages		Potassium-Calcium Ages [†]
	Carnegie	Tomlinson Das Gupta	M.I.T.	R=0.085	R=0.125	
850 ± 200 ^b 1500 ± 300	2050 ± 150	a	1390 ^d	2060* ^c	1710 ± 90* 1360 ± 70* ^e	1190 ± 90*
					lepidolite-1610 ^g 1260 muscovite-1730 microcline-1275	
950 ± 200 ^b	1980 ⁱ 1730 1700 1760 1790				1080 780 ⁱ (microcline)	1370 ± 150 1570 ± 130
2150 ^k	3040 ^l 3340 ± 300 ^b			3060* ^m	3140 2500 ⁱ (lepidolite)	1980 ± 100*
				1290* ^m		1190 ± 150*
5.	820 ± 40 (lepidolite)					
6.	1650 (biotite)					
7.	{1640 (muscovite)					
	{1900 (lepidolite)					
8.	1180 ± 90 (biotite) ^a					
9.	2150 ± 200 3740 ± 370				2610 (2150)	

j. Holmes (1954).

k. Ahrens and MacGregor (1951).

l. Davis and Aldrich (1953); their stated value was 3160. This was corrected to a value based on the same decay constants as the M.I.T. values.

m. Herzog, et al. (1955).

* Analyses made on the same lepidolite sample by different methods at M.I.T.

uranium-lead ages disagree, a number of age determinations in the same geological province (Aldrich, et al., (1955)) indicate an age of 1500 m.y. The true age of the Brown Derby sample is probably 1400-1600 m.y. No uranium-lead ages have been published for the Bikita Quarry pegmatites, but interlocking lead ages in the same geological province are of the order of 2650 m.y. (Holmes, 1954).

The Wilberforce, Ontario, ages interlock and may therefore be regarded as correct. In all other cases in Table 26 considerable variations in the different uranium-lead ages are apparent. In such cases, if it is assumed that the discrepancies are due to 1) recent lead leaching (Collins, et al., 1954), then the 207/206 age is "correct"; 2) ancient lead leaching (Kulp and Eckelmann, 1955), then the 207/206 age is a "minimum age"; 3) radon leakage (Kulp, et al., 1954), then the 207/238 age is "correct"; 4) a combination of factors, then the age is in doubt. A larger amount of data is required before a conclusion can be drawn, as to which assumption is most nearly correct, though many workers at present favor the second assumption.

Rubidium-Strontium Ages - Analytical Problems

A definite disagreement between Rb/Sr ages determined by optical spectrographic techniques and those determined by isotope dilution techniques is apparent. The reason for this disagreement has not yet been determined. Excellent agreement between the M.I.T. and Carnegie laboratories is indicated by their results on the Bob Ingersoll lepidolite and Bikita lepidolite. Similar agreement has been obtained on two other samples (Herzog, et al., 1955). Rb/Sr age given by Tomlinson and Das Gupta is considered to be too low. Before making their determination,

Tomlinson and Das Gupta boiled the lepidolite in aqua regia, but their young age was not due to a low strontium determination, but to a high rubidium determination!

It is suggested that the Rb/Sr ages given by M.I.T. and Carnegie in Table 26 should be considered analytically correct to within a few percent. The Rb⁸⁷ half-life used in most of the computations was about 60 billion years.

Rubidium-Strontium Age Relationships

The rubidium-strontium ages in Table 26 for localities for which "true" ages may be inferred are 12-28% high. The difference between Carnegie's Rb/Sr ages and the corresponding 207/206 ages varies from -10% to +60%, with all but two of the values lying above +15%. The data are thus consistent with the proposal (e.g., Kohman and Saito, 1955) that the adopted value (60 billion years) for the half-life of rubidium may be 15-30% high.

There is evidence of minor post-formational geochemical alteration of micas in the age of 1980 million years obtained by Carnegie for a fine-grained Brown Derby Mine lepidolite, and in the discrepancy between the muscovite and lepidolite ages for Bagdad, Arizona. These comparisons, combined with the general observation that Rb/Sr ages are high, suggest that rubidium may have been leached from fresh-appearing lepidolites sometime during their history. This conclusion is geochemically quite plausible in view of the abnormally large rubidium content of lepidolites.

Potassium-Argon Age Relationships

Many workers (for a summary see Wasserburg and Hayden, 1955) pioneering in the use of K/A ratios for geologic age determination, have

observed a consistent relationship between K/A "ages" of feldspars and related uranium-lead "ages." On the basis of these results, it was tentatively concluded that the branching ratio for K^{40} decay is lower (0.8 to 0.9) than has been indicated by physical measurements, and that argon is well-retained by feldspars. Recently, however, many anomalously low K/A ages have been found (Aldrich, et al., 1955, and oral communications) for feldspars. The Brown Derby microcline in Table 26 is an example. It thus now appears that feldspars may lose a variable amount of argon. The Carnegie group also found (Aldrich et al., 1955) that micas gave K/A ages consistently 0-15% lower than corresponding Rb/Sr ages when a branching ratio, $R = 0.085$, was assumed. Whether this relationship will persist as more comparisons are made remains to be seen.

On the basis of the scanty K/Ca age data obtained it now appears that the assumption that K/A "ages" are low because of an incorrect physical determination of the branching ratio is not justified.

Potassium-Calcium Age Relationships

The relationships found between K/Ca "ages" and those determined by other methods are summarized in Table 27. The following conclusions may be drawn:

- 1) K-Ca ages are lower than Rb-Sr ages to a variable degree, and in view of the estimated errors this variability is definitely significant;
- 2) K/Ca ages are generally lower than U/Pb ages, and the difference is probably variable;
- 3) K/Ca ages do not support the hypothesis that the physically determined value for the branching ratio of K^{40} decay is too high.

TABLE 27. Relationship of K-Ca Ages to Ages Obtained by other Methods

	<u>K/Ca Age</u>	<u>K/Ca Age</u>	<u>K/Ca Age</u>	
	<u>U/Pb Age</u>	<u>Rb/Sr Age</u>	<u>K/A Age</u>	<u>R-0.085 R-0.125</u>
Black Hills	0.75	0.58	0.70	0.88*
Brown Derby Mine, Colorado**	0.91 1.05	0.77 0.88
Bikita Quarry, Southern Rhodesia	0.75	0.65	0.65	0.79
Skuleboda, Sweden	0.92

*Using Strickland's result.

**Using a Rb-Sr age of 1775 m.y., and a U/Pb age of 1500 m.y.

The fact that K/Ca ages (and K/A ages, if a branching ratio greater than 0.1 is used) are relatively low may be due to several factors. The accepted value for the relative isotopic abundance of K^{40} may be too high (see Part III), though this factor would only amount to about four percent. It is possible that solutions with a normal crustal ratio (200) of potassium to rubidium might enrich a lepidolite in potassium while simultaneously removing rubidium. It is certainly possible that calcium could have been recently leached from these lepidolites, though it is difficult to see why strontium would not be similarly affected.

However, the absolute rate of the beta decay of K^{40} appears to be well established, and Birch (1951) actually considers the adopted value to be somewhat low.

Summary

K/Ca ages obtained for lepidolites from four localities were in variable disagreement with related ages obtained by other methods. The fact that the K/Ca ages are in general relatively low indicates that similar

relationships for K/A ages do not necessarily justify the adoption of a value of 0.085 for the branching ratio of K^{40} decay. The fact that K/Ca ages were low by a variable amount relative to ages obtained by other methods suggests that these lepidolites may have experienced post-formational geochemical alterations to a variable degree.

4. THE BRANCHING RATIO OF K^{40} DECAY

If the concentration of both radiogenic calcium and radiogenic argon are determined for the same mineral, a direct estimate of the branching ratio of K^{40} decay is obtained. The validity of the estimate depends on the extent to which the mineral tested has remained a closed system relative to argon and calcium. Since direct physical determinations depend on the exceedingly difficult quantitative observation of the low energy (3000-4000 e.v.) x-ray associated with potassium K-capture, and the extrapolation of the beta energy spectrum to zero energy, independent geological determinations of the branching ratio are extremely desirable.

Published Determinations

The published determinations of the branching ratio are given in Table 28. Values published through 1950 are taken from the tabulation by Birch (1951).

Experimental evidence (Sawyer and Wiedenbeck, 1950) and theoretical considerations (Morrison, 1951) indicate a one-to-one correspondence between K-capture events and gamma emissions. Therefore $\lambda_{\gamma}/\lambda_{\beta}$ should correspond to the branching ratio, and Endt and Kluyver's (1954) weighted average of this ratio is included.

Only the latest published values of Wasserburg and Shillibeer are given, since they are revisions of earlier published values which had been based on fewer data.

Published Results on Stassfurt Sylvite

Inghram, et al. (1950), measured the radiogenic calcium and argon concentration in a Stassfurt sylvite sample and obtained a branching ratio

TABLE 28. Published Determinations of the Branching Ratio of K^{40} Decay

A. Physical determinations

1. Measurements of gamma-emission	
Endt and Kluyver (1954)	
weighted average of all measurements through late 1953	0.12
2. Measurements of x-rays associated with K-capture	
Thompson and Rowland (1943)	(3 to 4)
Bleuler and Gabriel (1947)	(1.9 ± 0.4)
Ceccarelli, Quarcini, and Rostagni (1950)	0.07
Graf (1950)	0.127 to 0.67
Sawyer and Wiedenbeck (Auger electrons)(1950)	0.135
3. Method not stated	
Moljk, <u>et al.</u> (1955)	0.124-0.136

B. Geological determinations

1. Comparison of K/A ages with U/Pb ages	
Harteck and Suess (1947)	0.1
Aldrich and Nier (1948)	0.02 ± 0.09
Shillibeer, <u>et al.</u> (1954)	0.09
Wasserburg and Hayden (1955)	0.085 ± 0.005
2. Comparison of Radiogenic A^{40} and Ca^{40} concentrations in a single specimen	
Inghram, <u>et al.</u> (1950) - sylvite	0.126 ± 0.003
Strickland and Backus (1955) - lepidolite	0.15 ± 0.02
3. Other methods	
Ahrens and Evans (1948)	
(Based on total calcium in lepidolite)	$< 1.4 \pm 0.2$

of 0.126 ± 0.003 . If it is assumed that their sample was pure KCl, their results indicate an age for the Stassfurt sylvite of 89 million years (using $\lambda = 0.55 \times 10^{-9} \text{yr}^{-1}$, $R = 0.125$). For comparison, Moljk, et al. (1955), measured the A^{40} content of a sample of Stassfurt sylvite by a neutron activation method, and obtained an age of 52 million years (using $\lambda = 0.55 \times 10^{-9} \text{yr}^{-1}$, $R = 0.125$), though they did not give an estimate of their error.

Since Gentner, et al. (1953) have found evidence of argon leakage from sylvite, the branching ratio obtained by Inghram, et al., should be considered a minimum value.

Results of This Research

L. Strickland (1955) measured the radiogenic A^{40} content of the Bob Ingersoll lepidolite specimen discussed in Sections 2 and 3, and obtained a value, $A_{\text{radiogenic}}^{40} = 0.73 \times 10^{-3}$ 5% c.c. s.t.p. A comparison of this result with the measured quantity of $Ca_{\text{radiogenic}}^{40}$ is included in Table 29.

A value of $0.15 \pm .02$ was thus obtained for the branching ratio of K^{40} decay. The stated error is an estimate of the absolute accuracy of the analytical results, and is believed to be a realistic estimate. The probability of argon leakage and calcium leaching was discussed in Section 3. Since there is some evidence that lepidolites have been geochemically altered after original formation, additional geologic determinations of the branching ratio should be made to determine the nature of the alterations and establish the significance of such determinations. It is the opinion of the author that the escape of A^{40} is more likely than the removal of Ca^{40} , and that the values $R = 0.15 \pm 0.02$ should be regarded as a minimum value.

TABLE 29. A Determinations of the Branching Ratio of K^{40} Decay

<u>Sample</u>	<u>$A_{\text{radiogenic}}^{40}$ (ppm)</u>	<u>$Ca_{\text{radiogenic}}^{40}$ (ppm)</u>	<u>$\frac{A^{40}}{Ca^{40}}$</u>
Bob Ingersoll lepidolite	$1.305 \pm .065$	8.65 ± 0.90	$0.151 \pm .017$

Summary

A determination of the A^{40} content (Strickland, 1955) and the Ca^{40} content of the same lepidolite specimen indicates a branching ratio of $0.15 \pm .02$ for K^{40} decay. This result is in agreement with recent physical determinations, and disagrees with recent determinations based on a comparison of K/A ages and U/Pb ages.

PART V. RECOMMENDATIONS FOR FURTHER RESEARCH

Argon Measurements

Additional amounts of each of the lepidolite samples for which radiogenic Ca^{40} concentrations have been measured, are available for argon analysis. It is hoped that the argon analyses will be made at this laboratory in the near future. Such measurements would provide four additional independent geologic estimates of the branching ratio of K^{40} decay, and thus would be of considerable value.

Additional K/Ca Ages

The few K/Ca "ages" obtained in this research are related to ages obtained by other methods in a discrepant and inconsistent manner. However, the amount of data obtained is not large enough to support any definite conclusions concerning the causes of the discrepancies. It is therefore strongly recommended that a program of determination of Rb/Sr, K/A, and K/Ca "ages" for the same lepidolite specimens should be continued. It is also suggested that further work on the relative isotope abundances of potassium should be carried out (see Part III).

Mass Spectrometric Techniques

In order to critically study natural variations in the isotopic composition of "common" calcium, the development of a method of mass spectrometric measurement of the relative isotope abundances of calcium more precise than the method used in this research is desirable. It is suggested that the development of a less complex type of primary ion source, as discussed in Part I, Sections 2, 3, and 4, might result in such an increase in precision.

APPENDIX I. THERMAL BEHAVIOR OF FILAMENTS

In order to gain a better understanding of and a closer control over the thermionic ion source used in this work, it was necessary to make a rough temperature calibration of the filaments used in the source. Several different types of filaments, some with a coating of calcium compounds, were studied in an evacuated bell-jar (see Figure 25). Temperatures were measured approximately with a Leeds and Northrup #8622 optical pyrometer borrowed from the M.I.T. Heat Measurements Laboratory, and recorded as a function of filament current and voltage. It was found that filament temperature could be estimated from these parameters alone to within about 10-15%, and that there was an excellent short period linear relationship, with a reproducible slope, between temperature and resistance. In addition, it was found that due to the thermal conductivity of the filament, the temperature varied by about 10% over the region in which the sample was generally deposited. On the basis of these considerations, combined with the fact that the thermionic emission behavior was not expected to be highly reproducible in any case, the pyrometer calibration was considered good enough for the immediate purposes of this work.

Since black body conditions were not attained, it was necessary to correct the raw measured temperatures according to Wien's Law:

$$1/\theta - 1/D = (\lambda/C_2) \ln E_\lambda$$

where

θ = true temperature ($^{\circ}$ Kelvin)

D = measured temperature at wavelength

E_λ = spectral emissivity at wavelength

C_2 = 14360 micron-degrees

λ = 0.65 microns (for the instrument used)

The spectral emissivities used were 0.49 for the tantalum and 0.30 for platinum (Hodgman, 1952). The corrections were of the order of 5 per cent, and were therefore not critical.

The data obtained for one batch of platinum-plated tantalum filaments are shown in Figs. 26 and 27, in which the temperature at the center of the filament is plotted as a function of filament resistance and filament current. The points plotted represent measurements made during the initial heating and also those made after prolonged heating at high temperatures. Different batches of platinum-plated filaments were calibrated separately; several plain tantalum filaments and a wolfram filament like that used in the double filament source were also calibrated.

An excellent linear relationship was observed between temperature and filament resistance. The observed spread of points was due mainly to the loss of filament material during prolonged heating. However, during short periods, the linearity was good, and the slope obtained during short period measurements was quite reproducible. Therefore, though the uncertainty in the actual filament temperature was of the order of 10 per cent, the uncertainty in relative temperatures was considerably smaller.

Time Effects

The filaments were left running for various periods of time, and changes in current, resistance, and temperature were observed. Within a period of about fifteen minutes there was generally an increase of $\frac{1}{2}$ - 1% in temperature, with a corresponding increase in resistance. This was apparently due to the attainment of thermal equilibrium. In the initial heating cycle there was generally a large change in filament resistance (see temperature - current graphs) probably due to chemical changes at the filament interface, outgassing, etc. After this, there was a slow change at temperatures of the order of 2000°K,

but the temperature resistance relation was rather stable. Most of the emission measurements discussed in Part I, Section 3, were made on filaments in the stable phase. The increase of positive ion current with time generally observed in calcium runs may be partially attributed to slow period temperature increase, but this by no means can account entirely for the phenomenon.

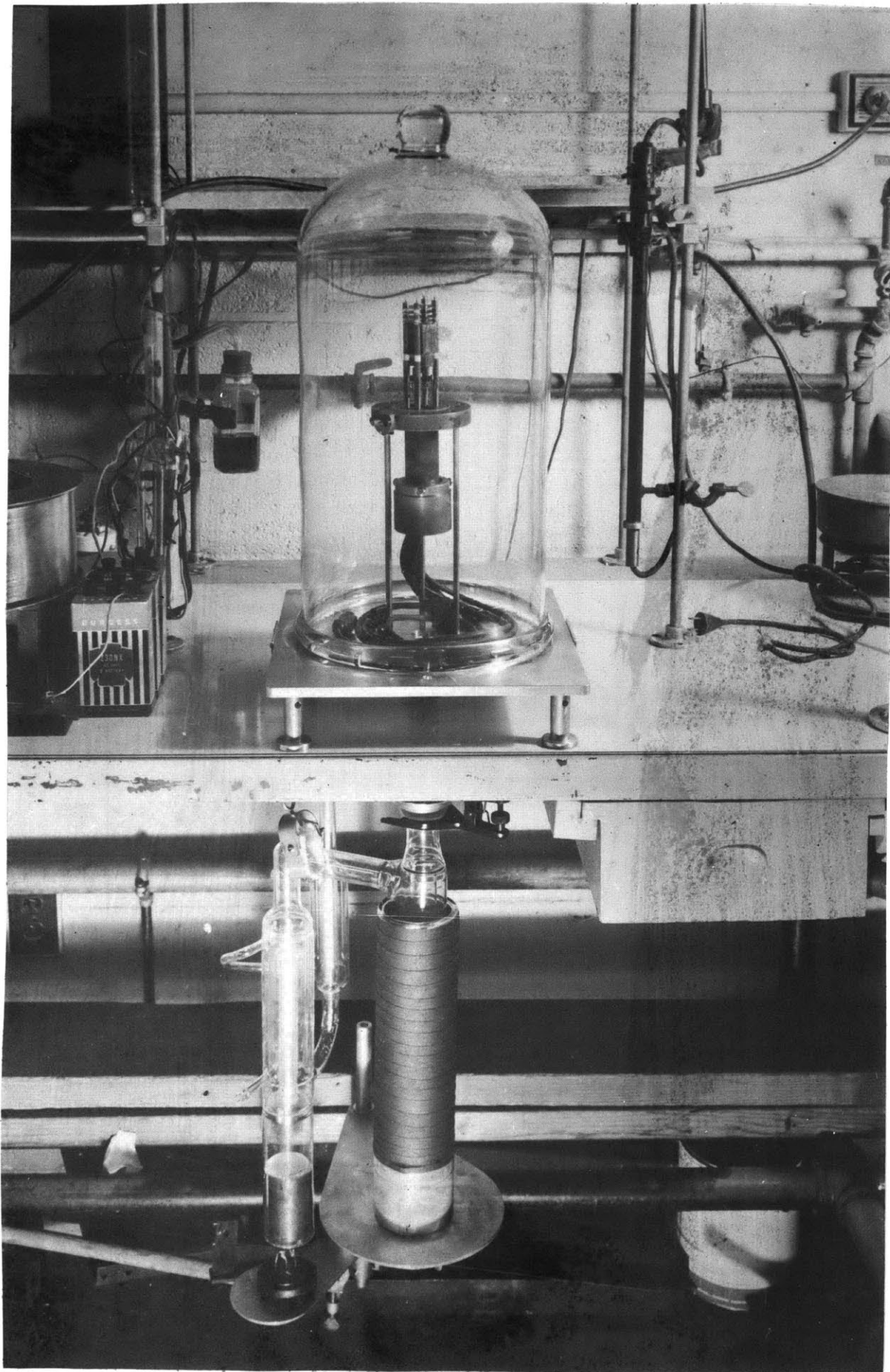


Figure 24. Auxiliary Vacuum System.

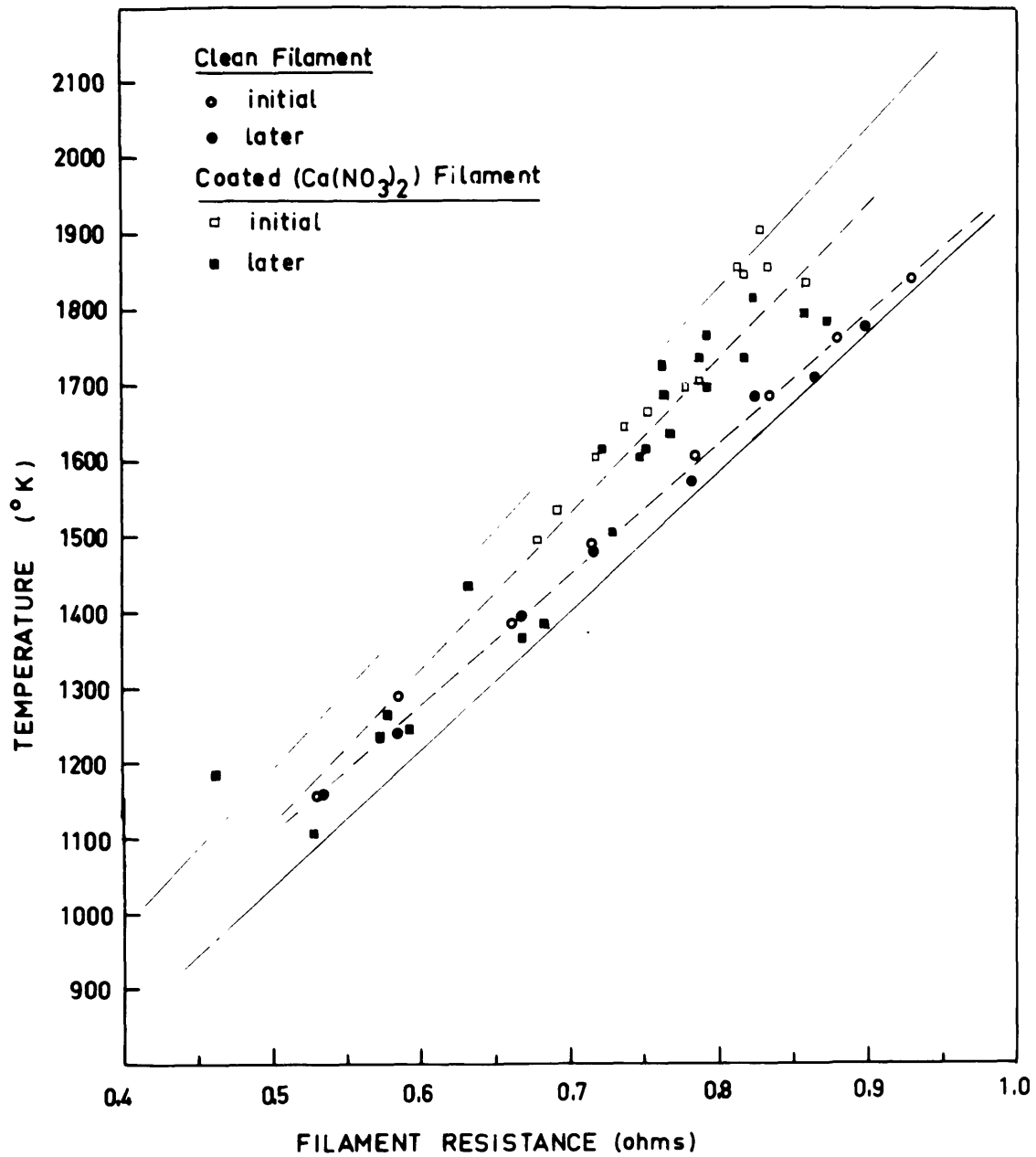


Figure 26. Temperature-Resistance Relationship For Platinum-plated Tantalum Filaments.

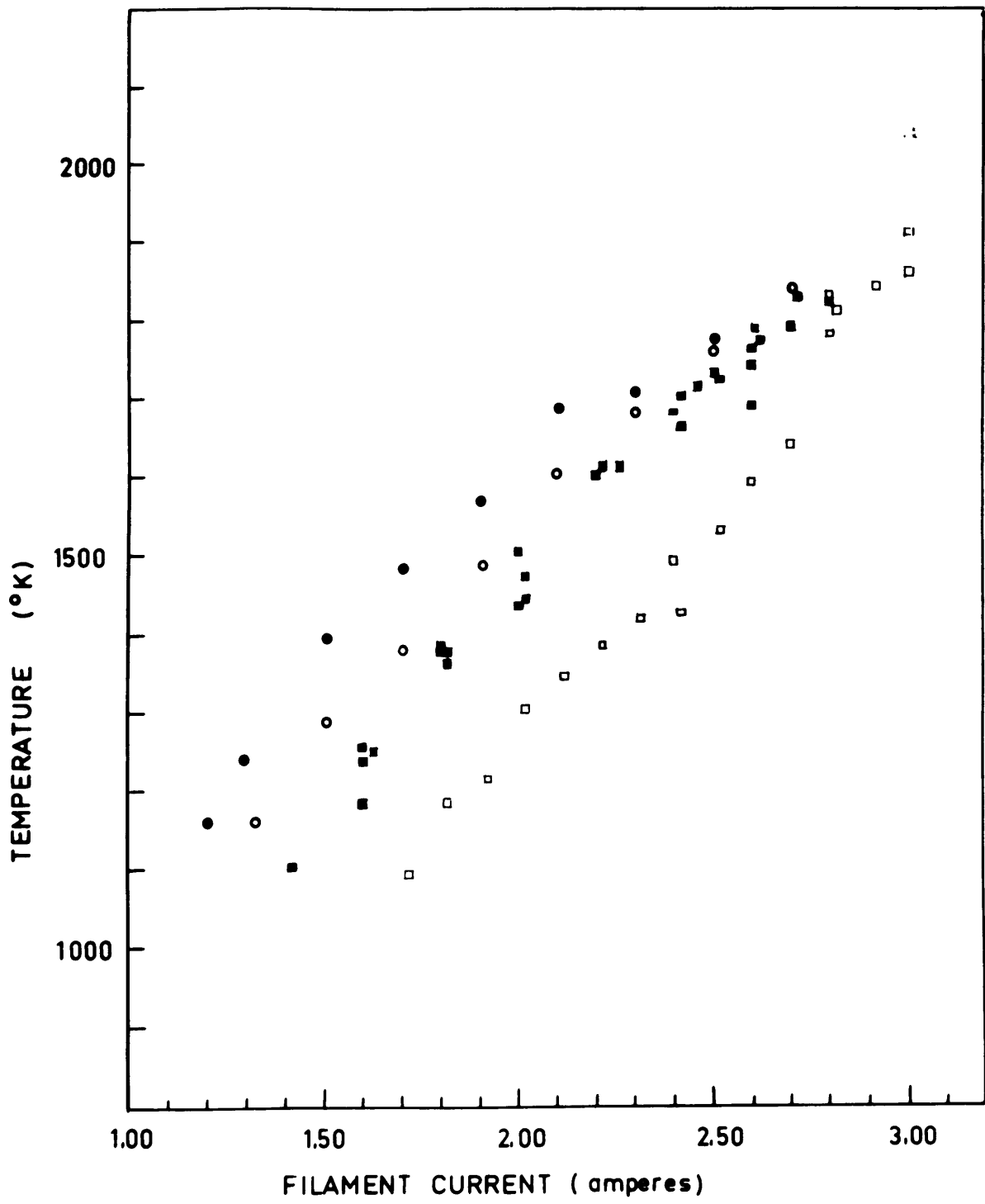


Figure 27. Temperature-Current Relationships For Platinum-plated Tantalum Filaments.

APPENDIX II. DISCARDED DATA

Three poor determinations of the relative isotope abundances of calcium in the calcium standard were not included in the discussion in Part IV, Section I. These results are given in Table 30, and are straight averages of all peak sets obtained for each run.

TABLE 30. DISCARDED DATA

<u>Date</u>	<u>No. of Peak Sets</u>	<u>$\frac{48}{40}$</u>	<u>$\frac{44}{40}$</u>	<u>$\frac{43}{40}$</u>	<u>$\frac{42}{40}$</u>
1. 10/30/53	11	0.00222	0.0228	0.00149	0.00688
2. 2/24/54	7		0.0232		0.00703
3. 3/2/54	6		0.00223		0.00679

In Determination No. 1, no measurements were made during the first part of the emission, and the results thus show an enrichment in the heavier isotopes. In runs 2 and 3 the ion current was very low intensity, and varied rapidly. All of the samples were applied to oxidized tantalum filaments as $\text{Ca C}_2 \text{O}_4$. All other discarded isotope determinations were thrown out for similar reasons.

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BIOGRAPHICAL NOTE

The author was born in Chicago, Illinois, on May 3, 1932. He obtained his secondary education at Thornton Township High School, in Harvey, Illinois, graduating in 1948. He graduated as a Bachelor of Science in geophysics from the Massachusetts Institute of Technology in June, 1952, and began post-graduate work at the Massachusetts Institute of Technology the following fall.

The author married Barbara Cairns in 1952, and has two children, Colleen and Marcia. He has one brother, George, who is at present engaged in research in astrophysics at the University of Chicago.

His professional experience includes one summer on a seismic exploration crew with Geophysical Services, Inc., and three years as a research assistant at the Massachusetts Institute of Technology. In addition to the work presented in this thesis, he has performed research in radioactivity measurements, and with Professor P.M. Hurley and Doctor H.C. Stetson presented a paper at the 1953 Geological Society of America meeting in Toronto entitled, "Radioactivity Relationships in Three Deep Sea Cores from the Gulf of Mexico."

The author was elected to Sigma Xi in 1952, and also holds memberships in the A.G.U. and the E.A.E.G.

Upon completion of requirements for the doctoral degree, he expects to be engaged in seismic research and engineering with Geophysical Services, Inc., Dallas, Texas.