

THE COMPOSITION AND ORIGIN OF TEKTITES

by

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B.S. University of Kansas  
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## The Composition and Origin of Tektites

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Submitted to the Department of Geology and Geophysics on August 28, 1961, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

**ABSTRACT**-Studies of the strontium isotopic composition and major element composition of tektites have been carried out.

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 average  $Sr^{87}/Sr^{86}$  ratio in 18 tektites is  $0.7190 \pm 0.0006$ , indicating the results of Pinson et al (1958), reporting no radiogenic strontium in tektites, were in error. Rb and Sr contents of tektites from a given locality are very similar, but differences exist between localities. The  $Sr^{87}/Sr^{86}$  ratios of tektites do not show variation of the magnitude expected in random fusion of terrestrial rocks. If tektites were derived from the Moon, and the 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 material. A second possibility is that the Moon has undergone recent differentiation. Tektites exhibit a direct correlation of  $Sr^{87}/Sr^{86}$  and Rb/Sr ratios, suggesting they differentiated from a common source material 175 m.y. ago.

37 tektites and 2 "americanites" were partially or completely analysed for major elements. Many chemical similarities are noted between the philippinites and indochinites, but the two groups appear different in  $SiO_2$ ,  $Al_2O_3$ ,  $TiO_2$  and, in particular, CaO contents. Tektites from two sites in the Philippine Islands are identical, within experimental error, in mean composition. 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 CaO and Sr contents of the philippinites are due to contamination of the parent material by limestone. Real variations, up to approximately 10% for some constituents, exist within the philippinites and indochinites, and even within tektites from restricted sites. A new tektite from Martha's Vineyard is remarkably similar chemically to the Georgia tektites and at least some of the Texas tektites. Evidence is presented that the Texas samples are not two geographically separate showers as suggested by Barnes (1960) but are intermixed.

The similar chemical compositions over wide areas, and direct correlation of  $Sr^{87}/Sr^{86}$  ratios with Rb/Sr ratios cannot be explained by any proposed terrestrial theory of origin.

Thesis supervisor: W.H. Pinson  
Associate Professor of Geology

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## **Part I**

**(Part I consists of two papers which will be submitted for publication. These papers have been abstracted from the complete description of the thesis investigation presented in Part II)**

## STUDIES OF TEKTITES I-VARIATIONS OF STRONTIUM ISOTOPES IN TEKTITES

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 average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in 18 tektites is  $0.7190 \pm 0.0006$ , indicating the results of Pinson et al (1958), reporting no radiogenic strontium in tektites, was in error. Rb and Sr contents of tektites from a given locality are very similar, but differences exist between localities. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of tektites do not show variation of the magnitude expected in random fusion of terrestrial rocks, particularly of shales or granites. If tektites were derived from the Moon, and the surface of the Moon is old (4.5 b.y.), the observed  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios could not have been developed by a chondritic, granitic, or tektitic surface material, but could have been generated by a basaltic type material. A second possibility is that the Moon has undergone recent differentiation. Tektites exhibit a direct correlation of  $\text{Sr}^{87}/\text{Sr}^{86}$  and Rb/Sr ratios, suggesting they differentiated from a common source material 175 m.y. ago.

### INTRODUCTION

Perhaps the majority of tektite investigators currently believe that tektites were formed by the fusion of terrestrial materials. Various mechanisms have been proposed, such as impact by meteorites (Spencer, 1933; Cohen, 1961) comets (Urey, 1957; Cherry and Taylor, 1961), and lightning (Hawkins, 1960). All of these theories are similar in that they all suggest a random process--the probability of fusing a certain type of material being in direct proportion to the extent of that material upon the earth's surface. In view of the large compositional variations one would expect if the fusions were random, the rather similar chemical compositions of tektites might be attributed to one of two possibilities. Perhaps only materials of a certain type would form durable

tektites; other materials would not form glasses, or tektites formed from these other materials would devitrify rapidly. Or perhaps selective volatilization of elements during the high temperature fusion would change the chemical composition of different materials toward some common composition, thus suppressing the chemical variations. In view of this second possibility it might not be possible to identify the parent material from the chemical composition of the tektite (Lovering, 1960, p. 1029).

However, selective fractionation should be essentially non-existent among the heavier isotopes during a high temperature fusion, and the relative isotopic composition of tektites should be the same as that of the parent material provided their composition has not been changed by radioactive transformations since the time of fusion. Thus it should be possible to test the theory of random fusion by comparing the variation of the isotopic composition of tektites with the variation observed in various proposed parent materials. The strontium isotopes are particularly suited for this type of investigation.  $\text{Sr}^{87}$  is formed by the decay of  $\text{Rb}^{87}$ , so that 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  $\text{Rb}/\text{Sr}$  ratio of the system, the initial abundance at an initial time, and the time elapsed since this initial time. Thus terrestrial materials, having different  $\text{Rb}/\text{Sr}$  ratios and different ages, have a wide range of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. K-Ar dating of

tektites gives ages of 30 m.y. or less for the moldavites, bediasites, and Georgia tektites, and less than 1 m.y. for the Pacific Ocean area tektites (Reynolds, 1960). According to the terrestrial fusion theories, these ages would be the times since fusion. As the half-life of the decay of  $\text{Rb}^{87}$  to  $\text{Sr}^{87}$  is quite long, approximately  $4.7 \times 10^{10}$  years (Glendenin, 1961), no measurable change has occurred in 30 m.y. in the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio so that the relative strontium isotopic composition of tektites should be the same as the parent material at the time of fusion.

Pinson et al (1956) suggested that the relative strontium isotopic composition 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 this would prove their extra-terrestrial origin, as this circumstance occurring in terrestrial rocks from different parts of the world would be highly improbable.

Later Pinson et al (1957) reported the rubidium and strontium, and strontium isotopic composition of three indochinites, two australites, and two philippinites. The  $\text{Sr}^{87}/\text{Sr}^{86}$  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  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios and the Rb/Sr ratios. The computed ages, assuming an initial ratio of 0.712 (this is called "normal strontium" as it is the ratio found in sea water), varied from 180 to 730 m.y., with estimated errors of  $\pm 50\%$ .

These values were later reported to be in error, and the corrected values for the  $\text{Sr}^{87}/\text{Sr}^{86}$  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, 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,  $60^\circ$  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, p. 237-244).

The X-ray fluorescence unit used was a North American Phillips instrument with a tungsten target X-ray tube. The crystal was  $\text{LiF}$  and the detector was a scintillation counter. The standards used were tektites which had been analysed 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 standard from the same area could be compared with no matrix effects.

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:  $\text{LiF}$  crystal; pulse height analyser: base volts = 41.5, window volts = 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 positions. 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-worker that the variations of  $\text{Sr}^{87}$  in tektites are small, if present, so that a reproducibility of  $\pm 0.001$  or less in the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio was desirable.

In an attempt to determine the precision of the strontium isotope ratio analyses, two tektites were analysed in triplicate. The results are shown in Table 1.

**Table 1 Triplicate Isotope Ratio Analyses**

(see Table 4, Part II, page 34)

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 (Nier, 1938). 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 given in the column headed  $(\text{Sr}^{87}/\text{Sr}^{86})$  corr.

It can be seen that in the two samples shown in Table 1 the precisions of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios were improved by about a factor of three by the application of the fractionation correction. This same correction procedure has been applied by other members of the M.I.T. Geochronology Laboratory with approximately the same results. (Faure, 1961, p. 178; Hart, 1960, p. 194). By elimination of this instrumental fractionation, standard deviations (of a single analysis) of approximately  $\pm 0.001$  ( $c = 0.14\%$ ) were achieved.

In an attempt to monitor the accuracy of the strontium isotope ratio determinations, and to determine if the correction applied by Pinson et al (1958) was valid, replicate analyses were made of a strontium carbonate standard (Elmer and Amend, lot #92327) during the period of the investigation. The average of nine determinations is compared with the results of other investigators on the same, or similar, material in Table 2. On the basis of the excellent agreement with the

**Table 2 Analyses of strontium isotopes from reagents**

**(See Table 6, Part II, page 40)**

results of the other laboratories no "pressure broadening correction," as applied by Pinson et al (1958) was used in this investigation. Had such a "correction" been made the results would have been far from those obtained by the other laboratories. The standard deviation of a single analysis of the strontium carbonate data was  $\pm 0.0009$  for the  $(\text{Sr}^{87}/\text{Sr}^{86})$  corr. ratio.

The tektite analyses were also interspersed with basalt analyses (by Faure), and the agreement between his results and the results of other investigators can be seen in Table 5. This work gives confidence in the tektite analyses and is further evidence that a "pressure broadening correction" should not be applied.

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). Interlaboratory 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 3 and 4. Eighteen tektites were analysed for strontium isotopic composition and 25 tektites were analysed for rubidium and strontium elemental contents. All errors are standard deviation of the mean. The number of scans pertain to the  $\text{Sr}^{87}/\text{Sr}^{86}$  and  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios; the  $\text{Sr}^{84}/\text{Sr}^{88}$  ratios were calculated from a much smaller number of scans--usually 12 to 36.

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 0.712 ("normal" strontium) or 0.700 (primordial strontium).

Five philippinites, from three different sites, have an average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.7181,  $\overline{\sigma} = 0.0006$ ,  $\sigma = 0.0013$ . The reproducibility ( $\sigma$ ) of strontium isotope analyses appears to be approximately  $\pm 0.001$ . Thus the variation of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in the philippinites is only slightly greater than one would expect from measurement error. Seven philippinites, including the five analysed for isotopic composition, have an average rubidium content of  $117 \pm 2$  ppm ( $\overline{\sigma}$ ) 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.

Five indochinites, from four different localities, also have homogeneous  $\text{Sr}^{87}/\text{Sr}^{86}$  values, averaging 0.7198,  $\overline{\sigma} = 0.0005$ ,

**Table 3 Rb and Sr Contents of Tektites**

(See Table 8, Part II, page 44)



**Table 4 Strontium Isotopic Ratio Results**

(See Table 10, Part II, page 50)

$\sigma = 0.0011$ . This variation is again about what one could expect from measurement error. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio for indochinites seems to be different from the ratio measured in the philippinites. If  $\bar{x} \pm \sqrt{\sigma_{\bar{x}}}$  and  $\bar{y} \pm \sqrt{\sigma_{\bar{y}}}$  are the measured values of two independent populations, there is only a 5% probability that  $(\bar{x} - \bar{y}) > 2\sqrt{\sigma_{(\bar{x}-\bar{y})}}$  if the difference between the true mean values is zero, where  $\sqrt{\sigma_{(\bar{x}-\bar{y})}} = \sqrt{\sigma_{\bar{x}}^2 + \sigma_{\bar{y}}^2}$  (Hoel, 1954, p. 109). In this case  $\bar{x} - \bar{y} = 0.0017$  and  $\sqrt{\sigma_{(\bar{x}-\bar{y})}} = \pm 0.0008$ . Since  $(\bar{x} - \bar{y}) > 2\sqrt{\sigma_{(\bar{x}-\bar{y})}}$  it can be tentatively concluded that at the usual 95% confidence limit these two populations are significantly different. However this conclusion is based on rather limited data and more samples should be analysed to test this point.

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 identical  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios at 0.7174 while a javanite has a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.7194. 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 analysed 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 three North American tektites have an average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of  $0.7166 \pm 0.0012$ . Unfortunately only small amounts of these samples were available and replicate runs could not be made in order to confirm the measurements. The Empire, Georgia  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, although significantly lower than the other tektites, was obtained from two exceptionally long and steady runs. A strontium carbonate standard was run immediately after the first of the Georgia analyses to check for any instrumental bias and the run was completely normal. The Massachusetts and Georgia tektites contain quite similar rubidium contents (78 and 74 ppm respectively) and strontium contents (177 and 170 ppm respectively). The two Texas samples contain 70 and 66 ppm rubidium and 152 and 153 ppm strontium--slightly less than the Massachusetts and Georgia samples--but the Rb/Sr ratios of the four are amazingly similar for samples from such widely separated localities.

The two moldavites analysed gave the highest  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of the tektites analysed, 0.7257 and 0.7235. Only one of these samples was analysed for rubidium and strontium, and it has the highest Rb/Sr ratio of any of the tektites analysed; viz. 1.07. Due to the small size of the sample available, the other moldavite (T3314) could not be analysed for rubidium and strontium. However, values of 130 ppm Rb and 136 ppm Sr were reported for this sample by Pinson et al (1958).

The average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio for all 18 tektites analysed is  $0.7190 \pm 0.0006$ .

### Discussion of Results

Although the analytical results reported by Pinson et al (1958) were partially in error, 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 terrestrial 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 in terrestrial materials.

The first question to be asked is, does the variation of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites correspond with the variation

one would expect by the random fusion of terrestrial materials?

$\text{Sr}^{87}/\text{Sr}^{86}$  ratios and Rb/Sr ratios in various types of terrestrial and extra-terrestrial materials are given in Table 5. Unfortunately, it has been common practice in age-dating to use only a few favorable minerals rather than the whole rock for analysis so that data of interest to this investigation is sparse.

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 analysed. Granites have a very large variation in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. As all but one of the 21 granites in Table 5 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 Rb/Sr ratios in the granites range from 0.25 to 6.0, averaging about 1.7 while the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios range from 0.72 to 1.25. 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 analysed.

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 analysed 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 analysed by Pinson and Bottino (1961) show a limited  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio ranging from 0.704 to 0.724, while the

**Table 5**  $\text{Sr}^{87}/\text{Sr}^{86}$  Ratios and Rb/Sr Ratios in Terrestrial  
and Extra-Terrestrial Materials

(See Table 13, Part II, page 69)

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).

Faure analysed two composite samples of Paleozoic shales from the east and west coasts of North America. The measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios are quite similar - 0.720 and 0.723. The Rb/Sr ratios were not determined in these samples. Turekian and Wadeohl (1961) and Faure (1961) have estimated the average Rb/Sr ratio in shale to be 0.47 and 0.50 respectively. Thus rocks of this high a Rb/Sr ratio (and undoubtedly having considerable variation in this ratio) and of varying ages should have highly varying  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. Such variations are suppressed between composite samples.

Chondrites have fairly high, varying  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. Unfortunately Gast (1960) did not analyse his five chondrites for rubidium and strontium, but it is assumed the variation shown by these specimens is due to slightly different Rb/Sr ratios and the ages are all the same--approximately  $4.5 \times 10^9$  years. This should be investigated further. Herzog and Pinson (1956) found the Rb/Sr ratios in two chondrites to be about 0.35.

Achondrites have extremely low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios which show almost no variation (See Table 5). Under the assumptions that 1) all terrestrial and meteoritic strontium was derived from a homogeneous parent material and thus had the same abundance of  $\text{Sr}^{87}$ , 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-worker 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 ( $\sim .005$ ) 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 (0.7004 - 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 next question that should be discussed is: How many independent fusions by the various mechanisms would the 18 tektite samples analysed for strontium isotopic composition represent? As they came from at least 14 different sites separated by more than ten miles, they would represent at least 14 independent fusions if they were formed by the energy of lightning randomly striking the earth. A few of the



samples such as the two labeled "North Cambodia" may have been collected from exactly the same site, but this is unlikely so the 18 samples probably would represent 18 fusions by lightning.

If the tektites were formed by the impact of meteorites all the tektites within several square miles, or even tens of square miles may have been formed from one impact. Thus, as the samples analysed are from 12 provinces, states, or countries, any of which is more than 100 miles from its nearest neighbor, they should represent 12 different meteorite impacts.

The number of impacts necessary to form the tektites by fusion by asteroids or comets is considerably less than either of the other two theories just discussed. Cohen (1961) suggested that all the Pacific Ocean area tektites were produced by one collision, all the North American tektites were the result of another, a third produced the moldavites, and a fourth the Ivory Coast tektites. Reynolds' (1960) K-Ar work implies at least five groups, while Baker (1959) claims the geological evidence points to eleven groups (including the Georgia field which he did not discuss, but excluding the Martha's Vineyard specimen). Urey (1957), in discussing the comet hypothesis, conceded that probably all the Pacific Ocean area tektites were not formed by one impact but suggests the comet head split and produced multiple, simultaneous impacts in the various tektite localities of the Pacific. Thus it is proposed that the 18 tektites analysed

would represent at least six separate impacts of asteroids or comets, these six impacts consisting of the moldavites, North American tektites (grouped on the basis of similarity of composition), australites, javanites, philippinites, and indochinites.

The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites given in Table 4 and the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios taken from the literature for various materials as given in Table 5 are plotted in Figure 1. The figure shows the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios for various materials from only 0.700 to 0.760, approximately the lower one-tenth of the range exhibited by the data in Table 5. 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 1.

It can be seen from this diagram that tektites do not show the variation one would expect if they are the product of random fusions of terrestrial materials - whether the tektites analysed represent 14, 12, or 6 separate random impacts. As mentioned above, some investigators maintain that only a certain type of material could produce tektites. For example a basic magma may crystallize even when undergoing rapid cooling but the more viscous acid melt may be unable to form crystals and remain as a glass. Of the more acidic rocks the ones most commonly mentioned as possible parents for the tektites include siliceous shale (Urey, 1959), granite (Mason, 1959), and granophyre (Lovering, 1960). But these are types that should have large variations in their  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. They have high average Rb/Sr ratios (approximately 0.5 in shales and 1 in granites, and also presumable granophyres)

**Figure 1**  $\text{Sr}^{87}/\text{Sr}^{86}$  Ratios in Tektites, Meteorites, and  
Terrestrial Rocks (Expanded View)

(See Figure 6, Part II, page 76)

and exhibit a wide range of Rb/Sr ratios. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in shales will vary according to the proportions of young low-ratio volcanic material, low-ratio limestone, old high-ratio granite, etc., that together contributed to make up the rock. For example, certainly a largely detrital micaceous shale derived from an ancient landmass would have a much greater  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio than a feldspathic shale with a high proportion of endogenic constituents or recent volcanics.

Thus the results of this investigation do not support the theory of tektite production by random fusion of terrestrial materials, particularly the random fusion of shale or granite.

## 2. 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; Chapman, 1960). Varsevsky (1958) calculated that possible trajectories exist by which lunar material may be focused to restricted portions of the Earth. It is interesting to use this data to test the theory that the tektites were derived from the Moon, again assuming that the Rb/Sr ratios have not changed since the tektites were formed.

It is proposed that the K-Ar ages date the period of second melting that is observed in some of the tektites. This second melting caused the melting of the surface and the build-up of a flange, probably heating the interior sufficiently to allow the diffusion of radiogenic argon from the interior,

but the melting was limited to the surface. Taylor's (1961) analyses of alkali elements in the flanges and cores of australites indicate considerable selective volatilization occurred. However, all the analyses in this work were performed on specimens that did not contain a flange--either the samples never experienced second melting or the flanges had since weathered away. In any event, it is believed the Rb/Sr ratios in the tektites analysed, and thus the rate of growth of their  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, were not changed during the heating that is dated by the K-Ar measurements, and thus the Rb/Sr ratios have remained unchanged since formation of the tektites.

Most students of the Moon (for example, Urey, 1952, p. 30; Spurr, 1948, p. 242; 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  $\text{Sr}^{87}/\text{Sr}^{86}$  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 to the present day the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, after a growth for 4.5 billion years from the primordial ratio of 0.700, would be between 0.78 and 0.90, far in excess of that actually found.

Conversely, the Rb/Sr ratio that would generate a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.719 (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 5), and the maria have commonly been theorized as being covered with basaltic lava flows. A basalt that had remained on the surface of the Moon for 4.5 billion years should have about the same  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio as is observed in tektites; viz. 0.719. It is difficult to reconcile such a radical change in Rb/Sr ratio (from 0.1 to between 0.44 and 1.1) 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 result 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 evidence has been used by most lunar investigators to conclude the maria are approximately 4.5 billion years old (Opik, 1960). Gilvarry's (1960) theory that the maria are composed of sedimentary rocks that were deposited by a hydrosphere which had a life time of the order of  $10^9$  years could account for observed Rb/Sr ratios in tektites. However, there seems to be little evidence to support this hypothesis.

In short, the Rb/Sr and  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios (and the lead isotopic composition as determined by Tilton, 1958) 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; theories advocating this differentiation have been advanced but they have not been widely accepted by lunar investigators. The present tektite Rb/Sr data is fairly consistent with such theories of recent and continuing differentiation of the Moon's crust.

3. Significance of the direct correlation of Rb/Sr ratios and  $Sr^{87}/Sr^{86}$  ratios in tektites.

Igneous rocks that are formed contemporaneously by crystal fractionation from a common source (e.g. Comagmatic series of volcanic rocks) will differ in Rb/Sr ratios. At the time of their formation they all had the same initial  $Sr^{87}/Sr^{86}$  ratio but after fractionation they each developed radiogenic strontium in accordance with each Rb/Sr ratio. If the  $Sr^{87}/Sr^{86}$  development lines are drawn for each rock type they form an array of lines which converge back in time, intersecting at a point whose coordinates are the time of differentiation and the  $Sr^{87}/Sr^{86}$  ratio of the parent material. The common origin of a series of igneous rocks can be tested in this manner. If the rocks crystallized from parent materials having different  $Sr^{87}/Sr^{86}$  ratios or at different times the probability of three or more development lines meeting at a common point is small. Two different points of intersection would indicate two different source regions. In this section such a test for a common source region is applied to the tektites.

Figure 2 is a graph of the  $Sr^{87}/Sr^{86}$  ratios plotted against time, showing the  $Sr^{87}/Sr^{86}$  development lines for four groups of tektites. The four areas represented, and the number of samples included by the average, are North America (3), Philippine Islands (5), Indo China (5), and Bohemia (2). The lines are drawn from the data given in Tables 3 and 4, with the error envelopes shown by dashed lines. The envelopes are



Figure 2  $\text{Sr}^{87}/\text{Sr}^{86}$  vs Time for Several Groups of Tektites

(See Figure 8, Part II, page 84)

computed on the basis of one standard deviation of the mean ( $\bar{v}$ ) for the  $\text{Sr}^{87}/\text{Sr}^{86}$  and  $\text{Rb}/\text{Sr}$  ratios. The australites were not included in this diagram because the two samples analysed had different  $\text{Rb}/\text{Sr}$  ratios and an average would not be very meaningful.

One basic assumption made in drawing these development lines is that the  $\text{Rb}/\text{Sr}$  ratios have not changed since the tektite first formed. This was discussed earlier. A second assumption is that the tektites from one locality are related, other than just geographically. Otherwise the average  $\text{Sr}^{87}/\text{Sr}^{86}$  development line would be meaningless. The constancy of the  $\text{Rb}/\text{Sr}$  ratio of a particular group, in contrast to the difference between groups, supports this assumption.

It can be seen from Figure 2 that the philippinites, indochinites, and North American tektite lines nearly intersect at a common point, with coordinates of  $\text{Sr}^{87}/\text{Sr}^{86} = 0.7135$  and time = 175 m.y. However, the error envelopes are so large that the overlap of any two of these three lines extend from 0 to 350 m.y. The error envelopes of the two lines with the smallest errors (the indochinites and philippinites) overlap from approximately 50 to 250 m.y. The moldavite line, perhaps the poorest determined as it is based on only two samples, does not cross the other three lines at their common point of intersection. It intersects the North American line at 300 m.y. with an error range of from 200 to 400 m.y., and crosses or is within the error envelope of the other two lines from 250 to 550 m.y.

The  $\text{Sr}^{87}/\text{Sr}^{86}$  development line for the upper mantle, as determined by Faure (1961), is shown on the same diagram. The tektite development lines cross this line at ages that range from 325 m.y. (indochinites) to 525 m.y. (North American tektites). The moldavite and philippinite lines actually intersect on this line and the indochinite, philippinite, and moldavite lines have error envelopes that overlap on this line; if  $2\sqrt{\quad}$  has been used the points of intersection of the tektite lines upon the upper mantle line would have all been within experimental error. Thus the tektites could have been derived from the upper mantle at the time indicated.

The primordial value of  $\text{Sr}^{87}/\text{Sr}^{86}$  determined from achondrites and discussed earlier, is also shown on Figure 2. Thus the maximum age for the tektites, given by the intersection of the tektite lines with the primordial line, range from 500 to 950 m.y.

In this discussion the term "tektite development line" has been used. The same remarks would apply to the parent material if the Rb/Sr ratio did not change either when the tektite formed from the parent or during the pre-tektite history of the parent.

It is interesting that Figure 2 shows a sympathetic variation of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios with the Rb/Sr ratios; if there was no sympathetic variation the lines would not converge back in time. Another way to show the sympathetic variation is given in Figure 3. In this figure the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios

Figure 3  $\text{Sr}^{87}/\text{Sr}^{86}$  vs Rb/Sr in Tektites

(See Figure 9, Part II, page 87)

are plotted against the Rb/Sr ratios for the various tektites analysed, and the averages for the different groups are shown. The standard deviation of the mean ( $\bar{\sigma}$ ) for the  $\text{Sr}^{87}/\text{Sr}^{86}$  and the Rb/Sr ratios are shown by the lengths of the vertical and horizontal lines respectively. In such a diagram all samples of equal age will lie on a straight line. Such a line, the 175 m.y. isochron, is drawn through the averages for the North American, Philippine, and Indo China samples. The moldavites lie above this line, reflecting the fact that in Figure 2 their development line was above the point of intersection of the other three lines. More experimental work is necessary to refine this data, especially to see if the moldavites actually lie above the 175 m.y. isochron (i.e. do not intersect with the other three lines at the common point), but the present data seems more than coincidental or circumstantial and suggest that the North American, Philippine and Indo China tektites differentiated from a common source material approximately 175 m.y. ago. CERTAINLY IT IS DIFFICULT TO RECONCILE THIS DATA WITH TEKTITE PRODUCTION WITHIN THE LAST 30 m.y. FROM RANDOM MATERIALS OF DIFFERENT AGES AND COMPOSITIONS. Sympathetic variation between the  $\text{Sr}^{87}/\text{Sr}^{86}$  and Rb/Sr ratios in such a case would be highly unlikely.

This homogeneity of age values, whether these are actual ages of the tektites or the parent material, is indeed difficult to reconcile with any terrestrial origin in view of their widespread geographic locations and varying K-Ar ages.

The extra-terrestrial theories are not much more attractive. One model that would explain their Rb/Sr -  $Sr^{87}/Sr^{86}$  ratio relations, K-Ar ages, lack of cosmic-ray induced radioactivity (Anders, 1960), distribution in restricted strewnfields, and second period of melting would be as follows:

1) The fusion and ejection of large bodies from the surface of the Moon or some other body in the solar system about 175 m.y. ago. The glassy blocks would have a common  $Sr^{87}/Sr^{86}$  ratio, which would be the same as the parent material, approximately 0.713. Due to differences in selective volatility the Rb/Sr ratios of the various bodies were different; however, it is certainly difficult to see why the Sr should vary and not the Rb. The  $Sr^{87}/Sr^{86}$  ratio of 0.713 is compatible with a basaltic surface 4.5 billion years old, but the compositional changes necessary to derive a tektite from basalt do not seem possible by high temperature fusion. A more plausible occurrence would be production of the large tektite bodies from material that was similar to tektites in composition due to recent differentiation or some change that increased its Rb/Sr ratio. Tilton (1958) after analyzing three tektites for lead isotopes and one tektite for uranium and thorium, reached the conclusion that the tektites, or parent material, had undergone differentiation within the last tens of millions of years. This work should be extended to check the apparent agreement with this investigation.

2) The bodies independently spiraled toward the Earth, arriving in the Earth's atmosphere 30 to less than 1 m.y. ago. Since their common origin each had developed  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in accordance with their different Rb/Sr ratios. Since each body was of considerable size, the interiors were protected from cosmic rays.

3) The large bodies broke up in the Earth's atmosphere and the tektites formed from a particular body fell in a specific strewnfield. The bodies probably entered the Earth's atmosphere along orbits nearly parallel to the surface of the Earth (O'Keefe, 1960) since considerable ablation of the individual tektite took place. During this ablation the tektites were heated sufficiently to cause the escape of argon, giving rise to the young argon ages.

The principal difficulty of any extra-terrestrial origin for tektites is the existence on some body in the solar system of suitable parent material. However, it is believed the Rb/Sr -  $\text{Sr}^{87}/\text{Sr}^{86}$  relationship, and the lack of large variations in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in tektites, makes any of the proposed terrestrial theories even more unattractive.

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## STUDIES OF TEKTITES-II MAJOR ELEMENT COMPOSITIONS OF TEKTITES

ABSTRACT-37 tektites and 2 "americanites" were partially or completely analysed for major elements. Included were 15 philippinites and 12 indochinites. 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, CaO contents. The CaO contents of the indochinites are distinctly lower, and the MgO contents higher, than the analyses 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. 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 CaO and Sr contents of the philippinites are due to contamination of the parent material by limestone. Negative correlations of  $\text{SiO}_2$  with the other major elements, which exhibit positive correlation among themselves, are exhibited by the tektites in agreement with Taylor et al (1961). A new tektite from Martha's Vineyard is remarkably similar chemically to the Georgia tektites and at least some of the Texas tektites. Evidence is presented that the Texas samples are not two geographically separate showers as suggested by Barnes (1960) but are intermixed.

### Introduction

Barnes (1940) compiled all the analyses of tektites available at that time. He listed 61 analyses, not including the questionable Darwin Glass and Libyan Desert Glass; these included 10 moldavites, 2 bediasites, 24 indochinites, 4 philippinites, 9 billitonites and associated tektites, 9 australites, and 3 Ivory Coast tektites. Since 1940 the only complete major element analyses of tektites to appear in the literature are one bediasite (Barnes, 1956), a new tektite from Martha's Vineyard, Massachusetts (Kaye, et al, 1961), and one Georgia tektite (Clarke and Carron, 1961). Pinson and Schnetzler (1959)

reported the average K, Na, Fe, Mn, and Ti contents of 11 philippinites and indochinites, and Taylor (1960) reported the alkali element contents of 14 australites.

From the published analyses it is obvious 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 is 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.

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 probable terrestrial origin.

### Chemical Analyses

#### Analytical Procedures

The majority of analyses reported in this paper were

made by the "rapid silicate" method of Shapiro and Brannock (1956). 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" Techniques

The rapid silicate procedures of Shapiro and Brannock (1956) are primarily colorimetric methods of analysis. The intensity of light passing through various colored complexes of  $SiO_2$ ,  $Al_2O_3$ , total Fe,  $TiO_2$ , MnO, and  $P_2O_5$  is determined on a spectrophotometer, while CaO and MgO are determined by photometric titration.  $Na_2O$  and  $K_2O$  are determined by flame photometry. The rapid silicate method is especially attractive because most of the determinations are independent of each other so that gross errors in one determination do not affect subsequent results. Also, the manipulations are simpler than in conventional methods of silicate analysis (there are no separations, precipitations, etc.) so that gross errors due to improperly performed procedures are not usually encountered.

Beckman Model B spectrophotometers were used in the colorimetric and photometric titration procedures, and a Perkin-Elmer Model 146 flame photometer was used in the determination of  $Na_2O$  and  $K_2O$ .

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 4). The spectrophotometric method is much faster and results in considerable saving of sample.

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) as 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) as 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 (Phinney, 1959). 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 analyzed in one day and the duplicate pairs from the other weighing on another day. The samples to be analyzed 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) have 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 favorable with the wet chemical results, being accurate only to 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 Pacific Ocean area tektites, 2) the tektites, being a fairly homogeneous glass, should not exhibit the inhomogeneity of particle size and mineralogical composition that would be found in a powdered rock sample, and 3) the machine available allows the rapid comparison of standard and sample, which was not the case in the machine used by Chodos and Engel, thus reducing instrumental drift.

One disadvantage of the X-ray fluorescent unit used is that the samples are inverted when put into the machine, making it necessary to have a mylar window over the sample holder to

contain the powdered sample within the holder. It was found the 0.5 mil mylar window cut the intensity of the beam for the silica K $\alpha$  radiation by a factor of  $\sim 10$  and for aluminum K $\alpha$  radiation by a factor of  $\sim 25$ . This reduction in beam intensity greatly increases the counting time necessary for the desired precision, and nullifies the advantage of speed this method originally promised. Some of the samples had not been completely powdered, and the solid portions were large enough to fill the aperture in the sample holder shield; thus they could be run as solids and the mylar window could be eliminated. However, the majority of the samples had been completely powdered. An attempt was made to press them into a brickette under high pressure, but the powdered tektite glasses would not form hard brickettes, and the danger of losing the whole sample was felt to be too great to pursue this approach. Thus it was decided to sacrifice speed, and use the mylar window with the powdered samples. Larger shields were used for the powdered samples than for the solids so that the counting rates for the powders were only a factor of 3 lower for silica and 8 lower for aluminum than the counting rates of the solids.

The preparation and packing of the powdered samples were essentially as described by Chodos and Engel (1961). A cut surface of the solid which was free from bubbles was polished to eliminate any effect of surface irregularity, and mounted behind a shield which did not have a mylar window.

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 volts = 1.50, window volts 6, flow proportional counter volts = 1650. Number of counts for powder: SiK $\alpha$  peak 51,200, background 800; Al K $\alpha$  peak 8000, background 800. Number of counts for solid: Si K $\alpha$  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. Table 1 compares the values obtained by the two methods. The numbers in parentheses are the number of determinations by the X-ray fluorescence method. It can be seen that the Al<sub>2</sub>O<sub>3</sub> results for the powdered samples as well as for the solid samples are in very good agreement. The maximum difference between the two methods is about 2% of the amount present, while the average difference is about 1% of the amount present. In the last two samples listed in Table 1 the Al<sub>2</sub>O<sub>3</sub> powder and solid X-ray fluorescence results are compared.

The SiO<sub>2</sub> X-ray fluorescence results, however, are 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 Al<sub>2</sub>O<sub>3</sub>, but not in SiO<sub>2</sub>.

However, the SiO<sub>2</sub> determinations in the solid samples are in good agreement with the values obtained by the rapid

**Table 1 Comparison of Rapid Silicate and X-ray Fluorescence  
Analyses for SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>**

(See Table 15, Part II, page 107)

silicate procedure. Another reason to believe the solid sample  $\text{SiO}_2$  results are acceptable, while the powdered sample values are not, is the fact that the constituents total close to 100% using the solid sample  $\text{SiO}_2$  results, while the totals, using the powdered sample  $\text{SiO}_2$  results, vary approximately between 95% and 107%.

From the data given in Table 1, and the confirmation by totaling to 100%, 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.

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 of uniform size--unfortunately, this was not checked.

#### Precision and Accuracy

Mercy (1956) presents an extensive discussion on the precision and accuracy of the rapid silicate method of analysis.

However, the procedures for Al, total Fe, Ti, Ca, and Mg have been changed since his work. Phinney (1959), Brownlow (1959) and Moore (1960) discuss the precision and accuracy found in routine analysis in the M.I.T. rapid silicate laboratory.

As most of the values reported in this paper are the mean of replicate determinations, an estimate of the precision is possible from the tektite data. In addition, the rock standard G-1 and W-1 (Fairbairn et al, 1953) were interspersed with the samples during the analyses to monitor the results, so an estimate of the accuracy may be obtained.

The standard deviation of the mean ( $\bar{c}$ ) is the most important statistic as all results, except some of the aluminum results obtained by X-ray fluorescence, are the mean of replicate analyses. The replicate tektite results, together with the analyses of G-1 and W-1, suggest that the average precision ( $\bar{c}$ ) of the rapid silicate data is approximately: SiO<sub>2</sub>, 0.2%; Al<sub>2</sub>O<sub>3</sub>, 1.4%; TiO<sub>2</sub>, 1.5%; total Fe, 0.5%; MgO, 1%; CaO, 1%; Na<sub>2</sub>O, 1%; K<sub>2</sub>O, 1%; and MnO, 2%. These values agree in general with those given by Mercy (1956, p. 168). The precision ( $\bar{c}$ ) of the photometric FeO determinations is approximately 2%, the SiO<sub>2</sub> X-ray fluorescence determinations 0.5%, and the Al<sub>2</sub>O<sub>3</sub> X-ray fluorescence determinations 1% or less.

The results of replicate analyses of G-1 and W-1 are given in Table 2. The columns labeled A, B, C, etc. represent different weighings, while the numbers in parentheses are the number of determinations that were made of the sample. The averages were calculated from the values given in columns A,

**Table 2 Analyses of G-1 and W-1**

(See Table 17, Part II, p 112)



B, C, etc., weighing each value by the number of determinations that were made of that solution. The accepted values ( $\bar{x}$ ) for G-1 and W-1, and the "acceptable range" ( $\bar{x} - S, \bar{x} + S$ ) are from Stevens (1960, p. 32). The only results that are outside the "acceptable range" are CaO in G-1 and SiO<sub>2</sub> in W-1. The high results for Na<sub>2</sub>O in both G-1 and W-1 (although they are both within the "acceptable range") are in excellent agreement with flame photometric determinations listed by Steven (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 all the analyses total close to 100%. The data in Tables 2 and 3, therefore, indicate that the accuracy of this work is acceptable.

## Results

The results of the chemical analyses are given in Table 3. Included are partial or complete analyses of 37 tektites and 2 "americanites." The specific gravity and total iron contents are also listed. The index of refraction is given for a few of the tektites.

A description of these samples can be found in Schnetzler (1961).

**Table 3 Analytical Results**

(See Table 19, Part II, page 117)

The columns labeled A and B in all but three cases represent duplicate weighings of the sample, and, as discussed above, for most of the constituents the result in each column is the average of duplicate analyses. Insufficient amounts of samples T4102, T4104, and T3310 were available to allow duplicate weighings; therefore the columns A and B in these three cases are duplicate analyses from only one weighing.

The results obtained by X-ray fluorescence are designated by an asterisk--all results not so designated were obtained by rapid silicate techniques. In most X-ray fluorescence  $\text{SiO}_2$  determinations, three independent measurements were made and all three are given in the table. If both rapid silicate and X-ray fluorescence determinations were made on a sample the rapid silicate results are given in Table 3. A comparison of the results obtained by the two methods in these samples is given in Table 1.

### Discussion

The average compositions for the various tektite localities calculated from the samples analyzed in this work are presented in Table 4 along with the averages calculated from the analyses compiled by Barnes (1940). In this table n is the number of samples from which the averages were computed except for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  where the number is given in parentheses.

As the sampling of the philippinites reported in this

**Table 4 Average Compositions of the Various Groups of  
Tektites**

(See Table 20, Part II, page 135)

paper is more extensive than that in Barnes it is felt the new average for this group is more representative of their composition. The differences between the old and new data are attributed to the small number of samples previously analyzed. Twenty-four indochinites had previously been analyzed, however, and it can be seen in Table 4 that the new and old averages are in close agreement for many of the constituents. The most notable exceptions are  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MgO}$ , and  $\text{CaO}$ .  $\text{Fe}_2\text{O}_3$  was reported in only 5 of the 24 indochinite analyses compiled by Barnes. Whether this constituent was not determined or not detected in the other 19 samples is not stated, but as it is usually determined by the difference between total iron and  $\text{FeO}$ , and as it is very difficult to prevent a small percent of the  $\text{Fe}^{+2}$  from oxidizing to  $\text{Fe}^{+3}$  during digestion of the sample, a small amount of  $\text{Fe}_2\text{O}_3$  usually appears in any rock analysis. Thus it is assumed the  $\text{Fe}_2\text{O}_3$  content was determined in only 5 samples and the discrepancy is not surprising considering the limited number of samples reported and the poor precision of the method at these low levels of concentration. As the total iron averages of the old and new data are very similar, the discrepancy between the  $\text{FeO}$  results is also explained if the analyst of the samples reported by Barnes assumed all the iron was in the +2 oxidation state rather than determining both  $\text{FeO}$  and total iron.

However, the  $\text{MgO}$  and  $\text{CaO}$  averages for the indochinites reported in this paper are distinctly different from the

averages from 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 of 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. In fact, the difference of CaO content between the philippinites and indochinites was not noticed until after all the analyses had been completed. Evidence that the CaO (and MgO) values reported here are not in error are: 1) the CaO values for the philippinites and australites 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, 1961), which has a close 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 data for 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.

It can be seen from the data in Table 3 that there appears to be some variation in the composition of the tektites, both between groups and within groups. It should now be determined whether this variation is real or merely analytical error. Table 5 compares the scatter of results, expressed as the relative deviation (c), of the philippinites and indochinites listed in Table 3 with the analytical precision as estimated from the data. The rubidium and strontium values are from Schnetzler (1961, Table 8).

In Table 5 it can be seen that  $Al_2O_3$ , MgO, CaO,  $Na_2O$ , and MnO exhibit a significantly greater variation in the philippinites than can be accounted for by purely analytical error, while all the major constituents in the indochinites exhibit a greater scatter of results than the estimate of analytical precision. The scatter of rubidium and strontium results in both the philippinites and indochinites is also greater than predicted from just analytical error. Thus, it appears there are real differences in composition within the

**Table 5 Comparison of Scatter of Analytical Results and Analytical Precision**

(See Table 22, Part II, page 140)



philippinite and indochinite groups. Taylor (1960) found the same order of magnitude of variation in the alkali elements in 14 australites. He found a relative deviation of 12.6% in Na, 7.6% in K, and 12.1% in Rb. The larger deviations than found here, particularly in the case of Rb, are probably due in part to the greater deviations in his analytical methods, viz. the emission spectrograph as compared to the mass spectrometer.

The first 6 samples (T3959 through T3965) listed in Table 3 are from one site in the Philippine Islands--the Santa Mesa site in Rizal Province. The next 7 samples (T3379 through T3984) come from another site--the Pugad-Babuy site in Bulacan Province. Both of these sites are on Luzon Island near Manila. Therefore, the opportunity exists to test if variations exist 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 3, and are shown in Table 6. By comparison of the relative deviation (c) values of this table with values estimated for the analytical procedures given in Table 5, 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,  $Al_2O_3$ , MgO, CaO, and  $Na_2O$  in the Santa Mesa samples, and CaO,  $Na_2O$ , and MnO in the Pugad-Babuy samples exhibit significantly greater variation than just analytical

**Table 6 Average Compositions of the Samples from the Santa Mesa site and Pugad-Babuy site, P.I.**

(See Table 23, Part II, page 142)

error. Thus the data suggest there are real differences in compositions, not only within a given locality such as Indo-China, but also within restricted tektite sites, although the average compositions of tektites from different groups may be identical.

Next to be considered is, does the data suggest the philippinites and indochinites are significantly different in composition to be considered two independent populations? According to the Null Hypothesis (Moroney, 1956), 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 indochinite and philippinite data it is found that five of the constituents exhibit differences that are definitely significant. The difference 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 does not suggest any significant differences in composition.

If the same test is applied to the data in Table 6 for the two sites in the Philippine Islands it is found that only 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 data suggest there is a real difference in the mean composition of the indochinites and philippinites analyzed, but no significant difference is demonstrated between the tektites from the Santa Mesa and Pugad-Babuy sites, although Beyer (1955) states that the samples from the two different sites have quite distinct differences in physical appearance.

Taylor (1960) 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 exhibit a uniform change of approximately 20%. Cohen (personal communication) believes this uniform change in composition supports his theory that the Pacific Ocean area tektites were formed by the impact of a large meteorite somewhere in China. The tektites represent the fused terrestrial material that was thrown high into the atmosphere and across southeast Asia and Australia, the alkali elements being selectively volatilized during their passage through the

atmosphere. Baker and Forester (1943, p. 399), assuming there was such a chemical change from their specific gravity determinations, suggest that the tektites were ablated from a meteorite which passed from west to east across Australia. Whatever the cause of this uniform change in chemical composition of the tektites across Australia, it is apparent from the data in Tables 3 and 4 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 does not indicate any selective volatilization of elements during passage of a parent body 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, Ca and Sr, would not be expected to be selectively volatilized without much greater volatilization of many of the other elements, e.g. the alkalis. 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.

Thus it is concluded that selective volatilization is not the cause of the differences observed between philippinites and indochinites. They might be completely independent groups, from completely different source materials, in which case their similarities would be just as difficult to explain. Considering these similarities (for example, 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?).

Several interesting features can be seen from the data in Table 3 that, although not entirely original with this work, confirm the observations of earlier investigators. One is that the Fe and Mg contents of the indochinites exhibit a much greater range than in the philippinites, but there appears to be no directional trend to the variation, in contrast to chromium and nickel which are present in much greater concentration in the southern than in the northern indochinites (Preuss, 1935; Ehmann, 1960). Ehmann feels these large differences in Cr and Ni are strong evidence that the indochinites represent two separate occurrences. The major elements reported here, however, do not indicate any grouping into two separate populations.

Taylor et al (1961) pointed out the inverse relationship between SiO<sub>2</sub> 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 3. 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 "americanites", T3967 and T3996 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.

Table 7 is a summary of the chemical analyses of North American tektites, taken from both the literature and this work. The first column is the analysis of sample T4091 from Martha's Vineyard, Massachusetts given in Table 3, and also in a paper by Kaye et al (1961). The second column is another analysis of the same sample by Clarke and Carron (1961). The excellent agreement between these two independent analyses is considered confirmation of the accuracy of the work. The Georgia sample listed on the third column was analyzed by Clarke and Carron (1961). This sample, U.S. National Museum no. 1396, has been analyzed for rubidium and strontium and strontium isotopes (Schnetzler, 1961), K-Ar age (Reynold, 1960), trace elements (Cohen, 1959; Clarke and Carron, 1961), magnetic susceptibility (Senftle and Thorpe, 1959), and absorption spectra

**Table 7 Chemical Compositions of Martha's Vineyard, Georgia  
and Texas tektites**

(See Table 24, Part II, page 148)



(Stair, 1955; 1956). A photograph of this sample is shown by Bruce (1959).

Barnes (1940) reported the analyses of two bediasites from Grimes County, and the average is given in the last column of Table 7. After 1940, tektites were found approximately 75 to 125 miles southwest of Grimes County in Fayette, Lee, and Gonzales counties, and an analysis of a sample from this newer area is given by Barnes (1956). This analysis is given in the fourth column of Table 7. Barnes (1960) suggests the two sites, considering their different compositions as indicated in columns 4 and 6, represent two separate showers. He also states the similarity in physical appearance between the Fayette County and Georgia samples suggest they could have come from the same shower. Clarke and Carron (1961), comparing the Martha's Vineyard and Georgia samples suggest that an artificial origin may explain their remarkable similarity. They believe the Grimes County samples are from an extensive and bonafide tektite strewn field, but that the Fayette and Gonzales County glasses cannot be considered true bediasites, and may also be of artificial origin (personal communication).

A tektite from Grimes County, T<sub>4</sub>106, was partially analyzed during this investigation and the results are given in the fifth column of Table 7. It can be seen that most of the constituents resemble the Fayette County sample more closely than the previously analyzed Grimes County samples. The MgO, and especially the CaO, contents are strikingly different from

the two older Grimes County analyses. T4106 appears closer to the older Grimes County analyses than to the Fayette County analysis only in total iron and  $TiO_2$ . This data suggest several possibilities. One, the MgO and CaO analyses of the two Grimes County bediasites in Barnes may be incorrect---perhaps due to incomplete precipitation of calcium, so that the bulk of the calcium was included in the MgO determination. The combined CaO and MgO values of all the Grimes and Fayette County samples are similar. A second possibility is that the two types of bediasites are not physically separated, as suggested by Barnes (1960), but intermixed, as T4106, which most closely resembles the Fayette County sample, was found in Grimes County. Or it may be that there are not two completely separate compositional types but a gradation over a wide range of composition. Many more samples from Texas need to be analyzed to determine the true chemical nature of this field. Mr. Sumner Wolfson of Boston University, who collected T4106, was quite emphatic that it came from Grimes County.

In any event, it appears that the Martha's Vineyard tektite, Georgia tektite, and at least some of the Texas samples are remarkably similar in composition. An artificial origin, suggested by Clarke and Carron (1961), is not supported because: 1) the Texas field, which appears to have samples quite similar in composition to the other two areas, is a large field and the similarities of the samples in this field with those of other recognized fields has been well documented (Barnes, 1940; 1960);

2) it is difficult to believe sufficient amounts of argon would be retained during recent melting to give K-Ar ages of 32 and 29 million years as given by the Georgia and Texas samples respectively (Reynolds, 1960); 3) the chemical composition is much different from normal man-made glass, and has an extremely high melting temperature; and 4) the similarity in composition seems even more strange if the objects are man-made, for it seems quite coincidental that three separate glass-makers would choose such similar, and odd ingredients.

It should be emphasized that the Martha's Vineyard sample is a single find and this area should not be considered a tektite locality until more are found. However, it is suggested that the most logical explanation of the similarities found in the North American samples analyzed to date is that they are part of the same shower. Confirmation of this awaits the discovery of more samples and additional analyses.

Although the 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. However, the small chemical variations that exist in tektites from a particular locality, the similarities between localities, and the type and degree of the differences that exist between localities, exhibited by the philippinites and indochinites analyzed in this investigation, are difficult to ascribe to a terrestrial origin.

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**Part II**

**(Complete description of thesis investigation)**



SECTION I  
INTRODUCTION

Interest in tektites has increased tremendously in the past few years; however, despite the growing volume of literature on the subject, the origin of tektites is still quite uncertain.

A short resume on tektites is given in this section, but no attempt has been made to present a complete summary of the papers concerning tektites that have appeared since they were first discovered 175 years ago. Comprehensive summaries, with extensive bibliographies, may be found in papers by Suess (1900), Barnes (1940) and Baker (1959). In addition Volume 14, Number 4, 1958, of *Geochemica et Cosmochemica Acta* contains a number of papers presented at a conference on tektites held under the auspices of the U. S. National Academy of Science.

Tektites are small glassy bodies which are found by the thousands in certain large areas of the world. They contain no crystals and many have regular shapes, such as spheres, disks, pears, rods, dumbbells, etc. They usually have a black to green highly vitreous appearance and thin chips exhibit a light green to brownish green tint. They vary in weight from less than a gram to several kilograms. (Lacroix, 1935)

Tektites occur in "strewn fields" which vary from several tens of square miles to sub-continental in area. Tektites are found in southern Australia, in varying degrees of concentration, over an area of 2,000,000 square miles, while none are found in

northern Australia. Each large group of tektites is usually given a local name; thus the accepted strewn fields, and the common name for the tektites of each, are, in Czechoslovakia (moldavites); Australia and neighboring islands to the south (australites); the islands of Borneo and Billiton, and the Malay Peninsula (billitonites); Indo-China, south China, and Siam (indochinites); the Philippine Islands (rizalites or philippinites); Texas (bediasites); Java (javanites); the Ivory Coast (no special name) and Georgia (no special name). A tektite was recently found in Massachusetts (Kaye et al, 1961) but until other tektites are found in the vicinity this area cannot be considered a tektite site. Beyer (1955) estimated that approximately 650,000 tektites have been collected from these localities, distributed thusly-- australites 40,000, bediasites 2000, billitonites 7500, indochinites 40,000, Ivory Coast tektites 200, javanites 7000, moldavites 5500, philippinites 500,000. Probably no more than 20 samples have been recovered from the Georgia site (Bruce, 1959).

Besides these groups of tektites there are other glassy objects that are considered tektites by some investigators. These include Darwin glass from Tasmania, which are highly vesicular and have no regular shape (Spencer, 1939); Lybian Desert glass, which is radically different in composition from any tektite, being almost pure silica (Spencer 1939); and the "americanites" from Peru and Columbia, which have small crystals (Martin and Koomans, 1955) and much more water than any tektites (Friedman, 1958). Other types of glassy objects that have been related to tektites

by some investigators (for example, Spencer, 1939, and Cohen, 1961) are the "impactites." These objects are found associated with meteorite craters in many parts of the world and are obviously formed by fusion of the terrestrial material upon impact by the meteorite (Nininger, 1952). They commonly exhibit incomplete fusion and do not have any regular shape. They also contain small spherules of nickel-iron. Tektites, however, are not found in close association with any known crater and no transitional forms between tektites and impactites have been reported.

Tektites seem to have no relation to the formations in which they occur. They are found upon, and occasionally in, superficial deposits which range in age from Tertiary to Recent. These deposits overlie rocks of very diverse character--igneous, metamorphic, and sedimentary, both acid and basic, and of almost every age from pre-Cambrian to Recent (Baker, 1959).

Beyer (1942) gives the following ages for the various groups of tektites, based upon geological evidence: Ivory Coast, late Mesozoic; bediasites, Eocene; moldavites, Middle Miocene; indochinites, billitonites, javanites, and philippinites, Middle Pleistocene; australites, Recent. Reynolds (1960) K-Ar dates supported these ages except for the australites. The ages he reported were: bediasites and Georgia tektites approximately 30 m.y., moldavites approximately 13 m.y., and all the Pacific Ocean tektites about  $0.5 \pm 0.2$  m.y.

Ehmann and Kohman (1958) measured the content of the cosmic ray produced nuclides  $Al^{26}$  and  $Be^{10}$  in tektites and

concluded they must have spent at least one million years in space. However the measurements were border line, and Anders (1960), using more sensitive instrumentation, was unable to confirm the results.

Tektites from all parts of the world are remarkably similar in chemical composition. They contain at least 65% silica, but usually have high iron, calcium, and magnesium, and low potassium and sodium in comparison to known terrestrial glasses of similar silica content. Friedman (1958) found the water content of tektites to be between 20 and 100 parts per million, much lower than any terrestrial rock.

The outer surfaces of tektites are marked to varying degrees with pits and grooves which have been interpreted by some (for example Oswald, from O'Keefe, p. 6, 1960) as the result of motion through the atmosphere and by others (for example Merrill, 1911) as the result of the etching action of soil acids. However, extensive studies on the shapes of tektites by Fenner (1938) and Baker (1959) indicate all the shapes can be explained as a sequence of forms characteristic of a fluid body in rapid rotation. In addition many australites and a few indochinites and javanites exhibit a second period of melting which is interpreted as due to ablation during motion through the atmosphere (Barnes, 1960).

The interiors of the tektites exhibit flow structures, strain, lechaeturite particles, and small bubbles (Barnes, 1960). Suess (1951) found the pressure inside these bubbles to be less than  $10^{-3}$  atmosphere making the designation "voids" more appropriate than "bubbles."

Many different theories have been formulated to account for the origin of tektites and they can be classified into two categories, one, assigning a terrestrial, and the other an extra-terrestrial origin. Most early investigators believed them to be a special form of obsidian (Dunn, 1935; Merrill, 1911), although they are often found far from any evidence of volcanism. Other early theories advanced included proposals that they were man-made (Hillebrand, 1910), concretions (Jensen, 1915), dehydrated silicate gellmasses (Easton, 1921) etc. These theories have been abandoned by almost all students of tektites.

Late in the 19th century several investigators proposed an extraterrestrial origin for tektites, the first being Verbeek's (1897) proposing that the billitonites were ejected from volcanoes on the moon. Suess (1900), on the basis of their surface markings and dissimilarity to terrestrial glasses, proposed that the three types of tektites known at that time were forms of glass meteorites. A modification of this theory is that tektites are the residual incombustible siliceous contents of combustible metallic meteorites that burned as they fell through the atmosphere (Fenner, 1938). Stair (1956) and Cassidy (1956) considered that tektites could have originated at the disruption of a planet similar to the Earth.

Nininger (1943), reflecting upon the craters on the Moon and the lengths of the rays emanating from these craters, proposed that tektites were knocked off the Moon by meteorite impacts. Varsavsky (1958) has calculated that possible trajectories

exist by which lunar material can be focused to restricted portions of the earth. O'Keefe (1960) noted that a reported fall near Igast, Esthonia had a chemical composition similar to tektites, and he suggested that tektites are ablated from similar meteorites as they come into the earths atmosphere in near satellite orbits. An orbit nearly horizontal with the earths surface allows the spread of tektites over great distances and allows deep melting to form the flanges observed in some tektites. He stated that the reflecting properties of lunar rays, the polarization of light from the Moon's surface, and the radar reflectivity of the Moon are best explained if the Moon's surface has a composition similar to tektites and the Igast object.

Suess (1951) proposed that tektites may be fragments of the head of a comet that was outgassed and fused by passage close to the sun.

Because of the peculiar distribution and chemical compositions exhibited by tektites, any terrestrial theory of origin postulates some sort of catastrophic event. The first serious challenge to the extra-terrestrial theories was proposed by Spencer's (1933) meteorite splash theory. He suggested that tektites were composed of terrestrial material which had been fused by meteorite impacts upon the Earth. Barnes (1940), reviving an early theory by Rutley (1885), proposed that tektites may be formed by lightning striking sedimentary rocks--that is, they are a form of fulgarite. Recently Hawkins (1960) has supported this theory.

In an attempt to explain the widespread distribution of apparently related tektites, and their chemical similarity to certain terrestrial material, Urey (1957) suggested that collisions of comets with the Earth would result in the fusion of large volumes of materials and this debris would be scattered over large areas. He pointed out that tektites could not have passed through space in a cluster, because a cluster of the density necessary to produce the observed distribution of australites would be unstable and would be torn apart by the Sun's gravitational attraction in a short time. A cluster of density sufficient for gravitational stability would pile up australites to a depth of  $100\text{gms/cm}^2$ . The explosion of the comet would occur high in the atmosphere and would fuse material over a wide area but probably produce only a small depression.

Cohen (1961) has also theorized that tektites were formed by a gigantic impact, but he believes the mechanism was the impact of giant meteorites or asteroids. He points to the 17 mile wide Ries Kessel crater as the point of impact that produced the moldavites, which extend from 150 to 400 miles east of the crater. The presence of coesite at this crater suggests that it is of meteoritic origin (Shoemaker and Chao, 1960). Cohen believes the chemical compositions and shapes of the moldavites vary from west to east in a manner consistent with his theory. He has associated the Ivory Coast tektites with the Bosumtvi crater in Ghana, and suggests there should be an immense crater in China which produced all the tektites in the Pacific Ocean area.

In summary, the majority of present day investigators believe the mechanism and materials are available to produce tektites on the Earth (Krinov, 1958; Rinehart, 1958; Friedman, 1958; Barnes, 1958; Hawkins, 1960; Urey, 1957, 1959; Cherry, Taylor, and Sachs, 1960; Cherry and Taylor, 1961; Taylor, 1960; Cohen, 1960, 1961; Tilton, 1958). However, other current investigators believe the similar compositions of tektites, and their widespread distribution suggest an extraterrestrial origin (Pinson, 1958; O'Keefe, 1960; Cassidy, 1956, 1958; Varsofsky, 1958; Chapman, 1960; Baker, 1959, 1960; Lowman, 1960), and some of these investigators believe the evidence points toward the Moon as the most probable source.

The following sections discuss two different studies of tektites. It was felt the strontium isotopic composition of tektites might suggest possible parent materials, and the variation of isotopic composition, compared to the variation observed in terrestrial materials, should test the feasibility of their being derived from pre-existing terrestrial rocks. This study is described in Section II. A study of the chemical composition of tektites is given in Section III. It was felt the variation in chemical composition between individual tektites, and between groups of tektites, could not be accurately determined from the published analyses, as these analyses are the work of many analysts of different skills using different methods, and in some cases only a few analyses of tektites from a given site have been reported. For example, only four



philippinites have been analyzed although approximately 500,000 have been collected. As the degree of uniformity of composition is an important factor that must be considered in any theory of origin, it was felt this uniformity should be investigated further.

SECTION II  
RUBIDIUM AND STRONTIUM CONTENTS, AND STRONTIUM  
ISOTOPIC COMPOSITION OF TEKTITES

A. Introduction

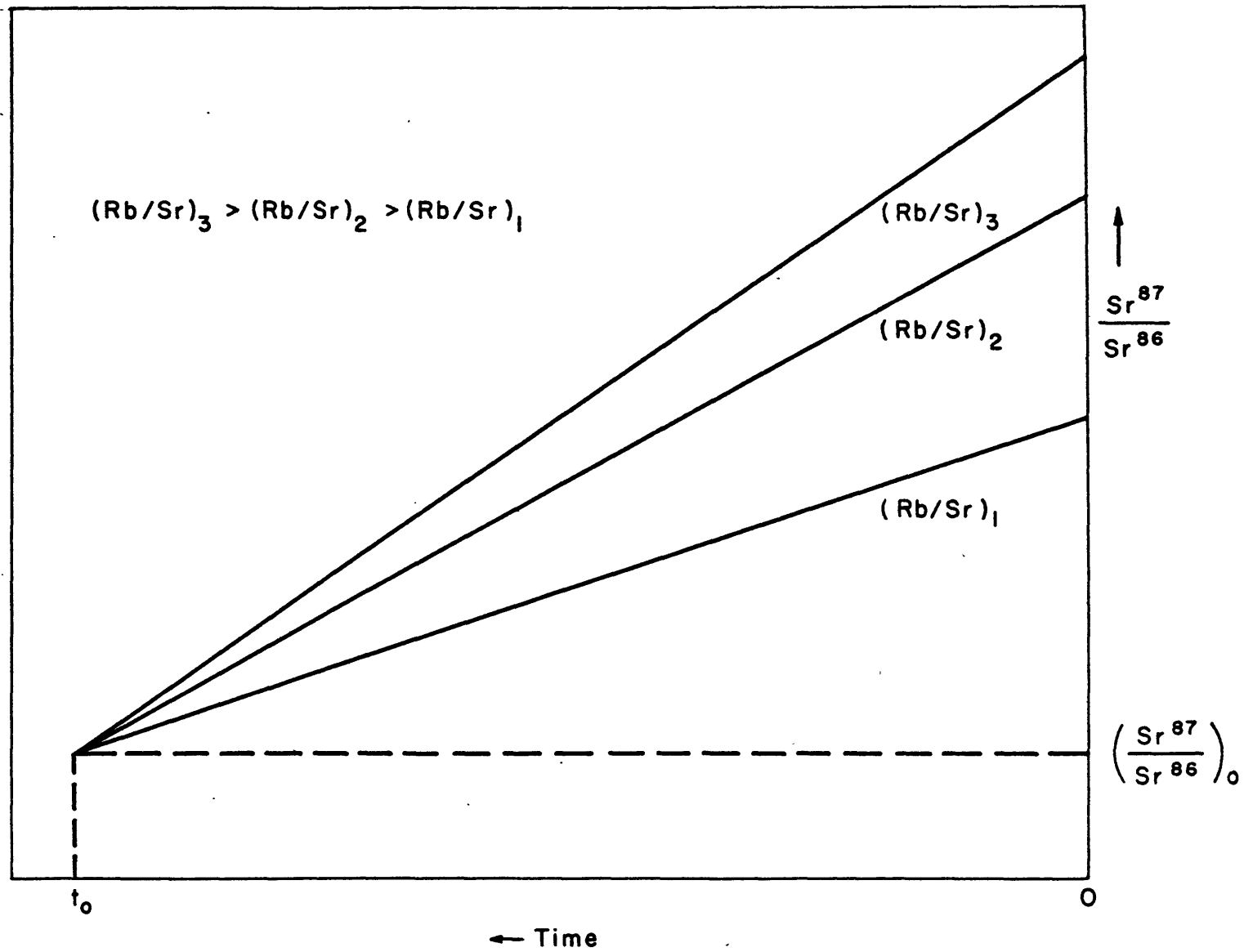
There are four natural isotopes of strontium--Sr<sup>84</sup>, Sr<sup>86</sup>, Sr<sup>87</sup>, and Sr<sup>88</sup>. The isotopes of mass 84, 86, and 88 are non-radiogenic (that is, they are not formed by the decay of another isotope) and non-radioactive. However the strontium isotope of mass 87 is formed by the decay of the rubidium isotope of mass 87. Thus the radiogenic Sr<sup>87</sup> content, conveniently expressed as the Sr<sup>87</sup>/Sr<sup>86</sup> ratio, increases with time in a closed system containing rubidium. The relative isotopic abundance of Sr<sup>87</sup> in a given system is determined by 1) the Rb/Sr ratio of the system, 2) the isotopic abundance at an initial time, and 3) the time elapsed since this initial time.

These quantities can be related by the following equation, which is derived in Appendix B:

$$(Sr^{87}/Sr^{86})_p = (Sr^{87}/Sr^{86})_o + 4.256 \times 10^{-2} \cdot (Rb/Sr)t$$

where  $(Sr^{87}/Sr^{86})_p$  is the ratio at the present time,  $(Sr^{87}/Sr^{86})_o$  is the ratio at some initial time, Rb/Sr is the elemental weight ratio, and t is the time, in billions of years, from the initial time to present.

If  $(Sr^{87}/Sr^{86})_p$  is plotted versus time on Cartesian coordinate graph paper this equation describes a family of straight lines which have slopes determined by the Rb/Sr ratios and which intersect at the initial Sr<sup>87</sup>/Sr<sup>86</sup> ratio,  $(Sr^{87}/Sr^{86})_o$ , when t=0. (Figure 1).



II

FIG. 1 INCREASE IN THE  $Sr^{87}/Sr^{86}$  RATIO WITH TIME AND INCREASING Rb/Sr RATIO

Pinson et al (1956) reported the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of a philippinite as  $0.731 \pm 0.003$ . At that time they suggested that the relative strontium isotopic composition of tektites from all known localities should be measured; if the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios are identical in correspondence to their Rb/Sr ratios this would prove their extra-terrestrial 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 contents and the strontium isotopic compositions of three indochinites, two australites, and two philippinites. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios for these seven tektites ranged from 0.718 to 0.735, averaging 0.724. The Rb/Sr ratios varied from 0.39 to 1.08, but there was no apparent sympathetic variation between the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios and the Rb/Sr ratios. The computed ages, assuming an initial ratio of 0.712 varied from 180 to 730 m.y., with estimated errors of  $\pm 50\%$ .

The value of 0.712 is often assumed in age dating for the initial ratio because this is the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio found in sea water by several investigators (Pinson et al, 1957b; Gast, 1960) and it is assumed this ratio is representative of the crust of the earth. If the material under investigation has a high  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio relative to 0.712 this assumption is usually satisfactory, but when the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is nearly equal to 0.712, as it is in tektites, a knowledge of the true initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is necessary if the age is to have any

meaning. Strontium that has a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.712 is often called "normal" strontium.

In 1958 Pinson et al reported that the  $\text{Sr}^{87}/\text{Sr}^{86}$  measurements discussed above were in error and the corrected values should be about 0.712, the same ratio as "normal" strontium. They reported a correction had to be made to compensate for insufficient resolution in the mass spectrometer which caused the "tail" of the large 88 peak to enhance the 87 peak. Since the corrected ratios were "normal" Pinson et al stated the tektites did not contain radiogenic strontium and had essentially a zero age. The authors stated, however, concerning the initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, "since we do not know the source material from which the tektites were derived it is speculative and arbitrary to select a value."

It is apparent from the research of Pinson and co-workers that the tektites are not favorable samples for age determinations. They do not have high Rb/Sr ratios and they apparently have young ages--thus they have low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, making an accurate knowledge of the initial  $\text{Sr}^{87}/\text{Sr}^{86}$  necessary. However, in view of the questionable validity of the correction that was applied and in view of the improvement in mass spectrometric techniques, it was thought a re-investigation of the strontium isotopic composition of tektites might prove fruitful. The variation of isotopic composition compared to possible parent materials would be particularly instructive. As the strontium isotopic composition is directly related to

the Rb/Sr ratio as well as the age, the elemental rubidium and strontium contents were also investigated.

## B. Analytical Techniques

### 1. Introduction

Rubidium and strontium were determined by the stable isotope dilution method and by X-ray fluorescence. The strontium isotopic compositions were determined mass spectrometrically on "raw" (unspiked) strontium extracted from the tektites.

The techniques used for the isotope dilution and isotope composition determinations have been described in the Annual Progress Reports of the M.I.T. Geochronology Laboratory and in the literature (Faure, 1961, p. 145-184; Hart, 1960, p. 182-192; Pinson, 1960; Herzog and Pinson, 1956). A general discussion of the stable isotope dilution method plus an extensive bibliography is given by Webster (1960). Briefly this method involves the use of a spike, a solution of the analysis element whose isotopic composition has been radically changed and is accurately known. A known amount of this spike is added to a known amount of sample and the isotopic composition of this mixture is determined on a mass spectrometer. From the measured isotopic ratio the amount of the element in the sample can be determined. This method is especially attractive because, once the spike and sample have been mixed, quantitative recovery of the mixture is not necessary.

In tektites, and samples with Rb/Sr ratios less than about 1, the enrichment of  $\text{Sr}^{37}$  will be quite small, and, in general, it is unsatisfactory to determine the isotopic composition from the spiked sample. The greatest accuracy in the

determination of  $\text{Sr}^{97}$  enrichment is obtained from unspiked strontium because the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is independent of spike calibration and pipetting errors. Thus the strontium isotopic composition and the elemental contents were determined on separate fractions of the sample.

Another portion of the powdered sample was used in the X-ray fluorescence rubidium and strontium determinations. In this analytical method the sample is irradiated with a beam of X-rays which cause the ejection of electrons from the inner shells of the atoms in the specimen. Electrons from the outer orbits may return to the vacant orbit and X-rays (called fluorescent X-rays) of wavelength characteristic of each element will be produced. A general discussion of X-ray fluorescence analytical techniques is given by Shalgosky (1960).

## 2. Materials and Equipment

Purity of Reagents: Demineralized water was used throughout these procedures. It was obtained by passing distilled water through a Barnstead Bantam demineralizer column. The ammonium hydroxide, hydrochloric acid and nitric acid used were distilled in a vycor still. The hydrofluoric acid and ammonium oxalate were analytical reagent grade.

Ion-exchange columns: The ion-exchange resins used were manufactured by the Dow Chemical Company, Midland, Michigan. The resin was Dowex 50, 8% cross-linked, 200-400 mesh hydrogen ion, cation exchange resin. This resin approximately half filled a 1" x 20" vycor column, and was supported in the column



by a small "wad" of vycor glass wool in the tip. The columns were washed with two column volumes of distilled 6N HCl and two column volumes of distilled 2N HCl between samples.

Sr<sup>85</sup> tracer: Sr<sup>85</sup> tracer was prepared by irradiating RbCl with 15 Mev deuterons in the M.I.T. Cyclotron. Sr<sup>85</sup> is produced by the reaction  $\text{Rb}^{85}(\text{d}, 2\text{n}) \text{Sr}^{85}$ , and has a half life of 65 days.

Approximately 0.8 grams of RbCl were packed in a small aluminum foil envelope. After a one hour irradiation, and a cooling period of several days, the envelope was opened in a fume hood in a beaker containing a small amount of water to reduce the possibility of the powder being blown into the air. HCl was added until the normality of the solution was approximately 2. The dissolved sample was then put on a cation exchange column and eluted with 2N HCl. As radioactive Rb<sup>86</sup> is also produced ( $\text{Rb}^{85}(\text{d}, \text{p}) \text{Rb}^{86}$ ) the progress of both the rubidium and strontium fractions in the column can be followed by monitoring their activities with a Geiger counter. The strontium fraction was collected, dried, redissolved in 2N HCl and put through the column again. The strontium fraction was again collected, diluted with 2N HCl to approximately 500 ml and stored in a polyethylene bottle. The preceding work was done in a fume hood with sufficient lead brick shield to protect the analyst. Less than five milliliters of this tracer per sample was necessary to give a clear indication on the Geiger

counter. This much tracer did not give detectable quantities of rubidium or strontium in the mass spectrometer.

Sr<sup>84</sup>, Sr<sup>86</sup>, and Rb<sup>87</sup> spike solutions: Comprehensive discussions of the preparation of the spikes used in the M.I.T. Geochronology Laboratory are given by Pinson (1960, p. 237-244) and Faure (1961, p. 149-165). The preparation of these spikes was the result of the combined efforts of members of the laboratory under the supervision of Professor W. H. Pinson.

The spikes were obtained from the Oak Ridge National Laboratory as salts that were enriched in a particular isotope. The salts were weighed, dissolved, and diluted to a known volume. However, as no guarantee of purity was given by Oak Ridge, it was necessary to calibrate the spikes against rubidium and strontium "shelf" solutions. The shelf solutions contain a known concentration of the element of normal isotopic composition.

The rubidium shelf solution was prepared from RbCl which was purified by passing it through an ion-exchange column. A weighted portion of this purified salt was then diluted to a known volume. After correction for a small potassium impurity the calculated concentration of rubidium was 140.9  $\mu\text{gm/ml}$ . Duplicate gravimetric analyses of this solution were in satisfactory agreement with this calculated value, averaging 142.5  $\mu\text{gm/ml}$ . Strontium carbonate (Eimer and Amend, lot 492327) was used for the strontium shelf solution. The concentration of this solution was 280  $\mu\text{gm Sr/ml}$ .

Triplicate isotope ratio and isotope dilution analyses to determine the rubidium isotopic composition and concentration of the Rb<sup>87</sup> spike gave the following results:

85/87 = .01760, .01789, .01787 averaging  $.01779 \pm .00009$  ( $\bar{\sigma}$ ).

Rb  $\mu\text{gm/ml}$  = 63.49, 64.07, 62.30 averaging  $63.30 \pm 0.52$  ( $\bar{\sigma}$ ).

The isotopic composition was identical, within experimental error, to the Oak Ridge analysis.

Triplicate determinations of the strontium isotopic composition of the Sr<sup>86</sup> spike are given in Table 1.

Table 1. Isotopic Ratio Analyses of the Sr<sup>86</sup> Spike

Date	84/88	86/88	87/88	Scans
6/60	--	12.4168	1.4176	70
7/60	.0074	12.4715	1.4002	72
2/61	.0077	12.3765	1.4002	90
Average	.0076	12.4216	1.4060	
$\bar{\sigma}$	$\pm .0001$	$\pm .0275$	$\pm .0058$	

The strontium concentration in this spike was determined by three independent isotope dilution analyses. The results were 21.54, 21.44 and 21.56  $\mu\text{gm Sr/ml}$ , averaging 21.51  $\mu\text{gm Sr/ml}$ .

The calculated strontium concentration in the Sr<sup>84</sup> spike was 19.8  $\mu\text{gm/ml}$  and an isotope dilution analysis was in very good agreement at 19.74  $\mu\text{gm/ml}$ . The atomic abundances of the isotopes of this spike, calculated from two isotope ratio measurements were 84 = 0.536, 86 = 0.140, 87 = 0.043, and 88 = 0.281.

The  $\text{Sr}^{86}$  spike was used in preference to the  $\text{Sr}^{84}$  spike to reduce the chance of isotope fractionation in the mass spectrometer. However, several samples were double spiked, that is spiked with both the  $\text{Sr}^{84}$  and  $\text{Sr}^{86}$  spikes, and the results based on the  $84/88$  and the  $86/88$  ratios were in good agreement.

Mass Spectrometer: The mass spectrometer used was a standard 6-inch radius,  $60^\circ$ -sector, solid source, single collector Nier type instrument. Amplification of the ion current was obtained by means of a vibrating reed electrometer. A Duo-Seal forepump coupled with a high capacity mercury diffusion pump using a liquid nitrogen cold trap were used to obtain the operating pressures in the range of  $10^{-6}$  to  $10^{-7}$  mm of Hg. The filament was 0.001" x 0.030" tantalum ribbon which was spot welded to posts in the source.

X-ray Fluorescence Unit: The analyses were made on a North American Phillips X-ray fluorescence unit with a tungsten target X-ray tube. The crystal was LiF and the detector was a scintillation counter. The analyses were made in an air atmosphere.

### 3. Rubidium and Strontium Isotope Dilution Procedures

The tektites were first washed with acetone to remove any laquers that may have been used to "preserve" them. They were then cleaned in hot 6N HCl for approximately 15 minutes, washed in demineralized water and dried. Any adhering clay or soil in their pitted surfaces was removed. The samples were

then crushed in a steel percussion mortar and powdered in a tungsten carbide mortar. From 0.2 to 0.8 grams of the dried powder were weighed accurately and transferred to a large platinum dish. Rubidium and strontium spike solutions were then added by pipette in amounts that were estimated to give  $\text{Rb}^{85}/\text{Rb}^{87}$  and  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios close to unity. For tektite analyses this was usually 2 mls of each spike. Approximately 2 mls of 1 + 1  $\text{H}_2\text{SO}_4$  and 20 mls of HF were added and the crucibles were placed on a steam bath. The samples were allowed to digest almost to dryness and then approximately 50 mls of demineralized water were added. This was to assure the complete removal of fluoride ion from the solution. The complete digestion procedure was accomplished in 4 to 5 hours, with occasional stirring of the sample. By this time the sample was in solution and the spike and sample thoroughly mixed so that quantitative recovery was no longer necessary. Approximately 20 mls of distilled 2N HCl was added after the water evaporated the second time. After the salts dissolved, the dish was removed from the steam bath and allowed to cool for several hours. The solution was then filtered and stored in a pyrex beaker (if the sample was to be put on the ion exchange column soon) or a polyethylene bottle (if there was to be a long delay in the procedure).

A few mls of the  $\text{Sr}^{85}$  tracer were added to the solution to enable the detection of the strontium in its progress through the column. The solution was then put on the column with a pipette so as not to disturb the top surface of the resin, which

had previously been leveled. After the solution had soaked into the resin the walls of the column were washed with approximately 20 mls of 2N HCl, again not disturbing the resin. After this, the sample was sufficiently washed down the column so that it was no longer necessary to exercise such care concerning the disturbance of the resin. The column was then eluted with 2N HCl. Fe, Al, Li, Na, K, Rb, Ca, Sr are eluted from the column in that order. The presence of potassium was detected by platinum wire flame test and when it was observed, four or five 20 ml portions were collected in pyrex beakers. The best rubidium fraction will be found in the portion following the last trace of potassium. The position of rubidium in the beakers was often checked on a flame photometer. The beaker which contained the most rubidium was evaporated to dryness and a few drops of  $\text{HNO}_3$  were added. One drop of this  $\text{RbNO}_3$  solution was then taken up in the glass tip of a small syringe and carefully put in the middle of the tantalum wire filament. A small current was then passed through the filament and the sample was dried to a cake. The sample was now ready for the mass spectrometer.

The eluted strontium, detected by the  $\text{Sr}^{85}$  activity, was also collected in 20 ml portions in pyrex beakers and evaporated to dryness. The 2 or 3 beakers with the highest activity were chosen and approximately 5 mls of 2N HCl was used to wash the strontium from these beakers into a 50 ml Vycor dish. This concentrate was then evaporated to dryness, and the resulting  $\text{SrCl}_2$  residue was dissolved in a drop of HCl and approximately 1 ml

of water. A small crystal of ammonium oxalate and several drops of ammonium hydroxide were added. In a few minutes a precipitate of strontium oxalate formed. The supernatant liquid was removed by a syringe with a clean glass capillary tip. The precipitate was washed several times with a few mls of ice-cold water, the solution removed each time by the syringe. This washing removes any soluble rubidium oxalate that may be present. The precipitate was then pulled up into the glass tip of the syringe and carefully placed in the middle of the tantalum wire filament. It was then dried by passing a small current through the filament. When the sample was dry, the current was increased until the filament was red hot (for only an instant) to convert the oxalate to the oxide. The sample was now ready to put in the mass spectrometer.

#### 4. Strontium Isotopic Ratio Chemical Procedures

The chemical procedures for the strontium isotopic ratio determinations were similar to the chemical procedures for the strontium isotope dilution determinations except in a few details. One difference was that the weight of the sample did not have to be determined accurately. Approximately 0.5 to 0.8 grams were usually sufficient for the recovery of 50 or more micrograms of Sr. The second, and most important difference, was that no rubidium or strontium spikes were used; the isotopic ratios were determined on the sample strontium alone with no addition of any foreign strontium, except the  $\text{Sr}^{85}$  tracer. To keep contamination from spike strontium to a minimum several

ion-exchange columns, a set of pyrex beakers, and several vycor dishes were used exclusively for isotope ratio work.

Quantitative recovery of the strontium in this procedure was not necessary. However, as much as possible of the strontium was collected from the ion-exchange column to reduce the effect of any possible isotopic fractionation in the column.

## 5. Mass Spectrometric Techniques

Once the chemical procedures described in the preceding sections were completed the source was re-assembled and put into the mass spectrometer. The pumps were turned on and when the pressure fell to approximately  $2 \times 10^{-5}$  mm Hg the filament temperature was slowly raised. If the run was a rubidium or strontium isotope dilution determination the peaks were immediately located, the ion beam was focused, and the magnetic sweep started. Approximately 40 to 50 sets of peaks (or scans) were recorded on a Brown Electric Strip Chart Recorder for the isotope dilution analyses. As rubidium is ionized off the filament at a much lower temperature than the strontium, no strontium was observed during a rubidium isotope dilution run. However, during the higher temperature strontium isotope dilution runs rubidium was usually observed, especially during the first part of the run. As the strontium isotopes of interest were those of mass 84 and 88 or 86 and 88, depending on which spike was used, the rubidium isotopes, 85 and 87, did not interfere.

If the run was an isotopic ratio determination it was necessary to burn off all the rubidium before strontium peaks



could be recorded, as the Rb<sup>87</sup> peak would enhance the Sr<sup>87</sup> peak. This was accomplished by setting the filament temperature just below the temperature at which strontium emission occurs. The sample was conditioned at this temperature for 2 or 3 hours. In addition to burning off the rubidium this conditioning seemed to improve the quality of the analysis--enabling longer, steadier runs than if the sample had not been conditioned.

This period of conditioning also allowed time for the pressure to fall below  $5 \times 10^{-6}$  mm Hg. It was found that pressures much above this resulted in poor resolution, caused by diffusion of the ion beam due to collisions between the ions and gas molecules in the tube. In particular the tall 88 peak overlaps the smaller 87 peak, giving false Sr<sup>87</sup>/Sr<sup>86</sup> ratios. This enhancement is what Pinson et al (1958) thought had happened during their analyses of tektites and was the reason for their "pressure broadening" correction.

After the conditioning period (the pressure was now about  $1$  or  $2 \times 10^{-6}$  mm Hg) the filament temperature was slowly raised until the strontium emission increased spontaneously. The magnet sweep was then turned on and the sets recorded. The optimum operating condition--that is the condition giving maximum precision and minimum chance of failure--seemed to be obtained when the emission was allowed to grow spontaneously to a peak height of 2 to 6 inches on the 100 millivolt scale (Sr<sup>86</sup> and Sr<sup>87</sup>) and 1000 millivolt scale (Sr<sup>88</sup>) of the vibrating reed electrometer (VRE). Usually the emission leveled off and 80 to 120 scans could be recorded without changing the filament

temperature. Runs made on lower VRE scales had a higher noise to signal ratio, thereby causing more uncertainty in the position of base lines and peak tops.

After a strontium isotope dilution or isotope ratio analysis the filament was cleaned by raising the filament temperature. Cleanliness of the filament was checked by scanning for strontium isotopes at a temperature higher than for a normal run. Using this method of cleaning it was possible to make as many as nine strontium determinations on a single filament, and it was possible to intersperse isotope dilution and isotope ratio runs with no apparent danger of contamination. However this practice was generally avoided. A new filament was employed for each Rb analysis.

## 6. X-ray Fluorescence Techniques

The powdered sample (-200 mesh) was packed into a depression 20 mm in diameter and 3.5 mm deep in a nylon sample holder and the surface was smoothed off. The sample holder was then put into a frame which contained a 0.5 mil mylar window which prevented the powder from falling out of the holder when the sample holder was inverted in the machine. After the sample was 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 analyser: base volts = 41.5, window volts = 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 positions. The calculated counts per second (cps) for the backgrounds were subtracted from the peak intensities to give a net peak intensity. The intensity value obtained for the standard samples were plotted against the ppm strontium, obtained by isotope dilution analyses, to yield a calibration curve (Figure 2). Strontium values for the unknowns were obtained by interpolation from this calibration curve. The rubidium values in the standard were too similar to enable a curve to be drawn, so an average value of counts per second per parts per million 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.

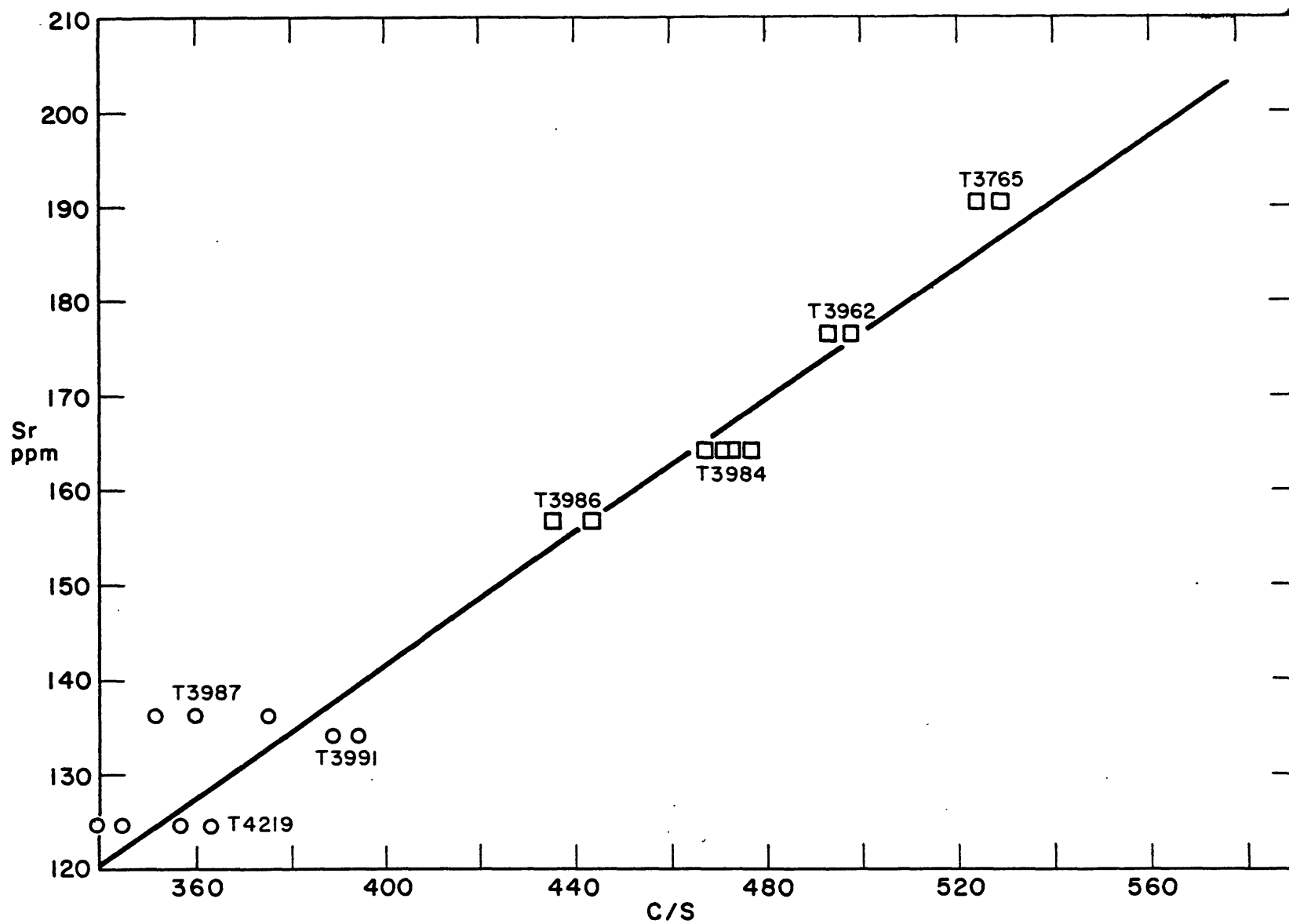


FIG. 2 STRONTIUM X-RAY FLUORESCENCE CALIBRATION CURVE.

### C. Precision and Accuracy

#### 1. Introduction

In this section the precision and accuracy of the elemental and isotopic results will be discussed. The precision of an analytical method contains only the effects of random errors. It is a measure of the reproducibility of the method and does not indicate how near the result is to the true value. The accuracy however also includes the effects of systematic errors, and is a measure of the degree of agreement with the true value. The evaluation of accuracy requires a material of known composition or the use of several distinctly different analytical procedures. It is assumed that several different procedures will not have similar systematic errors and agreement between results from different procedures indicate the systematic errors are negligible.

In other words, the precision is a measure of the performance of an analytical procedure while the accuracy is a measure of the confidence that can be put in the results from that analytical procedure (Youden, 1959, pg. 47).

Precision in this paper will be expressed in terms of the following expressions:

$$\text{Standard deviation (of a single analysis)} \quad \sigma = \sqrt{\frac{\sum d^2}{n-1}}$$

$$\text{Relative deviation (of a single analysis)} \quad C = \frac{\sigma}{\bar{X}} \quad (100)$$

$$\text{Standard deviation of the mean} \quad \bar{\sigma} = \sqrt{\frac{\sum d^2}{n(n-1)}}$$

$$\text{Relative deviation of the mean} \quad \bar{C} = \frac{\bar{\sigma}}{\bar{X}} \quad (100)$$

where  $n$  is the number of determination and  $d$  is the difference between each observation and the average ( $\bar{x}$ ) of all observations. The relative deviation is called the coefficient of variation or percent spread by some authors.

Statistics predict that two-thirds of all observations should fall within one  $\sqrt{}$  of the average and that 95% of all observations within  $2\sqrt{}$  of the average. As Ahrens (1954, p. 39) points out, this is true only if the distribution is normal (i.e. Gaussian). However, he states that if the dispersion is small ( $c < 15\%$ ) a normal distribution may be safely assumed as the general nature of the distribution is of little consequence. In this investigation a normal distribution is assumed as the relative deviations are certainly less than 15%.

## 2. Precision and accuracy of the isotope dilution analyses

The precision, or reproducibility, of the rubidium and strontium isotope dilution analysed was determined by making triplicate analyses of a tektite (T3987). These results are compared in Table 2 with precisions found by other investigators in the M.I.T. Geochronology Laboratory. The same routine procedures were used in all cases. As all the tektites except T3987 were analysed only once by isotope dilution the standard deviation of a single analysis ( $\sqrt{}$ ) is of major interest in evaluating the precision. It can be seen in Table 2 that relative deviations of about 2.5% were obtained for both rubidium and strontium in the tektite. Faure (1960) obtained rubidium relative deviations of about 2% in samples containing about an

Table 2. Replicate Rb and Sr Isotope Dilution Analyses

Sample no.	Rb ppm	Sr ppm
T3987 - Indochinite	117.7	138.0
	123.1	138.2
	118.9	180.9***
	<u>119.9</u>	<u>132.6</u>
Average		136.3
	$\bar{\Delta}$ ± 1.6	± 1.8
	$\Delta$ ± 2.8	± 3.2
	C ± 2.36%	± 2.33%
<hr/>		
*R1292- Olivine Basalt	9.76 Average of 3	398.6
	$\bar{\Delta}$ ± 0.11	± 2.0
	$\Delta$ ± 0.19	± 3.7
	C ± 1.98%	± 0.93%
<hr/>		
*R3111 - Eclogite	6.90 Average of 2	149.0
	$\bar{\Delta}$ ± 0.09	± 0.7
	$\Delta$ ± 0.128	± 0.99
	C ± 1.86%	± 0.665%
<hr/>		
*P3111 - Pyroxene	13.0 Average of 3	261.7
	$\bar{\Delta}$ ± 0.147	± 5.6
	$\Delta$ ± 0.255	± 9.6
	C ± 1.96%	± 3.67%
<hr/>		
*G3111 - Garnet	1.12 Average of 3	19.00
	$\bar{\Delta}$ ± 0.148	± 1.40
	$\Delta$ ± 0.257	± 2.42
	C ± 22.9%	± 12.7%
<hr/>		
**Rb shelf solution	69.3 Average of 3	
	$\bar{\Delta}$ ± 0.32	
	$\Delta$ ± 0.56	
	C ± 0.8%	

\* From Faure(1960),162-163. \*\* From Pinson(1960), 244.

\*\*\* Spiking in doubt. Omitted from average

order of magnitude less rubidium than the tektites; his strontium relative deviations, on samples whose strontium contents were equal to or greater than that in the tektites, ranged from less than 1% to almost 4%. Pinson (1960) stated the relative deviation of 0.8% on the rubidium shelf solution should be considered a minimum value as this sample was not subjected to all the chemical procedures used in the analysis of rock samples. From the evidence given in Table 2, Faure's conclusion (1960, p. 164) that the probable relative deviation for a single analysis is  $\pm 2\%$  for both rubidium and strontium seems valid for this investigation.

Accuracy, which is the degree of agreement between the measured value and the true value, includes systematic errors as well as random errors. A comparison of the value obtained at the M.I.T. Geochronology Laboratory on the rubidium shelf solution shown in Table 2 with the values obtained at two other laboratories is given in Table 3.

Table 3. Interlaboratory Comparison of Rb Isotope Dilution Results

M.I.T.	69.3 $\pm$ 0.6
Carnegie Institute	67.5
(P.Gast)U. of Minn.	<u>68.5</u>
Average	68.4
	$\bar{\sigma}$ $\pm$ 0.5
	$\sigma$ $\pm$ 0.9
	E 1.3%



This data suggests that the accuracy is about 1%. However, as mentioned above, this sample was not subjected to as much chemical processing as a rock sample, and 1% should be considered a minimum value. Also all three of these values were obtained by isotope dilution and would not reveal any systematic error that might be inherent in the general method. As these results were obtained on at least three different mass spectrometers, and using three different spike solutions, the data would suggest there were no systematic errors in the procedure.

Comparison of isotope dilution analyses for rubidium and strontium in G-1 and W-1 to the mean of a number of analyses by such methods as spectrochemical, flame photometry, neutron activation, and X-ray fluorescence (Steven, 1960, pgs. 97 and 99) indicate the accuracy might be about  $\pm 5\%$ . Webster (1960, p. 221) states that an absolute accuracy in the range of 1 to 5% should be possible.

### 3. Precision and accuracy of the strontium isotope ratio analyses

In an attempt to determine the precision of the strontium isotope ratio analyses, two tektites were analysed in triplicate. The results are shown in Table 4.

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 (Nier, 1938). 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

Table 4. Triplicate Isotope Ratio Analyses

Sample no.	Date	87/86	(87/86) corr	86/88	84/88	Scans	E <sub>87/86</sub>
T3987	8/25/60	0.7193	0.7202	0.1197	0.0072	108	0.04%
"	10/25/60	0.7174	0.7189	0.1199	-	88	0.06%
"	12/6/60	0.7221	0.7194	0.1185	0.0066	120	0.05%
Average		0.7196	0.7195	0.1194	0.0069		
	$\bar{v}$	$\pm 0.0014$	0.0004	0.0004			
	$\bar{c}$	$\pm 0.19\%$	0.06%	0.34%			
	$\bar{v}$	$\pm 0.0024$	0.0007	0.0008			
	$\bar{c}$	$\pm 0.33\%$	0.09%	0.64%			
T3990	10/23/60	0.7144	0.7186	0.1208	-	112	0.04%
"	10/31/60	0.7195	0.7174	0.1187	0.0066	108	0.06%
"	11/7/60	0.7161	0.7193	0.1205	0.0067	95	0.06%
Average		0.7167	0.7184	0.1200	0.0066		
	$\bar{v}$	$\pm 0.0016$	0.0006	0.0007			
	$\bar{c}$	$\pm 0.22\%$	0.08%	0.58%			
	$\bar{v}$	$\pm 0.0026$	0.0010	0.0011			
	$\bar{c}$	$\pm 0.36\%$	0.14%	0.94%			

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. This is because the mass difference between  $\text{Sr}^{87}$  and  $\text{Sr}^{86}$  is only half the difference between  $\text{Sr}^{86}$  and  $\text{Sr}^{88}$ .

The formula used for this correction is:

$$\left(\frac{87}{86}\right)_{\text{corr.}} = \left(\frac{87}{86}\right) \cdot \left(\frac{86/88 + .1194}{2(.1194)}\right)$$

It can be seen that in the two samples shown in Table 4 the precisions of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios were improved by about a factor of three by the application of the fractionation correction. This same correction procedure has been applied by other members of the M.I.T. Geochronology Laboratory with approximately the same results. A triplicate strontium isotope ratio determination by Hart (1960, p. 194) showed a relative deviation (c) for the measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.34%. The corrected  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio showed a relative deviation of 0.1%, while the average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio remained essentially unchanged by the correction procedure. Replicate analyses of a basalt by Faure (1961, p. 178) illustrated the same magnitude of improvement--the measure  $\text{Sr}^{87}/\text{Sr}^{86}$  relative deviation was 0.36% while the corrected  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio had a relative deviation of only 0.08%. Finally, replicate analyses of a strontium carbonate (Table 5) shows an improvement of the relative deviation from the average measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio (c = 0.22%) to the

corrected  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio ( $c = 0.12\%$ ) by a factor of about 2, while the average measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is identical to the corrected value. Thus in the five cases of replicate analyses to which this correction, or "normalizing" procedure has been applied by members of the Geochronology Laboratory in the past year, all have shown a marked improvement in the precision of the data without materially changing the value of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio. While the exact nature of the mass fractionation is not completely understood, it is felt the evidence presented above justifies the use of the correction procedure. Although the fractionation has been assumed to occur during the ionization of the isotopes off the filament, it may at least partly occur in the ion-exchange column. The data for the strontium carbonate, which was not passed through the ion-exchange column, indicate slightly less fractionation than the other samples, which were put through the column. However, the differences between the carbonate and other samples in the bulk and purity of the precipitate put on the filament may cause different degrees of fractionation.

It should be noted that the relative deviations (c) shown in Table 4 for the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios are about twice those of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, supporting the assumption made above that the 87/86 ratio is subject to only half the fractionation of the 86/88 ratio. The large error inherent in measuring the small  $\text{Sr}^{84}$  peak height masks the fractionation effect that should appear in the  $\text{Sr}^{84}/\text{Sr}^{88}$  ratio.

The column labeled  $E_{87/86}$  in Table 4 is a measure of the precision of the instrumental and measurement errors. It was obtained by use of the formula for  $\bar{c}$  but was given a different symbol because it does not represent the true precision of the analysis--it is not the precision of the  $Sr^{87}/Sr^{86}$  ratio averaged from independent replicate analyses. When the record was measured, the isotope ratios were calculated for each group of four or six sets. These groups were then used to calculate the final averages. The differences between the  $Sr^{87}/Sr^{86}$  for the groups and the overall average were calculated as a relative deviation,  $E_{87/86}$ . Therefore it is a measure of the variation of the machine and measurement errors and was used to judge the quality of the run. Other factors, such as the number of scans recorded, the pressure during the run, and evidence of excessive fractionation or contamination were also considered in evaluating the quality of the run. In general if  $E_{87/86}$  was greater than 0.2% the results were discarded and the analysis was repeated, if possible.

From the data in Tables 4 and 5 and from the replicate analyses by Hart and Faure the standard deviation of a single analysis ( $\sqrt{c}$ ) appears to be 0.001 ( $c = .14\%$ ) or better.

In an attempt to determine the accuracy of the strontium isotope ratio determination replicate analyses were made on a strontium carbonate standard (Eimer and Amend, lot 492327). These runs were made during the period of this investigation by several members of the M.I.T. Geochronology Laboratory

(Hart, Faure, Schnetzler, Pinson) on the same machine used to analyze the tektites. The results are shown in Table 5. Run number 3 was not included in the average. If it was averaged in, it would differ from the average by 2.5  $\mu$  and as Faure states (1961, p. 181) the probability that this value would occur in a population with such an average and standard deviation is less than 0.8%. By excluding run 8 the average (87/86) corr. ratio only changes from 0.7117 (including #8 in average) to 0.7121 (excluding #8) but the standard deviation goes from  $\pm 0.0016$  to 0.0009, while the 86/88 ratio remains unchanged at 0.1194.

The purpose of making the strontium carbonate runs was to determine if our analyses were comparable to those of other laboratories and to see if any systematic errors developed during the course of the investigation. A summary of the results obtained by the M.I.T. Geochronology Laboratory and other investigators on similar strontium compounds are shown in Table 6. While comparing these results is not a strict measure of the accuracy, since the results were all obtained by a single method, mass spectrometry, and since the samples did not go through the complete chemical procedure, the excellent agreement of our results with those of other laboratories gives confidence in the accuracy of the results reported in this thesis.

#### 4. Precision and accuracy of the X-ray fluorescence analyses

Replicate analyses were made by X-ray fluorescence on

Table 5

## Isotopic Composition of Eimer and Amend Strontium Carbonate

No.	Date	87/86	(87/86) corr	86/88	84/88	No. of Sets
1	5/3/60	0.7098	0.7116	0.1200	0.0068	-
2	5/15/60	0.7114	0.7117	0.1195	0.0066	64
3	6/30/60	0.7133	0.7130	0.1193	0.0064	80
4	7/20/60	0.7133	0.7127	0.1192	0.0062	48
5	8/21/60	0.7136	0.7127	0.1192	0.0069	84
6	10/17/60	0.7128	0.7116	0.1190	0.0069	76
7	12/1/60	0.7111	0.7102	0.1191	0.0067	84
8 *	2/13/61	0.7083	0.7077	0.1192	0.0064	-
9	2/27/61	0.7093	0.7123	0.1204	-	90
10	4/13/61	0.7146	0.7132	0.1189	-	54
Average		0.7121	0.7121	0.1194	0.0066	
	$\bar{r}$	$\pm 0.0006$	$\pm 0.0003$	$\pm 0.00017$	$\pm 0.0001$	
	$\bar{c}$	$\pm 0.086\%$	$\pm 0.044\%$	$\pm 0.14\%$	$\pm 1.52\%$	
	$\bar{v}$	$\pm 0.0018$	$\pm 0.0009$	$\pm 0.0005$	$\pm 0.0027$	
	$\bar{c}$	$\pm 0.26\%$	$\pm 0.13\%$	$\pm 0.42\%$	$\pm 4.09\%$	

\* Run 8 not included in average. (See text)

Table 6. Analyses of Strontium Isotopes from Reagents

Author	87/86	86/88	84/88	Remarks
Nier, 1938 p.277	0.712±.007	0.1194±.0012	.0068±.00014	Sr metal, 99.9% pure
Aldrich, et al, 1953 p.458	0.711±.0004	0.1195±.0003	.0067±.0005	SrCO <sub>3</sub> , Eimer and Amend Average of 6 analyses
Herzog, et al 1953 p.462	0.712	0.1196	.0070	SrCO <sub>3</sub> , Eimer and Amend Lot 492327
This work	0.7121±.0003	0.1194±.0002	.0066±.0001	SrCO <sub>3</sub> , Eimer and Amend Lot 492327. Average of 9 analyses.



several samples to determine the precision of the method. The data is shown in Table 7. It appears that the precision is about the same as obtained by isotope dilution. The relative deviations for the rubidium determinations seem to be fairly constant at about 2.2%, while the relative deviations of the strontium analyses range from 1% to about 3%. Two to four independent measurements were made on each of the tektites analysed; therefore the results given in the following section probably have a precision of  $\pm 2\%$  ( $\bar{c}$ ) or less.

The accuracy of the X-ray fluorescence data is directly related to the accuracy of the isotope dilution determination, since the latter were used as standards. Therefore the accuracy of the X-ray fluorescence results is considered to be the same as the accuracy of the isotope dilution results--better than  $\pm 5\%$ .

Table 7. Replicate Rb &amp; Sr Analyses by X-ray Fluorescence

		Rb	Sr
T3984	1)	111	167
	2)	116	170
	3)	115	166
	4)	116	168
	Averages	114.5	168
	11.2	± 0.9	
	± 1.0%	± 0.5%	
	± 2.4	± 1.7	
	± 2.1%	± 1.0%	
T4219	1)	110	127
	2)	113	129
	3)	109	121
	4)	107	123
	Averages	110	125
	± 1.3	± 1.8	
	± 1.2%	± 1.4%	
	± 2.5	± 3.6	
	± 2.3%	± 2.9%	
T3987	1)	113	125
	2)	118	128
	3)	117	133
	Averages	116	129
		± 1.5	± 2.3
	± 1.3%	± 1.8%	
	± 2.6	± 4.1	
	± 2.2%	± 3.2%	

Rb &amp; Sr in ppm by weight

#### D. Results

##### 1. Rubidium and strontium elemental compositions

A total of twenty-five tektites were analysed for rubidium and strontium, including samples from the Philippine Islands, Indo-China, Java, Australia, Georgia, Texas, Massachusetts, and Bohemia. In addition, an "americanite" from the Santa Mesa site in the Philippine Islands was analysed. The samples are described in Appendix A.

The results of the rubidium and strontium determinations are given in Table 8. Included in this table are both isotope dilution and X-ray fluorescence analyses. As previously discussed the X-ray fluorescence determinations were made using the samples analysed by isotope dilution as standards. It was found that due to the different matrices tektites from different localities could not be directly related, with the exception of the philippinites and indochinites. For example, in a plot of strontium in ppm, determined by isotope dilution, against counts per second, obtained by X-ray fluorescence, the philippinites and indochinites fell on a straight line (Figure 1) but samples from other areas plotted far from this line. Thus the X-ray fluorescence results for the indochinites and philippinites were obtained using a number of standards while the two australites, T4215 and T4216 were compared to the other two australites, T3313 and T4214, on which isotope dilution determinations were made, and the bediasite T4300 was compared to the isotope dilution results for T4106.

Table 8 Rb and Sr Content of Tektites

Sample No.	Locality	Rb (ppm)	Sr (ppm)	Rb/Sr
<b>PHILIPPINE ISLANDS</b>				
T3379	Santa Mesa Site Rizal, Prov.	115	174	0.66
T3962	Santa Mesa Site Rizal, Prov.	111 110*	487** 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
<b>INDO-CHINA</b>				
T3987	Kouang-Tcheou Wan	120# 116*	136# 129*	0.88
T3989	Kouang-Tcheou Wan	110*	132*	0.83
T3990	North Cambodia	116. 116*	171** 127*	0.91
T3991	North Cambodia	129 134*	134 139*	0.96
T3993	Annam	113. 112*	165** 130*	0.87
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

Table 8(cont)

Sample No.	Locality	Rb (ppm)	Sr (ppm)	Rb/Sr
T4104	Java	98	153	0.64
<b>AUSTRALIA</b>				
T3313	Charlotte Waters C. Australia	109	154	0.71
T4214	Nullarbor Plain	93	197	0.47
T4215	Nullarbor Plain	135*	205*	0.66
T4216	Nullarbor Plain	114*	218*	0.66
<b>NORTH AMERICA</b>				
T4091	Massachusetts	78	177	0.44
T4106	Texas	70	152	0.46
T4300	Texas	66*	153*	0.43
T4271	Georgia	74	170	0.44
T4090	Czechoslovakia (moldavite)	146	136	1.07
T3967	"Americanite" P.I.	181	98	1.85

\* X-ray fluorescence analysis. Others by isotope dilution.

\*\* Discarded isotope dilution-contamination.

# Average of 3- See Table 7

A previous isotope dilution determination was made of the rubidium and strontium contents of T3379 by Pinson et al (1958) and they reported  $104 \pm 6$  and  $112 \pm 6$  ppm Rb and  $162 \pm 8$  ppm Sr. The compositions reported in Table 8 are believed to be more accurate due to better knowledge of the spike composition--however the two results agree with the stated limits of error.

The X-ray fluorescence results shown in Table 8 are the average of from two to four independent measurements made on different days. Variation of any analysis from the average was less than 3% so only the averages are reported.

The Rb/Sr ratios given in Table 8 were calculated from the isotope dilution results in all cases where isotope dilution and X-ray fluorescence results are both reported. Ratios calculated from the X-ray fluorescence data would agree in almost all cases with the isotope dilution ratios and any disagreement would be slight.

Table 9 is a summary of the rubidium and strontium results compiled from Table 8, averaging the data for each locality.

Figure 3 is a graphical presentation of the rubidium and strontium results given in Table 8, while Figure 4 is a graphical presentation of the Rb/Sr ratios from the same table.

## 2. Strontium isotopic composition

Eighteen tektites were analysed for strontium isotopic composition. The results are given in Table 10. One run, T3379

Table 9  
Summary of Rb and Sr in Tektites

Locality	No. of Samples	Rb	Sr	Rb/Sr
Philippine Is.	7	117	173	0.68
		CANAI ± 1.9	4	0.017
		1.6%	2.3%	2.5%
		C ± 5	10.6%	0.044
		4.3%	6.1%	6.5%
Indo-China	8	118	132	0.89
		CANAI ± 2.5	1.75	0.013
		2.1%	1.33%	1.5%
		C ± 7	4.9	0.038
		5.9%	3.7%	4.3%
Java	1	98	153	0.64
Australia	4	120	194	0.62
		CANAI ± 11.7	13.9	0.053
		9.8%	7.2%	8.5%
		C ± 23.5	27.7	0.11
		20%	14.3%	17%
Bohemia	1	146	136	1.07
North America	4	72	163	0.44
		CANAI ± 2.6	6.2	0.0065
		3.6%	3.8%	1.5%
		C ± 5.2	12.5	0.013
		7.2%	7.7%	3%

Rb & Sr expressed as ppm by weight

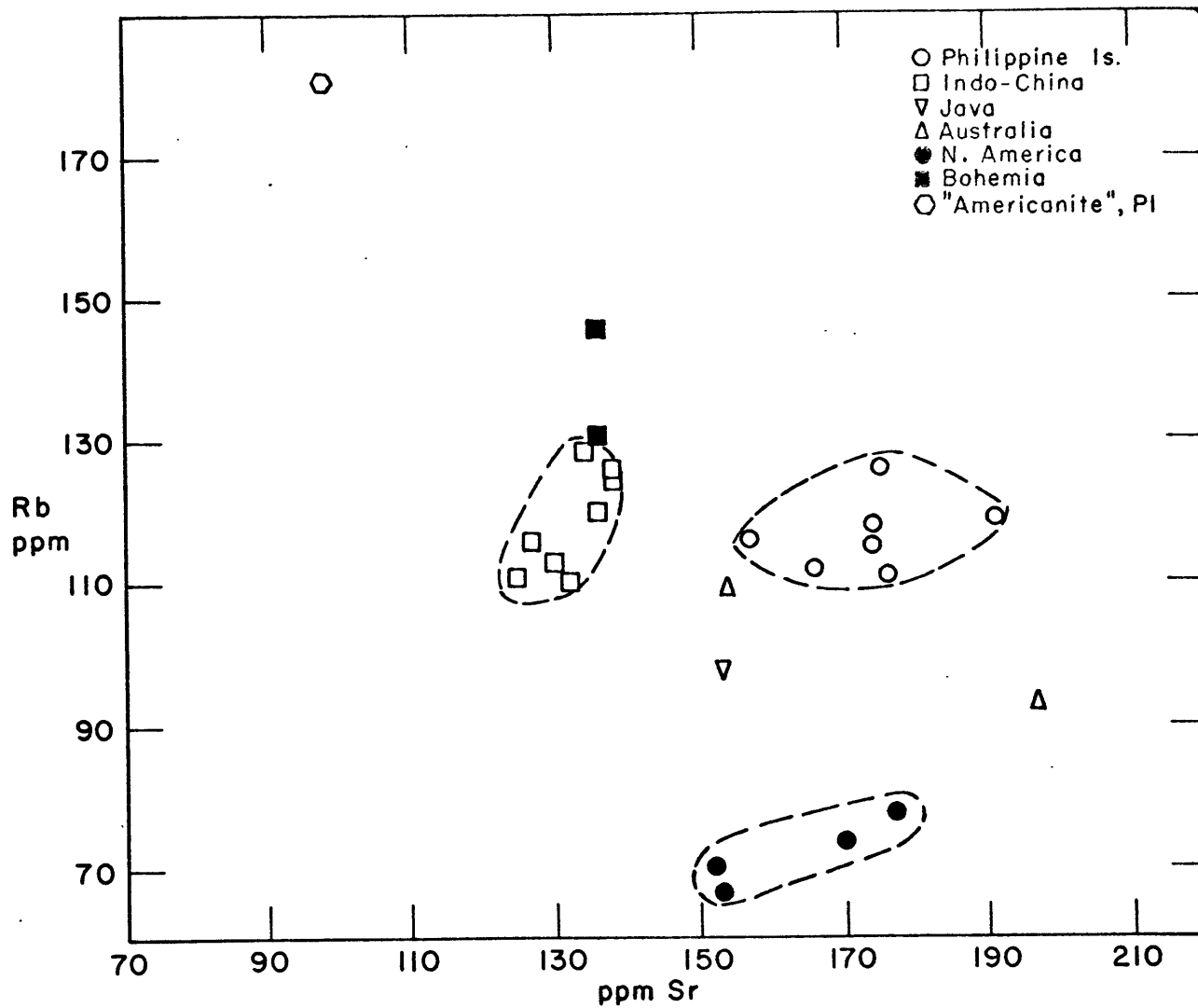


FIG. 3 Rb AND Sr CONTENTS OF TEKTITES



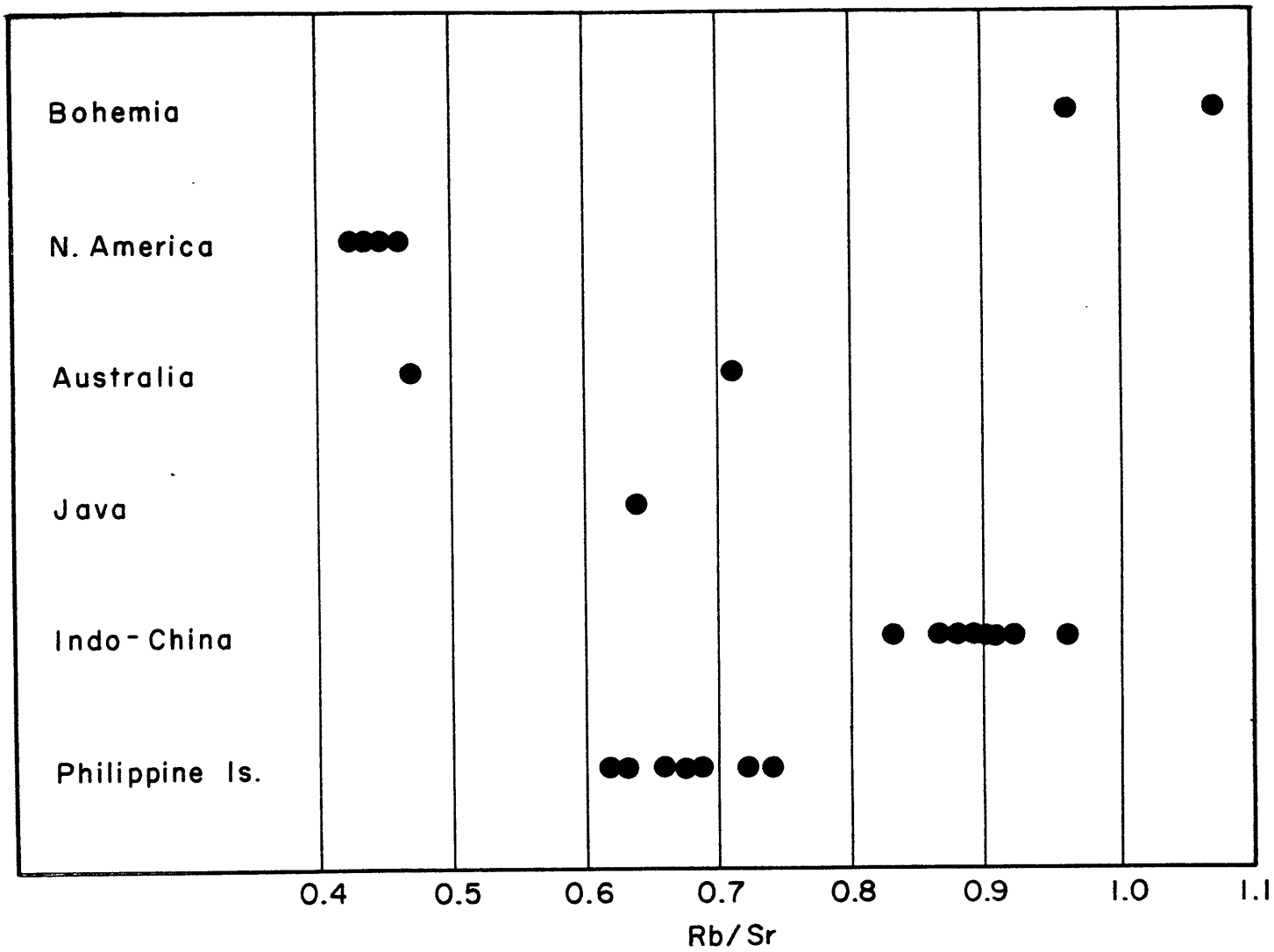


FIG. 4 Rb/Sr IN TEKTITES

Table 10 - Strontium Isotopic ratio results

No.	Locality	Date	87/88	(87/88) corr	86/88	84/88	Scans	E87/88
Philippine Islands								
T3379	Santa Mesa Site Rizal, Prov.	5/14/60	.7236	.7239	.1195	.0069	55	0.13% <sup>**</sup>
		10/20/60	.7011	-	.1233	.0067	-	*
		11/2/60	.7166	.7173	.1196	.0067	36	0.07%
		4/2/61	.7172	.7172	.1194	-	52	0.06%
Average for T3379			.7169	.7172	.1195	.0067		
T3962	Santa Mesa Site Rizal, Prov.	11/9/60	.7150	.7168	.1200	.0067	100	0.04%
T3984	Pugad-Babuy Site Bulakan, Prov.	7/5/60	.7261	.7249	.1190	.0068	42	0.23% <sup>**</sup>
		11/3/60	.7172	.7174	.1195	.0067	88	0.06%
T3765	Pugad-Babuy Site Bulakan, Prov.	3/24/61	.7192	.7192	.1194	-	96	0.11%
T3986	Busugana, Is.	7/29/60	.7181	.7193	.1198	.0072	66	0.14%
		11/17/60	.7241	.7204	.1182	.0065	92	0.06%
Average for T3986			.7211	.7198	.1190	.0068		

Table 10 - cont.

No.	Locality	Date	87/88	(87/88) corr	86/88	84/88	Scans	E87/88
Average for Philippinites			.7179	.7181	.1195	.0067		
		$\bar{\sigma}$	$\pm .0009$	$\pm .0006$	$\pm .0002$	$\pm .0001$		
		$\sigma$	$\pm .0021$	$\pm .0013$	$\pm .0004$	$\pm .0001$		
Indo-China								
T3987	Kouang-Tcheou- Wan	8/25/60	.7193	.7202	.1197	.0072	108	0.04%
		10/25/60	.7174	.7189	.1199	-	88	0.06%
		12/6/60	.7221	.7194	.1185	.0066	120	0.05%
Average for T3987			.7196	.7195	.1194	.0069		
T3990	North Cambodia	10/23/60	.7144	.7186	.1208	-	112	0.04%
		10/31/60	.7195	.7174	.1187	.0066	108	0.06%
		11/7/60	.7161	.7193	.1205	.0067	95	0.06%
Average for T3990			.7167	.7184	.1200	.0066		
T3991	North Cambodia	7/7/60	.7215	.7227	.1198	.0077	90	0.20% <sup>**</sup>
		11/20/60	.7213	.7195	.1188	.0065	90	0.05%

Table 10 - cont.

No.	Locality	Date	87/88	(87/88) corr	86/88	84/88	Scans	E87/88
T3993	Annam	8/23/60	.7230	.7215	.1189	.0068	116	0.05%
		11/15/60	.7245	.7214	.1184	-	80	0.12%
	Average for T3993			.7238	.7214	.1186	.0068	
T4219	Dalat, S. Viet-Nam	4/3/61	.7207	.7203	.1193	-	76	0.14%
Average for Indochinites			.7204	.7198	.1192	.0067		
			$\bar{\sigma}$ $\pm$ .0012	$\pm$ .0005	$\pm$ .0003	$\pm$ .0001		
			$\sigma$ $\pm$ .0026	$\pm$ .0011	$\pm$ .0006	$\pm$ .0002		
T4104	Java	2/19/60	.7219	.7194	.1186	-	106	0.06%
T3313	Charlotte Waters Central, Aust.	11/23/60	.7232	.7203	.1184	-	52	0.40%**
		12/2/60	.7232	.7174	.1175	-	64	0.16%
T4214	Mullarbor Plain	12/16/60	.7172	.7174	.1195	.0067	84	0.05%
Average for Australites			.7202	.7174	.1185	.0067		

Table 10 - cont.

No.	Locality	Date	87/86	(87/86) corr	86/88	84/88	Scans	E87/86
<b>North America</b>								
T4091	Massachusetts	7/1/60	.7175	.7169	.1192	.0071	90	0.15%
T4106	Texas	5/1/60	.7207	.7186	.1187	.0068	110	0.09%
T4271	Georgia	4/27/61	.7153	.7147	.1192	-	100	0.09%
		4/12/61	.7154	.7140	.1189	.0066	176	0.07%
Average of T4271			.7154	.7144	.1170	.0066		
Average for North America			.7179	.7166	.1190	.0068		
		$\bar{\sigma}$	$\pm .0015$	$\pm .0012$	$\pm .0002$			
		$\sigma$	$\pm .0027$	$\pm .0021$	$\pm .0003$			
<b>Czechoslovakia</b>								
T4090	Nechov, Bohemia	5/5/60	.7236	.7257	.1201	.0070	102	0.10%
T3314	"moldavite"	12/11/60	.7257	.7235	.1187	.0065	84	0.05%
Average for moldavites			.7246	.7246	.1194	.0068		

Table 10 - cont.

No.	Locality	Date	87/86	(87/86) <sub>88rr</sub>	86/88	84/88	Scans	37/86
Average for all tektites			.7198	.7190	.1192	.0067		
		$\bar{\sigma}$	$\pm .0007$	$\pm .0006$	$\pm .0002$	$\pm .0001$		
		$\sigma$	$\pm .0031$	$\pm .0026$	$\pm .0006$	$\pm .0002$		

\* Discarded - probable Sr<sup>86</sup> spike contamination

\*\*Discarded - poor run

(10/20/60), was discarded because the high  $\text{Sr}^{86}/\text{Sr}^{88}$  and low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios suggested possible contamination from  $\text{Sr}^{86}$  spike. Three other runs, T3984 (7/5/60), T3991 (7/7/60) and T3313 (11/23/60) were discarded due to the poor precision of the run as noted by the high value of  $\text{E}^{87}/^{88}$  (see page 37). Run T3379 (5/14/60) was judged to be of poor quality and discarded although the precision of the run was satisfactory. The 55 scans recorded were the sum of three short separate runs--each failing after only a small number of scans were recorded, after which more sample was put on the filament. Also the peak heights were small and the pressure was poor. Experience has indicated such runs often give spurious results and in view of the different results obtained by two runs of better quality the run was discarded.

In all except one case replicate runs of a sample were obtained by taking separate portions of the powdered tektite and putting each through the complete chemical and mass spectrometric procedure. The one exception was the analysis of T4271. The two determinations of this sample were made on two portions of the same strontium oxalate precipitate as not enough sample was available to make two completely independent determinations.

The ratios  $\text{Sr}^{87}/\text{Sr}^{86}$ ,  $\text{Sr}^{86}/\text{Sr}^{88}$ , and  $\text{Sr}^{84}/\text{Sr}^{88}$  are given in Table 10 exactly as measured from the record. The  $\text{Sr}^{87}/\text{Sr}^{86}$  and  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios are the averages of the number of sets indicated. The  $\text{Sr}^{84}/\text{Sr}^{88}$  ratios were determined from a smaller

number of sets, usually 18 to 30, and therefore are less precise. The  $(\text{Sr}^{87}/\text{Sr}^{86})$  corr. ratios were obtained by correcting, or normalizing, the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios to a constant, and applying half the correction to the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios (see page 33). The variation in the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios, attributed to instrumental fractionation, was in one case (T3990), as great as 1.7% between two independent runs. All discussions of this data in the following pages will be based upon the corrected value of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios; however, many of the general conclusions derived from this work would be the same if the raw  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios were used instead of the corrected  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios.

A correction for "pressure broadening" as applied by Pinson et al (1958) was not made in this investigation, and evidently should not have been made during the earlier investigation. Interspersed strontium carbonate analyses (see Table 5) and basalt analyses (by Faure, 1961) were used to monitor the tektites analyses. If corrections similar to those made by Pinson had been applied to the strontium carbonate and basalt analyses the results would have been far from the results obtained by other investigators on similar materials. Without such a "correction" the results are in excellent agreement with those of other laboratories (see Table 6 and Table 12). Another indication that this "correction" should not be made is found in the precision of the strontium carbonate runs. These runs exhibited different degrees of resolution, from cases where



the valley between the Sr<sup>87</sup> and Sr<sup>88</sup> peaks was almost completely down to the base line to cases where the valley was several inches above the true base. The procedure used by Pinson et al to correct for this seeming lack of resolution was to draw the baseline curving up from the flat portion between the 84 and 86 peaks to the valley between the 86 and 87 peaks (this valley was usually slightly above the base between the 84 and 86 peaks) and on up to the valley between the 87 and 88 peaks (which was normally considerably above the base between the 84 and 86 peaks). Had this curved base been drawn on the strontium carbonate runs, which showed considerable range in resolution, the precision of the runs would be very poor and the average of the runs would have been far below the accepted composition of this standard.

Pinson et al attributed the lack of resolution to diffusion of the ion beam due to ions striking gas molecules in their flight down the tube. This is undoubtedly a factor, but at pressures of less than  $5 \times 10^{-6}$  mm Hg it is believed the position of the sample on the filament, the size of the sample, and purity of the sample are the primary causes of peak overlap. Occasionally runs at pressures of  $5 \times 10^{-7}$  mm Hg showed greater peak overlap than runs at pressures of  $5 \times 10^{-6}$  mm Hg. In any event, it appeared that overlap to the extent that the 87-88 valley was half the height of the Sr<sup>87</sup> peak could be tolerated before the 88 curve actually began to add to the 87 peak.

A summary of the results of Table 10, plus the Rb/Sr results from Table 9, are given in Table 11.

Five philippinites, from three different sites, have an average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.7181,  $\bar{\sigma} = 0.0006$ ,  $\sigma = 0.0013$ . As discussed in the section on precision and accuracy the reproducibility ( $\sigma$ ) of strontium isotope analyses appears to be approximately  $\pm 0.001$ . Thus the variation of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in the philippinites is only slightly greater than one would expect from measurement error. Seven philippinites, including the five analysed 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  $0.68 \pm 0.02$ .

Five indochinites, from four different localities, also have homogeneous  $\text{Sr}^{87}/\text{Sr}^{86}$  values, averaging 0.7198,  $\bar{\sigma} = 0.0005$ ,  $\sigma = 0.0011$ . This variation is again about what one could expect from measurement error. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio for indochinites seems to differ from the ratio measured in the philippinites. If  $\bar{x} \pm \bar{\sigma}_{\bar{x}}$  and  $\bar{y} \pm \bar{\sigma}_{\bar{y}}$  are the measured values of two independent populations, there is only a 5% probability that  $(\bar{x} - \bar{y}) > 2\bar{\sigma}_{(\bar{x}-\bar{y})}$  if the difference between the true mean values is zero, where  $\bar{\sigma}_{(\bar{x}-\bar{y})} = \sqrt{\left(\frac{\bar{\sigma}_{\bar{x}}}{\bar{x}}\right)^2 + \left(\frac{\bar{\sigma}_{\bar{y}}}{\bar{y}}\right)^2}$

Table 11 Summary of the  $(\text{Sr}^{87}/\text{Sr}^{86})$  Ratio in Tektites

Locality	No. of Samples	$(87/86)_{\text{corr}}$	Rb/Sr <sup>*</sup>
Philippine Is.	5	0.7181 ± 0.0006	0.68 ± 0.017
Indo-China	5	0.7198 ± 0.0005	0.89 ± 0.013
Java	1	0.7194	0.64
Australia	2	0.7174	0.62±0.05
North America	3	0.7166 ± 0.0012	0.44 ± 0.0065
Czechoslovakia	2	0.7246 ± 0.0010	1.07
Average	18	0.7190 ± 0.0006	

1) Errors are standard deviation of the mean.

\* Taken from Table 9.

(Hoel, 1954, p. 109). In this case  $\bar{x} - \bar{y} = 0.0017$  and  $\overline{\sigma}(\bar{x}-\bar{y}) = \pm 0.0008$ . Since  $(\bar{x} - \bar{y}) > 2 \overline{\sigma}(\bar{x}-\bar{y})$  it can be tentatively concluded that at the usual 95% confidence limit these two populations are significantly different. However this conclusion is based on rather limited data and more samples should be analysed to test this point.

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.

Two australites have identical  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios at 0.7174 while a javanite has  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.7194. 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 analysed 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 three North American tektites have an average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of  $0.7166 \pm 0.0012$ . Unfortunately only small amounts of these samples were available and replicate runs could not be made in order to confirm the measurements. The Empire, Georgia  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, although significantly lower than the other tektites, was obtained from two exceptionally long and steady runs. The strontium carbonate standard (Run 10, Table 5) was run immediately after the first of the Georgia analyses to check for any instrumental bias. The Massachusetts and Georgia tektites contain quite similar rubidium contents (78 and 74 ppm respectively) and strontium contents (177 and 170 ppm respectively). The two Texas samples contain 70 and 66 ppm rubidium and 152 and 153 ppm strontium--slightly less than the Massachusetts and Georgia samples--but the Rb/Sr ratios of the four are amazingly similar for samples from such widely separated localities.

Two two moldavites analysed gave the highest  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of the tektites analysed, averaging 0.7246. Only one of these samples was analysed for rubidium and strontium, and it has the highest Rb/Sr ratio of any of the tektites analysed; viz. 1.07. Due to the small size of the sample available, the other moldavite (T3314) could not be analysed for rubidium and strontium. However, values of 130 ppm Rb and 136 ppm Sr were reported for this sample by Pinson et al (1958).

The average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio for all 18 tektites analysed is  $0.7190 \pm 0.0006$ .

### E. Discussion

Discussion of the rubidium and strontium elemental compositions determined in this investigation will be deferred to Section III, in which the chemical composition of tektites is treated. Due to the direct relationship between the Rb/Sr ratios and the strontium isotopic composition, it was necessary to present the data on the preceding pages, and the Rb/Sr ratios, as they pertain to the isotopic composition, will be discussed in this section.

#### 1. The existence of radiogenic strontium

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  $Sr^{87}/Sr^{86}$  ratio is greater than 0.712 ("normal" strontium) or 0.700 (primordial strontium). As the initial strontium isotopic ratio, that is the ratio when the tektites were formed, is not known, they cannot be directly dated. However, limitations upon their age, and a possible means of determining their initial ratio will be discussed in the following pages.

#### 2. Significance of the non-radiogenic strontium isotopes in tektites

Kohman (1958) proposed an extra-solar system origin for tektites and suggested a possible experimental test of the theory. He stated that due to the apparent variety of processes for the synthesis of elements in the universe and the continuing

level of such activity (Purbridge et al, 1957), it is likely that matter formed outside our solar system will have different isotopic composition from that observed in our solar system.

Since the publication of Kohman's hypothesis several investigators have indicated that tektites have the same isotopic composition as terrestrial material. Friedman (1958) found the deuterium content of the water in tektites to be in the same range as in terrestrial waters; Silverman (1951) found the oxygen isotopic composition in tektites similar to ratios found in terrestrial sediments; Tilton (1958) found the lead isotopic composition similar to modern terrestrial lead, and Pinson et al (1956, 1957a, and 1958) found the strontium isotopic composition to be normal. The similarity of the K/Rb ratio in tektites to terrestrial and meteoritic materials was noted by Taylor and Ahrens (1958), indicating that they were formed by similar processes.

During the period of this investigation the tektite analyses were interspersed with analyses of terrestrial rocks by G. Faure and strontium carbonate by various members of the M.I.T. Geochronology Laboratory. A total of 98 strontium isotope ratio determinations were made, including 26 tektites, 63 terrestrial rocks (mostly basic igneous rocks), and 9 SrCO<sub>3</sub> standards.

Therefore an excellent opportunity exists to compare the non-radiogenic strontium isotopic composition of tektites to that of terrestrial materials analysed in the same period

of time, on the same mass spectrometer, and using the same routine procedures.

A summary of the non-radiogenic isotope ratios obtained during this period is given in Table 12.

The  $\text{Sr}^{86}/\text{Sr}^{88}$  ratios were usually calculated from about 80 to 100 scans while the  $\text{Sr}^{84}/\text{Sr}^{88}$  ratios were calculated from only about 18 to 30 scans. Thus the precision error of the  $\text{Sr}^{84}/\text{Sr}^{88}$  ratios (as much as 5%) is much poorer than the precision error of the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio (approximately 0.5%). The numbers in parentheses beside the  $\text{Sr}^{84}/\text{Sr}^{88}$  ratios are number of analyses used to compute the average ratio, as the  $\text{Sr}^{84}/\text{Sr}^{88}$  ratio was not determined in all analyses.

It can be seen that the non-radiogenic strontium isotope ratios ( $\text{Sr}^{84}/\text{Sr}^{88}$  and  $\text{Sr}^{86}/\text{Sr}^{88}$ ) are not significantly different between the three types of materials at the 95% confidence limit ( $2\sigma$ ).

Thus it can be concluded that the strontium stable isotopic composition of tektites is essentially the same as terrestrial and meteoritic materials, and this information, combined with the findings of the earlier investigators, makes an extra-solar system origin highly improbable.

### 3. Significance of the variation of the $\text{Sr}^{87}/\text{Sr}^{86}$ ratio in tektites

The majority of tektite investigators currently believe that tektites were formed by the fusion of terrestrial materials. Different mechanisms for this fusion have been proposed, such as impact of meteorites or comets, and lightning. All of these



Table 12  
The  $\text{Sr}^{86}/\text{Sr}^{88}$  and  $\text{Sr}^{84}/\text{Sr}^{88}$  Ratios in Tektites and Terrestrial  
Materials

Material	86/88	84/88	No. of Samples
$\text{SrCO}_3$	0.1194	0.0066 (7)	9
	$\bar{\nabla} \pm 0.0002$	$\pm 0.0001$	
	$\nabla \pm 0.0005$	$\pm 0.0003$	
Terrestrial Rocks	0.1190	0.0066 (55)	63
	$\bar{\nabla} \pm 0.0001$	$\pm 0.00003$	
	$\nabla \pm 0.0006$	$\pm 0.0002$	
Tektites	0.1192	0.0067 (17)	26
	$\bar{\nabla} \pm 0.0002$	$\pm 0.0001$	
	$\nabla \pm 0.0006$	$\pm 0.0002$	

theories are similar in that they all suggest a random process, and they differ only in the magnitude of tektite production per fusion. The probability of fusing a certain type of material should be in direct proportion to the extent of that material on the earth's surface, unless the process of fusion was restricted to certain portions of the earth. Evidence indicates that the infall of meteorites (and therefore by analogy, comets and asteroids) is random (Krinov, 1960). The process of fusion by lightning might occur more often in certain regions than in others; Hawkins (1959, p. 6) points to the fact that tektites are found primarily in the temperate and equatorial regions of the earth where thunderstorms are most frequent, but certainly such regions contain a myriad of geological materials of all ages.

Clarke (1924, p. 34) estimated that 75% of the land surface of the earth is covered by sedimentary rocks and 25% by igneous rocks. Pettijohn (1957, p. 11) estimated the composition of sedimentary rocks to be shale, sandstone, and limestone in the proportion of 58, 22, and 20 respectively. The igneous rocks can be grouped roughly into two types: basic (basaltic) and acidic (granitic) that occur in the proportion of about 1:2 in the earth's crust. Thus the probability of a particular general type of rocks being fused by a random process should be roughly as follows: shale 44%, sandstone 16%, granite 16%, limestone 14%, basalt 9%.

In view of the large compositional variation one would

expect if the fusions were random, the rather similar chemical composition of tektites might be attributed to one of two possibilities. 1) Only materials of a certain type would form durable tektites; other materials would not form glasses (however George (1924) states that glasses ranging in  $SiO_2$  from 40 to 80% are known) or tektites formed from these other materials would devitrify rapidly. 2) Selective volatilization of elements during the high temperature fusion would change the chemical composition toward some common composition, thus suppressing the chemical variations. In view of this second possibility it might not be possible to identify the parent material from the chemical composition of the tektite (Lovering, 1960, p. 1029).

However, during a high temperature fusion there should be no selective fractionation of the isotopes, as the degree of fractionation decreases with increasing temperature and increasing mass. Thus the relative isotopic composition of the tektite should be the same as that of the parent provided this composition has not changed by radioactive transformations since the time of fusion. K-Ar dating of tektites, determined by Reynolds (1960) and Gentner and Zahringer (1959, 1960) give ages of 30 m.y. or less for the moldavites, bediasites and Georgia tektites, and less than 1 m.y. for the Pacific Ocean area tektites, i.e. philippinites, indochinites, javanites, australites, etc. According to the terrestrial fusion theories these ages must be the time of formation of the tektite. They might very well be the age since the second period of melting

which some tektites exhibit, but the terrestrial fusion theories suggest that the second period of melting, caused by the tektites falling through the atmosphere, immediately followed the first melting.

As the half-life of the decay of  $\text{Rb}^{87}$  to  $\text{Sr}^{87}$  is quite long, approximately  $4.7 \times 10^{10}$  years (Glendenin, 1961), and the Rb/Sr ratios in tektites are not large, no measurable increase in the Sr content could occur in 30 m.y. Therefore if the K-Ar ages represent the times since formation of the tektites from their parents, the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in the tektites will be the same as in the parents and comparison of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in tektites with that of various terrestrial and extra-terrestrial materials might suggest possible parent material and/or mode of origin.

$\text{Sr}^{87}/\text{Sr}^{86}$  ratios and Rb/Sr ratios in various types of terrestrial and extra-terrestrial materials are given in Table 13. Unfortunately, it has been common practice in age-dating to use only a few favorable minerals rather than the whole rock so that data of interest to this investigation is sparse.

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 analysed. Granites have a very large variation in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. As all but one of the 21 granites in Table 13 is over 1000 m.y. old it is apparent that the variation

Table 13  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios and Rb/Sr ratios in terrestrial and extra-terrestrial materials

Material & Reference	No. of Samples	Range $\text{Sr}^{87}/\text{Sr}^{86}$	Avg $\text{Sr}^{87}/\text{Sr}^{86}$	Range Rb/Sr	Avg Rb/Sr
<b>GRANITE</b>					
Gast (1960) <sup>1</sup>	10	.720-1.003	0.830	.35-3.9	1.64
Fairbairn et al (1961) <sup>2</sup>	11	.732-1.25	0.868	.25-6.0	1.78
<b>BASALT</b>					
Gast (1960)	5	.705-.711	0.708	-	-
Faure (1961) <sup>3</sup>	25	.705-.710	0.708	.02-.18	0.05
<b>OBSIDIANS</b>					
Pinson & Bottino (1961) <sup>4</sup>	9	.704-.724	0.714	1.2-31.	4.2
<b>LIMESTONE</b>					
Gast (1960)	5	.704-.712	0.709	-	-
<b>SHALE</b>					
Faure (1961) <sup>5</sup>	2	.720-.723	0.7215	-	-
<b>CHONDRITES</b>					
Herzog and Pinson (1956) <sup>6</sup>	2	.753-.755	0.754	.33-.36	0.345
Gast (1960)	5	.739-.811	0.764	-	-
<b>ACHONDRITES</b>					
Gast (1960)	3	.7004-.7027	0.7015	-	0.01
Herzog & Pinson (1956) <sup>7</sup>	1	-	0.703	-	-
<b>SEA WATER</b>					
Pinson et al (1957b) <sup>8</sup>	1	-	0.712	-	0.016

- 1 One age 200 m.y.-others 1000-2700 m.y.
- 2 Ages from 1200-2200 m.y.
- 3 Recent oceanic and continental basalts
- 4 Ages range from 0 to 60 m.y.
- 5 East and west coast composite samples
- 6 Homestead and Forest City chondrites
- 7 Pasamonte achondrite
- 8 Mid-Atlantic

shown is due to the variation in high Rb/Sr ratios. The Rb/Sr ratios in the granites range from 0.25 to 6.0, averaging about 1.7, while the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios range from 0.72 to 1.25. 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 analysed.

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 analysed by Faure were Recent basalts, but due to their low Rb/Sr ratios little change in the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios should be observed in older basalts. The range of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in the basalts analysed is from 0.704 to 0.711, averaging 0.708, while the Rb/Sr ratios range from 0.02 to 0.18, averaging 0.05.

Nine obsidians analysed by Pinson and Bottino show a limited  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 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. The Rb/Sr ratio in limestones is about 0.008 (Faure, 1961, p. 115).

Faure analysed two composite samples of Paleozoic shales from the east and west coasts of North America. The measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios are quite similar--0.720 and 0.723. The Rb/Sr ratios were not determined in these samples. Turekian and Wadepohl (1961) and Faure (1961) have estimated the average Rb/Sr ratio in shale to be 0.47 and 0.50 respectively. Thus

rocks of this high a Rb/Sr ratio (and undoubtedly having considerable variation in this ratio) and of varying ages should have highly varying  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. Such variations are suppressed between composite samples.

Chondrites have fairly high, varying  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios. Unfortunately Gast (1960) did not analyse his five chondrites for rubidium and strontium, but it is assumed the variation shown by these specimens is due to slightly different Rb/Sr ratios and the ages are all the same--approximately  $4.5 \times 10^9$  years. This should be investigated further.

Achondrites have extremely low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios which show almost no variation (See Table 13). Under the assumption that 1) all terrestrial and meteoritic strontium was derived from a homogeneous parent material and thus had the same abundance of  $\text{Sr}^{87}$  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-worker have demonstrated that these assumptions hold true in the case of lead, by analogy the assumption should be true for strontium. The achondrites have extremely low Rb/Sr ratios (.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 (0.7004) 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.

To complete this rather sparse summary of measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios found in terrestrial and extra-terrestrial materials, several estimates of the average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in the crust of the Earth should be mentioned. Gast (1960) assumed an initial ratio of 0.714, an average Rb/Sr ratio of 0.33 and an average age of 2 billion years and arrived at a present day  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.742 for the silicic crust.

Faure (1961, p. 139) in an estimate of the upper limit for the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in the crust assumed an initial ratio of 0.7004, a Rb/Sr ratio of 0.25 and an age of 4.5 billion years. The calculated  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio was 0.748. Reasoning that the continental masses are younger than 4.5 billion years, he set a lower limit to the average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio by assuming that the continents are only 1 billion years old and the initial ratio was 0.706 (calculated from basalt analyses). This lower limit calculated to be 0.717. He therefore concluded the average  $\text{Sr}^{87}/\text{Sr}^{86}$  value for the crust must be between 0.717 and 0.748.

Faure also calculated the average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of a geosynclinal assemblage of sedimentary and volcanic rocks. Based on Faldervart's model for rocks of young folded belts this  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is approximately 0.720, in excellent agreement with the analysed composite shales.



The next question that should be discussed is: How many independent fusions by the various mechanisms would the 18 tektite samples analysed for strontium isotopic composition represent? As they came from at least 14 different sites separated by more than ten miles, they would represent at least 14 independent fusions if they were formed by the impact of lightning randomly striking the earth. A few of the samples such as the two labeled "North Cambodia" may have been collected from exactly the same site, but this is unlikely so the 18 samples probably would represent 18 fusions by lightning.

If the tektites were formed by the impact of meteorites all the tektites within several square miles, or even tens of square miles may have been formed from one impact. Thus, as the samples analysed are from 12 provinces, states, or countries, any of which is more than 100 miles from its nearest neighbor, they should represent 12 different meteorite impacts.

The number of impacts necessary to form the tektites by fusion by asteroids or comets is considerably less than either of the other two theories just discussed. Cohen (1961) suggested that all the Pacific Ocean area tektites were produced by one collision, all the North American tektites were the result of another, a third produced the moldavites, and a fourth the Ivory Coast tektites. Reynolds' (1960) K-Ar work implies at least five groups, while Baker (1959) claims the geological evidence points to eleven groups (including the Georgia field which he did not discuss, but excluding the Martha's Vineyard specimen). Urey (1957), in discussing the comet hypothesis,

conceded that probably all the Pacific Ocean area tektites were not formed by one impact but suggests the comet head split and produced multiple, simultaneous impacts in the various tektite localities of the Pacific. Thus it is proposed that the 18 tektites analysed would represent at least six separate impacts of asteroids or comets, these six impacts consisting of the moldavites, North American tektites (grouped on the basis of similarity of composition), australites, javanites, philippinites, and indochinites.

The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites given in Table 10 and the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios taken from the literature for various materials as given in Table 13 are plotted in Figure 5. As most of the materials shown in this figure have low  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, an expanded picture, with the  $\text{Sr}^{87}/\text{Sr}^{86}$  scale running from 0.700 to only 0.760, is given in Figure 6. Figure 6 has only the lower one-tenth of the  $\text{Sr}^{87}/\text{Sr}^{86}$  scale of Figure 5.

It can be seen from these diagrams that tektites do not show the variation one would expect if they are the product of random fusions of terrestrial materials--whether the tektites analysed represent 11, 12, or 6 separate random impacts. As mentioned above some investigators maintain that only a certain type of material could produce tektites. For example Urey (1957) stated that a basic magma will crystallize even when undergoing rapid cooling but the more viscous acid melt will be unable to form crystals and remain as a glass. Of the more acidic rocks the ones most commonly mentioned as possible parents for the tektites include siliceous shale (Urey, 1959), granite

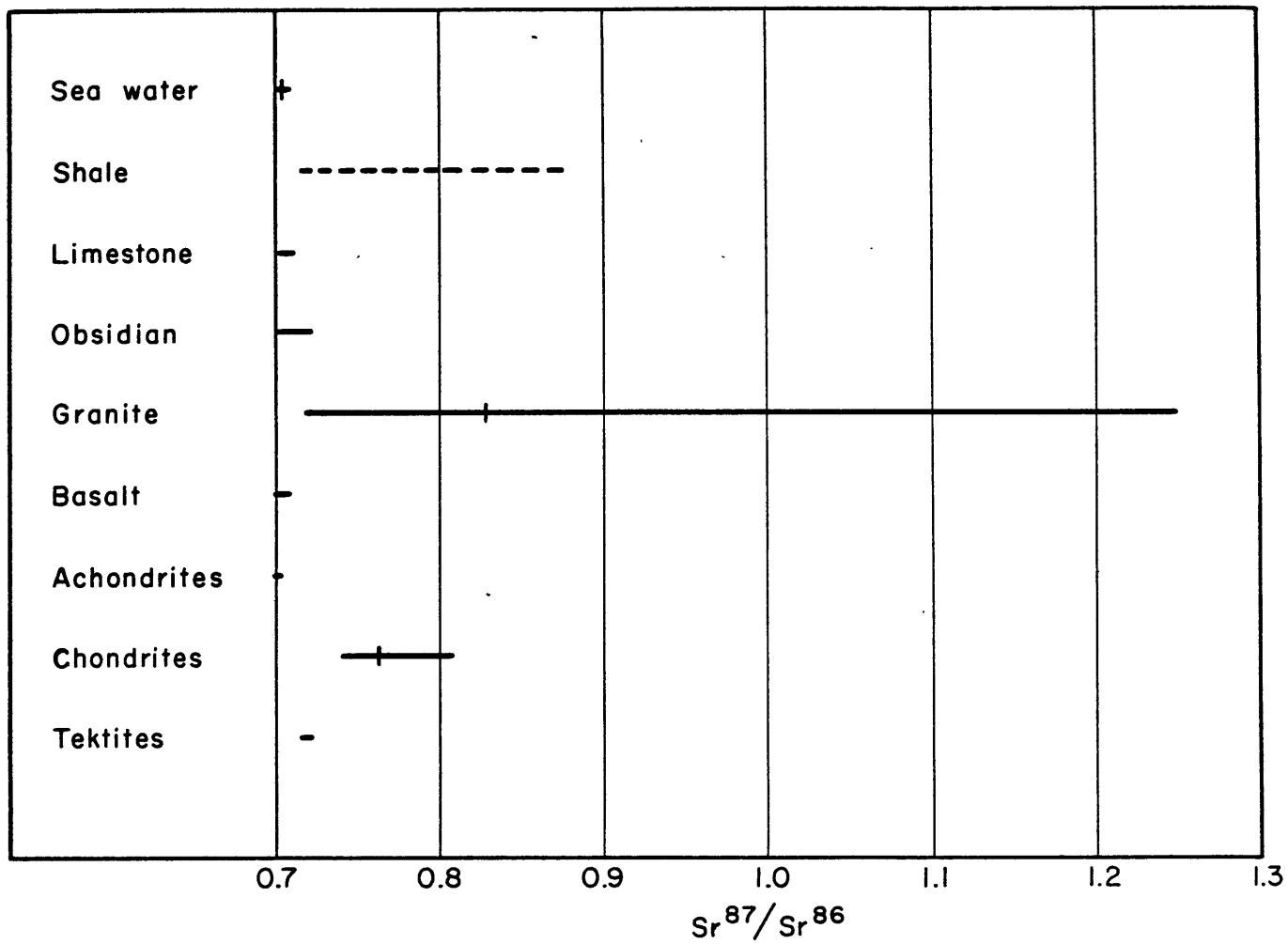


FIG. 5  $Sr^{87}/Sr^{86}$  IN TEKTTITES, METEORITES AND VARIOUS TERRESTRIAL MATERIALS

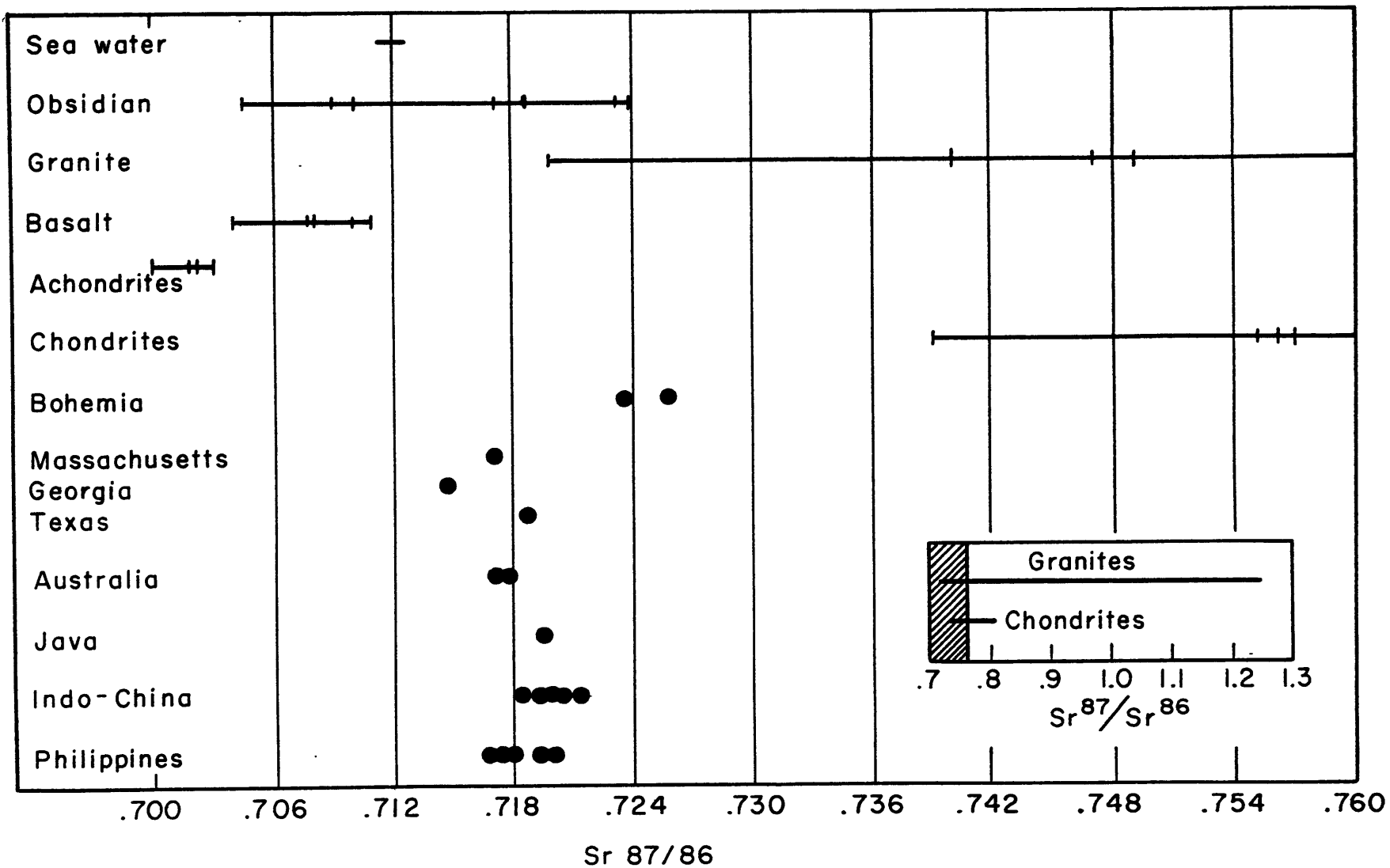


FIG. 6  $Sr^{87}/Sr^{86}$  IN TEKTITES, METEORITES, IGNEOUS ROCKS, AND SEA WATER

(Mason, 1959) and granophyre (Lovering, 1960). But these are types that should have large variations in  $\text{Sr}^{87}/\text{Sr}^{86}$ . They have high average Rb/Sr ratios (approximately 0.5 in shales and 1 in granites, and also presumable granophyres) and exhibit, or would be expected to exhibit, a wide range of Rb/Sr ratios. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in shales will vary according to the proportions of young low-ratio volcanic material, low-ratio limestone, old high-ratio granite, etc., that together contributed to make up the rock. For example, certainly a largely detrital micaceous shale derived from an ancient landmass would have a much greater  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio than a felspathic shale with a high proportion of endogenic constituents or recent volcanics.

Thus the results of this investigation do not support the theory of tektite production by random fusion of terrestrial materials, particularly the random fusion of shale or granite.

#### 4. Significance of the tektite $\text{Sr}^{87}/\text{Sr}^{86}$ ratio growth with time

It is interesting to see what conclusions can be drawn if it is assumed that the Rb/Sr ratios in tektites have not changed substantially since they were formed from a parent material.

It is proposed that the K-Ar ages date the period of second melting that is observed in some of the tektites. This second melting caused the melting of the surface and the build-up of a flange, probably heating the interior sufficiently to allow the diffusion of radiogenic argon from the interior, but the melting was limited to the surface. Taylor's (1961) analyses of

alkali elements in the flanges and cores of australites indicate considerable selective volatilization occurred. However, all the analyses in this work were performed on specimens that did not contain a flange--either the samples never experienced second melting or the flanges had since weathered away. In any event, it is believed the Rb/Sr ratios in the tektites analysed, and thus the rate of growth of their  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, were not changed during the heating that is dated by the K-Ar measurements, and thus the Rb/Sr ratios have remained unchanged since formation of the tektites.

Figure 7 shows generalized  $\text{Sr}^{87}/\text{Sr}^{86}$  growth lines for several types of materials, including a line for an average tektite which has a Rb/Sr ratio of 0.9 and a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.719. This diagram, and many of the conclusions derived from it, are the same as presented by Pinson et al (1958). They are repeated here to emphasize the fact that although the earlier data was partially incorrect many of their conclusions are still valid.

It can be seen that the tektite  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio development line does not intersect the chondrite line; accordingly the tektites could not have been derived from chondrites. However, as the five chondrites measured for  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios to date vary between 0.735 and 0.811, the probability that some chondrites have a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.720 or less cannot be excluded.

The generalized tektite growth line does intersect, however, the achondrite growth line, the time of intersection

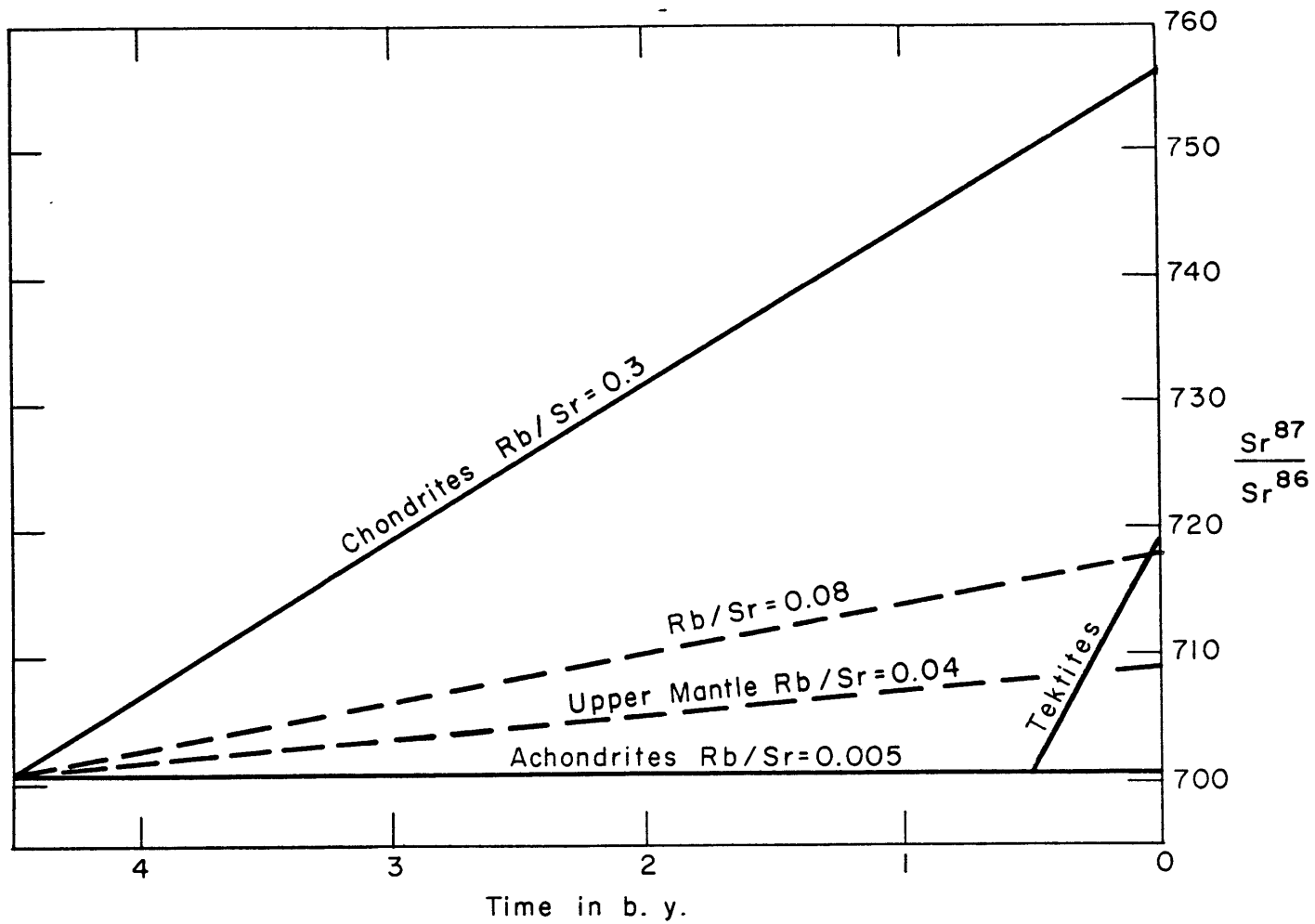


FIG. 7 VARIATION OF  $\text{Sr}^{87}/\text{Sr}^{86}$  WITH TIME FOR TEKTITES, METEORITES, AND UPPER MANTLE

being approximately 500 m.y. ago. Thus the tektites could have differentiated from achondritic material at this time. Several lines of evidence, including the strontium isotopic composition, support the theory that chondrites and achondrites developed simulatneously 4.5 billion years ago, but the tektites could not be a separate class of meteorite that developed contemporaneously with the other types--each remaining independent since that time.

Faure (1961) studied the isotopic composition of basalts and from this developed the theoretical upper mantle  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio development line shown in Figure 7. The tektites could have been differentiated from the mantle approximately 250 m.y. ago, as shown by the intersection of the tektite and the upper mantle line.

It is interesting to compare this data with the theory that the tektites were derived from the Moon, again assuming that the Rb/Sr ratios have not changed since the tektites were formed. Most students of the Moon (for example, Urey, 1952, p. 30; Spurr, 1948, p. 242; 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  $\text{Sr}^{87}/\text{Sr}^{86}$  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 generalized growth line as shown in Figure 7, and the present day  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio would be about 0.750, again in excess of that found in tektites. If it is assumed that the surface of the Moon has a chemical composition similar to tektites the present day  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, after a growth for 4.5 billion years from the primordial ratio of 0.700, would be between 0.78 and 0.90.

Conversely, if the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in tektites, approximately 0.719, is assumed to be representative of the lunar crust, and still assuming the Moon formed under the conditions discussed above, the Rb/Sr ratio of the material that would generate such a  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio from an initial ratio of 0.700 may be calculated. This growth line is shown on Figure 7 and the slope of this line corresponds to a Rb/Sr ratio of 0.1. The common terrestrial material whose Rb/Sr ratio most closely resembles this ratio is basalt (see Table 13), and the maria have commonly been theorized as being covered with basaltic lava flows. Thus a basalt that has remained on the surface of the Moon for 4.5 billion years should have about the same  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio as tektites. It is difficult to reconcile such a radical change in Rb/Sr ratio (from 0.1 to between 0.44 and 1.1) 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 (Lovering, 1960).

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 result of fusion of this differentiated material or the ejecta from volcanos during this time. As pointed out by Chapman (1960), 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. 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. However, the same evidence has been used by other investigators to conclude the maria are approximately 4.5 billion years old (Opik, 1960). Gilvarry's (1960) theory that the maria are composed of sedimentary rocks that were deposited by a hydrosphere which had a life time of the order of  $10^9$  years could account for observed Rb/Sr ratios in tektites.

In short, the Rb/Sr and  $Sr^{87}/Sr^{86}$  ratios (and the lead isotopic composition as determined by Tilton, 1958) 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; theories advocating this differentiation have been advanced but they have not been widely accepted by lunar investigators. The present

tektite Rb/Sr data is fairly consistent with such theories of recent and continuing differentiation of the Moon's crust.

5. Significance of the sympathetic variation of Rb/Sr ratios and  $Sr^{87}/Sr^{86}$  ratios in tektites.

Igneous rocks that are formed contemporaneously by crystal fractionation from a common source will differ in Rb/Sr ratios. At the time of their formation they all had the same initial  $Sr^{87}/Sr^{86}$  ratio but after fractionation they each developed radiogenic strontium in accordance with each Rb/Sr ratio. If the  $Sr^{87}/Sr^{86}$  development lines are drawn for each rock type they form an array of lines which converge back in time, intersecting at a point whose coordinates are the time of differentiation and the  $Sr^{87}/Sr^{86}$  ratio of the parent material. (See Figure 1). The common origin of a series of igneous rocks can be tested in this manner. If the rocks crystallized from parent materials having different  $Sr^{87}/Sr^{86}$  ratios or at different times the probability of three or more development lines meeting at a common point is small. Two different points of intersection would indicate two different source regions. In this section such a test for a common source region is applied to the tektites.

Figure 2 is a graph of the  $Sr^{87}/Sr^{86}$  ratios against time, showing the  $Sr^{87}/Sr^{86}$  development lines for four groups of tektites. The four areas represented, and the number of samples included by the average, are North America (3), Philippine Island (5), Indo China (5), and Bohemia (2). The lines are drawn from the data given in Table 11, with the error

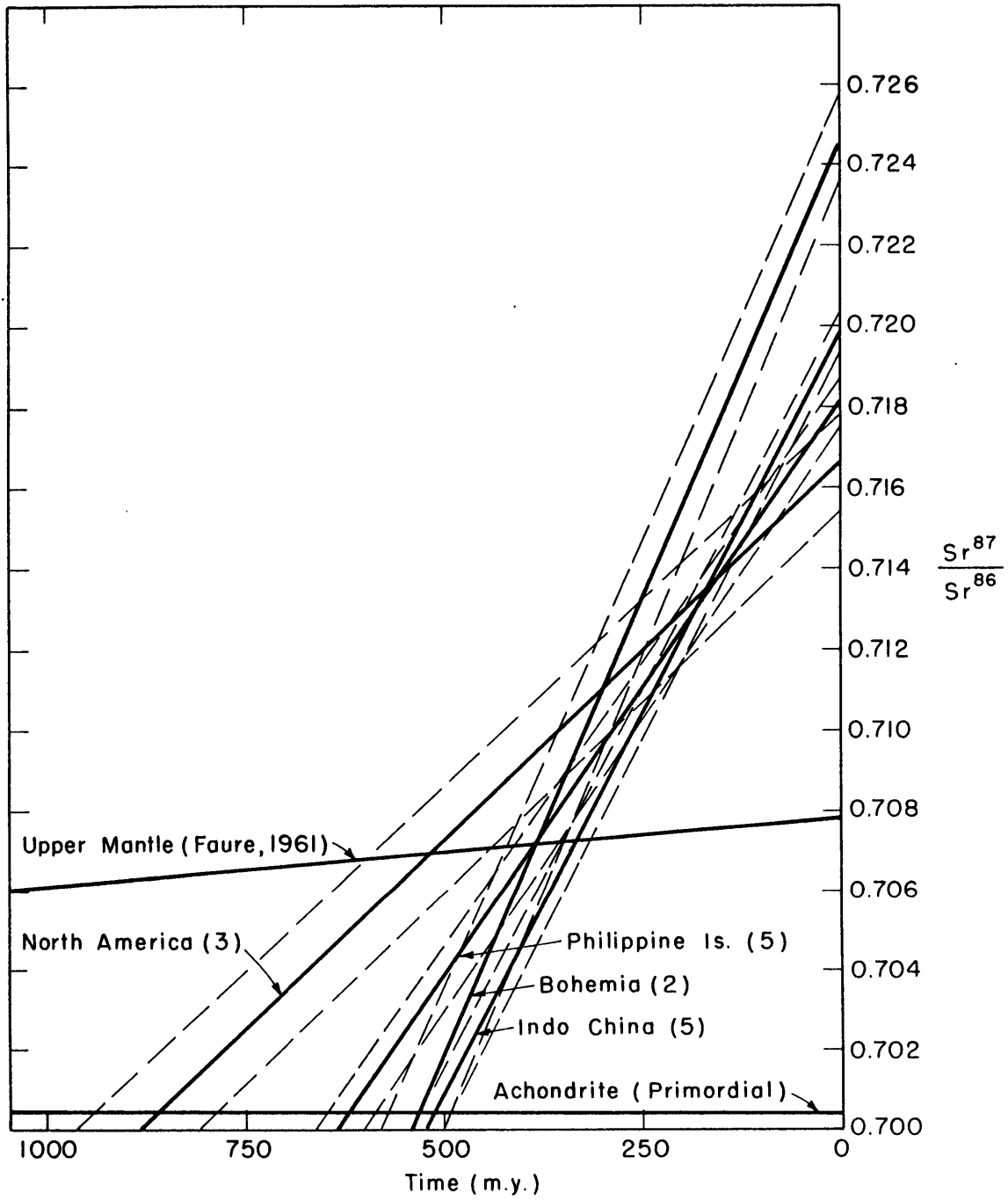


FIG. 8  $\text{Sr}^{87}/\text{Sr}^{86}$  vs TIME

envelopes shown by dashed lines. The envelopes are computed on the basis of one standard deviation of the mean ( $\bar{v}$ ) for the  $\text{Sr}^{87}/\text{Sr}^{86}$  and Rb/Sr ratios. The australites were not included in this diagram because the two samples analysed had different Rb/Sr ratios and an average would not be very meaningful.

One basic assumption made in drawing these development lines is that the Rb/Sr ratios have not changed since the tektite first formed. This was discussed earlier. A second assumption is that the tektites from one locality are related, other than just geographically. Otherwise the average  $\text{Sr}^{87}/\text{Sr}^{86}$  development line would be meaningless. The constancy of the Rb/Sr ratio of a particular group, in contrast to the difference between groups, supports this assumption. It can be seen from Figure 8 that the philippinites, indochinites, and North American tektite lines nearly intersect at a common point, with coordinates of  $\text{Sr}^{87}/\text{Sr}^{86} = 0.7135$  and time = 175 m.y. However, the error envelopes are so large the overlap of any two of these three lines extend from 0 to 350 m.y. The error envelopes of the two lines with the smallest errors (the indochinites and philippinites) overlap from approximately 50 to 250 m.y. The moldavite line, perhaps the poorest determined as it is based on only two samples, does not cross the other three lines at their common point of intersection. It intersects the North American line at 300 m.y. with an error range of from 200 to 400 m.y., and crosses or is within the error envelope of the other two lines from 250 to 550 m.y.

The  $\text{Sr}^{87}/\text{Sr}^{86}$  development line for the upper mantle, as determined by Faure (1961), is shown on the same diagram. The tektite development lines cross this line at ages that range from 325 m.y. (indochinites) to 525 m.y. (North American tektites). The moldavite and philippinite lines actually intersect on this line and the indochinite, philippinite, and moldavite lines have error envelopes that overlap on this line; if  $2\sqrt{\sigma}$  had been used the points of intersection of the tektite lines upon the upper mantle line would have all been within experimental error.

The primordial value of  $\text{Sr}^{87}/\text{Sr}^{86}$  determined from achondrites and discussed earlier, is also shown on Figure 8. Thus the maximum age for the tektites, given by the intersection of the tektite lines with the primordial line, range from 500 to 950 m.y.

In this discussion the term "tektite development line" has been used. The same remarks would apply to the parent material if the Rb/Sr ratio did not change either when the tektite formed from the parent or during the pre-tektite history of the parent.

It is interesting that Figure 8 shows a sympathetic variation of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios with the Rb/Sr ratios; if there was no sympathetic variation the lines would not converge back in time. Another way to show the sympathetic variation is given in Figure 9. In this figure the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios are plotted against the Rb/Sr ratios for the various

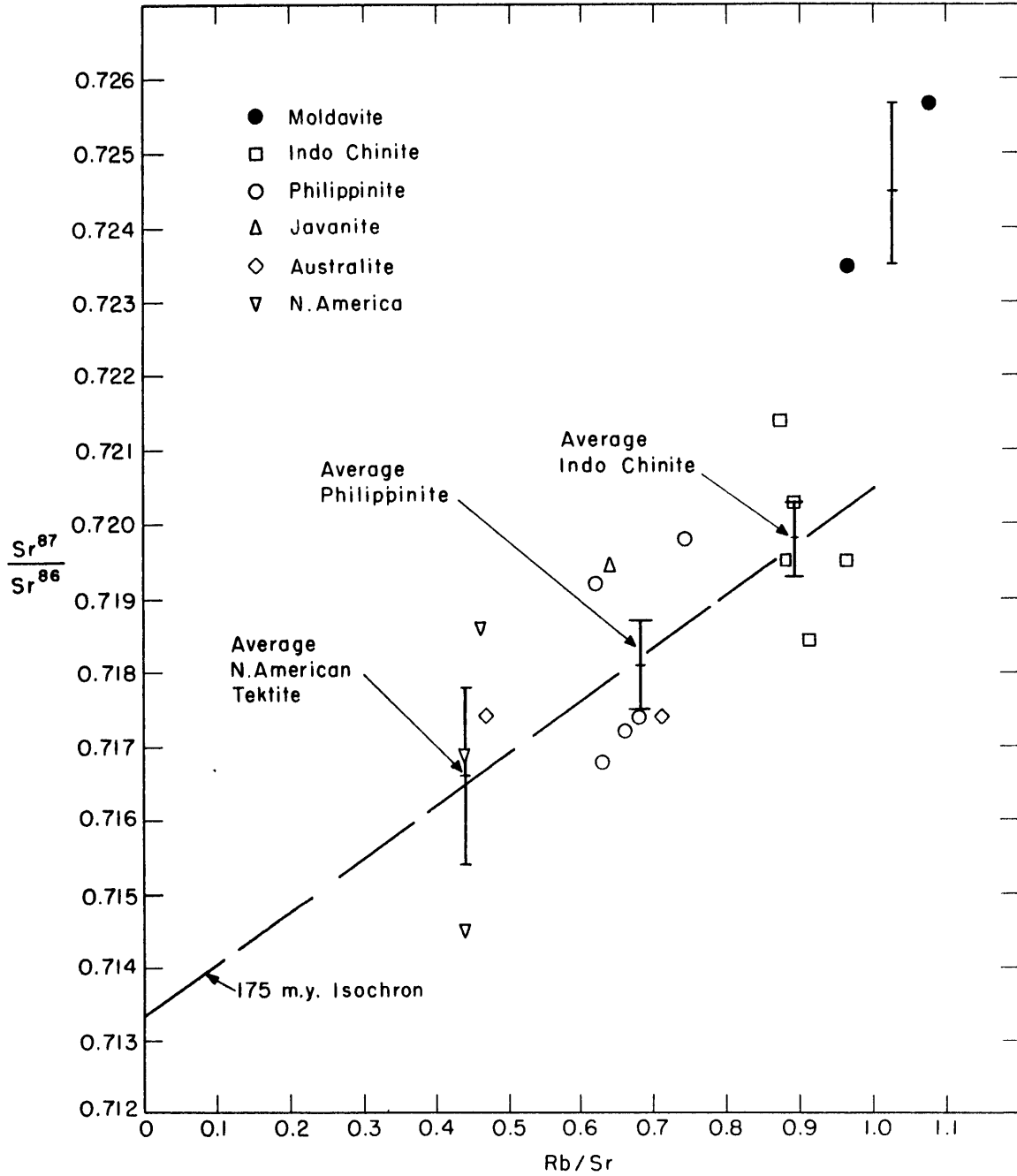


FIG. 9  $\frac{^{87}\text{Sr}}{^{86}\text{Sr}}$  vs Rb/Sr

tektites analysed, and the averages for the different groups are shown. The standard deviation of the mean ( $\bar{\sigma}$ ) for the  $\text{Sr}^{87}/\text{Sr}^{86}$  and the Rb/Sr ratios are shown by the lengths of the vertical and horizontal lines respectively. In such a diagram all samples of equal age will lie on a straight line. Such a line, the 175 m.y. isochron is drawn through the averages for the North American, Philippine, and Indo-China samples. The moldavites lie above this line, reflecting the fact that in Figure 8 their development line was above the point of intersection of the other three lines. More experimental work is necessary to refine this data, especially to see if the moldavites actually lie above the 175 m.y. isochron (i.e. do not intersect with the other three lines at the common point), but the present data seems more than coincidental or circumstantial and suggest that the North American, Philippine and Indo China tektites differentiated from a common source material approximately 175 m.y. ago. CERTAINLY IT IS DIFFICULT TO RECONCILE THIS DATA WITH TEKTITE PRODUCTION WITHIN THE LAST 30 m.y. FROM RANDOM MATERIALS OF DIFFERENT AGES AND COMPOSITIONS. Sympathetic variation between the  $\text{Sr}^{87}/\text{Sr}^{86}$  and Rb/Sr ratios in such a case would be highly unlikely.

This homogeneity of age values, whether these are actual ages of the tektites or the parent material, is indeed difficult to reconcile with any terrestrial origin in view of their widespread geographic locations and varying K-Ar ages. The extra-terrestrial theories are not much more attractive. One model that would explain their Rb/Sr-- $\text{Sr}^{87}/\text{Sr}^{86}$  ratio relations,



K-Ar ages, lack of cosmic-ray induced radio-activity, distribution in restricted strewnfields, and second period of melting would be as follows:

1) The fusion and ejection of large bodies from the surface of the Moon or some other body in the solar system about 175 m.y. ago. The glassy blocks would have a common  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio, which would be the same as the parent material, approximately 0.713. However, due to differences in selective volatility the Rb/Sr ratios of the various bodies were different. The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.713 is compatible with a basaltic surface 4.5 billion years old, but the compositional changes necessary to derive a tektite from basalt do not seem possible by high temperature fusion. A more plausible occurrence would be production of the large tektite bodies from material that was similar to tektites in composition due to recent differentiation or some change that increased its Rb/Sr ratio. Tilton (1959), after analyzing three tektites for lead isotopes and one tektite for uranium and thorium, reached the conclusion that the tektites, or parent material, had undergone differentiation within the last tens of millions of years. This work should be extended to check the apparent agreement with this investigation.

2) The bodies independently spiraled toward the Earth, arriving in the Earth's atmosphere 30 to less than 1 m.y. ago. Since their common origin each had developed  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in accordance with their different Rb/Sr ratios. Since each body was of considerable size, the interiors were protected from cosmic rays.

3) The large bodies broke up in the Earth's atmosphere and the tektites formed from a particular body fell in a specific strewnfield. The bodies probably entered the Earth's atmosphere along orbits nearly parallel to the surface of the Earth (O'Keefe, 1960) since considerable ablation of the individual tektite took place. During this ablation the tektites were heated sufficiently to cause the escape of argon, giving rise to the young argon ages.

The principal difficulty of any extra-terrestrial origin for tektites is the existence on some body in the solar system of suitable parent material. However, it is believed the Rb/Sr -  $\text{Sr}^{87}/\text{Sr}^{86}$  relationship, and the lack of large variations in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in tektites, makes any of the proposed terrestrial theories even more unattractive.

### F. Conclusions

1) The average  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in 18 tektites is  $0.7190 \pm 0.0006$ . Thus the earlier work of Pinson et al (1958) on the strontium isotopic composition of tektites was in error and tektites do contain radiogenic strontium.

2) As the non-radiogenic isotopes of strontium are perfectly normal the extra-solar system hypothesis of Kohman (1958) is not supported.

3) Rubidium and strontium contents of tektites from a given locality are very similar, but small differences exist between localities. The Rb/Sr ratios in tektites are within the range found in shale and granite but do not show the variation that is observed in these materials.

4) Tektites do not exhibit the variation in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios one would expect to find if they are the result of random fusion of terrestrial materials, particularly acid rocks such as granites or siliceous shale.

5) Tektites could not have been derived from any chondrites which have been measured. They could have been derived from achondrites approximately 500 to 1000 m.y. ago, or from the upper mantle approximately 350 to 500 m.y. ago.

6) If the tektites were derived from the Moon the results of this investigation suggest either (a) the tektites must have been formed somehow from a basaltic type parent material if the surface of the Moon is old (i.e.  $\sim 4.5$  b.y.) or (b) there must have been recent differentiation of the surface of the Moon (i.e. within the last 500 m.y.). If the Moon's

surface has remained unchanged for the longer period the tektites could not have formed from chondritic, granitic, or tektitic type material.

7) Sympathetic variation of the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios with the  $\text{Rb}/\text{Sr}$  ratios occurs in tektites and strongly suggests that the tektites differentiated from a common source material approximately 175 m.y. ago. This coupled with their widespread geographic distribution and young K-ar ages make a terrestrial origin quite unlikely.

## SECTION III

## A STUDY OF THE CHEMICAL COMPOSITION OF TEKTITES

A. Introduction

Barnes (1940) compiled all the analyses of tektites available at that time. He listed 61 analyses, not including the questionable Darwin Glass and Lybian Desert Glass; these included 10 moldavites, 2 bediasites, 24 indochinites, 4 philippinites, 9 billitonites and associated tektites, 9 australites, and 3 Ivory Coast tektites. Since 1940 the only complete major element analyses of tektites to appear in the literature are one bediasite (Barnes, 1956), a new tektite from Martha's Vineyard, Massachusetts (Kaye, et al, 1961), and one Georgia tektite (Clarke and Carron, 1961). Pinson and Schnetzler (1959) reported the average K, Na, Fe, Mn, and Ti contents of 11 philippinites and indochinites, and Taylor (1960) reported the alkali element contents of 14 australites.

From the published analyses it is obvious 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 is 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.

Therefore, it seemed desirable to analyse 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 probable terrestrial origin.

Unfortunately the present tektite collections in this country are rather small. Therefore, it was not possible to obtain a thorough sampling of all the major fields; however, a sufficient number of indochinites and philippinites were obtained to test for variations within, and between, these two groups. Taylor's (1960) study of the alkali elements in australites was the first phase of proposed complete chemical analyses, so it should be possible to compare the philippinites and indochinites with the australites when his completed work appears. The analyses reported in this paper on the philippinites are especially important as only four analyses of this group have been published. It is by far the largest, in number of samples, of any of the tektite groups. As stated in Section I, approximately 500,000 tektites have been collected from the

Philippine Islands. A number of samples were obtained from two rather restricted sites in the Philippines, so it is possible to study the variation of composition within a restricted group, as well as between the larger localities.

## B. Chemical Analyses

### 1. Analytical Procedures

The majority of analyses reported in this paper were made by the "rapid silicate" method of Shapiro and Brannock (1956). 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. As both silica and aluminum are determined from a different weighing from the rest of the constituents in the rapid silicate procedure, considerable time and effort would be saved if silica was analysed by X-ray fluorescence techniques at the same time as the aluminum. This was done in approximately 10 of the silica analyses.

### "Rapid silicate" Techniques

The rapid silicate procedures of Shapiro and Brannock (1956) are primarily colorimetric methods of analysis. The intensity of light passing through various colored complexes of  $SiO_2$ ,  $Al_2O_3$ , total Fe,  $TiO_2$ , MnO, and  $P_2O_5$  is determined on a spectrophotometer, while CaO and MgO are determined by photometric titration.  $Na_2O$  and  $K_2O$  are determined by flame photometry. The rapid silicate method is especially attractive because most of the determinations are independent of each



other so that gross errors in one determination do not affect subsequent results. Also, the manipulations are simpler than in conventional methods of silicate analysis (there are no separations, precipitations, etc.) so that gross errors due to improperly performed procedures are not usually encountered.

Beckman Model B spectrophotometers were used in the colorimetric and photometric titration procedures, and a Perkin-Elmer Model 146 flame photometer was used in the determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .

In the method of Shapiro and Brannock (1956)  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  are determined from a solution obtained by fusing approximately 50 mg. of powdered sample with  $\text{NaOH}$  in a nickel crucible, and diluting to 1 liter.  $\text{SiO}_2$  is determined colorimetrically as the molybdenum blue complex, and  $\text{Al}_2\text{O}_3$  is determined colorimetrically as the orange complex of calcium and Alizarine red-S. Small corrections for the amounts of iron and titanium in the sample are applied to the aluminum results. National Bureau of Standards soda felspar no. 99 is used as the standard in both the silica and aluminum procedures.

All the other major elements, except  $\text{FeO}$ , are determined on aliquots of a solution made by digesting approximately 0.5 grams of powdered sample with  $\text{HF}$  and  $\text{H}_2\text{SO}_4$  in a platinum dish over a steam bath, and diluting to 250 mls.

Total iron is determined photometrically as the orange ferrous orthophenanthroline complex using ferrous ammonium sulphate for the standard.

$TiO_2$  is determined photometrically as the yellow complex produced by the reaction of titanium with tiron after reduction of the blue ferric tiron complex with sodium dithionite. National Bureau of Standards titanium dioxide no. 154 is used as the standard.

$MnO$  is determined photometrically after the manganese has been oxidized to permanganate by potassium periodate. The standard used is National Bureau of Standards manganese ore no. 25b.

$P_2O_5$  is determined photometrically as the yellow molybdivanadophosphoric acid complex. The standard is National Bureau of Standard phosphate rock no. 120.

The automatic photometric titration procedure, employing a spectrophotometer and recorder, as described by Shapiro and Brannock (1956), 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.

Na<sub>2</sub>O and K<sub>2</sub>O are determined on a flame photometer, using Li as an internal standard. Standards covering the concentration range of the samples are prepared from analytical reagent grade sodium chloride and potassium acid phthalate.

The FeO determination, as described in the rapid silicate procedure of Shapiro and Brannock (1956) is the classical dichromate titration procedure. It consists of decomposing approximately 0.5 grams of the powdered sample in a boiling mixture of sulfuric and hydrofluoric acid in a closed platinum crucible, and then titrating the solution with potassium dichromate. Diphenylamine sulfonic acid is used as the indicator. As the FeO is rather easily oxidized by air, and as the method is slow and necessitates great care, Shapiro (1960) has devised a spectrophotometric method of determining FeO which requires less sample and can be carried out much faster. 10 mg. of sample plus approximately 20 mg. of powdered orthophenanthroline are dissolved in HF and H<sub>2</sub>S<sub>2</sub>O<sub>4</sub> on a steam bath, the orthophenanthroline complexing the Fe<sup>+2</sup> as it goes into solution. The absorbance of the resulting orange complex is measured on a spectrophotometer, and compared with the absorbance of a rock standard. W-1 was used as standard in this work. A comparison of the two methods

of FeO analyses is shown in Table 14, which gives the results for five samples that were analysed both photometrically and by titration. There appears to be very good agreement between the two methods. Although the precision is poorer in the photometric method the time saved by using this method allows more replicate analyses to be made, and the saving in sample is important in cases where the sample available is limited.

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.

Fe<sub>2</sub>O<sub>3</sub> is determined by difference between the FeO and total iron results. Thus MgO and Fe<sub>2</sub>O<sub>3</sub> are the only determinations that are not independent, except for small corrections for iron and titanium that must be applied to the aluminum results.

Sample solutions were made in duplicate from two separate portions of the powdered tektite, which had previously been dried in an oven at 105° C for 1 to 2 hours. The solutions were stored in polyethylene bottles. In the SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, total iron, CaO, (CaO + MgO) as MgO, Na<sub>2</sub>O, and K<sub>2</sub>O determinations duplicate portions of each solution were analysed, 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

Table 14

Comparison of titration and photometric determinations  
for FeO

Sample No.	Titration	Average	Spectrophotometric	Average
T4091	2.18, 2.27	2.22	2.15	2.15
T3379	4.30, 4.46	4.38	4.36, 4.50, 4.10, 4.44	4.35
T3993	4.88, 4.89	4.88	4.67, 4.74, 4.77	4.73
T3985	4.31, 4.30	4.30	4.28	4.28
T3965	4.78, 4.84	4.81	5.02, 4.80	4.91

determinations were made from 16 instrument readings in total. One titration of CaO and (CaO + MgO) as 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 (Phinney, 1959). 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 be analysed in any one day were picked at random; therefore the tektites from any particular area were analysed at various times during the period of the investigation and not as a group.

#### X-ray fluorescence techniques

Chodos and Engel (1961) have 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 only to about 5% of the amount present. They attributed this error to matrix effects, as their samples varied considerably in major element composition.

Professor John Hower of the M.I.T. Geology Department has also been working on the application of this method of analysis to major elements, and has primarily been concerned with determination of the enhancement and absorption corrections that must be applied if this method is to be used over wide ranges of composition. He suggested that tektites, with their very limited compositional range, would be ideal materials to analyse by X-ray fluorescence techniques. As all the major elements except silica and aluminum had been analysed in the samples, and as the aluminum determination is perhaps the least satisfactory of the rapid silicate procedures, it was decided to attempt to analyse for these two elements by X-ray

fluorescence. It was believed this method might be successful in this investigation, where it had failed for Chodos and Engel (1961), for three reasons: 1) the matrix problem should be essentially non-existent, at least among the Pacific Ocean area tektites, 2) the tektites, being a fairly homogeneous glass, should not exhibit the inhomogeneity of particle size and mineralogical composition that would be found in a powdered rock sample, and 3) the machine available allows the rapid comparison of standard and sample, which was not the case in the machine used by Chodos and Engel, thus reducing instrumental drift.

One disadvantage of the X-ray fluorescent unit used is that the samples are inverted when put into the machine, making it necessary to have a mylar window over the sample holder to contain the powdered sample within the holder. It was found the 0.5 mil mylar window cut the intensity of the beam for the silica  $K\alpha$  radiation by a factor of  $\sim 10$  and for aluminum  $K\alpha$  radiation by a factor of  $\sim 25$ . This reduction in beam intensity greatly increases the counting time necessary for the desired precision, and nullifies the advantage of speed this method originally promised. Some of the samples had not been completely powdered, and the solid portions were large enough to fill the aperture in the sample holder shield; thus they could be run as solids and the mylar window could be eliminated. However, the majority of the samples had been completely powdered so an attempt was made to press them into a brickette under high



pressure. This procedure had been successfully applied to mixtures of oxides, and a few powdered rocks, by Hower and his assistants, but the powdered tektite glasses would not form hard brickettes, and the danger of losing the whole sample was felt to be too great to pursue this approach. An attempt to coat a porcelain plate with the powdered sample in an ultra-high speed centrifuge failed due to apparent contamination of the sample with aluminum and silica from the plate. Thus it was decided to sacrifice speed, and use the mylar window with the powdered samples. Larger shields were used for the powdered samples than for the solids so that the counting rates for the powders were only a factor of 3 lower for silica and 8 lower for aluminum than the counting rates of the solids.

The preparation and packing of the powdered samples were the same as described in Section II. A cut surface of the solid which was free from bubbles was polished to eliminate any effect of surface irregularity, and mounted behind a shield which did not have a mylar window. The sample was exposed to the X-ray beam through a 0.4 inch square aperture in the shield. It was found the area of this aperture varied by as much as 6% between the largest and smallest used, so that it was necessary to accurately determine the differences in area and make a corresponding correction to the data.

The X-ray fluorescent unit, and general procedures, are described in Section II. The operating conditions were: ENDT crystal; pulse height analyser base volts = 1.50, window volts 6; flow proportional counter volts = 1650. Number of

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

The standards used were selected tektites which had been analysed for silica and aluminum by rapid silicate procedures. Table 15 compares the values obtained by the two methods. The numbers in parentheses are the number of determinations by the X-ray fluorescence method. It can be seen that the  $\text{Al}_2\text{O}_3$  results for the powdered samples as well as for the solid samples are in very good agreement. The maximum difference between the two methods is about 2% of the amount present, while the average difference is about 1% of the amount present. In the last two samples listed in Table 15 the  $\text{Al}_2\text{O}_3$  powder and solid X-ray fluorescence results are compared. The good  $\text{Al}_2\text{O}_3$  agreement between rapid silicate and X-ray fluorescent methods is rather surprising considering the spread of values obtained for  $\text{Al}_2\text{O}_3$  on replicate determinations by the rapid silicate procedure, but suggests the average of four photometric determinations is quite good.

The  $\text{SiO}_2$  X-ray fluorescence results, however, are 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  $\text{SiO}_2$ .

However, the  $\text{SiO}_2$  determinations in the solid samples are in good agreement with the values obtained by the rapid silicate procedure. Another reason to believe the solid sample

Table 15

Comparison of Rapid Silicate and X-ray Fluorescence Analyses

Sample no.	for SiO <sub>2</sub> & Al <sub>2</sub> O <sub>3</sub>			
	Al <sub>2</sub> O <sub>3</sub>		SiO <sub>2</sub>	
	Rap.Sil.Avg.	X-ray Fl.Avg.	Rap.Sil.Avg.	X-ray Fl.Avg
<b><u>Powders</u></b>				
T3379	13.34	13.34 (1)	71.8	69.9 (2)
T3995	12.28	12.29 (1)	71.2	74.9 (3)
T3993	12.96	12.84 (5)	72.9	73.2 (3)
T3985	12.96	12.98 (12)	72.3	72.9 (17)
T3987	12.77	12.53 (1)	-	-
T3959	13.90	14.06 (1)	71.1	73.1 (5)
T3965	15.23	15.40 (1)	68.9	68.0 (2)
<b><u>Solids</u></b>				
T3983	13.82	13.93 (2)	70.8	70.6 (3)
T3984	-	-	71.2	71.1 (3)
T3988	-	-	73.0	73.1 (3)
T4215	15.20 *	15.32 (2)	-	-
T3990	13.62 *	13.56 (2)	-	-

\* Value determined as powder by X-ray fluorescence

$\text{SiO}_2$  results are acceptable, while the powdered sample values are not, is the fact that the constituents total close to 100% using the solid sample  $\text{SiO}_2$  results, while the totals using the powdered sample  $\text{SiO}_2$  results vary approximately between 95% and 107%.

From the data given in Table 15, and the confirmation by totaling to  $\sim 100\%$ , 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.

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 of uniform size--unfortunately, this was not checked. However, they should not have exhibited the extreme variation found in the square windows used for the solid samples, since the wells were round and it is much easier to machine a round hole than cut a square hole to a standard size.

## 2. Precision and Accuracy

Mercy (1956) presents an extensive discussion on the precision and accuracy of the rapid silicate method of analysis. However, the procedures for Al, total Fe, Ti, Ca, and Mg have been changed since his work. Phinney (1959), Brownlow (1959) and Moore (1960) discuss the precision and accuracy found in routine analysis in the M.I.P. rapid silicate laboratory.

As most of the values reported in this paper are the mean of replicate determinations, an estimate of the precision is possible from the tektite data. In addition, the rock standard G-1 and W-1 (Fairbairn et al, 1953) were interspersed with the samples during the analyses to monitor the results, so an estimate of the accuracy may be obtained.

The statistical terms used in this section have been defined in Section II. In order to illustrate the precision, or reproducibility of the analyses, the sample having the greatest precision error for each element was determined by inspection, and is given in Table 16. In addition the precision for each element was calculated for a sample picked at random. These are also shown in Table 16. The first row for each element represents the most pessimistic order of precision while the second row is probably more representative of the general precision of the data. The standard deviation of the mean ( $\bar{\sigma}$ ) is the most important statistic as all results, except some of the aluminum results obtained by X-ray fluorescence, are the mean of replicate analyses. These results, together with the data in Table 18 on the precision of the analyses of G-1 and

Table 16 Precision of the Analytical Results

	Sample no	n	$\bar{x}$	$\sigma$	C	$\bar{\sigma}$	$\bar{C}$
<b>RAPID SILICATE</b>							
SiO <sub>2</sub>	T3995	8	71.2	0.72	1.0%	0.25	0.35%
	T3379	4	71.8	0.25	0.34%	0.12	0.17%
Al <sub>2</sub> O <sub>3</sub>	T3985	6	12.96	0.40	3.1%	0.16	1.2%
	T3959	4	13.90	0.29	2.1%	0.15	1.0%
Total Fe	T3993	4	5.93	0.15	2.5%	0.07	1.2%
	T3978	4	5.32	0.05	0.9%	0.03	0.5%
MgO	T3983	4	2.51	0.09	3.7%	0.05	1.9%
	T3995	4	2.96	0.04	1.2%	0.02	0.6%
CaO	T4216	4	3.47	0.13	3.8%	0.07	1.9%
	T3379	4	2.98	0.06	2.2%	0.03	1.1%
Na <sub>2</sub> O	T4216	4	1.84	0.08	4.0%	0.04	2.0%
	T3995	4	1.54	0.03	2.0%	0.02	1.0%
K <sub>2</sub> O	T3993	4	2.27	0.07	3.2%	0.04	1.6%
	T3987	6	2.49	0.03	1.2%	0.01	0.5%
MnO	T4104	2	0.122	0.006	5.2%	0.005	3.6%
	T3986	3	0.102	0.003	2.5%	0.001	1.0%
<b>FeO SPECTROPHOTOMETRICALLY</b>							
	T3379	4	4.35	0.18	4.1%	0.09	2.1%
	T3993	3	4.73	0.05	1.1%	0.03	0.7%
<b>X-RAY FLUORESCENCE</b>							
SiO <sub>2</sub>	T3991	4	73.68	1.11	1.5%	0.56	0.76%
	T3983	3	70.57	0.50	0.7%	0.29	0.41%
Al <sub>2</sub> O <sub>3</sub>	T3993	5	12.84	0.29	2.3%	0.13	1.0%
	T3985	12	12.98	0.27	2.1%	0.09	0.7%

W-1, suggest that the average precision ( $\bar{c}$ ) of the rapid silicate data presented in this section is approximately:  $\text{SiO}_2$ , 0.2%;  $\text{Al}_2\text{O}_3$ , 1.4%;  $\text{TiO}_2$ , 1.5%; total Fe, 0.5%;  $\text{MgO}$ , 1%;  $\text{CaO}$ , 1%;  $\text{Na}_2\text{O}$ , 1%;  $\text{K}_2\text{O}$ , 1%; and  $\text{MnO}$ , 2%. These values agree in general with those given by Mercy (1956, p. 168). The precision ( $\bar{c}$ ) of the photometric  $\text{FeO}$  determinations is approximately 2%, the  $\text{SiO}_2$  X-ray fluorescence determinations 0.5%, and the  $\text{Al}_2\text{O}_3$  X-ray fluorescence determinations 1% or less.

The results of replicate analyses of G-1 and W-1 are given in Table 17, and the statistical calculations of precision of the data are given in Table 18. The columns in Table 17 labeled A, B, C, etc. represent different weighings, while the numbers in parentheses are the number of determinations that were made of the sample. The values given the column headed "average" were calculated from the values given in columns A, B, C, etc., weighing each value by the number of determinations that were made of that solution. The accepted values ( $\bar{x}$ ) for G-1 and W-1, and the "acceptable range" ( $\bar{x} - S$ ,  $\bar{x} + S$ ) are from Stevens (1960, p. 32). The only results that are outside the "acceptable range" are  $\text{CaO}$  in G-1 and  $\text{SiO}_2$  in W-1. 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 flame photometric determinations listed by Steven (1960, p. 36). The discrepancy between conventional and flame photometric determinations of this oxide should be investigated.

As most of the analytical procedures used are independent of each other a total of the constituents close to 100% is

Table 17 Analyses of G-1 and W-1

G-1	A	B	C	D	E	Average (weighed)	Accepted Value	x-s x+s
SiO <sub>2</sub>	72.57 (2)	-	-	-	-	72.57 (2)	72.35	{ 71.87 72.83
Al <sub>2</sub> O <sub>3</sub>	15.40 (1)	13.71 (4)	14.22 (4)	-	-	14.12 (9)	14.32	{ 13.95 14.69
TiO <sub>2</sub>	-	0.21 (3)	0.24 (2)	-	-	0.22 (5)	0.26	{ 0.22 0.30
FeO	0.91 (1)	-	-	-	-	0.91 (1)	0.98	{ 0.89 1.10
Total Fe**	1.98 (8)	2.08 (2)	1.95 (4)	-	-	1.98 (14)	2.04	{ 1.76 2.32
MgO	0.37 (6)	0.38 (3)	-	0.44 (1)	-	0.38 (10)	0.40	{ 0.27 0.53
CaO	1.19 (6)	1.28 (4)	-	1.30 (2)	1.23 (2)	1.23 (14)	1.40	{ 1.28 1.52
Na <sub>2</sub> O	3.52 (3)	3.42 (6)	3.45 (2)	-	3.43 (5)	3.45 (16)	3.31	{ 3.08 3.54
K <sub>2</sub> O	-	5.39 (2)	5.58 (2)	-	5.34 (2)	5.44 (6)	5.42	{ 5.03 5.81
MnO	0.030 (2)	-	0.020 (2)	-	0.026 (2)	0.025 (6)	0.03	{ 0.02 0.04
P <sub>2</sub> O <sub>5</sub>	0.08 (2)	-	-	0.06 (4)	0.10 (2)	0.07 (8)	0.10	{ 0.04 0.16
						99.39	99.52	

\* Average Fe<sub>2</sub>O<sub>3</sub> value 0.97, accepted value 0.95



Table 17 -cont

W-1	A	B	C	D	Average (weighed)	Accepted Value	x-s x s
SiO <sub>2</sub>	53.15 (4)	53.04 (6)	-	-	53.09 (14)	52.40	{ 52.07 52.73
Al <sub>2</sub> O <sub>3</sub>	14.72 (4)	-	-	16.22 (1)	15.02 (5)	15.11	{ 14.98 15.74
TiO <sub>2</sub>	1.08 (4)	1.12 (1)	1.08 (4)	1.07 (2)	1.08 (11)	1.07	{ 0.87 1.27
FeO	8.57 (1)	8.53 (1)	-	-	8.55 (2)	8.63	{ 8.22 9.04
Total Fe*	-	11.14 (2)	11.04 (6)	-	11.09 (8)	11.22	{ 10.94 11.50
MgO	6.79 (2)	-	-	6.58 (2)	6.68 (4)	6.58	{ 6.23 6.93
CaO	10.78 (6)	-	10.96 (1)	-	10.81 (7)	10.97	{ 10.81 11.13
Na <sub>2</sub> O	2.23 (3)	2.24 (4)	2.26 (8)	2.24 (5)	2.25 (20)	2.07	{ 1.87 2.27
K <sub>2</sub> O	-	0.69 (2)	0.84 (3)	0.75 (4)	0.77 (9)	0.67	{ 0.54 0.80
MnO	0.165(2)	0.174(2)	0.174(2)	0.162(2)	0.169(8)	0.17	{ 0.12 0.22
P <sub>2</sub> O <sub>5</sub>	0.12 (6)	-	-	0.14 (2)	0.13 (8)	0.15	{ 0.09 0.21
					100.14	99.44	

\* Average Fe<sub>2</sub>O<sub>3</sub> value 1.60, accepted value 1.62

Table 18 Precision of Analyses of G-1 and W-1

G-1	$\bar{X}$	n	$\bar{\sigma}$	$\bar{C}$	$\sigma$	C
SiO <sub>2</sub>	72.57	2				
Al <sub>2</sub> O <sub>3</sub>	14.12	9	0.19	1.3%	0.57	4.0%
TiO <sub>2</sub>	0.22	5	0.01	4.1%	0.02	9.0%
Total Fe	1.98	14	0.03	1.3%	0.09	4.7%
MgO	0.38	10	0.01	3.2%	0.04	9.7%
CaO	1.23	14	0.02	1.5%	0.07	5.7%
Na <sub>2</sub> O	3.45	16	0.02	0.51%	0.07	2.0%
K <sub>2</sub> O	5.44	6	0.05	0.9%	0.12	2.2%
MnO	0.025	6	0.003	11.0%	0.007	26.0%
P <sub>2</sub> O <sub>5</sub>	0.07	8	0.008	12.0%	0.023	33.0%
<hr/>						
W-1						
SiO <sub>2</sub>	53.09	14	0.13	0.25%	0.50	0.94%
Al <sub>2</sub> O <sub>3</sub>	15.02	5	0.35	2.3%	0.77	5.1%
TiO <sub>2</sub>	1.08	11	0.006	0.5%	0.02	1.7%
Total Fe	11.09	8	0.02	0.2%	0.06	0.5%
MgO	6.68	4	0.06	0.9%	0.13	1.9%
CaO	10.80	7	0.04	0.4%	0.11	1.0%
Na <sub>2</sub> O	2.25	20	0.008	0.34%	0.04	1.66%
K <sub>2</sub> O	0.77	9	0.04	4.8%	0.11	14.0%
MnO	0.169	8	0.002	1.4%	0.006	3.8%
P <sub>2</sub> O <sub>5</sub>	0.13	8	0.01	9.8%	0.04	28.0%

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 19 that all the analyses total close to 100%. The data in Tables 17 and 19, therefore, indicates that the accuracy of this work is acceptable.

### 3. Results

The results of the chemical analyses are given in Table 19. Included are partial or complete analyses of 37 tektites, 2 "americanites," 1 sample of soil from a tektite site in Texas, and 6 obsidians. The specific gravity and total iron contents are also listed. The index of refraction is given for a few of the tektites.

The columns labeled A and B in all but three cases represent duplicate weighings of the sample, and, as discussed above, for most of the constituents the result in each column is the average of duplicate analyses. Insufficient amounts of samples T4102, T4104, and T3310 were available to allow duplicate weighings; therefore the columns A and B in these three cases are duplicate analyses from only one weighing.

The results obtained by X-ray fluorescence are designated by an asterisk--all results not so designated were obtained by rapid silicate techniques. In most X-ray fluorescence SiO<sub>2</sub> determinations, three independent measurements were

made and all three are given in the table. If both rapid silicate and X-ray fluorescence determinations were made on a sample the rapid silicate results are given in Table 19. A comparison of the results obtained by the two methods in these samples is given in Table 15.

Figure 10 shows in graphical form the results listed in Table 19 for Si, Al, total Fe, Mg, Ca, Na, and K. The data has been recomputed from the oxide to the element. Figure 10 was drawn to enable the reader to quickly comprehend the type of variation and degree of scatter exhibited by each locality and the differences between each locality. The samples are grouped along the abscissa by localities. The order of the samples within each group is completely arbitrary, and the order of the groups is also completely arbitrary. This diagram is not a variation diagram in the usual sense of the word as there is no physical or chemical basis for listing the samples in any particular order. The average contents for the various elements are shown by dashed lines for the indochinites and philippinites. The rubidium and strontium results were obtained from Table 8. Also included in this diagram is an analyses of a Georgia tektite by Clarke and Carron (1961) - the complete analysis is given in Table 24.

Table 19 Analytical Results

## PHILIPPINITES

	T3959			T3960			T3961		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>	70.6	71.3	71.0	72.4	71.8	72.1	71.6	70.2	70.9
Al <sub>2</sub> O <sub>3</sub>	14.16	13.64	13.90	12.11	12.89	12.50	13.90	13.38	13.64
TiO <sub>2</sub>	0.78	0.79	0.78	0.77	0.79	0.78	0.79	0.79	0.79
Fe <sub>2</sub> O <sub>3</sub>	0.75	0.99	0.37	0.66	0.78	0.72	0.68	0.95	0.82
FeO	4.19	4.39	4.29	4.34	4.23	4.23	4.30	4.06	4.18
MgO	2.68	2.71	2.70	2.61	2.56	2.58	2.61	2.73	2.67
CaO	2.95	2.75	2.95	2.92	2.88	2.90	3.26	3.14	3.20
Na <sub>2</sub> O	1.38	1.37	1.37	1.29	1.31	1.30	1.35	1.37	1.36
K <sub>2</sub> O	2.36	2.38	2.37	2.34	2.38	2.36	2.32	2.31	2.31
MnO	0.084	0.095	0.089	0.093	0.091	0.091	0.080	0.078	0.079
P <sub>2</sub> O <sub>5</sub>	0.081	0.078	0.080	0.088	0.092	0.090	0.090	0.100	0.095
total			100.40			99.70			100.05
Fe <sup>o</sup>			3.95			3.83			3.82
S.G.			2.460			2.455			2.456
n			n.d.			1.5074			n.d.

Table 19 - cont

PHILIPPINITES									
T3962			T3964			T3965			
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	70.4	70.0	70.2	-	-	-	69.3	68.5	68.9
Al <sub>2</sub> O <sub>3</sub>	14.04	14.14	14.09	14.01	-	14.01*	14.93	15.53	15.23
TiO <sub>2</sub>	0.81	0.84	0.83	0.77	0.76	0.76	0.84	0.86	0.85
Fe <sub>2</sub> O <sub>3</sub>	0.80	0.80	0.80	0.55	0.51	0.53	0.54	0.47	0.50
FeO	4.15	4.20	4.18	4.14	4.51	4.33	4.78	4.84	4.81
MgO	2.68	2.66	2.67	2.31	2.33	2.32	2.77	2.65	2.71
CaO	3.25	3.34	3.30	3.34	3.43	3.38	3.34	3.19	3.27
Na <sub>2</sub> O	1.27	1.33	1.30	1.77	1.75	1.76	1.28	1.30	1.29
K <sub>2</sub> O	2.28	2.34	2.31	2.55	2.57	2.56	2.47	2.45	2.46
MnO	0.092	0.099	0.096	0.090	0.087	0.088	0.095	0.069	0.082
P <sub>2</sub> O <sub>5</sub>	0.104	-	0.104	n.d.	n.d.	-	0.062	-	0.062
Total			99.88						100.16
Fe <sup>o</sup>			3.80			3.74			4.09
S.G.			2.454			2.411			2.429
n			1.511			n.d.			n.d.

\* Determined by X-ray fluorescence analysis

Table 19 - cont

## PHILIPPINITES

	T3379			T3765			T3978		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	71.6	72.0	71.8				69.50	70.52 70.37	70.13
Al <sub>2</sub> O <sub>3</sub>	13.63	13.06	13.34	14.11	-	14.11*	14.68	14.64	14.66
TiO <sub>2</sub>	0.76	0.78	0.77	0.74	0.84	0.79	0.80	0.81	0.80
Fe <sub>2</sub> O <sub>3</sub>	0.72	0.54	0.63	0.94	0.92	0.93	0.69	0.61	0.65
FeO	4.30	4.46	4.38	4.08	4.17	4.13	4.18	4.24	4.21
MgO	2.64	2.56	2.60	2.49	2.56	2.53	2.41	2.48	2.44
CaO	2.95	3.01	2.98	3.58	3.50	3.54	3.29	3.27	3.28
Na <sub>2</sub> O	1.35	1.31	1.33	1.31	1.33	1.32	1.55	1.54	1.55
K <sub>2</sub> O	2.32	2.38	2.35	2.49	2.52	2.51	2.59	2.54	2.56
MnO	0.077	0.091	0.084	0.118	0.119	0.118	0.093	0.100	0.096
P <sub>2</sub> O <sub>5</sub>	0.081	0.054	0.068	n.d.	n.d.	-	n.d.	n.d.	-
Total			100.33						100.35
Fe <sup>0</sup>			3.85			3.85			3.72
S.G.			n.d.			2.452			2.432
n			n.d.			n.d.			1.5105

\* Determined X-ray fluorescence

## PHILIPPINITES

Table 16 - cont

	T3979			T3981			T3983		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	70.73	70.44	70.5*	70.6	70.4	70.5	70.78	70.93	70.6*
Al <sub>2</sub> O <sub>3</sub>	70.39 14.63	14.55	14.59*	13.53	13.43	13.48	70.0 13.81	13.83	13.82*
TiO <sub>2</sub>	0.79	0.77	0.78	0.78	0.78	0.78	0.87	0.81	0.84
Fe <sub>2</sub> O <sub>3</sub>	0.92	0.93	0.93	0.64	0.62	0.63	0.55	0.59	0.57
FeO	4.06	4.01	4.04	4.28	4.30	4.29	4.42	4.42	4.42
MgO	2.61	2.61	2.61	2.46	2.36	2.41	2.44	2.58	2.51
CaO	3.12	3.16	3.14	3.31	3.38	3.34	3.03	3.09	3.06
Na <sub>2</sub> O	1.35	1.34	1.34	1.54	1.57	1.56	1.26	1.27	1.27
K <sub>2</sub> O	2.40	2.39	2.40	2.52	2.58	2.56	2.34	2.36	2.35
MnO	0.088	0.093	0.090	0.093	0.100	0.097	0.101	0.106	0.104
P <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	-	0.127	0.099	0.113	0.064	0.070	0.067
Total			100.42			99.64			99.61
Fe <sup>o</sup>			3.78			3.78			3.83
S.G.			2.439			2.379			2.455

\* Determined by X-ray fluorescence



Table 19 - cont

PHILIPPINITES									
	T3984			T3985			T3986		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	70.53	72.45	71.1*	72.7	71.4	72.1	71.10	70.91	71.0*
Al <sub>2</sub> O <sub>3</sub>	70.39 14.10	14.17	14.13*	13.45	12.66 12.76	12.96	13.43	13.69	13.56*
TiO <sub>2</sub>	0.77	0.81	0.80	0.74	0.76	0.75	0.77	0.76	0.76
Fe <sub>2</sub> O <sub>3</sub>	0.77	0.73	0.75	0.70	0.71	0.71	0.44	0.55	0.50
FeO	4.30	4.21	4.26	4.31	4.30	4.30	4.38	-	4.38
MgO	2.64	2.66	2.65	2.91	2.95	2.93	2.60	2.72	2.66
CaO	2.87	2.86	2.86	2.50	2.50	2.50	2.61	2.67	2.64
Na <sub>2</sub> O	1.33	1.35	1.34	1.18	1.18	1.18	1.39	1.39	1.39
K <sub>2</sub> O	2.35	2.34	2.35	2.19	2.15	2.17	2.41	2.40	2.40
MnO	0.099	0.099	0.099	0.087	0.092	0.092	0.104	0.099	0.102
P <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	-	0.103	0.072	0.087	n.d.	n.d.	-
Total			100.34			99.78			99.39
Fe <sup>o</sup>			3.83			3.84			3.75
S.G.			2.456			2.445			2.437
n			n.d.			1.5074			n.d.

\* Determined by X-ray fluorescence

Table 19 - cont

## INDOCHINITES

	T3987			T3988			T3989		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	-	-	n.d.	73.36	73.23	73.3*	71.87	70.89	71.33*
Al <sub>2</sub> O <sub>3</sub>	12.77	12.53	12.65	73.31 12.22	12.56	12.39*	71.15 13.66	13.70	13.68*
TiO <sub>2</sub>	0.70	0.75	0.72	0.79	0.75	0.77	0.76	0.72	0.74
Fe <sub>2</sub> O <sub>3</sub>	0.68	0.67	0.68	0.54	0.55	0.54	0.49	0.44	0.47
FeO	4.33	4.12	4.22	4.16	4.16	4.16	4.59	5.13	4.86
MgO	2.44	2.46	2.45	2.37	2.31	2.34	2.95	2.90	2.93
CaO	2.05	2.08	2.06	2.01	2.08	2.04	1.95	1.94	1.94
Na <sub>2</sub> O	1.57	1.59	1.58	1.51	1.55	1.53	1.35	1.38	1.37
K <sub>2</sub> O	2.48	2.50	2.49	2.47	2.45	2.46	2.33	2.35	2.34
MnO	0.101	0.101	0.101	0.095	0.095	0.095	0.086	0.102	0.094
P <sub>2</sub> O <sub>5</sub>	0.069	0.066	0.067	n.d.	n.d.	-	n.d.	n.d.	-
Total						99.63			99.73
Fe <sup>o</sup>			3.75			3.61			4.10
S.G.			2.435			2.425			2.445

\* Determined by X-ray fluorescence

Table 19 - cont

## INDOCHINITES

	T3990			T3991			T3992		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	71.54 71.33	72.41	71.8*	75.19 72.60	73.74 73.19	73.7*	77.53	77.41	77.5*
Al <sub>2</sub> O <sub>3</sub>	13.64	13.48	13.56*	13.39	13.25	13.32	11.48	11.70	11.59
TiO <sub>2</sub>	0.77	0.85	0.81	0.75	0.75	0.75	0.65	0.67	0.66
Fe <sub>2</sub> O <sub>3</sub>	0.69	0.71	0.70	0.77	0.86	0.82	0.78	0.86	0.82
FeO	4.84	4.81	4.82	3.70	3.83	3.77	3.25	-	3.25
MgO	2.87	2.84	2.85	1.87	1.94	1.90	1.64	1.60	1.62
CaO	1.85	1.86	1.86	1.88	1.85	1.86	1.54	1.60	1.57
Na <sub>2</sub> O	1.42	1.43	1.43	1.44	1.46	1.45	1.05	1.07	1.06
K <sub>2</sub> O	2.49	2.49	2.49	2.59	2.64	2.62	2.10	2.10	2.10
MnO	0.107	0.106	0.106	0.092	0.094	0.093	0.079	0.077	0.078
P <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-
Total			100.43			100.28			100.25
Fe <sup>o</sup>			4.22			3.50			3.10
S.G.			2.446			n.d.			n.d.

\* Determined by X-ray fluorescence

Table 19 - cont

## INDOCHINITES

	T3993			T3994			T3995		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	73.0	72.8	72.9	71.3	72.7	72.0	70.8	71.6	71.2
Al <sub>2</sub> O <sub>3</sub>	12.27	13.66	12.96	13.29	12.75	13.02	12.34	12.21	12.28
TiO <sub>2</sub>	0.73	0.74	0.74	0.72	0.74	0.73	0.73	0.75	0.74
Fe <sub>2</sub> O <sub>3</sub>	0.51	0.50	0.50	0.68	0.69	0.68	0.71	0.74	0.72
FeO	4.88	4.89	4.88	4.65	4.64	4.65	4.71	4.68	4.70
MgO	2.80	2.69	2.74	2.67	2.67	2.67	2.97	2.95	2.96
CaO	1.79	1.88	1.83	1.85	2.02	1.94	1.96	1.90	1.93
Na <sub>2</sub> O	1.29	1.37	1.33	1.44	1.47	1.45	1.52	1.56	1.54
K <sub>2</sub> O	2.33	2.21	2.27	2.30	2.33	2.32	2.40	2.36	2.38
MnO	0.110	0.102	0.106	0.092	0.088	0.090	0.095	0.092	0.094
P <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	-	n.d.	n.d.	-	n.d.	n.d.	-
Total			100.26			99.55			98.54
Fe <sup>o</sup>			4.15			4.09			4.15
S.G.			2.448			2.439			2.447

Table 19 - cont

## INDOCHINITES

	T4218			T4219			T4220		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	-	-	n.d.	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	13.40	-	13.40*	12.38	-	12.38*	12.76	-	12.76*
TiO <sub>2</sub>	0.75	0.78	0.76	0.64	0.62	0.63	0.70	0.70	0.70
Fe <sub>2</sub> O <sub>3</sub>	0.58	0.57	0.58	0.76	0.77	0.76	0.35	0.39	0.37
FeO	4.21	-	4.21	4.50	-	4.50	4.63	4.19	4.41
MgO	2.23	2.27	2.25	2.81	2.80	2.80	2.28	2.28	2.28
CaO	2.01	2.04	2.03	1.86	1.89	1.88	2.02	2.06	2.04
Na <sub>2</sub> O	1.55	1.53	1.54	1.55	-	1.55	1.56	-	1.56
K <sub>2</sub> O	2.50	2.50	2.50	2.32	2.33	2.32	2.47	2.54	2.50
MnO	0.090	0.092	0.091	0.091	0.100	0.096	0.072	0.090	0.079
Fe <sup>o</sup>			3.67			4.03			3.69

\* Determined by X-ray Fluorescence

Table 19 - cont

## JAVANITES

	Th102			Th104		
	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	11.15	-	11.15*	13.43	-	13.43*
TiO <sub>2</sub>	0.62	0.65	0.64	0.70	0.75	0.72
Fe <sub>2</sub> O <sub>3</sub>	0.77	0.79	0.78	0.64	0.66	0.65
FeO	5.33	5.48	5.41	6.47	6.13	6.30
MgO	3.96	3.98	3.97	4.95	4.97	4.96
CaO	2.34	2.31	2.33	2.61	2.58	2.60
Na <sub>2</sub> O	1.19	1.19	1.19	1.00	1.02	1.01
K <sub>2</sub> O	2.04	2.00	2.02	1.94	1.87	1.91
MnO	0.111	0.122	0.116	0.117	0.126	0.122
Fe <sup>o</sup>			4.75			4.34
S.G.			2.437			2.438

\* Determined by X-ray fluorescence

Table 19 - cont

## AUSTRALITES

	T3310			T3313			T4214		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	-	-	n.d.	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	13.21	-	13.21*	-	-	n.d.	13.82	-	13.82*
TiO <sub>2</sub>	0.73	-	0.73	0.66	0.68	0.67	0.81	0.77	0.79
Fe <sub>2</sub> O <sub>3</sub>	0.61	0.70	0.66	0.59	0.68	0.63	0.88	0.89	0.88
FeO	3.79	3.98	3.89	3.49	3.36	3.43	3.80	-	3.80
MgO	1.97	2.11	2.04	1.62	1.66	1.64	2.43	2.43	2.43
CaO	5.10	5.11	5.10	2.14	2.16	2.15	3.57	3.61	3.59
Na <sub>2</sub> O	1.27	1.29	1.28	1.33	1.33	1.33	1.13	1.12	1.12
K <sub>2</sub> O	2.41	2.37	2.39	2.39	2.37	2.38	2.06	2.08	2.07
MnO	0.115	0.115	0.115	0.079	0.087	0.083	0.087	0.086	0.086
Fe <sup>o</sup>			3.48			3.11			3.57

\* Determined by X-ray fluorescence

Table 19 - cont

AUSTRALITES

	Th215			Th216		
	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	69.19 68.46	69.35	69.0*	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	15.36	15.28	15.32*	13.48	-	13.48*
TiO <sub>2</sub>	0.83	0.80	0.81	0.59	0.59	0.59
Fe <sub>2</sub> O <sub>3</sub>	0.36	0.39	0.38	0.68	0.73	0.71
FeO	4.49	-	4.49	-	4.13	4.13
MgO	2.29	2.27	2.28	2.13	2.14	2.13
CaO	3.18	3.16	3.17	3.36	3.58	3.47
Na <sub>2</sub> O	1.54	1.58	1.56	1.78	1.90	1.84
K <sub>2</sub> O	2.49	2.50	2.50	2.61	2.61	2.61
MnO	0.092	0.091	0.091	0.084	-	0.084
Total			99.61			
Fe <sup>o</sup>			3.75			3.75

\* Determined by X-ray fluorescence



Table 19 - cont.  
BEDIASITE

	MASSACHUSETTS			BEDIASITE			MOLDAVITE		
	T4091			T4106			T4090		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	80.97	80.40	80.68	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	11.38	11.47	11.43	12.69	-	12.69*	9.59	-	9.59*
TiO <sub>2</sub>	0.51	0.51	0.51	0.74	0.74	0.74	0.32	0.30	0.31
Fe <sub>2</sub> O <sub>3</sub>	0.75	0.69	0.72	0.77	0.78	0.77	0.48	0.49	0.49
FeO	2.18	2.27	2.22	3.26	3.03	3.15	1.35	1.32	1.34
MgO	0.73	0.73	0.73	0.61	0.62	0.61	2.19	2.20	2.19
CaO	0.48	0.52	0.50	0.57	0.56	0.56	2.65	2.69	2.67
Na <sub>2</sub> O	1.12	1.16	1.14	1.58	1.50	1.54	0.38	0.41	0.40
K <sub>2</sub> O	2.44	2.44	2.44	2.10	2.11	2.10	3.52	3.42	3.47
MnO	0.047	0.047	0.047	0.041	0.044	0.042	0.063	0.069	0.066
P <sub>2</sub> O <sub>5</sub>	0.06	0.06	0.06	-	-	n.d.	-	-	n.d.
Total			100.48						
Fe <sup>o</sup>			2.23			2.99			1.38
S.G.			2.337			2.42			

\* Determined by X-ray fluorescence

Table 19- cont

	"AMERICANITES"			T3996 Peru			TEXAS SEDIMENT		
	T3967	P.I		T3996	Peru		4109		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	72.8	72.6	72.7	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	11.96	13.54	12.75	-	-	n.d.	-	-	n.d.
TiO <sub>2</sub>	0.05	0.07	0.06	0.05	0.04	0.04	0.34	0.36	0.35
Fe <sub>2</sub> O <sub>3</sub>	0.71	0.67	0.69	0.27	0.29	0.28	0.75	0.87	0.81
FeO	0.93	0.96	0.95	0.42	0.40	0.41	0.51	-	0.51
MgO	0.07	0.16	0.11	0.03	0.03	0.03	0.44	0.43	0.44
CaO	0.86	0.87	0.86	0.25	0.24	0.25	0.45	0.48	0.47
Na <sub>2</sub> O	3.89	3.80	3.85	4.60	4.57	4.59	0.90	0.89	0.90
K <sub>2</sub> O	5.13	5.20	5.18	3.71	3.67	3.69	1.56	1.56	1.56
MnO	0.048	0.056	0.052	0.060	0.058	0.059	0.011	0.013	0.012
Total			97.20						
Fe <sup>o</sup>			1.22			0.52			0.97
S.G.			2.461			2.363			n.d.
n			1.4879			n.d.			n.d.

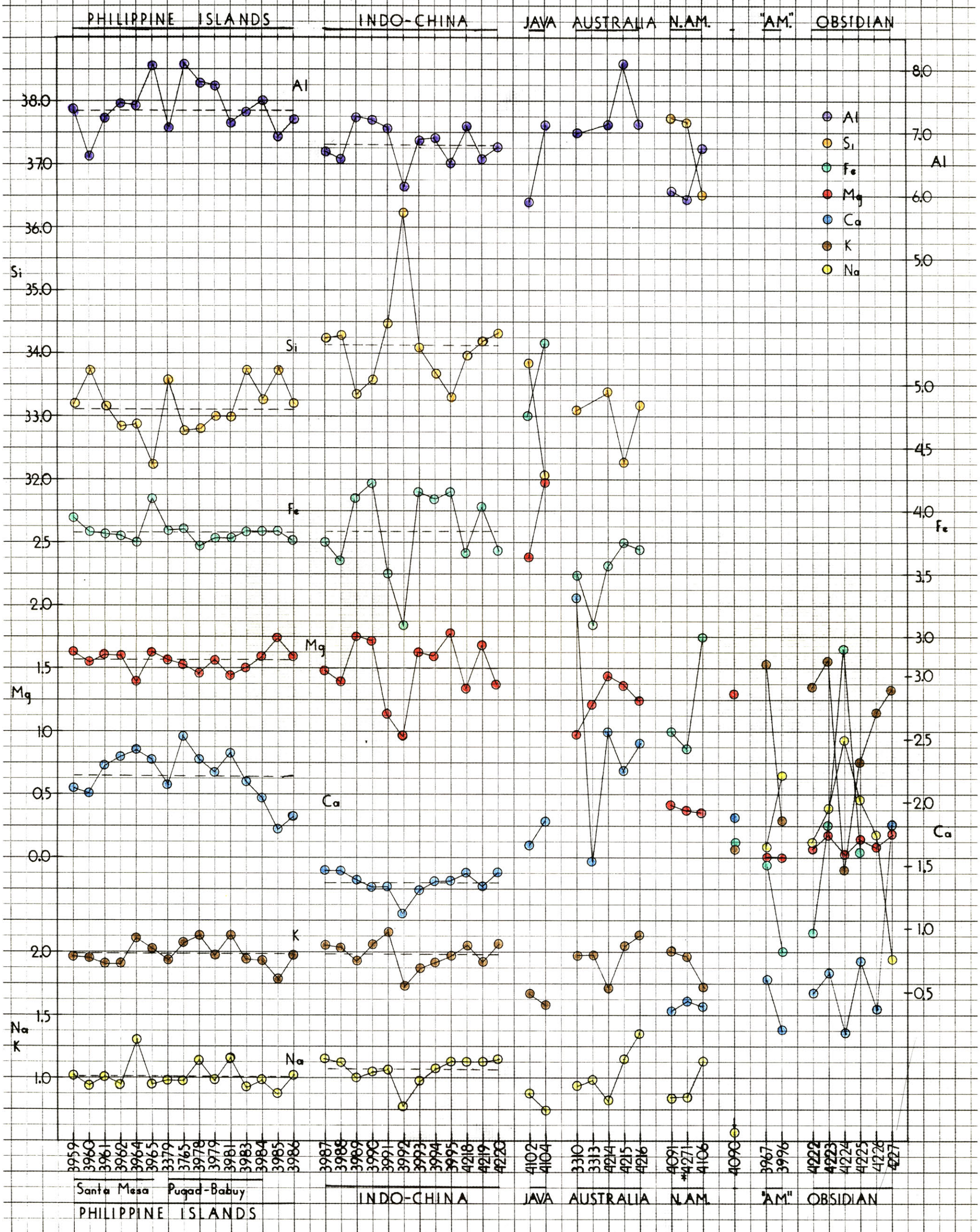
Table 19 - cont

OBSIDIANS									
	R4222B			R4223			R4224		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	-	-	n.d.	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	-	-	n.d.	-	-	n.d.	-	-	n.d.
TiO <sub>2</sub>	0.22	0.21	0.22	0.11	0.10	0.10	0.20	0.20	0.20
Fe <sub>2</sub> O <sub>3</sub>	0.62	0.68	0.65	1.00	1.01	1.00	1.91	1.91	1.91
FeO	0.32	0.28	0.30	1.18	0.94	1.06	-	2.02	2.02
MgO	0.16	0.21	0.19	0.25	0.30	0.27	0.05	0.10	0.08
CaO	0.70	0.70	0.70	0.93	0.97	0.95	0.24	0.26	0.25
Na <sub>2</sub> O	3.91	3.85	3.88	4.22	4.25	4.24	4.97	4.95	4.96
K <sub>2</sub> O	4.93	4.95	4.94	5.22	5.22	5.22	3.19	3.21	3.20
MnO	0.052	0.052	0.052	0.065	0.066	0.066	0.091	0.084	0.088
Fe <sup>0</sup>			0.98			2.18			4.15

Table 19 - cont

	OBSIDIANS								
	Rh225			Rh226			Rh227		
	A	B	Avg	A	B	Avg	A	B	Avg
SiO <sub>2</sub>	-	-	n.d.	-	-	n.d.	-	-	n.d.
Al <sub>2</sub> O <sub>3</sub>	-	-	n.d.	-	-	n.d.	-	-	n.d.
TiO <sub>2</sub>	0.14	0.13	0.14	0.06	0.06	0.06	0.09	0.09	0.09
Fe <sub>2</sub> O <sub>3</sub>	1.78	1.80	1.79	-	-	n.d.	-	-	n.d.
FeO	0.08	0.07	0.08	0.09	0.11	0.10	0.26	0.20	0.23
MgO	0.27	0.24	0.25	0.12	0.13	0.13	0.31	0.34	0.32
CaO	1.07	1.08	1.08	0.55	0.53	0.55	2.56	2.60	2.58
Na <sub>2</sub> O	4.28	4.36	4.32	3.97	3.94	3.95	2.61	2.61	2.61
K <sub>2</sub> O	4.24	4.22	4.23	4.69	4.73	4.71	4.98	4.93	4.95
MnO	0.031	0.032	0.032	0.201	0.189	0.195	0.063	0.058	0.060
Fe <sup>o</sup>			1.88			n.d.			n.d.

Figure 10 Graphic presentation of the results



\* From Clarke & Carron (1961)

Si not determined in all samples; in these cases it was obtained by subtraction from 100%.

### C. Discussion

The average compositions for the various tektite localities calculated from the samples analysed in this work are presented in Table 20 along with the averages calculated from the analyses compiled by Barnes (1940). In this table  $n$  is the number of samples from which the averages were computed except for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  where the number is given in parentheses.

As the sampling of the philippinites reported in this paper is more extensive than that in Barnes it is felt the new average for this group is more representative of their composition. The differences between the old and new data are attributed to the small number of samples previously analysed. Twenty-four indochinites had previously been analysed, however, and it can be seen in Table 20 that the new and old averages are in close agreement for many of the constituents. The most notable exceptions are  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MgO}$ , and  $\text{CaO}$ .  $\text{Fe}_2\text{O}_3$  was reported in only 5 of the 24 indochinite analyses compiled by Barnes. Whether this constituent was not determined or not detected in the other 19 samples is not stated, but as it is usually determined by the difference between total iron and  $\text{FeO}$ , and as it is very difficult to prevent a small percent of the  $\text{Fe}^{+2}$  from oxidizing to  $\text{Fe}^{+3}$  during digestion of the sample, a small amount of  $\text{Fe}_2\text{O}_3$  usually appears in any rock analysis. Thus it is assumed the  $\text{Fe}_2\text{O}_3$  content was

Table 20 Average compositions of the various groups of tektites

This work

	n	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	Fe <sup>o</sup>
Philippinites	15	70.8 <sup>(3)</sup>	13.85	0.70	4.30	2.60	3.09	2.40	1.38	0.79	0.094	3.83
Indochinites	12	73.0 <sup>(4)</sup>	12.83	0.64	4.37	2.48	1.91	2.40	1.45	0.73	0.094	3.84
Javanites	2	-	-	0.71	5.86	4.47	2.47	1.96	1.10	0.68	0.119	5.05
Australites	5	-	-	0.65	3.95	2.11	3.50	2.39	1.43	0.72	0.092	3.52
Moldavites	1	-	-	0.49	1.34	2.19	2.67	3.46	0.40	0.31	0.065	1.38

From Barnes (1940)

Philippinites	4	71.2	12.57	1.10*	4.19	2.90	3.19	1.93	1.52	0.89	0.11	3.98
Indochinites	24	73.1	12.48	0.19*	4.98	2.00	2.51	2.40	1.45	0.94	0.13	3.90
Javanites	6	71.2	12.22	0.82*	4.84	2.89	3.06	2.32	1.86	0.77	0.17	4.33
Australites	9	73.3	12.75	0.50	4.25	1.98	3.01	2.05	1.25	0.67	0.16	3.65
Moldavites	10	79.6	11.02	0.23*	2.24	1.30	1.92	2.90	0.51	0.80	0.11	1.90

\* Fe<sub>2</sub>O<sub>3</sub> not reported in all analyses

determined in only 5 samples and the discrepancy is not surprising considering the limited number of samples reported and the poor precision of the method at these low levels of concentration. As the total iron averages of the old and new data are very similar, the discrepancy between the FeO results is also explained if the analyst of the samples reported by Barnes assumed all the iron was in the +2 oxidation state rather than determining both Fe<sup>2+</sup> and total iron.

However, the MgO and CaO averages for the indochinites reported in this paper are distinctly different from the averages from 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 (Ca = 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 of 2.00 calculated from the literature. It should again be stated that the samples were analysed in a completely random fashion, with a mixture of indochinites, philippinites, australites, etc. in each group of samples analysed in any particular day. In fact, the difference of CaO content between the philippinites and indochinites was not noticed until after all the analyses had been completed. Evidence that the CaO (and MgO) values reported here are not in error are: 1) the CaO values for



the philippinites and australites 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, which has a close 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 analysed 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 data for 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.

It can be seen from the data in Table 19 and Figure 10 that there appears to be some variation in the composition of the tektites, both between groups and within groups. It should now be determined whether this variation is real or merely analytical error. Table 21 gives the average composition of the 15 philippinites and 12 indochinites listed in Table 19, and the variation exhibited by each constituent. The numbers in parentheses by the silica and aluminum results are the number of samples averaged, as these constituents were not

determined in all samples. Table 22 compares the scatter of results, expressed as the relative deviation (c), with the analytical precision as estimated from the data presented in Tables 16 and 18. The precisions of the rubidium and strontium analytical procedures are discussed in Section II.

In Table 22 it can be seen that  $Al_2O_3$ ,  $MgO$ ,  $CaO$ ,  $Na_2O$ , and  $MnO$  exhibit a significantly greater variation in the philippinites than can be accounted for by purely analytical error, even using the most pessimistic estimates of precision shown in Table 16, while all the major constituents in the indochinites exhibit a greater scatter of results than the most pessimistic estimates of analytical precision. The scatter of rubidium and strontium results in both the philippinites and indochinites is also greater than predicted from just analytical error. Thus, it appears there are real differences in composition within the philippinite and indochinite groups. Taylor (1960) found the same order of magnitude of variation in the alkali elements in 14 australites. He found a relative deviation of 12.6% in Na, 7.6% in K, and 12.1% in Rb. The larger deviations than found here, particularly in the case of Rb, are probably due in part to the greater deviations in his analytical methods, viz. the emission spectrograph as compared to the mass spectrometer.

The first 6 samples (T3959 through T3965) listed in Table 19 are from one site in the Philippine Islands--the Santa Mesa site in Rizal Province. The next 7 samples (T3379 through T3984) come from another site--the Pugad-Rabuy site in Bulakan

Table 21

## Average Composition of the Philippinites and Indochinites

## Philippinites

	Average	$\bar{V}$	$\bar{C}$	$\bar{V}$	$\bar{C}$
SiO <sub>2</sub>	70.8	0.24	0.34%	0.88	1.24%
Al <sub>2</sub> O <sub>3</sub>	13.85	0.20	1.44%	0.72	5.2%
TiO <sub>2</sub>	0.79	0.007	0.9%	0.03	3.7%
Fe <sub>2</sub> O <sub>3</sub>	0.70	0.035	5.0%	0.14	19.6%
FeO	4.30	0.045	1.0%	0.17	4.0%
MgO	2.60	0.03	1.3%	0.13	5.1%
CaO	3.09	0.07	2.4%	0.30	9.8%
Na <sub>2</sub> O	1.38	0.04	2.7%	0.14	10.4%
K <sub>2</sub> O	2.40	0.03	1.2%	0.11	4.6%
MnO	0.094	0.003	2.7%	0.010	10.4%
Total Fe(Fe <sub>2</sub> O <sub>3</sub> )	5.48	0.03	0.6%	0.13	2.4%
*Rb ppm	117	1.9	1.6%	5	4.3%
*Sr ppm	173	4	2.3%	10.6	6.1%

## Indochinites

	Average	$\bar{V}$	$\bar{C}$	$\bar{V}$	$\bar{C}$
SiO <sub>2</sub>	73.0	0.73	0.99%	2.05	2.81%
Al <sub>2</sub> O <sub>3</sub>	12.83	0.22	1.75%	0.67	5.2%
TiO <sub>2</sub>	0.73	0.014	1.9%	0.05	6.6%
Fe <sub>2</sub> O <sub>3</sub>	0.64	0.04	6.4%	0.14	22.2%
FeO	4.37	0.14	3.2%	0.49	11.1%
MgO	2.48	0.12	4.9%	0.42	17.1%
CaO	1.91	0.04	2.0%	0.14	7.1%
Na <sub>2</sub> O	1.45	0.04	2.9%	0.15	10.1%
K <sub>2</sub> O	2.40	0.04	1.6%	0.14	5.7%
MnO	0.094	0.002	2.6%	0.009	9.0%
Total Fe(Fe <sub>2</sub> O <sub>3</sub> )	5.49	0.14	2.6%	0.49	8.9%
*Rb ppm	118	2.5	2.1%	7	5.9%
*Sr ppm	132	1.75	1.3%	4.9	3.7%

\* From Table 9

**Table 22 Comparison of a Scatter of Analytical Results and Analytical Precision**

	Relative deviation* of Philippinites	Relative deviation* of Indochinites	Est. relative deviation** of analytical method
SiO <sub>2</sub>	±1.2%	±2.8%	±<1%
Al <sub>2</sub> O <sub>3</sub>	5.2	5.2	3
TiO <sub>2</sub>	3.7	6.6	3
Total Fe as Fe <sub>2</sub> O <sub>3</sub>	2.4	8.9	2
FeO	4.0	11.1	2
MgO	5.1	17.1	2
CaO	9.8	7.1	3
Na <sub>2</sub> O	10.4	10.1	2
K <sub>2</sub> O	4.6	5.7	3
MnO	10.4	9.0	4
Rb	4.3	5.9	2
Sr	6.1	3.7	2

\* Relative deviation of a single analysis (C)

Province. Both of these sites are on Luzon Island near Manila. Therefore, the opportunity exists to test if variations exist 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 19, and are shown in Table 23. By comparison of the relative deviation (c) values of this table with values estimated for the analytical procedures given in Table 22, 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 as shown in Table 16,  $Al_2O_3$ ,  $MgO$ ,  $CaO$ , and  $Na_2O$  in the Santa Mesa samples, and  $CaO$ ,  $Na_2O$ , and  $MnO$  in the Pugad-Babuy samples exhibit significantly greater variation than just analytical error. Thus the data suggests there are real differences in compositions, not only within a given locality such as Indo-China, but also within restricted tektite sites, although the average compositions of tektites from different groups may be identical.

Next to be considered is, does the data suggest the philippinites and indochinites are significantly different in composition to be considered two independent populations? According to the Null Hypothesis (Moroney, 1956), as described in Section II, there is only a 5% probability that the difference between the average of two groups is equal to two standard

Table 23 Average compositions of the samples from the  
Santa Mesa site and the Pugad Babuy site, P.I.

	Santa Mesa site, P.I. (6)				Pugad-Babuy site, P.I. (7)			
	$\bar{x}$	$\bar{v}$	$\bar{v}$	$\bar{c}$	$\bar{x}$	$\bar{v}$	$\bar{v}$	$\bar{c}$
SiO <sub>2</sub>	70.7	0.53	1.2	1.7%	70.8	0.24	0.60	0.8%
Al <sub>2</sub> O <sub>3</sub>	13.88	0.35	0.86	6.2	14.02	0.19	0.51	3.6
TiO <sub>2</sub>	0.80	0.014	0.035	4.4	0.79	0.007	0.023	2.9
Total Fe as Fe <sub>2</sub> O <sub>3</sub>	5.54	0.07	0.18	3.3	5.44	0.03	0.07	1.3
FeO	4.35	0.098	0.24	5.5	4.25	0.05	0.13	3.2
MgO	2.61	0.06	0.15	5.7	2.54	0.04	0.09	3.5
CaO	3.17	0.08	0.20	6.3	3.17	0.09	0.23	7.3
Na <sub>2</sub> O	1.40	0.07	0.18	12.9	1.39	0.05	0.12	8.6
K <sub>2</sub> O	2.40	0.04	0.10	4.2	2.44	0.04	0.10	4.1
MnO	0.88	0.024	0.06	6.8	0.98	0.042	0.11	11.0

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 indochinite and philippinite data in Table 21 it was found that five of the constituents exhibited differences that are definitely significant. The difference 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 equaled 9 standard deviations, and the difference in CaO values equaled 15 standard deviations of the difference. The data for the other constituents does not suggest any significant differences in composition.

If the same test is applied to the data in Table 23 for the two sites in the Philippine Islands it is found that only 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 data suggests there is a real difference in

the mean composition of the indochinites and philippinites analysed, but no significant difference is demonstrated between the tektites from the Santa Mesa and Pugad-Babuy sites.

Ehmann (1960) analysed one tektite from each of three sites in the Philippine Islands, including the Santa Mesa and Pugad-Babuy sites, for Ni and Fe, and concluded that there was no significant difference in the Ni/Fe ratios, although, as he points out, Beyer (1955) states the samples from the different sites have quite distinct differences in physical appearance.

Taylor (1960) 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 exhibit a uniform change of approximately 20%. Cohen (personal communication) believes this uniform change in composition supports his theory that the Pacific Ocean area tektites were formed by the impact of a large meteorite somewhere in China. The tektites represent the fused terrestrial material that was thrown high into the atmosphere and across southeast Asia and Australia, the alkali elements being selectively volatilized during their passage through the atmosphere. Baker and Forester (1943, p. 399), assuming there was such a chemical change from their specific gravity determinations, suggest that the tektites were ablated from a meteorite which passed from west to east across Australia.



Whatever the cause of this uniform change in chemical composition of the tektites across Australia, it is apparent from the data in Table 19 and Figure 10 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 does not indicate any selective volatilization of elements during passage of a parent body 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, Ca and Sr, would not be expected to be selectively volatilized without much greater volatilization of many of the other elements, e.g. the alkalis. 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.

Thus it is concluded that selective volatilization is not the cause of the differences observed between philippinites

and indochinites. They might be completely independent groups, from completely different source materials, in which case their similarities would be just as difficult to explain. Considering these similarities (for example, total Fe, Mg, K<sub>2</sub>O, Na<sub>2</sub>O, Mn) 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?).

Several interesting features are apparent from Figure 10 that, although not entirely original with this work, confirm the observations of earlier investigators. One is that the Fe and Mg contents of the indochinites exhibit a much greater range than in the philippinites, but there appears to be no directional trend to the variation, in contrast to chromium and nickel which are present in much greater concentration in the southern than in the northern indochinites (Preuss, 1935; Ehmann, 1960). Ehmann feels these large differences in Cr and Ni are strong evidence that the indochinites represent two separate occurrences. The major elements reported here, however, do not indicate any grouping into two separate populations.

Taylor et al (1961) pointed out the inverse relationship between SiO<sub>2</sub> 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 shown in Figure 10. 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. However, the fact that such associations exist is obvious from an examination of Figure 10.

The similarity of the two "americanites," T3967 and T3996 to obsidian is obvious from Table 19 and Figure 10. Koomans (1938) proposed the name "pseudo-americanites" for this type of material from the Philippine Islands, suggesting a similarity to the "americanites" from Peru and Columbia. 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.

4109, a sample of the Wellborn sandstone from Texas, was partially analysed to determine if it had any chemical similarity to bediasites. Hawkins and Wolfson (1960) state that tektites have been seen embedded in this formation, and they suggest the tektites were formed by lightning fusing the sediment. It can be seen that most of the constituents do not resemble the bediasites, and that the relative proportions of the  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  would have to increase during formation of the tektites from the sandstone - an unlikely occurrence.

Table 24 is a summary of the chemical analyses of North American tektites, taken from both the literature and

Table 24. Chemical Composition of Martha's Vineyard, Georgia,  
and Texas Tektites

	Martha's Vineyard (1) Th.091	(2)	Georgia (2)	Texas (3) Fayette Co.	Texas (4) Th.106 Grimes Co.	Texas, (5) Grimes Co Avg of 2
SiO <sub>2</sub>	80.68	80.6	80.54	81.31	n.d.	75.64
Al <sub>2</sub> O <sub>3</sub>	11.43	11.3	11.21	10.96	n.d.	14.59
Fe <sub>2</sub> O <sub>3</sub>	0.72	0.4	0.33	0.15	0.77	0.41
FeO	2.22	2.2	2.40	2.29	3.15	4.00
MgO	0.73	0.7	0.65	0.53	0.61	1.29
CaO	0.50	0.7	0.61	0.50	0.56	0.05
Na <sub>2</sub> O	1.14	1.1	1.16	1.50	1.54	1.35
K <sub>2</sub> O	2.44	2.4	2.38	2.17	2.10	1.85
TiO <sub>2</sub>	0.51	0.5	0.43	0.53	0.74	0.81
P <sub>2</sub> O <sub>5</sub>	0.06	-	-	0.01	-	-
MnO	0.047	0.05	0.05	0.03	0.042	0.01
	100.48	99.95	99.76	99.98		100.00
*Rb ppm	78		74		70	
*Sr ppm	177		170		152	
density (g/cm <sup>3</sup> )	2.337	2.332	2.330 2.332			
Fe <sup>o</sup>	2.23		2.10	1.88	2.99	3.40

(1) Kaye, Schmetzler, and Chase (1961) and this investigation

(2) Clarke and Carron (1961)

(3) Barnes (1956)

(4) This investigation

(5) Barnes (1940)

\* From Table 8

this work. The first column is the analysis of sample T4091 from Martha's Vineyard, Massachusetts given in Table 19, and also in a paper by Kaye et al (1961). The second column is another analysis of the same sample by Clarke and Carron (1961). The excellent agreement between these two independent analyses is considered confirmation of the accuracy of the work. The Georgia sample listed in the third column was analysed by Clarke and Carron (1961). This sample, U.S. National Museum no. 1396, was analysed for rubidium and strontium and strontium isotopes during this investigation and the results were reported in Section II under M.I.T. no. T4271. This same sample has been analysed for K-Ar age (Reynold, 1960), trace elements (Cohen, 1959; Clarke and Carron, 1961), magnetic susceptibility (Senftle and Thorpe, 1959), and absorption spectra (Stair, 1955; 1956). A photograph of this sample is shown by Bruce (1959).

Barnes (1940) reported the analyses of two bediasites from Grimes County, and the average is given in the last column of Table 24. After 1940, tektites were found approximately 75 to 125 miles southwest of Grimes County in Fayette, Lee, and Gonzales counties, and an analysis of a sample from this newer area is given by Barnes (1956). This analysis is given in the fourth column of Table 24. Barnes (1960) suggests the two sites, considering their different compositions as indicated in columns 4 and 6, represent two separate showers. He also states the similarity in physical appearance between the Fayette County and Georgia samples suggest they could have come from

the same shower. Clarke and Carron (1961), comparing the Martha's Vineyard and Georgia samples suggest that an artificial origin may explain their remarkable similarity. They believe the Grimes County samples are from an extensive and bonafide tektite strewn field, but that the Fayette and Gonzales County glasses cannot be considered true bediasites, and may also be of artificial origin (personal communication).

A tektite from Grimes County, T4106, was partially analysed during this investigation and the results are given in the fifth column of Table 24. It can be seen that most of the constituents resemble the Fayette County sample more closely than the previously analysed Grimes County samples. The MgO, and especially the CaO, contents are strikingly different from the two older Grimes County analyses. T4106 appears closer to the older Grimes County analyses than to the Fayette County analysis only in total iron and TiO<sub>2</sub>. This data suggests several possibilities. One, the MgO and CaO analyses of the two Grimes County bediasites in Barnes may be incorrect--perhaps due to incomplete precipitation of calcium, so that the bulk of the calcium was included in the MgO determination. The combined CaO and MgO values of all the Grimes and Fayette County samples are similar. A second possibility is that the two types of bediasites are not physically separated, as suggested by Barnes (1960), but intermixed, as T4106, which most closely resembles the Fayette County sample, was found in Grimes County. Or it may be that there are not two completely

separate compositional types but a gradation over a wide range of composition. Many more samples from Texas need to be analysed to determine the true chemical nature of this field. Mr. Sumner Wolfson of Boston University, who collected T<sub>H</sub>106, was quite emphatic that it can from Grimes County.

In any event, it appears that the Martha's Vineyard tektite, Georgia tektite, and at least some of the Texas samples are remarkably similar in composition. An artificial origin, suggested by Clarke and Carron (1961), is not supported because: 1) the Texas field, which appears to have samples quite similar in composition to the other two areas, is a large field and the similarities of the samples in this field with those of other recognized fields has been well documented (Barnes, 1940; 1960); 2) it is difficult to believe sufficient amounts of argon would be retained during recent melting to give K-Ar ages of 32 and 29 million years as given by the Georgia and Texas samples respectively (Reynolds, 1960); 3) the chemical composition is much different from normal man-made glass, and has an extremely high melting temperature; and 4) the similarity in composition seems even more strange if the objects are man-made, for it seems quite coincidental that three separate glass-makers would choose such similar, and odd ingredients.

It should be emphasized that the Martha's Vineyard sample is a single find and this area should not be considered a tektite locality until more are found. However, it is

suggested that the most logical explanation of the similarities found in the North American samples analysed to date is that they are part of the same shower. Confirmation of this awaits the discovery of more samples and additional analyses.



D. Summary

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

- 1) The philippinites, analysed for the first time in any substantial number during this investigation, have many chemical similarities to the indochinites.
- 2) However, the philippinites and indochinites analysed here differ significantly in  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ , 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  $\text{CaO}$  contents of the indochinites analysed in this investigation are distinctly lower, and the  $\text{MgO}$  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 (1960) for the australites.
- 5) These two sites in the Philippine Islands do not differ significantly in average chemical composition and are probably parts of the same population.

6) No decrease is observed in the alkali element contents from Indo-China to the Philippine Islands (i.e. west to east) as Taylor (1960) observed across Australia, indicating selective volatilization is not the mechanism for the differences between the two groups.

7)  $\text{SiO}_2$  displays a negative correlation with the other oxides, which show positive correlations among themselves in the philippinites and indochinites, similar to the correlations found by Taylor et al (1961) for the australites.

8) A new tektite find from Martha's Vineyard, Massachusetts was analysed during this investigation, and it has a remarkable chemical similarity to the Georgia tektites and at least some of the Texas tektites.

9) The partial analysis of a tektite from Grimes County, Texas, resembles the analysis reported in the literature for a Fayette County tektite (and also the Martha's Vineyard and Georgia tektites), and suggests that there are not two separate types of Texas tektites, separated by approximately 100 miles, as suggested by Barnes (1960), but that there is a mixture of the two types or a complete gradation of composition with the group.

In conclusion, the work of the preceding section on the strontium isotopic composition of tektites and this section on their major element compositions do not support the theory of formation by random fusion of terrestrial materials, whether

impact of meteorites, asteroids, comets, or lightning. The quite similar chemical compositions, limited range of strontium isotopic compositions, and, in particular, sympathetic  $\text{Sr}^{87}/\text{Sr}^{86}$  -- Rb/Sr ratio variations for the various groups of tektites are not features one would expect from the random fusion of various types of terrestrial materials. The sympathetic variation of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios with the Rb/Sr ratios observed in tektites suggest they differentiated from a common, or similar, source material approximately 175 m.y. ago. But their K-Ar ages indicate they were last heated less than 30 m.y. ago. These two "ages," together with their similar composition and widespread distribution cannot be explained by any proposed theory of terrestrial origin.

Thus this writer is forced to tentatively accept an extra-terrestrial origin for the formation of tektites, fully aware that an extra-terrestrial origin raises many new questions. In particular, what extra-terrestrial source could have produced the tektites? The Moon is often suggested as the parent body. If the lunar surface is approximately 4.5 b.y. old the observed  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites must have been generated by a material having a low Rb/Sr ratio, such as basalt. But how were tektites produced from a basaltic lunar surface? Another possibility is that the surface of the Moon has undergone recent differentiation, an occurrence that is contrary to most theories of lunar history. Perhaps new studies of the Moon will be able to answer some of these questions, but at present it appears that all suggested theories of the origin of tektites contain difficulties.

Appendix ADescription of Samples

The samples are listed in numerical order.

T3310	Australite.	Given by I. Friedman, U.S.G.S. Friedman no. 97-2. 2.5 grams.
T3313	Australite.	Charlotte Waters, Central Australia. Given by I. Friedman. No Friedman no. 2.7 grams.
T3314	Moldavite.	Given by I. Friedman, U.S.G.S.
T3379	Philippinite.	Pugad-Babuy site, Bulakan Province. Given by C. Frondel, Harvard Museum Collection.
T3765	Philippinite.	Pugad-Babuy site, Bulakan Province. Collected by Beyer. Given by Rankama. 203.5 grams.
T3959	Philippinite.	Santa Mesa site, Rizal Province. Given by I. Friedman, U.S.G.S. 5.3 grams.
T3960	Philippinite.	Same description as T3959. 1.9 grams.
T3961	Philippinite.	Same description as T3959. 2.8 grams.
T3962	Philippinite.	Same description as T3959. 4.1 grams.
T3964	Philippinite.	Santa Mesa site. Rizal Province. Collected by Beyer. Given by C. Frondel, Harvard Museum Collection #92703. 4.5 grams.
T3965	Philippinite.	Same description as T3964. 5.7 grams.
T3967	"Americanite"	Santa Mesa site. Rizal Province, P.I. Collected by Beyer. Given by C. Frondel. Harvard Museum Collection #92703. 4.9 grams.
T3978	Philippinite.	Pugad-Babuy site, Bulakan Province. Collected by Beyer. Given by C. Frondel, Harvard Museum Collection #92703. 13.9 grams.
T3979	Philippinite.	Same description as T3978. 10.3 gms.
T3981	Philippinite.	Same description as T3978. 7.9 gms.
T3983	Philippinite.	Same description as T3978. 9.8 gms.

- T3984 Philippinite. Same description as T3978. 22.8 gms.
- T3985 Philippinite. Busuanga Island. Collected by Beyer. Given by C. Frondel, Harvard Collection. 3.4 grams.
- T3986 Philippinite. Same description as T3985. 18.3 gms.
- T3987 Indochinite. Kouang-Tcheou-Wan. Given by C. Frondel, Harvard Museum Collection. 12.1 gms.
- T3988 Indochinite. Same description as T3987. 10.6 gms.
- T3989 Indochinite. Same description as T3987. 25.9 gms.
- T3990 Indochinite. North Cambodia. Given by C. Frondel, Harvard Museum collection. 24.5 gms.
- T3991 Indochinite. Same description as T3990. 19.1 gms.
- T3992 Indochinite. Same description as T3990.
- T3993 Indochinite. Annam. Given by C. Frondel, Harvard Museum Collection. 11.5 grams.
- T3994 Indochinite. Same description as T3993. 9.7 gms.
- T3995 Indochinite. Same description as T3993. 7.6 gms.
- T3996 Americanite. Peru. Collected by Martin. Given by Rankama. 26.6 grams.
- T4090 Moldavite. Nechov, Bohemia. Given by A. Cohen of Mellon Institute. 4.5 grams.
- T4091 Tektite. From Gay Head, Martha's Vineyard, Massachusetts. Collected by J. Chase. Given by C. Kaye of U.S.G.S. 17.8 gms. Description and photograph in Kaye et al (1961).
- T4102 Javanite. From Pithecanthropus erectus beds. Given by J. G. Lester of Emory University. 1.76 grams.
- T4104 Javanite. Same description as T4102. 1.82 gms.
- T4106 Bediasite. Grimes County, Texas. Given by G. S. Hawkins of Boston University. B.U. no. 10. 12.05 grams. Photograph in Hawkins et al (1960).

- 4109 Sandstone. From the Wellborn formation, Texas. Given by G. S. Hawkins. Boston University.
- T4214 Australite. Nullarbor Plain. Purchased from American Meteorite Laboratory, Denver, Colorado. 6.5 grams.
- T4215 Australite. Same description as T4214. 8.1 gms.
- T4216 Australite. Same description as T4214. 5.5 gms.
- T4218 Indochinite. Collected near Dalat, South Viet-Nam. Purchased from American Meteorite Laboratory. 6 grams.
- T4219 Indochinite. Same description as T4218. 10.4 gms.
- T4220 Indochinite. Same description as T4218.
- R4222B Obsidian. Pellets from Tuff, Tonopah, Nevada.
- R4223 Obsidian. Spherulitic, from Yellowstone National Park.
- R4224 Obsidian. Dufferin Island, British Columbia.
- R4225 Obsidian. Red, from Teotihuacan, Mexico.
- R4226 Obsidian. Rhyolitic, from Silver Cliff, Colorado.
- R4227 Obsidian. Rhyolitic, from Eureka Pit, Ruth district, Nevada.
- T4271 Tektite From Empire, Georgia. Given by E. Henderson, National Museum #1396. Photograph in Bruce (1959).
- T4300 Bediasite. Grimes County Texas. Given by G. S. Hawkins of Boston University. B.U. no. 9. 9.65 grams. Photograph in Hawkins, et al (1960).

Appendix FDerivation of the Sr<sup>87</sup>/Sr<sup>86</sup> growth equation

In the decay of a radioactive isotope, the rate of decay,  $-\frac{dN}{dt}$  (where  $N$  is the number of unchanged atoms at time  $t$ ) is proportional to the number of atoms present:

$$-\frac{dN}{dt} = \lambda N \quad (1)$$

where  $\lambda$  is the constant of proportionality for the particular radioactive nuclide.

Integrating, with appropriate limits

$$N = N_0 \int_{N_0}^N \frac{dN}{N} = - \int_{t=0}^t \lambda dt \quad (2)$$

where  $N_0$  is the number of atoms present at time  $t = 0$  yields:

$$\ln \frac{N}{N_0} = -\lambda t \quad \text{or} \quad N = N_0 e^{-\lambda t} \quad (3)$$

In the case of Rb<sup>87</sup> decay this equation becomes:

$$Rb^{87} = Rb_0^{87} e^{-\lambda t} \quad (4)$$

The number of radiogenic Sr<sup>87</sup> daughter atoms formed during time  $t$  is given by:

$$*Sr^{87} = Rb_0^{87} - Rb^{87} \quad (5)$$

Substituting (4) into (5):

$$*Sr^{87} = Rb_0^{87} (e^{\lambda t} - 1) \quad (6)$$

The total number of Sr<sup>87</sup> atoms is given by the sum of the Sr<sup>87</sup> atoms at  $t = 0$ ,  $Sr_0^{87}$ , and the number of Sr<sup>87</sup> atoms formed since  $t = 0$  by the decay of Rb<sup>87</sup>,  $*Sr^{87}$

$$Sr^{87} = Sr_0^{87} + *Sr^{87} \quad (7)$$

Substituting (6) into (7):

$$\text{Sr}^{87} = \text{Sr}_o^{87} + \text{Rb}^{87} (e^{\lambda t} - 1) \quad (8)$$

As it is convenient to relate the concentration of  $\text{Sr}^{87}$  in a sample to the non-varying  $\text{Sr}^{86}$  content, both sides of equation (8) are divided by this constant:

$$\frac{\text{Sr}^{87}}{\text{Sr}^{86}} = \left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_o + \left( \frac{\text{Rb}^{87}}{\text{Sr}^{86}} \right) \cdot (e^{\lambda t} - 1) \quad (9)$$

The atomic ratio  $\text{Rb}^{87}/\text{Sr}^{86}$  can be transformed into a total Rb/Sr weight ratio as follows:

$$\frac{\text{Rb}^{87}}{\text{Sr}^{86}} = \left( \frac{\text{Rb}}{\text{Sr}} \right)_{\text{wt}} \times \frac{\text{At. wt. Sr}}{\text{At. wt. Rb}} \times \frac{(\text{Rb}^{87}/\text{Rb})_{\text{atomic}}}{(\text{Sr}^{86}/\text{Sr})_{\text{atomic}}}$$

The atomic weight of Sr and the fraction of  $\text{Sr}^{86}$  in the total Sr depend upon the amount of radiogenic  $\text{Sr}^{87}$  in the sample, and should be evaluated for each sample. However, in most samples only a small error is introduced if the values of "normal" strontium ( $\text{Sr}^{87}/\text{Sr}^{86} = 0.712$ ) are used. For example if  $\text{Sr}^{87}/\text{Sr}^{86} = 0.725$ , which is about the greatest ratio found in this work, an error of  $\sim .1\%$  is introduced if the figure for normal strontium is used. Thus:

$$\frac{\text{At wt Sr}}{\text{At wt Rb}} \times \frac{(\text{Rb}^{87}/\text{Rb})_{\text{atomic}}}{(\text{Sr}^{86}/\text{Sr})_{\text{atomic}}} = \frac{87.710}{85.557} \times \frac{0.2785}{0.0986} = 2.8962$$

and equation (9) becomes

$$\text{Sr}^{87}/\text{Sr}^{86} \simeq \left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_o + \left( \frac{\text{Rb}}{\text{Sr}} \right)_{\text{wt}} \times 2.8962 (e^{\lambda t} - 1) \quad (10)$$

$e^{\lambda t}$  can be expanded in the power series:

$$e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2} + \frac{(\lambda t)^3}{3} + \dots \quad (11)$$



If  $t = 1 \times 10^9$  years and  $\lambda = 1.49 \times 10^{-11}$  years<sup>-1</sup> an error of only 0.01% is introduced if only the first two terms are used instead of the first three.

Introducing the first two terms of the power series and the constant for  $\lambda$  into equation (10) gives:

$$\frac{\text{Sr}^{87}}{\text{Sr}^{86}} \approx \left( \frac{\text{Sr}^{87}}{\text{Sr}^{86}} \right)_0 + 4.256 \times 10^{-2} \left( \frac{\text{Rb}}{\text{Sr}} \right)_{\text{wt}} t \quad (12)$$

where  $t$  is in billions of years.

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### Biography

The author was born on June 3, 1930 in East Chicago, Indiana. In 1933 he moved with his family to Neodesha, Kansas, where he received his elementary and secondary education in the public school system. He received a Bachelor of Science degree in Geology from the University of Kansas in 1952.

From 1952 to 1956 the author served in the U.S. Navy as a Photographic Interpretation Officer. In 1956 he began graduate study at M.I.T.

His professional experience includes two and a half academic years as a half-time research assistant and two summers as a full time research assistant at M.I.T. He also spent a summer on a seismic crew with the Gulf Oil Company.

The writer is a member of Sigma Gamma Epsilon, honorary earth science fraternity, and Sigma Xi.

He has co-authored the following papers:

Pinson, W.H. and Schmetzler, C.C. (1959) Chemical and physical studies of tektites. Bull. Geol. Soc. Amer. 70, 1656 (abstract). Paper presented at the Pittsburg meeting of the GSA, 1959

Kaye, C.A., Schmetzler, C.C., and Chase, J.N. (1961) Tektite from Martha's Vineyard, Massachusetts. Geol. Soc. Amer. Bull. 72, 339-340

Pinson, W.H. and Schmetzler, C.C. (1961) Rb-Sr correlations of tektites. J. Geophys. Res. 66, 2539. (Abstract) Paper presented at the Washington meeting of the AGU, 1961

In December, 1951 he married Miss Sammy Johnson of Sibley, Missouri, and has four children, Margaret, Robert, William, and Ann.