

92P

INTERIM REPORT TO NASA

Grant No. NSG-222-61

Attention: Mr. Robert P. Bryson

Subject: Physical and Chemical Studies of Tektites

Principal

Investigators: Professor W.H. Pinson, Jr. and Dr. C.C. Schnetzler, Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge, Mass.

Submitted: November 5, 1963

William H. Pinson, Jr.

William H. Pinson, Jr.  
Associate Professor of Geology.

OTS PRICE

XEROX \$ 3.00 ES  
MICROFILM \$ .75 MF

FACILITY FORM 608	N 65 10526	
	(ACCESSION NUMBER)	(THRU)
	72 (PAGES)	1 (CODE)
	NASA CR 58865 (NASA CR OR TMX OR AD NUMBER)	13 (CATEGORY)

## CONTENTS

This report consists of preprints of two papers which have been submitted to Geochimica et Cosmochimica Acta for publication on October 29, 1963.

These papers are entitled:

- (1) Variations of Strontium Isotopes in Tektites, by C.C. Schnetzler and W.H. Pinson, Jr.
- (2) A report on Some Major Element Analyses in Tektites, by C.C. Schnetzler and W.H. Pinson, Jr.

Also included in this Report is a bibliography of the papers published during the two years of operation under NASA Grant No. NSG-222-61.

A Statement of Progress is included.

A Distribution List for this Interim Report is included.

## Statement of Progress

Dr. Charles Schnetzler has been employed under this NASA Grant at M.I.T. as a Research Associate for the past two years. This fall Dr. Schnetzler took a job with the Theoretical Division of the Goddard Space Flight Center of NASA, having accomplished his major aims in tektite research at M.I.T.

Several graduate students at M.I.T. have been employed using funds from this Grant. These students were employed as Research Assistants. Their names and dates of employment are:

Mr. Dave Jackson, 1961-1962

Mrs. Marla Moody Heath, 1962-1963

Mr. John Philpotts, June 1963 to present

Mr. Robert Shields, September, 1963-November, 1963

Mr. Shields is presently being supported by other funds.

Mr. Philpotts plans to begin work on a Ph.D. thesis on tektites upon completion of his General Examination this fall. For this purpose we have obtained a very fine collection of moldavites, representing 13 geographical localities.

**Bibliography of Published Papers  
under NASA Grant No.  
NSG-222-61**

- (1) Rubidium-strontium correlation of three tektites and their supposed sedimentary matrices, (1962), Pinson, W.H., and Schnetzler, C.C., Nature, London, 193, pp.233-234
  
- (2) The lanthanum, europium and dysprosium contents on two tektites (1963), Chase, J.W., Schnetzler, C.C., Czamenske, G.K., and Winchester, J.W., Journal of Geophysical Research, 68, pp.577-579.
  
- (3) The Chemical Composition of Tektites, (1963), Schnetzler, C.C., and Pinson, W.H., Chapter 4 in the book Tektites, Edited by John A. O'Keefe, University of Chicago Press, 1963, pp.95-129.

Distribution List

No. of Copies

Recipients at NASA

3

Mr. Robert P. Bryson, S.L.

1

Mr. Ryan, of RASPO

1

Dr. C.C. Schnetzler

Recipients at M.I.T.

1

Professor R.R. Shrock

1

Mr. Frank Conroy

1

Mr. Milton Holzman

1

Professor P.M. Hurley

1

Professor W.H. Pinson, Jr.

VARIATION OF STRONTIUM ISOTOPES IN TEKTITES #

C. C. Schnetzler\* and W. H. Pinson, Jr.  
Department of Geology + Geophysics  
Massachusetts Institute of Technology  
Cambridge, Massachusetts

N 65 10527

10521 over

ABSTRACT -- The rubidium, strontium, and strontium isotopic compositions have been determined in tektites from Indo-China, Philippine Islands, Java, Australia, Texas, Georgia, Massachusetts, and Czechoslovakia. The range of  $Sr^{87}/Sr^{86}$  ratios in 18 tektites is from 0.7121 to 0.7223, indicating the results of Pinson et al. (1958), reporting no radiogenic strontium in tektites, were not of sufficient precision to study the problem definitively. This range of  $Sr^{87}/Sr^{86}$  ratios is quite small compared to the range found in nature, in general agreement with previous studies of oxygen and silicon isotopes in tektites. Rb and Sr contents of tektites from a given locality are very similar, but differences exist between localities. There is indicated, however, a sympathetic variation of the  $Sr^{87}/Sr^{86}$  and Rb/Sr ratios; i.e., the tektite groups have age values of approximately 400 m.y. If tektites were derived from the Moon, and surface of the Moon is old (4.5 b.y.), the observed  $Sr^{87}/Sr^{86}$  ratios could not have been developed by a chondritic, granitic, or tektitic surface material, but could have been generated by a basaltic type

-----

#M.I.T. Age Studies No. 39

\*Present address: Theoretical Division, National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Maryland.

material. However, production of tektites from a basaltic type surface material during a high temperature fusion implies extreme fractionation in a direction contrary to expectation. A second possibility is that the Moon has undergone differentiation within the last 500 m.y.

*Author*

INTRODUCTION -- Several elements whose isotopic compositions vary for reasons other than radioactivity, i.e., due to physical-chemical fractionation, have been isotopically analyzed in tektites. These include hydrogen (Friedman, 1958), oxygen (Silverman, 1951; Taylor and Epstein, 1962, 1963), and silicon (Tilles, 1961). The values obtained were compared to the isotopic composition of different types of terrestrial and extra-terrestrial material in the hope of obtaining a clue to the origin of tektites.

Although the variation of strontium isotopes in nature is due to radioactivity, the half life of the decay of  $Rb^{87}$  to  $Sr^{87}$  is so long, approximately  $4.7 \times 10^{10}$  years (Glendenin, 1961), no measurable change has occurred in the  $Sr^{87}$  content since the tektites were formed from their parent material. This formation of the tektites is assumed to have occurred at the time dated by the K-Ar method, i.e., less than 35 m.y. ago (Zahringer, 1963). Also, as strontium is much heavier than hydrogen, oxygen, or silicon it should not be as subject to fractionation during the high temperature fusion (Taylor and Epstein [1963] found a slight increase in the  $O^{18}/O^{16}$  ratio during fusion of tektite glass). Thus, the strontium isotopic composition of the tektites now should be the same as the parent material at the time of fusion.

The relative isotopic abundance of  $\text{Sr}^{87}$ , conveniently expressed as the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, in a given system is determined by the Rb/Sr ratio of the system, the initial abundance at an initial time, and the time elapsed since this initial time. Thus terrestrial materials, having different Rb/Sr ratios, different initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, and different ages, have a wide range of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. In this respect the study of strontium isotopes may be more informative than the study of oxygen, hydrogen, or silicon which show a rather small range of variation in nature.

In addition, of course, a knowledge of the relative isotopic abundances of strontium, and the Rb and Sr elemental contents enable the calculation of an age value for the sample. In the case of samples such as tektites whose association or past geologic history are in doubt, however, a number of assumptions must be made and such age values must be interpreted with discretion.

Previous studies of strontium in tektites have been made in this laboratory, but have been plagued with analytical difficulties. Pinson et al. (1956) suggested that the relative Sr isotopic composition of a representative sampling of tektites from all known localities be measured; if the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios are identical in correspondence to their Rb/Sr ratios (all lying on the same isochron) this would prove their extraterrestrial origin, as this circumstance occurring in terrestrial rocks from different parts of the world would be highly improbable.



Later Pinson et al. (1957a) reported the rubidium and strontium, and strontium isotopic composition of three indochinites, two australites, and two philippinites. The  $Sr^{87}/Sr^{86}$  ratios varied from 0.718 to 0.735, while the Rb/Sr ratios ranged from 0.39 to 1.08, but there was no apparent sympathetic variation between the  $Sr^{87}/Sr^{86}$  ratios and the Rb/Sr ratios. The computed age values, assuming an initial ratio of 0.712 (this was called "normal strontium" as it was the ratio found in sea water), varied from 180 to 730 m.y., with estimated errors of  $\pm 50\%$ , the large error being due chiefly to the poor precision in the  $Sr^{87}/Sr^{86}$  mass spectrometric determinations.

These values were later reported to be in error, and the corrected values for the  $Sr^{87}/Sr^{86}$  ratios were given as 0.712 (Pinson et al. 1958). The corrections were thought necessary due to suspected lack of mass discrimination in the mass spectrometer. In view of the questionable validity of the correction that was applied, the rather large errors in the precision of the measurements and in view of improvement in mass spectrometric techniques, it was thought a re-investigation of the strontium isotopic composition of tektites might prove fruitful. As the strontium isotopic composition is directly related to the Rb/Sr ratio, the elemental rubidium and strontium contents were also investigated.

Techniques

Rubidium and strontium were determined mass spectrometrically by the stable isotope dilution method, and by X-ray fluorescence techniques. The strontium isotopic compositions were determined mass spectrometrically on a separate portion of "raw" (i.e. unspiked) strontium extracted from the tektites. The techniques used in this investigation for the mass spectrometric determinations are essentially the same as described by Herzog and Pinson (1955, 1956). The mass spectrometer used was a standard 6-inch radius, 60° sector, solid source, single collector Nier-type instrument. Amplification of the ion current was obtained by means of a vibrating reed electrometer.

The  $\text{Sr}^{84}$ ,  $\text{Sr}^{86}$ , and  $\text{Rb}^{87}$  spikes used in the isotope dilution analyses were prepared and calibrated as described by Pinson (1960, 1962).

The X-ray fluorescence unit used was a North American Phillips instrument with a tungsten target X-ray tube. The crystal was LiF and the detector was a scintillation counter. The standards used were tektites which had been analyzed for rubidium and strontium by isotope dilution. It was found that tektites from a given locality were similar enough in major element composition so that unknowns and standards from the same area could be compared with no matrix effects, and a precision and accuracy comparable to the mass spectrometric analytical work was achieved.

The powdered sample was packed into a nylon sample holder, covered with a 0.5 mil mylar sheet and put in the X-ray beam. The region of  $K\alpha$  radiation of rubidium and strontium was scanned to

determine the exact location of the peaks, and to pick the angles on both sides of the peaks where background could be obtained free of any interfering element emission. Operating conditions were: LiF crystal; pulse height analyzer: base = 41.5, window = 5.60; number of counts on peak and background = 102,400.

The goniometer was set at the proper angles and the times necessary to accumulate the fixed number of counts were measured at the peak and background position. The calculated counts per second (cps) for the backgrounds were subtracted from the peak intensities to give a net peak intensity. The intensity values obtained for the standard samples were plotted against the ppm strontium, obtained by isotope dilution analyses, to yield a calibration curve. Strontium values for the unknowns were obtained by interpolation from this calibration curve. The rubidium values in the standards were too similar (the Rb varied only from 111 to 129 ppm) to enable a curve to be drawn, so an average value of cps/ppm rubidium was calculated, and this value was used to calculate the rubidium contents of the unknowns.

It was found that only samples of quite similar major element composition could be compared in this manner. The indochinites and philippinites could be compared but samples from other localities gave spurious results when compared with samples from these two localities. This matrix effect could have been eliminated by the addition of an internal standard. However, it was found that the

tektites from a given locality were similar enough so that unknowns and standards from the area could be compared.

It was apparent from the earlier investigations of Pinson and co-workers that the variations of  $\text{Sr}^{87}$  in tektites are small, if present at all. It was also apparent that complete resolution between the large mass 88 peak and the smaller mass 87 peak ( $88/87 \approx 12$ ) was not obtained -- i.e., the 88 peak "tail" was enhancing the 87 peak. Improved vacuum conditions and re-alignment of the mass spectrometer have improved discrimination so that ratios of minimum ion current between the 87 and 88 peaks to the ion current at the 87 peak of 1/600 or better are obtained routinely. A small portion of a typical record are shown in Figure 1 to demonstrate the resolution obtained.

The precision of the strontium isotopic analysis runs can be estimated from replicate runs on several samples shown in Table 1. The Homestead meteorite runs were made of three separate portions of a powdered sample, each receiving independent chemical treatment. The  $\text{SrCO}_3$  standard runs were made on separate portions of a liquid sample and did not undergo any chemical purification before analysis. The standard deviation of a single analysis ( $\sigma$ ) of the  $(\text{Sr}^{87}/\text{Sr}^{86})_N$  ratio in both cases is  $\pm 0.0006$ , or approximately 0.085%.

An isotopic fractionation correction was applied to the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios on the assumption that the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio is a constant and equal to 0.1194. The run-to-run variations of the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio from this value were attributed to instrumental fractionation, chiefly fractionation of the isotopes of different mass off the filament.

Half of any correction necessary to re-adjust the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio to 0.1194 was applied to the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio. The corrected, or normalized,  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios are listed in the tables in columns headed  $(\text{Sr}^{87}/\text{Sr}^{86})_N$ , while the ratios as actually measured are listed in columns simply headed by  $\text{Sr}^{87}/\text{Sr}^{86}$ .

The  $\text{SrCO}_3$  standard (Eimer and Amend Company lot #492327) was also used to monitor the accuracy of the isotope ratio determinations. Five laboratories have informally reported that they find a value of  $(\text{Sr}^{87}/\text{Sr}^{86})_N$  in the range of 0.708 to 0.709 (Hurley et al., 1963). The average value shown for this standard in Table 1 indicates there are no systematic errors between this laboratory and the other reporting laboratories.

Replicate analyses of a tektite by isotope dilution, and by X-ray fluorescence, indicate the rubidium and strontium results have a precision of approximately  $\pm 2\%$  (relative deviation of a single analysis). Inter-laboratory analyses of a standard sample indicate the accuracy of the isotope dilution analyses is about  $\pm 1\%$  (Pinson, 1960, p. 244). By comparison of the strontium and rubidium values for G-1 and W-1 obtained by the M.I.T. Geochronology Laboratory with the results obtained by other methods of analysis (Stevens, 1960, p. 97 and 99) a conservative estimate of the accuracy would be  $\pm 5\%$ .

### Results

The analytical results obtained in this investigation are presented in Tables 2 and 3. Eighteen tektites were analyzed for strontium isotopic composition and 27 tektites were analyzed for rubidium and strontium elemental contents.

Four philippinites, from three different sites, have  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios varying only from 0.7168 to 0.7182, and average 0.7173. As the reproducibility ( $\sigma$ ) of strontium isotope analyses appears to be approximately  $\pm 0.0006$ , the variation in the philippinites is only slightly greater than one would expect from measurement error.

Seven philippinites, including the four analyzed for isotopic composition, have an average rubidium content of  $117 \pm 2$  ppm ( $\bar{\sigma}$ ) and an average strontium content of  $173 \pm 4$  ppm. The variations are greater than measurement error so some differences exist between the samples in rubidium and strontium contents. However, these differences are small and the Rb/Sr ratios are remarkably uniform, averaging  $0.68 \pm 0.02$  for the seven samples.

Four indochinites, from four different localities, also have homogeneous  $\text{Sr}^{87}/\text{Sr}^{86}$  values, ranging from 0.7182 to 0.7185 and averaging 0.7184. This variation is even less than one could expect from measurement error. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of indochinites seems to be slightly higher than the ratio measured in philippinites, but not enough samples have been analyzed to determine if this difference is real. There is no doubt, however, that the Rb/Sr ratio of the

indochinites differs significantly from the Rb/Sr ratio of the philippinites. Eight indochinites have an average Rb/Sr ratio of  $0.89 \pm 0.013$ . The rubidium and strontium contents average  $118 \pm 3$  ppm and  $132 \pm 2$  ppm respectively, the variation again only slightly greater than measurement variation. It should be noted that the average rubidium contents of the indochinites and philippinites are identical within experimental error but that the strontium content of the indochinites is significantly lower than the strontium content of the philippinites. It is thought that alternation of the order of analysis throughout the analysis period excludes any possibility of a systematic error.

Two australites have similar  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of 0.7162 and 0.7172 while a javanite has a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.7182. The Rb/Sr ratios of the two australites are dissimilar however--0.47 and 0.71, and the Rb/Sr ratio of the javanite is 0.64, similar to the philippinites. Two other australites, which were not analyzed for isotope ratios have identical Rb/Sr ratios of 0.66. The four australites have an average Rb/Sr ratio of  $0.62 \pm .05$ , similar to the philippinites but exhibiting much larger variation. However, more sampling is needed of this important group of tektites.

The four North American tektites have an average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.7125, and the range exhibited -- from 0.7121 to 0.7130 -- could be attributed to analytical error. The Massachusetts and Georgia tektites contain quite similar rubidium contents (78 and 74 ppm

respectively) and strontium contents (177 and 170 ppm respectively). The three Texas samples contain slightly less rubidium and strontium than the Massachusetts and Georgia samples, but the Rb/Sr ratios of the five are amazingly similar for samples from such widely separated localities.

The three moldavites analyzed gave the highest  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of the tektites analyzed, averaging 0.7216. Again the range, 0.7208 to 0.7223, is about what one would expect from analytical error. The moldavites also have the highest Rb/Sr ratios, approximately one, of any group analyzed. Due to the small size of the sample available, one moldavite (T3314) could not be analyzed for rubidium and strontium. However, values of 130 ppm Rb and 136 ppm Sr were reported for this sample by Pinson et al. (1958).

An "amerikanite" from the Santa Mesa site in the Philippine Islands was analyzed for rubidium and strontium contents. "Amerikanites" are found intermixed with the true philippinites at this site and exhibit a sculptured tektite-like external appearance. However, they show an internal structure typical of ordinary obsidian, and are considered such by Beyer (1935). Certainly the rubidium and strontium contents of the sample analyzed are dissimilar to the philippinites and are more characteristic of obsidian than tektites. The major element contents of this sample (Schnetzler and Pinson, 1963) are also typical of obsidian and unlike tektites.



Discussion of Results

The first conclusion that can be reached from this investigation is that the work of Pinson et al. (1958) was in error and that tektites do contain radiogenic strontium-- in the limited sense that their  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is greater than "primordial" strontium (approximately 0.700 -- see following discussion) or "normal reagent" strontium (approximately 0.708 to 0.711). However, many of their conclusions were valid and will not be discussed here. It should only be mentioned that the results of this investigation substantiate their conclusions that it is possible, from the viewpoint of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, for the tektites to have been derived from basalt and achondrites, but not from any chondrite yet measured for strontium isotopic composition.

1. Comparison of the variation of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites with the variation of terrestrial materials.

The variation in the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio measured in tektites, from 0.7121 to 0.7223, is certainly real, i.e., not due to analytical error, as the spread is approximately 16 times the reproducibility ( $\sigma$ ). It is of interest to compare this variation with the spread observed in nature and, particularly with the variation one might expect assuming various terrestrial fusion models.

$\text{Sr}^{87}$  and  $\text{Sr}^{86}$  ratios and Rb/Sr ratios reported in the literature for various types of terrestrial and extraterrestrial materials are given in Table 4. A complete literature survey has not been attempted. Unfortunately it has been common practice in Rb-Sr dating to use only a few favorable minerals rather than the whole rock for analysis so

that data of interest to this investigation are sparse, or non-existent, for some rock types.

It can be seen that certain types of rocks show a very limited range of  $\text{Sr}^{87}/\text{Sr}^{86}$  values while others exhibit a considerable range. This is due to the magnitude of the Rb/Sr ratio, the range of the Rb/Sr ratio, and the range of the age of the samples analyzed. Granites have a very large variation in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. As all but one of the 21 granites in Table 4 are over 1000 m.y. old it is apparent that the variation shown is due primarily to the variation in high Rb/Sr ratios. The average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.85 is undoubtedly not a representative number for average granite but is a reflection of the great age of the samples analyzed.

Basalts, however, do not show this extreme range in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios due primarily to their low Rb/Sr ratios. The basalts analyzed by Faure were Recent basalts, but due to their low Rb/Sr ratios little change in the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio would appear in older samples.

Nine obsidians analyzed by Pinson and Bottino (1961) show a limited  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, ranging from 0.704 to 0.724, while the Rb/Sr ratios are quite high--from 1.2 to 31. The low  $\text{Sr}^{87}/\text{Sr}^{86}$  values are due to the young ages of the samples, and since obsidians generally devitrify quickly (geologically speaking) high  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios similar to that observed in granites would not be expected.

Limestones, both young and old, have low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios due to their extremely low Rb/Sr ratios. The Rb/Sr ratio in limestones averages about 0.008 (Faure, 1961, p. 115).

The shales analyzed by Whitney (1962), all from the Hamilton Group of Middle Devonian age, show a considerable spread in both Rb/Sr ratio and  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio. Faure's (1961) analyses are on two composites of Paleozoic shales from the east and west coasts of North America. Variations are suppressed between such composite samples.

Chondrites have fairly high, varying  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. Currently, analyses of stony meteorites are being carried out at M.I.T. Variations from about 0.73 to 0.96 have been found in chondrites.

Achondrites have extremely low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios which show almost no variation (See Table 4). Under the assumptions that 1) all terrestrial and meteoritic strontium was derived from a homogeneous parent material and thus had the same abundance of initial  $\text{Sr}^{87}$ , and 2) the meteorites have existed as closed chemical systems since their formation approximately 4.5 b.y. ago, the achondrites probably give us a good approximation of the initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio. As Patterson (1956) and his co-workers have demonstrated that these assumptions hold true in the case of lead, by analogy the assumptions should be true for strontium. The achondrites have extremely low Rb/Sr ratios ( $\sim 0.005$ ) so their initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio has remained essentially unchanged for  $4.5 \times 10^9$  years. The lowest value found for achondrites (0.700 - Gast, 1960) is accepted here as the primordial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio.

From the above discussion it is obvious that the data is too meager to define the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in the various rock types. The data does show, however, that a great deal of variation does exist.

The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites given in Table 3 and the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios taken from the literature for various materials as given in Table 4 are plotted in Figure 2. The figure shows the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios for various materials from only 0.700 to 0.780, approximately the lower one-seventh of the range exhibited by the data in Table 4. The full range of the data is shown in the inset; the shaded portion of the inset is that part of the scale which has been expanded in Figure 2.

It can be seen that the variation of strontium isotopic composition, although measurable, is quite small compared to the variation observed in nature. This is in qualitative agreement with the constancy of oxygen isotope ratios (Taylor and Epstein, 1962; 1963) and silicon isotope ratios (Tilles, 1961) recently demonstrated in tektites. The strontium isotopic compositions are particularly homogeneous when compared to the isotopic compositions of the acid rocks most commonly mentioned as possible parents for the tektites: siliceous shales (Urey, 1959), granite (Mason, 1959) and granophyre (Lovering, 1960).

It has been suggested that tektites were formed by many independent fusions of terrestrial material in a random manner by such processes as lightning (Hawkins, 1960) or small meteoritic impacts (Spencer, 1933). The probability of fusing a certain type of

material should be in direct proportion to the extent of that material's occurrence upon the earth's surface. Such modes of production should produce tektites exhibiting a wide variation in Sr isotopic composition. However, in recent years it has become apparent that there are only a few independent tektite occurrences. K-Ar ages of tektites (Zahringer, 1963), chemical and specific gravity determination (Schentzler, 1961; Chapman et al., 1963) and aerodynamic evidence (Chapman, 1963) strongly indicate that there are a maximum of four known independent groups of tektites. These are the North American tektites, the moldavites, the Australasian tektites, and possibly the Ivory Coast tektites. Therefore, the tektites listed in Table 3 would represent only three large scale impacts. The variation of isotopic composition between groups could be quite small for several reasons. 1) Naturally, the smaller the number of impacts the greater the probability of striking the same general type of material; it could be merely chance that the different groups of tektites have similar and characteristic compositions. 2) Widespread surficial deposits of quite uniform compositions have been proposed for the parent material in an effort to explain the lack of chemical variation in tektites; soil (Schwarcz, 1962) and loess (Taylor, 1962) have been specifically suggested. The variations in isotopic composition of these particular materials are not known. However, the young sediments which cover much of the earth's surface represent a possible source that has been at least partially homogenized with respect to strontium isotopic composition. 3) The impact may have fused and mixed a very large

volume of material, incorporating a number of rock types, thereby suppressing variations. The larger the volumes fused, the closer the materials' composition would be to crustal abundances. Tektites are strikingly similar in chemical composition to estimates of crustal abundances (Suess, 1963), and it is interesting that the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites are quite similar to recent estimates of the crustal average (Faure, 1961). However, if a large volume of rather heterogeneous material was fused, an almost incredible degree of mixing must have occurred before the liquid parent material solidified into the individual tektites. The tektites of any particular group demonstrate over wide areas a surprising homogeneity with respect to strontium isotopic composition, and it is difficult to imagine such mixing during the short time the material was molten.

Variation of the strontium isotopic composition of tektites do not point specifically to a terrestrial or extraterrestrial origin, but emphasize again how completely homogeneous these objects are. Not enough is known of the strontium isotopic composition of various widespread surficial materials, or the degree of mixing which can occur during high temperature fusion by impact to indicate if such constancy is impossible to explain by a terrestrial impact origin.

## 2. Rb-Sr age values of tektites

It is interesting that the data presented in Tables 2 and 3 suggest a positive correlation of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios with Rb/Sr ratios in the tektites. This is illustrated in Figures 3 and 4.

To quantitatively test the degree of association between the Rb/Sr ratios and the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, the co-efficient of correlation

(Moroney, 1956, pgs. 289-291) was calculated. If all 18 samples are considered independent (Figure 3) the coefficient of correlation ( $r$ ) is +0.91 (when  $r=+1$  there is perfect direct relationship and when  $r=0$  there is no relationship --a random scatter). This coefficient of correlation is significant at less than the 0.1% level-- i.e., the probability of this high correlation coefficient arising by chance in this large a population is less than one in a thousand. If the samples are assumed to represent three independent groups (for reasons discussed above)--the australasian tektites, North American tektites, and moldavites--and the average values for each group is used (Figure 4), the correlation coefficient is +1.0. The small number of groups involved precludes a calculation of the statistical significance of this correlation but the Rb/Sr -  $Sr^{87}/Sr^{86}$  correlation seems more than coincidental or circumstantial. Certainly it is difficult to reconcile this correlation with tektite production within the last 35 m.y. from random materials of different ages, compositions, and geologic histories. It seems quite unlikely that the variables which determine the present  $Sr^{87}/Sr^{86}$  ratios (initial Sr, isotopic composition, Rb/Sr ratios, and ages) would be just in the right combinations to cause unrelated groups of tektites to lie on a particular line.

This correlation suggests the tektites from different areas are related, and might have a common origin. Rocks formed at the same time from a common material (for example, by fractional crystallization from a magma) will develop with time, from a common  $Sr^{87}/Sr^{86}$  ratio,

different  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in relation to their different Rb/Sr ratios. Such a series of rocks, when plotted on a graph of  $\text{Sr}^{87}/\text{Sr}^{86}$  vs Rb/Sr lie on a straight line which is an isochron. The slope of the isochron gives the time since differentiation from the common source, while the intercept of the line on the  $\text{Sr}^{87}/\text{Sr}^{86}$  axis (at zero Rb/Sr) is the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of the source material at the time of differentiation.

If the direct correlation of the Rb/Sr ratios with the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites is due to their derivation from a common source, and if they have remained closed systems to Rb and Sr since that time, age values can be calculated without having to assume a particular initial  $\text{Sr}^{87}/\text{Sr}^{86}$  value. The "least square" line through all 18 points shown in Figure 3 corresponds to the 310 m.y. isochron ( $\lambda_{\text{Rb}} = 1.47 \times 10^{-11} \text{ year}^{-1}$ ). The "least squares" line in Figure 4 through the points representing the averages of the three groups is the 400 m.y. isochron. It is interesting that the initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.705 is within the narrow range of values reported for volcanic rocks of recent origin--that is, this initial ratio is typical of the source region of igneous rocks (Hurley et al., 1962)

The assumption that the tektites and/or their parent material have remained closed systems since their derivation from a common source presents a serious objection to the validity of the age value. If tektites were formed by high temperature fusion at a time dated by the K-Ar method (35 m.y. to less than 1 m.y. ago) then the assumption is that the Rb and Sr contents, and isotopic contents of the strontium in the parent material were not disturbed by this fusion. In a



sense we are looking through this "metamorphic" event to the time of formation of the parent material. The fact that the points do lie on an isochron suggests that extensive selective fractionation might not have occurred during the fusion process as its occurrence would add another variable to those already mentioned (initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, parent Rb/Sr ratios, and age) which must be in a particular combination to cause unrelated samples to lie upon an isochron. In fact, in normal Rb-Sr dating, the isochronal relationship of samples is usually regarded as evidence of closed systems. In view of the assumptions involved, and the small number of groups of tektites, the most that should be stated at this time is that the data suggests the different groups of tektites, or their parent materials, have developed from a common type of source material. The initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of the source was 0.705, and the time since this development has been approximately 400 m.y.

Independent of the validity of a particular isochron age for tektites, it is clear that tektites have undergone differentiation within the last  $10^9$  years. Tilton (1958) pointed out that the U and Th in tektites have increased relative to Pb within the last tens of millions of years, while this investigation has demonstrated that Rb has increased relative to strontium within the last hundreds of million years. If after this differentiation a high temperature fusion took place one might expect Pb to be lost preferentially to U and Th, and/or Rb lost preferentially to Sr. Analyses would yield U-Pb ages that are too young and Rb-Sr ages that are too old; this might be an explanation for the quantitative disagreement in these ages. The

Rb-Sr ages however would be maximum values. The maximum age since the tektites obtained their present Rb/Sr ratio is obtained by assuming an initial ratio equal to the primordial value found in achondrites (0.700). The age calculated is approximately 700 m.y., making them distinctly younger than stony meteorites.

3. Comparison of the data with a possible lunar origin for tektites

Some investigators have suggested that tektites were ejected from the Moon's surface by meteorite impacts (Nininger, 1943; O'Keefe, 1960; and others). Most students of the Moon (for example, Urey, 1952, p. 30; Baldwin, 1949, p. 194) have concluded that the present lunar surface was formed soon after the origin of the Moon, and the Moon has remained relatively cool since that time. Also, the age of the Moon is generally assumed to be the same as the rest of the solar system - approximately 4.5 billion years. Assuming these conditions, it is possible to calculate the present-day  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio for various hypothetical lunar crustal materials.

Granitic material, with an average Rb/Sr ratio of 1 (Faure, 1961, p. 106) and an initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.700 would have, after 4.5 billion years, a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of about .890, far greater than that found in tektites. Chondritic material would have a present day  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of about 0.750, (which is approximately the ratio found in chondrites) again in excess of that found in tektites. If it is assumed that the surface of the Moon has had a chemical composition similar to tektites since its formation the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio would be between 0.78 and 0.90, again far in excess of that found in tektites.

Conversely, the Rb/Sr ratio that would generate a  $Sr^{87}/Sr^{86}$  ratio of 0.718 (average actually observed in tektites) in 4.5 b.y. from a primordial ratio of 0.700 is approximately 0.1. The common terrestrial material whose Rb/Sr ratio most closely resembles this ratio is basalt (see Table 4), and the maria have commonly been theorized as being covered with basaltic lava flows. Thus a basalt that had remained on the surface of the Moon for 4.5 billion years should have about the same  $Sr^{87}/Sr^{86}$  ratio as is observed in tektites. It is difficult, however, to reconcile such a radical change in Rb/Sr ratio (from 0.1 to between 0.44 and 1.1) and other radical changes in composition such as increase in K and Si with any mechanism that would throw the tektites from the Moon, especially high temperature fusion where the alkali elements would be expected to volatilize preferentially to the alkaline earth elements.

Perhaps a more reasonable hypothesis, if tektites come from the Moon, is that there has been differentiation of the Moon since the start of the Paleozoic era and that tektites are the results of fusion of this differentiated material or the ejecta from volcanos during this time. The recent spectroscopic evidence of gas escaping from Alphonsus crater and the existence of a temporary surface temperature of 1200-1500°K in this crater have raised serious doubts concerning the widely held theory that the Moon is cold, without any remnants of volcanic activity (Kozyrev, 1961). By comparing the number of craters on the maria with the number of meteorites of various sizes that fall on the Earth per year, Kreiter (1960) has concluded the maria are about 200 m.y. old. But the same data has been used by

most lunar investigators to conclude the maria are approximately 4.5 billion years old (Opik, 1960).

In short, the low Rb-Sr and U-Pb ages in tektites are difficult to explain if the tektites were derived from the Moon, if the conventional model of a cold undifferentiating body is accepted. Recent differentiation of the Moon is almost required if tektites were produced from its surface.

In conclusion, the slight variation in strontium isotopic compositions exhibited in tektites suggests that if they are terrestrial in origin they must be derived from a uniform widespread source material. The direct correlation of Rb/Sr ratios with  $Sr^{87}/Sr^{86}$  ratios (i.e., the homogeneity of age values) is, however, difficult to reconcile with any terrestrial origin in view of their widespread geographic locations and varying K-Ar ages. As the isochron relationship is based upon only 3 points, the analysis of the fourth possible independent group, the Ivory Coast tektites, is quite critical to this discussion; unfortunately none have been available. It would also be interesting to look for possible uniform source materials which have apparent ages of approximately 300 to 500 m.y., using 0.705 as the initial ratio. The recent suggestions of soil (Schwarcz, 1962) and loess (Taylor, 1962) might be possibilities. Equally germane to this discussion would be the comparison of variations of strontium isotopes in tektites with that observed in known impactites, and the comparison of tektites with postulated source regions, such as the moldavites with the Ries crater, and the Ivory Coast tektites with the Bosumtwi crater (Cohen, 1961). Some of this work is already in progress.

Acknowledgements

The support of the Lunar-Planetary Exploration Branch of the Geophysics Research Directorate, Air Force Cambridge Research Laboratories, Bedford, Massachusetts, under Contract No. AF19(604)-6135, and the National Aeronautics and Space Administration under grant NSG-222-61 is gratefully acknowledged.

The analytical work was performed in the geochronology laboratory at M.I.T., on mass spectrometers and equipment financially supported by the United States Atomic Energy Commission. The authors wish to express their appreciation to Professor P. M. Hurley and the Atomic Energy Commission for the use of the facilities.

Thanks are also due the following individuals and organizations who generously supplied samples: Clifford Frondel (Harvard University); Irving Friedman (U.S.G.S.); Alvin Cohen (Mellon Institute); Edward Henderson (U. S. National Museum); K. Rankama (Helsinki); Clifford Kaye (U.S.G.S.); Gerald Hawkins (Boston University); and J. G. Lester (Emory University).

References

- Baldwin, R. B., (1949) The Face of the Moon, The University of Chicago Press.
- Beyer, H. O. (1935) Philippine tektites, Philippine Magazine 32, 331-334.
- Chapman, D. R. (1963) On the unity and origin of the Australasian tektites, Second International Symposium on Tektites Program Pittsburgh, Pa., p. 17., (Abstract).
- Chapman, D. R., Larson, H. K., and Scheiber, L. C. (1963) Population polygons of tektite specific gravity for various localities in Australasia, Second International Symposium on Tektites Program, Pittsburgh, Pa., p. 16 (Abstract).
- Cohen, A. J. (1961) A semi-quantitative asteroid impact hypothesis of tektite origin. Journal of Geophy. Res. 66 (abstract), 2521.
- Fairbairn, H. W., Hurley, P.M., and Pinson, W. H. (1961) The relation of discordant Rb-Sr mineral and whole rock ages in an igneous rock to its time of crystallization and to the time of subsequent  $Sr^{87}/Sr^{86}$  metamorphism. Geochim. et Cosmochim. Acta 23, 135-144.
- Faure, G. (1961) The  $Sr^{87}/Sr^{86}$  ratio in oceanic and continental basalts and the origin of igneous rocks. Ph.D. thesis, Dept. of Geology and Geophysics, M.I.T.
- Friedman, I. (1958) The water, deuterium, gas, and uranium content of tektites. Geochim. et Cosmochim. Acta 14, 316.
- Gast, P. W. (1960) Limitations on the composition of the upper mantle. J. Geophy. Res. 65, 1287.
- \_\_\_\_\_ (1961) Strontium and rubidium in stone meteorites, in Problems Related to Interplanetary Space, NAS-NRC publication 845, p. 85-89.
- Glendenin, L. E. (1961) Present status of the decay constants. Geochronology of Rock Systems, Annals of the N.Y. Academy of Sciences 19, 166-180.
- Hawkins, G. S. (1960) Tektites and the earth. Nature 185, 300-301.
- Herzog, L. F. and Pinson, W. H., (1955) The Sr and Rb contents of the granite G-1 and the diabase W-1. Geochim. et Cosmochim. Acta, 8, 295-298.

- (1956) Rb/Sr age, elemental and isotopic abundance studies of stony meteorites. *Am. J. Sci.* 254, 555-566.
- Hurley, P. M., Hughs, H., Faure, G., Fairbairn, H. W., and Pinson, W. H. Jr., (1962) Radiogenic strontium - 87 model of continent formation. *J. Geophys. Res.* 67, 5315 - 5334.
- Hurley, P. M., Pinson, W. H. Jr., and Fairbairn, H. W. (1963) Progress report on analytical accuracy of  $\text{Sr}^{87}/\text{Sr}^{86}$  measurement. *Trans. Am. Geophys. Union* 44, 111-112 (Abstract).
- Kozrev, N. A. (1962) Physics and Astronomy of the Moon, edited by Kopal, Z., Chapter 9, Academic Press.
- Kreiter, F. J. (1960) Dating lunar surface features by using crater frequencies. *Astron. Soc. of the Pac.* 72, 393-398.
- Lovering, J. F. (1960) High-temperature fusion of possible parent material for tektites. *Nature*, 186, 1028-1030.
- Mason, B. (1959) Chemical composition of tektites. *Nature*, 183, 254.
- Moroney, M. J. (1956) Facts from figures, 3rd edition. Pelican Press.
- Nininger, H. H. (1943) Tektites and the Moon. *Sky and Telescope*, 2.
- O'Keefe, J. A. (1960) The origin of tektites. NASA Tech. Note D-490.
- Opik, E. J. (1960) The lunar surface as an impact counter. *Mon. Notice Roy. Astron. Soc.*, 120, 404-411.
- Patterson, C. (1956) Age of meteorites and the earth. *Geochim. et Cosmochim. Acta*, 10, 230-237.
- Pinson, W. H., Herzog, L. F., and Cormier, R. F. (1956) Age study of a tektite, *Bull. Geol. Soc. Amer.* 67, 1725 (Abstract).
- Pinson, W. H., Fairbairn, H. W., Herzog, L. F., and Cormier, R. F. (1957a), Sr/Rb age study of tektites. *Bull. Geol. Soc. Amer.* 68, 1780, (Abstract).
- Pinson, W. H., Herzog, L. F., Anderson, P. A., and Cormier, R. F., (1957b), Rb, Sr, Ca, and K contents and isotopic relative abundances of Ca and Sr in a sea water sample. *Bull. Geol. Soc. Amer.* 68, 1781-1782, (Abstract).

- Pinson, W. H., Herzog, L. F., Fairbairn, H. W., and Cormier, R. F. (1958) Sr/Rb age study of tektites. *Geochim. et Cosmochim. Acta* 14, 331-339.
- Pinson, W. H. (1960) Sources of error in the preparation of spike and shelf solutions for geochronometric work. Eighth Annual Progress Report for 1960, U. S. Atomic Energy Commission, Contract AT (30-1)-1381.
- Pinson, W. H. and Bottino, M. L. (1961) Rb-Sr ages of Tertiary volcanic rocks. *Geol. Soc. Amer. Program of 1961 Annual Meeting*, 122A-123A. (Abstract).
- Pinson, W. H. Jr. (1962) A review of the preparation and calibration of shelf and spike solutions currently in use at MIT in the Geochronology Laboratory, Tenth Annual Progress Report for 1962, U. S. Atomic Energy Commission, Contract AT (30-1) - 1381.
- Schnetzler, C. C. (1961) Chemical composition and origin of tektites. Ph.D. Thesis, Department of Geology and Geophysics, M.I.T.
- Schnetzler, C. C. and Pinson, W. H. Jr. (1963) Report of some recent major element analyses of tektites, *Geochim. et Cosmochim. Acta*.
- Schwarcz, H. P. (1962) A possible origin of tektites by soil fusion at impact sites. *Nature* 194, 8-10.
- Silverman, S. R. (1951) The isotope geology of oxygen. *Geochim. et Cosmochim. Acta* 2, 26.
- Spencer, L. J. (1933) Origin of tektites. *Nature*, 131, 117-118.
- Stevens and others (1961) Second report on a cooperative investigation of the composition of two silicate rocks U.S.G.S. Bull. 1113.
- Suess, H. E. (1963) Well-known facts about tektites, Second International Symposium on Tektites Program, Pittsburgh, Pa. p. 22. (Abstract).
- Taylor, H. P. Jr., and Epstein S. (1962) Oxygen isotope studies on the origin of tektites. *J. Geophys. Res.* 67, 4485-4490.
- Taylor, H. P. Jr. and Epstein S. (1963) Comparison of  $O^{18}$  /  $O^{16}$  ratios in tektites, soils, and impact glasses. *Trans. Am. Geophys. Union* 44, 93 (Abstract).



Taylor, S. R. (1962) Chemical composition of australites, *Geochim. et Cosmochim. Acta* 26, 685-722.

Tilles, D. (1961) Natural variations in isotopic abundances of silicon. *J. Geophys. Res.* 66, 3003.

Tilton, G. R. (1958) Isotopic composition of lead from tektites. *Geochim et Cosmochim. Acta*, 14, 323-330.

Urey, H. C. (1952) The Planets. New Haven: Yale University Press, 245 pages.

\_\_\_\_\_, (1959) Chemical composition of tektites. *Nature*, 183, 114.

Whitney, P. R. (1962) Whole rock Rb/Sr age determinations for shales and the problem of inherited radiogenic strontium, Ph.D. Thesis, Dept. of Geology and Geophysics, M.I.T.

Zahringer, J. (1963) K-Ar measurements of tektites, Radioactive Dating, International Atomic Energy Agency, Vienna, 1963.

TABLE 1. Replicate  $(\text{Sr}^{87}/\text{Sr}^{86})_N$  Ratio Analyses

<u>Homestead Meteorite</u>	<u>SrCO<sub>3</sub> Standard</u>
0.7503	0.7070
0.7507	0.7076
0.7515	0.7071
	0.7084
Avg. = 0.7508	0.7085
	0.7076
$\sigma = \pm 0.0006_1$	Avg. = 0.7077
E% = $\pm 0.08\%$	$\sigma = \pm 0.0006_3$
	E% = $\pm 0.09\%$

Table 2 Rb and Sr Content of Tektites

Sample No.	Locality	Rb(ppm)	Sr(ppm)	Rb/Sr
PHILIPPINE ISLANDS				
T3379	Santa Mesa Site Rizal, Prov.	115	174	0.66
T3962	Santa Mesa Site Rizal, Prov.	111 110*	176 176*	0.63
T3964	Santa Mesa Site Rizal, Prov.	126*	175*	0.72
T3765	Pugad-Babuy Site Bulakan, Prov.	119 118*	191 188*	0.62
T3979	Pugad-Babuy Site Bulakan, Prov.	118*	174*	0.68
T3984	Pugad-Babuy Site Bulakan, Prov.	112 115*	164 168*	0.68
T3986	Busuanga Island	116 115*	157 157*	0.74
INDO-CHINA				
T3987	Kouang-Tcheou Wan	118 123 119 116*	138 138 133 129*	0.88
T3989	Kouang-Tcheou Wan	110*	132*	0.83
T3990	North Cambodia	116 116*	127*	0.91
T3991	North Cambodia	129 134*	134 139*	0.96
T3993	Annam	113 112*	130*	0.87

\*X-ray fluorescence analysis. All others by isotope dilution.

Table 2 (Con't)

T4219	Dalat, S. Viet-Nam	111 110*	125 125*	0.89
T4220	Dalat, S. Viet-Nam	124*	138*	0.90
T4218	Dalat, S. Viet-Nam	125*	138*	0.91
T4104	Java	98	153	0.64
AUSTRALIA				
T3313	Charlotte Waters, Central Australia	109	154	0.71
T4214	Nullarbor Plain	93	197	0.47
T4215	Nullarbor Plain	135*	205*	0.66
T4216	Nullarbor Plain	144*	218*	0.66
NORTH AMERICA				
T4106	Grimes Co., Texas	70	152	0.46
T4300	Grimes Co., Texas	64	134	0.48
T5129	Lee Co., Texas	63*	134*	0.47
T4271	Empire, Georgia	74	170	0.44
T4091	Martha's Vineyard, Mass.	78	177	0.44
CZECHOSLOVAKIA				
T4090	Nechov, Bohemia	146	136	1.07
T3314	"moldavite"	130†	136†	0.96
T4575	Ratiborova Lhota, Bohemia	136	143	0.95
"AMERIKANITE"				
3967	Philippine Is.	181	98	1.85

\*X-ray fluorescence analysis. All others by isotope dilution.

†From Pinson et al. (1958).

TABLE 3 - STRONTIUM ISOTOPIC RATIO RESULTS

MT No.	Locality	Date	86/88	87/86	(87/86) <sub>N</sub>	Scans	E 87/86
PHILIPPINE ISLANDS							
T3379	Santa Mesa Site Rizal Province	6/25/63	.1208	.7129	.7172	72	0.06%
T3962	Santa Mesa Site Rizal Province	5/14/63	.1200	.7153	.7171	54	0.03%
T3984	Pugad-Babuy Site Bulakan Province	7/23/63	.1200	.7150	.7168	60	0.03%
T3986	Busugana Is.	6/3/63	.1199	.7167	.7182	54	0.05%
	Average for Philippinites		.1202	.7150	.7173		
INDO-CHINA							
T3987	Koung-Tcheou-Wen	7/24/63	.1207	.7144	.7183	66	0.03%
T3991	North Cambodia	7/11/63	.1194	.7182	.7182	66	0.03%
T3993	Annam	5/9/63	.1203	.7158	.7185	72	0.02%
T4219	Dalat, S. Viet-Nam	8/3/63	.1196	.7178	.7185	58	0.03%
	Average for Indochinites		.1200	.7166	.7184		
JAVA							
T4104	Java	8/13/63	.1190	.7193	.7182	54	0.02%

MIT No.	Locality	Date	86/88	87/86	(87/86)N	Scans	E 87/86
---------	----------	------	-------	-------	----------	-------	---------

AUSTRALIA

T3313	Charlotte Waters Central Australia	8/1/63	.1204	.7142	.7172	72	0.06%
T4214	Nullarbor Plain	5/16/63	.1199	.7148	.7162	72	0.04%
	Average for Australites		.1202	.7145	.7167		

NORTH AMERICA

T4106	Grimes Co., Texas	3/11/63	.1194	.7122	.7122	72	0.05%
T5129	Lee Co., Texas	4/2/63	.1196	.7114	.7121	72	0.03%
T4271	Empire, Georgia	8/16/63	.1197	.7119	.7127	66	0.04%
T4091	Martha's Vineyard, Mass.	6/6/63	.1199	.7115	.7130	72	0.02%
	Average for N. America		.1196	.7118	.7125		

CZECHOSLOVAKIA

T4090	Nechov, Bohemia	5/28/63	.1203	.7196	.7223	72	0.02%
T3314	"moldavite"	8/15/63	.1199	.7194	.7208	64	0.05%
T4575	Ratiborova Lhota, Bohemia	3/12/63	.1193	.7221	.7218	62	0.04%
	Average for moldavites		.1198	.7204	.7216		

Table 4. Some  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios and  $\text{Rb}/\text{Sr}$  ratios reported for terrestrial and extraterrestrial materials

<u>Material and Reference</u>	<u>No. of Samples</u>	<u>Range <math>\text{Sr}^{87}/\text{Sr}^{86}</math></u>	<u>Avg <math>\text{Sr}^{87}/\text{Sr}^{86}</math></u>	<u>Range <math>\text{Rb}/\text{Sr}</math></u>	<u>Avg. <math>\text{Rb}/\text{Sr}</math></u>
<b>GRANITE</b>					
Gast (1960) <sup>a</sup>	10	0.720 - 1.00	0.830	0.35 - 3.9	1.64
Fairbairn et al. (1961) <sup>b</sup>	11	0.732 - 1.25	0.868	0.25 - 6.0	1.78
<b>BASALT</b>					
Gast (1960)	5	0.705 - 0.711	0.708	-	-
Faure (1961) <sup>c</sup>	25	0.705 - 0.710	0.708	0.02 - 0.18	0.05
<b>OBSIDIANS</b>					
Pinson and Bottino (1961) <sup>d</sup>	9	0.704 - 0.724	0.714	1.2 - 31.	4.2
<b>LIMESTONE</b>					
Gast (1960)	5	0.704 - 0.712	0.709	-	-
<b>SHALE</b>					
Faure (1961) <sup>e</sup>	2	0.720 - 0.723	0.7215	-	-
Whitney (1962)	20	0.712 - 0.755	0.735	0.34 - 2.67	1.57
<b>CHONDRITES</b>					
Herzog and Pinson (1956)	2	0.753 - 0.755	0.754	0.33 - 0.36	0.345
Gast (1960, 1961)	5	0.739 - 0.960	0.796	0.26 - 1.37	0.54
<b>ACHONDRITES</b>					
Herzog and Pinson (1956)	1	-	0.703	-	-
Gast (1960, 1961)	3	0.700 - 0.703	0.7015	0.002 - 0.005	0.003
<b>SEA WATER</b>					
Pinson et al. (1957b) <sup>f</sup>	1	-	0.712	-	0.016

- a. One age 200 m.y. - others 1000 - 2700 m.y.  
 b. Ages from 1200 - 2200 m.y.  
 c. Recent oceanic and continental basalts.  
 d. Ages range from 0 to 60 m.y.  
 e. East and west coast composite samples.  
 f. Mid-Atlantic.

### Figure Captions

- Figure 1. Portion of a mass spectrometer isotope ratio analysis record. The  $^{85}\text{Sr}$  and  $^{87}\text{Sr}$  mass peaks are amplified 10 times in relation to the  $^{86}\text{Sr}$  mass peak.
- Figure 2.  $\text{Sr}^{87}/\text{Sr}^{86}$  in tektites, meteorites, terrestrial rocks and sea water. Inset shows the full range of measurements reported in the literature for granites and chondrites.
- Figure 3.  $\text{Sr}^{87}/\text{Sr}^{86}$  plotted against  $\text{Rb}/\text{Sr}$  for all eighteen individual tektites. Least squares line through these points is the 310 m.y. isochron.
- Figure 4.  $\text{Sr}^{87}/\text{Sr}^{86}$  plotted against  $\text{Rb}/\text{Sr}$  for averages of tektites from three groups. Least squares line through these points is the 400 m.y. isochron. The vertical and horizontal lines represent the range of the  $\text{Sr}^{87}/\text{Sr}^{86}$  and  $\text{Rb}/\text{Sr}$  ratios respectively, while the hash lines represent the value of the particular parameter for each sample. Numbers in parentheses are the number of samples from each area.



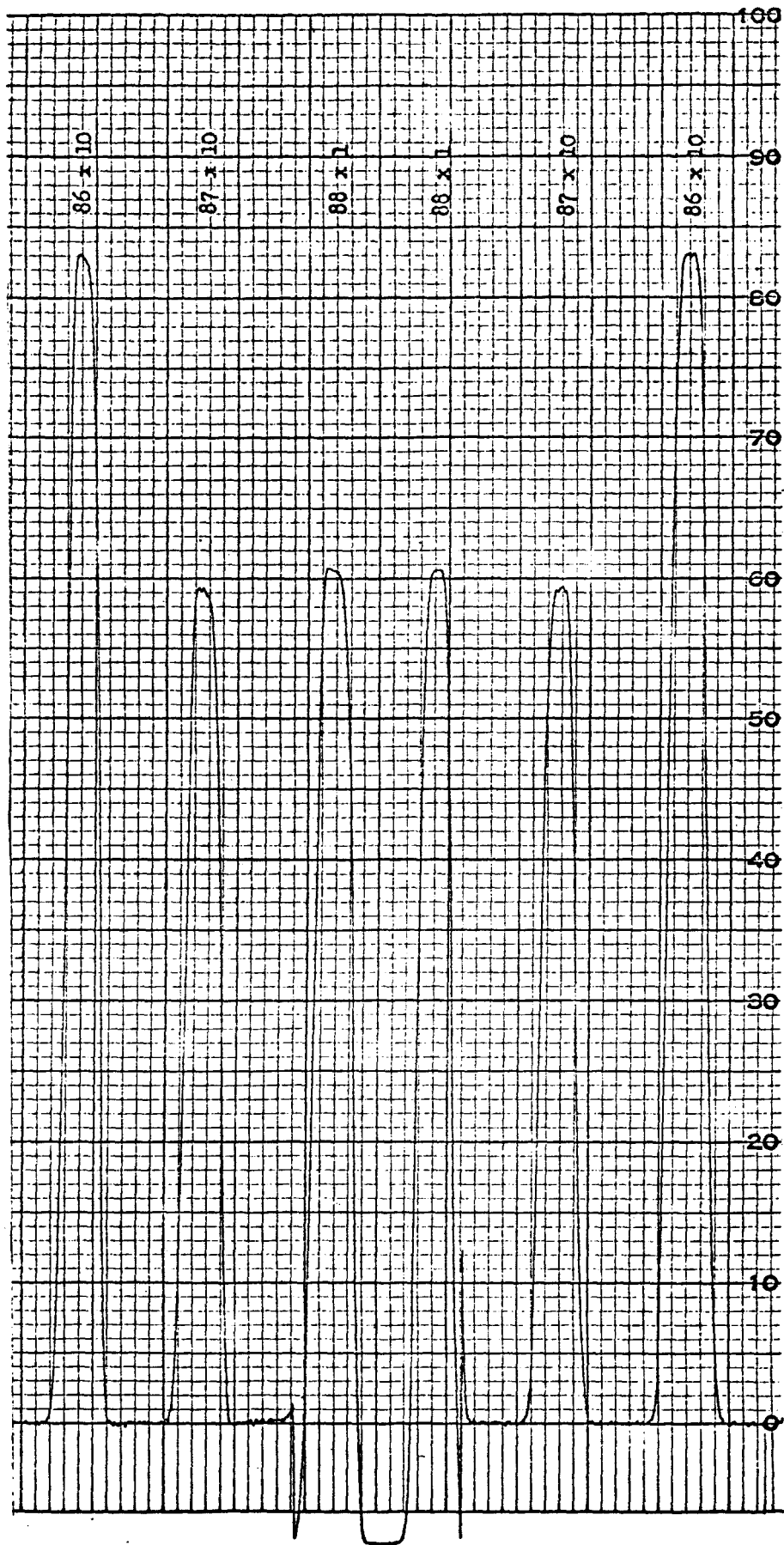


Fig. 1

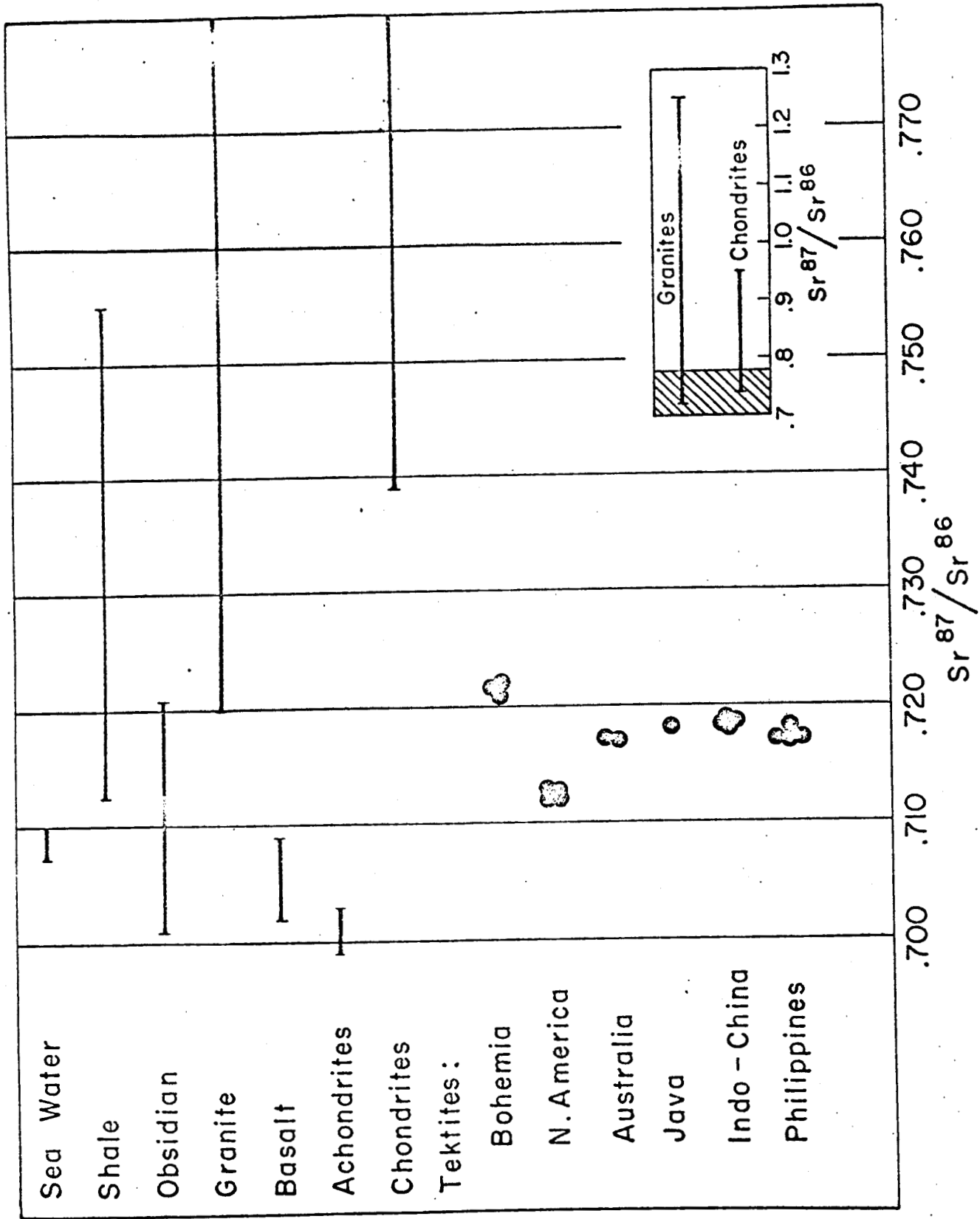


Fig. 2

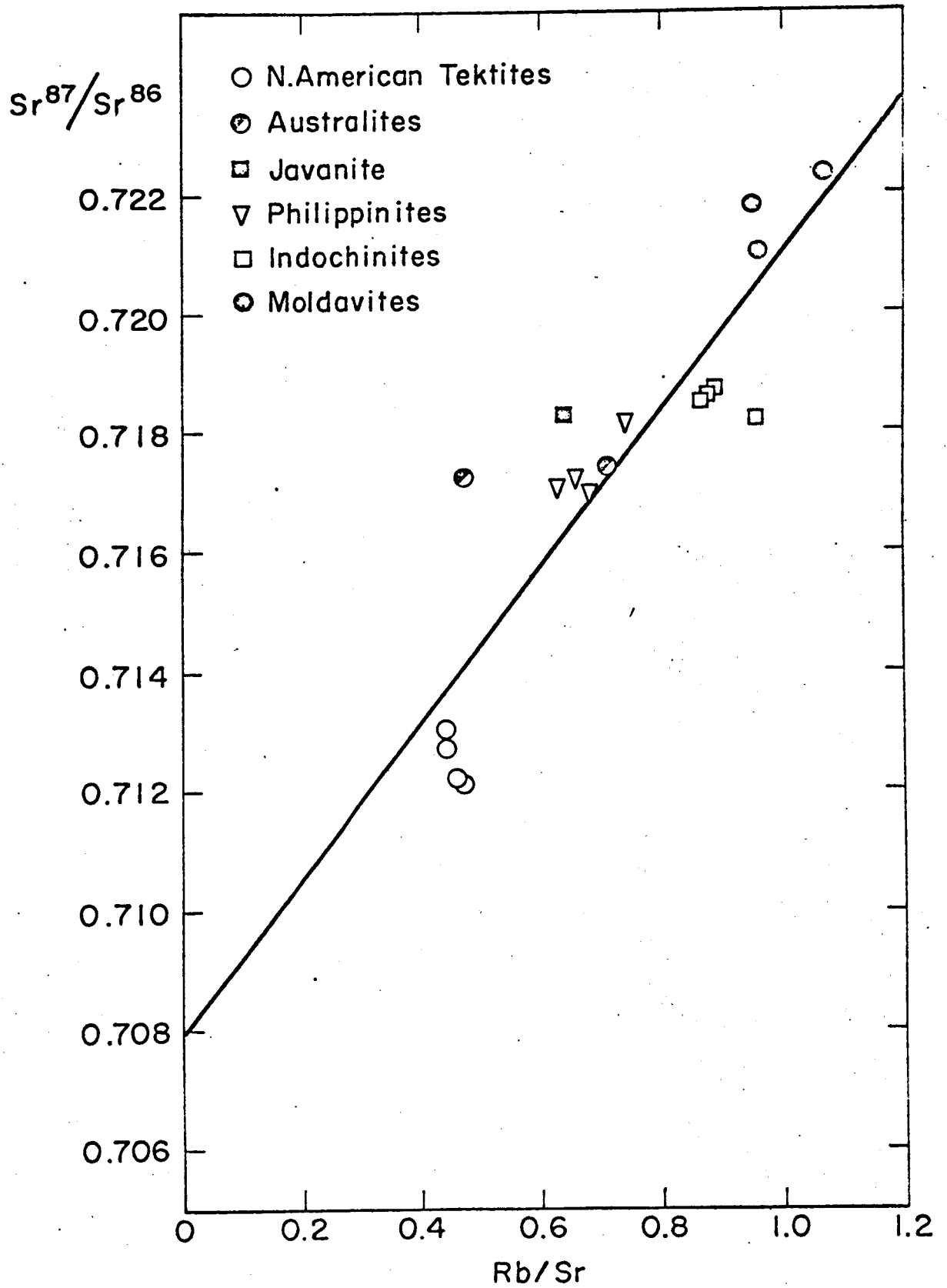


Fig. 3

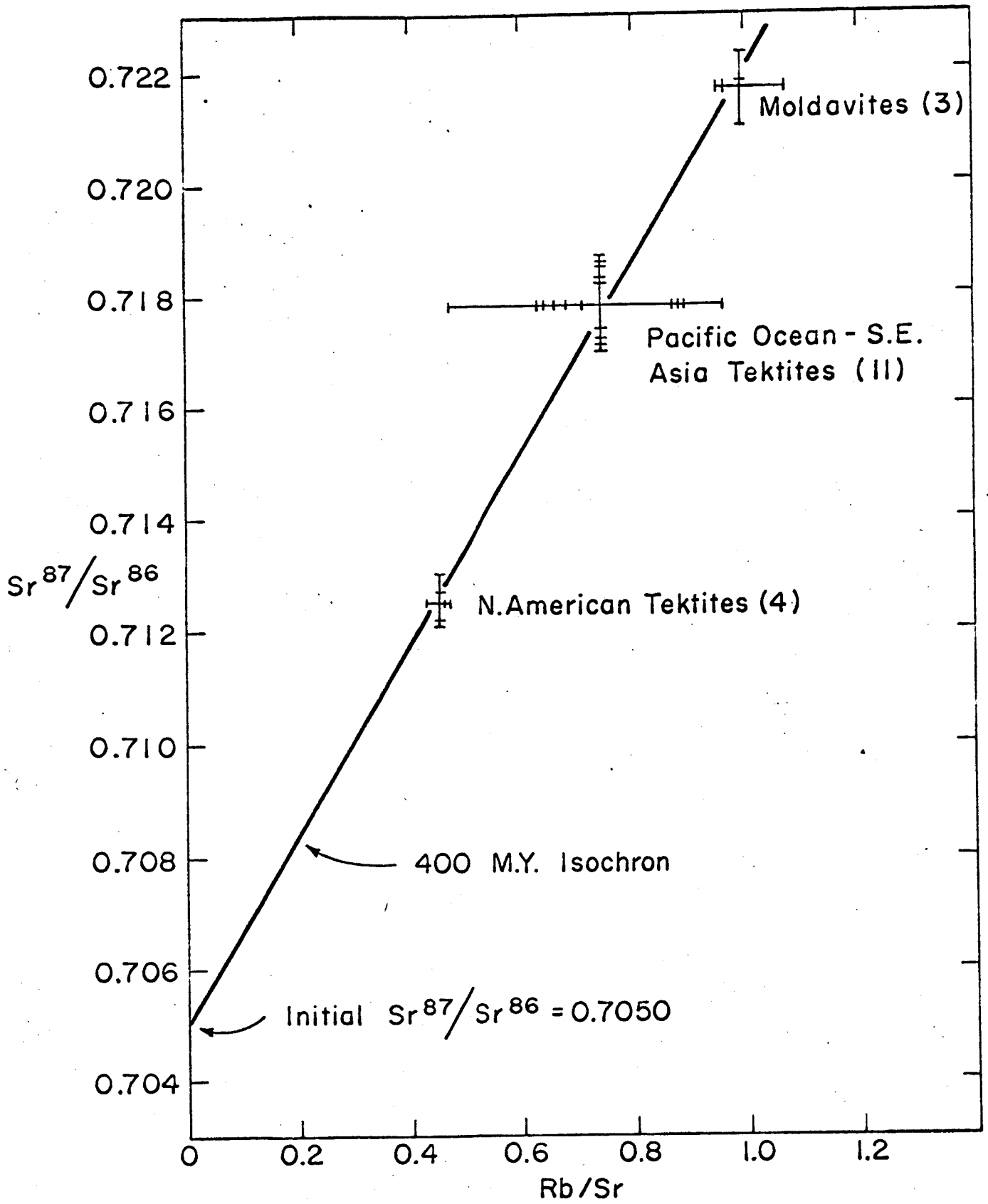


Fig. 4

A REPORT ON SOME RECENT MAJOR ELEMENT ANALYSES OF TEKTITES

C. C. Schnetzler\* and W. H. Pinson, Jr.

Department of Geology and Geophysics  
Massachusetts Institute of Technology  
Cambridge, Mass.

N 65 10528

10528

ABSTRACT-- Forty-two tektites and two "amerikanites" were partially or completely analyzed for major elements. Included were 7 moldavites, 1 bediasite, 2 javanites, 15 philippinites, 12 indochinites, and 5 australites. Many chemical similarities are noted between the philippinites and indochinites, but the two groups appear different in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  and, in particular,  $\text{CaO}$  contents. No decrease in alkali element content is observed from Indo-China to the Philippine Islands (i.e., west to east) as is observed across Australia. Selective volatilization cannot account for the differences in the two groups. Perhaps the higher  $\text{CaO}$  and  $\text{Sr}$  contents of the philippinites are due to contamination of the parent material by limestone. The  $\text{CaO}$  contents of the indochinites analyzed are distinctly lower, and the  $\text{MgO}$  contents higher, than the analyses reported in Barnes (1940). Real variations, up to approximately 10% for some constituents, exist within the philippinites and indochinites, and even within tektites from restricted sites. Tektites from two sites in the Philippine Islands are identical, within experimental error, in mean composition. The unity of chemical character of the australites and the southeast Asian tektites strongly suggest that they represent one large strewn field. New moldavite analyses do not indicate any systematic chemical variation across the Czechoslovakian strewn field.

*Author*

---

\*Present address: Theoretical Division, National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt, Maryland.

## INTRODUCTION

The purpose of this paper is to report some major element analyses of tektites that have been obtained in the rapid silicate analysis laboratory at the Massachusetts Institute of Technology. When we decided in 1959 to start a study of tektites it was apparent that more chemical data was necessary. From the published analyses it could be seen that the tektites from a given locality are quite similar in chemical composition, and that there is some similarity between the different groups of tektites. However, it was difficult, if not impossible, to define the limits of variability among the several groups of tektites from the published analyses, as each analyst worked on only a few specimens, and undoubtedly different methods of chemical analysis were used by the various analysts. Also, many areas were poorly sampled- for example, only four philippinites were listed in Barnes' (1940) compilation of analyses.

Therefore, it seemed desirable to analyze a representative number of tektites from several different localities by uniform methods of analysis, making use of reliable rock standards to monitor the accuracy of the work. From such a study it should be possible to define the limits of variation in the chemical composition of tektites both within a group and between groups. As Taylor (1960, p. 85) states, "Uniformity of composition for groups of tektites, if established, would have far-reaching implications." Certainly, if, in addition to their peculiar composition, widely separated localities had essentially the same composition, it would be difficult to postulate any terrestrial origin.

Unfortunately, due to the scarcity of tektites in this country prior to the last several years, we could obtain only a limited number of tektites for destructive analysis. An adequate number of samples could

be obtained from only the tektite rich areas of Indo-China and the Philippine Islands, and even here a larger collection from which to pick samples for analysis would have been desirable. The work of Taylor (1962) on the australites and Chao (1963) on the bediasites have recently supplied extensive data in these fields.

#### ANALYTICAL TECHNIQUES

Most of the analyses reported in this paper were made by "rapid silicate" procedures. A large number of anomalous  $Al_2O_3$  results were obtained using this method so it seemed desirable to determine this constituent by some other means. It was found that aluminum, as well as silica under certain conditions, could be determined by X-ray fluorescence techniques with no loss in accuracy and considerable improvement in precision (in the case of aluminum) over the rapid silicate method.

#### Rapid Silicate Procedures

The rapid silicate procedures used in this investigation were exactly as described by Shapiro and Brannock (1956) except for  $CaO$ ,  $MgO$ , and  $FeO$ .

The automatic photometric titration procedure, employing a spectrophotometer and recorder, as described by Shapiro and Brannock, was used in the determination of  $CaO$  and  $MgO$ . However, they have since modified the chemical procedures, eliminating the separation of iron and aluminum necessary under the system described in their paper, and they have supplied the M.I.T. rapid silicate laboratory with the necessary details. In the modified procedure iron and aluminum are complexed with a mixture of sodium cyanide and triethanolamine, and do not interfere with the calcium and magnesium titrations by Versene. Calcium is titrated at a pH between 12 and 12.7, using murexide as an indicator. ( $CaO+MgO$ )

as MgO is titrated with Versene at a pH of approximately 9.5 using Eriochrome Black T as an indicator. The result obtained for CaO (changed to the corresponding amount of MgO) is subtracted from the result for (CaO+MgO) as MgO to obtain the amount of MgO. Thus the accuracy of the MgO determination is dependent upon the accuracy of the CaO determination. The standard used for both the CaO and (CaO+MgO) as MgO analyses is the National Bureau of Standard dolomite no. 88.

FeO was determined in most samples by the spectrophotometric method of Shapiro (1960) rather than the chemical dichromate titration procedure described by Shapiro and Brannock (1956). Results obtained by the two methods on the same samples were in good agreement (Schnetzler, 1961, Table 14.)

H<sub>2</sub>O was not determined in the tektites as Friedman (1958) showed their water content to be extremely low (approximately 3 to 100 ppm), far below the detectable limit of the Penfield method.

Sample solutions were made in duplicate from two separate portions of the powdered tektite. In the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, total iron, CaO, (CaO+MgO), Na<sub>2</sub>O, and K<sub>2</sub>O determinations duplicate portions of each solution were analyzed, making a total of four aliquots of each sample. Four spectrophotometer readings were made on each aliquot in the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and total iron determinations, while an average of four flame photometer readings were made for each Na<sub>2</sub>O and K<sub>2</sub>O determinations. Thus the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, total iron, Na<sub>2</sub>O, and K<sub>2</sub>O determinations were made from 16 instrument readings in total. One titration of CaO and (CaO+MgO) was made from each aliquot, making a total of four for each sample. The MnO and TiO<sub>2</sub> determinations were made from only one aliquot of each sample solution, as the precision was sufficiently high in these procedures to



allow fewer replicate determinations. Four spectrophotometric readings were made of each aliquot in the MnO determinations, and two spectrophotometer readings were made of each aliquot in the TiO<sub>2</sub> determinations. P<sub>2</sub>O<sub>5</sub> was determined from two aliquots of each weighing but this element proved to be so low in tektites that the method was unreliable, and in the majority of samples it was not determined. FeO was determined by titration or photometrically on two separate weighings of the sample. In the photometric determinations two instrument readings were made in each determination.

The above scheme was followed in most analyses. Occasionally, however, the lack of sufficient sample necessitated the determination from only one weighing, or if duplicate weighings were made they were diluted to smaller volumes, so that fewer aliquots could be taken for some of the determinations. Also, when the precision appeared to be poor, the sample solutions were rerun, so some results are an average of a greater number of aliquot determinations than discussed in the scheme above.

Duplicate pairs from one weighing were usually analysed in one day and the duplicate pairs from the other weighing on another day. The samples to analysed in any one day were chosen at random; therefore the tektites from any particular area were analyzed at various times during the period of the investigation and not as a group.

#### X-ray fluorescence techniques

Chodos and Engel (1961) determined the total iron, CaO, MgO, K<sub>2</sub>O, TiO<sub>2</sub>, and MnO contents of amphibolite rocks by fluorescent X-ray spectrography, and the results are in acceptable agreement with wet chemical analyses of the same samples. However, they found that the silica and

aluminum results did not compare favorably with the wet chemical results, being accurate to only about 5% of the amount present. They attributed this error to matrix effects, as their samples varied considerably in major element composition.

As the variation of the major elements in tektites is small, it was felt the matrix effects should be negligible in these samples. Since the aluminum determination is the least satisfactory of the rapid silicate procedures it was decided to attempt to analyze for this element by the X-ray fluorescence method, and as the determination of silica by this procedure would eliminate one of the sample solutions in the rapid silicate procedure, this element was also attempted by the X-ray fluorescent method. It was believed this method might be successful in this investigation, while it had failed for Chodos and Engel (1961), for three reasons: 1) the matrix problem should be essentially non-existent, at least among the Australasian tektites, 2) the tektites, being a fairly homogeneous glass, would not exhibit the inhomogeneity of particle size and mineralogical composition that would be found in a powdered rock sample, and 3) the machine available allowed the rapid comparison of standard and sample, which was not the case in the machine used by Chodos and Engel, thus reducing instrumental drift.

An attempt was first made to analyze powdered samples. The preparation and packing of the samples were essentially as described by Chodos and Engel (1961). Agreement between the X-ray fluorescence and rapid silicate results were satisfactory for aluminum; the maximum difference between the two methods was about 2% of the amount present, while the average difference was slightly less than  $\pm 1\%$  (Schnetzler, 1961, Table 15)

The  $\text{SiO}_2$  X-ray fluorescence results, however, were not satisfactory in the powdered samples. As silica is the predominant constituent in tektites relatively more precise values are desired than for the other constituents. A 1 or 2% error is permissible in  $\text{Al}_2\text{O}_3$ , but not in  $\text{SiO}_2$ . There are several possible causes for the poor  $\text{SiO}_2$  results on the powdered samples. Probably the greatest error is in the packing of the sample in the holder. Chodos and Engel (1961) state that duplicate packings should agree within about 1%. Duplicate packings in this investigation disagreed by as much as 2%. Differences in grain size, resulting in differences in surface area exposed to the beam, might have been a minor factor. The sample holder wells might not have been uniform size—unfortunately this was not checked.

In view of this difficulty an attempt was made to analyse a cut surface of the solid tektite which was free of bubbles and which had been polished to eliminate any effect of surface irregularity. Using this procedure, triplicate results for  $\text{SiO}_2$  were in agreement with the rapid silicate results to  $\pm 0.47\%$  of the amount present, or better. (Schnetzler, 1961, Table 15). Therefore it was concluded that the X-ray fluorescence  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  determinations on the solid samples, and the  $\text{Al}_2\text{O}_3$  determinations on the powdered samples were acceptable, and comparable to the rapid silicate determinations. However, the  $\text{SiO}_2$  determinations on the powdered samples were not comparable to determinations by the rapid silicate procedure, and were not reported.

The X-ray fluorescent unit used was a North American Phillips instrument with a tungsten target tube. The operating conditions were: EDDT crystal; pulse height analyser base = 1.50, window = 6, flow proportional counter = 1650. Number of counts for powder;  $\text{SiK}\alpha$  peak

51,200, background 800; Al K $\alpha$  peak 8000, background 800. Number of counts for solid: SiK $\alpha$  peak 102,400, background 800; Al K $\alpha$  25,600, background 800.

The standards used were selected tektites which had been analyzed for silica and aluminum by rapid silicate procedures.

#### Precision and Accuracy

Mercy (1956) presents an extensive discussion on the precision and accuracy of the rapid silicate method of analysis. A good estimate of the precision of this work can be obtained as each sample was analyzed in replicate and the rock standard G-1 and W-1 were repeatedly analyzed during the course of the investigation. The results have approximately the following precision (expressed as the relative deviation of a single analysis): SiO<sub>2</sub>  $\pm$  0.5%; Total Fe, photometrically determined FeO, MgO, and Na<sub>2</sub>O  $\pm$  2%; Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CaO, and K<sub>2</sub>O  $\pm$  3%; MnO  $\pm$  4%. The X-ray fluorescence results have a precision of approximately: SiO<sub>2</sub>  $\pm$  0.8%; Al<sub>2</sub>O<sub>3</sub>  $\pm$  2%. These values agree in general with estimates of precision given by Mercy (1956, p. 168)

The results of replicate analyses of G-1 and W-1 are given in Table 1. Most of these results are the average of determinations made on several different weighings. The numbers of analyses are given in parentheses. The accepted values listed are from Steven (1960, p. 32). The only values that lie outside the "acceptable range", as defined by Stevens, are SiO<sub>2</sub> in W-1 and CaO in G-1. The SiO<sub>2</sub> values in W-1 were determined during preliminary stages of the analytical period, using National Bureau of Standard feldspar #99 as standard. Perhaps the poor accuracy was due to the extreme difference in matrices. During the tektite analyses G-1 was used as standard, as its SiO<sub>2</sub> content

is well known and its composition is similar to tektites, while NBS #99 was used to monitor the results. These analyses gave acceptable values for  $\text{SiO}_2$  in the NBS feldspar. The CaO values for G-1 were consistently low in four different weighings of the sample; no explanation could be found. However, the CaO values for W-1 are satisfactory. The high results for  $\text{Na}_2\text{O}$  in both G-1 and W-1 (although they are both within the "acceptable range") are in excellent agreement with other flame photometric determinations as listed by Stevens (1960, p. 36).

As most of the analytical procedures used are independent of each other a total of the constituents close to 100% is much more indicative of accuracy than in conventional methods of analysis where a constituent may be incompletely precipitated at one point and later precipitated with another constituent, and still give a good summation. It can be seen in Table 3 that the analyses total close to 100%.

### RESULTS

The results of the chemical analyses are given in Table 2. Included are partial or complete analyses of 12 tektites and 2 "amerikanites". The total iron contents, denoted in the table as  $\text{Fe}^0$ , the specific gravity, and specimen weight are also given.

The results obtained by X-ray fluorescence are designated by astericks; all results not so designated were determined by rapid silicate techniques. The X-ray fluorescence results are the average of several independent measurements, usually three for  $\text{SiO}_2$  and two for  $\text{Al}_2\text{O}_3$ . If both rapid silicate and X-ray fluorescence determinations were made on a sample, the rapid silicate results are given in Table 2.

The  $\text{SiO}_2$  values given in parentheses were obtained by subtraction

from 100%.

There appears to be general agreement between the analyses in Table 2 and the analyses reported by Barnes (1940). The differences between the old and new data can be attributed in most cases to the small number of samples and the variation within a group. However, the MgO and CaO averages for the 12 indochinites reported in this paper are distinctly different from the averages of the 24 indochinites listed by Barnes; the CaO averages of this work are lower and the MgO correspondingly higher than the data from Barnes. None of the CaO results reported here approach the average from the literature (CaO = 2.06 is the highest value found as compared with the literature average of 2.51) and only 4 of the 24 CaO values from the literature are in the range found by the new analyses. Only two of the MgO contents reported here are as low or lower than the average 2.00 calculated from the literature. It should again be stated that the samples were analyzed in a completely random fashion, with a mixture of indochinites, philippinites, australites, etc. in each group of samples analyzed in any particular day. Evidence that the CaO (and MgO) values reported here are not in error are: 1) the CaO values for the philippinites, australites and moldavites, appear to be in fair agreement with the literature—at least they are not all lower than the literature analyses, and 2) the values obtained for strontium (Schnetzler and Pinson, 1963), which has a geochemical coherence to calcium, are distinctly lower in the indochinites than the values obtained for the philippinites. In the conventional method of rock analysis, calcium and magnesium are separated by the precipitation of calcium oxalate and the determination of magnesium is from the filtrate. As 23 of the 24 indochinites from Barnes were analyzed by one analyst, it is suggested that consistent incomplete separations may have caused

high CaO and correspondingly low MgO results. The methods used in the analyses reported here do not require the separation of calcium and magnesium, and the monitoring with G-1 and W-1 suggest that the CaO and MgO determinations were essentially correct. Thus, it is suggested that the CaO and MgO results reported in the literature for the indochinites are in error and the averages reported here should be considered closer to the true average for the group.

Table 3 gives the average values of the indochinites and philippinites, with calculations of the spread of results expressed as standard ( $\sigma$ ) and relative (C) deviation of a single analysis. Comparison of the relative deviations with estimates of analytical precision given above indicate that the spread of results in almost all cases are greater than can be expected from analytical error. Total iron and TiO<sub>2</sub> in the philippinites are the possible exceptions. Taylor (1962) found the same order of magnitude in the variation of most major constituents of australites.

The first six philippinites (T3959 through T3965) listed in Table 2 are from one site on the island of Luzon--the Santa Mesa site in Rizal Province. The next seven samples (T3379 through T3984) come from another site--the Pugad-Babuy site in Bulakan Province. Both of these sites are near Manila. Therefore the opportunity exists to test if variations occur within small areas, and between two areas which, due to their proximity, might be assumed to have a common origin and/or parent material. The average composition for each site, and the statistical computations, have been calculated from the data in Table 2 and are shown in Table 4. By comparison of the relative deviation (C) values of this table with values estimated for the analytical procedures it appears that many of the constituents have a greater variation than can be accounted for

by analytical error. Even if these deviations are compared with the most pessimistic estimates of analytical precision  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{Na}_2\text{O}$  in the Santa Mesa samples, and  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{MnO}$  in the Pugad-Babuy samples exhibit significantly greater variation than just analytical error. Thus the data suggest there are real differences in composition, not only within a given locality such as Indo-China, but also within restricted tektite sites.

The average compositions of the two sites, as listed in Table 4, are quite similar. It is possible to test the degree of similarity by the Null Hypothesis (Moroney, 1956). According to the Null Hypothesis there is only a 5% probability that the difference between the average of two groups is equal to two standard deviations of the difference if the actual difference between the two groups is zero. Moroney (1956, p. 220) regards this occurrence as "probably significant" while a difference of three or more standard deviations can be regarded as "definitely significant", the probability being less than one half of one percent that so great a difference should occur by chance in random sampling of one population. Applying this hypothesis to the data in Table 4 for the two sites in the Philippine Islands it is found that only  $\text{MnO}$  reaches the "probably significant" level--the difference equaling two standard deviations of the difference. As the probability of this occurring if the actual difference between the groups is zero is approximately one in twenty, and as there were ten pairs of constituents tested, it is felt the occurrence of only this much difference in one pair is not significant. Thus the two sites cannot be considered independent on the basis of their chemical composition, although Beyer (1955) states that the samples from the two sites have quite distinct differences in physical appearance.



If the same test is applied to the indochinite and philippinite data of Table 3, it is found that five of the constituents exhibit differences that are definitely significant. The differences in the means of the two groups for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  equals approximately three standard deviations of the difference, while the difference in strontium values equals 9 standard deviations, and the difference in  $\text{CaO}$  values equals 15 standard deviations of the difference. The data for the other constituents do not suggest any significant differences in composition.

Cohen (1963b) has stated that there appears to be a relation between composition and size for samples within a given site. He refers specifically to the 6 samples from the Santa Mesa site, the 7 from the Pugad-Babuy site, and the 3 from Kouang-Tcheou-wan. The supposed correlation of decreasing silica with increasing sample weight is theorized to be related to differences in ballistic trajectory (and thus temperature) of samples of various masses having the same flight distance. It can be seen from Table 2 that the three Kouang-Tcheou-wan tektites <sup>show</sup> some correlation between  $\text{SiO}_2$  and mass, and that the Santa Mesa samples suggest a correlation. However, considering the analytical precision of the analyses, we feel the Pugad-Babuy samples do not exhibit any discernible correlation, and more samples must be analyzed before any such correlations could be considered statistically significant.

The data on the southeast Asian tektites presented in this paper do not suggest to us a regional change in composition of the type noted by Taylor (1960) in the australites. He found a decrease in alkali element content in 14 australites from west to east, parallel to the decrease in specific gravity reported by Baker and Forster (1943). Over

a distance of approximately 1300 miles all the alkali elements exhibited a uniform change of approximately 20%. It is apparent from the data in Tables 2 and 3 that sodium, potassium and rubidium do not show any significant decrease from Indo-China to the Philippine Islands (i.e., west to east), despite the fact that these two localities are approximately 800 miles apart. There also appears to be no uniform change in composition in a north-south direction since the Kouang-Tcheou-wan samples are quite similar in composition to the Dalat samples which lie approximately 650 miles to the south.

Thus the data presented here do not indicate any selective volatilization of elements during passage of the material from west to east (or in any other direction), as suggested by the compositional changes in australites. The two elements which exhibit the greatest difference between the two groups, calcium and strontium, would not be expected to be selectively volatilized without much greater volatilization of many of the other elements, e.g., the alkalies. As Lovering (1960) points out, it is reasonable to assume that the relative volatilities would correspond to the boiling points of the normal oxides, and the order might be approximately  $MgO, CaO < Al_2O_3 < SiO_2, FeO < Na_2O, K_2O$ . Fusion studies by Lovering (1960) and Friedman et al. (1960) suggest that this order is essentially correct.

The philippinites and indochinites might be completely independent groups, from completely different source materials; in this case their similarities would be just as difficult to explain. Considering these similarities (i.e., total Fe, MgO, K<sub>2</sub>O, Na<sub>2</sub>O, MnO) it might be more reasonable to consider the higher calcium and strontium contents of the philippinites due to contamination, by some unknown means, by a high calcium-strontium source—limestone.

Combining the data presented in this paper with previously reported analyses of southeast Asian tektites, Cohen (1963b) reaches the conclusion that these tektites represent two strewn fields having a common center of origin. One strewn field incorporates the tektites of Indo-China and Java while the other includes the tektites of Thailand, the South China Islands (Kouang-Tcheou-wan) and the Philippine Islands. He postulates a second, independent, impact to produce the australites. However, the delineation between the two southeast Asian strewn fields is not apparent from the major element analyses. Indeed, we believe the major element analyses reported to date show that tektites from the Australasian area have a unity of composition which is most readily explained by a common source or origin, rather than two as proposed by Cohen.

The moldavites in Table 2 are listed in order of geographic location from west to east. Cohen (1963a) states that the analyses of moldavites in the literature indicate a decrease in silica from west to east, and he interprets this as supporting evidence for the production of tektites by asteroid or comet impact at the Ries Kessel, which lies to the west of the moldavite strewn field. The new data reported in this paper do not clarify any geographic trend in moldavite major element composition. Any trend among the moldavite macroanalyses now available, which have accurate location data -- seven from Barnes (1940), four others listed by Cohen (1963a), and the seven new analyses given in this paper -- is due to one tektite in the western part of the field (Radomilice, Bohemia) which has 84.5%  $\text{SiO}_2$  and one tektite toward the eastern edge (Senorady, Moravia) which has only 74.9%  $\text{SiO}_2$ . The other 16 moldavites have  $\text{SiO}_2$  contents, in ~~scarcely~~ <sup>seemingly</sup> random geographic order, from approximately 77.1% to 82.3%.

Five of the available moldavite analyses are of samples from

Radomilice, and these samples have rather unusual compositions when compared to the other 13 moldavite analyses. For example, four of the five have distinctly lower  $K_2O$  contents than the tektites from the other localities.

Taylor et al. (1961) pointed out the inverse relationship between  $SiO_2$  and the other major constituents in australites, and the positive correlations the other constituents show among themselves. These relationships can be seen in most of the elements in Table 2. The correlation coefficients of the various pairs are not as statistically significant as those reported by Taylor, largely because the variations exhibited by indochinites and philippinites are not as great as those in the australites and the analytical error masks the small variations.

The similarity of the two "amerikanites", 3967 and 3996, to obsidian and dissimilarity to tektites is apparent. In view of the analyses reported by Martin and Koomans (1955) and those reported here, it is believed these objects are merely stream worn obsidian pebbles and they should not be considered as possible tektites.

#### SUMMARY

Although the following results of this investigation do not point toward a specific mode of origin for tektites, they add to the limiting factors that must be accounted for in any proposed theory of origin.

1. The philippinites, analyzed for the first time in any substantial number during this investigation, have many chemical similarities to the indochinites.
2. However, the philippinites and indochinites analyzed here differ significantly in  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ,  $CaO$ , and  $Sr$  contents, and there is

a very high probability that they represent different populations. In particular, the calcium and strontium contents are distinctly lower in the indochinites than in the philippinites, suggesting that the two may have come from the same source, but the philippinite melt was contaminated, by some unknown means, by limestone.

3. The CaO contents of the indochinites analyzed in this investigation are distinctly lower, and the MgO contents higher, than the analyses in the literature.

4. Real variations, up to approximately 10% for some constituents, exist within the philippinites and indochinites, and even within the restricted Santa Mesa and Pugad-Babuy sites of the Philippine Islands, in agreement with the variations found by Taylor (1962) for the australites.

5. The two sites in the Philippine Islands do not differ significantly in average chemical composition and are probably parts of the same population.

6. No particular geographic trends are observed in the chemical compositions of the various groups. The new moldavite analyses do not confirm the supposed  $\text{SiO}_2$  decrease from west to east as suggested by Cohen (1963a).

7. The similarity in major element composition between the southeast Asian tektites and the australites (Taylor, 1962) is striking. This unity of chemical character is strong evidence in itself, exclusive of aerodynamic or age data (Chapman, 1963; Zahringer, 1963), that the australasian tektites had a common origin and represent one large strewn field.

## ACKNOWLEDGEMENTS

This work was supported by the Lunar and Planetary Exploration Branch of the Geophysics Research Directorate, Cambridge Air Force Research Center, Bedford, Massachusetts under Contract No. A.F. 19 (604)-6135, and the National Aeronautics and Space Administration under grant NSG-222-61.

The authors are grateful to the following individuals and organizations who provided samples: Clifford Frondel (Harvard University), Irving Friedman (U.S.G.S.), K. Rankama (Helsinki), Alvin Cohen (Mellon Institute), G. S. Hawkins (Boston University), and J. G. Lester (Emory University).

The assistance of Professor John Hower in the X-ray fluorescence analyses and Mr. John Philpots in some of the rapid silicate analyses is gratefully acknowledged.

## REFERENCES

- Baker G. and Forster H. C. (1943) The specific gravity relationships of australites. *Amer. J. Sc.* 241, 377-406.
- Barnes V. E. (1940) North American tektites. *Univ. Texas Publ. No.* 3945, 477-582.
- Beyer H. O. (1955) The relation of tektites to archaeology (Special reprint with revisions in 1954) *Natl. Res. Council Philippines, Univ. Philippines, Deliman, Quezon City.*
- Chao E. C. T. (1963) The petrographic and chemical characteristics of tektites. Chapter 3 of Tektites, ed. by J. O'Keefe, pp 51-94.
- Chapman D. R. (1963) On the unity and origin of the australasian tektites. *Second International Symposium on Tektites program, Pittsburgh, Pa., 17 (Abstract).*
- Chodos A. A. and Engel C. G. (1961) Fluorescent X-ray spectrographic analysis of amphibolite rocks. *Am. Mineralogist* 46, 120-133.
- Cohen A. J. (1963a) Asteroid- or comet-impact hypothesis of tektite origin: the moldavite strewn field. Chapter 9 of Tektites, ed. by J. O'Keefe, *Univ. of Chicago Press*, pp 189-211.
- Cohen A. J. (1963b) Asteroid-impact hypothesis of tektite origin III, The southeast Asian strewn fields. Space Research III, Proc. 3<sup>rd</sup> Int. Space Sci. Symp., ed. W. Priester, *North Holland Publ. Co.*, pp 950-973.
- Friedman I. (1958) The water, deuterium, gas, and uranium contents of tektites. *Geochim. et Cosmochim. Acta* 14, 316-322.
- Friedman I., Thorpe A., and Senftle F. E. (1960) Comparison of the chemical composition and magnetic properties of tektites and glasses formed by fusion of terrestrial rocks. *Nature* 187, 1089-1092.
- Lovering J. F. (1960) High-temperature fusion of possible parent material for tektites. *Nature* 186, 1028-1030.
- Martin R. and De Sitter-Koomans G. (1955) Pseudotectites from Colombia and Peru. *Leidsche Geol. Meded.* 20, 151.
- Mercy E. L. P. (1956) The accuracy and precision of "rapid methods" of silicate analysis. *Geochim. et Cosmochim. Acta* 9, 161-173.
- Moroney M.J. (1956) *Facts from Figures*. 3rd edition. Pelican Press.
- Schnetzler C. C. (1961) The composition and origin of tektites. Ph.D. thesis, Dept. of Geol. & Geophys., M.I.T., Cambridge, Mass.
- Schnetzler C. C. and Pinson W. H. Jr. (1963) Variation of strontium isotopes in tektites. *Geochim. et Cosmochim. Acta*

- Shapiro L. and Brannock W. W. (1956) Rapid analysis of silicate rocks. U.S.G.S. Bull. 1036-C.
- Shapiro L. (1960) A spectrophotometric method for the determination of FeO in rocks. Geological Survey Research 1960, Short papers in the Geological sciences.
- Stevens and others (1961) Second report on a cooperative investigation of the composition of two silicate rocks. U.S.G.S. Bull. 1113.
- Taylor S. R. (1960) Abundance and distribution of alkali elements in australites. Geochim. et Cosmochim. Acta 20, 85-100.
- Taylor S. R. (1962) The chemical composition of australites. Geochim. et Cosmochim. Acta 26, 685-722.
- Taylor S. R., Sachs M., and Cherry R. D. (1961) Studies of tektite composition-I. Inverse relationship between SiO<sub>2</sub> and the other major constituents. Geochim. et Cosmochim. Acta 22, 155-163.
- Zahringer J. (1963) K-Ar measurements of tektites. Radioactive Dating. International Atomic Energy Agency, Vienna, 1963. pp 289-305.



TABLE 1. ANALYSES of G-1 and W-1

	G-1		W-1	
	This work	Accepted Value	This Work	Accepted Value
SiO <sub>2</sub>	72.57 (2)	72.35	53.09 (14)	52.40
Al <sub>2</sub> O <sub>3</sub>	14.12 (9)	14.32	15.02 (5)	15.11
Total Fe	1.98 (14)	2.04	11.09 (8)	11.22
FeO	0.91 (1)	0.98	8.55 (2)	8.63
MgO	0.38 (10)	0.40	6.68 (4)	6.58
CaO	1.23 (14)	1.40	10.81 (7)	10.97
Na <sub>2</sub> O	3.45 (16)	3.31	2.25 (20)	2.07
K <sub>2</sub> O	5.44 (6)	5.42	0.77 (9)	0.67
TiO <sub>2</sub>	0.22 (5)	0.26	1.08 (11)	1.07
MnO	0.03 (6)	0.03	0.17 (8)	0.17
P <sub>2</sub> O <sub>5</sub>	0.07 (8)	0.10	0.13 (8)	0.15
Total	99.39	99.52	100.14	99.44

TABLE 2. Major Element Analyses of Tektites

MOLDAVITES

Locality	Ratiborova Lhotka, Bohemia	Strpi, Bohemia	Radomilice, Bohemia	Kroclov, Bohemia	Koroseky, Bohemia	Nechov, Bohemia	Slavice, Moravia
Sample #	T4575	T4572	T4574	T4570	T4571	T4090	T4573
SiO <sub>2</sub>	78.59	79.99	84.48	80.12	78.93	79.26	81.35
Al <sub>2</sub> O <sub>3</sub>	10.99	10.36	7.79	9.70	10.42	10.28	10.98
Fe <sub>2</sub> O <sub>3</sub>	0.10	0.10	0.21	0.14	0.27	0.49	0.28
FeO	1.75	1.52	0.98	1.49	1.56	1.34	1.55
MgO	2.38	1.75	1.72	1.91	1.88	2.19	1.23
CaO	2.85	2.17	1.90	2.47	2.36	2.67	0.95
Na <sub>2</sub> O	0.47	0.42	0.20	0.46	0.51	0.40	0.59
K <sub>2</sub> O	3.44	3.32	2.40	3.57	3.62	3.47	3.57
TiO <sub>2</sub>	0.32	0.32	0.22	0.27	0.30	0.31	0.32
MnO	0.08	0.07	0.05	0.06	0.06	0.07	0.03
P <sub>2</sub> O <sub>5</sub>	0.03	0.03	0.01	0.04	0.03	-	0.01
Total	101.01	100.05	99.96	100.23	99.94	100.48	100.86
Fe <sup>o</sup>	1.43	1.25	0.91	1.26	1.40	1.38	1.41
Wt. (gms)	5.1	4.2	6.2	5.1	2.7	4.5	5.5

Table 2 cont.

Locality	"AMERIKAVITES"		BEDIASITE	JAVANITES		PHILIPPINITES	
	Philippine Islands	Peru		Grimes, Co. Texas		Santa Mesa site,	
Sample #	3967	3996	T4106	T4102	T3959	T3960	T3961
SiO <sub>2</sub>	72.7	—	(77.80)	(72.39)	71.0	72.1	70.9
Al <sub>2</sub> O <sub>3</sub>	12.75	—	12.69*	11.15*	13.90	12.50	13.64
Fe <sub>2</sub> O <sub>3</sub>	0.69	0.28	0.77	0.78	0.87	0.72	0.82
FeO	0.95	0.41	3.15	5.41	4.29	4.28	4.18
MgO	0.11	0.03	0.61	3.97	2.70	2.58	2.67
CaO	0.86	0.25	0.56	2.33	2.95	2.90	3.20
Na <sub>2</sub> O	3.85	4.59	1.54	1.19	1.37	1.30	1.36
K <sub>2</sub> O	5.18	3.69	2.10	2.02	2.37	2.36	2.31
TiO <sub>2</sub>	0.06	0.04	0.74	0.64	0.78	0.78	0.79
MnO	0.05	0.06	0.04	0.12	0.09	0.09	0.08
Total	97.20	—	(100)	(100)	100.40	99.70	100.05
Fe <sup>o</sup>	1.22	0.52	2.99	4.75	3.95	3.83	3.82
S.G.	2.461	2.363	2.42	2.437	2.460	2.455	2.456
Wt. (gms.)	4.9	26.6	12.05	1.76	5.3	1.9	2.8

\* by X-ray fluorescence

Table 2-- con't.

Locality	PHILIPPINES								
	Santa Mesa site		Pugad-Babuy site						
Sample #	T3962	T3964	T3965	T3979	T3978	T3979	T3981	T3983	T3984
SiO <sub>2</sub>	70.2	(70.26)	68.9	71.8	(70.02)	70.13	70.5	70.6*	71.1*
Al <sub>2</sub> O <sub>3</sub>	14.09	14.01*	15.23	13.34	14.11*	14.66	14.59†	13.48	13.82*
Fe <sub>2</sub> O <sub>3</sub>	0.80	0.53	0.50	0.63	0.93	0.65	0.93	0.63	0.57
FeO	4.18	4.33	4.81	4.38	4.13	4.21	4.04	4.29	4.42
MgO	2.67	2.32	2.71	2.60	2.53	2.44	2.61	2.41	2.51
CaO	3.30	3.38	3.27	2.98	3.54	3.28	3.14	3.34	3.06
Na <sub>2</sub> O	1.30	1.76	1.29	1.33	1.32	1.55	1.34	1.56	1.34
K <sub>2</sub> O	2.31	2.56	2.46	2.35	2.51	2.56	2.40	2.56	2.35
TiO <sub>2</sub>	0.83	0.76	0.85	0.77	0.79	0.80	0.78	0.78	0.84
MnO	0.10	0.09	0.08	0.08	0.12	0.10	0.09	0.10	0.10
Total	99.88	(100)	100.16	100.33	(100)	100.35	100.42	99.64	100.34
Fe <sup>o</sup>	3.80	3.74	4.09	3.85	3.85	3.72	3.78	3.78	3.83
S.G.	2.454	2.411	2.429	-	2.452	2.432	2.439	2.379	2.455
Wt. (gms.)	4.1	4.5	5.7	-	203.5	13.9	10.3	7.9	9.8

\* by X-ray fluorescence

Table 2- con't.

Locality	INDOCHINITES											
	PHILIPPINES			Kouang-Tcheou-Kan			North Cambodia			Annam		
	Busuanga Island			T3987		T3988	T3989	T3990	T3991	T3992	T3993	T3994
Sample #	T3985	T3986	T3987	T3988	T3989	T3990	T3991	T3992	T3993	T3994	T3995	
SiO <sub>2</sub>	72.1	71.0*	(72.98)	73.3*	71.33*	71.8*	73.7*	77.5*	72.9	72.0	71.2	
Al <sub>2</sub> O <sub>3</sub>	12.96	13.56*	12.65	12.39*	13.68*	13.56*	13.32	11.59	12.96	13.02	12.28	
Fe <sub>2</sub> O <sub>3</sub>	0.71	0.50	0.68	0.54	0.47	0.70	0.82	0.82	0.50	0.68	0.72	
FeO	4.30	4.38	4.22	4.16	4.86	4.82	3.77	3.25	4.88	4.65	4.70	
NgO	2.93	2.66	2.45	2.34	2.93	2.85	1.90	1.62	2.74	2.67	2.96	
CaO	2.50	2.64	2.06	2.04	1.94	1.86	1.86	1.57	1.83	1.94	1.93	
Na <sub>2</sub> O	1.18	1.39	1.58	1.53	1.37	1.43	1.45	1.06	1.33	1.45	1.54	
K <sub>2</sub> O	2.17	2.40	2.49	2.46	2.34	2.49	2.62	2.10	2.27	2.32	2.38	
TiO <sub>2</sub>	0.75	0.76	0.72	0.77	0.74	0.81	0.75	0.66	0.74	0.73	0.74	
MnO	0.09	0.10	0.10	0.10	0.09	0.11	0.09	0.08	0.11	0.09	0.09	
Total	99.78	99.39	(100)	99.63	99.73	100.43	100.28	100.25	100.26	99.55	98.54	
Fe <sup>o</sup>	3.84	3.75	3.75	3.61	4.10	4.22	3.50	3.10	4.15	4.09	4.15	
S.G.	2.445	2.437	2.435	2.425	2.445	2.446	-	-	2.448	2.439	2.447	
Wt. (gms.)	3.4	18.3	12.1	10.6	25.9	24.5	19.1	-	11.5	9.7	7.6	

\* By X-ray fluorescence.

Table 2- con't.

Locality	INDOCHINITES			AUSTRALITES			Charlotte Waters
	Dalat, S. Viet-Nam			Nullarbor Plain			
	T4218	T4219	T4220	T4214	T4215	T4216	
SiO <sub>2</sub>	(72.64)	(73.08)	(73.30)	(71.41)	69.0*	(70.96)	-
Al <sub>2</sub> O <sub>3</sub>	13.40*	12.38*	12.76*	13.82*	15.32*	13.48*	-
Fe <sub>2</sub> O <sub>3</sub>	0.58	0.76	0.37	0.88	0.38	0.71	0.63
FeO	4.21	4.50	4.41	3.80	4.49	4.13	3.43
MgO	2.25	2.80	2.28	2.13	2.28	2.13	1.64
CaO	2.03	1.88	2.04	3.59	3.17	3.47	2.15
Na <sub>2</sub> O	1.54	1.55	1.56	1.12	1.56	1.84	1.33
K <sub>2</sub> O	2.50	2.32	2.50	2.07	2.50	2.61	2.38
TiO <sub>2</sub>	0.76	0.63	0.70	0.79	0.81	0.59	0.67
MnO	0.09	0.10	0.08	0.09	0.09	0.08	0.08
Total	(100)	(100)	(100)	(100)	99.61	(100)	-
Fe <sup>o</sup>	3.67	4.03	3.69	3.57	3.75	3.70	3.11
S.G.	-	-	-	-	-	-	-
Wt. (gms.)	6.0	10.4	-	6.5	8.1	5.5	2.7

\* By x-ray fluorescence.

TABLE 3

## Average Composition of the Philippinites and Indochinites

## Philippinites (15)

	Average	$\sigma$	C
SiO <sub>2</sub>	70.8	±0.88	±1.2%
Al <sub>2</sub> O <sub>3</sub>	13.85	0.72	5.2%
TiO <sub>2</sub>	0.79	0.03	3.7%
Fe <sub>2</sub> O <sub>3</sub>	0.70	0.14	19.6%
FeO	4.30	0.17	4.0%
MgO	2.60	0.13	5.1%
CaO	3.09	0.30	9.8%
Na <sub>2</sub> O	1.38	0.14	10.4%
K <sub>2</sub> O	2.40	0.11	4.6%
MnO	0.094	0.010	10.4%
Total Fe (Fe <sub>2</sub> O <sub>3</sub> )	5.48	0.13	2.4%
*Rb ppm	117	5.0	4.3%
*Sr ppm	173	10.6	6.1%

## Indochinites (12)

	Average	$\sigma$	C
SiO <sub>2</sub>	73.0	±2.05	±2.8%
Al <sub>2</sub> O <sub>3</sub>	12.83	0.67	5.2%
TiO <sub>2</sub>	0.73	0.05	6.6%
Fe <sub>2</sub> O <sub>3</sub>	0.64	0.14	22.2%
FeO	4.37	0.49	11.1%
MgO	2.48	0.42	17.1%
CaO	1.91	0.14	7.1%
Na <sub>2</sub> O	1.45	0.15	10.1%
K <sub>2</sub> O	2.40	0.14	5.7%
MnO	0.094	0.009	9.0%
Total Fe (Fe <sub>2</sub> O <sub>3</sub> )	5.49	0.49	8.9%
*Rb ppm	118	7	5.9%
*Sr ppm	132	4.9	3.7%

\* From Schnetzler and Pinson (1963)