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The absolute abundance of the titanium isotopes in nature

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THE ABSOLUTE ABUNDANCE OF THE TITANIUM
ISOTOPES IN NATURE

by

Harold Arthur Belsheim

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In Charge of Major Work

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1968

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I. INTRODUCTION

One purpose of this work is to investigate natural variations in the isotopic abundance of titanium. In the periodic table titanium lies between calcium, for which variations of 5.5 per cent have been reported (60) in the $^{40}\text{Ca}/^{44}\text{Ca}$ ratio, and chromium, for which no natural variation was found (37, p. 45). Variations in the abundance of the molybdenum isotopes have been ascribed (26) to incomplete mixing of terrestrial elements having different stellar sources. Theories of nucleogenesis indicate that the titanium isotopes may also have multiple sources. There are thus two major reasons for thinking that variations might be found in titanium. Background material in these areas is presented in this Introduction, as well as information on the measurement of abundances.

The second objective of this work is to place the measurements on an absolute scale. Titanium is one of the few remaining elements for which the atomic weight is based on chemical determinations, primarily because the previous mass spectrometric measurements were relative and because there is a discrepancy between the results by chemical and physical means. An absolute determination would aid in resolving the difference.

A. Element Formation and Distribution

1. Nucleogenesis

It is a tribute to man's tenacity that he continues to investigate the stars, since it appears that he will never be afforded direct confirmation of what occurs within them. It has been known for many years that nuclear reactions provide the only energy source capable of maintaining stars at their observed radiation levels for lengths of time comparable to the age of the earth. Details of many of these reactions have been determined in the laboratory, and their place in stellar evolution is inferred from demands of various stellar models. The consequences of these reactions on the origin and abundance of the elements have engendered interest in a lively field of research.

The fruits of this research which are of present interest are several theories of the origin and abundance of the elements. Of these only the multiple process theories of Burbidge, Burbidge, Fowler, and Hoyle (commonly called B^2FH) (14) and Cameron (21) are developed in full detail. Many investigators have advanced explanations covering groups of elements or particular processes; their theories will not, in the main, be covered here. An excellent review by Alpher and Herman (4) covers the early work. Early theories can be divided into equilibrium and non-equilibrium classes. In the former it is assumed that thermodynamic equilibrium exists among the nuclear species. While a set of conditions can be found for which the calculated isotopic abundance of

any element agrees with that observed, it is also found that such a set is quite different even for neighboring light elements. Among the heavy elements agreement is obtained over a greater number of elements, up to a range of perhaps 20 mass units (80). For reasons such as these, interest in equilibrium theory is presently confined to the region of high elemental abundance peaking at ^{56}Fe , and non-equilibrium theories are invoked to explain the remaining abundances.

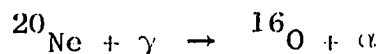
The non-equilibrium theories incorporate a variety of reactions. Proton, alpha, and heavier charged particle reactions, spallations, and neutron captures both slow and fast with respect to intervening beta decays are the main reactions of interest. Because of the observation that, starting with Se, the lightest isotope of those elements with even atomic numbers is the least abundant (except immediately following a neutron shell closure), nearly all investigators agree that some process involving excess neutrons is necessary to explain this abundance distribution. A second and probably more cogent reason is that charged particle reactions would have to overcome increasingly large coulombic barriers.

The theory of B^2FH seems to be retaining a basic position in the field. Most workers are willing to keep the general structure and suggest improvements in limited areas. The eight processes proposed by B^2FH are as follows:

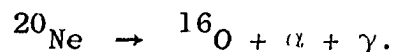
- 1) H burning; forms He and some isotopes of C, N, O, F, Ne, Na.
- 2) He burning; forms ^{12}C , ^{16}O , ^{20}Ne , possibly some ^{24}Mg .
- 3) α process; differs from He burning in that the source of He is $^{20}\text{Ne} (\gamma, \alpha) ^{16}\text{O}^*$; forms ^{24}Mg , ^{28}Si , ^{32}S , ^{36}Ar , ^{40}Ca , ^{44}Ca , ^{48}Ti .
- 4) e process; forms isotopes of V, Cr, Mn, Fe, Co, Ni by nuclear reactions at statistical equilibrium.
- 5) s process; forms isotopes in the ranges $23 \leq A \leq 46$ and $63 \leq A \leq 209$ by neutron captures which are slow with respect to intervening β decays.
- 6) r process; forms isotopes mainly in the range ^{68}Fe to ^{254}Cf by rapid neutron captures.
- 7) p process; uses (p, γ) and (γ, n) reactions to form nuclei with $A > 74$ which cannot be made in s and r processes.
- 8) x process; attempts to outline processes by which D, Li, Be, and B may be formed.

It was later found that He burning stops at ^{16}O because an anticipated resonance in ^{20}Ne is spin-forbidden. This gap can be filled by another process, C burning, which B²FH ignored.

* An abbreviation for the reaction



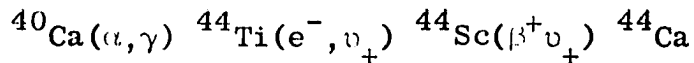
Had there been no comma, the reaction indicated would be the hypothetical decay



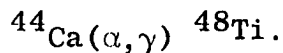
Both B²FH and Clayton et al. (23) find that at least two s process events are needed to obtain correlation with abundance data. B²FH find it reasonable that one r process event is sufficient, but Seeger, Fowler, and Clayton (73) find that two such events are necessary, and Marshall (54) suggests three events. Suess (80), however, has raised objections both to any multiple source argument and to the particular processes proposed by B²FH for $A \geq 50$. His arguments are not conclusive, but do bear considerable weight; they are summarized below. Multiple sources are contraindicated by the constancy of isotopic compositions, implying extreme homogeneity of the solar system nebula, by abundance similarities around nuclear shell closures, and by the smooth decrease in abundance with atomic mass of nuclides having the same neutron excess, both of the latter implying a fortuitous mixture of nuclides made by different processes. For s process nuclides it is hard to understand not only the smooth abundance curve through even A and odd N or Z species but also the sharp decrease in abundances beyond the proton shell closure at $Z = 50$. The abundance hump centered at $A=128$ can readily be explained by r process reactions occurring on material near the $N=82$ shell closure, but the very similar hump around $A=102$ is not connected with any nuclear feature. This tends to discredit the assumed correlation of the r process and shell closures.

The position of titanium in nucleogenesis schemes is one which is hard to treat. B²FH propose varying contributions

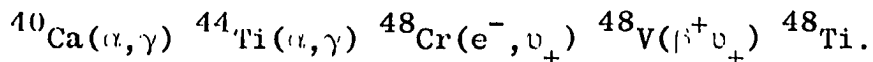
from four processes, α , e^- , s , and r , and they would thereby seem to gain great latitude in fitting calculations to observed abundances. In this case the gain is only apparent because of the difficulty in application: the processes are at their limits of application or are in a region outside of their normal use. The α process is at least straightforward and will be covered first (14). An ideal α process can be thought of as one in which the nuclei formed have mass numbers divisible by four and atomic numbers divisible by two. Such a process would form ^{40}Ca , ^{44}Ti , ^{48}Cr , as well as nuclei of lesser mass, but since ^{40}Ca is the last stable nuclide in this series, the further progress of the process will depend on the relative lifetimes for α -capture and β^+ -decay (or e^- -capture). If α -capture is relatively slow, then



is followed by



If it is relatively fast, then the path is



In the latter case the expected increase in coulomb barrier occurs so that one would expect a decrease in abundance in going from ^{44}Ca (from unreacted ^{44}Ti) to ^{48}Ti , whereas in the former case the barriers for the calcium isotopes are roughly the same and one would expect roughly equal abundances

of ^{44}Ca and ^{48}Ti . The abundances somewhat favor ^{48}Ti (see Table 1) which indicates that the slow pathway is followed. At the time B²FH published their theory, the estimated half life of ^{44}Ti was 1000 years. This lifetime has recently been determined by Wing et al. (88) and by Moreland and Heymann (61) who report that the average of their determinations is 47.3 years. Thus the latitude for the α process time scale is increased by a factor of 20. Burbidge (15) has revised events in the α process region to give much of it over to heavy ion reactions, reserving only $36 < A$ for α reactions; this does not affect the main argument presented here.

Table 1. Abundances of α process nuclei^a

Author	Nuclide							
	^{20}Ne	^{24}Mg	^{28}Si	^{32}S	^{36}Ar	^{40}Ca	^{44}Ca	^{48}Ti
Suess and Urey ^b	840	78	100	39	14	5.2	0.11	0.19
Cameron ^c	290	89	100	62	22	7.8	0.16	0.25
Aller ^d	-	68	100	65	-	4.7	0.10	0.12

^aNumbers are normalized to 100 ^{28}Si nuclei

^bReference (81)

^cReference (18)

^dReference (3, p. 122)

The e process abundances calculated by B²FH for the titanium isotopes are smaller than the observed abundances by factors of 20 to 100, but the pattern is similar to that observed. Clifford and Tayler (24) have recalculated abundances in this region for a wide range of conditions. Their figures indicate that the titanium isotopes cannot be formed exclusively by this process, but that major contributions could be made to the abundances of all isotopes.

Neutron capture processes are not well covered in the titanium region. No r process path has been plotted below ⁵⁶Fe because of the great uncertainty in extrapolating scanty nuclear data in this region. Only three nuclides (formed only by r process) aside from some of the titanium isotopes have been assigned by B²FH to this process. Interest in both s and r processes has centered on nuclides formed from ⁵⁶Fe "seed". This encompasses all of the elements heavier than iron, and offers many possibilities for testing the validity of the processes. B²FH have tentatively assigned ^{47,49,50}Ti to the r process, and have calculated s process abundance curves from ²³Ne to ⁴⁶Ti. The curve which best fits the abundances of the lighter nuclides rapidly falls below the abundances of nuclides beyond the last point of fit at A=43. B²FH note that calculated contributions to the abundance of ⁴⁶Ti from both s and e processes are still below the measured abundance.

2. Origin of the solar system

The origin of the solar system seems to be clouded by as much controversy as the origin of the elements, with the added hindrance that no theory has risen to a predominant position. It is of some benefit to note that the group of theories requiring interaction of another body with an already formed sun are not favored now. The remaining group of theories deals with systems isolated in the sense that no such interaction occurs. These theories generally consider condensation of an interstellar gas cloud of about 10^3 solar masses and its fragmentation into protostars. A point of concern now arises in that most theorists proceed with systems like the solar system and appear to ignore the large number of binary stars. Kuiper (50) estimates that binary systems are more numerous than single stars, and Kopal (47) concludes that both probably form at the same time and by similar processes. Cameron's treatment (19,20) is the only one noted which takes account of binary system formation; indeed he indicates that this may seriously limit the number of planetary systems formed. It is mainly for this reason that his theory is selected for presentation here.

Before condensation the gas cloud is presumably homogeneous in composition, primarily because no particular reason can be found for it to be inhomogeneous. The cause of its gravitational collapse is probably external, although somewhat larger clouds could condense spontaneously. External sources of

pressure considered are the presence of surrounding H II (ionized hydrogen) regions formed by radiation from nearby type O and B stars and the passage of the shell of matter ejected from a supernova. Only the latter can introduce inhomogeneity, although this may be inconsequential. If subcondensations form by simple fragmentation then the gradient, which is linear, is reduced by about a factor of 10 on geometrical grounds and further reduced by various mixing processes. Alternately, McCrea (53) considers agglomeration of turbulent blobs from many regions of the cloud. In this case the gradient is essentially that of the cloud itself, and greater reliance is placed on mixing to reduce it. In either case no evidence has been found to indicate inhomogeneity surviving in the solar system from this early stage (80).

By whichever means, then, a gas cloud condenses and breaks into further condensing fragments which are protostars. These either have or develop a nebular disk, which does not fractionate while gaseous. Opik (67) has shown that in this case loss of thermally excited molecules from an exospheric layer is insignificantly small and that loss from a hot nebula is purely mass transfer, that is, a "blowing-off" of whole layers. After partial solidification there is obvious fractionation since hydrogen and helium are strongly depleted in the inner planets of the solar system. It may be assumed that a similar separation occurs in other systems. If there is a concurrent isotopic fractionation, it has not yet

been discovered. It is difficult even to envision the equivalent number of theoretical stages involved in such phase separations. Cameron (20) considers that condensation precedes nebular dissipation, while Fowler, Greenstein, and Hoyle (38) believe that these are roughly concurrent processes. The former appears to be at most a single stage, while the latter could be several. Fowler, Greenstein, and Hoyle (38) note Boato's determinations (11) of the deuterium hydrogen ratio in carbonaceous chondrites, and attribute the variations to probable fractionation effects, rather than effects of solar irradiation of the nebula. They expect the irradiation to be nearly uniform within the volume occupied by the terrestrial planets, and consequently to have produced only small abundance variations, if any. Boato (11) concluded that no extensive isotopic fractionation of hydrogen occurred, since his results were not significantly different from ratios of earth samples. Investigations of other elements, presumably in the condensed phase at the time of the hypothesized irradiation, have revealed no significant variations in isotopic abundance in meteoritic material (16, 22, 28, 29, 30, 31, 35, 48, 64, 74, 86, 89) except for xenon (68). (It must be noted that irradiation runs counter to Cameron's theory (20) since he believes that a supernova injected radioactive isotopes at that time.)

The steps from this point to the final formation of planetary bodies are vague or missing in the theories

presented, but it can be said that there is apparently little further opportunity for fractionation. Thus while it may be tentatively concluded that little isotopic fractionation occurred during the formation of the solar system, there is no reason to believe that any initial inhomogeneities were dissipated.

B. Geology of Titanium

Titanium is the ninth most abundant element in the earth's crust. It is present to the amount of 0.44 per cent by weight (55, p. 45) and it is thus the most abundant minor element. It is found in many independent minerals, of which the predominant ones are ilmenite, rutile, and sphene. It also occurs to a lesser extent in pyroxenes, amphiboles, and biotite, where it substitutes for aluminum, iron(III), and magnesium. In all of these cases titanium occupies octahedral sites. The previously held concept that titanium commonly replaces silicon in tetrahedral sites is now limited to such replacement only in certain titaniferous garnets (27, pp. 90-92).

It has been estimated (70, p. 559) that over 90 per cent of the titanium in igneous rocks occurs as ilmenite. Since about 95 per cent of the crust is igneous rock, ilmenite is by far the most common titanium mineral. It is most abundant in gabbroic rocks; indeed, it is in gabbros and anorthosites that the major hard-rock titanium ores occur. In these ores the ilmenite occurs with magnetite or in some cases with

hematite. In most cases the oxides crystallized later than the silicates, and Lister (52) has suggested that these ores are commonly segregations or injections of an immiscible iron-titanium-rich liquid. A few ilmenite-apatite (nelsonite) deposits are also known, which appear to be similar in origin; they too are associated with anorthosite.

Rutile is frequently found as a major constituent of nelsonite, in which case it is usually of interest as a titanium ore. However, most rutile probably occurs in igneous rocks as an accessory mineral in gabbro pegmatites.

Sphene is more commonly found as a titanium-bearing accessory mineral than rutile. It occurs in some diorites - instead of ilmenite - and in many granites and syenites. Many substitutions are possible in the sphene structure (40, p. 416). Some of the more interesting ones are NaNb for CaTi and FeY for CaTi .

Perovskite is often found in silica-poor and calcium-rich rocks, such as those containing melilite; it undergoes substitutions like those given for sphene. Perovskite and the remaining titaniferous minerals are comparatively rare, and tend to occur in the less common rocks.

In sediments and sedimentary rocks only ilmenite and rutile are of importance, although minor amounts of sphene and the polymorphs of rutile are found. The prominent occurrence is in the black sands of many beaches, where wave action has concentrated the resistant heavy minerals. Some

of these are of sufficient extent and concentration to serve profitably as sources of titanium, and nearly all commercial rutile is derived from beach deposits.

A predominant amount of the titanium in sediments is found in the hydrolyzates, where it occurs mainly as tiny needles of rutile. Bauxites and laterites are especially rich, the titanium being concentrated in roughly the same ratio as is the aluminum (40, pp. 419-420).

Ingerson (45) discusses isotopic fractionation and the mechanisms by which it may have occurred in nature. Of the physical methods he notes, many do not appear applicable to titanium; these are evaporation, sublimation, atmospheric diffusion, and gravity diffusion. All that remains is non-atmospheric diffusion under thermal or concentration gradients, which might include metasomatism and granitization. Chemical exchange reactions make up the second group of processes; they appear about as reasonable as diffusion processes for titanium. Biological processes are nothing more than the above groups of processes operating under the guidance of a life force; they are quite effective. They are not important for titanium since no organism is known to require it. Several organisms, such as the tunicates Ciona intestinalis and Ascidia ceratodes, are known to concentrate titanium, but this action seems to be no more than the taking in of a useless element coupled with the lack of an efficient mechanism for getting rid of it.

It cannot be said whether any of these processes are operative for titanium, but it should be noted that among minerals only chemical exchange processes are seen for oxygen (34). It seems probable that processes for fractionating titanium are similarly restricted. Aside from that, fractionation might be expected anywhere there is titanium. The present author feels, however, that sedimentary titanium minerals will retain the isotopic ratios which they had on entering the sedimentary cycle. This is based on the implication that no titanium is lost in the alteration of ilmenite (83) and on the observation that the titanium aluminum ratio is relatively constant in the sedimentary cycle. From these points it is inferred that there is no mobile titanium available for exchange reactions.

C. Isotopic Abundance Measurements

The methods of measuring isotopic abundance may be divided into two groups, those dependent on nuclidic properties and those dependent on properties of the isotopic mixture. In the first group, useful properties are mass, radioactivity, and nuclear, atomic and molecular levels. In the second group are all of the gross properties, such as density, index of refraction, or chemical atomic weight. The most used of all of these properties is the mass. Direct observation of mass differences is possible in a mass spectrometer, which also provides a convenient measure of the relative numbers at each mass. Thus both identity and assay are inherent in mass spectrometric measurements.

Isotopic assay by measurement of radioactivity is limited to elements having isotopes which are all radioactive. Uranium (1) and the transuranium elements are good examples. Other elements could be so analyzed, but only by combining this method with another, such as chemical assay of the element. Radioactivation analysis, in which the sample is made radioactive by particle bombardment, is commonly done to determine the amount of an element present, the activated isotope being assumed to have normal abundance. But if the elemental determination is done in another way, then the activation analysis yields the abundance of the activated isotope. Elements investigated by this method include calcium (25) argon (33,85) and several elements the origin of which was suspected to be partly radiogenic (58).

The use of energy levels is arbitrarily separated here from those methods depending upon radioactivity. The latter depend on detection of emitted particles or gamma radiation, while the former requires measurement of electromagnetic radiation other than gamma which is emitted or absorbed. In both methods the useful emission (or absorption) is of energy characteristic of a particular isotope.

The optical region of the electromagnetic spectrum is used almost to the exclusion of the remainder. Nuclear magnetic resonance has been little applied to isotopic analysis although it has been found of value in assaying deuterium substituted compounds for isotopic purity (5,75). Microwave

spectroscopy has not yet fulfilled the wave of postwar optimism concerning its application. Only a few exploratory analyses are reported (77). Much work has been reported in the optical region. Many applications of interest in the field of atomic energy are noted by Rodden (71), while the Russians (90, pp. 523-677) provide their usual theoretical introduction to a review of practical work in the same field. Atomic spectra are preferred because they are easy to obtain, but they commonly require use of an interferometer to attain sufficient resolution. Their use is also limited to elements showing a sufficiently large isotope effect which is not masked by hyperfine interactions. Molecular spectra of isotopic species are different enough so that spectrographs of only moderate resolution can be used; the main problem is in finding molecules to analyze.

A major advantage of all of the above methods is that only routine purity is required, because the nuclidic properties are insensitive to the surroundings. The purity is needed mostly to reduce interference. In mass spectrometry, for example, chromium is removed from titanium samples so that CrO_2F^+ and CrOF_2^+ cannot interfere at the masses of TiF_3^+ . In contrast, the methods based on measurement of gross properties are critically dependent on purity, since the change with isotopic concentration is much less than with impurity concentrations. For example, the density of water is increased about 0.01 per cent by the addition of either 0.1 mole per

cent of deuterium oxide or only 0.004 mole per cent of sodium chloride. The gross properties also suffer from the disadvantage of being an average, and therefore of yielding the abundance of only biisotopic elements. For these and other reasons these methods are almost exclusively applied to hydrogen isotope assays of water.

Precision measurements of isotopic abundance are nearly always made with magnetic deflection mass spectrometers. This seems to be due more to greater development of this type of instrument than to any inherent advantage. For example, the quadrupole mass spectrometer has only recently been brought into commercial production - one measure of the development effort expended - and such an instrument, albeit a research machine, was recently used in a determination of the isotopic abundances in xenon (13). On the other hand those interested in time-of-flight instruments seem to have left abundance measurements to others.

Most variations of the basic deflection machine have been used in abundance work. The most important components involved in these variations are the ion source and the ion detection system. The analyzer, which is actually the heart of a mass spectrometer, is commonly an object of indifference. Basically it must only resolve ions sufficiently well so that an isotope does not contribute significantly to the abundance of its neighbor. In certain instruments this apparently simple requirement has been extended to such

length that ions of abundance 10^{-8} that of ions at a neighboring mass can be detected (87), whereas a ratio of 10^{-5} is about the limit for an average instrument.

The two most used ion sources are the electron impact source and the thermal ionization source. In the first of these, the sample is introduced as a gas or vapor or is vaporized from a furnace close to the source, and is ionized while in the gas phase by a beam of energetic electrons. In an ideal case the gas flow can be easily regulated and samples can be interchanged rapidly, thus permitting comparisons of samples, one of which may be a reference sample, in a time which is short compared to the drift time of the mass spectrometer detection system. Ideality in this sense is primarily a function of reactivity and vapor pressure of the sample. The transition metal halides investigated in this laboratory are quite corrosive, and maintaining an even gas flow is difficult. Memory effects are also troublesome in this case. Therefore this type of compound is the practical limit of application of this kind of ion source.

The thermal ionization source is the logical alternative to consider in such cases, since among its attributes are the use of a small amount of a relatively involatile substance, small memory effects, and a low background of extraneous peaks. This source operates by the partial ionization of material evaporated from a hot filament according to the Saha-Langmuir (51,72) equation

$$n_+/n_0 = A \exp [(\phi - I)/kT]$$

in which n_+ and n_0 are the number of positive ions and neutral particles, A is a constant, ϕ is the work function of the surface, I is the ionization potential of the element or molecule, k is the Boltzmann constant, and T is the absolute temperature. It can be seen that for $I < \phi$, T should be just high enough to evaporate the sample. For $I > \phi$, T should be as high as possible, and this is best attained by using an auxiliary filament at a lower temperature to evaporate the sample at the desired rate. This increases the total efficiency even though only part of the evaporated sample strikes the hot filament. Thermal ionization is a popular source of ions, particularly so wherever many different elements are analyzed. Its popularity is tempered by some disadvantages, among which are difficulties in maintaining steady ion currents, the necessity of replacing filament assemblies with each sample, and low ion currents.

Detector systems begin with an ion collector, commonly a Faraday cup or the conversion electrode of an electron multiplier. The Faraday cup offers some advantage in retaining secondary electrons, but usually a suppressor electrode just in front of the collector is kept negatively biased to ensure their retention. The ion collector signal is ordinarily fed to an electrometer amplifier in instruments with an electron impact source. Vibrating reed electrometers must be used with the smaller ion current obtained from a

thermal ionization source, or this type of system can be abandoned in favor of an electron multiplier system, which offers even greater sensitivity but has the disadvantage of being mass-sensitive. A correction which is proportional to the square root of the mass of the impinging ion can be applied although this simple mass correlation is not always precise. This obstacle can be overcome by pulse counting at very low ion currents.

Dual collection is relatively simple when a plate or Faraday cup system is used. The second collector is placed behind a slit in the first collector. Electron multipliers are not so easily fitted into the restricted space, so their use in dual collection is limited to a few ingenious applications (36).

In spite of scrupulous care taken to eliminate bias in mass spectrometer ion sources, collectors, and ion current read-out systems, some uncertainties are not amenable to direct correction. Accordingly, it is the usual practice to calibrate an overall mass spectrometer system with materials of known isotopic abundances. These are generally produced by mixing separated isotopes.

II. EXPERIMENTAL WORK

A. The Samples

1. Sources

Samples were obtained from most of the ore-producing areas of the world, and were supplemented with a few specimens from other regions. The samples are described in Table 2. World resources are estimated to be 290 million tons^{**} of TiO_2 , of which over 158 million tons are represented by samples used in this work. If the tonnage for those deposits which are not now economically recoverable is subtracted from these totals, then the representation ratio becomes 143/190. Figures for annual production from individual deposits are not available, but they would show roughly the same representation ratio. That six of the seven continents are represented further indicates the broad coverage.

The major types of deposits are all included. As was noted earlier (p. 12) the predominant hard-rock deposit is ilmenite-magnetite or ilmenite-hematite associated with anorthosite or gabbro, and all of the rock samples excepting those from Virginia fall into this category. The deposits at Piney River are dike-like bodies of nelsonite in anorthosite

^{**}The range given in reference (59) was modified by more precise data for Canada (78) and the United States (69); the value for Sierra Leone (79) was added. Neither this nor the total from Table 2 include a figure for Tanganyika since only a reconnaissance survey was made there (59).

Table 2. Description of natural samples

Sample Number	Location	Type of Deposit	Resources ^a (million tons of contained TiO ₂)
AC-1	Piney River, Va.	ilmenite in nelsonite	5.
DUP-1	Starke, Fla.	ilmenite in beach placer	8. ^b
DUP-2	Western Australia	ilmenite in beach placer	0.55
DUP-3	Eastern Australia	rutile in beach placer	2.5
GSR-1A	Roseland, Va.	rutile in anorthosite	0.15
GSR-2A	Roseland, Va.	ilmenite in anorthosite	(see AC-1)
GSR-3	Graves Mt., Ga.	rutile in kyanite-quartz	- ^c
MGS-1	Poplar Lake, Cook Co., Minn.	magnetite-ilmenite in gabbro	14.4 ^c
M-123	Langesundsfjord, Norway	ilmenite-magnetite in gabbro	- ^c
M-594	Gratton, Ont.	sphene	- ^c
NJZ-1	Allard Lake, Que.	ilmenite-hematite in anorthosite	52.5 ^d
NJZ-3	Florida	ilmenite in beach placer	-
NJZ-4	Tellnes, Norway	ilmenite-magnetite in anorthosite	18.7
NL-4	California	ilmenite-magnetite in anorthosite	1.0 ^c
NL-5	Tanganyika	ilmenite-magnetite in anorthosite or gabbro	(170.7)
NL-7	Quilon, India	ilmenite in beach placer	31.9

^aReference 59 unless otherwise specified.

^bReference 69.

^cNot commercial.

^dReference 78.

Table 2. (Continued)

Sample Number	Location	Type of Deposit	Resources ^a (million tons of contained TiO ₂)
NL-9	MacIntyre dev., N.Y.	ilmenite-magnetite in anorthosite	20.
NL-10	Cumuxatiba, Brazil	ilmenite in beach placer	- ^c
NL-15	Baie St. Paul, Que.	ilmenite-hematite in anorthosite	0.48
PPG-1	Sierra Leone	rutile in alluvium	3. ^e

^eReference 79.

and extend into the surrounding gneiss. Nelsonite is a rock composed principally of ilmenite and apatite. The Roseland deposit is in the same anorthosite mass and consists of rutile and ilmenite disseminations.

Among the sedimentary deposits, beach placers are well represented with several ilmenite samples and one rutile sample, the latter from the area which supplies most of the world's rutile. The only other sample from a sedimentary source is the Sierra Leone rutile. The geology of this deposit has not been published, but the degree of rounding shown by the grains indicates an alluvial origin.

The Graves Mt. rutile occurs as crystals disseminated in a kyanite-quartz rock; the crystals have long been popular as mineral specimens. The sphene represents only a different mineral form containing titanium, since nothing is known

concerning the geology of this particular sample. All of the other forms in which titanium occurs, as in exotic minerals or as a concealed element in common minerals, are left for other investigators.

Two samples of purified titanium dioxide remain to be described. One of these, F-1, is the reference sample to which all of the others were compared. It is reagent grade TiO_2 from lot number 734701 of Fisher Scientific Co., Pittsburgh. It was probably made from ore from the MacIntyre development, N.Y.* The other one is sample NI-1394, a portion of titanium dioxide from the material used to prepare TiBr_4 in one (10) of the two chemical determinations (9,10) on which the present value for the atomic weight of titanium is based (17). The origin of this sample cannot be traced beyond the Valentine Valspar Co., who supplied it to Baxter and Butler (10).

2. Chemical treatment

The ideal chemical treatment of samples would be no treatment at all. This has several advantages. One is that a minimum opportunity is provided for contamination of the element under analysis by reagents, atmospheric dust, handling, or apparatus. A second is that no operations are done which might lead to isotopic fractionation; hence no compulsion

*Mountsier, S. R., Jr., Whittaker, Clark, and Daniels, Inc., New York, N.Y. Probable source of titanium dioxide. Private communication. 1965.

exists to make these operations quantitative to avoid fractionation. Finally it is faster.

In nearly all cases this ideal is not attainable. In some instances this is true because natural processes are inefficient, and interfering elements occur in the samples. In other cases the natural samples are not in a form amenable to direct analysis. Some processing is necessary, and it becomes profitable to minimize the amount of processing for the same reasons as given earlier. In addition it is useful to treat all samples in the same way. Since a reagent grade chemical is often used as a reference material it is further desirable to attain a high purity in processing so that the samples are also similar to the reference material. Even if the reference material itself is a natural sample, it is useful to maintain a rigorous process, both to reduce possible interfering elements to a minimum and to obtain samples of parallel purity. This latter point may be amplified: it is better to use a rigorous process than run the risk that some variant sample will emerge with substantially different purity.

The specific process used to obtain titanium tetrafluoride from ore samples will now be described. Most specimens were received as sands or ores ground to pass a 30 mesh screen. These were divided by the cone-and-quarter method to a sample of about 30 g. Fragments were broken from massive specimens to give a similar size sample, and these fragments were

crushed in a Plattner mortar to about minus 20 mesh. Each sample was ground in an electric mortar grinder (model MG-1, The Torsion Balance Co., Clifton, N.J.) for at least one hour; this was sufficient to reduce the two samples upon which tests were made to minus 200 mesh. It was found that the sample caked after a short grinding period, and that grinding was inefficient thereafter. Hence sufficient acetone was added to give a thin paste which allowed easy comminution. Samples were poured from the mortar, dried, and stored in plastic vials.

A 1 g portion of each sample was fused with 10-20 g of KHSO_4 in a Vycor crucible. The cooled melt was crushed and dissolved in concentrated hydrochloric acid, and the solution was charged to an ion exchange column. The column itself was made by sealing a fritted glass disc and tubulation to the bottom of a suitable length of 30 mm diameter Pyrex glass. About 600 ml of resin were used in each of several columns, giving a column length of about 110 cm. One column was made with Dowex 1-X8, minus 100 mesh (Dow Chemical Corp., Midland Mich.) and the other columns were made with the equivalent resin, Amberlite IRA-400, minus 20 mesh (Rohm and Haas Co., Philadelphia, Pa.). These strongly basic anion resins were supplied and used in the chloride form. The resin, which is stored in a column filled with water, was first treated with one column volume of 12 M HCl. The sample solution was added, and sulfate as well as all slightly adsorbed metals were

eluted with another column volume of 12 M HCl. The titanium was eluted with one column volume of 9 M HCl, and the remaining metals (mostly iron) were stripped off with 1/2 volume of 1 M HCl, 1/2 volume of 0.1 M HCl, and one volume of water. This method was developed from the work of Kraus and coworkers on anion exchange; see especially reference (49). The titanium began to appear in the effluent shortly after the 9 M acid reached the bottom of the column, and was almost completely eluted in the first 150 ml of effluent. In some cases a faint positive titanium test* was noted just before Fe(III) appeared in the effluent, and for this reason this portion was collected separately from the majority of the titanium effluent and re-treated in a smaller column (about 42 ml of Dowex-1 in a 50 ml buret) according to the procedure just outlined. This portion was added to the main portion only if it gave a positive peroxide test for titanium after evaporation to a few ml. The total titanium-bearing effluent was evaporated to about 25 ml, and the titanium was precipitated with cupferron using the method of Murphy et al. (63). The essential difference between this and the conventional cupferron precipitation is that this is done at 65°C. The precipitate was collected on ashless filter paper (SandS no. 589 black ribbon), dried, and slowly brought to 700°C. The product was pure

*A drop of effluent was caught on a spot plate and treated with a drop of 5 per cent H_2O_2 . Immediate change to orange or red indicates the presence of titanium.

TiO₂, which was stored in that form as a supply for subsequent preparations.

The preparation of the analysis form, TiF₄, was undertaken individually just before the sample was introduced into the mass spectrometer; in fact the reaction apparatus was attached to the sample inlet of the spectrometer so that no transfer was needed. Each such sample preparation was paralleled by a reference preparation. The reaction tube is a 6 1/2 inch length of 1/4 inch outside diameter copper tubing flattened and sealed at one end with silver-copper eutectic solder and flared at the other end to attach to a 90° elbow brass flare fitting. This is connected to the mass spectrometer inlet system by a horizontal condenser tube made from 16 inches of 1/4 inch outside diameter copper tubing flared at both ends.

About 10 to 30 mg of TiO₂ was mixed in an alundum mortar with 1.5 to 2 g of CoF₃. The mortar was used primarily to break up the coarse fragments from the ignition; it was not an especially efficient mixer, nor was such needed. This operation, as well as the transfer of the mixture to a reaction tube, was performed in a glove box kept at low humidity by an open dish of anhydrous Mg(ClO₄)₂. The filled reaction tube was removed from the box and the mixture was capped with a small square of knitted copper ribbon tamped into place to retain the mixture on evacuation. The tube was fitted with a condenser tube and the assembly was attached

to the instrument inlet system and slowly evacuated. See Figure 1 for an illustration of this assembly. For each analysis these operations were performed serially using reference TiO_2 and a sample TiO_2 . When both preparations had been evacuated, the condenser tubes were bent so that the reaction tubes were parallel and contiguous, and so that a small vertical tube furnace could be raised to envelop them. The furnace was so raised and heated to 250 to 300°C, at which temperature an oxygen-producing reaction occurs. After this reaction had subsided, a facial tissue was wrapped around the condenser tube, covering approximately that part of the tube from four to eight inches from the inlet connection. The tissue was kept saturated with water during the remaining reaction. The furnace temperature was then raised to 650°C and held there while a Bunsen flame was played over the elbow and adjacent tubing. The main portion of the reaction occurs 500-550°C. Notice in the figure that the thermocouple was not affixed to the reaction tube; since the latter was connected to a more efficient heat sink, it was undoubtedly cooler than the temperatures cited here. However, the reaction phenomena were reproducible. The furnace was then lowered to allow the reaction tube to cool. The valve through which the system had been kept evacuated was closed, and the reaction tube and elbow replaced with a brass plug fitting. This abbreviated system, containing the sublimed TiF_4 reaction product, was then re-evacuated. A short (two foot length)

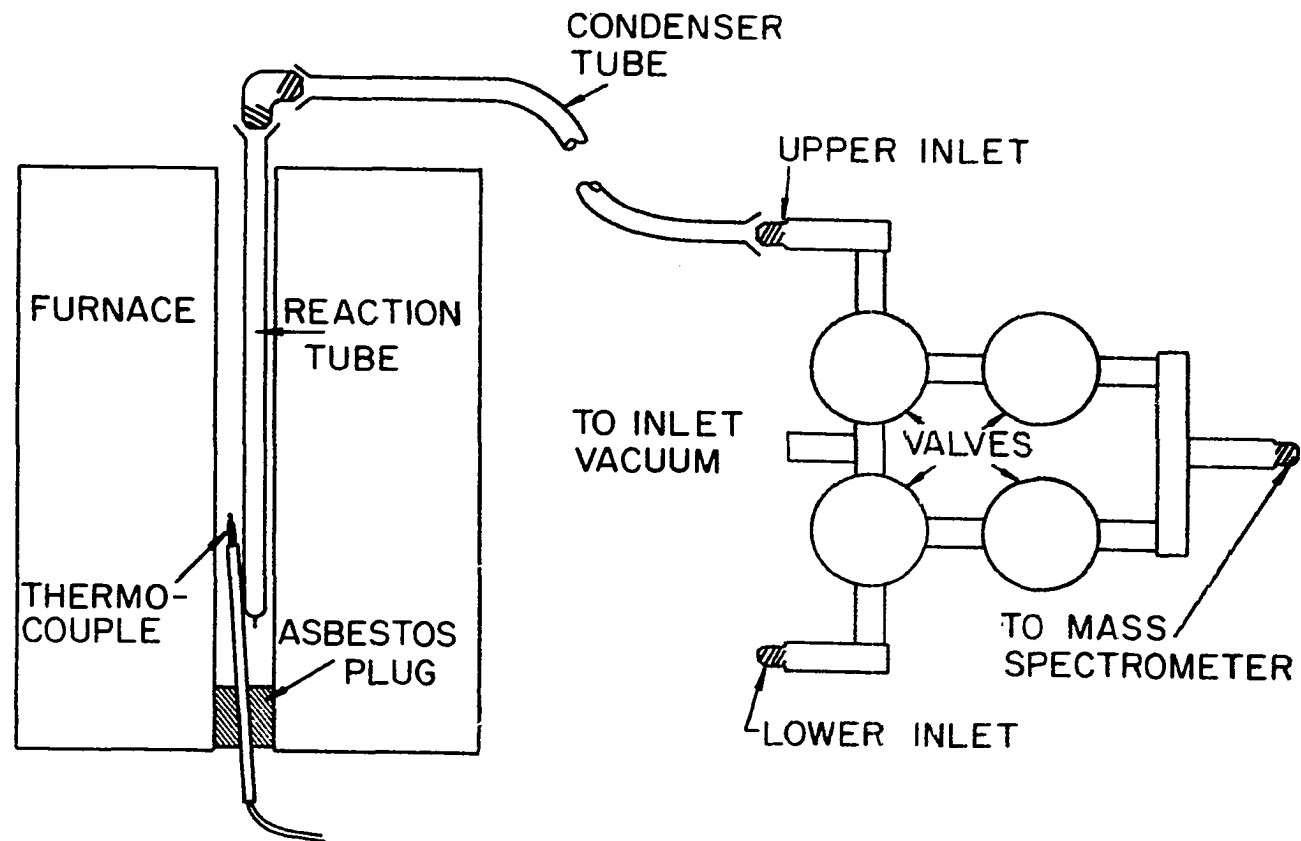


Figure 1. Sample preparation and inlet systems

electrical heating tape was affixed to the plugged end of this system in such a way that the tubing was sandwiched between parallel halves of the tape. This assembly was wrapped with a layer of asbestos tape. Upon heating the tape, TiF_4 could be sublimed directly into the ion source of the mass spectrometer.

B. The Instrument

The mass spectrometer used in this research is a 180° , 5 inch radius instrument (Consolidated Electrodynamics Corporation model 21-220) which was modified in this laboratory by substituting for the original fixed current magnet power supply a variable current supply.* This supply achieves regulation by comparing the IR drop across a motor-driven potentiometer with the voltage developed across a standard resistor in series with the magnet. After being used for several years the supply was tested and found to regulate the magnet current to within one part in 60,000 for about 1/2 hour, after which the test was terminated.

Two other modifications were made for this study. One was the substitution of a new inlet system, made necessary by the low vapor pressure of TiF_4 . The other was the use of an external feedback control and null indicator in place of the recording potentiometer and attenuation system, desirable

*The supply was designed and built in this laboratory by the Electronics Shop, and is designated by circuit number MF-33.

for increased precision and ease of operation.

The new inlet system consisted of two pairs of Hoke series 413A valves; these are packless valves with a diaphragm seal. They were altered in this laboratory by removing the aluminum gasket and electron beam welding the diaphragm to the valve body. They were interconnected by Monel fittings so as to permit either one or both samples to be connected to the inlet vacuum system and/or to the mass spectrometer (see Figure 1). The two valves on the inlet vacuum side of the assembly were modified by drilling a 3/16 inch hole to the center of each valve and at 90° to the existing inlet holes. This permits flow through the valve body at all times. Thus when the valve is open, for example to remove gaseous products evolved during the fluorination of a sample, the valve laterally adjacent to it may be partially opened to allow an aliquot of the evolved gas to enter the mass spectrometer for analysis or estimation of partial pressure of O₂. When the valve is closed, as for sample analysis, all gas and vapor flow through the adjacent valve, which is fully opened to avoid possible mass discrimination due to molecular flow through the orifice at the valve seat.

The unrestricted flow path is the primary difference between this inlet system and the previous one used with the mass spectrometer. In the latter the presence of a capillary leak assures viscous flow of (gaseous) samples into the ion source chamber so the sample composition does not change with

time. Then differential pumping* out of the source chamber establishes the desired reproducible conditions in the source. For this case the conditions are that the concentration of a species in the source is directly proportional to the original concentration times the square root of its mass. Since the differential pumping is not affected by the inlet system, it remains only to be shown that the present system provides conditions equivalent to viscous flow in order that the same correction can be applied to measurements reported herein. Mulliken and Harkins (62) have discussed isotopic separation by diffusion and similar processes, and concluded that an irreversible distillation is equivalent to molecular effusion in separating species according to the square root of their mass ratio. They showed that such a distillation could be approximated by vacuum distillation, and that this did produce a change in the density of mercury. Since then many workers have confirmed this phenomenon in mass spectrometry, especially in the evaporation of a sample from a hot filament. Few, however, have explicitly remarked on the physical state of their sample during evaporation. Svec and Anderson (82) did this; they noted that their ${}^6\text{Li}/{}^7\text{Li}$ ratios remained constant for several days when the temperature of the sample (LiI) was kept below its melting point. In other experiments

*This is pumping under conditions of molecular flow, in which molecules diffuse out of the chamber at a rate inversely proportional to the square root of their mass.

Anderson* has noted that these ratios remain constant until the sample is roughly 80 per cent sublimed, at which time it is also necessary to increase the filament temperature to maintain the desired ion current. In the present work, ratios in a sample of TiF_4 were compared over a period of 12 weeks with ratios in freshly prepared samples; no variation was found. Again, these samples were always well below the normal sublimation temperature of TiF_4 . While not conclusive, these investigations strongly indicate that fractionation does not occur in these cases. The reason is undoubtedly that diffusion in the solid cannot maintain the initial preferential sublimation according to $(M_1/M_2)^{1/2}$, and that the specific surface is insufficient to maintain it. Hence all but the initial (and final) sample vapor has the same isotopic composition as the solid, and this system is equivalent to a system of gas introduction by viscous flow.

The feedback control and associated circuitry are shown in Figure 2; they were designed and built by Gerald D. Flesch of this laboratory in 1964. The circuit denoted Δ reference provides a variable voltage which is inserted in the reference voltage circuit of the high voltage power supply or the magnet power supply. Its purpose is to permit rapid switching between two peaks. The high/low switch gives the potentiometer equal sensitivity in voltage and magnetic switching.

*Anderson, Arthur R., Jr., Ames Laboratory of the U.S. Atomic Energy Commission, Ames, Iowa. Mass spectrometric behavior of LiI samples. Private communication. 1967.

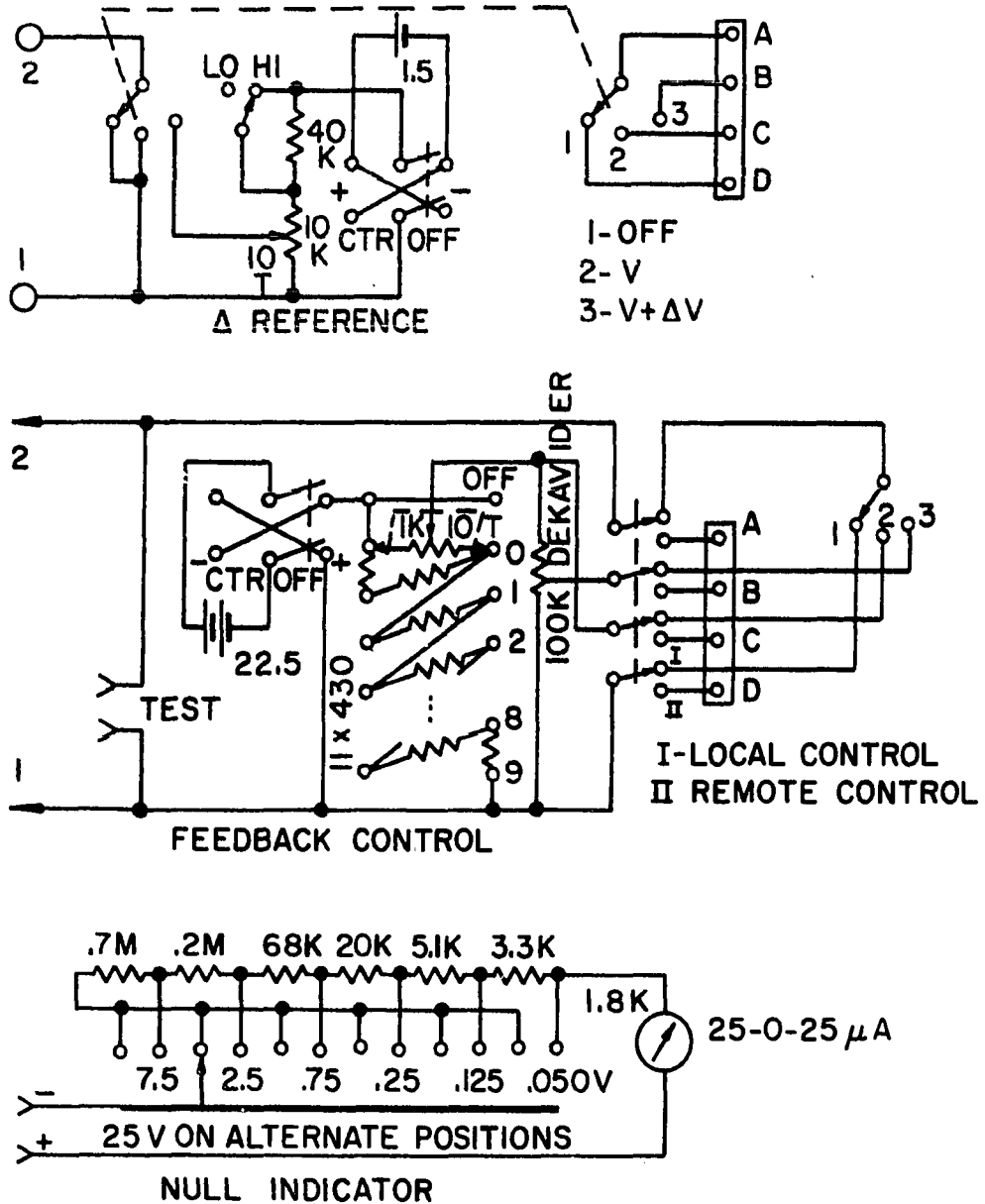


Figure 2. Feedback control and associated circuitry

In normal operation connections are made to the various collectors and amplifiers as shown in Figure 3. In the modified operation the recorder and high current amplifier are interchanged. The null indicator is inserted in parallel with the panel meter, which normally indicates the output from the number one collector. The feedback control is inserted in the feedback loop originating in the high current amplifier, and terminating in the modified scheme in the number two preamplifier. The potentiometer and resistor assembly of the control fulfill the same functions as the attenuation controls of the mass spectrometer. The addition of the Dekavider* and suitable switching, however, permits direct reading of a ratio of ion currents from one collector.

A typical sequence of operations follows: Plug in the Δ reference, feedback control, and null indicator circuits in the appropriate places; also interconnect the first two at terminals A, B, C, D. With Δ reference set at "V", find the maximum of the larger peak whose ratio is desired by adjusting the mass spectrometer controls. Adjust the potentiometer and resistor string of the feedback control until the null indicator shows no ion current at its most sensitive setting. Switch Δ reference to "V + Δ V" and use its potentiometer to maximize the lesser peak. Adjust the Dekavider to zero

*Electro-Measurements, Inc., Portland, Oregon provided a model DV-411 with especially selected resistors to give an accuracy of ± 0.01 per cent instead of the normal ± 0.05 per cent.

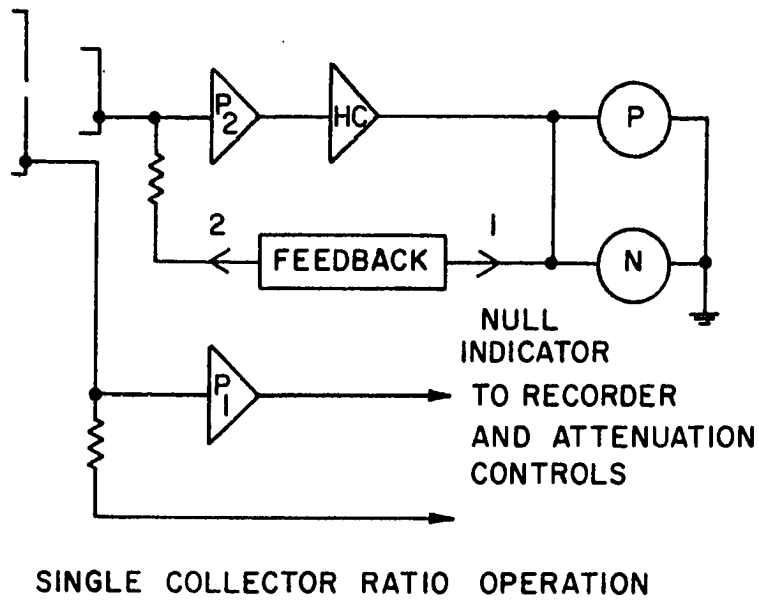
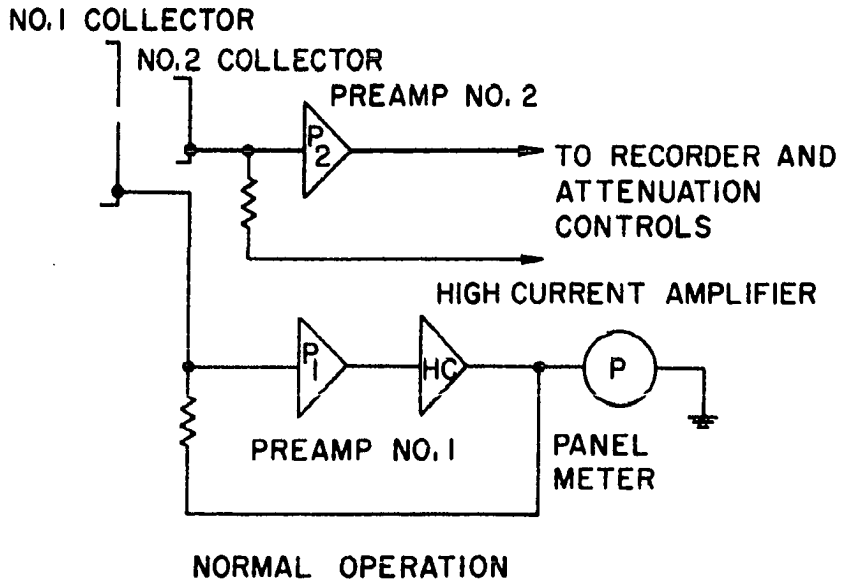


Figure 3. Collector and amplifier connections

current on the null indicator, and read the ratio of peak heights from the Dekavider dials. For better statistical control, repeat the sequence of operations following the plugging in of the circuits, noting that it is usually not necessary to check the peak maxima within a set of five or fewer ratio measurements.

C. The Method

Single collector methods were used in this work. The highly precise feedback control made this method attractive. The mass separation of ions in the region of interest is such that when ions of nominal mass x are falling on the number two collector, ions of mass $x-2$ are falling on the edge of the number one collector. Hence direct reading of ratios would be highly inaccurate. A suitable mask could have been installed to permit reading of direct ratios accurately, but it was decided that the sequential ratio measurement necessary when using only one collector was sufficiently accurate. This also had the advantage that all measurements would involve a single amplifier thus obviating determination of input resistor ratios.

The TiF_3^+ ion is the largest peak in the mass spectrum of TiF_4 , and this ion was therefore used for analysis. The TiF_4 pressure was adjusted by manually regulating the sample temperature; this was done by changing the voltage applied to the heating tape around the sample with an autotransformer.

When the pressure was such that a reasonably constant $^{48}\text{TiF}_3^+$ ion current of roughly 10^{-10} amp (3-5 volts developed across a 4×10^{10} ohm feedback resistor) was obtained, collection of data was started.

In the course of this work data on relative abundances were amassed under three sets of conditions. In the first two sets the source focusing controls were set at optimum operating values at the start of the first set, and were left alone thereafter. In the last set it was necessary to adjust the controls frequently to maintain a stable ion current. Ample stability was maintained by adjusting the controls or checking their adjustment just before running each sample. The second set differs from the first primarily by a one week interval, but can more readily be distinguished by the appearance of an unexplained bias associated with the lower inlet.

The method by which ratios are measured has already been described under operation of the feedback control (see p. 35). This scheme was followed for ions of mass 107, 103, 104, and 106 (the ions are $^{50}\text{TiF}_3^+$, $^{46}\text{TiF}_3^+$, $^{47}\text{TiF}_3^+$, and $^{49}\text{TiF}_3^+$ respectively) in turn, each being compared with the $^{48}\text{TiF}_3^+$ ion at mass 105. The order of measurement only represents one convenient sequence. Ten ratios were measured for each mass before going to the next mass. After these 40 ratios were measured, the amplifiers were switched to normal operation and peaks of mass 105, 104, 86, and 85 were scanned on the recorder. These data were used to correct the 104/105

ratio for a contribution to the 104 peak height by $^{28}\text{SiF}_4^+$. A correction for contributions from the other silicon isotopes was not made because it was small compared to the random error.

When these data had been collected for the first sample run on a particular day (whether this was the reference or an ore sample was determined randomly) then that sample valve was closed. The ion current was allowed to decay to about 1/3 to 1/10 of its operating value before the other sample valve was opened; this took about 15 minutes. Then the pressure of the second sample was adjusted as described previously. This generally required three hours. Conditions sufficiently stable to permit collection of data could have been attained in one to one and one half hours, but the data would have been about four times less precise. The reading of ratios and correction peaks was done for the second sample. Its introduction valve was closed, and both samples were removed and discarded. Two new samples were made up as described in the latter part of the section on chemical treatment (p. 29). They were maintained under vacuum and with a small current flowing through the heating tapes overnight so that they would be degassed and ready for analysis on the following day.

The procedural changes made when the sample of mixed isotopes were analyzed are noted below. Appropriate amounts of each isotope as the oxide were weighed into the

mixing mortar, where they were thoroughly mixed with a small amount of CoF_3 before being mixed with the main portion of CoF_3 . Since only three isotopes were used, the ratios are not near normal. The slow approach to the different ratios (memory effect) made it impractical to use a reference sample. Therefore several sets of ratios were read, both on the same day and on succeeding days, in order to establish a statistical basis for comparing these with normal samples.

D. The Results

1. Relative measurements

The primary results of this part of the work are the isotopic abundance ratios. These are presented here, along with certain other results of an auxiliary nature. The uncorrected ratios (excepting 104/105; see below) are given in Table 3, in which each sample is listed in the order in which its ratios were determined. Each ratio is identified by the mass ratio of the ions measured. Thus 103/105 is the ratio of ion currents for the ions $^{46}\text{TiF}_3^+$ and $^{48}\text{TiF}_3^+$. All ratios are with respect to the major isotope, ^{48}Ti . Immediately following each column of ratios is a column containing ratios of ratios in which each measurement of a particular sample is referred to that of a reference sample, F-1, made on the same day. For example, R49 denotes the ratio of ratios for the ^{49}Ti -containing ions, with the reference sample ratio always in the denominator. As a specific example, the second entry in this column is obtained from $0.07501/0.07476 = 1.00334$. In

Table 3. Titanium abundance ratios

Sample	Ratios								Inlet ^a	Date
	103/105 x10 ⁵	R46	104/105 x10 ⁵	R47	106/105 x10 ⁵	R49	107/105 x10 ⁵	R50		
DUP-3	10794	0.98991	09913	0.99468	07509	1.00455	07324	1.01090	L	16 Sep.
F-1	10904		09966		07475		07245		U	1966
F-1	10781		09876		07476		07267		L	22 Sep.
AC-1	10798	1.00158	09898	1.00223	07501	1.00334	07293	1.00358	U	
F-1	10793		09898		07504		07299		U	23 Sep.
NL-4	10803	1.00093	09906	1.00081	07495	0.99880	07297	0.99973	L	
F-1	10810		09929		07503		07282		L	24 Sep.
NJZ-1	10792	0.99833	09898	0.99688	07534	1.00413	07331	1.00673	U	
NL-10	10806	0.99576	09914	0.99809	07534	1.00641	07286	1.00303	U	25 Sep.
F-1	10852		09933		07486		07264		L	
F-1	10914		09969		07479		07221		L	26 Sep.
NJZ-4	10727	0.98287	09853	0.98836	07514	1.00468	07348	1.01759	U	
F-1	10793		09908		07509		07286		U	27 Sep.
DUP-2	10816	1.00213	09933	1.00252	07570	1.00812	07328	1.00576	L	
F-1	10784		09913		07519		07324		U	28 Sep.
NL-9	10841	1.00529	09933	1.00202	07498	0.99721	07281	0.99413	L	
F-1	10876		09983		07487		07256		L	29 Sep.
PPG-1	10735	0.98704	09890	0.99068	07526	1.00521	07353	1.01337	U	
F-1	10856		09937		07493		07261		L	30 Sep.
NL-7	10784	0.99337	09919	0.99819	07500	1.00093	07326	1.00895	U	

^aL = lower inlet. U = upper inlet.

Table 3. (Continued)

Sample	Ratios								Inlet ^a	Date
	103/105 x10 ⁵	R46	104/105 x10 ⁵	R47	106/105 x10 ⁵	R49	107/105 x10 ⁵	R50		
F-1	10789		09924		07516		07301		L	2 Oct.
NI-1394	10718	0.99342	09881	0.99567	07526	1.00133	07356	1.00753	U	
F-1	10687		09856		07524		07367		L	11 Oct.
NI-1394	10688	1.00009	09859	1.00030	07519	0.99934	07364	0.99959	U	
NI-1394	10812	1.01056	09939	1.00699	07527	0.99761	07297	0.99090	L	13 Oct.
F-1	10699		09870		07545		07364		U	
NI-1394 ^b	10732	1.00346	09882	1.00182	07536	0.99973	07348	0.99810	L	15 Oct.
F-1 ^b	10695		09864		07538		07362		U	
F-1	10724		09870		07518		07345		L	19 Oct.
NL-10	10692	0.99702	09854	0.99838	07512	0.99920	07353	1.00109	U	
F-1	10714		09873		07523		07353		L	20 Oct.
NL-4	10704	0.99907	09867	0.99939	07517	0.99920	07362	1.00122	U	
GSR-2A	10705	0.99972	09872	0.99929	07513	0.99920	07344	0.99864	L	25 Oct.
F-1	10708		09879		07519		07354		U	
F-1	10696		09864		07511		07359		U	26 Oct.
NJZ-1	10715	1.00178	09866	1.00020	07513	1.00027	07346	0.99823	L	
DUP-1	10724	1.00215	09875	1.00091	07527	1.00213	07346	0.99878	L	27 Oct.
F-1	10701		09866		07511		07355		U	
DUP-3	10694	0.99276	09860	0.99516	07513	1.00107	07355	1.00396	U	28 Oct.
F-1	10772		09908		07505		07326		L	

^bA redetermination using the same sample preparation as was used for the ratios immediately above in the same inlet position.

Table 3. (Continued)

Sample	Ratios								Inlet ^a	Date
	103/105 x10 ⁵	R46	104/105 x10 ⁵	R47	106/105 x10 ⁵	R49	107/105 x10 ⁵	R50		
F-1 ^b	10764		09905		07509		07312		L	
DUP-3 ^b	10717	0.99563	09868	0.99626	07514	1.00067	07343	1.00424	U	
NL-9	10778	1.00738	09899	1.00334	07521	0.99880	07316	0.99389	L	30 Oct.
F-1	10699		09866		07530		07361		U	
F-1	10704		09848		07533		07356		U	1 Nov.
PPG-1	10734	1.00280	09877	1.00294	07530	0.99960	07347	0.99878	L	
NL-5	10703	0.99786	09864	0.99757	07514	0.99867	07348	1.00014	U	4 Nov.
F-1	10726		09888		07524		07347		L	
F-1	10781		09910		07552		07321		U	5 Nov.
AC-1	10779	0.99981	09899	0.99889	07510	0.99444	07314	0.99904	L	
NI-1394	10722	0.99916	09877	0.99899	07522	0.99907	07341	1.00068	U	7 Nov.
F-1	10731		09887		07529		07336		L	
NJZ-4	10784	1.00419	09906	1.00162	07514	0.99841	07314	0.99619	L	8 Nov.
F-1	10739		09890		07526		07342		U	
MGS-1	10726	0.99935	09873	0.99768	07515	0.99973	07343	1.00328	U	9 Nov.
F-1	10733		09896		07517		07319		L	
F-1	10778		09917		07516		07310		L	10 Nov.
NJZ-3	10747	0.99712	09888	0.99708	07533	1.00226	07335	1.00342	U	
F-1	11153		10057		07365		07063		U	15 Dec.
GSR-1A	11219	1.00592	10086	1.00288	07345	0.99728	07029	0.99519	L	
F-1	11137		10055		07367		07058		L	17 Dec.
DUP-2	11070	0.99398	10001	0.99463	07390	1.00312	07106	1.00680	U	
M-594	11137	1.00370	10052	1.00319	07365	0.99743	07062	0.99437	L	18 Dec.
F-1	11096		10020		07384		07102		U	
F-1	11119		10068		07384		07064		L	20 Dec.

Table 3. (Continued)

Sample	Ratios								Inleta	Date
	103/105 x10 ⁵	R46	104/105 x10 ⁵	R47	106/105 x10 ⁵	R49	107/105 x10 ⁵	R50		
F-1	11062	0.99487	10013	0.99454	07398	1.00190	07107	1.00609	U	
F-1 ^b	11082	0.99820	10028	0.99850	07393	1.00068	07113	0.99916	L	
F-1 ^b	11045		09999		07394		07103		U	21 Dec.
F-1 ^b	11027	1.00163	10018	0.99810	07403	0.99878	07139	0.99496	L	
NL-15	11046	0.99343	10011	0.99642	07396	1.00339	07125	1.00821	U	22 Dec.
F-1	11119		10047		07371		07067		L	
F-1	11047		10022		07395		07122		U	23 Dec.
M-123	11078	1.00281	10039	1.00170	07392	0.99959	07105	0.99761	L	
F-1	10961		09974		07414		07164		U	27 Dec.
NL-7	11100	1.01268	10034	1.00602	07370	0.99407	07086	0.98911	L	
F-1	11037		10022		07388		07123		L	28 Dec.
GSR-3	11055	1.00163	10003	0.99810	07387	0.99986	07106	0.99761	U	
F-1	11079		10038		07381		07093		L	29 Dec.
F-1	10989	0.99188	10007	0.99691	07417	1.00488	07145	1.00733	U	
F-1 ^b	11108	0.98929	10033	0.99741	07371	1.00624	07074	1.01004	L	
F-1 ^b	11083	0.99775	10007	0.99741	07394	1.00312	07094	1.00283	U	

certain cases (20, 21, 29 December) both samples were of reference material; here the ratio is of the sample on the upper inlet to the sample on the lower inlet for adjacent runs on the same day. No entry in the date column indicates that that sample was run on the date last entered.

Each of the ratios in this table is the mean of ten individual measurements. The standard deviation of each set of individual measurements was estimated from

$$s = \left[\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{n}}{n - 1} \right]^{1/2}$$

in which s is the standard deviation estimator of "Student" (41), x_i is a single measurement, and n is the number of measurements. The average value of s for all sets is 4.8×10^{-5} and the range is $(1.4 - 13) \times 10^{-5}$. All means involve raw data except for ratios 104/105, which have been corrected for the contribution of $^{28}\text{SiF}_4^+$ to the 104 peak height.

The SiF_4 correction was made in the following way. The simultaneous equations,

$$\text{P.H.}_{85} = A(^{47}\text{TiF}_2^+)X + A(^{28}\text{SiF}_3^+)Y = W + Z$$

and

$$\text{P.H.}_{86} = A(^{48}\text{TiF}_2^+)X + A(^{29}\text{SiF}_3^+)Y$$

were solved for W and Z from the measured peak heights, P.H., at masses 85 and 86 and the accepted values (39) for isotopic abundance, A . Values of W and Z were combined with

fragmentation data (see Table 4) to give a simulated 104 peak height,

$$\begin{aligned} \text{P.H.}_{104} = & ([^{47}\text{TiF}_3^+]/[^{47}\text{TiF}_2^+])W \\ & + ([^{28}\text{SiF}_4^+]/[^{28}\text{SiF}_3^+])Z = a + b \end{aligned}$$

In this equation the brackets indicate an appropriate entry of relative abundance from Table 4. The measured 104/105 was multiplied by $a/\text{P.H.}_{104}$ to give the corrected 104/105. Since these operations were programmed on a desk computer, the value of the multiplying factor, $a/\text{P.H.}_{104}$, is not now available without extensive recomputation. However, the difference between raw and corrected ratios is available. The average difference is 0.00066 with range 0.00007 to 0.00237. The fragmentation patterns of SiF_4 and TiF_4 were obtained under the same operating conditions as were used for the ratio determinations.

The mass spectrometer was operated under essentially the same conditions as were used by Flesch (37, pp. 17-19). Ions were accelerated by 1600 volts. The ion acceleration voltage was set before each run by measuring with a potentiometer the voltage drop across a portion of the high voltage divider supplying ion source electrode voltages. It should be noted that the ratios so far presented were obtained by voltage scanning. In this case the $^{48}\text{TiF}_3^+$ ion was accelerated by 1600 volts, and the ions of the minor isotopes were accelerated by a greater or lesser voltage.

Table 4. Fragmentation patterns^a

Ion	Relative abundance	Ion	Relative abundance		
SiF ₄ ⁺	2.04	TiF ₄ ⁺	1.06	1.09	1.14
SiF ₃ ⁺	100. ^b	TiF ₃ ⁺	100. ^c	100. ^d	100. ^e
SiF ₂ ⁺	0.58	TiF ₂ ⁺	8.43	8.55	7.84
SiF ⁺	2.83	TiF ⁺	10.36	10.48	9.67
Si ⁺	3.26	Ti ⁺	6.04	6.03	5.63
SiF ₃ ⁺⁺	0.90	TiF ₃ ⁺⁺	0.58	0.57	0.59
SiF ₂ ⁺⁺	2.57	TiF ₂ ⁺⁺	6.62	6.54	6.04
SiF ⁺⁺	0.26	TiF ⁺⁺	2.57	2.56	2.27
Si ⁺⁺	0.15	Ti ⁺⁺	2.97	2.96	2.43

^aOnly peaks of the major isotopes, ²⁸Si and ⁴⁸Ti, are presented. SiF₄⁺⁺ and TiF₄⁺⁺ were not detected.

^bThis base peak was 9.7 volts high.

^cPeak height, 1.15v.

^dPeak height, 1.05v.

^ePeak height, 2.5v.

The electron accelerating voltage was 70 volts. In the first two sets (see p.40) of ratios, 200 μA of ionizing current was used, while in the third set the current was set daily at whatever value (in the range 130 to 170 μA) gave the greatest ion current.

In attempting to determine more exactly the differences between the three sets of ratios (mentioned on p.40) it was discovered that a relatively constant difference exists between ratios measured on the upper and lower sample inlets.

If the ratios of ratios, R , are recast into a form in which they are always the ratios of ratios measured on the upper inlet to ratios measured on the lower inlet without regard for sample origin, then the average R values from the three sets are indistinguishable according to the t test at the 5 per cent level. However, most of the pairs of standard deviations exceed the limits of the F test at the same confidence level. It was decided to ignore these results on the basis that most of the exceeding values were comparisons with the first set, and that the measurement techniques had apparently not hardened into a routine at the time this set was taken. Thus the conclusion was reached that all R 's are a sample of the same population.

Since sample identity was ignored in the above comparison, the result could not be used to obtain a correction factor if the results were to be examined for differences between reference and ore samples. Therefore the six R 's involving only the reference sample were averaged and fitted by least squares to a line of the form

$$R_c = 1 + b(m - 105)$$

in which m is the mass of the minor fragment ion involved in the ratio, R_c . The constant, b , of this line has the value $(2106 \pm 274)10^{-6}$. The fitted values for the correction factor, R_c , are given in Table 5, along with the averages of the individually corrected sample ratios. Since the effect of R_c is to transform a ratio measured on the lower inlet into

Table 5. Inlet correction factors and corrected ratio of ratios averages

Identity	Ratios			
	R46	R47	R49	R50
R_c	0.99579±55	0.99789±28	1.00211±28	1.00421±55
R_{corr}				
L/U	0.99903±488	0.99964±275	1.00136±338	1.00181±512
U/L	0.99997±478	0.99895±317	0.99956±236	1.00058±490
average	0.99952±478	0.99928±296	1.00041±299	1.00116±497
average less two ^a	1.00030±363	0.99973±232	1.00016±284	1.00039±389

^aThe first and sixth sets of ratios in Table 6 were omitted from this average.

its equivalent on the upper inlet, it follows that the 17 R's in Table 3 in which the ore sample was on the lower inlet must be multiplied by the proper value of R_c , and that the 19 others must be divided. The averages of these operations are entered in Table 5 as R_{corr} , L/U and U/L respectively. They were tested by t and F tests and found to be within the 5 per cent limits, indicating that the overall average shown is a valid one. The hypothesis that each average R_{corr} is exactly one was also tested and found to be true within the same limits.

The individual values of R_{corr} are given in Table 6. It is interesting to note that 26 values are more than one standard deviation from the averages, and an additional 9 exceed two standard deviations. However, if only two sets

Table 6. Corrected ratios of ratios

Sample	Ratio			
	R46 _{corr}	R47 _{corr}	R49 _{corr}	R50 _{corr}
DUP-3	0.98574	0.99258	1.00667	1.01516
AC-1	1.00581	1.00435	1.00123	0.99937
NI-4	0.99672	0.99870	1.00091	1.00394
NJZ-1	1.00255	0.99899	1.00202	1.00251
NL-10	0.99997	1.00020	1.00429	0.99882
NJZ-4	0.98703	0.99045	1.00256	1.01332
DUP-2	0.99791	1.00040	1.01025	1.00999
NL-9	1.00106	0.99991	0.99931	0.99832
PPG-1	0.99121	0.99277	1.00309	1.00912
NL-7	0.99757	1.00030	0.99882	1.00472
NI-1394	0.99762	0.99778	0.99922	1.00331
NI-1394	1.00432	1.00242	0.99724	0.99540
NI-1394	1.00631	1.00487	0.99971	0.99507
NI-1394	0.99924	0.99971	1.00184	1.00230
NL-10	1.00124	1.00049	0.99710	0.99689
NL-4	1.00329	1.00150	0.99710	0.99702
GSR-2A	0.99551	0.99718	1.00131	1.00284
NJZ-1	0.99756	0.99809	1.00238	1.00243
DUP-1	0.99793	0.99880	1.00424	1.00298
DUP-3	0.99696	0.99726	0.99896	0.99975
DUP-3	0.99984	0.99837	0.99856	1.00003
NL-9	1.00314	1.00122	1.00091	0.99807
PPG-1	0.99858	1.00082	1.00171	1.00298
NL-5	1.00208	0.99968	0.99657	0.99595
AC-1	0.99560	0.99678	0.99654	1.00325
NI-1394	1.00338	1.00110	0.99697	0.00648
NJZ-4	0.99996	0.99951	1.00052	1.00038
MGS-1	1.00358	0.99979	0.99763	0.99907
NJZ-3	1.00134	0.99919	1.00015	0.99921
GSR-1A	1.00169	1.00076	0.99938	0.99938
DUP-2	0.99818	0.99673	1.00101	1.00258
M-594	0.99947	1.00107	0.99953	0.99856
NL-15	0.99763	0.99853	1.00128	1.00398
M-123	0.99859	0.99959	1.00170	1.00181
NL-7	1.00842	1.00390	0.99617	0.99327
GSR-3	1.00586	1.00021	0.99775	0.99343

of ratios (the first and sixth in Table 6) are omitted, the latter figure drops from 9 to 2 (before recomputation of s). Perhaps it would be profitable to exclude these sets from the data; it is true that the averages and deviations look better if this is done (see Tables 5 and 7). On the other hand ratios for these two samples were among those replicated, and the replicate determinations show no significant difference from the averages. Further, the numbers of ratios exceeding various limits indicates that the distribution deviates only slightly from a normal distribution. It was therefore decided to retain all data.

Table 7. Distribution of R values

Average Limit	Number exceeding limit					Total	Normal
	46	47	49	50			
all $\pm s$	8	7	11	9	35	46	
	2	3	2	2	9	7	
less two $\pm s$	8	9	11	9	37	43	
	2	2	1	2	7	6	

It was also noted that such deviations tend to fall in groups, that is, if one ratio of a set exceeded one standard deviation, it was probable that most of the other ratios would also exceed their respective standard deviations. Since no sample showed consistent behavior in this respect in replicate determinations, this was taken to indicate the presence of

another systematic error, probably one connected with behavior of the mass spectrometer. It is suspected that this error could have been largely eliminated had it been possible to change from one sample to another in a shorter time.

To sum up, then, there are three sets of ratios, separable by the dates on which they were determined (see below for further evaluation of the difference). This difference does not extend to ratios of ratios, for which it appears that one set encompasses all of the data. There was a difference between upper and lower sample inlet ratios, which also seems to affect all of the results equally.* When ratios obtained on one sample inlet were normalized to the other sample inlet by means of a correction factor, the ratios of ratios again formed a single set, in which no experimental sample was significantly different from the reference sample.

From strict statistical inference, it can be asserted that, if one more set of ratios is measured for a new experimental sample and the reference sample, and ratios of ratios computed from them, then a chosen percentage of the time the whole experiment is done the values will lie within t s of R_{corr} where $R_{\text{corr}} \pm s$ are from Table 5 and t is an appropriate

*This effect can be rationalized on the grounds that a difference in temperature probably existed between the two inlets because the heating tape wrapped about the inlets was also the only insulation they had.

entry from a table of the Student t distribution. Thus for 95 per cent confidence limits and 35 degrees of freedom (number of ratios of ratios less one) the value of t is 2.03. By the term "the whole experiment" it is meant that new values must be used for another group of R_{corr} if a second new sample is to be compared (2, pp. 45-48). Acton (2, pp. 45-48) has also pointed out that it is commonly desired to make several comparisons with one original group of data, as in the use of a calibration curve, and that for this purpose tolerance limits must be established, which in general differ from the confidence limits used in the simple case. Bowker (12) has stated that tolerance limits "... are computed in such a way that in a fraction γ [confidence coefficient] of the samples from which they are computed they will include at least a fraction P of the items in the distribution." Applied to the present problem this can be restated as with confidence γ it can be predicted that P of the next measured ratios of ratios will fall within $R_{\text{corr}} \pm Ks$. The 95 per cent limits were chosen for both γ and P , and $K = 2.48$ for 36 measurements was read from the table of Bowker (12). Thus any new sample for which ratios of ratios fall outside these limits is probably of different isotopic composition. The present author is 95 per cent confident that 19 of 20 natural terrestrial titanium samples have isotopic ratios within the following percentages of the ratios of the reference sample:

46	47	49	50
1.18	0.73	0.74	1.23

2. Absolute measurements

It would have been preferable to use the parent ion for all analyses so that there need be no concern about a difference in isotopic bond energy causing a perturbation of observed abundances. Similarly, magnetic scans of the isotopic peaks would have skirted the perturbation introduced by voltage scans, which appears to be caused by nonlinear effects of these voltage changes within the ion source. Both of these things would have introduced difficult experimental problems, so all of the data were taken in a simple way, and special experiments were made to determine the value of the necessary corrections.

There are two approaches to these correction or calibration experiments. One approach is to measure the effect of every known systematic error by "standard means", and to determine thereby a correction factor for each error. The term "standard means" is meant to include such things as comparison of voltages via standard cells and comparison of isotopic ratios from parent ions with ratios from fragment ions. This method was used by Flesch (37, pp. 46-54) and is described in detail by him. The other approach is to calibrate the system in toto by measuring mixtures of separated isotopes of the element under analysis. This method has the obvious advantage of being direct and it eliminates the possibility of overlooking an unsuspected source of error. The method is used whenever practical.

Because of previous experience in this laboratory, it was suspected that a calibration using separated titanium isotopes might prove impractical. For this reason, and also for satisfaction of curiosity, some experiments were done to determine correction factors for use of fragment ions and electrostatic focussing. In all of these experiments, ratios were measured as described in the section on relative measurements except that in specified cases ions were focussed magnetically instead of electrostatically, and also that the parent ions (masses 124 ± 2) were measured as well as the principal fragment ions (masses 105 ± 2). The notation used is similar to that used in Table 3, the subscript denoting the ions involved and the method of focussing. Thus

$$R_{47}^{pm/fe} = ([^{47}\text{TiF}_4^+]/[^{48}\text{TiF}_4^+]) / ([^{47}\text{TiF}_3^+]/[^{48}\text{TiF}_3^+])$$

in which the numerator ratio was scanned magnetically, the denominator ratio electrostatically. The data collected in these experiments are presented in Table 8; these are again raw data, each number being the average of ten measurements. Where the ratio 47/48 refers to the fragment ion, the ratio has been corrected for the presence of $^{28}\text{SiF}_4^+$ as described previously. The average correction ratios from these data are presented in Table 9. The overall average was computed from the equation

$$\bar{R}_{pm/fe} = \frac{4R_{pm/fe} + 9R_{fm/fe} R_{pm/fm}}{13}$$

Table 8. Correction data

Scan ^a	Ratios				Date
	46/48	47/48	49/48	50/48	
pm	0.11478±13	0.10096±10	0.07436±7	0.07116±9	13 Jan
fe	0.11024±2	0.10022±3	0.07383±4	0.07116±2	1967
fe	0.10969±6	0.10000±6	0.07401±5	0.07135±7	14 Jan.
pm	0.11445±13	0.10049±18	0.07416±13	0.07063±6	
pm	0.11846±23	0.10082±13	0.07473±36	0.07192±14	25 Jan.
fe				0.07155±3	
fe	0.10560±9	0.09800±4	0.07560±4	0.07455±4	6 Feb.
fm	0.10763±8	0.09900±6	0.07502±8	0.07327±7	
fe	0.10554±8	0.09800±5	0.07550±6	0.07463±4	
fe	0.10558±3	0.09801±5	0.07568±5	0.07453±4	7 Feb.
fm	0.10757±6	0.09892±6	0.07502±3	0.07332±7	
fm	0.10754±6	0.09886±4	0.07503±6	0.07321±5	
fe	0.10559±4	0.09797±5	0.07564±3	0.07461±4	
fe	0.10568±7	0.09805±9	0.07560±5	0.07449±4	8 Feb.
fm	0.10749±5	0.09899±4	0.07499±5	0.07317±4	
fm	0.10757±9	0.09890±7	0.07496±6	0.07322±6	9 Feb.
fe	0.10577±6	0.09816±3	0.07562±5	0.07447±3	
fe	0.10572±6	0.09812±3	0.07566±4	0.07441±3	14 Feb.
fm	0.10753±7	0.09898±8	0.07496±3	0.07308±4	
fm	0.10756±10	0.09891±13	0.07491±4	0.07323±7	15 Feb.
pm	0.1126±3	0.1002±1	0.0749±1	0.0720±1	
fm	0.10757±12	0.09897±6	0.07488±4	0.07319±6	17 Feb.
pm	0.11284±11	0.10062±18	0.07453±8	0.07195±13	

^aThe symbol p is parent ion, f is fragment ion, m is magnetic scan, e is electrostatic scan.

Table 9. Average correction ratios

Ratio	Isotope			
	46	47	49	50
$R_{pm/fe}$	1.0423±16	1.0062±18	1.0046±37	0.9984±78
$R_{fm/fe}$	1.0182±11	1.0092±9	0.9919±9	0.9825±9
$R_{pm/fm}$	1.0480±15	1.0148±26	0.9976±33	0.9832±1
$\bar{R}_{pm/fe}$	1.0595	1.0186	0.9942	0.9760
$R^{\circ}_{pm/fe}$	1.0383±130	1.0191±65	0.9809±65	0.9617±130
R_{flow}	1.00816	1.00406	0.99599	0.99203
R_{cal}	1.0353±586	1.0176±293	0.9824±293	0.9647±586

in which the weighting factors were arrived at by considering that the seven measurements of $R_{fm/fe}$ and two of $R_{pm/fm}$ contribute equally to the product, and thus the product has a weight of (7+2)/2. The two measurements of $R_{pm/fe}$ gave it a weight of two. Values of $\bar{R}_{pm/fe}$ were fitted by least squares to the line

$$\bar{R}_{pm/fe} = 1 + b (n-48)$$

in which n is the mass number of the minor titanium isotope for the corresponding ratio. The fitted values of this correction factor are entered in Table 9 as $R^{\circ}_{pm/fe}$. The effect of this factor is to transform a fragment ion ratio focussed electrostatically to the equivalent parent ion ratio focussed magnetically, thus to remove the perturbing effects of using fragment ions and of scanning electrostatically.

The problem of gas flow in the source region has already been discussed (p.33). One conclusion of that discussion will be restated here: no change of composition was observed in a sample of TiF_4 flowing continuously into the mass spectrometer for 12 weeks. In addition the physical details of the source region and exhaust pump and tubing are unchanged from the experiments of Flesch (37). These items provide the basis for concluding that the correction for gas flow discrimination is the same as that used by Flesch (37, pp. 50-54), that is, that all ratios must be multiplied by the inverse square root of the masses of the molecules involved to correct for effusive flow out of the ion source. This correction, R_{flow} , is shown in Table 9.

Before discussing these corrections further, it will be useful to describe the experiments on absolute calibration so that the two results can be compared. Three preparations of separated isotopes were purchased from the Oak Ridge National Laboratory, Oak Ridge, Tenn., for these experiments. They were supplied in the oxide form. Analyses for isotopes and impurities were made by that laboratory, and their results are summarized in Tables 10 and 11. It would have been preferable to use ^{50}Ti , but the most highly enriched sample of this isotope assayed only about 70 per cent. It was decided that the advantage of using the highest mass isotope was outweighed by the advantage of using a more highly enriched isotope, so ^{49}Ti was used. At the low mass

Table 10. Isotopic analyses of separated isotopes

Isotope	Atom per cent in separated isotope				
	46	48	48a	49	49 ^b
46	84.5 ±0.1	0.25 ±0.02	0.28 ±0.04	1.2	1.163 ±0.012
47	2.71 ±0.05	0.26 ±0.02	0.27 ±0.04	1.2	1.196 ±0.010
48	10.7 ±0.1	99.13 ±0.05	99.01 ±0.08	11.5	12.055 ±0.031
49	0.99 ±0.05	0.19 ±0.02	0.23 ±0.04	83.9	83.416 ±0.022
50	1.11 ±0.05	0.17 ±0.02	0.21 ±0.03	2.2	2.171 ±0.007

^aValues in this column are the average and standard deviation of two determinations made in this laboratory on a Nuclide Corporation Graf 2 mass spectrograph, converted from the measured ratio to atom per cent.

^bValues in this column are derived from my measurements. They are further discussed in the text (p. 62).

Table 11. Spectrographic analyses of separated isotopes^a

Element	Weight per cent		
	46	48	49
B		0.01	
Ca	0.02		
Cb	0.2		
Fe	0.02		
Mg	<0.02		0.01
Na	<0.01		
Si	<0.05	0.03	0.05
Zr	0.1		

^aAbout 28 elements were looked for. Only those for which a spectral line was seen are entered here.

end this problem did not exist, and ^{46}Ti was used. The desire here is of course to use isotopes of greatest and least mass to enhance the sensitivity of any mass-dependent correction.

Amounts of each separated isotope were weighed on a single-pan semimicro analytical balance, the amounts being chosen so that the ratios 46/48 and 49/48 would be close to those observed in ordinary titanium. Weighings were arranged so that only the optical scale of the balance was used. Each weighing was corrected by subtracting the known impurities as listed in Table 11; for example, 0.34 per cent for ^{46}Ti . Weights are given in Table 12. The atomic weight of each separated isotope was calculated from the Oak Ridge abundances for separated isotopes 46 and 48, my abundances for 49, and the atomic masses (56). These data were combined to give the calculated isotopic ratios in each mixed sample, STD-1 and STD-2. The ratios are given in Table 13, along with the experimental ratios. In this case each of the latter is the average of five individual determinations.

It is appropriate to insert here a description of the analysis of separated isotope 49 before continuing the description of the calibration experiment. The isotopic analysis for this separated isotope was given by ORNL with few significant figures and no indication of their precision. Hence it was decided to try an analysis on the same mass spectrometer used throughout this work. Although at the time

Table 12. Weights of separated isotopes

Sample	Isotope	Raw weight, mg	Corrected weight, mg	Computed weight, mg
STD-1	46	6.80	6.777	6.540
STD-1	48	55.03	55.008	55.030
STD-1	49	5.08	5.077	5.306
STD-2	46	6.55	6.528	6.623
STD-2	48	51.41	51.389	51.111
STD-2	49	4.98	4.977	5.160

it was known that residual normal titanium was only slowly removed when an enriched sample was introduced, it was hoped that all normal titanium would be flushed out within a day or two. This was not so. However, it was possible to obtain consistent values for the abundance of each isotope by the following calculation, in which it is assumed that the measured values can be obtained by mixing a fraction of normal titanium with the enriched. Here is a step-by-step description of the computation, with some further discussion. Table 14 contains the measured isotopic ratios, again an average of five determinations of each ratio. The ratios were converted to fractional abundances, with M denoting abundances measured in the analysis and N denoting abundances from the normal ratios.* The the equation,

$$Nx + OR(1 - x) = M$$

*Ratios of normal titanium were measured several times shortly before the enriched isotope was analyzed. The ratios are: 103/105, 0.10564±8; 104/105, 0.09804±7; 106/105, 0.07561±6; 107/105, 0.07452±8.

Table 13. Isotopic ratios in standard samples

Sample	Ratio				Date
	103/105	104/105	106/105	107/105	
STD-1	0.11235	0.01024	0.08220	0.00742	5 Apr. 1967
	0.11093	0.00930	0.08193	0.00670	
	0.10922	0.00829	0.08160	0.00607	6 Apr.
	0.10841	0.00940	0.08193	0.00713	
	0.10828	0.00895	0.08172	0.00655	
	0.10822	0.00867	0.08164	0.00631	
	0.10792	0.00835	0.08151	0.00614	7 Apr.
	0.10725	0.00803	0.08109	0.00598	
	0.10620	0.00780	0.08094	0.00575	
	0.10576	0.00763	0.08097	0.00556	11 Apr.
	0.10577	0.00765	0.08096	0.00562	12 Apr.
	0.10600	0.00766	0.08087	0.00555	
	0.10608	0.00760	0.08069	0.00547	13 Apr.
	0.10610	0.00758	0.08071	0.00550	14 Apr.
	0.10614	0.00763	0.08066	0.00549	
	Average of last six	0.10598 ±0.00017	0.00762 ±0.00003	0.08081 ±0.00014	0.00553 ±0.00006
Calculated	0.10969	0.00703	0.07757	0.00501	
STD-2	0.11514	0.01003	0.08349	0.00733	26 June 1967
	0.11551	0.00883	0.08389	0.00641	
	0.11541	0.00846	0.08406	0.00609	
	0.11512	0.00822	0.08442	0.00592	27 June
	0.11511	0.00815	0.08430	0.00587	

Table 13. (Continued)

Sample	Ratio				Date
	103/105	104/105	106/105	107/105	
STD- 2	0.11498	0.00814	0.08441	0.00591	
	0.11506	0.00807	0.08440	0.00584	28 June
	0.11499	0.00807	0.08442	0.00580	
	0.11489	0.00794	0.08453	0.00573	30 June
Average of last six	0.11502 ±0.00009	0.00810 ±0.00010	0.08441 ±0.00007	0.00584 ±0.00007	
Calculated	0.11292	0.00719	0.08122	0.00513	

Table 14. Measured abundance ratios of ^{49}Ti

103/106	104/106	105/106	107/106	Date
0.07145	0.06791	0.6913	0.06624	25 Feb. 1967
0.06558	0.06235	0.6340	0.06195	
0.06172	0.05861	0.5946	0.05893	
0.05376	0.05112	0.5219	0.05372	
0.05134	0.04887	0.4982	0.05199	
0.05016	0.04794	0.4869	0.05109	26 Feb.
0.05236 ^a	0.05006	0.5065	0.05255	27 Feb.
0.04079	0.03906	0.3971	0.04455	

^aThe temperature of the analyzer tube was increased before this series, which increased the amount of normal titanium introduced and reversed the trend in prior ratios.

in which x is the fraction of normal titanium contributing to the measured abundance and OR denotes the abundances supplied by ORNL, was solved for x for each of the 40 abundances, M . Eight averages were calculated, corresponding with the eight determinations. The fact that the standard deviations of these averages were only one to two per cent of the average values supported the belief that this method was valid. Each of these averages, \bar{x} , was combined with the corresponding individual abundances, M , to give a first corrected ORNL abundance, OR_1 , according to the equation,

$$OR_1 = (M - N\bar{x}) / (1 - \bar{x})$$

The results of these computations were eight values of abundance for each of the five isotopes. The average values and their standard deviations are shown in Table 10. The whole computation was repeated, using OR_1 in place of OR .

The values of OR_2 thus found were identical with OR_1 for four isotopes and differed by 0.001 atom per cent for the fifth. The high degree of internal consistency is a strong indication that this method is valid. Therefore these abundances were used in preference to the ORNL abundances.

In the calibration experiment it was hoped that a similar correction for admixture of residual normal titanium would help to bring measured and calculated ratios into agreement, but such was not the case. Fractions of normal titanium necessary to make the abundances agree varied widely among the several isotopes, and some fractions were negative - a physical impossibility. It was concluded that some other systematic error was swamping out this source of error. The values of the fractions indicated that the other error was connected with the amounts of separated isotopes. No method excepting trial and error could be devised to connect this possible error source with the measured values by a forward calculation. However, the reverse calculation is quite straightforward, and was done as follows: an equation was set up for each isotope using as unknowns the mole fractions of the three separated isotopes plus normal titanium, and using as coefficients the abundances given in Table 10 for the separated isotopes and the average of the first 22 ratios of Table 3 for normal titanium;* the constants used

*Measurements of normal titanium at the time of this experiment agreed well with these ratios.

were the measured abundances; these five equations in four unknowns were augmented by the equation defining mole fraction, and the six were solved by the method of least squares; separate solutions were obtained for each standard sample; the mole fractions thus derived were used to compute the least squares abundances. The last computation is a check. It gave abundances identical to the measured abundances, which indicates that the least squares numbers are a good fit to the data. It also tends to confirm the suppositions that some normal titanium was present and that the amounts weighed were not in proportion to the amounts indicated by the measurements.

Weights of each separated isotope were calculated from these mole fractions using the normalizing convention that the same total number of moles is present. These computed weights are shown in Table 12, from which it is apparent that a reasonable weighing error cannot account for the discrepancies and that all of the error cannot be put on the same separated isotope for the two samples. It is felt that the most reasonable explanation is that a part of each sample remained unreacted in the solid-solid reaction between TiO_2 and CoF_3 , probably because of inefficient mixing.

This is a disappointing result. In hopes of salvaging something of value the ratios of the calculated ratio to the measured ratio were computed and fitted to least squares lines of the same type used to obtain the electrostatic

scan-fragment ion correction. The slope of the line for STD-1 is -0.022 ± 0.020 ; that for STD-2 is -0.013 ± 0.036 ; that for both samples taken together is -0.0176 ± 0.0293 . This is in remarkably good agreement with the correction line just mentioned, for which the slope is -0.0191 ± 0.0065 . If the gas flow correction is combined with this the slope becomes approximately -0.023 . This figure includes all of the known remaining sources of systematic error (it excludes the impurity correction because this applies to only one isotope; it excludes the inlet correction, R_c , because this applies to only samples on the lower inlet) and is thus the proper correction term to compare with the calibration term of -0.0176 . The correlation is still good, and is taken to confirm the validity of the calibration experiment. The latter is therefore accepted as correct. Least squares values of the calibration factor, R_{cal} , for each isotope are given in Table 9.

The calibration factor is to be applied to the ratios of the reference sample in the single measurement of 23 March 1967 (see Table 15) because this measurement was made under the same operating conditions as were the measurements in the calibration experiment.

The other data in Table 15 were collected so that some conclusion could be drawn concerning the uncertainty of the 23 March measurement. Essentially all measurements on both reference and ore samples are included. Each set contains

Table 15. Averages of sets of ratios

Dates	103/105	104/105	106/105	107/105	Number in set
27 June - 7 July 1966	0.10794±35	0.09907±17	0.07523±25	0.07302±31	13
26 July - 14 Sep.	0.10745±32	0.09889±17	0.07539±14	0.07328±25	8
16 Sep. - 2 Oct.	0.10785±45	0.09906±28	0.07515±22	0.07312±32	22
11 Oct. - 10 Nov.	0.10704±29	0.09870±18	0.07530±12	0.07357±17	36
15-29 Dec.	0.11056±49	0.10017±20	0.07394±15	0.07113±29	23
13-14 Jan. 1967	0.10996±39	0.10011±16	0.07392±13	0.07126±13	2
6-14 Feb.	0.10564±8	0.09804±7	0.07561±6	0.07453±8	7
23 March	0.10800±124	0.09918±60	0.07500±38	0.07283±76	1
Average of 1-3	0.10780±43	0.09903±24	0.07522±23	0.07312±31	

a group of measurements separable from adjoining sets by a period of time, by a suspected difference in averages, or by a known change in the mass spectrometer. The first two sets are from miscellaneous experiments on the reference sample, the next three are from Table 3, the next two are the "fe" scans from Table 8, and the last is the single measurement just mentioned. Where necessary, ratios were normalized to the upper sample inlet by using the factor R_c of Table 5. The known changes in the mass spectrometer and the dates on which they were made are: electrometer tubes replaced on 15 September 1966, ion source cleaned and filament replaced on 28 November 1966, filament replaced on 1 February 1967, filament replaced on 10 March 1967.

The t test was applied to adjacent sets. The results indicate that the first three sets are from the same population, and that sets five and six can also be grouped. From this it is concluded that replacing the filament introduces a bias, that replacing electrometer tubes has no effect, and that there remains an unexplained difference between sets three and four. Since this is a small difference, and since the large differences have all been explained, it will be assumed that only a small difference could have occurred between 23 March and the conclusion of the calibration experiment on 30 June 1967.

The standard deviation in the averages of sets one to three will be taken as the random error in the measurement of 23 March, and the difference between set-three averages and set-four averages will be taken as a measure of the systematic error, and will be added to the random error. It is this overall estimated error which is shown for the 23 March measurement. The conclusions drawn have nothing to do with the fact that this measurement happens to agree with these sets; in great part these sets were chosen because the measurements comprising them were taken over a time span comparable to that taken in the calibration experiment.

When the products of R_{cal} and the ratios of 23 March are transformed to abundances the results are

$${}^{46}\text{Ti} = 8.24 \pm 0.44 \text{ per cent}$$

$${}^{47}\text{Ti} = 7.44 \pm 0.21$$

$${}^{48}\text{Ti} = 73.71 \pm 0.47$$

$${}^{49}\text{Ti} = 5.43 \pm 0.16$$

$${}^{50}\text{Ti} = 5.18 \pm 0.31$$

These abundances and in particular the error terms apply to the reference sample only.

The measurements of natural abundance can also be placed on an absolute scale. It has been shown that natural and reference ratios are the same, so the abundance figures are unchanged. Error terms are derived by normal propagation procedures applied to the product

$$\begin{aligned}
 R_{\text{natural, absolute}} &= R_{\text{cal}} \times R_{23 \text{ Mar}} \times R_{\text{corr}} \\
 &= R_{\text{reference, absolute}} \times R_{\text{corr}}
 \end{aligned}$$

From this the absolute abundances of natural terrestrial titanium are

$${}^{46}\text{Ti} = 8.24 \pm 0.45 \text{ per cent}$$

$${}^{47}\text{Ti} = 7.44 \pm 0.22$$

$${}^{48}\text{Ti} = 73.71 \pm 0.48$$

$${}^{49}\text{Ti} = 5.43 \pm 0.16$$

$${}^{50}\text{Ti} = 5.18 \pm 0.31$$

It is obvious that the calibration experiment contributes the controlling quantity to the errors. Just how large the error terms are can be seen from the following tabulation, in which the percentage error from each source is shown for ${}^{46}\text{Ti}$.

5.7 calibration experiment

1.15 ratio of 23 March

(0.40 relative error plus

0.75 estimated absolute error)

1.18 corrected ratio of ratios

5.9 root of sum of squares

III. DISCUSSION

The isotopic abundance of titanium has been determined several times, in each case by mass spectroscopic means. Aston (6) measured the titanium abundances near the end of the period embracing his pioneering work in the discovery of isotopes and determination of their abundance. His values were obtained by photometric determination of line density on a mass spectrogram. The sample he used was titanium fluoride prepared by the reaction of pure oxide with hydrofluoric acid (7)*. The Ti^+ ion was used for analysis; it was formed by electron bombardment of a mixture of the sample and graphite which was pressed into the hollow anode of a gas discharge bulb, the discharge being maintained and stabilized by iodine vapor introduced through a capillary. In this way Aston became the first to observe the five natural isotopes of titanium, but the accuracy of his abundance determinations was quickly superseded by the work of Nier. The abundance measurements of Aston and others are shown in Table 16 in chronological order.

In the middle thirties Nier started a program of measuring abundances accurately and of setting upper abundance limits at other isotopic positions. This work included titanium (65). The fluoride, TiF_3 , was vaporized

*According to a recent report (84) this reaction yields the oxyfluoride, $TiOF_2$.

Table 16. Titanium isotopic abundances

Author	Ion	Per cent abundance				
		46	47	48	49	50
Aston ^a	Ti ⁺	8.5	7.8	71.3	5.5	6.9
Nier ^b	TiF ₃ ⁺	7.95	7.75	73.45	5.51	5.34
Hibbs ^c	Ti ⁺	8.22±0.13	7.42±0.05	73.38±0.11	5.56±0.04	5.41±0.05
	TiBr ⁺	7.92±0.07	7.50±0.07	73.09±0.13	5.90±0.13	5.59±0.11
Matraw and Pachucki ^d	Ti ⁺	7.87	7.25	73.9	5.56	5.43
Hogg ^e	TiCl ₃ ⁺	7.99±0.02	7.32±0.02	73.99±0.07	5.46±0.02	5.25±0.05
Drawin ^f	TiO ⁺	8.00±0.05	7.29±0.04	73.98±0.08	5.38±0.05	5.35±0.04
this work ^g	TiF ₃ ⁺	8.24±0.45	7.44±0.22	73.71±0.48	5.43±0.16	5.18±0.31

^aReference (6).

^bReference (65).

^cReference (43). Error cited is "L. E. (\bar{X} , 0.05)" (95 per cent confidence level?).

^dReference (57).

^eReference (44). Error cited is standard deviation.

^fReference (32). Error cited is standard deviation.

^gSee p. 73 for the individual contributions to each error term.

from a small furnace in the source region and ionized by electron bombardment. The resulting molecular ions were analyzed in a 180° magnetic analyzer by changing the accelerating voltage. Nier (66) felt that because the electrode potentials in his ion source were obtained in proportion to the accelerating voltage by means of a resistor string, all ions arriving at the collector would have followed the same path and no isotopic discrimination should have occurred from this cause.

Hibbs was concerned with establishing methods for assay of separated isotopes. He used material of natural abundance primarily for testing these methods. The report of work on titanium (43) contains no information about the mass spectrometer or its operating conditions, but a report (42) immediately previous notes that a Nier type, 60° mass spectrometer was in use and that magnetic scans were made. Single collector methods appear to have been used. The fragment ions Ti^+ and TiBr^+ were measured after electron bombardment of TiBr_4 vapor introduced through a heated delivery tube from a supply at -26°C .

The next published work on titanium was done by Matraw and Pachucki (57) who used $\text{Ni}(\text{CO})_4$ and TiCl_4 as volatile metal compounds to test their unmodified General Electric [Analytical] Mass Spectrometer. It is not known to the author that this company made any instrument other than one using a 60° deflection, a magnetic scan, and a single

collector. Abundances were reported for the Ti^+ ion.

The first to use natural samples was Hogg (44) who reported analyses of five minerals, four of which were from known localities. He found no variation among them, nor any difference between them and a reference sample of "chemically pure" oxide. He used a 180° mass spectrometer, but gave no details about how it was used. Again, it appears that single collector methods were used. The $TiCl_3^+$ ion, obtained by electron bombardment of $TiCl_4$ vapor, was used for analysis. The data were first split and used to find the chlorine isotope ratio giving the best fit. This was then taken as a constant in the recombined data, which were analyzed by a least squares method for the titanium isotope abundances.

Drawin (32) made a number of changes in the methods used heretofore, the main ones being use of thermal ionization source and a dual collector. He used a 60° sector instrument (Atlas-Werke model CH-3/57). The sample was TiO_2 prepared by dissolving the metal in a mixture of HCl and H_2SO_4 and boiling in order to hydrolyze the titanium. The sample was fused onto a filament with borax and the TiO^+ ion was analyzed.

A glance at Table 16 is sufficient to show that the results of Aston are not of sufficient precision to merit further consideration. The lack of precision reflects nothing more than that photographic detection is inherently less precise than electrical detection. In addition, the value for ^{50}Ti

is very doubtful, probably because of CF_2^+ formed by reaction within the anode mixture. All of the other work seems to be of roughly comparable precision, and, as no rigorous attempts were made to place any work on an absolute scale, it can only be judged in terms of the various systematic errors which may have been present. This is an onerous task for the present author since such judgments can only be made in terms of personal experience, and his experience is such that he must reject that set of abundances in which he has the most faith.

Some sources of error are definite, while others can only be inferred. In the work of Nier, his statement (see p. 76) concerning voltage discrimination was subsequently shown to be incorrect (8, pp. 69-85). Hence there is a definite possibility that some voltage discrimination was present. This is contrasted with the work of Hibbs (and of Matraw and Pachucki and Drawin) in which part of the advantage of magnetic scanning may have been offset by the use of a permanent magnet to collimate the ionizing electron beam. The presence of the magnet can only be inferred from common practice. Another definite source of error is the use of fragment ions by all except Nier. Little is known about the cause of this discrimination, but it is suspected that the effect is enhanced by breaking a greater number of bonds. Thus the results of Hogg would be less affected than those of Hibbs and Matraw and Pachucki. Drawin's work is exempted on the grounds that the effect is different for thermal ionization. Finally it

is inferred that in all but the work of Drawin the high resistance resistors in the preamplifier circuits may not have been ohmic in response to different ion currents.

Another type of error is that inferred by intercomparison of results. This is exemplified by Aston's result for ^{50}Ti noted above. Another example is found in Nier's result for ^{47}Ti , which is higher than the average, and could be brought closer to the average by a postulated correction for $^{28}\text{SiF}_4^+$. The presence of this source of error is suggested by the use of fluorides by both Nier and the present author, by the presence of glass (as a source of silicon) in both instruments, and by the necessity for the correction in the present work. The last example of this type of error is in the work of Drawin, in which it was noted that the results for ^{49}Ti and ^{50}Ti are anomalously close to each other. In a paper otherwise exemplary in noting sources of error, Drawin makes no mention of a correction for the oxygen isotopes. If this was overlooked, then a crude calculation shows that ^{50}Ti should be changed to 5.20 per cent and ^{48}Ti to 74.13 per cent to account for the contribution of $^{48}\text{Ti}^{18}\text{O}^+$ to $^{50}\text{Ti}^{16}\text{O}^+$. The other corrections appear to be less than the random error.

It is concluded that the results of Hogg are least affected by systematic errors, and thus represented the best available estimate of the abundance of the titanium isotopes. The results of the present work are thought to be more reliable than those of Hogg because of the extensive attempts to place

the measurements on an absolute basis. Admittedly, these attempts gave results with large error terms, but they are the only absolute measurements available. The principal contribution to the large error terms was from the calibration experiments.

The relative measurements presented here represent a considerable extension of the work of Hogg (44) in seeking natural variations. Not only were more samples measured, but also the samples were selected to cover the majority of commercial sources of titanium. Since no variations were found, it can only be concluded that none exist in the samples measured within the stated limits of precision. This is the same conclusion that was reached by Hogg. The implications concerning nucleogenesis and geologic fractionation are meager. If more than one source of titanium exists, and if the sources are different in isotopic composition, then mixing has smoothed out these differences to less than the stated limits. Such fractionation as may exist has not caused differentiation exceeding these limits. Probably the most profitable conclusion to draw from this is that measurements of greater precision might well show differences of interest.

Such differences are being discovered. As noted earlier, calcium and molybdenum have been found to show natural isotopic variations, and quite recently tellurium (76) was added to this group. These discoveries lead the author to believe that a new period in abundance measurement has begun, in which

instrumental methods of increased precision are being used to uncover isotopic variations previously hidden.

In the present work, the fact that the methods were being pushed probably beyond their limits accounts for much of the lack of precision in the results. Primary factors here are the highly corrosive nature of TiF_4 and the necessity for subliming it directly into the source region. These lead to difficulty in controlling ion currents, to memory effects, and to a slow switchover from one sample to another. Lack of time in part precluded investigation of other compounds of titanium which might have given better results in the instrument available. A direct insertion vacuum lock (such as described by Junk and Svec (46)) might also have helped avoid some of the difficulties involved in working with TiF_4 .

It is very interesting to note that the TiO_2 used by Baxter and Butler (10) in their work on the atomic weight of titanium appears to be isotopically identical with the reference sample used in this work. This is the first time that material used in a chemical determination of atomic weight has been examined mass spectroscopically. The fact that this sample is isotopically normal enhances the value of the chemical determination.

It is unfortunate that the absolute abundance experiment was of such low precision. The author is therefore reluctant to compute an atomic weight from the results. However, if this is

done using the abundances on page 73 and masses from the 1964 atomic mass table (56) the mass spectrometric atomic weight is

$$47.87 \pm 0.37$$

This result certainly offers no real competition to the chemically determined weight (because of the large error in the calibration experiment) but it does tend to confirm the previous mass spectrometric atomic weight, 47.88, rather than the internationally accepted value of 47.90 (17).

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*Abbreviations used in this list conform to the usage of Chemical Abstracts as published by Chemical Abstracts Service, Columbus, Ohio, in the book, *List of periodicals abstracted by Chemical Abstracts*, 1956.

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