

THE CHEMICAL COMPOSITION AND ORIGIN OF MOLDAVITES

by

JOHN ALDWYN PHILPOTTS  
B.Sc. McGill University  
(1959)  
M.Sc. McGill University  
(1961)



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

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

March, 1965

Signature of Author \_\_\_\_\_  
Department of Geology and Geophysics, March, 1965

Certified by \_\_\_\_\_  
Thesis Supervisor

Accepted by \_\_\_\_\_  
Chairman, Departmental Committee  
of Graduate Students

## The Chemical Composition and Origin of Moldavites

by

John A. Philpotts

Submitted to the Department of Geology and Geophysics in March, 1965, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

**Abstract:** Twenty three new major-element analyses of moldavites are reported. The samples include seventeen Bohemian and six Moravian tektites. The ranges in the contents of the various oxides are as follows:  $\text{SiO}_2$ , 75.5 - 80.6;  $\text{Al}_2\text{O}_3$ , 9.62 - 12.64;  $\text{TiO}_2$ , 0.268 - 0.460;  $\text{Fe}_2\text{O}_3$ , 0.12 - 0.31;  $\text{FeO}$ , 1.42 - 2.36;  $\text{MgO}$ , 1.13 - 2.50;  $\text{CaO}$ , 1.46 - 3.71;  $\text{Na}_2\text{O}$ , 0.31 - 0.67;  $\text{K}_2\text{O}$ , 3.26 - 3.81. The Rb and Sr contents and the Rb/Sr ratios are also reported for the 23 specimens; the ranges are as follows: Rb, 120 - 160 ppm; Sr, 130 - 156 ppm; Rb/Sr, 0.82 - 1.20. The specific gravity and refractive index values range from 2.3312 to 2.3718  $\text{gm/cm}^3$  and from 1.486 to 1.495, respectively.

In contrast to the australites, the moldavites display significant negative correlations between the alkali metals (Na and Rb) and the alkaline earths. The variations in the chemical composition of moldavites would seem to be unlike those of sedimentary or igneous rocks. It is suggested that the parent material of the moldavites was of constant chemical composition throughout and that the present variations in composition are due largely to selective volatilization. The wide range of Rb/Sr ratios in conjunction with the uniformity of the Sr isotopic composition supports this suggestion. The australite data is briefly examined in terms of selective volatilization. It is suggested that the Nordlingen Ries crater may have been produced by the impact of the moldavite parent-body.

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

## TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ii
LIST OF TABLES	vi
LIST OF FIGURES	viii
 <u>Part I</u> (to be submitted for publication)	
The Chemical Composition and Origin of Moldavites	
Abstract	1
ACKNOWLEDGEMENTS	2
INTRODUCTION	3
ANALYTICAL TECHNIQUES	4
Refractive index and specific gravity determinations	4
Sample preparation	4
Rapid silicate procedures	5
X-ray fluorescence	5
Precision and accuracy of the chemical analyses	8
RESULTS	12
DISCUSSION	17
SUMMARY	31
REFERENCES	33

Part II (to be submitted for publication)

## K/Rb Ratios in Tektites

Abstract	1
Introduction	2
Analytical Results	3
Discussion of the results	5
Acknowledgements	8
References	14

Part III (to be submitted for publication)

## Rb-Sr Age Study of Moldavites

Abstract	1
INTRODUCTION	3
ANALYTICAL RESULTS	4
DISCUSSION	5
REFERENCES	9

Part IV

## The Chemical Composition and Origin of Moldavites

CHAPTER 1 INTRODUCTION	1
CHAPTER 2 PHYSICAL CHARACTERISTICS	4
2.1 Form	4
2.2 Sculpture	5
2.3 Colour	8
2.4 Specific Gravity and Refractive Index	9
CHAPTER 3 CHEMICAL ANALYSES	14
3.1 Sample preparation	14



3.2 Analytical techniques	14
A. "Rapid silicate" procedures	14
B. X-ray fluorescence procedures	16
3.3 Precision and accuracy	21
3.4 Results	32
CHAPTER 4 ELECTRON MICROPROBE STUDIES	42
CHAPTER 5 DISCUSSION OF RESULTS. THEORIES OF ORIGIN	46
5.1 Variations in chemical composition within and between the Bohemian and Moravian "strewn fields".	46
5.2 Correlations	50
5.3 Variation in chemical composition	59
5.4 Nature of the parent material	77
5.5 Theory of origin	83
CHAPTER 6 SUMMARY	91
APPENDIX Analyses of glass standard 191 AIK and 191 ALA	94
ACKNOWLEDGEMENTS	95
REFERENCES	97
BIOGRAPHY	104

LIST OF TABLES

	<u>Page</u>
<u>Part I</u>	
1. Analyses of G-1 and W-1	9
2. Analytical Results	13
3. Correlation coefficients (r) and levels of significance, for various pairs of constituents in moldavites	20
<u>Part II</u>	
1. K and Rb Contents and K/Rb Ratios in Tektites	9
2. K and Rb Contents of G-1 and W-1 Determined throughout the Analysis Period of the Present Work	12
<u>Part III</u>	
1. Rb and Sr contents in ppm of moldavites as determined by two methods of analysis	6
2. Sr isotopic composition of moldavites	7
3. Summary of Rb-Sr data for nine completely analyzed moldavites	8
<u>Part IV</u>	
1. Some physical properties of 26 moldavites	13
2. Analyses of G-1 on separate weighings	25
3. Analyses of W-1 on separate weighings	26
4. Precision of the analyses of G-1 and W-1	27
5. K analyses by x-ray fluorescence and by flame photometry	28

6. $\text{Al}_2\text{O}_3$ analyses by x-ray fluorescence and by spectrophotometry	29
7. $\text{SiO}_2$ analyses by x-ray fluorescence and by spectrophotometry	29
8. Rb and Sr analyses by x-ray fluorescence and by mass spectrometry (in ppm by weight)	31
9. Analytical Results	33
10. Comparison of observed spread and analytical precision	47
11. Correlation coefficients (r) and levels of significance, for various pairs of constituents in moldavites	51

LIST OF FIGURES

	<u>Page</u>
<u>Part I</u>	
1. CaO vs. FeO for 23 moldavites	19
2. Na <sub>2</sub> O vs. K <sub>2</sub> O for 23 moldavites	26
3. Rb/Sr vs. K/Rb for 23 moldavites	27
<u>Part II</u>	
1. K/Rb weight ratios for fifty-four tektites	13
<u>Part IV</u>	
1. CaO vs FeO for 23 moldavites	54
2. Na <sub>2</sub> O vs K <sub>2</sub> O for 23 moldavites	55
3. MgO vs. Sr for 23 moldavites	56
4. Rb vs. CaO for 23 moldavites	57
5. Na <sub>2</sub> O vs. FeO for 23 moldavites	58
6. Rb/Sr vs. MgO for 23 moldavites	68
7. Rb/Sr vs. FeO for 23 moldavites	69
8. Rb/Sr vs. Na <sub>2</sub> O for 23 moldavites	70
9. Rb/Sr vs. Sp. G. for 23 moldavites	71
10. Rb/Sr vs. K/Rb for 23 moldavites	72

The Chemical Composition and Origin of Moldavites.

J. A. Philpotts and W. H. Pinson, Jr.

Department of Geology and Geophysics

Massachusetts Institute of Technology, Cambridge, Mass.

Abstract:

Twenty three new major-element analyses of moldavites are reported. The samples include seventeen Bohemian and six Moravian tektites. The ranges in the contents of the various oxides are as follows:  $\text{SiO}_2$ , 75.5 - 80.6;  $\text{Al}_2\text{O}_3$ , 9.62 - 12.64;  $\text{TiO}_2$ , 0.268 - 0.460;  $\text{Fe}_2\text{O}_3$ , 0.12 - 0.31;  $\text{FeO}$ , 1.42 - 2.36;  $\text{MgO}$ , 1.13 - 2.50;  $\text{CaO}$ , 1.46 - 3.71;  $\text{Na}_2\text{O}$ , 0.31 - 0.67;  $\text{K}_2\text{O}$ , 3.26 - 3.81. The Rb and Sr contents and the Rb/Sr ratios are also reported for the 23 specimens; the ranges are as follows: Rb, 120 - 160 ppm; Sr, 130 - 156 ppm; Rb/Sr, 0.82 - 1.20. The specific gravity and refractive index values range from 2.3312 to 2.3718  $\text{gm/cm}^3$  and from 1.486 to 1.495, respectively.

In contrast to the australites, the moldavites display significant negative correlations between the alkali metals (Na and Rb) and the alkaline earths. The variations in the chemical composition of moldavites would seem to be unlike those of sedimentary or igneous rocks. It is suggested that the parent material of the moldavites was of constant chemical composition throughout and that the present variations in composition are due largely to selective volatilization.

The wide range of Rb/Sr ratios in conjunction with the uniformity of the Sr isotopic composition supports this suggestion. The australite data is briefly examined in terms of selective volatilization. It is suggested that the Nordlingen Ries crater may have been produced by the impact of the moldavite parent-body.

#### ACKNOWLEDGEMENTS

This research was sponsored by the N.A.S.A. Research Grant No. Nsg222-61. The mass spectrometric analyses were financed by the U.S. Atomic Energy Commission under Contract AT(30-1)-1381, which is under the supervision of Professor P. M. Hurley. The x-ray fluorescence analyses for rubidium and strontium were performed on equipment granted to M.I.T. by a National Science Foundation grant, under the supervision of Professor H. W. Fairbairn. Preliminary major element x-ray fluorescence analyses were performed at Harvard University under the supervision of Professor Clifford Frondel and Mrs. Frondel. X-ray fluorescence analyses for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were performed in the Geochemistry Laboratory, Goddard Space Flight Centre, N.A.S.A., Greenbelt, Md. To the above individuals and organizations the authors express their appreciation.

## INTRODUCTION

Published analyses have shown that tektites from a particular geographic group are quite similar in chemical composition and that there is some similarity between tektites from different groups. Compilations in the literature, of older analyses by various investigators using different analytical techniques, have tended to obscure real variations within and between the tektite groups. There existed a need for precise analyses of representative numbers of samples by uniform techniques, preferably utilizing accepted rock standards to monitor accuracy. This need has been satisfied in the case of the australites (Taylor, 1960; Taylor et al, 1961; Cherry and Taylor, 1961; Taylor, 1962; Taylor and Sachs, 1964), the bediasites (Chao, 1963), and various South East Asian tektites (Schnetzler and Pinson, 1964a). The purpose of this paper is to report a number of internally consistent chemical analyses of Czechoslovakian tektites. Seventeen moldavites from the Bohemian "strewn field" and 6 moldavites from the Moravian field were analyzed for major element contents. The rock standards G-1 and W-1 were used as analytical monitors. Analyses of the trace elements Rb and Sr were also performed. The refractive indexes and specific gravities of the 23 tektites were also determined.

## ANALYTICAL TECHNIQUES

Refractive index and specific gravity determinations

Refractive index values for the 23 moldavites were obtained on powders by the immersion oil method. Most powders gave a range of refractive indexes and the reported values are an estimate of the mean value for each sample. Because of the estimate involved in the determinations, accuracy is thought to be about  $\pm 0.002$ .

The specific gravities of the moldavites were determined by weighing the bulk samples in air and in distilled water on a high-precision chain balance. Duplicate determinations were made on six samples; the mean difference between duplicates was  $0.0004 \text{ gm/cm}^3$ . The precision and accuracy of the specific gravity determinations are thought to be better than  $\pm 0.001 \text{ gm/cm}^3$ .

Sample preparation

The moldavites were prepared for chemical analysis in the following manner. The samples were washed in acetone, in distilled water, and in hot, six normal HCl; they were broken on a steel plate and a portion of each tektite was crushed in a flat-surfaced, hardened steel, percussion mortar; a hand magnet was passed over the crushed fragments in order to remove any incorporated steel; the samples were powdered in a boron carbide mortar and homogenized.



### Rapid silicate procedures

Total Fe, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> were determined by the rapid silicate procedures described by Schnetzler and Pinson (1964a). Two weighings of each tektite sample, except T 5296d, were used in the determinations; a single weighing of T 5296d was used. FeO was determined by the spectrophotometric method of Shapiro (1960). Only a few determinations of P<sub>2</sub>O<sub>5</sub> were made because the method proved unreliable at the low concentrations found in the moldavite samples. For the same reason, determinations of MnO, H<sub>2</sub>O and CO<sub>2</sub> were not undertaken.

### X-ray fluorescence

It was decided to determine SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> by x-ray fluorescence techniques because of the number of determinations required to obtain a reliable SiO<sub>2</sub> value, and because of the frequently anomalous Al<sub>2</sub>O<sub>3</sub> results obtained by the "rapid silicate" method. This decision was made in light of the successful x-ray fluorescence analyses for light elements by Volborth (1963), Rose et al (1963), Schnetzler and Pinson (1964a), and Welday et al (1964). It was further decided to forego the fusion technique of sample preparation because tektites are relatively homogeneous glasses produced by a natural fusion process, and because tektites from the same locality (ie. Czechoslovakia) are quite similar in chemical composition.

Preliminary x-ray fluorescence investigations were done at the Hoffman Laboratory, Harvard, on a helium path, Phillips unit, under the supervision of Dr. J. W. Frondel. In order to determine the suitability of the moldavite powdered samples for x-ray fluorescence analysis, they were first analyzed for K; flame photometric data on K were available for comparison. The moldavite powders were packed into lucite trays by pressing the surface with a glass slide. The  $KK_{\alpha}$  radiation of each sample was rapidly scanned (1 degree per minute) from  $40^{\circ}$  to  $42^{\circ}$ , using a tungsten target and an ADP crystal. A comparison of the x-ray K results (obtained from a least squares fit) and the flame photometric K results for the same 23 moldavites is presented elsewhere (Pinson et al, 1965). It was next decided to analyze for  $Al_2O_3$ . A tungsten target and a gypsum crystal were used. Four sets of 50 second counts were taken at three goniometer settings corresponding to two background positions and the Al  $K_{\alpha}$  peak. Unfortunately only a few samples could be run because of other demands upon the x-ray unit.

The  $Al_2O_3$  determinations were continued on a General Electric, vacuum, x-ray unit in the Geochemistry Laboratory at the Goddard Space Flight Centre. The moldavite samples were prepared for analysis by briquetting 50% mixture of sample powder and boric acid at 10,000 psi for one minute.

A chromium target, PET crystal and plexiglass sample holders were used in the  $\text{Al}_2\text{O}_3$  determinations. Three sets of 100 second counts were taken at a background setting and on the  $\text{AlK}\alpha$  peak. This corresponded to a total of about 7500 counts on the background and 75,000 counts on the  $\text{AlK}\alpha$  peak for each sample. Moldavites previously analyzed for  $\text{Al}_2\text{O}_3$  spectrophotometrically were used as standards.  $\text{SiO}_2$  was determined using a chromium target and a PET crystal. Three sets of 100 second counts were made at each of the two background settings, and three 20 second counts were made at the  $\text{SiK}\alpha$  peak. This corresponded to a total of about 3000 counts on each of the backgrounds and about 90,000 counts on the  $\text{SiK}\alpha$  peak for each sample briquette. Some samples gave anomalous background counts. Most of these anomalous counts were obtained on samples run in the same sample-holder. An empirical correction factor, equal to the average background count divided by the observed background count, was applied to the peak counts in these cases. Moldavites which had been analyzed for  $\text{SiO}_2$  by the "rapid-silicate" method were used as standards.

Rb and Sr were determined on the North American Phillips x-ray fluorescence unit at M.I.T. under the supervision of Professor H. W. Fairbairn. Powdered samples were used. A molybdenum target, topaz crystal, and scintillation counter were employed. Three sets of counts were registered on

three background settings, the  $\text{RbK}\alpha$  peak, and the  $\text{SrK}\alpha$  peak. A total of 6000 counts were taken at each of the background settings and a total of 12,000 counts were taken on both of the peaks, for each sample. Each run on four samples included a standard; the Rb and Sr contents of the three "unknowns" were determined by comparison of peak heights with those of the standard that was run with them. The standards used were moldavites for which Rb and Sr contents had been (or were later) determined by mass spectrometric stable isotope dilution analyses (Schnetzler and Pinson, 1964b; Pinson et al, 1965). Each moldavite sample was packed and run two or three times in the x-ray fluorescence analyses for Rb and Sr.

#### Precision and accuracy of the chemical analyses

The precision and accuracy of the rapid silicate procedures employed in this investigation have been discussed by Schnetzler and Pinson (1964a). The most meaningful expressions of precision and accuracy of the analyses are derived from the results of replicate analyses of the rock standards G-1 and W-1 which were prepared and run with the tektites. Results of the analyses of G-1 and W-1 are given in Table 1. The accepted values for the monitors are taken from Fleischer and Stevens (1962). The precision and the accuracy of the tektite analyses are believed to be as good (for comparable concentrations) as those of the analyses of

Table 1 Analyses of G-1 and W-1

G-1	Accepted Value	$\bar{x}$	n	$\nabla$	W-1	Accepted Value	$\bar{x}$	n	$\nabla$
SiO <sub>2</sub>	72.41	72.32	6	0.55					
Total Fe as FeO	1.76	1.74	6	0.04	10.01	9.94	6	0.06	
MgO	0.41	0.26	6	0.07	6.62	6.47	6	0.12	
CaO	1.39	1.41	6	0.10	10.96	10.88	6	0.07	
Na <sub>2</sub> O	3.32	3.31	6	0.04	2.07	2.13	6	0.07	
K <sub>2</sub> O	5.45	5.53	6	0.07	0.64	0.65	6	0.01	
TiO <sub>2</sub>	0.26	0.24	6	0.007	1.07	1.08	6	0.008	
FeO	0.98	0.98	9	0.01	8.74	8.62	6	0.11	
Fe <sub>2</sub> O <sub>3</sub>	0.87	0.85			1.41	1.46			

$\bar{x}$  is the average value from this work

n is the number of weighings

$$\nabla = \sqrt{\frac{(x - \bar{x})^2}{n - 1}}, \text{ the standard deviation of a single analysis}$$

G-1 and W-1, if not better, because of the ease with which tektite glass goes into solution.

The accuracy of the x-ray fluorescence determinations of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  depends upon the accuracy of the spectrophotometric determinations of these constituents in the standard moldavites. The average difference between the spectrophotometric values and the x-ray fluorescence values (obtained from a least squares fit) for  $\text{Al}_2\text{O}_3$  in the 4 standard moldavites was less than 0.1%  $\text{Al}_2\text{O}_3$ . The average difference between the spectrophotometric and the x-ray fluorescence values for  $\text{SiO}_2$  in the 5 standards was 0.5%  $\text{SiO}_2$ .

The Rb x-ray fluorescence analyses of the moldavites have a precision (c) of about  $\pm 2\%$ ; the Sr x-ray analyses have a precision of about  $\pm 3\%$ . These conclusions are based upon numerous replicate analyses of G-1 and W-1 by Professor H. W. Fairbairn (M.I.T., 1964, unpublished). The accuracy of the x-ray fluorescence analyses for Rb and Sr depends upon the accuracy of the mass spectrometric determinations of these constituents in the standard moldavites. Results obtained on G-1 and W-1 in the M.I.T. Geochronology Laboratory, when compared with results obtained elsewhere by various reliable methods of analysis (Fleischer and Stevens, 1962), suggest an accuracy of better than  $\pm 5\%$  for the mass spectrometric determinations of Rb and Sr.

Direct evidence of the overall accuracy of the moldavite

analyses is given by the fact that summations of the values of the constituent oxides fall between 99% and 101% for 20 out of the 23 samples analyzed; it should be noted that only the CaO and MgO and the FeO and Fe<sub>2</sub>O<sub>3</sub> determinations are dependent. A conservative estimate of the overall precision ( $C = \frac{\sigma}{\bar{x}} (100)$ ) of the analyses is as follows: SiO<sub>2</sub>, ±1%; Al<sub>2</sub>O<sub>3</sub>, ±3%; TiO<sub>2</sub>, ±3%; MgO, ±5%; CaO, ±4%; Na<sub>2</sub>O, ±15%; K<sub>2</sub>O, ±2%; total Fe as FeO, ±2%; Rb, ±2%; Sr, ±3%.

## RESULTS

The results of the chemical analyses of the 23 moldavites are given in Table 2 along with the specific gravity and refractive index values. The results are presented in order of sample occurrence from west to east in the "strewn fields". The major element contents are reported in Table 2 as weight % of the oxides; a summation of the constituent contents is included. Total Fe contents, as % FeO, TiO<sub>2</sub> contents, and the contents of Rb and Sr in parts per million, are also reported. The results of the P<sub>2</sub>O<sub>5</sub> analyses are not given because these analyses proved to be of poor quality; the 15 samples analyzed for P<sub>2</sub>O<sub>5</sub> gave results ranging from 0.00 to 0.06 with a mean value of 0.03.

The values reported in Table 2 for the various constituents show the following ranges: SiO<sub>2</sub>, 75.5 - 80.6; Al<sub>2</sub>O<sub>3</sub>, 9.62 - 12.64; TiO<sub>2</sub>, 0.268 - 0.460; Fe<sub>2</sub>O<sub>3</sub>, 0.12 - 0.31; FeO, 1.42 - 2.36; MgO, 1.13 - 2.50; CaO, 1.46 - 3.71; Na<sub>2</sub>O, 0.31 - 0.67; K<sub>2</sub>O, 3.26 - 3.81; total Fe as FeO, 1.53 - 2.61; Rb, 120 - 160 ppm; Sr, 130 - 156 ppm. All of these values fall within the ranges given in the literature (Barnes, 1940; Schnetzler and Pinson, 1963, 1964a, 1964b; Bouška and Povondra, 1964) with the exception of one K<sub>2</sub>O analysis and four Rb analyses. The K<sub>2</sub>O analyses all fall in the upper region of the range reported in the literature. The specific gravity and refractive index values of the 23 moldavites range from 2.3312 to 2.3718 gm/cm<sup>3</sup> and from 1.486 to 1.495, respectively.



Table 2 Analytical Results

	T 5296a Ihenice	T 5296b Ihenice	T 5296c Ihenice	T 5296d Ihenice	T 5296e Ihenice	T 5296f Ihenice	T 5309 Ihenice	T 5310 Ihenice
SiO <sub>2</sub>	79.2	77.3	76.7	75.7*	78.4	75.5	79.6	78.5*
Al <sub>2</sub> O <sub>3</sub>	10.93	10.89	11.28	11.04	10.76	11.12	10.73	10.54
TiO <sub>2</sub>	0.307	0.336	0.331	0.314	0.303	0.313	0.300	0.294
Fe <sub>2</sub> O <sub>3</sub>	0.16	0.31	0.20	0.28	0.12	0.29	0.18	0.21
FeO	1.54	1.63	1.73	1.47	1.62	1.50	1.46	1.46
MgO	1.48	2.09	1.99	2.50	2.13	2.20	1.90	1.58
CaO	2.02	2.91	2.79	3.58	3.27	3.40	2.78	2.64
Na <sub>2</sub> O	0.51	0.51	0.63	0.45	0.45	0.48	0.37	0.41
K <sub>2</sub> O	3.64	3.74	3.71	3.44	3.66	3.68	3.48	3.62
<b>Total</b>	<b>99.79</b>	<b>99.72</b>	<b>99.36</b>	<b>98.77</b>	<b>100.71</b>	<b>98.48</b>	<b>100.80</b>	<b>99.25</b>
Total Fe as FeO	1.68	1.91	1.91	1.72	1.73	1.76	1.62	1.65
Rb ppm	148	146	144	120	136	140	131	139
Sr ppm	133	156	142	140	148	144	138	139
R.I.	1.486	1.491	1.492	1.495	1.492	1.494	1.492	1.492
Sp. G.	2.3350	2.3654	2.3521	2.3718	2.3635	2.3664	2.3493	2.3451

Table 2 continued

	№ 5311	№ 5312	№ 5313	№ 5314	№ 5315	№ 5316	№ 5317	№ 5318
	Doñi Chrastany	Habl'1	Habl'1	Slavce	Vrabce	Vrabce	Kroolov	Korošaky
SiO <sub>2</sub>	78.6	77.6	78.4	80.6*	77.0	79.55	77.1*	78.4
Al <sub>2</sub> O <sub>3</sub>	10.77	11.13	10.30	10.09	10.28	9.94	10.43	10.11
TiO <sub>2</sub>	0.307	0.331	0.300	0.295	0.287	0.286	0.285	0.268
Fe <sub>2</sub> O <sub>3</sub>	0.26	0.21	0.13	0.12	0.16	0.13	0.14	0.18
FeO	1.46	1.75	1.63	1.42	1.49	1.55	1.49	1.50
MgO	1.66	2.10	1.90	1.38	2.19	1.63	2.33	2.12
CaO	2.35	3.12	3.07	2.00	3.50	2.16	3.69	3.71
Na <sub>2</sub> O	0.42	0.51	0.45	0.45	0.35	0.50	0.31	0.38
K <sub>2</sub> O	3.59	3.75	3.74	3.58	3.65	3.71	3.44	3.65
Total	99.42	100.50	99.92	99.94	98.91	99.46	99.22	100.32
Total Fe as FeO	1.69	1.94	1.75	1.53	1.63	1.67	1.62	1.66
Rb ppm	138	141	140	145	129	149	121	135
Sr ppm	134	146	144	130	147	139	147	147
R.I.	1.491	1.495	1.494	1.488	1.493	1.489	1.494	1.493
Sp. g.	2.3440	2.3647	2.3708	2.3312	2.3653	2.3413	2.3681	2.3644

Table 2 continued

	T 5319 Něchov	T 5320 Slavice	T 5321 Kožichovice	T 5322 Slavetice	T 5323 Dukovany	T 5324 Dukovany	T 5325 Dukovany
SiO <sub>2</sub>	80.3	79.8	80.2	79.4*	78.8	76.7*	80.0
Al <sub>2</sub> O <sub>3</sub>	9.62	11.04	11.02	11.24	10.99	12.64	11.43
TiO <sub>2</sub>	0.284	0.402	0.337	0.364	0.326	0.460	0.361
Fe <sub>2</sub> O <sub>3</sub>	0.20	0.26	0.14	0.16	0.17	0.28	0.23
FeO	1.49	2.03	1.64	1.83	1.60	2.36	1.71
MgO	1.57	1.24	1.25	1.33	1.61	1.15	1.13
CaO	2.52	1.57	1.68	1.50	2.46	1.57	1.46
Na <sub>2</sub> O	0.42	0.60	0.53	0.53	0.39	0.67	0.58
K <sub>2</sub> O	3.68	3.69	3.47	3.57	3.26	3.81	3.53
Total	100.08	100.63	100.27	99.92	99.61	99.64	100.43
Total Fe as FeO	1.67	2.26	1.77	1.97	1.75	2.61	1.92
Rb ppm	150	148	138	142	122	160^	149
Sr ppm	133	134	135	137	146	133^	134
R.I.	1.489	1.490	1.487	1.489	1.491	1.492	1.489
Sp. G.	2.3414	2.3474	2.3351	2.3388	2.3484	2.3609	2.3372

## Table 9 continued

\* spectrophotometric determination of  $\text{SiO}_2$

^ mass spectrometric isotope dilution analysis by Professors  
W. H. Pinson, Jr., and H. W. Fairbairn.

Note: Tektites 5296a - 5319 are from Bohemia, tektites 5320 -  
5325 are from Moravia.

## DISCUSSION

The results reported in Table 2 indicate variations in the contents of all constituents. The observed scatter of the moldavite analyses, expressed in terms of the same function  $C$  as was used to evaluate precision, is as follows:  $\text{SiO}_2$ ,  $\pm 2\%$ ;  $\text{Al}_2\text{O}_3$ ,  $\pm 4\%$ ;  $\text{TiO}_2$ ,  $\pm 13\%$ ; total Fe as FeO,  $\pm 13\%$ ;  $\text{MgO}$ ,  $\pm 23\%$ ;  $\text{CaO}$ ,  $\pm 29\%$ ;  $\text{Na}_2\text{O}$ ,  $\pm 19\%$ ;  $\text{K}_2\text{O}$ ,  $\pm 4\%$ ; Rb,  $\pm 7\%$ , Sr,  $\pm 4\%$ . It is evident that the observed scatter is greater than the analytical error for all constituents, and indeed, it is considerably greater for most constituents. It is therefore concluded that real differences in chemical composition exist between the moldavites analyzed in this investigation.

The Moravian tektites were found to have higher average contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , FeO and  $\text{Na}_2\text{O}$ , and lower average contents of  $\text{MgO}$ ,  $\text{CaO}$ , and Sr, than the Bohemian tektites. The specific gravities of the Moravian samples were lower, in general, than those of the Bohemian samples; this is in accord with the results of the specific gravity study by Chapman *et al* (1964). The major distinction between moldavites from the two localities is that the Moravian samples have high and variable FeO and  $\text{TiO}_2$  contents with low and relatively constant  $\text{CaO}$ ,  $\text{MgO}$ , and Sr, whereas the Bohemian samples have high and variable alkaline earth contents with low and constant FeO and  $\text{TiO}_2$ . This difference is illustrated

for the pair CaO - FeO in Figure 1. The overall similarity between tektites from the two groups, however, suggests that a common origin is highly probable. The data do not indicate any clear regional trends in composition within either of the "strewn fields". This is not surprising in view of the facts that moldavites of all colours occur in most localities (Paul and Bouška, 1963), and that tektites from Habří showed a wide range of specific gravities (Chapman *et al.*, 1964).

Certain relationships exist between the various constituents of moldavites. In Table 3, correlation coefficients and degrees of significance are presented for various pairs of constituents. The alkalis show positive correlations amongst themselves, as do the alkaline earths. Na<sub>2</sub>O and Rb are inversely correlated with the alkaline earths. SiO<sub>2</sub> shows negative correlations of various significances with the alkaline earths, Al<sub>2</sub>O<sub>3</sub>, refractive index and specific gravity. FeO (actually total Fe as FeO) has significant positive correlations with TiO<sub>2</sub> and with Na<sub>2</sub>O.

The variations in the chemical composition of moldavites reflect variations in the parent material and/or differential changes in composition brought about during fusion. Taylor (1962), partly on the basis of significant negative correlations of most constituents with SiO<sub>2</sub>, concluded that the australite parent material consisted of a mixture of 75% homogeneous shale and 25% quartz. Such a mixture is not

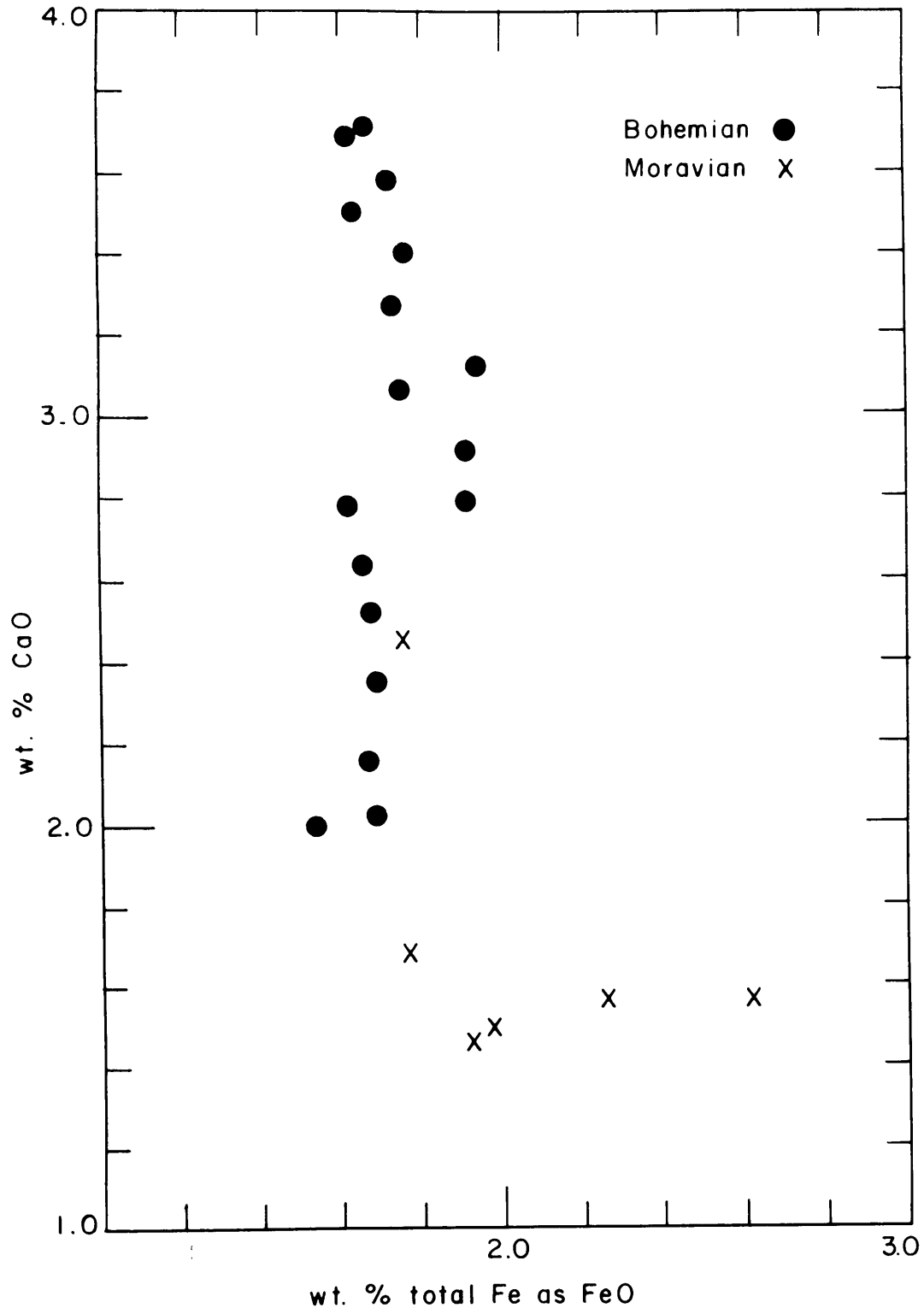


Fig. 1 CaO vs. FeO for 23 moldavites.

Table 3 Correlation coefficients (r) and levels of significance, for various pairs of constituents in moldavites.

	Moravia		Bohemia		Combined data	
	r	signi- ficance	r	signi- ficance	r	signi- ficance
Na <sub>2</sub> O-K <sub>2</sub> O	+0.96	<1%	+0.63	<1%	+0.47	<5%
Na <sub>2</sub> O-Rb	+0.99	<0.1	+0.61	<1	+0.73	<0.1
K <sub>2</sub> O-Rb	+0.94	<1	+0.75	<0.1	+0.72	<0.1
MgO-CaO	+0.91	1	+0.81	<0.1	+0.96	<0.1
MgO-Sr	+0.98	<0.1	+0.72	<0.1	-	-*
CaO-Sr	+0.91	1	+0.56	<5	-	-*
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	not significant		-0.65	<1	-	-*
SiO <sub>2</sub> -MgO	-0.93	<5"	-0.83	0.1	-0.88	<0.1 <sup>^</sup>
FeO <sup>X</sup> -TiO <sub>2</sub>	+0.99	<0.1	+0.85	<0.1	+0.96	<0.1
FeO <sup>X</sup> -Na <sub>2</sub> O	+0.83	<5	+0.70	<1	+0.79	<0.1
Na <sub>2</sub> O-MgO	-0.91	1	not significant		-0.53	1
Na <sub>2</sub> O-CaO	-0.83	<5	not significant		0.64	0.1
Rb-CaO	-0.83	<5	-0.73	<0.1	-	-*
Rb-Sr	-0.90	<5	-0.50	<5'	-0.61	<1 <sup>^</sup>

\* combined data not applicable

" n = 5

<sup>^</sup> n=22

<sup>X</sup> Total Fe as FeO

' n=16



suggested by the moldavite data because  $\text{SiO}_2$  is not inversely correlated with the alkalis or with  $\text{FeO}$ . In fact, the non-linear correlations of certain pairs of constituents (eg.  $\text{CaO-FeO}$ , Figure 1;  $\text{Na}_2\text{O-FeO}$ ) cannot be explained in terms of any two-phase mixing process, including the mixing of immiscible liquids. The data could be explained in terms of a complicated mixing process but the significant correlations between many pairs of constituents indicate that a simple cause was responsible for the observed variations in chemical composition. In any case, sedimentary parent materials would seem to be ruled out by the oxygen isotope data. Taylor and Epstein (1962, 1963) concluded on the basis of the oxygen data that tektites are either extra-terrestrial or they are fused terrestrial granitic rocks with changed chemical composition.

Superficially, the variations in chemical composition of the moldavites resemble the variations in acid igneous rock sequences. In such sequences, however, the alkalis have positive correlations with  $\text{SiO}_2$ , and iron is positively correlated with the alkaline earths and with  $\text{Al}_2\text{O}_3$ . These correlations are not displayed by the moldavites. In addition, there is no evidence for the erstwhile existence of discrete phases in tektites, with the exception of a  $\text{SiO}_2$  phase. The presence of lechatelierite is of interest because melts of moldavite composition would presumeably

lie within the  $\text{SiO}_2$  field and differentiation would occur by  $\text{SiO}_2$  phase separation. Products of this  $\text{SiO}_2$  subtraction would exhibit inverse correlations of all constituents with  $\text{SiO}_2$ . This is not the case for moldavites. Another objection to the origin of the observed variations in chemical composition by igneous differentiation is the fact that these variations also occur over small distances within individual tektites. A preliminary electron microprobe study of moldavites indicated that variations in composition, comparable to those between bulk samples, occur over distances of  $100\mu$  or so, within individual samples. This is supported by the refractive index data of this present work and of that by Cohen (1963).

In view of the failure of other processes to satisfactorily explain the variations in chemical composition of the moldavites, it is suggested that these variations are, for the most part, the result of selective volatilization. Many investigators (eg. Cohen, 1960; Lovering, 1960; Lowman, 1962; Greenland and Lovering, 1962; Chao, 1963) have appealed to selective volatilization in order to account for various features of the chemical compositions of tektites. Perhaps the best evidence of extensive changes of composition by selective volatilization is the apparent discrepancy between the U-Pb and Rb-Sr ages (Schnetzer and Pinson, 1964b).

Experimental data concerning selective volatilization

are meagre. Experiments by Lovering (1960), Friedman et al (1960), and Walter and Carron (1964), and optical spectrograph studies (Ahrens and Taylor, 1961) on silicate materials have indicated the following order of volatility, from most to least volatile: Alkalis  $>$  Si, Fe  $>$  Al, alkaline earths. It therefore seems probable that selective volatilization of tektite material would reduce the concentrations of alkalis and increase those of the alkaline earths. The content of a particular alkali or alkaline earth constituent could be used as an index of the extent of the process' action. There is the possibility, however, that some of the variation in concentration of the constituent could be inherited from the parent material. For example, the addition or subtraction of  $\text{SiO}_2$  from an otherwise homogeneous material would affect the concentration of another constituent; it would not, however, affect the weight ratio of any two constituents (excluding  $\text{SiO}_2$ ). A ratio of two constituents would therefore serve as a better index of volatilization.

The moldavite data was interpreted in terms of Rb/Sr ratio for the following reasons: 1. Rb and Sr are inversely correlated and therefore their ratio shows wide variation; 2. Rb and Sr were determined separately from all other constituents and therefore relationships between the Rb/Sr ratio and other constituents cannot be due to analytical idiosyncracies; 3. the Rb/Sr ratio is believed to be as

good if not better than the individual Rb and Sr determinations with respect to precision and accuracy. In addition, even though the Rb/Sr ratio varies from 0.77 to 1.20, eight out of nine  $\text{Sr}^{87}/\text{Sr}^{86}$  analyses of moldavites fell within a range of only 0.0011, which is two standard deviations of a single analysis (Pinson et al., 1965). It is suggested that the most attractive explanation of the moldavite Rb-Sr data is that the parent material had a constant Rb/Sr ratio throughout as indicated by the uniformity of the Sr isotopic composition, and that the Rb/Sr ratio was decreased by various amounts by selective volatilization during the thermal event dated by the K-A age.

Bohemian tektites with lower Rb/Sr ratios have lower  $\text{SiO}_2$ ,  $\text{Na}_2\text{O}$ , and Rb contents, and higher alkaline earth contents.  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , FeO, and  $\text{K}_2\text{O}$  do not vary appreciably with decreasing Rb/Sr. Moravian tektites with lower Rb/Sr ratios have lower  $\text{SiO}_2$ ,  $\text{TiO}_2$ , FeO, and alkali contents, and higher alkaline earth contents. Sample 5324 is exceptional in that it has the highest Rb/Sr ratio (1.20) and yet has lower  $\text{SiO}_2$  and higher  $\text{Al}_2\text{O}_3$  than the other 5 Moravian samples. The intercepts of trend lines in plots of pairs of constituents indicate relative volatilities. Thus in Figure 2 the trend line gives an intercept of about 3%  $\text{K}_2\text{O}$  and this indicates that  $\text{Na}_2\text{O}$  was more volatile than  $\text{K}_2\text{O}$ . Another method of determining relative volatilities is by examination

of constituent ratio changes with changing Rb/Sr. K/Rb was found to increase with decreasing Rb/Sr (Figure 3), and this indicates that Rb was more volatile than K. The relative volatilities of the chemical constituents, as indicated by the correlations, were as follows, from most to least volatile:  $\text{Na}_2\text{O}$ , Rb,  $\text{K}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , Sr, MgO, and CaO. This order is in essential agreement with the available experimental evidence. The relationships of iron with other constituents suggest that initially iron was the most volatile constituent and was rapidly lost until an equilibrium value of about 1.7% total Fe as FeO was attained.

It is difficult to account for the relationships among the chemical constituents of moldavites by means other than selective volatilization. This process might have masked preexisting variations. The authors feel, however, that such initial variations would involve the addition or subtraction of  $\text{SiO}_2$ . The inverse correlations of the alkalis and alkaline earths in moldavites suggests that variations of  $\text{SiO}_2$  in the parent material of moldavites were very limited. The presence of lechatelierite inclusions might indicate that the parent material consisted of an aphanitic or hyaline matrix containing a few phenocrysts of a pure  $\text{SiO}_2$  phase. Differences between the Bohemian and the Moravian tektites probably reflect different histories during the thermal event. The parent material of moldavites was

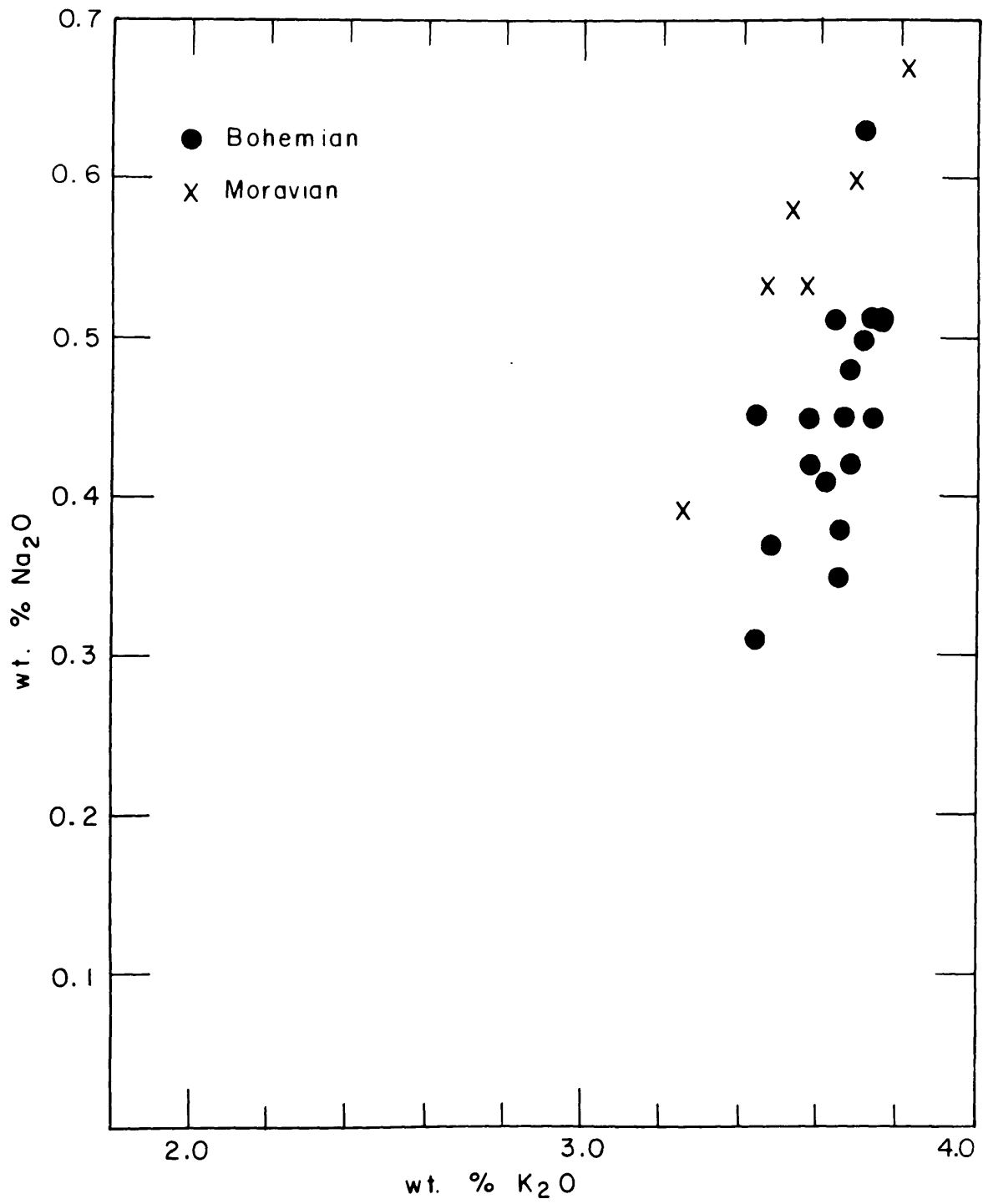


Fig. 2 Na<sub>2</sub>O vs. K<sub>2</sub>O for 23 moldavites

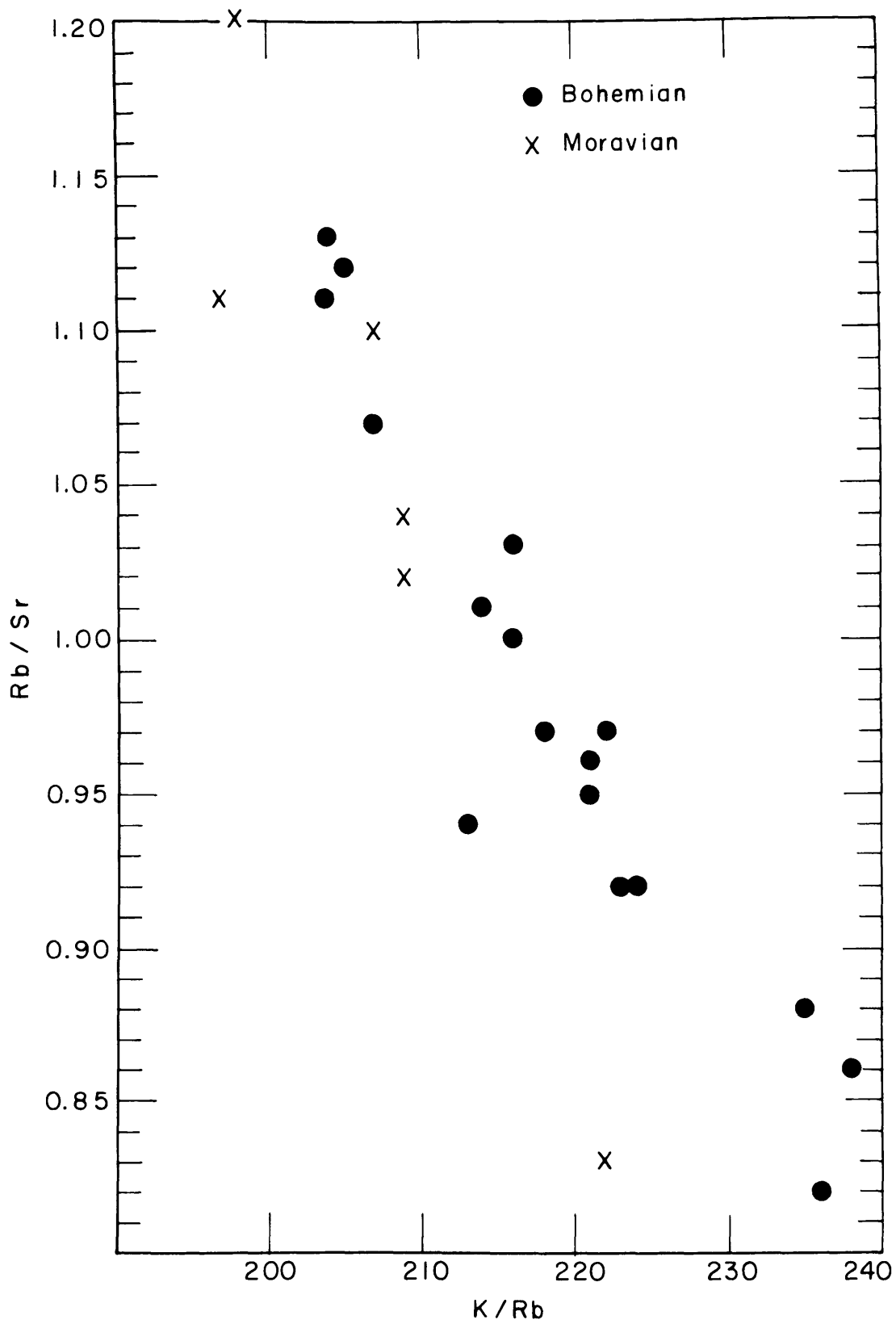


Fig. 3 Rb/Sr vs. K/Rb for 23 moldavites

probably homogeneous throughout.

Selective volatilization may have affected the chemical composition of tektites from other geographical groups. Taylor (1962) found an inverse correlation of most chemical constituents with  $\text{SiO}_2$  in australites, and this was interpreted in terms of a proposed quartz-shale parent mixture. Igneous differentiation of melts with tektite composition might well take place by  $\text{SiO}_2$  phase separation. The sedimentary mixing of pure  $\text{SiO}_2$  with a homogeneous phase (shale), and the igneous process of subtracting  $\text{SiO}_2$  from a homogeneous phase (melt), both yield products with inverse correlations between  $\text{SiO}_2$  and all other constituents. The addition or subtraction of  $\text{SiO}_2$ , however, does not completely account for the australite data. It does not account for the variation in ratios of constituents other than  $\text{SiO}_2$ . Some other process, such as selective volatilization, must be invoked to explain these ratio variations. In addition, not all of the constituents in australites are inversely correlated with  $\text{SiO}_2$  (Taylor, 1962; Taylor and Sachs, 1964). Loss of Ga and Cu, both of which are relatively volatile, to equilibrium concentrations might account for their lack of correlation with  $\text{SiO}_2$ . The lack of definite relationships with  $\text{SiO}_2$  in the cases of CaO and Sr, which are both relatively involatile, might be accounted for if  $\text{SiO}_2$  were also involatile. The positive correlation of  $\text{SiO}_2$  and Zr, and the high concentration of Zr in australites, would then also be



explained. The positive correlation of  $\text{Fe}^{3+}$  and  $\text{SiO}_2$  might also best be explained in terms of volatilization. It is concluded that the variations in the chemical composition of australites might also be the result of selective volatilization.

The probability of fusing terrestrial material, with the appropriate chemical composition, oxygen isotopic composition (Taylor and Epstein, 1962, 1963) and strontium isotopic composition (Schnetzler and Pinson, 1964b, 1965; Pinson et al, 1965), in four, large-scale, separate events, is low. In addition, aerodynamic ablation evidence (Chapman and Larson, 1963; Adams and Huffaker, 1964; Chao, 1964), petrographic data (Chao, 1963), and water content (O'Keefe, 1964), all seem to indicate an extra-terrestrial origin of tektites. Yet the moldavites have the same K-A age (Zahringer, 1963), within the experimental error, as the Nordlingen Ries impact crater, which is about 300 km west of the strewn field. This K-A data has been interpreted to mean that the moldavites were blasted out of the Ries crater (Cohen, 1963). The diverse rock types found rimming this crater (Shoemaker and Chao, 1961), however, would seem to be unsuitable parents, chemically and isotopically (Taylor and Epstein, 1963), for the moldavites. Perhaps, as O'Keefe (1963) has suggested on the basis of stratigraphic relations, the moldavites and the Ries crater are not of identical age.

If they are the same age it could be fortuitous but the Ivory Coast tektites have the same K-A age (Gentner et al, 1964) as the Bosumtwi crater, which is about 275 km east of the strewn field. Perhaps the Ries crater was formed by the impact of the moldavite parent-body. Such an origin might best explain the alignment of the moldavite strewn field with the Ries crater. In the case of the Ivory Coast tektites, however, there is ancillary evidence to support a hypothesis of terrestrial origin. Not only do the Ivory Coast tektites have the same K-A age as the Bosumtwi crater, but they would also seem to have the same Rb - Sr age as rocks in that part of Africa (Schnetzler and Pinson, 1965).

## SUMMARY

New analyses for nine major elements and for the trace elements Rb and Sr in 17 Bohemian and 6 Moravian moldavites have been reported. The refractive indexes and bulk specific gravities of the 23 moldavites have also been reported. Real variations in chemical composition and physical properties were found.

The Moravian tektites that were analyzed had higher average contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , FeO and  $\text{Na}_2\text{O}$ , and lower average contents of MgO, CaO and Sr than had the Bohemian tektites. The major distinction between samples from the two strewn fields is that Moravian tektites have high and variable FeO and  $\text{TiO}_2$  contents with low and relatively constant MgO, CaO, and Sr, whereas Bohemian tektites have high and variable alkaline earth contents, with low and constant FeO and  $\text{TiO}_2$ . The overall similarity between tektites from the two groups suggests that a common origin is highly probable. No clear regional trends in composition within the strewn fields were found.

The relationships between the concentrations of the various constituents were examined. It was concluded that the variations in chemical composition within and between individual moldavites are best explained in terms of selective volatilization that occurred during the brief thermal event dated by the K-A age. The wide range of Rb/Sr ratios and the uniformity of the Sr isotopic composition support

this conclusion. The variations in chemical composition were re-examined using the Rb/Sr ratio as an index of the extent of the proposed selective volatilization process. It was concluded that the parent material of the moldavites was probably of uniform composition throughout. It was suggested that selective volatilization may have been an important factor in the origin of other tektite groups.

It is thought that the chemical, isotopic, petrographic and aerodynamic ablation data on tektites favours, in general, an extra-terrestrial origin of these objects. It was suggested that the Ries crater might have been produced by impact of the moldavite parent-body. The preliminary Rb-Sr data on Ivory Coast tektites in conjunction with the K-A data would seem to strongly favour a terrestrial origin. If tektites are of terrestrial origin, some fundamental point would seem to have been so far overlooked.

## REFERENCES

- Adams E. W. and Huffaker R. M. (1964) Aerodynamic analysis of the tektite problem. Geochim. et Cosmochim. Acta 28, 881 - 892.
- Ahrens L. H. and Taylor S. R. (1961) Spectrochemical Analysis. Addison - Wesley, Reading, Mass.
- Barnes V. E. (1940) North American Tektites. Univ. Texas Publ. No. 3945, 477 - 582.
- Bouška V. and Povondra P. (1964) Correlation of some physical and chemical properties of moldavites. Geochim. et Cosmochim. Acta 28, 783 - 791.
- Chao E. C. T. (1963) The petrographic and chemical characteristics of tektites. Tektites (Ed. J. O'Keefe) Chapter 3, 51 - 94, Univ. of Chicago Press, Chicago.
- Chao E. C. T. (1964) Spalled, aerodynamically modified moldavite from Slavice, Moravia, Czechoslovakia. Science 146, 790 - 791.
- Chapman D. R. and Larson H. K. (1963) On the lunar origin of tektites. J. Geophys. Res. 68, 4305 - 4358.
- Chapman D. R., Larson H. K. and Scheiber L. C. (1964) Population polygons of tektite specific gravity for various localities in Australia. Geochim. et Cosmochim. Acta 28, 821 - 839.
- Cherry R. D. and Taylor S. R. (1961) Studies of tektite composition - II. Derivation from a quartz - shale mixture. Geochim. et Cosmochim. Acta 22, 164 - 168.
- Cohen A. J. (1960) Germanium content of tektites and other natural glasses. Implications concerning the origin of tektites. Rept. 21st Internat. Geol. Congr., Copenhagen, Part I, 30 - 39.
- Cohen A. J. (1963) Asteroid - or comet - impact hypothesis of tektite origin: the moldavite strewn fields. Tektites (Ed. J. O'Keefe) Chapter 9, 189 - 211, Univ. of Chicago Press, Chicago.
- Faul H. and Bouška V. (1963) Statistical study of moldavites. 2nd Internat. Symp. on Tektites, Pittsburgh, Pa. (Abstract).

- Fleischer M. and Stevens R. E. (1962) Summary of new data on rock samples G-1 and W-1. Geochim. et Cosmochim. Acta 26, 525 - 543.
- Friedman I., Thorpe A. and Senftle F. E. (1960) Comparison of the chemical composition and magnetic properties of tektites and glasses formed by fusion of terrestrial rocks. Nature, Lond. 187, 1089 - 1092.
- Gentner von W., Lippolt H. J. and Müller O. (1964) Das Kalium-Argon-Alters des Bosumtwi-Kraters in Ghana und die chemische Beschaffenheit seine Gläser. Z. Naturforschg. 19a, 150 - 153.
- Greenland L. and Lovering J. F. (1963) The evolution of tektites: elemental volatilization in tektites. Geochim. et Cosmochim. Acta 27, 249 - 259.
- Lovering J. F. (1960) High temperature fusion of possible parent materials for tektites. Nature, Lond. 186, 1028 - 1030.
- Lowman P. D. Jr. (1962) The relation of tektites to lunar igneous activity. J. Geophys. Res. 67, 1646.
- O'Keefe J. A. (1963) The origin of tektites. Tektites (Ed. J. O'Keefe) Chapter 8, 167 - 188, Univ. of Chicago Press, Chicago.
- O'Keefe J. A. (1964) Water in tektite glass. J. Geophys. Res. 69, 3701-3707.
- Pinson W. H. Jr., Philpotts J. A. and Schnetzler C. C. (1965) K/Rb ratios in tektites. To be submitted for publication in J. Geophys. Res.
- Pinson W. H. Jr., Schnetzler C. C., Philpotts J. A. and Fairbairn H. W. (1965) Rb-Sr correlation study of the moldavites. To be presented at annual meeting of Amer. Geophys. Un., Washington, D.C. (Abstract).
- Rose H. J. Jr., Adler I. and Flanagan F. J. (1963) X-ray fluorescence analysis of the light elements in rocks and minerals. Applied Spectroscopy 17, 81 - 85.
- Schnetzler C. C. and Pinson W. H. Jr. (1963) The chemical composition of tektites. Tektites (Ed. J. O'Keefe) Chapter 4, 95 - 129, Univ. of Chicago Press, Chicago.

- Schnetzler C. C. and Pinson W. H. Jr. (1964a) Report of some recent major element analyses of tektites. Geochim. et Cosmochim. Acta 28, 793 - 806.
- Schnetzler C. C. and Pinson W. H. Jr. (1964b) Variation of strontium isotopes in tektites. Geochim. et Cosmochim. Acta 28, 953 - 969.
- Schnetzler C. C. and Pinson W. H. Jr. (1965) Rb-Sr age study of Ivory Coast tektites. To be presented at annual meeting of Amer. Geophys. Un., Washington, D. C. (Abstract).
- Shapiro L. (1960) A spectrophotometric method for the determination of FeO in rocks. U.S.G.S. Prof. Paper 400B, 496 - 497.
- Shoemaker E. M. and Chao E. C. T. (1961) New evidence for the impact origin of the Ries Basin, Bavaria, Germany. J. Geophys. Res. 66, 3371 - 3378.
- Taylor H. P. Jr. and Epstein S. (1962) Oxygen isotope studies on the origin of tektites. J. Geophys. Res. 67, 4485 - 4490.
- Taylor H. P. Jr. and Epstein S. (1963) Comparison of  $^{18}O/^{16}O$  ratios in tektites, soils, and impact glasses. Trans. Amer. Geophys. Un. 44, 93. (Abstract).
- Taylor S. R. (1960) Abundance and distribution of alkali elements in australites. Geochim. et Cosmochim. Acta 20, 85 - 100.
- Taylor S. R., Sachs, Maureen, and Cherry R. D. (1961) Studies of tektite composition - I. Inverse relationship between  $SiO_2$  and the other major constituents. Geochim. et Cosmochim. Acta 22, 155 - 163.
- Taylor S. R. (1962) The chemical composition of australites. Geochim. et Cosmochim. Acta 26, 685 - 722.
- Taylor S. R. and Sachs, Maureen (1964) Geochemical evidence for the origin of australites. Geochim. et Cosmochim. Acta 28, 235 - 264.
- Volborth A. (1963) X-ray spectrographic determination of all major oxides in igneous rocks and precision and accuracy of a direct pelletizing method. Nevada Bur. of Mines Rept. 6, 1 - 72.

- Walter L. S. and Carron M. K. (1964) Vapor pressure and vapor fractionation of silicate melts of tektite composition. Geochim. et Cosmochim. Acta 28, 937 - 951.
- Welday E. E., Baird A. K., McIntyre D. B. and Madlem K. W. (1964) Silicate sample preparation for light element analysis by x-ray spectrography. Amer. Min. 49, 889 - 903.
- Zahringer J. (1963) Isotopes in tektites. Tektites (Ed. J. O'Keefe) Chapter 6, 137 - 149, Univ. of Chicago Press, Chicago.



## K/Rb Ratios in Tektites \*

Pinson, W. H., Jr., Philpotts, J. A., and Schnetzler, C. C.\*\*

Department of Geology and Geophysics

Massachusetts Institute of Technology

Cambridge, Massachusetts.

\*\*Theoretical Division, Goddard Space Flight Center, NASA

Greenbelt, Maryland

### Abstract:

K/Rb weight ratios and individual K and Rb contents are reported for 54 tektites. Twenty-nine of these are new analyses. The ranges of K/Rb ratios found in the present investigation for the different tektite localities are as follows: australites, 151-185, 4 samples; javanite, 162; philippinites, 169-174, 7 samples; indochinites, 166-178, 8 samples; Ivory Coast, 209; moldavites 197-238, 30 samples; North American, 249-267, 3 samples. Thus the Pacific Area, North American and Czechoslovakian tektites fall into three distinctive K/Rb ratio groups.

Potassium was determined flame photometrically, with 23 of the moldavite analyses being confirmed by x-ray fluorescence. Rubidium was determined by x-ray fluorescence, with standardization and numerous cross-checks by mass spectrometric stable isotope dilution analyses. G-1 and W-1 were used as analytical monitors. Precision and accuracy for the

---

\* M.I.T. Age Studies No. 65

ratios are better than  $\pm 4\%$ .

Variations of the K/Rb ratios within a group are interpreted as resulting from differential volatilization rates for K and Rb during high temperature fusion, whereas differences between the geographical groups reflect initial compositional variations in the parent materials.

### Introduction

The significance of the K/Rb ratio for theories of tektite origin was discussed by Taylor and Ahrens (1959). Their data for tektites was limited to about 5 specimens. They concluded that tektites are of solar system origin because their K/Rb ratios lie within the range  $220 \pm 50$  (Herzog and Pinson, 1955, 1956; Taylor and Heier, 1958; Ahrens, et al, 1952). The argument was based on the theoretical likelihood that had tektites formed in a planetary system resulting from the condensation of another stellar dust cloud, a different K/Rb might have resulted. The K/Rb ratios for the solar system may well be unique. The underlying idea is that stellar composition is dependent on place of origin, time, and the particular evolutionary history involved. Since 1959 it has become generally accepted that tektites are in fact of solar system origin, the evidence being chiefly that tektites do not contain measurable cosmogenic, radioactive elements (Anders, 1960). Furthermore it has been demonstrated

that tektites contain spherules of meteoritic Fe-Ni (Spencer, 1933; Chao, 1962, 1964) and this has been interpreted to mean that tektites are the result of meteoritic impact on a planetary surface, probably the earth, and possibly the moon.

### Analytical Results

In Table 1 we have compiled K/Rb ratios taken from Schnetzler and Pinson (1964a, 1964b), and new results for an Ivory Coast tektite and 28 moldavites. The K/Rb ratios are plotted graphically for the different localities in Figure 1.

The Rb values reported in Table 1 were obtained by a combination of mass spectrometric stable isotope dilution analyses and by x-ray fluorescence. The potassium contents were determined by flame photometry using Li as internal standard, and checked in part (for the moldavites) by x-ray fluorescence. All of these analyses for K and Rb were done in our Laboratory and the results are internally consistent in that common standards were used throughout. All analyses for K and Rb in the tektites were monitored with the rock standards G-1 and W-1 throughout the analysis period. The results of this monitoring and a listing of recommended values for these elements is tabulated in Table 2. Our flame photometric value of K in G-1 is 0.3% higher than the recommended value (see footnote to Table 2). The flame photometric determinations for K in the tektites have a pre-

cision of 1%, and all analyses were made on at least duplicate weighings. The x-ray determinations of K in the mol-davites agree in all but one case out of 23 analyses within 3% of the flame photometric analyses. Our value of 212.5 ppm Rb in G-1 is based on an exhaustive set of analyses by mass spectrometry. Published values, other than those by emission optical spectrography have ranged from 205 to 224. The precision of our mass spectrometric analyses for Rb in the tektites is 2%, this large error resulting almost entirely from instrumental fractionation of the measured  $\text{Rb}^{85}/\text{Rb}^{87}$  ratio. The precision of the x-ray fluorescence analyses for Rb is 2% for the concentrations found in tektites, based on results of replicate analyses for Rb in G-1 by Professor H. W. Fairbairn of M.I.T. (unpublished). Gentner, et al (1964) reported 64 ppm Rb by x-ray fluorescence in the Ivory Coast tektite (MIT sample No. T 5462) which we analysed. Our Rb analyses by mass spectrometric stable isotope dilution analysis was 64.8 ppm Rb, for this sample. This inter-laboratory comparison serves specifically as a check on the accuracy of our Rb analyses.

The K/Rb ratios tabulated in Table 1 were calculated on the following bases. Chemical values (rather than x-ray fluorescence) for potassium were used throughout. For those samples for which there were several isotope dilution analyses as well as an x-ray analysis we have averaged, without,

weighting, all of the analyses to obtain a rubidium value to use in calculating the K/Rb weight ratio.

### Discussion of the results

The four major tektite groups, namely the Pacific Area, North American, Czechoslovakian, and Ivory Coast fall into three distinct K/Rb ratio classes. The fact that the K/Rb ratio for the Ivory Coast sample falls near the mean of the Czechoslovakian sample ratio is probably fortuitous, because there is great dissimilarity in the general chemical compositions of samples from the two areas (Barnes, 1940; Schnetzler and Pinson, Table 4, 1963).

Although the number of samples is small, there appears to be a wider spread of K/Rb ratios for the indochinites than for the philippinites, especially if the javanite sample is included with the former group. Schnetzler and Pinson (1964a, Table 3) demonstrated from major element analyses that for most elements the indochinites show greater sample to sample chemical variability than do the philippinites (Sr and Ca are exceptions). A much larger spread in chemical composition for the australites was found (Schnetzler and Pinson, 1964a, Table 2), and this has been demonstrated conclusively in the work of Taylor (1962, 1964) for both minor and major elements. The precision of the K/Rb ratio measurements in australites in both Taylor's and our own work is sufficiently good to indicate that this ratio is much more

variable from sample to sample than is the case for tektites from other Pacific area localities. Our K/Rb ratio measurements for 4 australites average to the mean value for the other Pacific areas, viz about 170, but spread considerably on either side of this mean.

Taylor's (1960) data for the australites reveals K/Rb ratios ranging from about 210 to 235, with no overlap with our data. Whether this is due to analytical bias between data from the two laboratories, or is due to insufficient sampling is not known. On the other hand, Chao (1963) has published K and Rb analyses for the bediasites which give K/Rb ratios ranging from 240 to 365, and which average 282. There is an overlap in this case with our four samples. Both Chao's and Taylor's Rb analyses were made by emission optical spectroscopy.

There appears to be a difference in the K/Rb ratios for the tektites from Moravia and those from Bohemia - strewn fields that are separated by about 65 kilometers. The difference is shown graphically in Figure 1, with the group average being lower for the Moravian samples. The small number of samples, however, makes this conclusion tentative.

The range of values of the K/Rb ratio in tektites which we report in Table 1 is from 150 to 265, with only two australites lying outside the limit of  $220 \pm 50$  observed for common terrestrial rocks.

It is fairly well established by the ferrous-ferric iron

ratios (Abou-El-Azm, 1954; and Friedman et al, 1960) that tektites have been heated to temperatures probably in excess of 2000° C in an atmosphere of low oxygen pressure. At such temperatures tektite glass will lose material by vaporization. The experimental evidence of Walter and Carron (1964) and Lovering (1960) suggests that there is a preferential rate at which any given element vaporizes off. Although there is as yet no experimental verification that there is a differential rate of loss of Rb relative to K, we suspect that this is the most likely explanation of the range in K/Rb ratios found within any group of tektites. We do not think that the parent materials from which the four groups of tektites were fused initially had identical K/Rb ratios. The presently observed, post-fusion, K/Rb ratios probably reflect the initial ratios in the parent materials, later altered by the high temperature fusion event. It is known that the Na/K ratios vary widely between the different major tektite locality groups, and for the australites and moldavites especially there are rather wide variations of this ratio between individual tektites within a group. Walter and Carron (1964) have demonstrated experimentally that at low oxygen pressures and at temperatures of about 2000°C sodium is lost relative to potassium. A somewhat similar phenomenon might be expected to alter the relative concentrations of potassium and rubidium, although the experimental work necessary to test

this hypothesis for K and Rb has not yet been published.

### Acknowledgements

This research was sponsored by the NASA Research Grant No. Nsg222-61. Part of the analytical work, namely the mass spectrometry, was financed by the U.S. Atomic Energy Commission under Contract AT (30-1)-1381, which is under the supervision of Professor P.M. Hurley. The x-ray fluorescence analyses for rubidium were performed on equipment granted to M.I.T. by a National Science Foundation equipment grant, under the supervision of Professor H.W. Fairbairn. The potassium x-ray fluorescence analyses were performed at Harvard University under the supervision of Professor Clifford Frondel and Mrs. Frondel. To the above individuals and organizations we wish to express our appreciation.

We wish to thank the following individuals and institutions for the donation of samples: Professor Clifford Frondel of Harvard, Professor Alvin Cohen of the University of Pittsburg, Professor J. G. Lester of Emory University, and Dr. E.P. Henderson of the United States National Museum.



TABLE 1

## K and Rb Contents and K/Rb Ratios in Tektites

Geographical Group and MIT No.	Locality	K% Flame Photometry	K% X-ray Fluorescence	Rb ppm Isotope Dilution	Rb ppm X-ray Fluorescence	K/Rb Wt. Ratio
Australia						
3313	Charlotte Waters	1.98	-	109	-	181
4214	Nullarbor Plain	1.72	-	93	-	185
4215	" "	2.08	-	-	135	154
4216	" "	2.17	-	-	144	151
Java						
4104	Java	1.59	-	98	-	162
Philippines						
3379	Santa Mesa Site, Rizal Province	1.95	-	115	-	170
3962	" "	1.92	-	111	110	174
3964	" "	2.13	-	-	126	169
3765	Pugad-Babuy Site, Bulakan Province	2.08	-	119	118	176
3979	" "	1.99	-	-	118	169
3984	" "	1.95	-	112	115	172
3986	Busuanga Island	1.99	-	116	115	173
Indochina						
3987	Kouang-Tcheou Wan	2.07	-	118 123 119	116	172
3989	" "	1.94	-	-	110	177
3990	North Cambodia	2.07	-	116	116	178

Table 1 continued

Geographical Group and M.I.T. No.	Locality	K% Flame Photometry	K% X-ray Fluorescence	Rb ppm Isotope Dilution	Rb ppm X-ray Fluorescence	K/Rb Wt. Ratio
Indochina cont'd						
3991	North Cambodia	2.18	-	129	134	166
3993	Annam	1.88	-	113	112	168
4218	Dalat, S. Viet Nam	2.08	-	-	125	166
4219	" " "	1.93	-	111	110	174
4220	" " "	2.08	-	-	124	167
Ivory Coast						
5462	20-30 Km. South southwest of Ouelle	1.34*	-	64.3 65.4	- 64*	209
Czechoslovakia						
4575	Ratiborova Lhotka Bohemia	2.86	-	136	-	210
5296a	These six samples are from Lhenice, Bohemia, about 1 km east of the village, in fields	3.02	2.98	-	148	204
" b		3.10	3.15	-	146	213
" c		3.08	3.01	-	141	214
" d		2.86	2.91	-	120	238
" e		3.04	2.99	-	136	223
" f	right side of road to Chrástany.	3.05	3.13	-	140	218
5309	Lhenice, Bohemia	2.89	2.90	-	131	221
5310	" "	3.00	3.00	146	139	216**
5311	Dolni Chrástany Bohemia	2.98	3.04	-	138	216
4572	Strpi, Bohemia	2.76	-	132	-	209
4574	Radomilice, Bohemia	1.99	-	96	-	208

Table 1 continued

Geographical Group and M.I.T. No.	Locality	K% Flame Photometry	K% X-ray Fluorescence	Rb ppm Isotope Dilution	Rb ppm X-ray Fluorescence	K/Rb Wt. Ratio
Czechoslovakia cont'd						
5312	Habří, Bohemia	3.11	3.09	-	141	221
5313	" "	3.10	3.02	-	140	222
5314	Slávče, Bohemia	2.97	3.00	-	145	205
5315	Vrábče, Bohemia	3.03	3.00	-	129	235
5316	" "	3.08	3.05	-	149	207
5317	Kroclov, Bohemia	2.86	2.85	121	122	236
4570	" "	2.96	-	138	-	215
4571	Koroseky, Bohemia	3.01	-	148	-	203
5318	" "	3.03	3.05	-	135	224
4090	Něchov, Bohemia	2.88	-	146	-	197
5319	" "	3.05	3.03	-	150	204
5320	Slavice, Moravia	3.06	2.99	-	148	207
4573	" "	2.96	-	148	-	200
5321	Kožichovice, Moravia	2.88	3.01	-	138	209
5322	Slavetice, Moravia	2.96	3.03	-	142	209
5323	Dukovany, Moravia	2.71	2.73	-	122	222
5324	" "	3.16	3.09	160	161	198
5325	" "	2.93	2.97	-	149	197
North America						
4106	Grimes County, Texas	1.74	-	70	-	249
4271	Empire, Ga.	1.98	-	74	-	267
4091	Martha's Vineyard, Mass.	2.03	-	78	-	260

\* Gentner, et al, X-ray fluorescence values for K and Rb. Our isotope dilution values.

\*\* X-ray value used in computing K/Rb

TABLE 2

K and Hb contents of G-1 and W-1 Determined throughout the Analysis Period of the Present work

	% K (Present work period)	% K (Recommended Value)*	Rb (Present work period)	Rb (Recommended Value)**
G-1	4.52 ± 0.10 (Schnetzler and Pinson)	4.52	212.5 (Pinson, and Fairbairn, H. W.)	220
W-1	Not used as a monitor For K in this work	-	22.5 (Pinson)	22

\* (Fleischer and Stevens, 1962) and (Stevens and Miles, 1960). The recommended value of Stevens and Miles is 4.52% K in G-1, for the arithmetic mean of analyses published prior to 1959. Fleischer and Stevens have compiled all K analyses for G-1 published after 1959. The arithmetic mean of 12 of these analyses (we excluded 2 or 2 analyses that were made by methods not expected to yield a high accuracy) is also 4.52% K in G-1.

\*\* Ahrens and Fleischer (1960). Fleischer and Stevens state that changes in the recommended value given by Ahrens and Fleischer in 1960 are not warranted.

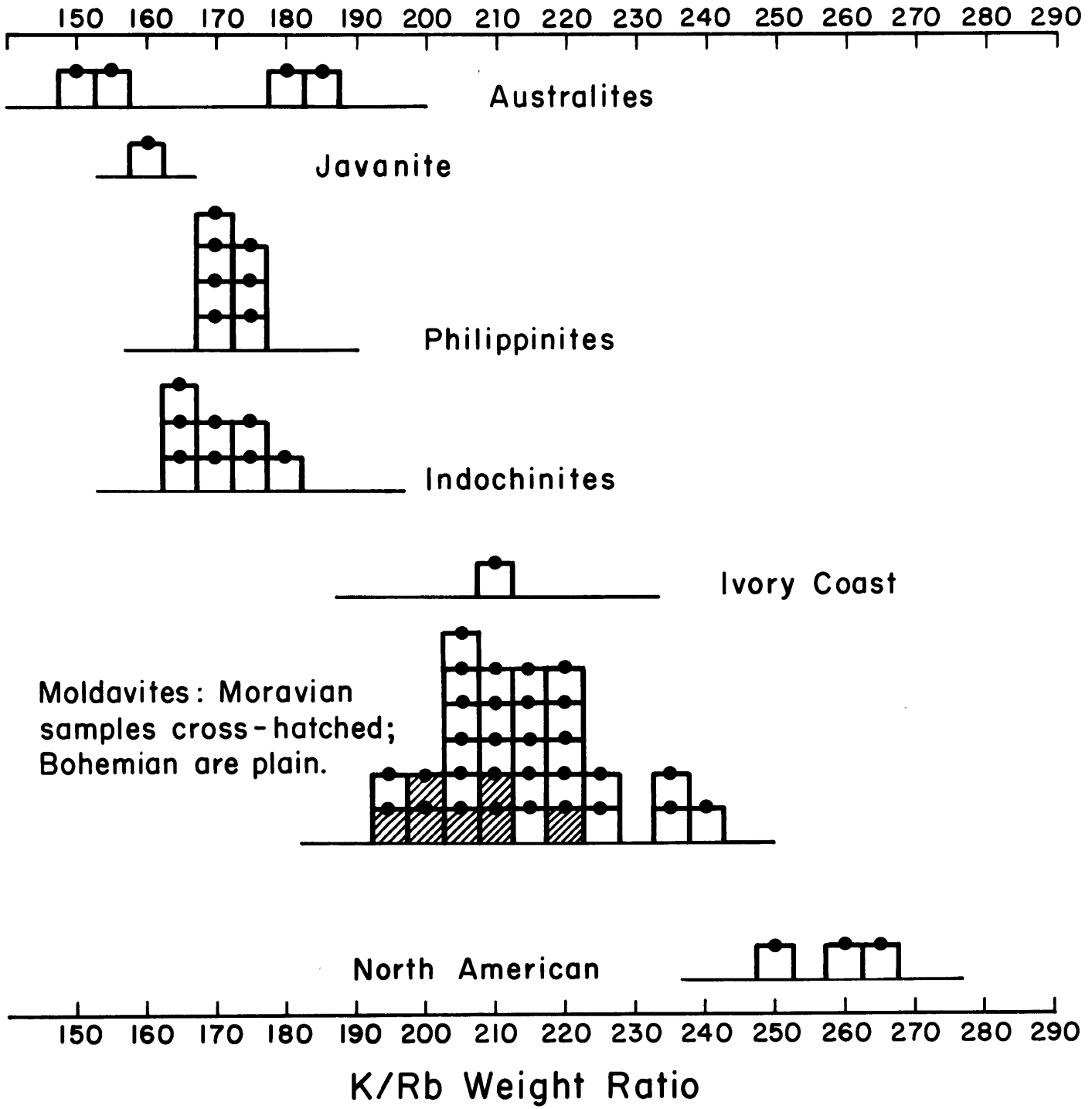


Fig. 1 K/Rb weight ratios for fifty-four tektites

## REFERENCES

- Abou-El-Azm, A. (1954) Spectrophotometric and magnetic studies of glasses containing iron, in relation to their structure - III. J. Soc. Glass Tech. 38, 197-243.
- Ahrens, L. H., Pinson, W. H., and Kearns, M. M. (1952) Association of Rb and K and their abundance in common igneous rocks and meteorites. Geochim. et Cosmochim. Acta 2, 229-242. (See revision of this paper in Herzog and Pinson, 1955).
- Ahrens, L. H. and Fleischer, M. (1960) Report on trace constituents in granite G-1 and diabase W-1. Pages 83-111 in U.S. Geol. Surv. Bull. 1113.
- Anders, E. (1960) On the presence of aluminum 26 in meteorites and tektites. Geochim. et Cosmochim. Acta 19, 53-62.
- Barnes, V. E., (1940) North American Tektites, University of Texas Publ. No. 3945, 477-582.
- Chao, E. C. T., (1963) The petrographic and chemical characteristics of tektites. Chapter 3 in the book Tektites, edited by John A. O'Keefe, University of Chicago Press, 51-94.
- Chao, E. C. T., Adler, I., Dwornik, E. J., and Littler, Janet (1962) Metallic spherules in tektites from Isabela, the Philippine Islands., Science 135, (3498), 97-98.
- Chao, E. C. T., Dwornik, Edward J., and Littler, Janet (1964) New data on the nickel-iron spherules from Southeast Asian tektites and their implications. Geochim. et Cosmochim. Acta 28, 971-980.
- Clarke, R. S., Jr., and Carron, M. K. (1961) Comparison of tektite specimens from Martha's Vineyard, Mass., and Empire, Georgia, Journal of Geophys. Res. 66, 2520.
- Fleischer, Michael and Stevens, R. E. (1962) Summary of new data on rock samples G-1 and W-1. Geochim. et Cosmochim. Acta 26, 525-543.
- Friedman, I., Thorpe, A. and, Senftle, F. E. (1960) Comparison of the chemical composition and magnetic properties of tektites and glasses formed by fusion of terrestrial rocks. Nature, London 187, 1089-1092 .

- Gentner, von W., Lippolt, H. J., and Müller, O. (1964) Das Kalium-Argon-Alters des Bosumtwi-kraters in Ghana und die chemische Beschaffenheit seine Glaser. Z. Naturforschg. 19a, 150-153.
- Herzog, L. F. and Pinson, W. H., (1955) The Sr and Rb contents of the granite G-1 and the diabase W-1 Geochim. et Cosmochim. Acta, 8, 295-298.
- Herzog, L. F. and Pinson, W. H. (1956) Rb/Sr age, elemental and isotopic abundance studies of stony meteorites. Amer. J. Sci. 254, 555-566.
- Lovering, J. F. (1960) High temperature fusion of possible parent materials for tektites. Nature, London 186, 1028 - 1030.
- Schnetzler, C. C. and Pinson, W. H. (1963) The chemical composition of tektites. Chapter 4 in the book Tektites, edited by John A. O'Keefe, University of Chicago Press, 95-129.
- Schnetzler, C. C., and Pinson, W. H. (1964a) A report on some recent major element analyses of tektites. Geochim. et Cosmochim. Acta 28, 793-806.
- Schnetzler, C. C., and Pinson, W. H. (1964b) Variations of strontium isotopes in tektites. Geochim. et Cosmochim. Acta 28, 953-969.
- Spencer, L. J. (1933) Origin of tektites. Nature, London 132, 571.
- Steven, R. E., and Niles, W. W. (1960) Chemical analyses of the granite and diabase. Pages 3-43 in the U.S. Geol. Surv. Bull. 1113
- Taylor, S. R. and Heier, K. S. (1958) Rubidium depletion in feldspars, Nature, London 182, 202-203
- Taylor, S. R. and Ahrens, L. H. (1959) The significance of K/Rb ratios for theories of tektite origin. Geochim. et Cosmochim. Acta, 15, 370-372.
- Taylor, S. R. (1962) The chemical composition of australites. Geochim. et Cosmochim. Acta 26, 685-722.

Taylor, S. R. (1960) Abundance and distribution of alkali elements in australites. Geochim. et Cosmochim. Acta 20, 85-100.

Taylor, S. R. and Sachs, M. (1964) Geochemical evidence for the origin of australites. Geochim. et Cosmochim. Acta 28, 235-264.

Walter, L. S. and Carron, M. K. (1964) Vapor pressure and vapor fractionation of silicate melts of tektite composition. Geochim. et Cosmochim. Acta 28, 937-951.



## Rb- Sr Age Study of Moldavites

W. H. Pinson, Jr., C. C. Schnetzler\*, J. A. Philpotts and  
H. W. Fairbairn

Department of Geology and Geophysics

Massachusetts Institute of Technology, Cambridge, Massachusetts

\*Goddard Space Flight Center, Theoretical Division,  
Greenbelt, Maryland

### Abstract:

Rb contents from 96-160 ppm and Sr from 124-157 have been determined for 31 moldavites. Rb/Sr ratios range from 0.77 - 1.20. Precision of the ratios, is 4%. Nine of the samples have been analysed isotopically.  $\text{Sr}^{87}/\text{Sr}^{86}$  normalized to 0.1194 for  $\text{Sr}^{86}/\text{Sr}^{88}$ , ranges from 0.7208 - 0.7224. Excepting one analysis, the range of the other eight analyses is 0.0011, which is two standard deviations of a single analysis. There is no sympathetic variation between Sr isotopic compositions and Rb/Sr ratios. We interpret this to mean that during fusion either Rb or Sr was lost differentially. The fusion event would not fractionate the Sr isotopes. Both the Bohemian and Moravian strewn fields are represented in the sampling, and the Rb - Sr data do not distinguish the two areas.

Two hypotheses are suggested. Firstly, the parent material was chemically and geochronologically homogeneous, over the whole crater area and in depth. This is incom-

patible with the hypothesis that the moldavites were blasted out of the Nordlingen-Ries crater, for the rim rocks there exhibit a great variety of types. Furthermore, there is apparently no chemical relation between the crater impact glass and the moldavites. The second hypothesis is that a remarkable homogenization of the parent-material Sr occurred during the fusion event, which, however, allowed a variation in chemical compositions to arise through selective volatilization of the elements. However, lechatelierite occurs in the moldavites, and survival of discrete phases might not be expected in material having undergone such thorough homogenization. Under this second hypothesis the presence of lechatelierite might best be explained as a post-mixing separation - a phenomenon which is, however, not predicted and has not been demonstrated experimentally.

## INTRODUCTION

The purpose of this paper is to report Rb/Sr ratios for 31 moldavites and the Sr isotopic compositions for 9 of these samples. Previous Rb/Sr age correlation studies of tektites (Schnetzler and Pinson, 1964) indicated that the North American, Pacific Area, and Czechoslovakian tektites all lie on a rough isochron whose slope suggests a common age of about 400 m.y. Only three moldavites had been analyzed for Rb - Sr data and it was felt that a larger sampling was needed. Recently, Schnetzler and Pinson (1965) have analyzed two Ivory Coast tektites and obtained a 2.0 b.y. isochron, with an initial  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio of 0.705, which is within the range found for mantle derived rocks. This work demonstrated that the Ivory Coast tektites lie far off the isochron formed by the other three major groups. Of further interest was the observation that the 2 b.y. age of the Ivory Coast tektites is coincident with the Rb - Sr ages of the basement complex rocks in the vicinity of the Bosumtwi crater (Bonhomme, 1962; Vachette, 1964).

The present survey of Rb/Sr ratios in 31 moldavites revealed a range of about 35%, and it was wondered whether or not  $\text{Sr}^{87}/\text{Sr}^{86}$  would vary sympathetically with Rb/Sr. The data presented in this paper indicates that within experimental error the Sr isotopic composition of moldavites is apparently constant.

## ANALYTICAL RESULTS

The Rb and Sr contents of the 31 moldavites were determined by a combination of x-ray fluorescence and mass spectrometric stable isotope dilution analyses. Standardization was by the latter method. The x-ray fluorescence analyses were made using a molybdenum target and topaz crystal. In general, the two analytical methods yield results of comparable precision. This was previously demonstrated in analyses of other tektites by Schnetzler and Pinson (1964). During the analysis period the following values for Rb and Sr were found in G-1 and W-1: for G-1, Rb = 213 ppm, Sr = 255 ppm; for W-1, Rb = 22 ppm and Sr = 194 ppm. These values are in close agreement with the recommended values in Fleischer and Stevens (1962). The results of the Rb and Sr analyses of the 31 moldavites are given in Table 1.

The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of 9 moldavites are presented in Table 2. These ratios were obtained by mass spectrometric analysis of unspiked Sr extracted from the moldavites. The same mass spectrometric methods as were used by Schnetzler and Pinson (1964) were used in this present investigation. The measured  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios were normalized to a value of 0.1194 for  $\text{Sr}^{86}/\text{Sr}^{88}$ . Standard Sr ( $\text{SrCO}_3$ , Eimer and Amend, Lot No. 492327), for which a mean value of  $0.708 \pm 0.0006$  for the normalized  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio was obtained during the analysis period, was used to monitor the Sr isotope analyses.

The  $\text{Sr}^{84}$ ,  $\text{Sr}^{86}$  and  $\text{Rb}^{87}$  spikes used in the isotope dilution analyses were prepared and calibrated as described by Pinson (1960, 1962). The  $\text{Rb}^{87}/\text{Sr}^{86}$  and  $\text{Sr}^{87}/\text{Sr}^{86}$  normalized ratios for the nine completely analyzed moldavites are given in Table 3.

### DISCUSSION

It is apparent that the Sr isotopic composition of moldavites is virtually constant (ie.  $\text{Sr}^{87}/\text{Sr}^{86} = 0.722 \pm 0.001$ ), whereas the Rb/Sr ratio ranges from 0.77 - 1.20. This situation cannot have long existed. Recently, almost certainly within the last 30 m.y., either Rb and Sr have been fractionated relative to each other, or the Sr has been isotopically homogenized. This most probably occurred during fusion of the moldavite parent-material 14.7 m.y. ago as dated by K-A (Zahringer, 1963). Extensive fractionation of Sr isotopes during fusion is most unlikely. Isotopic homogenization of Sr during fusion is a possibility, but it seems unlikely that lechatelierite inclusions, especially the stringers, would survive such a thorough homogenization, and there is no evidence to support a post-mixing  $\text{SiO}_2$  phase separation. It therefore seems probable that prior to fusion the Sr isotopic composition of the moldavite parent-material was constant throughout. This implies a constant Rb/Sr ratio throughout. In either case the variation in the Rb/Sr ratio is best explained in terms of selective volatilization.

Table 1 Rb and Sr contents (in ppm) of moldavites as determined by two methods of analysis.

M.I.T. Sample No.	Locality*	Rb (x-ray)	Rb (I.D.)	Sr (x-ray)	Sr (I.D.)	Rb/Sr (x-ray)	Rb/Sr (I.D.)
4575	Bohemia	-	136	-	143	-	0.95
5296a	"	148	-	133	-	1.11	-
5296b	"	146	-	156	-	0.94	-
5296c	"	144	-	142	-	1.01	-
5296d	"	120	-	140	-	0.86	-
5296e	"	136	-	148	-	0.92	-
5296f	"	140	-	144	-	0.97	-
5309	"	131	-	138	-	0.95	-
5310	"	139	146	139	151	1.00	0.97
5311	"	138	-	134	-	1.03	-
4572	"	-	132	-	131	-	1.01
4574	"	-	96	-	124	-	0.77
5312	"	141	-	146	-	0.96	-
5313	"	140	-	144	-	0.97	-
5314	"	145	-	130	-	1.12	-
5315	"	129	-	147	-	0.88	-
5316	"	149	-	139	-	1.07	-
5317	"	122	121	147	-	0.82	-
4570	"	-	138	-	132	-	1.05
4571	"	-	148	-	132	-	1.12
5318	"	135	-	147	-	0.92	-
4090	"	-	146	-	136	-	1.07
5319	"	150	-	133	-	1.13	-
5320	Moravia	148	-	134	-	1.10	-
4573	"	-	148	-	124	-	1.19
5321	"	138	-	135	-	1.02	-
5322	"	142	-	137	-	1.04	-
5323	"	122	-	146	-	0.83	-
5324	"	161	160	133	133	1.20	1.20
5325	"	149	-	134	-	1.11	-
3314	Unknown	130	-	136	-	0.96	-

\* See Part I for details of sample localities.

Table 2 Sr isotopic composition of moldavites

M.I.T. Sample No.	Locality	$\text{Sr}^{86}/\text{Sr}^{88}$ (measured)	$\text{Sr}^{87}/\text{Sr}^{86}$ (measured)	$\text{Sr}^{87}/\text{Sr}^{86}$ (normalized)*
4575	Bohemia	0.1193	0.7221	0.7218
5310	"	0.11955	0.72185	0.7223
4574	"	0.1194	0.7220	0.7220
5317	"	0.12013	0.71981	0.7220
4570	"	0.1194	0.7224	0.7224
4571	"	0.1183	0.7242	0.7213
4090	"	0.1203	0.7196	0.7223
4573	Moravia	0.1195	0.7221	0.7224
3314	Unknown	0.1199	0.7194	0.7208

\* The  $\text{Sr}^{87}/\text{Sr}^{86}$  measured ratio has been normalized to a value of 0.1194 for the measured  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio on the assumption that instrumental fractionation would affect the  $\text{Sr}^{86}/\text{Sr}^{88}$  ratio twice as much as it would affect the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio.

Table 3 Summary of Rb - Sr data for nine completely analyzed moldavites.

MIT Sample No.	Locality	Rb <sup>87</sup> /Sr <sup>86</sup>	Sr <sup>87</sup> /Sr <sup>86</sup> (normalized)
4575	Bohemia	2.75	0.7218
5310	"	2.81	0.7223
4574	"	2.23	0.7220
5317	"	2.38	0.7220
4570	"	3.04	0.7224
4571	"	3.25	0.7213
4090	"	3.10	0.7223
4573	Moravia	3.45	0.7224
3314	Unknown	2.78	0.7208



## REFERENCES

- Bonhomme, M. (1962) Contribution a L'étude géochronologique de la plate-forme de l'ouest Africain. Annales de la Faculté des Sciences de l'Université de Clermont.
- Fleisher, M. and Stevens, R. E. (1962) Summary of new data on rock samples G-1 and W-1. Geochim. et Cosmochim. Acta 26, 525 - 543.
- Pinson, W. H., Jr. (1960) Sources of error in the preparation of spike and shelf solutions for geochronometric work. Eighth Annual Progress Report for 1960, U.S. Atomic Energy Commission Contract At(30-1)-1381.
- Pinson, W. H., Jr. (1962) A review of the preparation and calibration of shelf and spike solutions currently in use at M.I.T. in the Geochronology Laboratory. Tenth Annual Progress Report for 1962, U.S. Atomic Energy Commission Contract AT(30-1)-1381.
- Schnetzler, C. C., and Pinson, W. H., Jr. (1964) Variation of strontium isotopes in tektites. Geochim. et Cosmochim. Acta 28, 953 - 969.
- Schnetzler, C. C., and Pinson, W. H., Jr. (1965) Rb-Sr age study of Ivory Coast tektites. To be presented at annual meeting of Amer. Geophys. Un., Washington, D. C.
- Vachette, M. (1964) Nouvelles mesures d'âges absolus de granites d'age eburnéen de la côte d'Ivoire. Comptes Rendus Acad. Sc. Paris, Groupe 9, t. 258, 1569-1571.
- Zahringer, J. (1963) Isotopes in tektites. Chap. 6 of Tektites, edited by John A. O'Keefe, University of Chicago Press, 137-149.

PART IV

The Chemical Composition and Origin of Moldavites

by

John A. Philpotts

## CHAPTER 1

### INTRODUCTION

Tektites first came to the attention of scientists about 175 years ago. During the past 10 years, tektite research has expanded at an ever increasing rate because of the possible extra-terrestrial origin of these objects. The imminent prospect of exploring earth's nearest neighbour further heightens interest in the problem.

The voluminous data on tektites are very curtly summarized in this chapter. Comprehensive summaries and bibliographies have been given by Suess (1900), Barnes (1940), and Baker (1959). In addition, Volume 14, Number 4, 1958, and Volume 28, Number 6, 1964, of *Geochimica et Cosmochimica Acta*, and the book *Tektites*, edited by John A. O'Keefe, University of Chicago Press, 1963, are entirely devoted to tektite studies.

Tektites are small, holohyaline objects. Their weights range from fractions of a gram up to 3 kgm, but most tektites weigh from 1 to 20 gm. Colour ranges from green to amber in transmitted light; most tektites appear black in reflected light. Some tektites possess forms that have been interpreted in terms of aerodynamic analysis (Chapman and Larson, 1963; Adams and Huffaker, 1964). Most tektites have characteristic surficial markings.

Tektite "strewn fields" occur in four major geographic locations: South East Asia, the Ivory Coast, Czechoslovakia,

and eastern North America. Further subdivisions of geographic locality have been made. Tektites from the four groups can generally be distinguished on the basis of chemical composition and their K-A ages.

Tektites are highly siliceous, usually consisting of 70-80%  $\text{SiO}_2$ . Compared with terrestrial glasses of similar  $\text{SiO}_2$  content, such as obsidians, tektites have lower alkali contents and generally have higher CaO, MgO, and FeO contents. In addition, tektites contain very little water (Friedman, 1963) and unusually low ferric to ferrous iron ratios. Tektites from a particular geographic group show less variation in chemical composition than acid igneous rock suites.

Tektites do not contain measurable amounts of radioactive, cosmogenic nuclides (Anders, 1960). This suggests that tektites originated within the earth-moon system, and indeed, the occurrence of tektites within restricted strewn fields is unlike the random distribution of meteorites. It has not yet been discovered whether tektites are of terrestrial or lunar origin. It is generally accepted that tektites have undergone a brief, high temperature thermal event. Ni-Fe spherules have been found in tektites (Spencer, 1933; Chao et al, 1962, 1964) and this has been interpreted to mean that tektites are the result of meteorite impact.

Because tektites from a particular geographic group show relatively little variation in chemical composition, the

compilations in the literature, of older analyses by various investigators using various analytical techniques, have tended to obscure real variations within and between the tektite groups. There existed a need for precise analyses of representative numbers of samples by uniform techniques, preferably utilizing accepted rock standards to monitor accuracy. This need has been satisfied in the case of australites (Taylor, 1960; Taylor et al, 1961; Cherry and Taylor, 1961; Taylor, 1962; Taylor and Sachs, 1964), bediasites (Chao, 1963), and various South East Asian tektites (Schnetzler and Pinson, 1964a). This thesis attempts to satisfy the need for a representative number of internally consistent analyses of Czechoslovakian tektites. 17 moldavites from the Bohemian "strewn field" and 6 moldavites from the Moravian field were analyzed for major element contents. The rock standards G-1 and W-1 were used as analytical monitors. Analyses of the trace elements Rb and Sr were also performed. The weights, refractive indexes and specific gravities of the 23 tektites were also determined.

## CHAPTER 2

## PHYSICAL CHARACTERISTICS

The physical properties of glasses are directly related to their chemical composition. Measurements of some of the physical properties of the 26 moldavites in the M.I.T. collection were made. These measurements are reported in this chapter and are related to the physical properties of tektites in general and moldavites in particular.

### 2.1 Form

Tektites exhibit a wide variety of forms. Characteristic forms are spherical, ellipsoidal, dumb-bell, drop-like and tabular. Tektite forms have been classified (Baker, 1963) as primary, secondary and tertiary. The primary forms presumably originated during unimpeded flight of viscous blobs with various rotation rates (Baker, 1963; Chapman and Larson, 1963). Fenner (1934) likened them to the shapes acquired by silicate smoke-bombs ejected from coal-burning railway engines. The secondary forms are aerodynamic ablation modifications that originated during high-speed flight through the earth's atmosphere. These aerodynamic forms are best preserved on australites of the button type. Chapman and Larson (1963) have produced artificial buttons in an electric-arc-jet-tunnel that are identical to the australite buttons with respect to the ring-waves on the ablated anterior surface, the circum-

ferential flange, and the unaffected posterior surface. The interpretation of the aerodynamic ablation evidence is of prime importance in a consideration of the origin of tektites and will be discussed later. The tertiary forms are those resulting from impact and subsequent terrestrial erosion.

The appearance of moldavites, including their shapes, has been described by Suess (1900), Hanuš (1928), and Oswald (1942), among others. Cohen (1963) compared the sizes and shapes of 297 moldavites from different sites and came to the conclusion (a) that tektites are more prevalent in Bohemia than Moravia, (b) that oblate spheroids are more common in Bohemia than Moravia and that their size decreases eastward, and (c) that spheroids and ellipsoids are more common in Moravia than Bohemia. Recently a spalled, aerodynamically modified, teardrop shaped moldavite from Slavice, Moravia, has been described (Chao, 1964).

The shapes and weights of the 26 moldavites studied by the author are reported in Table 1.

## 2.2 Sculpture

Most tektites show a remarkable similarity of surface markings although each geographical group has specific peculiarities. Sculpture has been discussed by many authors including Barnes (1940) and Baker (1963). The characteristic

sculpture of tektites consists of combinations of the following features: pits of various dimensions, furrows, ridges, mounds, frosted surfaces, and fresh conchoidal fractures. The detailed mode of formation of such unusual sculptures is not well known. Some investigators, following Suess (1900), consider that the pits and ridges originated during high-speed flight through the earth's atmosphere. Most investigators, however, attribute all of the sculpture to terrestrial erosion.

Barnes (1958) stated that a discussion of surface sculpture is most irrelevant so far as the origin of tektites is concerned because these features are acquired through etching and other erosive agencies after the tektites came to rest. Krinov (1958) and Baker (1963) concurred on this point. Part of the evidence in favour of this hypothesis consists of obsidian pebbles (Rost, 1964) and even artificial glass (Němec, 1933) with tektite-like sculpture. In addition Chao (1964) has observed sculpture on various Pacific area tektites that was formed subsequent to terrestrial rounding of these specimens. Several investigators (Ježek, 1911; Merrill, 1911; Baker, 1961; Rost, 1964) have produced tektite-like sculpture by HF etching of obsidians and tektites. Hence there is good cause to believe that the sculptures observed on tektites were produced by terrestrial erosion and that small differences between specimens from various groups are due to their particular erosional histories.



There are, however, several arguments in favour of an aerodynamic origin. O'Keefe (1963), in a restatement of Suess' (1900) ideas on the problem, pointed out that in the majority of cases the internal flow structure, as often revealed by fine streaks on the surface, is not related to the dominant sculpture pattern. It was also pointed out that certain regularities exist between the pattern and the curvature of the surface on which it has developed. These observations are borne out by the 26 samples examined by the author. However, Rost (1964) demonstrated that the smooth walls of bubbles etched at a slower rate than other surfaces, whereas the anisotropic region around lechatelierite particles etched relatively quickly. It therefore seems probable that etch patterns reflect not only differential composition but also smoothness of the surface and strain in the glass. Different sculptures on different surfaces of individual tektites may also reflect the affect of preferred orientation during erosion. O'Keefe (1963) mentioned two other pertinent facts, namely the striking resemblance between the sculpture of some tektites and that of nose cones, and the similarity of sculpture of tektites dredged from the sea with that of tektites found on land.

In conclusion it seems that the evidence favours the terrestrial erosion hypothesis rather than the aerodynamic ablation hypothesis for the production of the sculpture

pattern of tektites. The question is still open, however, and considering its significance with respect to theories of origin, there is a need for further detailed investigation.

### 2.3 Colour

The absorption spectra of tektites have been measured by Stair (1955) and Cohen (1958). It seems almost certain that iron is the major source of colour in tektites. Absorption of ferrous iron yields the green colour of some tektites. A recent analysis (Thorpe and Senftle, 1964) of the colour of tektites in terms of magnetic susceptibility measurements has shown that the dark brown to black colour of many tektites can be ascribed to light scattering and absorption by either dispersed ferric iron and/or submicroscopic metallic spherules.

Moldavites have been classified by Bouška and Povondra (1964) into five colour shades: pale green, light green, bottle green, olive green and brown. These authors found a close relation between colour and iron content. This is also true of the moldavites in the M.I.T. collection, in that the three specimens with browner hue (T5320, 5322, & 5324) were subsequently found to contain the highest iron. A statistical study of moldavites (Faul and Bouška, 1963) demonstrated that all colours could be found in most localities although some colours were more common in some areas than others; it was concluded that colour was a more important guide to the physical and chemical properties of moldavites than locality.

#### 2.4 Specific Gravity and Refractive Index

Specific gravity and refractive index data on tektites have been summarized by Barnes (1940), Baker and Forster (1943), Baker (1959), Chao (1963), Bouška and Povondra (1964), and Chapman et al (1964). The refractive indexes of tektites approximately range from 1.48 to 1.53; the bulk specific gravities range from 2.29 to 2.56 gm/cm<sup>3</sup>. The refractive indexes of moldavites range from 1.48 to 1.50; the bulk specific gravities range from 2.29 to 2.39 gm/cm<sup>3</sup>. The specific gravity and index of refraction of tektites show a nearly linear, positive relationship (Ježek and Woldrich, 1910; Tilley, 1922; Preuss, 1935; Spencer, 1939; Barnes, 1940; Chao, 1963). Density reflects the major element composition and varies inversely with SiO<sub>2</sub> content, and refractive index is a direct function of the FeO content, which is generally inversely proportional to the SiO<sub>2</sub> content. It is of interest to note that Barnes (1940) reported a refractive index range in a bediasite chip from 1.483 to 1.512 and this is about the same as the range found in bulk refractive index for the whole bediasite group. Similarly, Baker (1961) reported a range of refractive indexes for a single australite from 1.495 to 1.500. Chao (1963) stated that for many tektites (many philippinites and indochinites) the bulk specific gravity is low because of vesicularity. However, Chapman et al (1964) and Baker and Forster (1943) voiced

the opinion that chemistry dominates cavities in bulk specific gravity determinations and that only about 5% of the specimens from most geographic groups have grain specific gravity appreciably higher than the bulk specific gravity. Most obsidians can be distinguished from tektites on the basis of specific gravity and refractive index (Barnes, 1940); the reverse is not true.

The specific gravities of the 26 moldavites investigated in the present thesis are given in Table 1. An attempt was made to determine specific gravity by flotation: 1. the tektite was sunk in bromoform-acetone solution, 2. bromoform was added to the solution until the tektite just floated, 3. the density of the solution was then measured with a hydrometer. This method, however, proved to be unreliable, the results having poor precision and accuracy. The specific gravity values reported in Table 1 were obtained in the following manner: 1. The specimen was tied to a single fibre of human hair, 2. the specimen and the hair were weighed on a high-precision chain balance, 3. the surface of the specimen was completely wetted with acetone, 4. the specimen was then successively dunked into several beakers containing distilled water, 5. the specimen, suspended on the hair, was weighed in distilled water of known temperature, 6. the weight in air was divided by the difference of the weight in air and the weight in water; the result

was then multiplied by the temperature correction yielding the specific gravity of the specimen. The effect of the hair (buoyancy, surface tension) was negligible. Duplicate determinations were made on six samples; the mean difference between duplicates was  $0.0004 \text{ gm/cm}^3$ . The precision and accuracy of the specific gravity results in Table 1 are thought to be better than  $\pm 0.001 \text{ gm/cm}^3$ . Chao (1963) reported precisions of Jolly balance determinations of  $\pm 0.005 \text{ gm/cm}^3$  for tektites weighing more than 5 gm and of  $\pm 0.015 \text{ gm/cm}^3$  for smaller samples. Chapman et al (1964) reported a precision of  $\pm 0.001 \text{ gm/cm}^3$  and an accuracy of  $\pm 0.003 \text{ gm/cm}^3$  for determinations of specific gravity by heavy-liquid flotation (zinc iodide in tap water).

The refractive index values given in Table 1 were obtained on powders by the use of immersion oils. Most powders gave a range of refractive indexes and the reported values are an estimate of the mean value for each sample. The oils were calibrated to  $\pm 0.0005$ . Because of the estimate involved in the determinations, accuracy is thought to be about  $\pm 0.002$ . This may be compared with the precision of  $\pm 0.0004$  for determinations of the bulk refractive index of tektite wafers in a Valentine refractometer (Chao, 1963).

The specific gravity and refractive index values listed in Table 1 range from 2.3312 to 2.3718  $\text{gm/cm}^3$  and from 1.486 to 1.495 respectively. The refractive indexes and specific

gravities of these twenty-six tektites fall within the ranges reported for moldavites in the literature. There is a positive correlation between refractive index and specific gravity. Both refractive index and specific gravity were subsequently found to vary inversely with  $\text{SiO}_2$  content. No correlation was found between  $\text{FeO}$  content and refractive index for the Bohemian tektites; this may be due to the low and relatively invariant  $\text{FeO}$  contents of these samples.

Chapman et al (1964) gave population polygons of specific gravity (ie. % frequency vs. specific gravity in  $0.01 \text{ gm/cm}^3$  increments) for 108 moldavites from Habřív, Bohemia, and for 37 moldavites from Moravia. The Habřív samples gave a 40% mode at  $2.365 \text{ gm/cm}^3$  (ie. 2.36 to 2.37), and the Moravian samples gave a 30% mode at  $2.355 \text{ gm/cm}^3$ . The frequency distribution of the specific gravity values of the Bohemian tektites listed in Table 1 is bimodal with a 40% mode at  $2.365 \text{ gm/cm}^3$  (the two samples from Habřív fell within this polygon) and a 30% mode at  $2.345 \text{ gm/cm}^3$ . The number of Moravian tektites investigated in the current study was too small to draw any significant conclusions as to the frequency distribution. The Moravian tektites did in general, however, have lower specific gravities than those from Bohemia.

Table 1 Some physical properties of 26 moldavites

M.I.T. Sample No.	Locality	Weight gm	Specific gravity gm/cm <sup>3</sup>	Refractive index	Form
<u>Bohemia</u>					
5296a	These 9 samples were collected near Ihenice, in fields near farm complex on right side of road to Chrásťany, about 1 km east of the village	3.19	2.3350	1.486	irregular fragment
5296b		2.97	2.3654	1.491	" "
5296c		2.61	2.3521	1.492	" "
5296d		2.18	2.3718	1.495	" "
5296e		2.16	2.3635	1.492	" "
5296f		2.10	2.3664	1.494	" "
5296g		1.20	2.3627	1.493	" "
5296h		1.05	2.3597	1.493	" "
5296i		0.74	2.3488	1.489	" "
5309	Ihenice	12.566	2.3493	1.492	irregular ellipsoid
5310	"	12.728	2.3492		
5311	Dolní Chrásťany	15.961	2.3451	1.492	distorted oval plate
5312		8.208	2.3440	1.491	square plate
5313	Habří	2.708	2.3647	1.495	irregular fragment
5314	"	2.708	2.3708	1.494	plate
5315	Slávče	11.356	2.3312	1.488	oblate spheroid
5316	Vrábče	4.163	2.3656	1.493	short rod
5317	"	4.770	2.3649		
5318	Kroclov	4.964	2.3410	1.489	curved triangular plate
5319	Koroseky	9.107	2.3416		
5320	Něchov	7.969	2.3681	1.494	nondescript chunk
5321			2.3644	1.493	oblate spheroid
5322			2.3415	1.489	oblate spheroid
5323			2.3412		
<u>Moravia</u>					
5320	Slavice	24.337	2.3475	1.490	nondescript chunk
5321			2.3472		
5322	Kožichovice	13.208	2.3351	1.487	wedge
5323	Slavětice	24.185	2.3387	1.489	ellipsoid
5324			2.3389		
5325	Dukovany	5.645	2.3484	1.491	tear-drop
5326	"	4.550	2.3609	1.492	spheroid
5327	"	7.052	2.3372	1.489	tear-drop

## CHAPTER 3

### CHEMICAL ANALYSES

#### 3.1 Sample Preparation

The moldavites in the M.I.T. collection were prepared for analysis in the following manner: 1. the samples were washed in acetone, 2. the samples were scrubbed with a nylon brush in distilled water, 3. remaining surficial contamination was removed with a needle, 4. the samples were washed in hot, six normal HCl and rinsed with distilled water, 5. each tektite was then broken on a steel plate, 6. a portion of each tektite was crushed in a flat-surfaced, hardened steel, percussion mortar, 7. a hand magnet was passed over the crushed fragments in order to remove any incorporated steel, 8. the samples were powdered in a boron carbide mortar, 9. the powders were sieved through nylon cloth and coarser particles were re-powdered, 10. the powders were homogenized then stored in glass vials.

#### 3.2 Analytical Techniques

##### A. "Rapid silicate" procedures

The "rapid silicate" procedures used in this investigation were those described by Shapiro and Brannock (1956) except for CaO, MgO and FeO. CaO and MgO were determined by automatic photometric titration according to the modified procedure of Shapiro and Brannock (Schnetzler and Pinson, 1964a).



FeO was determined by the spectrophotometric method described by Shapiro (1960).

These "rapid silicate" procedures are mostly colourimetric, the absorption of light by various coloured complexes being measured with a spectrophotometer. Beckman Model B spectrophotometers were used in this investigation. Na<sub>2</sub>O and K<sub>2</sub>O were determined with a Perkin-Elmer Model 146 flame photometer using Li as internal standard. Most of the "rapid silicate" determinations of the several elements are independent of each other so that errors in one determination will not affect the others. For this reason a summation of the weight percents has more significance than a summation in the case of conventional analysis methods, wherein determinations are obtained by difference.

Prior to the preparation of solutions A and B (Shapiro and Brannock), the sample powders were dried in an oven at 105° C for about two hours. Sometimes zirconium crucibles were used instead of nickel ones in the preparation of solution A, and sometimes teflon dishes were used instead of platinum ones in the preparation of solution B; these substitutions did not noticeably affect the results. Duplicate solutions B from separate weighings were made for each tektite sample (only one was made for T 5296d because the powder was temporarily misplaced) and from one to three solutions A were made from those tektites analyzed by "rapid sil-

icate" techniques for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . In the determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , two aliquots were taken for each solution A and four transmission readings were made on each aliquot. Total Fe,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ , CaO,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  were all determined on a single aliquot of each solution B whereas as many as three aliquots were used in the MgO determination because of poor precision. Four instrument readings were made in the determination of total Fe,  $\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}$  and single readings were made for  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$ . Two or three FeO determinations were made on each tektite powder, with two transmission readings being taken in each determination. The analysis of solutions for a particular element was carried out in random fashion.

Only a few determination of  $\text{P}_2\text{O}_5$  were made because the method proved unreliable at the low concentrations found in the moldavite samples. For the same reason, determinations of MnO,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were not undertaken.

#### B. X-ray fluorescence procedures

The determination of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  by the "rapid silicate" method is not altogether satisfactory. In the course of analyzing tektites during the summer of 1963, the author came to the conclusion that repeated fusions were necessary before a good value for  $\text{SiO}_2$  could be obtained. In addition,  $\text{Al}_2\text{O}_3$  values determined by the "rapid silicate" procedure frequently had to be normalized to the accepted values for

the standards. Therefore, because of the number of determinations required to obtain a reliable  $\text{SiO}_2$  value, and because of the anomalous  $\text{Al}_2\text{O}_3$  results obtained by the "rapid silicate" method, it was decided to determine these constituents by x-ray fluorescence techniques. This decision was made in light of the successful x-ray fluorescence analyses of light elements by Volborth (1963), Rose et al (1963), Schnetzler and Pinson (1964a), Welday et al (1964), among others.

Dr. J. W. Frondel kindly offered the use of the Phillips x-ray equipment at the Hoffman Laboratory, Harvard. The following work was done under her supervision. In order to determine the suitability of the moldavite powdered samples for x-ray fluorescence analyses it was decided to analyze for K; flame photometric data on K were available for comparison. The tektite powders were consecutively placed in lucite trays about 2 mm in depth. The powders were packed by pressing the surface with a glass slide. The  $\text{K K}\alpha$  radiation of each sample was rapidly scanned (1 degree per min.) from  $40^\circ$  to  $42^\circ$ . The x-ray operating conditions were as follows: tungsten target, ADP crystal, base line voltage = 2v, window out, detector (flow proportional counter) voltage = 1.8kv, helium path. Peak heights were determined graphically by subtracting the average background values from the peaks. The x-ray K

results (obtained from a least squares line) and the "rapid silicate" K values are given in Table 5.

Determination of  $\text{Al}_2\text{O}_3$  was next attempted. The samples were packed as for the K analyses. Operating conditions were as follows: tungsten target, gypsum crystal, base line voltage = 2v, window out, detector voltage = 1.9Kv, helium path, Four sets of 50 second counts were taken at  $65^\circ$ ,  $66.85^\circ$  ( $\text{AlK}_\alpha$ ) and  $68^\circ$ . This corresponded to over 2000 counts on each of the background settings and about 3000 counts on the  $\text{AlK}_\alpha$  peak. The mean background was subtracted from the peak to obtain peak height in counts. The x-ray  $\text{Al}_2\text{O}_3$  values for the standards, obtained from a least squares fit of peak height and %  $\text{Al}_2\text{O}_3$ , are given in Table 6 with spectrophotometric values. Due to other demands upon the machine, only a few  $\text{Al}_2\text{O}_3$  determinations on "unknowns" were made at Harvard.

The  $\text{Al}_2\text{O}_3$  determinations were continued on equipment in the Theoretical Division, Goddard Space Flight Centre. The x-ray fluorescence unit was a General Electric, vacuum instrument. Versatile as this unit is, it is not well suited to the study of powdered samples because of the angle at which the samples are held and because of the jar occasioned when the sample holder rotates into place. For this reason and on the advice of H. Rose and I. Adler, the tektite samples were briquetted as follows: 1. approximately 0.95 gm of sample was mixed with about 1 gm of powdered boric acid, 2. the mixture was poured onto a 5 gm backing of

boric acid, in a pressure mold of  $1\frac{1}{4}$  in. diameter, 3. the sample mixture and backing were briquetted at 10,000 psi for one minute.

$Al_2O_3$  was determined using the following operating conditions: chromium target, PET crystal, baseline voltage = 2V, window out, detector (flow proportional counter) voltage = 1.6 Kv, vacuum path. Plexiglass sample holders were used. Three sets of 100 second counts were taken at  $142.6^\circ$  and  $144.06^\circ$  ( $AlK\alpha$ ). This corresponded to a total of about 7500 counts on the background and about 75,000 counts on the  $AlK\alpha$  peak for each briquette. The samples analyzed for  $Al_2O_3$  at Harvard were used as standards.

$SiO_2$  was determined employing the following operating conditions: chromium target, PET crystal, baseline voltage = 2v, window out, detector voltage = 1.7 Kv, vacuum path. Three sets of 100 second counts were made at  $105^\circ$  and  $112^\circ$  and three 20 second counts were made at  $108.4^\circ$ , the  $SiK\alpha$  peak. This corresponded to a total of about 3000 counts at  $105^\circ$ , 2400 counts at  $112^\circ$ , and 90,000 counts on the  $SiK\alpha$  peak for each briquette. Some samples gave anomalous background counts. Most of these anomalous samples were run in the same sample holder (there were four sample holders altogether). An empirical correction factor, equal to the average background count divided by the observed background count, was applied to the peak counts in these cases. Samples, which

had been analyzed for  $\text{SiO}_2$  by the "rapid silicate" method were used as standards. The x-ray fluorescence values (obtained from a least squares line of peak height vs. %  $\text{SiO}_2$ ) and the "rapid silicate" values for the  $\text{SiO}_2$  content of the standards are given in Table 1.

Rb and Sr were determined on the North American Phillips x-ray fluorescence unit at M.I.T. under the supervision of Professor H.W. Fairbairn. Powdered samples were used. The nylon sample holders were circular and about 3 mm in depth. The powders were packed by alternately tapping the sample holder and smoothing the surface of the powder with a spatula. Mylar sheets were used to retain the powders when the sample holders were inverted for the analyses. X-ray operating conditions were as follows: molybdenum target, topaz crystal, approximate baseline voltage = 6v, window = 8v, scintillation counter, air path. Three sets of counts were registered at 5 goniometer settings (corresponding to background,  $\text{RbK}\alpha$  peak, background,  $\text{SrK}\alpha$  peak, and background). A total of 6000 counts were taken at each of the background settings and a total of 12,000 counts were taken on both of the peaks, for each sample. Background values (in counts per second) under the peaks were obtained graphically; backgrounds were subtracted from peaks to give peak heights in counts per second. Each run on four samples included a standard; the Rb and Sr contents of the three "unknowns"

were determined by comparison of peak heights with those of the standard that was run with them. The standards used were moldavites for which Rb and Sr contents had been (or were later) determined by mass spectrometric stable isotope dilution analyses (see Schnetzler and Pinson, 1964b). Initially, all of the samples were run using T 4575 as the standard. Six of the samples were run twice. In Table 8 the Rb and Sr contents and the Rb/Sr ratios determined by x-ray fluorescence by the method described above, for three samples, are compared with isotope dilution values that were subsequently obtained on the same samples. All of the samples were rerun using all four standards; samples were run with the standard having a Rb/Sr ratio closest to their own.

### 3.3 Precision and Accuracy

Precision is a measure of the reproducibility of an analytical method. It indicates the spread in the results of replicate analyses. Precision in this thesis is expressed as follows:

$$\sigma = \sqrt{\frac{\sum d^2}{n-1}} \quad , \text{the standard deviation of a single analysis,}$$

$$C = \frac{\sigma}{\bar{x}} (100) \quad , \text{the relative deviation of a single analysis,}$$

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

$$\text{and, } \bar{C} = \frac{\bar{\sigma}}{\bar{x}} (100) \quad , \text{the relative deviation of the mean}$$

where  $d$  is the difference between a determined value  $x$  and the mean value,  $\bar{x}$ , of all determinations, and  $n$  is the number of determinations.

Accuracy is a measure of the agreement of a determined value with the true value. Accuracy in this work is evaluated in terms of the accepted values for the rock standards G-1 and W-1 (Fairbairn, 1953; Stevens and Niles, 1960; Fleischer and Stevens, 1962). These accepted values are the means of analytical results obtained by different and reliable methods in several laboratories.

The precision and accuracy of chemical analysis of silicate rocks has been discussed by Fairbairn (1953), Ahrens (1957), and others. It has been clearly demonstrated that the relative deviation ( $c$ ) increases with decreasing concentration of the constituent (as shown by the log-log plot of Ahrens, 1957). Mercy (1956) discussed the accuracy and precision of the "rapid silicate" method of analysis (Shapiro and Brannock). The "rapid silicate" procedures have been improved for many elements since Mercy's criticism, but it is unlikely that the deviations reported have been greatly altered for most elements.

In this investigation only a few determinations were made for any particular element in each of the moldavite samples. For this reason it is not possible to obtain statistically significant expressions for precision from the tek-



tite data although some idea may be obtained from a comparison of the duplicate analyses reported in Table 9. A more meaningful expression of analytical precision is derived from the results of replicate analyses of the rock standards G-1 and W-1 which were prepared and run with the tektites. Results of the analyses of G-1 and W-1 are given in Tables 2 and 3, respectively. The accepted values for the monitors are taken from Fleischer and Stevens (1962). The precision of the analyses of G-1 and W-1 is given in Table 4. The precision and the accuracy of the tektite analyses are believed to be as good (for comparable concentrations) as those of the analyses of G-1 and W-1, if not better, because of the ease with which tektite glass goes into solution.

The x-ray fluorescence analyses of amphibolite rock powders for Fe, Ca, Mg, K, Ti and Mn by Chodos and Engel (1961) had a precision and accuracy comparable to that of routine chemical analyses. However, Chodos and Engel found Si to be accurate only within 3 - 5% of the amount present, and Al only within 5 - 10% of the amount present; this was attributed to the matrix affect and it was suggested that this problem could be alleviated through the utilization of the borax fusion method of sample preparation proposed by Claisse (1956). The fusion technique has been improved by Rose et al (1963), who have analyzed a wide variety of rock types by x-ray fluorescence and obtained results of a quality that compares favorably with the quality of routine chemical

analyses. Welday et al (1964) have also performed x-ray fluorescence analyses of high quality, using the fusion technique.

Tektites, however, are the result of a natural fusion process and in addition the chemical variations within individual tektites and between tektites from the same group are relatively limited. It was therefore decided to forego the fusion technique of sample preparation. Schnetzler and Pinson (1964a) determined  $\text{Al}_2\text{O}_3$  in tektite powders by x-ray fluorescence with a precision of  $\pm 2\%$ . The  $\text{Al}_2\text{O}_3$  determinations made on powders by the author are believed to be of comparable precision. Comparisons of x-ray fluorescence powder analyses and "rapid silicate" analyses are given in Table 5 for K and in Table 6 for  $\text{Al}_2\text{O}_3$ .

The x-ray fluorescence analyses performed on the briquetted samples were of somewhat poorer quality than the powder determinations. Results obtained on four briquettes manufactured from the same sample were in good agreement for all elements. The poorer quality of the briquette analyses can only be attributed to differences in grain size between the different samples. The grain size affect was exaggerated by the briquetting procedure; this was demonstrated by analyzing three powders of different grain size which were obtained from the same sample, and then briquetting the three fractions and reanalyzing them. This affect would have been eliminated had the fusion method of sample preparation been

Table 2 Analyses of G-1 on separate weighing

	1	2	3	4	5	6	Average	Accepted value
SiO <sub>2</sub>	73.27	72.37	71.98	71.66	72.14	72.52	72.32	72.41
MgO	0.24	0.22	0.39	0.20	0.22	0.28	0.26	0.41
CaO	1.44	1.45	1.22	1.47	1.48	1.41	1.41	1.39
Na <sub>2</sub> O	3.34	3.32	3.23	3.34	3.33	3.32	3.31	3.32
K <sub>2</sub> O	5.60	5.45	5.63	5.57	5.49	5.48	5.53	5.45
TiO <sub>2</sub>	0.23	0.24	0.25	0.24	0.24	0.24	0.24	0.26
Total Fe as FeO	1.72	1.81	1.72	1.75	1.71	1.75	1.74	1.76
FeO	0.98	0.98	0.97	1.01	0.98	0.98	0.98	0.98
Fe <sub>2</sub> O <sub>3</sub>							0.85	0.87

Table 3 Analyses of W-1 on separate weighings.

	1	2	3	4	5	6	Average	Accepted Value
MgO	6.45	6.37	6.31	6.54	6.50	6.63	6.47	6.62
CaO	10.93	10.91	10.90	10.84	10.95	10.76	10.88	10.96
Na <sub>2</sub> O	2.07	2.16	2.19	2.17	2.16	2.02	2.13	2.07
K <sub>2</sub> O	0.65	0.64	0.64	0.66	0.66	0.64	0.65	0.64
TiO <sub>2</sub>	1.09	1.09	1.09	1.08	1.08	1.07	1.08	1.07
Total Fe as FeO	9.94	10.05	9.97	9.91	9.90	9.87	9.94	10.01
FeO	8.63	8.63	8.71	8.56	8.74	8.45	8.62	8.74
Fe <sub>2</sub> O <sub>3</sub>							1.46	1.41

Table 4 Precision of the analyses of G-1 and W-1

	$\bar{x}$	n	$\bar{v}$	$\bar{c}$	$\sigma$	C
G-1						
SiO <sub>2</sub>	72.32	6	0.23	0.31	0.55	0.77
Al <sub>2</sub> O <sub>3</sub>	14.32	4	0.10	0.68	0.19	1.36
Total Fe as FeO	1.74	6	0.02	0.90	0.04	2.21
MgO	0.26	6	0.03	11.20	0.07	27.40
CaO	1.41	6	0.04	2.79	0.10	6.82
Na <sub>2</sub> O	3.31	6	0.02	0.53	0.04	1.29
K <sub>2</sub> O	5.54	6	0.03	0.52	0.07	1.27
TiO <sub>2</sub>	0.24	6	0.003	1.24	0.007	3.02
FeO	0.98	9	0.004	0.38	0.01	1.14
Fe <sub>2</sub> O <sub>3</sub>	0.85					
W-1						
Total Fe as FeO	9.94	6	0.03	0.26	0.06	0.64
MgO	6.47	6	0.05	0.73	0.12	1.79
CaO	10.88	6	0.03	0.26	0.07	0.64
Na <sub>2</sub> O	2.13	6	0.03	1.29	0.07	3.17
K <sub>2</sub> O	0.65	6	0.004	0.63	0.01	1.54
TiO <sub>2</sub>	1.08	6	0.003	0.32	0.008	0.78
FeO	8.62	6	0.04	0.50	0.11	1.22
Fe <sub>2</sub> O <sub>3</sub>	1.46					

Table 5 K analyses by x-ray fluorescence and by flame photometry.

M.I.T. Sample No.	K% Flame photometry	K% X-ray fluorescence
5296a	3.02	2.98
" b	3.10	3.15
" c	3.08	3.01
" d	2.86	2.91
" e	3.04	2.99
" f	3.05	3.13
5309	2.89	2.90
5310	3.00	3.00
5311	2.98	3.04
5312	3.11	3.09
5313	3.10	3.02
5314	2.97	3.00
5315	3.03	3.00
5316	3.08	3.05
5317	2.86	2.85
5318	3.03	3.05
5319	3.05	3.03
5320	3.06	2.99
5321	2.88	3.01
5322	2.96	3.03
5323	2.71	2.73
5324	3.16	3.09
5325	2.93	2.97

Table 6  $\text{Al}_2\text{O}_3$  analyses by x-ray fluorescence and by spectrophotometry.

M.I.T. Sample No.	% $\text{Al}_2\text{O}_3$ spectrophotometry	% $\text{Al}_2\text{O}_3$ X-ray fluorescence
T4575	10.99	11.07
T4570	9.70	9.71
T4572	10.36	10.30
T4571	10.42	10.47
T4575	10.99	10.91

Table 7  $\text{SiO}_2$  analyses by x-ray fluorescence and by spectrophotometry.

M.I.T. Sample No.	% $\text{SiO}_2$ spectrophotometry	% $\text{SiO}_2$ X-ray fluorescence
5310	78.51	78.33
5314	80.62	80.92
5317	77.09	76.58
5322	79.38	79.39
5324	76.72	76.12

employed. The results of the briquette analyses were, however, acceptable. A comparison of the x-ray fluorescence briquette analyses and the "rapid silicate" analyses for  $\text{SiO}_2$  is given in Table 7.

The accuracy of the major element x-ray fluorescence determinations depends upon the accuracy of the determinations of the standards, which were analyzed by the "rapid silicate" method. Comparison of the determined values with the accepted values for the analytical monitors G-1 and W-1 (Tables 2 and 3) indicates an accuracy which is comparable to that reported for "rapid silicate" analysis in the literature. Direct evidence of the overall accuracy of the moldavite analyses reported in Table 9 is given by the fact that summations of the constituent oxides fall between 99% and 101% for 20 out of the 23 samples analyzed; it should be noted that only the CaO and the MgO and the FeO and  $\text{Fe}_2\text{O}_3$  determinations are dependent.

The Rb x-ray fluorescence analyses of moldavites have a precision (c) of about  $\pm 2\%$ ; the Sr x-ray analyses have a precision of about  $\pm 3\%$ . These conclusions are based upon numerous replicate analyses of G-1 and W-1 by Professor H. W. Fairbairn (M.I.T., 1964, unpublished).

The precision of the x-ray fluorescence analyses is about the same as that of the mass spectrometric stable isotope dilution analyses, based on the results of many investigators



in the M.I.T. Geochronology Laboratory. X-ray fluorescence values for Rb, Sr and the Rb/Sr ratio, standardized with T 4575, and isotope dilution values for the same samples are reported in Table 8.

The accuracy of the x-ray fluorescence analyses for Rb and Sr depends upon the accuracy of the mass spectrometric determinations of Rb and Sr in the standard moldavites. results obtained on G-1 and W-1 in the M.I.T. Geochronology Laboratory, when compared with results obtained by various methods of analysis (Fleischer and Stevens, 1962), suggest an accuracy of better than  $\pm 5\%$  for the mass spectrometric determinations of Rb and Sr.

A conservative estimate of the overall precision (c) of the analyses is as follows:  $\text{SiO}_2$ ,  $\pm 1\%$ ;  $\text{Al}_2\text{O}_3$ ,  $\pm 3\%$ ;  $\text{TiO}_2$ ,  $\pm 3\%$ ;  $\pm \text{MgO}$ ,  $\pm 5\%$ ;  $\text{CaO}$ ,  $\pm 4\%$ ;  $\text{Na}_2\text{O}$ ,  $\pm 15\%$ ;  $\text{K}_2\text{O}$ ,  $\pm 2\%$ ; total Fe as FeO,  $\pm 2\%$ ; Rb,  $\pm 2\%$ ; Sr,  $\pm 3\%$ .

Table 8 Rb and Sr analyses by x-ray fluorescence and by mass spectrometry (in ppm by weight).

M.I.T. Sample No.	Rb I.D.	Rb x-ray	Sr I.D.	Sr x-ray	Rb/Sr I.D.	Rb/Sr x-ray
4575	136	-	143	-	0.95	-
5310	146	139	151	139	0.97	1.00
5317	121	122	-	147	-	0.85
5324	160	161	133	136	1.20	1.19

### 3.4 Results

The results of the chemical analyses of 17 Bohemian and 6 Moravian moldavites are given in Table 9. The analyses are listed by occurrence from west to east in the strewn fields. The columns designated A and B represent analyses of duplicate solutions B (see "rapid silicate" procedures). The major element contents are reported in Table 9 as % of the oxides; a summation of the results is included. Also reported are the total Fe contents, as % FeO, and the contents of Rb and Sr in parts per million. TiO<sub>2</sub> analyses are given. MnO and P<sub>2</sub>O<sub>5</sub> analyses are not given because the former constituent was not determined and the P<sub>2</sub>O<sub>5</sub> analyses proved to be of poor quality; the 15 samples analyzed for P<sub>2</sub>O<sub>5</sub> gave results ranging from 0.00 to 0.06 with a mean P<sub>2</sub>O<sub>5</sub> content of 0.03.

The values reported in Table 9 for the various constituents show the following ranges: SiO<sub>2</sub>, 75.5 - 80.6; Al<sub>2</sub>O<sub>3</sub>, 9.62 - 12.64; TiO<sub>2</sub>, 0.268 - 0.460; Fe<sub>2</sub>O<sub>3</sub>, 0.12 - 0.31; FeO, 1.42 - 2.36; MgO, 1.13 - 2.50; CaO, 1.46 - 3.71; Na<sub>2</sub>O, 0.31 - 0.67; K<sub>2</sub>O, 3.26 - 3.81; total Fe as FeO, 1.53 - 2.61; Rb, 120 - 160 ppm; Sr, 130 - 156 ppm.

The ranges given in the literature (Barnes, 1940; Schnetzler and Pinson, 1963, 1964a, 1964b; Bouska and Povonfra, 1964) for the individual constituents are as follows: SiO<sub>2</sub>, 75.0 - 84.5; Al<sub>2</sub>O<sub>3</sub>, 7.79 - 13.80; TiO<sub>2</sub>, 0.22 - 1.40;

Table 9 Analytical Results

	T 5296a			T 5296b			T 5296c		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			79.2			77.3			76.7
Al <sub>2</sub> O <sub>3</sub>			10.93			10.89			11.28
TiO <sub>2</sub>	0.305	0.309	0.307	0.335	0.336	0.336	0.336	0.328	0.331
Fe <sub>2</sub> O <sub>3</sub>			0.16			0.31			0.20
FeO			1.54			1.63			1.73
MgO	1.51	1.45	1.48	2.06	2.12	2.09	2.03	1.95	1.99
CaO	2.04	2.01	2.02	2.91	2.90	2.91	2.71	2.86	2.79
Na <sub>2</sub> O	0.51	0.50	0.51	0.52	0.51	0.51	0.62	0.64	0.63
K <sub>2</sub> O	3.69	3.59	3.64	3.74	3.74	3.74	3.68	3.74	3.71
Total			99.79			99.72			99.36
Total Fe as FeO	1.71	1.66	1.68	1.92	1.90	1.91	1.92	1.90	1.91
Rb ppm			148			146			144
Sr ppm			133			156			142

Table 9 continued

	T 5296d	T 5296e			T 5296f		
		A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>	75.7 *			78.4			75.5
Al <sub>2</sub> O <sub>3</sub>	11.04			10.76			11.12
TiO <sub>2</sub>	0.314	0.301	0.305	0.303	0.316	0.309	0.313
Fe <sub>2</sub> O <sub>3</sub>	0.28			0.12			0.29
FeO	1.47			1.62			1.50
MgO	2.50	2.17	2.09	2.13	2.19	2.21	2.20
CaO	3.58	3.28	3.26	3.27	3.41	3.39	3.40
Na <sub>2</sub> O	0.45	0.45	0.45	0.45	0.48	0.49	0.48
K <sub>2</sub> O	3.44	3.65	3.68	3.66	3.67	3.70	3.68
Total	98.77			100.71			98.48
Total Fe as FeO	1.72	1.74	1.72	1.73	1.76	1.77	1.76
Rb ppm	120			136			140
Br ppm	140			148			144

Table 9 continued

	T 5309			T 5310			T 5311		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			79.6			78.5*			78.6
Al <sub>2</sub> O <sub>3</sub>			10.73			10.54			10.77
TiO <sub>2</sub>	0.303	0.296	0.300	0.295	0.293	0.294	0.310	0.304	0.307
Fe <sub>2</sub> O <sub>3</sub>			0.18			0.21			0.26
FeO			1.46			1.46			1.46
MgO	1.94	1.85	1.90	1.58	1.57	1.58	1.72	1.61	1.66
CaO	2.80	2.76	2.78	2.66	2.63	2.64	2.36	2.35	2.35
Na <sub>2</sub> O	0.38	0.37	0.37	0.42	0.41	0.41	0.43	0.42	0.42
K <sub>2</sub> O	3.40	3.56	3.48	3.59	3.65	3.62	3.59	3.59	3.59
Total			100.80			99.25			99.42
Total Fe as FeO	1.64	1.61	1.62	1.65	1.65	1.65	1.68	1.69	1.69
Rb ppm			131			139			138
Sr ppm			138			139			134

Table 9 continued

	T 5312			T 5313			T 5314		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			77.6			78.4			80.6*
Al <sub>2</sub> O <sub>3</sub>			11.13			10.30			10.09
TiO <sub>2</sub>	0.334	0.328	0.331	0.300	0.300	0.300	0.304	0.286	0.295
Fe <sub>2</sub> O <sub>3</sub>			0.21			0.13			0.12
FeO			1.75			1.63			1.42
MgO	2.11	2.09	2.10	1.95	1.85	1.90	1.44	1.32	1.38
CaO	3.15	3.10	3.12	3.06	3.10	3.07	2.00	2.00	2.00
Na <sub>2</sub> O	0.51	0.51	0.51	0.45	0.46	0.45	0.44	0.45	0.45
K <sub>2</sub> O	3.77	3.73	3.75	3.74	3.73	3.74	3.55	3.61	3.58
Total			100.50			99.92			99.94
Total Fe as FeO	1.94	1.94	1.94	1.75	1.76	1.75	1.52	1.53	1.53
Rb ppm			141			140			145
Sr ppm			146			144			130

Table 9 continued

	T 5315			T 5316			T 5317		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			77.0			79.55			77.1*
Al <sub>2</sub> O <sub>3</sub>			10.28			9.94			10.43
TiO <sub>2</sub>	0.289	0.285	0.287	0.293	0.279	0.286	0.285	0.284	0.285
Fe <sub>2</sub> O <sub>3</sub>			0.16			0.13			0.14
FeO			1.49			1.55			1.49
MgO	2.20	2.19	2.19	1.60	1.67	1.63	2.24	2.41	2.33
CaO	3.51	3.50	3.50	2.16	2.17	2.16	3.74	3.64	3.69
Na <sub>2</sub> O	0.34	0.36	0.35	0.52	0.49	0.50	0.29	0.33	0.31
K <sub>2</sub> O	3.63	3.66	3.65	3.69	3.72	3.71	3.37	3.51	3.44
Total			98.91			99.46			99.22
Total Fe as FeO	1.65	1.62	1.63	1.67	1.66	1.67	1.62	1.62	1.62
Rb ppm			129			149			121 <sup>^</sup>
Sr ppm			147			139			147

Table 9 continued

	T 5318			T 5319			T 5320		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			78.4			80.3			79.8
Al <sub>2</sub> O <sub>3</sub>			10.11			9.62			11.04
TiO <sub>2</sub>	0.266	0.269	0.268	0.278	0.289	0.284	0.403	0.401	0.402
Fe <sub>2</sub> O <sub>3</sub>			0.18			0.20			0.26
FeO			1.50			1.49			2.03
MgO	2.12	2.12	2.12	1.55	1.58	1.57	1.21	1.27	1.24
CaO	3.75	3.68	3.71	2.51	2.54	2.52	1.61	1.53	1.57
Na <sub>2</sub> O	0.39	0.38	0.38	0.43	0.41	0.42	0.60	0.61	0.60
K <sub>2</sub> O	3.65	3.66	3.65	3.68	3.67	3.68	3.68	3.69	3.69
Total			100.32			100.08			100.63
Total Fe as FeO	1.66	1.66	1.66	1.66	1.67	1.67	2.27	2.25	2.26
Rb ppm			135			150			148
Sr ppm			147			133			134



Table 9 continued

	T 5321			T 5322			T 5323		
	A	B	Avg.	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			80.2			79.4*			78.8
Al <sub>2</sub> O <sub>3</sub>			11.02			11.24			10.99
TiO <sub>2</sub>	0.342	0.331	0.337	0.363	0.364	0.364	0.326	0.326	0.326
Fe <sub>2</sub> O <sub>3</sub>			0.14			0.16			0.17
FeO			1.64			1.83			1.60
MgO	1.23	1.27	1.25	1.39	1.26	1.33	1.56	1.65	1.61
CaO	1.72	1.65	1.68	1.47	1.54	1.50	2.47	2.45	2.46
Na <sub>2</sub> O	0.52	0.53	0.53	0.52	0.54	0.53	0.40	0.38	0.39
K <sub>2</sub> O	3.45	3.49	3.47	3.60	3.54	3.57	3.27	3.26	3.26
Total			100.27			99.92			99.61
Total Fe as FeO	1.77	1.77	1.77	1.96	1.98	1.97	1.75	1.75	1.75
Rb ppm			138			142			122
Sr ppm			135			137			146

Table 9 continued

	T 5324			T 5325		
	A	B	Avg.	A	B	Avg.
SiO <sub>2</sub>			76.7*			80.0
Al <sub>2</sub> O <sub>3</sub>			12.64			11.43
TiO <sub>2</sub>	0.465	0.455	0.460	0.362	0.359	0.361
Fe <sub>2</sub> O <sub>3</sub>			0.28			0.23
FeO			2.36			1.71
MgO	1.17	1.14	1.15	1.13	1.13	1.13
CaO	1.55	1.59	1.57	1.46	1.47	1.46
Na <sub>2</sub> O	0.67	0.67	0.67	0.57	0.60	0.58
K <sub>2</sub> O	3.78	3.85	3.81	3.46	3.58	3.53
Total			99.64			100.43
Total Fe as FeO	2.61	2.61	2.61	1.93	1.91	1.92
Rb ppm			160 <sup>^</sup>			149
Sr ppm			133 <sup>^</sup>			134

\*spectrophotometric determination of SiO<sub>2</sub>

<sup>^</sup>mass spectrometric isotope dilution analysis by Professors W. H. Pinson, Jr., and H. W. Fairbairn.

Note: Tektites 5296a-5319 are from Bohemia, T 5320 - 5325 are from Moravia. Locations are given in Table 1.

$\text{Fe}_2\text{O}_3$ , 0.10 - 0.54;  $\text{FeO}$ , 0.98 - 3.36;  $\text{MgO}$ , 0.98 - 2.74;  $\text{CaO}$ , 0.95 - 3.81;  $\text{Na}_2\text{O}$ , 0.20 - 2.43;  $\text{K}_2\text{O}$ , 2.20 - 3.76;  $\text{Rb}$ , 130 - 1000 ppm;  $\text{Sr}$ , 80 - 1000 ppm. (This data is based upon a total of 35 complete and partial analyses of moldavites).

It is apparent that the analyses of the 23 moldavites investigated in the present study fall within the ranges reported in the literature except for one  $\text{K}_2\text{O}$  and four  $\text{Rb}$  analyses. The  $\text{K}_2\text{O}$  analyses all fall in the upper region of the reported range. Schnetzler (unpublished, 1964) has recently determined the  $\text{Rb}$  and the  $\text{Sr}$  contents of five moldavites by mass spectrometry and found ranges of 96 - 148 and 124 - 132 respectively. It would seem that determinations of  $\text{Rb}$  and  $\text{Sr}$  by methods other than mass spectrometry or x-ray fluorescence are somewhat unreliable. The upper limits given in the literature for the  $\text{Na}_2\text{O}$  and  $\text{TiO}_2$  contents are probably too high. The ranges in the values of  $\text{MgO}$  and  $\text{CaO}$  are very similar in both sets of data.

## CHAPTER 4

## ELECTRON MICROPROBE STUDIES

Tektites are composed of glass. The heterogeneity of tektite glass has been discussed by many investigators and a summary has been given by Chao (1963). Different tektites from the same geographical group exhibit small but measurable differences in chemical composition. In addition, the composition of the glass varies within individual tektites. Some of this internal variation may be ascribed to the presence of lechatelierite, which was first identified in tektites by Barnes (1940), and of other highly siliceous inclusions. The matrix glass surrounding these inclusions is also of variable composition; this is indicated by the omnipresent flow structure of tektites.

Almost all studies of chemical variations within tektites have been based on refractive index determinations. The refractive index of a glass is a direct function of composition. The exact nature of a change in composition cannot, however, be determined by measurements of refractive index. For this reason it was decided to obtain electron microprobe studies of tektites. The only other microprobe study known to the author is by I. Adler and E. J. Dwornik (unpublished, but reported in Chao, 1963, p. 60) who showed that the siliceous inclusions in an indochinite specimen were pure  $\text{SiO}_2$ .

The work was performed for the author on ARL (Applied

Research Laboratories Inc.) electron microprobes at the Hoffman Laboratory, Harvard, and at the Goddard Space Flight Centre; the respective operators were Cornelius Klein and Frank Wood. A polished section and a polished thin section of T 5320, and a polished section of T 5322 were used in the analyses. These tektites were selected because they displayed the most obvious flow structure. Both are Moravian. Corning glass standards 191 AIK and 191 ALA were used. However, the results obtained by "rapid silicate" analysis of these standards by the author did not agree for all constituents with the reported values (Appendix A). In addition, microprobe analyses of the standards indicated some heterogeneity. For these reasons the probe analyses were calculated in terms of the chemical compositions determined by the author for the samples. Microprobe tracks were run along and across the flow structure. Various steps from  $2\mu$  to  $50\mu$  were used, and 30 sec. or 100 sec. counts were taken at each step. Six elements, in groups of three, were determined. Some tracks were repeated so that data on all six elements were obtained along the same track.

Variations in the concentrations of all six constituents were observed. The following variations, given as % spread (ie.  $\frac{\text{spread}}{\text{mean value}} \times 100$ ), were common:  $\text{SiO}_2$ , 6%;  $\text{Al}_2\text{O}_3$ , 20%; total Fe as FeO, 20%; CaO, 25%; MgO, 25%;  $\text{K}_2\text{O}$ , 8%. These variations were observed across the flow structure and re-

peated themselves at intervals of about 100 to 200 $\mu$ . The variations are thought to be real on the basis of the following considerations: 1. all of the MgO and a considerable part of the Al<sub>2</sub>O<sub>3</sub> variations might have been due to analytical error, whereas the variations of the other constituents are believed to be greater than those arising from this error. (Instrument drift is not thought to have been a contributing factor because of the short distances and correspondingly short analysis periods over which the variations occurred); 2. traces along the flow structure did not show similar variations; 3. the fluctuation cycle seemed to be independent of the step-distance used; and 4., certain correlations were evident among the constituents.

It is interesting to note that the variation of K<sub>2</sub>O is less than that of total iron in terms of FeO which in turn is less than the variation observed for CaO. This same situation holds when variations of chemical constituents between moldavites are considered (Chapter 5). The probe analyses showed a clear inverse relationship between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. A weaker inverse relationship was observed between SiO<sub>2</sub> and the other constituents although in one trace SiO<sub>2</sub> and K<sub>2</sub>O were positively correlated. Several lechatelierite particles were identified and proved to be pure SiO<sub>2</sub>. One of the lechatelierite inclusions measured 130 $\mu$  across and was surrounded by a transition zone of about 60 $\mu$ . (The

microprobe analysis area was less than  $5\mu$  in diameter.)

It is concluded that real variations in chemical composition occur over distances of  $50\mu$  or more within individual tektites. These variations appear to be comparable in amount and direction to differences in bulk chemical composition between tektites. The flow structure is thought to be a physical manifestation of the observed chemical variations. These conclusions are tentative because of the preliminary nature of the investigation. It is planned to continue this work.

## CHAPTER 5

## DISCUSSION OF RESULTS. THEORIES OF ORIGIN

The results reported in Table 9 indicate variations in all constituents. Before these results can be discussed it is necessary to determine whether these variations are real or are merely manifestations of analytical error. In Table 10 conservative estimates of analytical precision, in terms of the relative deviation of a single analysis (c), are given alongside the observed scatter of the moldavite results, expressed in terms of the same function c. It is evident that the observed scatter is greater than the analytical error for all constituents, and indeed is considerably greater for most constituents. It is therefore concluded that real differences in chemical composition do exist between the moldavites analyzed in this investigation.

5.1 Variations in chemical composition within and between the Bohemian and Moravian "strewn fields"

Cohen (1963), after examining 8 complete chemical analyses of moldavites, suggested that the  $\text{SiO}_2$  contents of moldavites decrease as the sample localities trend eastward across the strewn fields and that the other constituents increase roughly with decreasing  $\text{SiO}_2$ . Cohen also determined Ga, Ge, Ni, Fe and refractive index in 18 moldavites; he concluded that 1. the Ga/Ge ratios and the Ga and the Ge contents showed no trend, 2. refractive index increased



Table 10 Comparison of observed spread and analytical precision

	Spread of moldavite analyses	Analytical precision
	C	C
SiO <sub>2</sub>	± 2%	± 1%
Al <sub>2</sub> O <sub>3</sub>	4	3
TiO <sub>2</sub>	13	3
Total Fe as FeO	13	2
MgO	23	5
CaO	29	4
Na <sub>2</sub> O	19	15
K <sub>2</sub> O	4	2
Rb	7	2
Sr	4	3

roughly from west to east and the higher refractive indexes of the Moravian samples indicated higher Fe, Mn and Ti contents in these tektites than in those from Bohemia, 3. Ni and the Ni/Fe ratio increased eastward. Cohen (1963) recognized the need for systematic chemical analyses of tektites from many sites before definite trends could be established.

Bouška and Povondra (1964) report chemical analyses of 14 moldavites; these analyses support Cohen's suggestion that SiO<sub>2</sub> content of the Moravian samples is lower than that of the Bohemian samples. However, Chapman *et al* (1964) determined the specific gravities of 37 Moravian tektites and of 108 samples from Habří, Bohemia; they found that the Moravian tektites had a lower average specific gravity than that of the Habří tektites and concluded that Moravian tektites have higher average SiO<sub>2</sub> contents. The specific gravity results obtained by the author (Table 1) tend to confirm the findings of Chapman *et al*. The evidence of the specific gravity results was later corroborated by determinations of SiO<sub>2</sub> contents. The average SiO<sub>2</sub> content of the Moravian samples studied by the author is higher than that of the Bohemian samples.

The analytical data presented in Table 9 for the 23 moldavites (17 samples from 8 locations in Bohemia, 6 samples from 4 locations in Moravia) lead to the following conclusions concerning the differences in chemical composition between the Bohemian and the Moravian samples and the trends which

appear in the Bohemian strewn field. The Moravian tektites have higher average contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{FeO}$  and  $\text{Na}_2\text{O}$  than do the Bohemian tektites. The Moravian tektites have lower average contents of  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Sr}$  than do the Bohemian tektites. The major distinction between samples from the two strewn fields is that Moravian tektites have high and variable  $\text{FeO}$  and  $\text{TiO}_2$  contents, with low and constant  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{Sr}$ , whereas Bohemian tektites have high and variable alkaline earth contents, with low and constant  $\text{FeO}$  and  $\text{TiO}_2$ . This distinction is brought out graphically in Figure 1 for the pair  $\text{CaO} - \text{FeO}$ . The only constituent that shows an apparent trend within the Bohemian strewn field is  $\text{TiO}_2$ ;  $\text{TiO}_2$  contents decrease roughly as the localities trend eastward. The  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  and  $\text{Na}/\text{Rb}$  ratios decrease eastwards.  $\text{MgO}/\text{CaO}$  also shows a weak eastward decrease. It is of some interest to note that all three of these ratios are higher in tektites from the Moravian strewn field which lies to the east, than they are in tektites from Bohemia. The specific gravities of the 17 Bohemian tektites showed no regional trend.

Germane to the subject of trends in composition within the moldavite strewn fields is the statistical study of Faul and Bouška (1963); this study demonstrated that although tektites of certain colours are more common in some areas than others, tektites of all colours can be found in most

localities. Similarly, Chapman et al (1964) found a wide range of specific gravities for samples from Habří. It is therefore apparent that considerable differences in composition exist between samples from the same locality. This is supported by the chemical data given in Table 9 (eg. for the eight samples from Lhenice and for the three samples from Dukovany). In addition, the electron microprobe results indicate considerable variations in chemical composition within individual moldavites. These variations in composition are also suggested by variations in refractive index across individual moldavites, as noted by Cohen (1963) and the author.

It is concluded that, 1. differences in chemical composition exist between the average Bohemian and the average Moravian tektites, 2. the overall similarity between tektites from the two groups suggests that a common origin is highly probable, and, 3. regional compositional trends within both strewn fields are vague or non-existent, and hence of dubious significance.

## 5.2 Correlations

Taylor, in a series of excellent papers concerning the chemical composition of australites (1960, et al 1961, 1962), has discussed the relationships that exist between the various constituents. An attempt was made to treat the moldavite data obtained in this investigation in a similar manner.

Table 11 Correlation coefficients (r) and levels of significance, for various pairs of constituents in moldavites.

	Moravia		Bohemia		Combined data	
	r	signi- ficance	r	signi- ficance	r	signi- ficance
Na <sub>2</sub> O-K <sub>2</sub> O	+0.96	<1%	+0.63	<1%	+0.47	<5%
Na <sub>2</sub> O-Rb	+0.99	<0.1	+0.61	<1	+0.73	<0.1
K <sub>2</sub> O-Rb	+0.94	<1	+0.75	<0.1	+0.72	<0.1
MgO-CaO	+0.91	1	+0.81	<0.1	+0.96	<0.1
MgO-Sr	+0.98	<0.1	+0.72	<0.1	-	-*
CaO-Sr	+0.91	1	+0.56	<5	-	-*
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	not significant		-0.65	<1	-	-*
SiO <sub>2</sub> -MgO	-0.93	<5"	-0.83	0.1	-0.88	<0.1 <sup>^</sup>
FeO <sup>x</sup> -TiO <sub>2</sub>	+0.99	<0.1	+0.85	<0.1	+0.96	<0.1
FeO <sup>x</sup> -Na <sub>2</sub> O	+0.83	<5	+0.70	<1	+0.79	<0.1
Na <sub>2</sub> O-MgO	-0.91	1	not significant		-0.53	1
Na <sub>2</sub> O-CaO	-0.83	<5	not significant		-0.64	0.1
Rb-CaO	-0.83	<5	-0.73	<0.1	-	-*
Rb-Sr	-0.90	<5	-0.50	<5'	-0.61	<1 <sup>^</sup>

\* combined data not applicable

" n = 5

<sup>^</sup> n = 22

<sup>x</sup> Total Fe as FeO

' n = 16

The correlation coefficients and levels of significance for the associations investigated are given in Table 11. The coefficient of correlation (Taylor, 1960; Moroney, 1956) is given by the equation;

$$r = \frac{\sum [(x - \bar{x})(Y - \bar{Y})]}{\sqrt{[\sum (x - \bar{x})^2 \sum (Y - \bar{Y})^2]}}$$

where  $\bar{x}$  and  $\bar{y}$  are the mean concentrations of the two constituents under consideration and  $x$  and  $y$  are the individual concentrations. A coefficient of 0 indicates no correlation (random distribution); a coefficient of +1 indicates a perfect positive correlation; a coefficient of -1 indicates a perfect negative (inverse) correlation. The significance of a correlation was obtained from a graph of the Student's  $t$  function (Moroney, 1956). This function was calculated from the equation

$$t = \frac{r \sqrt{(n - 2)}}{\sqrt{(1 - r^2)}}$$

where  $n$  is the number of determinations. Significance at the 0.1% level means that there is one possibility in a thousand of the correlation arising fortuitously. Data for the Moravian tektites, the Bohemian tektites and for the whole group of moldavites are presented separately in Table 11 because differences in correlations occur in many cases.

The alkali elements (Na, K & Rb) show a significant positive correlation amongst themselves. The relationship for the pair  $\text{Na}_2\text{O} - \text{K}_2\text{O}$  is demonstrated in Figure 2. The alkaline earth elements (Mg, Ca & Sr) show a

significant positive correlation amongst themselves. Figure 3 demonstrates the relationship between the MgO and the Sr contents of the 23 moldavites investigated. Sodium and rubidium are inversely correlated with the alkaline earths. This negative correlation is shown graphically in Figure 4 for the pair Rb-CaO. Potassium shows no significant correlations with the alkaline earths.

SiO<sub>2</sub> shows good negative correlations with the alkaline earths with Al<sub>2</sub>O<sub>3</sub> and with specific gravity. The alkaline earths, Al<sub>2</sub>O<sub>3</sub>, and specific gravity, show positive correlations amongst themselves of various significances. SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> do not have significant correlations with FeO or the alkalis.

FeO displays somewhat unexpected relationships with other constituents. Total Fe as FeO was used in the calculations because the precision of the total Fe determinations was better than the precision of the FeO determinations. FeO and TiO<sub>2</sub> contents show a highly significant positive correlation. A positive correlation exists between FeO and Na<sub>2</sub>O; the significance of this correlation is actually higher than the values reported in Table 11 because the FeO and Na<sub>2</sub>O contents plot along a curve; this is illustrated in Figure 5. The FeO - Rb and FeO - K<sub>2</sub>O relationships resemble that of FeO - Na<sub>2</sub>O for the Moravian tektites but for the Bohemian tektites the relationships are nearly random.

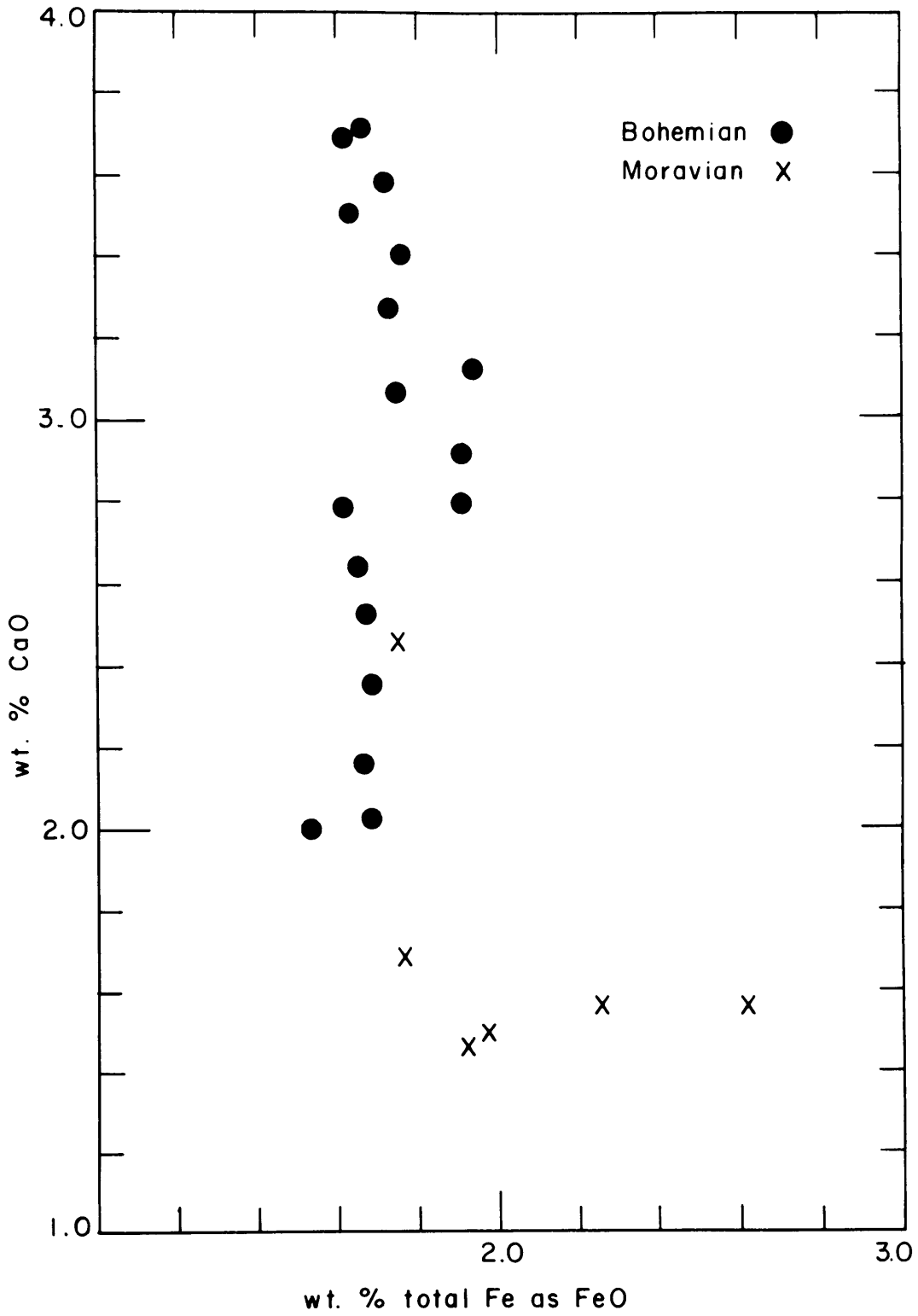


Fig. 1 CaO vs. FeO for 23 moldavites.



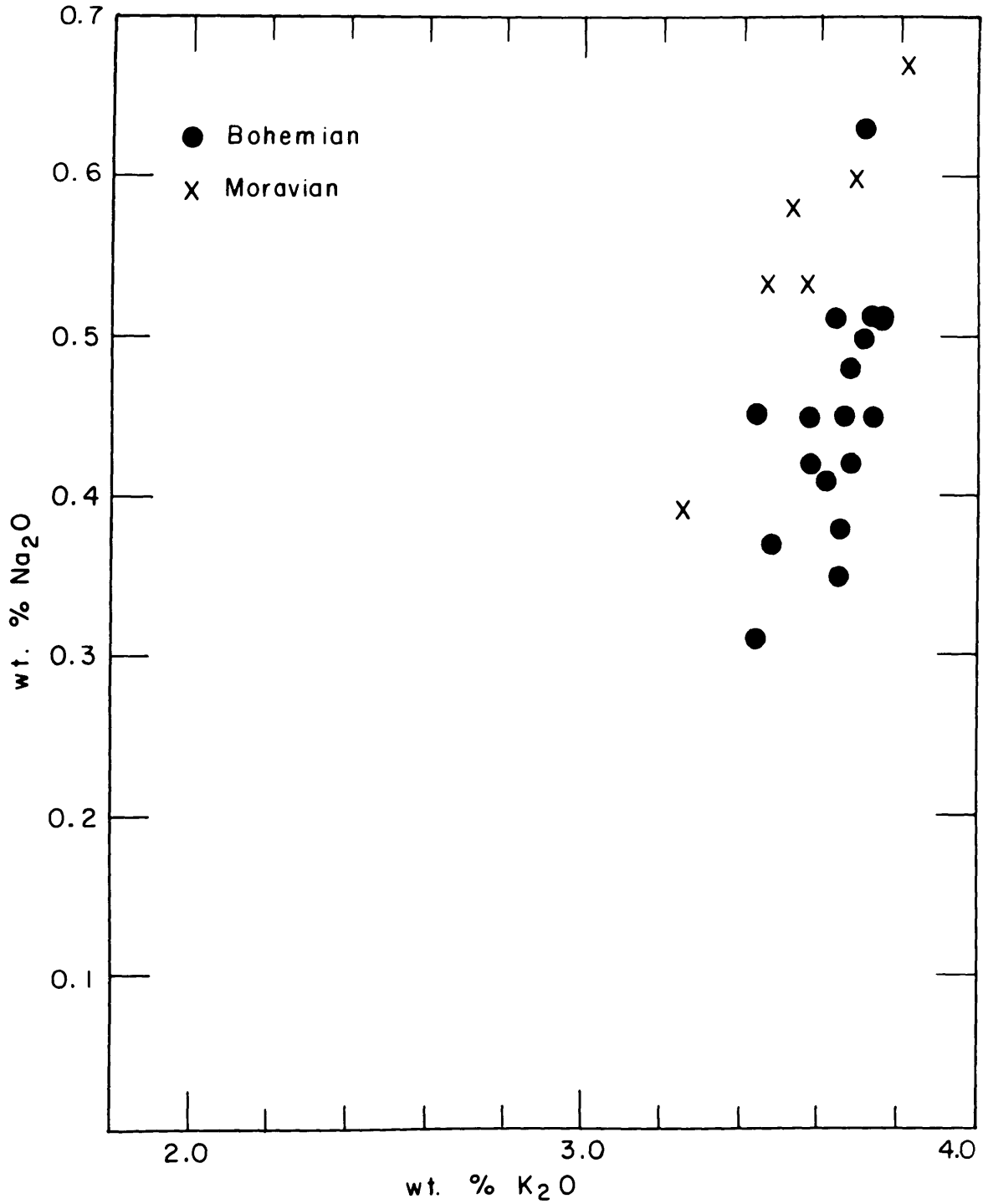


Fig. 2  $\text{Na}_2\text{O}$  vs.  $\text{K}_2\text{O}$  for 23 moldavites

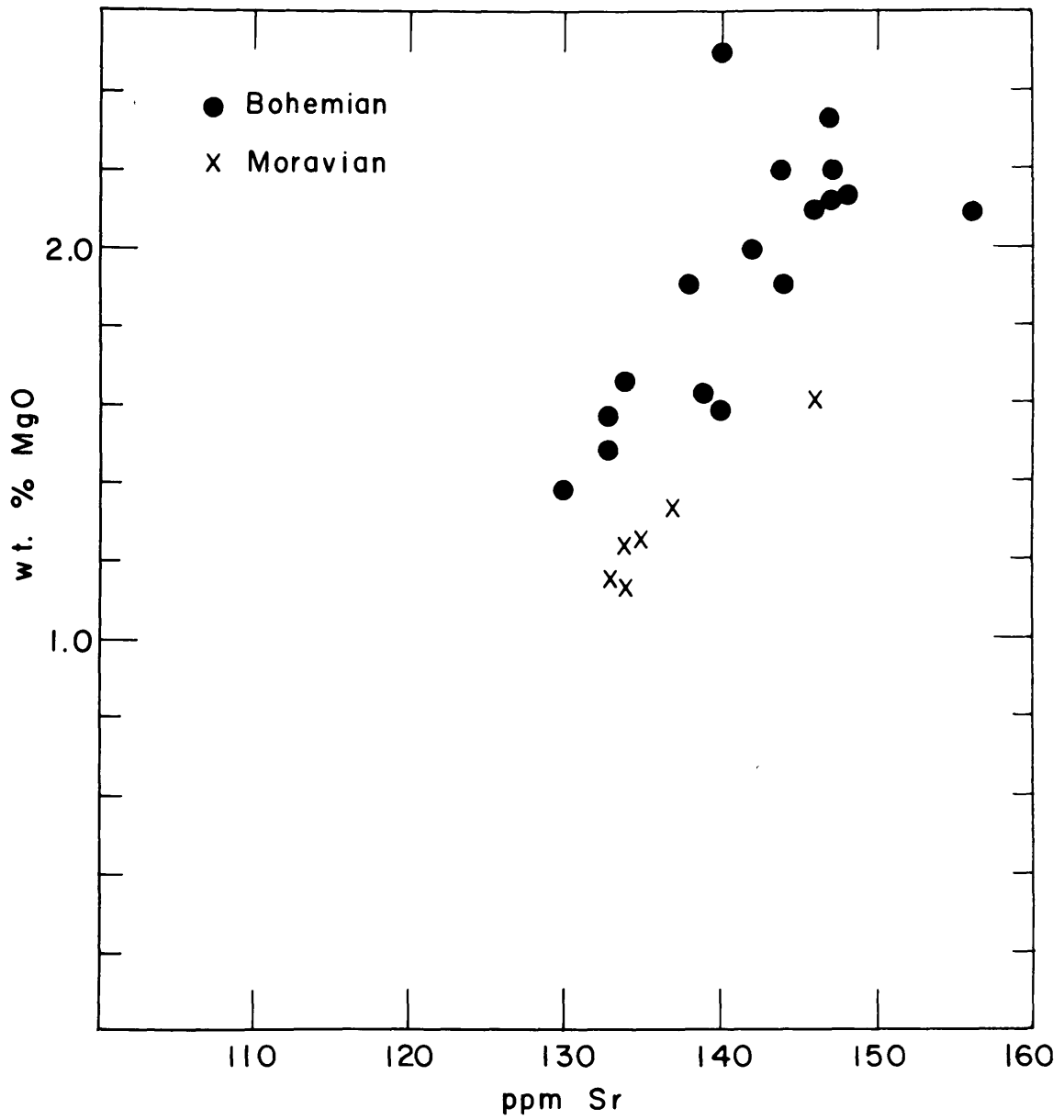


Fig. 3 MgO vs Sr for 23 moldavites.

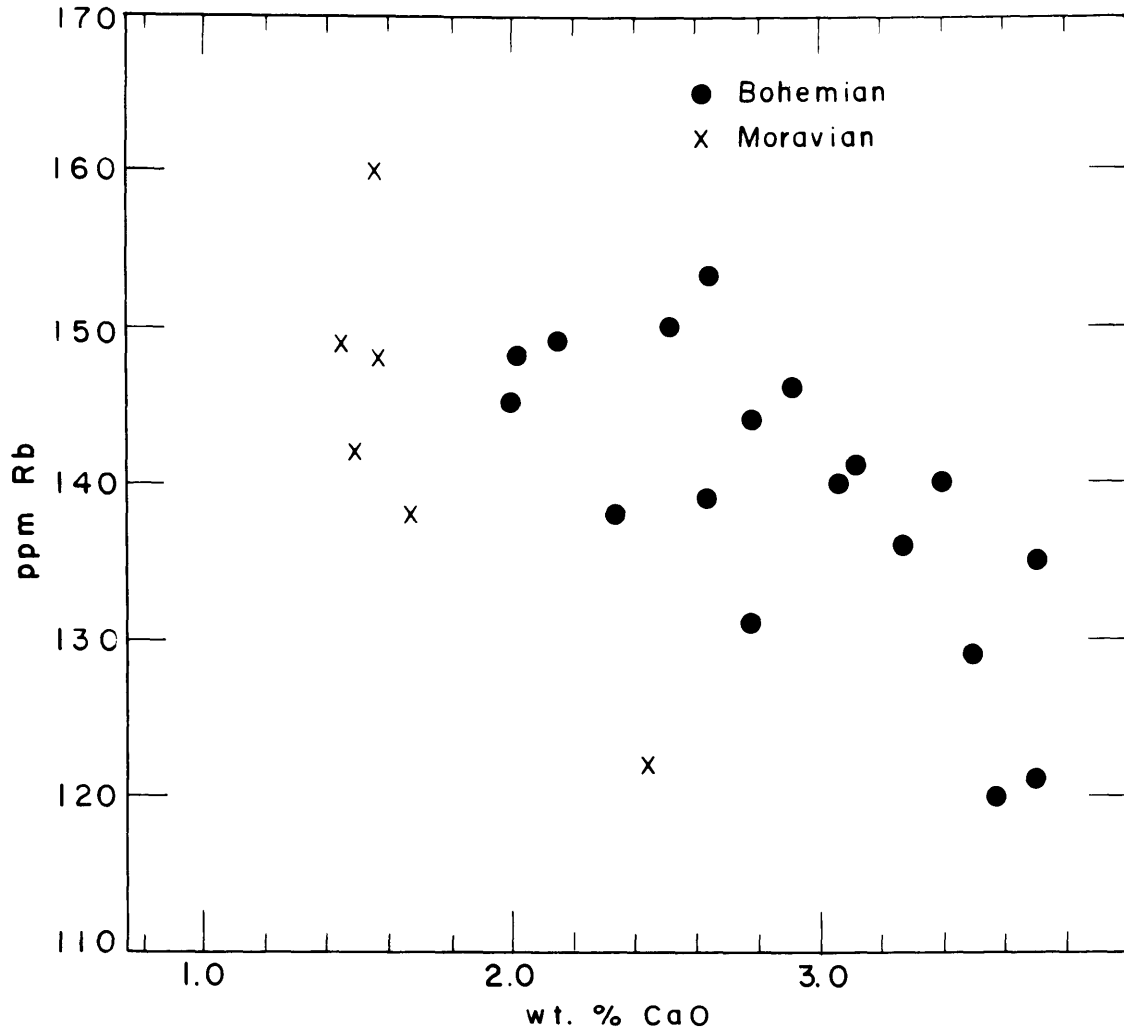


Fig. 4 Rb vs. CaO for 23 moldavites.



The relationships between FeO and the alkaline earths reveal a distinct difference between the Moravian and the Bohemian tektites. The Moravian tektites have low and constant alkaline earth contents with variable FeO, whereas the Bohemian tektites have relatively constant FeO with the alkaline earths varying over a wide range. Figure 1 illustrates this point for the pair CaO - FeO .

### 5.3 Variation in chemical composition

Real differences in chemical composition exist between tektites. Composition also varies within individual tektites, as indicated by refractive index and electron microprobe studies (Chapter 4). These variations in chemical composition reflect variations in the parent material and/or differential changes in composition brought about during fusion.

Taylor (1962), partly on the basis of significant inverse correlations of most constituents with SiO<sub>2</sub>, concluded that the australite parent material consisted of a mixture of 75% shale and 25% quartz. Such a mixture is not suggested by the moldavite data because SiO<sub>2</sub> is not inversely correlated with the alkalis or with FeO. In fact, the non-linear correlations of certain pairs of constituents (eg. Fig. 5, Na<sub>2</sub>O - FeO; Fig. 1, CaO - FeO) cannot be explained in terms of any two-phase mixing process, including the mixing of

immiscible liquids. The data could be explained in terms of a complicated mixing process but the significant correlations between many pairs of constituents indicate that a simple cause was responsible for the observed variations in chemical composition.

Igneous differentiation (fractional crystallization, crystal separations, etc) has been suggested by some authors (eg. Chao, 1963) as the cause of the varying concentrations of some chemical constituents in tektites. There is, however, no evidence for the erstwhile existence of crystalline phases in tektites, with the possible exception of  $\text{SiO}_2$ . In addition, the small-scale variations in composition within individual tektites are difficult to interpret in terms of igneous differentiation processes. Superficially, the variations in composition of the moldavites resemble the variations in acid igneous rock sequences. In such sequences, however, the alkalis have positive correlations with  $\text{SiO}_2$ , and iron is positively correlated with the alkaline earths and with  $\text{Al}_2\text{O}_3$ . These correlations are not displayed by the moldavites. However, igneous differentiation of melts with moldavite composition (ie. about 80%  $\text{SiO}_2$ ) would not follow the normal course. These melts would presumably lie within the  $\text{SiO}_2$  field and differentiation would occur by  $\text{SiO}_2$  phase separation. Products of this  $\text{SiO}_2$  subtraction would exhibit inverse correlations of all constituents with  $\text{SiO}_2$ . This is not the

case for moldavites.

Many investigators have appealed to selective volatilization in order to account for various features of the chemical composition of tektites. The low alkali content of tektites relative to the high  $\text{SiO}_2$  content (Lovering, 1960; Lowman, 1962a), and the positive correlations amongst the alkali elements (Chao, 1963) have been explained in terms of this process. Barnes (1962, oral communication, see Chao, 1963, p. 53) suggested that the siliceous "finger" inclusions in australites have undergone more volatilization than the matrix glass. The Ga/Ge ratios (Cohem, 1960) and the Zn/Cu ratios (Greenland and Lovering, 1962) of tektites have been interpreted on the basis of selective volatilization. Greenland and Lovering (1962) suggested that the positive correlation of mass and specific gravity for bediasites and australites indicated changes in composition brought about by volatilization. Taylor (1962), however, concluded that there was no evidence of any substantial changes of this nature for australites. Taylor (1962) also pointed out that complete loss of alkalis from granitic material would not appreciably affect the concentrations of most of the other constituents. The constancy of alkali contents in South East Asian tektites other than australites indicated a lack of selective volatilization to Schnetzler and Pinson (1964a). Direct evidence of limited selective volatilization is given

by the flanged australites. The flanges were found to have higher Ga/Ge ratios (Cohen, 1960) and SiO<sub>2</sub> contents (Baker, 1959) and lower alkali contents (Taylor, 1961) than the cores. Perhaps the best evidence of extensive changes of chemical composition by selective volatilization in tektites is the discrepancy between the U-Pb and Rb-Sr ages (Schnetzler and Pinson, 1964b).

Experimental data concerning selective volatilization are meagre. Optical spectrograph studies of silicate materials (Ahrens and Taylor, 1961, p.82) have indicated the following order of volatility, from most to least volatile: alkalis > Si, Fe > Mg > Al, alkaline earths. Lovering (1960) repeatedly fused granite in a solar furnace and observed a slight depletion of alkalis and small increases in alkaline earth and aluminum contents. Lovering concluded that extensive changes could occur in large meteorite impacts. Friedman et al (1960) performed a similar experiment using a variety of rock types and obtained equivalent results. Friedman found that the melts did not approach tektites in composition and concluded that tektites are probably similar chemically to their parent materials unless the materials were heated to very high temperatures. In a more extensive investigation, the relative volatility from tektite melts of the oxides of Na, K, Fe, Al and Si was determined as a function of temperature, total pressure and oxygen fugacity (Walter



and Carron, 1964). The relative volatility of  $\text{SiO}_2$  was found to decrease with decreasing oxygen pressure. Surprisingly enough, the alkalis were not significantly lost in runs made at atmospheric pressure ( $P_{\text{O}_2} = 0.21$  atm). Walter and Carron suggested that the alkalis in tektites have been reduced to an equilibrium value by fractional volatilization. This would nicely explain the low and constant alkali contents of tektites.

In view of the failure of simple mixing or normal igneous differentiation to satisfactorily explain the variations in chemical composition of the moldavites, it is suggested that these variations are, in part at least, the result of selective volatilization.

In this connection, the Rb - Sr data on tektites are of interest. The range of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios found within three of the four geographic groups is very limited and for the Czechoslovakian and South East Asian tektites wide variations in Rb/Sr ratios have been found (Schnetzler and Pinson, 1964b; Schnetzler and Pinson, 1965; Pinson, et al, 1965; this work). For example, eight out of nine  $\text{Sr}^{87}/\text{Sr}^{86}$  analyses of moldavites fell within a range of 0.0011, which is two standard deviations of a single analysis (Pinson et al, 1965); Rb/Sr ratios of moldavites range from 0.77 (Schnetzler, personal communication, 1964) to 1.20 (this work). No sympathetic variation of  $\text{Sr}^{87}/\text{Sr}^{86}$  with Rb/Sr has been found

within the North American, Czechoslovakian, or South East Asian tektite groups. On the basis of two samples, a sympathetic variation apparently does exist among Ivory Coast tektites (Schnetzler and Pinson, 1965).

The variable Rb/Sr ratios in conjunction with an almost constant  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio for the moldavites is a situation that cannot have existed long. Recently, certainly within the last 50 m.y., either homogenization of Sr or fractionation of Rb and Sr, or both processes, must have occurred. This event probably occurred between 30 and 15 m.y. (K-A age of moldavites, Zahringer, 1963) ago. The most obvious event that occurred during this time period was the fusion event itself. The simplest explanation of the moldavite Rb-Sr data is that the Rb/Sr ratio of the parent material was changed from a constant value by selective volatilization during fusion. There are other possible explanations. The Rb/Sr ratios could reflect initial variations in the parent material and the constant  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio could be interpreted as due to homogenization or fractionation. Arguments have, however, already been presented against the sedimentary or normal igneous origin of the observed constituent variations in moldavites. Fractionation of Sr during the fusion event is very unlikely. Homogenization of Sr during fusion is possible but then the survival of discrete phases such as lechatelierite must be accounted for and there is no evidence to support a post fusion  $\text{SiO}_2$  phase

separation. If homogenization of Sr during the thermal event occurred, then the observed Rb/Sr ratios must be due to fractional volatilization. It is concluded that the most attractive explanation of the moldavite Rb-Sr data is the assumption, 1. of a parent material with the same Rb/Sr ratio throughout which accounts for the observed invariance of  $\text{Sr}^{87}/\text{Sr}^{86}$ , and, 2. that the observed range of Rb/Sr ratios in moldavites was caused by selective volatilization during the thermal event dated by the K-A age.

The question next arises of how to interpret the moldavite data in terms of the proposed fractionation process. The loss of a particular constituent by volatilization depends upon the breaking of chemical bonds, diffusion through the melt, escape at the melt-vapor interface, and time. Hence the loss will be a function of temperature, pressure, partial pressures, concentration of the particular constituent, bulk composition, turbulence in the melt, time, etc. The effects of these variables on vaporization of silicate material are poorly understood at present. In addition, one can only speculate upon the conditions under which tektites were produced. Any suggestions as to the direction of vapor fractionation in tektite material must therefore be considered tentative. In light of the experimental data, however, it seems probable that this process would decrease the contents of the alkalis and increase the contents of the alkaline earths during the initial stages.

The moldavites show significant variations in the concentrations of the alkalis. It is assumed that those moldavites with lower alkali contents have undergone more of the selective vaporization process. The content of a particular alkali constituent could be used as an index of the extent of the process' action. There is the possibility, however, that some of the variation in concentration of the constituent could be inherited from the parent material. For instance, the addition or subtraction of  $\text{SiO}_2$  from an otherwise homogeneous material would not affect the weight ratio of any two other constituents but it would affect their concentrations. A ratio of two constituents would therefore serve as a better index of volatilization. The Rb/Sr ratio was selected as the index for the following reasons: 1. the Rb/Sr ratio was probably the same throughout the parent material as indicated by the uniformity of the Sr isotopic composition; 2. Rb and Sr are inversely correlated in moldavites and therefore their ratio shows much variation; 3. Rb and Sr were determined separately from all other constituents and therefore relationships between the Rb/Sr ratio and other constituents cannot be due to analytical idiosyncracies; 4. the Rb/Sr ratio is thought to be as good if not better than the individual Rb and Sr determinations with respect to precision and accuracy. It is assumed that the Rb/Sr ratio decreased during the fractionation process.

The following conclusions are based upon plots of Rb/Sr ratios versus the contents of other constituents. The SiO<sub>2</sub> content of the Bohemian tektites decreases with the Rb/Sr ratio although the points are scattered. The Moravian tektites in general display a smaller decrease in the SiO<sub>2</sub> contents; T 5324, which has the highest Rb/Sr ratio (1.20), possesses lower SiO<sub>2</sub> than the other five Moravian samples. The Al<sub>2</sub>O<sub>3</sub> contents of the Bohemian tektites and of five of the Moravian samples show no trend; T 5324 is considerably higher than the other tektites with respect to both the Rb/Sr ratio and the Al<sub>2</sub>O<sub>3</sub> content. MgO, CaO, and Sr contents all show similar and very definite increases with decreasing Rb/Sr. MgO is plotted in Figure 6. Total Fe as FeO varies very little within the Bohemian samples; in the Moravian samples it decreases with the Rb/Sr ratio until it attains a value similar to those of the Bohemian samples. These relationships for iron are demonstrated in Figure 7. Na<sub>2</sub>O, K<sub>2</sub>O, and Rb decrease linearly with Rb/Sr for the six Moravian samples. The Bohemian tektites show a similar significant trend for Rb, a much weaker trend for Na<sub>2</sub>O, and no apparent trend for K<sub>2</sub>O. Rb/Sr vs Na<sub>2</sub>O is plotted in Figure 8. Rb/Sr vs. Specific gravity is plotted in Figure 9; this plot is almost the reverse of SiO<sub>2</sub> plot and shows an increase in specific gravity for Bohemian tektites with decreasing Rb/Sr. Weight appeared to be unrelated to the Rb/Sr ratio.

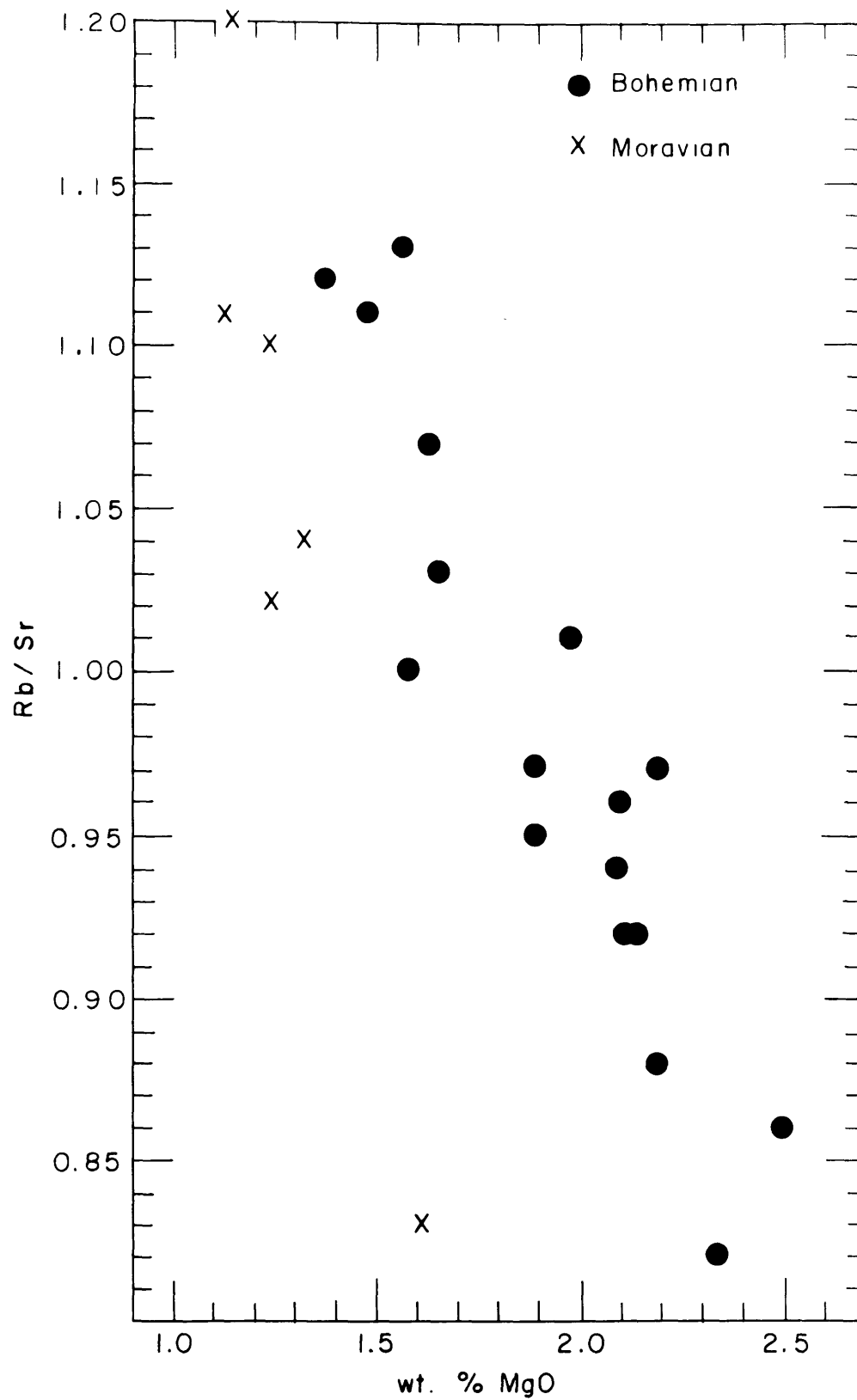


Fig. 6 Rb/Sr vs. MgO for 23 moldavites

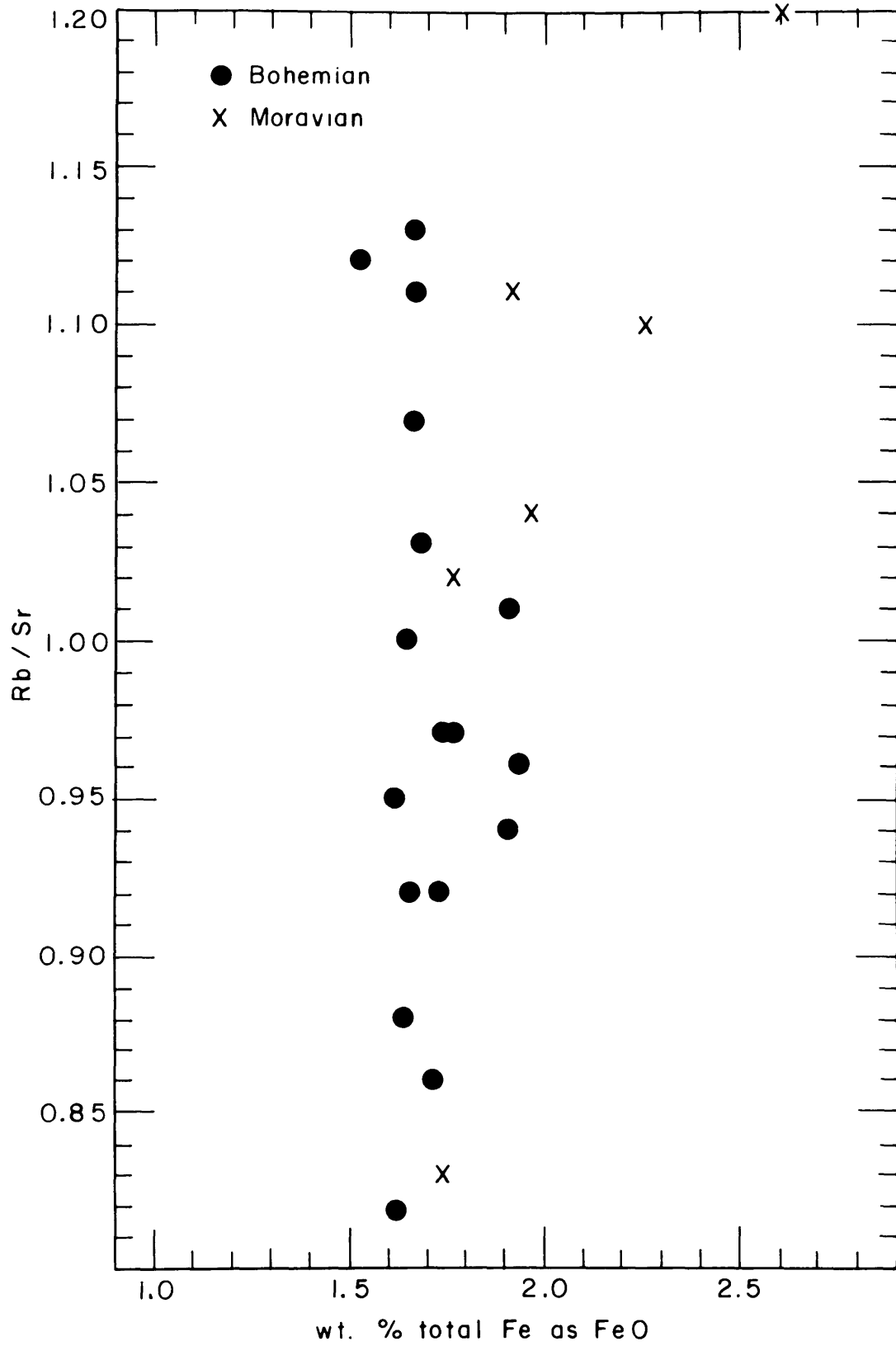


FIG. 7 Rb/Sr vs. FeO for 23 moldavites.

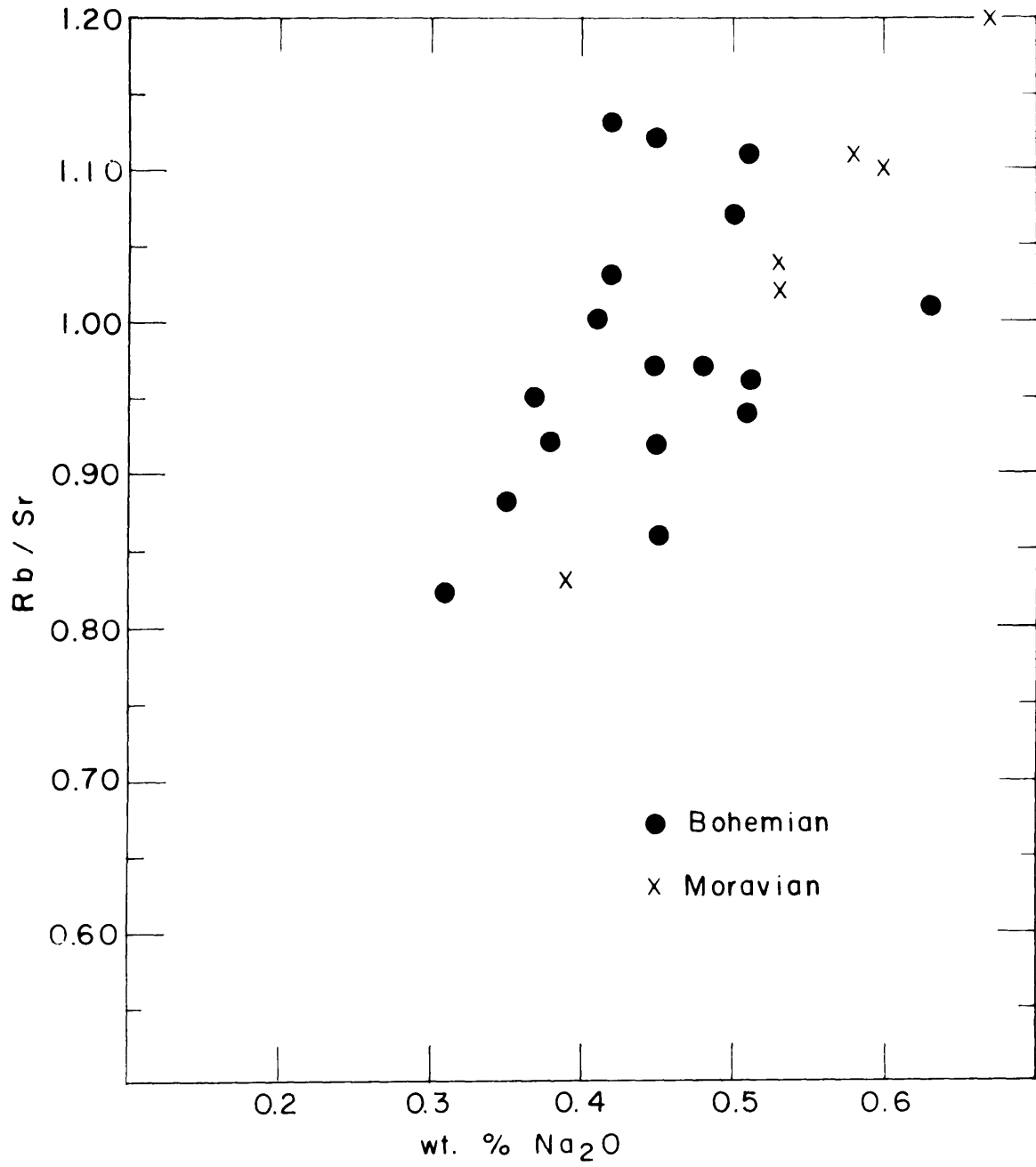


Fig. 8 Rb/Sr vs. Na<sub>2</sub>O for 23 moldavites.



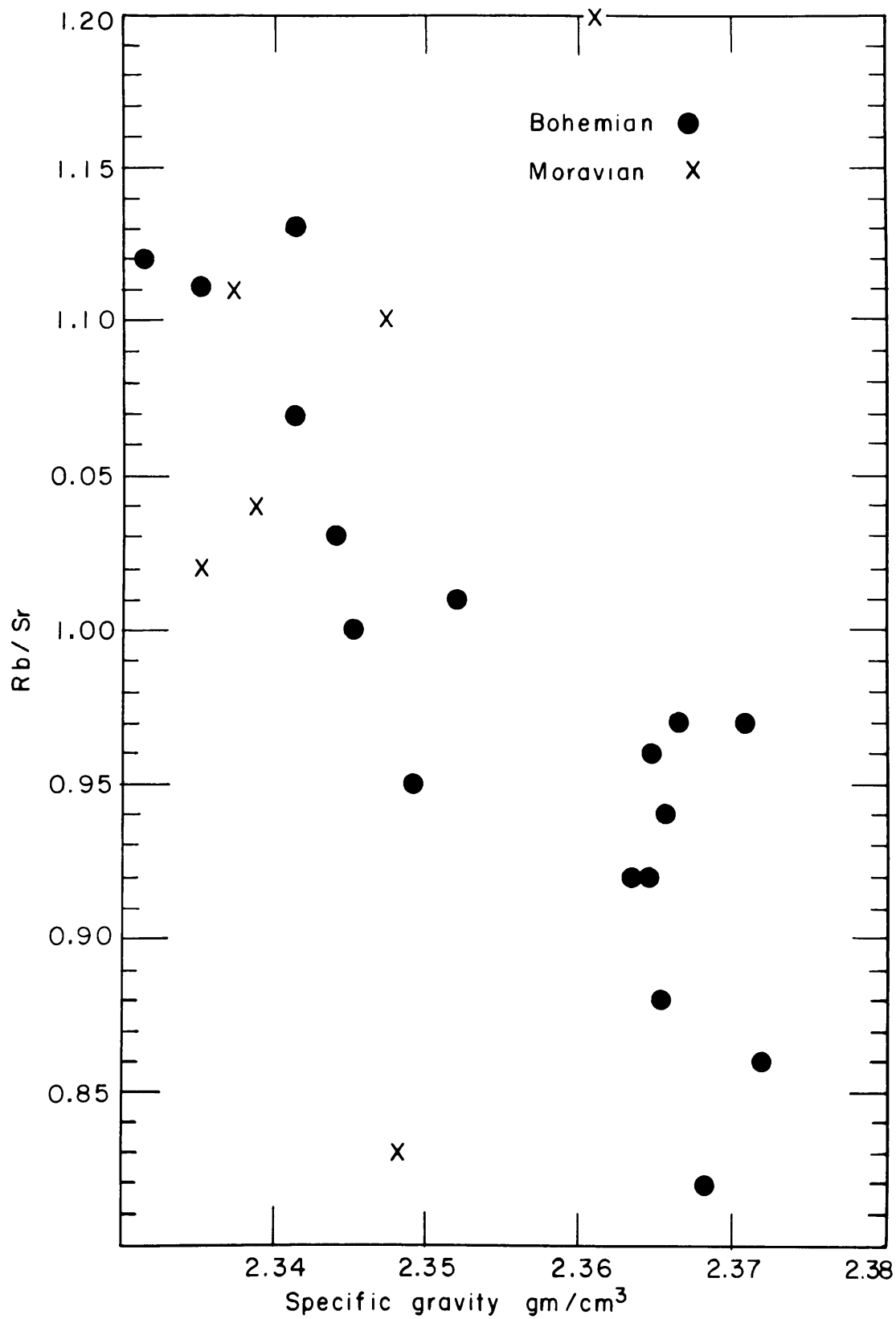


Fig. 9 Rb/Sr vs. Specific gravity for 23 moldavites

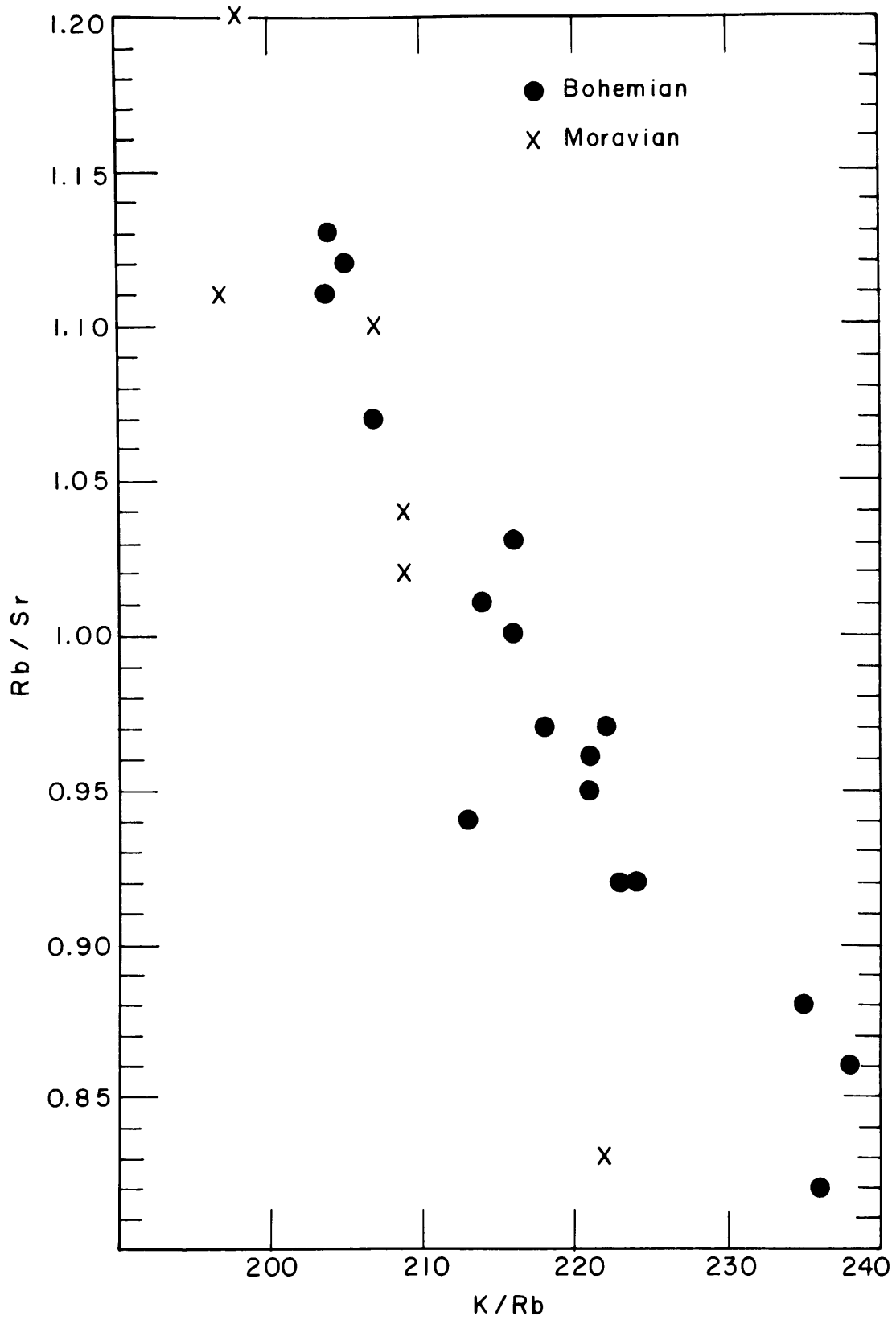


Fig. 10 Rb/Sr vs. K/Rb for 23 moldavites

No relationship was observed between the Rb/Sr and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios.  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  and  $\text{Na}_2\text{O}/\text{Rb}$  have significant positive correlations with Rb/Sr for the Moravian tektites.  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  has a similar trend for the Bohemian tektites, but with much scatter. No trend is apparent for  $\text{Na}_2\text{O}/\text{Rb}$  vs. Rb/Sr in the Bohemian samples. The K/Rb ratios of both Bohemian and Moravian samples increase with decreasing Rb/Sr ratios. K/Rb vs. Rb/Sr is plotted in Figure 10.

It is difficult to account for the relationships among the chemical constituents of moldavites by means other than selective volatilization. It might be argued that this process has masked preexisting variations. The author feels, however, that such initial variations would involve the addition or subtraction of  $\text{SiO}_2$  and hence would be manifested by inverse correlations of all constituents with  $\text{SiO}_2$ . The inverse correlation of the alkalis and alkaline earths in moldavites suggests that variations of  $\text{SiO}_2$  in the parent material of moldavites were very limited. Differences between the Bohemian and the Moravian tektites, with respect to constituent variations, probably reflect different histories during the thermal event. The relative volatilities of the chemical constituents, as indicated by the correlations, were as follows, from most to least volatile:  $\text{Na}_2\text{O}$ , Rb,  $\text{K}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , Sr, MgO, and CaO. This order is in essential agreement with the available experimental evidence. The

unusual relationships of total Fe as FeO with other constituents (see Fig. 1, Fig. 5, and Fig. 7) may be interpreted in terms of the volatility of iron. It is suggested that iron was the most volatile constituent initially and was rapidly lost in most of the moldavite material until an equilibrium value of about 1.7% total Fe as FeO was attained and that thereafter the iron content did not change appreciably.

If it is agreed that the Rb/Sr ratio of the moldavite parent material was the same throughout, and that the Rb/Sr ratio was continuously lowered during the thermal event, then it is possible to calculate the approximate composition of the moldavite parent material. An inspection of Fig. 3 (MgO vs Sr) suggests that a reasonable estimate of the Sr content of the parent material is 125 ppm. This in turn suggests a MgO initial content of about 0.8%. From the correlations among the various constituents it is possible to calculate the concentrations of the other constituents. It is suggested that the parent material of the moldavites may have had approximately the following composition: SiO<sub>2</sub>, 82%; Al<sub>2</sub>O<sub>3</sub>, 9%; TiO<sub>2</sub>, 0.5%; total Fe as FeO, 3%; MgO, 0.8%; CaO, 0.8%; Na<sub>2</sub>O, 0.7%; K<sub>2</sub>O, 4%; Rb, 160 ppm; Sr, 125 ppm; Rb/Sr = 1.3. This composition was calculated on the assumption that constituent concentrations varied in the same direction throughout the volatilization process. This assumption may not be valid. For example, T 5324 has the highest

Rb/Sr ratio (1.20) and might, therefore, be closest in composition to the parent material. T 5324, however, contains 77% SiO<sub>2</sub> and 13% Al<sub>2</sub>O<sub>3</sub>. This suggests that SiO<sub>2</sub> may have gone through a maximum and Al<sub>2</sub>O<sub>3</sub> through a minimum as Rb/Sr decreased.

It is interesting to speculate upon the possible effects of selective volatilization on tektites from other geographical groups. It has already been mentioned that Taylor (1962) found in australites an inverse correlation of most chemical constituents with SiO<sub>2</sub>. This was interpreted in terms of a proposed 75% shale - 25% quartz parent mixture. Taylor pointed out that the observed relationships were unlike those of differentiated rock series. However, igneous differentiation of melts with tektite compositions might well take place by SiO<sub>2</sub> phase separation. The sedimentary mixing of pure SiO<sub>2</sub> with a homogeneous phase (shale), and the igneous process of subtracting SiO<sub>2</sub> from a homogeneous phase (melt), both yield products with inverse correlations between SiO<sub>2</sub> and all other constituents. Moreover, the addition or subtraction of SiO<sub>2</sub> does not completely account for the correlations Taylor obtained. It does not account for the variations in constituent ratios (eg. K/Rb ratios range from 210 to 235). In other words if the australites truly reflected a mixture of quartz and homogeneous shale then plots of any pair of constituents other than SiO<sub>2</sub> should give trend lines that extrapolate through the origin.

This is not the case for all constituents in the australites and the deviations would seem to exceed those attributable to analytical error. For example  $\text{Na}_2\text{O}$  vs.  $\text{K}_2\text{O}$  gives an intercept at about 1%  $\text{K}_2\text{O}$ . Perhaps the best way to explain these deviations is through the agency of selective volatilization. It must then be wondered, in view of the significant correlations that Taylor obtained, whether all the variations might not be due to selective volatilization.

Not all of the constituents in australites are inversely correlated with  $\text{SiO}_2$  (Taylor, 1962). Some of these are the more volatile constituents. Taylor and Sachs (1964) pointed out that the low concentration of elements such as Ga and Cu in australites might be due to selective loss during melting. Reduction of these elements to equilibrium concentrations by volatilization might account for the lack of correlation with  $\text{SiO}_2$ . The lack of this correlation in the cases of CaO and Sr, which are both relatively involatile, might be accounted for if  $\text{SiO}_2$  were also involatile. The possibility of  $\text{SiO}_2$  being involatile receives some support from the higher  $\text{SiO}_2$  contents of australite flanges (Baker, 1959), the presence of siliceous "fingers" in australites, and from the fusions by Walter and Carron (1964) in oxygen poor environments. The positive correlation of  $\text{SiO}_2$  and Zr, and the high concentration of Zr in australites, would then also be nicely explained. The positive correlation of  $\text{Fe}^{-3}$  and

$\text{SiO}_2$  might also best be explained in terms of selective volatilization.

In conclusion, the variations in chemical composition of the moldavites were probably caused by preferential volatilization of constituents that occurred during the high temperature fusion event dated by the K-A age. The parent material of the moldavites was probably of uniform composition throughout. In view of the overall similarity of tektites from all geographic groups a common process of origin should be considered. Several aspects of the australite data (Taylor, 1962; Taylor and Sachs, 1964) that might best be interpreted in terms of selective volatilization have been mentioned. However, the australites and the bediasites (Chao, 1963) do not show clear relationships between the Rb/Sr ratios and the contents of other constituents and therefore cannot be treated in the same manner as the moldavites.

#### 5.4 Nature of the parent material

The chemical composition of tektites reflect the compositions of the parent materials and any changes in composition that occurred during fusion.

Numerous suggestions have been made as to the nature of the parent material. The compositions of tektites have matched with those of the following sedimentary materials:

soil (Preuss, 1935; Schwarcz, 1962; Taylor, 1962), sedimentary rocks (Barnes, 1940; Urey, 1958), "three parts shale - one part quartz" rock (Taylor, 1962). Tektite compositions have also been matched with those of acid igneous rocks (Barnes, 1940; Mason, 1959; Lovering, 1960; Greenland and Lovering, 1962; Chao, 1963) and intermediate igneous rocks (Lowman, 1962a). Tektites are in general more similar to terrestrial sedimentary rocks in composition than they are to fairly common igneous rocks. Taylor's (1962) shale-quartz rock fits the composition of tektites very well for most elements. Most authors, who have proposed igneous parents, however, invoked selective loss of alkalis and other volatile elements during the high temperature event; in this way the lack of fit for some elements in a comparison of tektite compositions with those of common acid igneous rocks was explained.

Arguments against each of these proposed parent materials have been presented in the literature. A major objection is variability of chemical composition because tektites show a relatively limited range of composition, especially if considered group by group. It is doubted that those proposed parent materials that are abundant enough to warrant serious consideration would be as chemically homogeneous as tektites throughout the required volume. Igneous rocks show a less erratic, smaller variation in



composition than sediments and for this reason have been preferred as parent material by some investigators (eg. Chao, 1963). However, Lowman (1962b) examined the variation in chemical composition in tektites, igneous rocks and sedimentary rocks and came to the conclusion that tektites have not been formed from terrestrial materials by any natural process thus far suggested. This conclusion receives support from the available isotopic data on O and Sr.

The  $O^{18}/O^{16}$  ratios of tektites fall within a unique and narrow range with  $\Delta=8.9$  to  $10.5\%$  relative to Hawaiian sea water (Silverman, 1951; Taylor and Epstein, 1962, 1963). Taylor and Epstein (1962) pointed out that tektites plot very nicely with igneous rocks on an  $O^{18}/O^{16}$  vs  $SiO_2$  diagram. Tektite oxygen closely resembles that of igneous quartz. The only sedimentary rocks that match tektites with respect to oxygen composition are orthoquartzites consisting of fresh (ie. non-authigenic) igneous quartz ( $\Delta=10.2\%$ ). The following ranges of  $\Delta$  were found for sedimentary materials and soils: sediments,  $10.2$  to  $18.2\%$ ; metasediments,  $12.1$  to  $15.7\%$ ; soils  $12.3$  to  $15.8\%$ . The distinct difference between these materials and tektites is apparent. On the other hand the  $O^{18}/O^{16}$  ratios of acid igneous rocks fall within a relatively narrow range ( $8 - 9.5\%$ ) and approach those of tektites. This data suggests that if tektites are terrestrial then acid igneous rocks are the only possible parent

materials. It is possible, of course, that the isotopic composition of O was changed during fusion. Taylor and Epstein (1963) found a very small increase (about 1‰) in the  $O^{18}/O^{16}$  ratio after fusion of two soil samples. The magnitude and direction of this change, and the composition of tektite oxygen lead Taylor and Epstein to conclude that tektites are either extraterrestrial or they are fused terrestrial granitic rocks with changed chemical composition. Selective volatilization would best explain such changes.

If tektites condensed from a vapour phase their oxygen would probably be lighter than that of the parent material which might then be sedimentary or metasedimentary rocks. The existence of lechatelierite inclusions argues against such an origin of tektites. Complete homogenization of material during fusion would explain the limited range in the isotopic composition of O from tektites of a particular geographic group. It would not explain why all tektite O falls within a very narrow range in the terrestrial spectrum. It might be argued that homogenization of vast quantities of material would produce oxygen approaching a "crystal-average" value in composition, but complete homogenization becomes less likely, the larger the amount of material involved. In addition, lechatelierite inclusions would probably not survive thorough homogenization and there is no evidence to support a post-fusion phase separation of  $SiO_2$ . It is concluded, as it was by Taylor and Epstein, that if tektites

are terrestrial then the oxygen isotope data indicates that the parent material was of granitic composition.

The range of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios in tektites from 0.712 to 0.723 is quite small compared to the range found in nature (Schnetzler and Pinson, 1964b; Schnetzler and Pinson, 1965; Pinson et al, 1965). The range of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios within the individual tektite groups is even more limited. Eight out of nine moldavite analyses fall within a range of 0.0011, which is two standard deviations of a single analysis (Pinson et al, 1965). The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios of 11 "australasian" tektite range from 0.7162 to 0.7185 (Schnetzler and Pinson, 1964b) and would seem to cluster into two groups with means of 0.7172 and 0.7183. Four North American tektites possessed ratios from 0.7121 to 0.7130 (Schnetzler and Pinson, 1964b). The Ivory Coast tektites show the most variation in  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios; the two samples analyzed to date have ratios of 0.719 and 0.723 (Schnetzler and Pinson, 1965). The Ivory Coast tektites are unique in that a sympathetic variation apparently exists between the Rb/Sr and  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios, although only two specimens have to date been analyzed. Interestingly enough, this sympathetic variation indicates a "differentiation" age of about 2 billion years for the Ivory Coast tektites, and this is the dominant Rb-Sr age of rocks in that region of Africa (Bonhomme, 1962; Vachette, 1964). The  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios within the other three tektite groups do not vary

sympathetically with the Rb/Sr ratios. The moldavites, for example, have Rb/Sr ratios from 0.77 to 1.20 (Schnetzer, 1964, personal communication; this investigation) whereas the  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio is virtually constant. Schnetzer and Pinson (1964b), however, did find a sympathetic variation of the  $\text{Sr}^{87}/\text{Sr}^{86}$  and Rb/Sr ratios between the North American, South East Asian, and Czechoslovakian tektite groups. A common Rb-Sr age of about 400 m.y. was indicated for these three tektite groups. The Ivory Coast tektites fall far off the isochron (Schnetzer and Pinson, 1965). Taylor and Sachs (1964) have pointed out that the tektite isochron data show much scatter; this might be explained by selective volatilization, which is suggested by the variable Rb/Sr ratios in conjunction with a constant  $\text{Sr}^{87}/\text{Sr}^{86}$  ratio in the Czechoslovakian and South East Asian groups. The isotopic composition of Sr in tektites most probably reflects that of the parent material. Sr, being heavier than O, should be less subject to fractionation, although this might be affected by the site stability of radiogenic  $\text{Sr}^{87}$ .

The oxygen data indicated that granitic rocks were the only possible terrestrial material from which tektites could have originated. A cursory examination of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios given in the Annual Reports of the M.I.T. Geochronology Laboratory for granitic rocks indicated that less than 50%

of such rocks have ratios that fall within the tektite range. Granitic rocks cover about 15% of the land surface of the earth (Schnetzler, 1961, p.66). It is apparent that the probability of fusing terrestrial material, having the O and Sr isotopic compositions of tektites, in four random events, separated in time and space, is very low. The fact that three of the four tektite groups fall upon a Rb-Sr isochron, albeit with much scatter, further reduces the probability of terrestrial origin.

#### 5.5 Theory of origin

Tektites do not contain measurable amounts of radioactive, cosmogenic nuclides (Anders, 1960) and therefore they probably originated within the earth-moon system.

It is generally accepted that tektites have undergone a high-temperature thermal event. The evidence for this is as follows: 1. tektites have been fused; 2. the very low ferric to ferrous iron ratio of tektites indicates that temperatures of at least 1700°C were attained (Abou-El-Asm, 1954; Friedman et al., 1960); 3. some tektites contain stringers of very siliceous glass and these, presumably, were once highly fluid. The actual temperature reached by the tektite material was probably considerably in excess of the lower limit suggested by the above data because evidence

indicates that tektites were only briefly at high temperature and were cooled rapidly. This is indicated by their being glass and by the coexistence of glasses of various compositions, including lechatelierite, within individual tektites. Barnes (1960) was able to dissolve lechatelierite inclusions in their matrix glasses by relatively brief reheatings of tektites to moderate temperatures. The lack of homogeneity in tektite glass implies very limited diffusion and hence rapid quenching. It is therefore concluded, as it has been by other authors (eg. Chao, 1963), that tektite material was briefly heated to high temperatures and quickly cooled.

Proposed causes of such a thermal event within the earth-moon system include lightning (Barnes, 1940; Hawkins, 1960), volcanic explosion (Verbeek, 1897), and meteorite or comet impact (Spencer, 1933; Nininger, 1943; Urey, 1957; Cohen, 1961). Tektites are almost certainly not fulgurites. Theories of volcanic origin must account for the disequilibrium glass assemblages. Variations in the chemical composition of the matrix glass within and between tektites might be accounted for by selective volatilization of constituents during the thermal event. However, the occurrence of lechatelierite inclusions poses a strong argument against tektites being volcanic ejecta. The possibility that tektites were produced by terrestrial volcanism is further ruled out by the low ferric to ferrous iron ratio, the low water content,

and the aerodynamic ablation evidence. With the discovery of Ni-Fe spherules in some tektites (Spencer, 1933; Chao, et al., 1962, 1964), it has become widely accepted that tektites originated in meteorite impacts. The Ni content of these spherules, however, is lower than that of meteoritic iron. In addition, Taylor (1962) has criticized the meteorite impact theory on the basis of the Ni content of tektites. The comet impact theory is free from this objection, although the efficacy of this process has yet to be demonstrated.

Aerodynamic ablation studies and trajectory calculations are highly relevant to any discussion of the origin of tektites. Chapman and Larson (1963) were able to produce ablation forms in an electric-arc-jet-tunnel that were identical to the natural australite buttons. On the basis of the aerodynamic ablation features of australite buttons, Chapman and Larson were able to calculate the angle of entry into the earth's atmosphere, the entry velocity and other flight characteristics of these australites. Other South East Asian tektites (Chapman, 1964), a bediasite (E. King, oral communication, 1964), and a moldavite (Chao, 1964), have been identified as spalled cores. Thus the conclusions reached for the flanged australites are probably valid for tektites from other groups. According to Chapman and Larson (1963), and Adams and Huffaker (1964), the aerodynamic ablation features exclude a terrestrial origin of tektites. Urey (1957), how-

ever, pointed out that if tektites came from the moon they would be expected to occur over the entire surface of the earth rather than in restricted strewn fields. Varsavsky (1958) showed that it was possible for material ejected from an impact crater on the moon to arrive at a localized region on the earth. Hawkins (1963), however, noted that this computation was invalid because the rotation of the earth was neglected. A more sophisticated treatment of possible lunar trajectories has recently been presented (Chapman, 1964). The suggestion of a skipping parent-body (O'Keefe, 1963; Adams and Huffaker, 1964) neatly explains the restricted strewn fields.

Tektites are remarkably similar in chemical composition to the crustal average of the earth (Taylor and Sachs, 1964). Yet there is a very low probability of fusing terrestrial material, having the O and Sr isotopic compositions of tektites, in four random events (Section 5.4). In addition, if tektites were terrestrial, one might expect to find material intermediate in composition between tektites and their most probable parent, namely granite; this is not the case. O'Keefe (1964) has recently criticized the theory of the terrestrial origin of tektites on the basis of their water content; O'Keefe suggested that sufficient loss of water from terrestrial materials by bubble transfer, diffusion, or volatilization followed by



condensation, is improbable in the tektite formation process. The petrographic characteristics of tektites also do not support a terrestrial origin. Fusion of material by meteorite or comet impact would likely produce peripheral material that was only partially fused. Such material has not been discovered in association with true tektites. The petrographic and chemical differences between tektites and impactites have been discussed by Chao (1963). Taylor and Epstein (1963) found an  $O\Delta$  value of 7.9% for suevite from the Ries crater and this is distinctly different from the  $\Delta$  values of moldavites. Other impactites have oxygen with  $\Delta$  values ranging up to 14.4. Not only do tektites not contain crystalline inclusions, but there is no indication in tektites of the prior existence of discrete phases other than those consisting of pure  $SiO_2$ . The parent material of tektites might, therefore, possibly have consisted of an aphanitic or hyaline matrix containing phenocrysts of a  $SiO_2$  phase.

Perhaps the strongest evidence in support of a terrestrial origin of tektites is the similarity in K-A ages of tektites and nearby impact craters. Thus the moldavites have the same K-A age, within the experimental error, as the Nordlingen Ries crater (Zahringer, 1963), which is about 300 km west of the strewn field. Similarly, the Ivory Coast tektites have the same K-A age as the Bosumtwi crater ((Gentner et al., 1964) which is about 275 km east of the

strewn field. O'Keefe (1963) has questioned the proposal that the moldavites and the Ries crater have identical ages on the basis of stratigraphic relations. Other authors (eg. Cohen, 1963), however, have thought that the K-A data indicated that the moldavites and the Ivory Coast tektites, respectively, were blasted out of the Ries crater and out of the Bosumtwi crater. The diverse rock-types found rimming the Ries crater (Shoemaker and Chao, 1961) are thought to be unsuitable parents, chemically and isotopically, for the moldavites. The correspondence of K-A ages might be fortuitous. Perhaps a better explanation would be that the crater was formed by the impact of the tektite parent-body or by impact of a large "tektite" which accompanied the tektite swarm. Such an origin might best explain the alignment of the moldavite strewn field with the Ries crater.

In the case of the Ivory Coast tektites, however, there is ancillary evidence to support a theory of terrestrial origin. Not only do the Ivory Coast tektites have the same K-A age as the Bosumtwi crater, but they also have the same Rb-Sr age (based on two samples) as the rocks in that part of Africa (Section 5.4). The Ivory Coast tektites are somewhat unique. They are the only group that apparently shows a sympathetic variation of Rb/Sr with  $\text{Sr}^{87}/\text{Sr}^{86}$  amongst samples. They fall far off the Rb-Sr isochron based upon the other three geographic groups. The lowest  $\text{SiO}_2$  content,

the highest FeO content, and the lowest K<sub>2</sub>O content for tektites have been reported for Ivory Coast samples. In addition, the only tektites that have more Na<sub>2</sub>O than K<sub>2</sub>O have come from the Ivory Coast. In view of the similarity in chemical composition and physical properties of all tektites, the aforementioned features of the Ivory Coast tektites may have little significance. On the other hand these features could indicate that the Ivory Coast tektites originated by a different process, either in degree or kind, than those that produced the other tektites.

A consideration of the available data leads the author to conclude that tektites most probably originated by meteorite or comet impact in very acid, extrusive igneous rocks on the surface of the moon. If further analyses substantiate the 2 b.y. isochron for the Ivory Coast tektites, this will constitute persuasive evidence, in conjunction with the K-A data, for the terrestrial origin of this group. If tektites are terrestrial it is surprising that there is so much evidence that suggests otherwise. Perhaps some fundamental point has so far been overlooked in considerations of the origin of tektites. It is possible that the impending exploration of the moon will result in as many objections to theories of lunar origin as now exist for theories of terrestrial origin.

## CHAPTER 6

## SUMMARY

New analyses for nine major elements and for the trace elements Rb and Sr in 17 Bohemian and 6 Moravian moldavites have been reported. The refractive indexes and bulk specific gravities of the 23 moldavites have also been reported. Real variations in chemical composition and physical properties were found. A preliminary electron microprobe study indicated that variations in chemical composition, comparable to those between tektites, occur over distances of  $50\mu$  or more within individual tektites. The range of refractive indexes found within individual moldavites supports this conclusion.

The Moravian tektites that were analyzed have higher average contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , FeO and  $\text{Na}_2\text{O}$ , and lower average contents of MgO, CaO and Sr than do the Bohemian tektites. The major distinction between samples from the two strewn fields is that Moravian tektites have high and variable FeO and  $\text{TiO}_2$  contents with low and constant MgO, CaO and Sr, whereas Bohemian tektites have high and variable alkaline earth contents, with low and constant FeO and  $\text{TiO}_2$ . The overall similarity between tektites from the two groups suggests that a common origin is highly probable. No clear regional trends in composition within the strewn fields were found.

The alkali element contents of moldavites show signi-

## CHAPTER 6

## SUMMARY

New analyses for nine major elements and for the trace elements Rb and Sr in 17 Bohemian and 6 Moravian moldavites have been reported. The refractive indexes and bulk specific gravities of the 23 moldavites have also been reported. Real variations in chemical composition and physical properties were found. A preliminary electron microprobe study indicated that variations in chemical composition, comparable to those between tektites, occur over distances of  $50\mu$  or more within individual tektites. The range of refractive indexes found within individual moldavites supports this conclusion.

The Moravian tektites that were analyzed have higher average contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , FeO and  $\text{Na}_2\text{O}$ , and lower average contents of MgO, CaO and Sr than do the Bohemian tektites. The major distinction between samples from the two strewn fields is that Moravian tektites have high and variable FeO and  $\text{TiO}_2$  contents with low and constant MgO, CaO and Sr, whereas Bohemian tektites have high and variable alkaline earth contents, with low and constant FeO and  $\text{TiO}_2$ . The overall similarity between tektites from the two groups suggests that a common origin is highly probable. No clear regional trends in composition within the strewn fields were found.

The alkali element contents of moldavites show signi-

ficant positive correlations amongst themselves, as do the alkaline earths. Sodium and rubidium are inversely correlated with the alkaline earths.  $\text{SiO}_2$  shows good negative correlations with the alkaline earths, with  $\text{Al}_2\text{O}_3$  and with specific gravity.  $\text{FeO}$  shows significant positive correlations with  $\text{TiO}_2$  and with  $\text{Na}_2\text{O}$ .

It was concluded that the variations in chemical composition within and between individual moldavites are best explained in terms of selective volatilization that occurred during the brief thermal event dated by the K-A age. The wide range of Rb/Sr ratios and the uniformity of the Sr isotopic composition support this conclusion. The variations in chemical composition were re-examined using the Rb/Sr ratio as an index of the extent of the selective volatilization process. It was concluded that the parent material of the moldavites was probably of uniform composition throughout, and an estimate of this composition was given. It was suggested that selective volatilization may have been an important factor in the origin of other tektite groups.

It was concluded on the basis of chemical, isotopic, petrographic, and aerodynamic considerations that tektites are probably not of terrestrial origin, although preliminary Rb-Sr data on Ivory Coast tektites (Schnetzler and Pinson, 1965) suggest otherwise. It was suggested that craters, with K-A ages identical with those of nearby tektites, might have

been produced by impacts of the tektite parent-bodies. It was also suggested that the parent material of tektites might have consisted of an aphenitic or hyaline matrix enclosing phenocrysts of a crystalline  $\text{SiO}_2$  phase. It was concluded that tektites probably originated by meteorite impact in very acid, extrusive igneous rocks on the surface of the moon. If tektites are terrestrial, some fundamental point would seem to have been overlooked.

Further investigations that might lead to a solution of the tektite problem include: a. electron microprobe studies of variations in chemical composition within individual tektites, b. controlled experimental studies of selective volatilization, c. detailed investigations of impactites, and, d. a study of the chemical compositions of a representative number of Ivory Coast tektites.

## APPENDIX

Analyses of glass standards 191 AIK and 191 ALA

Analyses of Corning glass standards 191 AIK and 191 ALA were performed with the tektite analyses. These two standards are as yet not suitable for use as analytical monitors because the concentrations of the various chemical constituents are not well known. A comparison of the determined values for the various constituents with the given values is presented below.

	<u>191 AIK</u>		<u>191 ALA</u>	
	<u>Given</u>	<u>Determined</u>	<u>Given</u>	<u>Determined</u>
Fe <sub>2</sub> O <sub>3</sub>	0.55	0.9	0.5	0.7
FeO	4.34	4.3	4.4	4.2
CaO	2.99	2.9	2.7	2.6
MgO	1.62	1.5	1.8	1.6
Na <sub>2</sub> O	1.02	1.2	1.2	1.2
K <sub>2</sub> O	1.89	2.0	2.0	2.0
TiO <sub>2</sub>	0.49	0.8	0.5	0.5



## ACKNOWLEDGEMENTS

This research was sponsored by the N.A.S.A. Research Grant No. Nsg222-61. The mass spectrometric analyses were financed by the U.S. Atomic Energy Commission under Contract AT(30-1)-1381, which is under the supervision of Professor P. M. Hurley. The x-ray fluorescence analyses for rubidium and strontium were performed on equipment granted to M.I.T. by a National Science Foundation grant, under the supervision of Professor H. W. Fairbairn. Preliminary major element x-ray fluorescence analyses were performed at Harvard University under the supervision of Professor Clifford Frondel and Mrs. Frondel. X-ray fluorescence analyses for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were performed in the Geochemistry Laboratory, Goddard Space Flight Centre, N.A.S.A., Greenbelt, Md. The electron microprobe analyses were performed by Cornelius Klein at Harvard and by Frank Wood at the Goddard Space Flight Centre. To the above individuals and organizations the author expresses his appreciation.

The author acknowledges the assistance given by many of the staff and students in the Department of Geology and Geophysics at M.I.T., the members of the Geochemistry Laboratory at the Goddard Space Flight Centre, and Dr. George Beall of Corning Glass. He takes particular pleasure in acknowledging the guidance and stimulation readily given by his thesis director, Professor W. H. Pinson. Special thanks also go to

Dr. Charles Schnetzler of the Goddard Space Flight Centre, for first introducing the author to the subject of tektites and for his continued interest.

Finally the author is indebted to his parents for insisting that he obtain an education, and to his wife, for the use of her nylons in sieving samples, for the use of her hair in the specific gravity determinations, for typing this thesis, and for helping him through a difficult period.

## REFERENCES

- Abou-El-Azm A. (1954) Spectrophotometric and magnetic studies of glasses containing iron, in relation to their structure - III. J. Soc. Glass Tech. 38, 197 - 243.
- Adams E. W. and Huffaker R. M. (1964) Aerodynamic analysis of the tektite problem. Geochim. et Cosmochim. Acta 28, 881 - 892.
- Ahrens L. H. (1957) A survey of the quality of some of the principal abundance data of geochemistry. Physics and Chemistry of the Earth 2, 30, Pergamon Press.
- Ahrens L. H. and Taylor S. R. (1961) Spectrochemical Analysis, Addison - Wesley, Reading, Mass.
- Anders E. (1960) On the presence of aluminum 26 in meteorites and tektites. Geochim. et Cosmochim. Acta 19, 53 - 62.
- Baker G. and Forster H. C. (1943) The specific gravity relationships of australites. Amer. J. Sci. 241, 377 - 406.
- Baker G. (1959) Tektites. Mem. Nat. Mus. Vict. 23, 1 - 313.
- Baker G. (1961) Einige Erscheinungen des Atzverhaltens der Australite. Chem. Erde. 21, 101 - 117.
- Baker G. (1963) Form and sculpture of tektites. Tektites (Ed. J. O'Keefe) Chapter 1, 1 - 24, Univ. of Chicago Press, Chicago.
- Barnes V. E. (1940) North American Tektites. Univ. Texas Publ. 3945, 477 - 582.
- Barnes V. E. (1958) Properties of tektites pertinent to their origin. Geochim. et Cosmochim. Acta 14, 267 - 278.
- Barnes V. E. (1960) Significance of inhomogeneity in tektites. Proc. 21st Internat. Geol Congr. 13, 328 - 338.
- Bonhomme M. (1962) Contribution a L'etude géochronologique de la plate-forme de l'ouest Africain. Annales de la Faculté des Sciences de l'Université de Clermont.
- Bouška V. and Povondra P. (1964) Correlation of some physical and chemical properties of moldavites. Geochim. et Cosmochim. Acta 28, 783 - 791.

- Chao E. C. T., Adler I., Dwornik E. J. and Littler, Janet (1962) Metallic spherules in tektites from Isabela, the Philippine Islands. Science 135, 97 - 98.
- Chao E. C. T. (1963) The petrographic and chemical characteristics of tektites. Tektites (Ed. J. O'Keefe) Chapter 3, 51 - 94, Univ. of Chicago Press, Chicago.
- Chao E. C. T., Dwornik E. J. and Littler, Janet (1964) New data on the nickel-iron spherules from Southeast Asian tektites and their implications. Geochim. et Cosmochim. Acta 28, 971 - 980.
- Chao E. C. T. (1964) Spalled, aerodynamically modified moldavite from Slavice, Moravia, Czechoslovakia. Science 146 790 - 791.
- Chapman D. R. and Larson H. K. (1963) On the lunar origin of tektites. J. of Geophys. Res. 68, 4305 - 4358.
- Chapman D. R., Larson H. K. and Scheiber L. C. (1964) Population polygons of tektite specific gravity for various localities in Australia. Geochim. et Cosmochim. Acta 28, 821 - 839.
- Chapman D. R. (1964) On the unity and origin of Australasian tektites. Geochim. et Cosmochim. Acta 28, 841 - 880.
- Cherry R. D. and Taylor S. R. (1961) Studies of tektite composition - II. Derivation from a quartz - shale mixture. Geochim. et Cosmochim. Acta 22, 164 - 168.
- Chodos A. A. and Engel C. G. (1961) Fluorescent x-ray spectrographic analyses of amphibolite rocks. Amer. Min. 46, 120 - 133.
- Claisse F. (1956) Accurate x-ray fluorescence analysis without internal standard. Province of Quebec Dept. of Mines Publ. Rept. 327.
- Cohen A. J. (1958) The absorption spectra of tektites and other natural glasses. Geochim. et Cosmochim. Acta 14, 279 - 286.
- Cohen A. J. (1960) Germanium content of tektites and other natural glasses. Implications concerning the origin of tektites. Proc. 21st Internat. Geol. Congr. 1, 30 - 39.
- Cohen A. J. (1961) A semi-quantitative asteroid impact hypothesis of tektite origin. J. Geophys. Res. 66, 2521.

- Cohen A. J. (1963) Asteroid - or comet - impact hypothesis of tektite origin: the moldavite strewn fields. Tektites (Ed. J. O'Keefe) Chapter 9, 189 - 211, Univ. of Chicago Press, Chicago.
- Fairbairn H. W. (1953) Precision and accuracy of chemical analysis of silicate rocks. Geochim. et Cosmochim. Acta 4, 143 - 156.
- Faul H. and Bouška V. (1963) Statistical study of moldavites. Oral presentation at 2nd Internat. Symp. on Tektites. Pittsburgh, Pennsylvania.
- Fenner C. (1934) Australites. Part I: classification of the W. H. C. Shaw collection. Trans. Roy. Soc. S. Aust. 58, 62.
- Fleischer M. and Stevens R. E. (1962) Summary of new data on rock samples G-1 and W-1. Geochim. et Cosmochim. Acta 26, 525 - 543.
- Friedman I., Thorpe A. and Senftle F. E. (1960) Comparison of the chemical composition and magnetic properties of tektites and glasses formed by fusion of terrestrial rocks. Nature, Lond. 187, 1089 - 1092.
- Friedman I. (1963) The physical properties and gas content of tektites. Tektites (Ed. J. O'Keefe) Chapter 5, 130 - 136, Univ. of Chicago Press, Chicago.
- Gentner von W., Lippolt H. J. and Müller O. (1964) Das Kalium-Argon-Alters des Bosumtwi-Kraters in Ghana und die chemische Beschaffenheit seine Gläser. Z. Naturforschg. 19a, 150 - 153.
- Greenland L. and Lovering J. F. (1963) The evolution of tektites: elemental volatilization in tektites. Geochim. et Cosmochim. Acta 27, 249 - 259.
- Hanus F. (1928) O moldavitech čili vltavínech Čech a Moravy. Rozpr. České Akad. 37, 1 - 83.
- Hawkins G. S. (1960) Tektites and the earth. Nature 185, 300 - 301.
- Hawkins G. S. (1963) A study of tektites. J. Geophys. Res. 68, 895 - 910
- Ježek B. (1911) Dnešní stav otázky vltavínové. 41 výr. Zpráva Klubu Přírodovědeckého 14.

- Krinov E. L. (1958) Some considerations on tektites. Geochim. et Cosmochim. Acta 14, 259 - 266.
- Lovering J. F. (1960) High temperature fusion of possible parent materials for tektites. Nature, Lond. 186, 1028 - 1030.
- Lowman P. D. Jr. (1962a) The relation of tektites to lunar igneous activity. J. Geophys. Res. 67, 1646.
- Lowman P. D. Jr. (1962b) Tektites vs. terrestrial rocks: a comparison of variance in compositions. Geochim. et Cosmochim. Acta 26, 561 - 579.
- Mason B. (1959) Chemical composition of tektites. Nature 183, 254 - 255.
- Mercy E. L. P. (1956) The accuracy and precision of "rapid-methods" of silicate analysis. Geochim. et Cosmochim. Acta 9, 161 - 173.
- Merrill G. P. (1911) On the supposed origin of the moldavites and like sporadic glasses from various sources. Proc. U.S. Nat. Mus. 40, 481 - 486.
- Moroney M. J. (1956) Facts from Figures, Pelican, London.
- Němec F. (1933) Druhé sklo s povrchem vltavínovým z Třebíče. Cas. Příroda 26, 2.
- Nininger H. H. (1943) Tektites and the moon. Sky and Telescope 2.
- O'Keefe J. A. (1963) The origin of tektites. Tektites (Ed. J. O'Keefe) Chapter 8, 167 - 188, Univ. of Chicago Press, Chicago.
- O'Keefe J. A. (1964) Water in tektite glass. J. Geophys. Res. 69, 3701 - 3707.
- Oswald J. (1942) Meteorické Sklo. Praha: Nákladem České Akad. věd a Umění, 1 - 95.
- Pinson W. H. Jr., Schnetzler C. C., Philpotts J. A. and Fairbairn H. W. (1965) Rb-Sr correlation study of the moldavites. To be presented at annual meeting of Amer. Geophys. Un., Washington, D. C. (Abstract).
- Preuss E. (1935) Spektralanalytische Untersuchung der Tektite. Chemie der Erde B. 9, 365 - 416.
- Rose H. J. Jr., Adler I. and Flanagan F. J. (1963) X-ray fluorescence analysis of the light elements in rocks and minerals. Applied Spectroscopy 17, 81 - 85.

- Rost R. (1964) Surfaces of and inclusions in moldavites. Geochim. et Cosmochim. Acta 28, 931 - 936.
- Schnetzler C. C. (1961) The Composition and Origin of Tektites. Ph.D. thesis, Dept. of Geol. and Geophys. M.I.T., Cambridge, Mass.
- Schnetzler C. C. and Pinson W. H. Jr. (1963) The chemical composition of tektites. Tektites (Ed. J. O'Keefe) Chapter 4, 95 - 129, Univ. of Chicago Press, Chicago.
- Schnetzler C. C. and Pinson W. H. Jr. (1964a) Report of some recent major element analyses of tektites. Geochim. et Cosmochim. Acta 28, 793 - 806.
- Schnetzler C. C. and Pinson W. H. Jr. (1964b) Variation of strontium isotopes in tektites. Geochim. et Cosmochim. Acta 28, 953 - 969.
- Schnetzler C. C. and Pinson W. H. Jr. (1965) Rb-Sr age study of Ivory Coast tektites. To be presented at annual meeting of Amer. Geophys. Un. Washington, D.C. (Abstract)
- Schwarcz H. P. (1962) A possible origin of tektites by soil fusion at impact sites. Nature, Lond. 194, 8 - 10.
- Shapiro L. and Brannock W. W. (1956) Rapid analysis of silicate rocks. U.S.G.S. Bull 1036-C.
- Shapiro L. (1960) A spectrophotometric method for the determination of FeO in rocks. U.S.G.S. Prof. Paper 400B, 496 - 497.
- Shoemaker E. M. and Chao E. C. T. (1961) New evidence for the impact origin of the Ries Basin, Bavaria, Germany. J. Geophys. Res. 66, 3371 - 3378.
- Silverman S. R. (1951) The isotope geology of oxygen. Geochim. et Cosmochim. Acta 2, 26 - 42.
- Spencer L. J. (1933) Origin of tektites. Nature, Lond. 132, 571.
- Spencer L. J. (1939) Tektites and silica-glass. Miner. Mag. XXV, 425 - 440.
- Stair R. (1955) The spectral-transmissive properties of some of the tektites. Geochim. et Cosmochim. Acta 7, 43 - 50.
- Stevens R. E. and Niles W. W. (1960) Chemical Analyses of the granite and diabase. Pages 3 - 43 in U.S.G.S. Bull. 1113.

- Suess F. E. (1900) Die Herfunft der Moldavite and verwandter Glaser. Jb. Geol. Reichsanst. Bundesanst., Wien 50, 193 - 382.
- Taylor H. P. Jr. and Epstein S. (1962) Oxygen isotope studies on the origin of tektites. J. Geophys. Res. 67, 4485 - 4490.
- Taylor H. P. Jr. and Epstein S. (1963) Comparison of  $O^{18}/O^{16}$  ratios in tektites, soils, and impact glasses. Trans. Amer. Geophys. Un. 44, 93 (Abstracts).
- Taylor S. R. (1960) Abundance and distribution of alkali elements in australites. Geochim. et Cosmochim. Acta 20, 85 - 100.
- Taylor S. R. (1961) Distillation of alkali elements during formation of australite flanges. Nature, Lond. 189, 630 - 633.
- Taylor S. R., Sachs, Maureen and Cherry R. D. (1961) Studies of tektite composition - I. Inverse relationship between  $SiO_2$  and the other major constituents. Geochim. et Cosmochim. Acta 22, 155 - 163.
- Taylor S. R. (1962) The chemical composition of australites. Geochim. et Cosmochim. Acta 26, 685 - 722.
- Taylor S. R. and Sachs, Maureen (1964) Geochemical evidence for the origin of australites. Geochim. et Cosmochim. Acta 28, 235 - 264.
- Thorpe A. N. and Senftle F. E. (1964) Submicroscopic spherules and color of tektites. Geochim. et Cosmochim. Acta 28, 981 - 994.
- Tilley C. E. (1922) Density, refractivity and composition relations of some natural glasses. Miner. Mag. XIX, 275 - 294.
- Urey H. C. (1957) Origin of tektites. Nature, Lond. 179, 556 - 557.
- Urey H. C. (1958) Origin of tektites. Nature, Lond. 182, 1078.
- Vachette M. (1964) Nouvelles mesures d'âges absolus de granites d'age eburéen de la côte d'Ivoire. Comptes Rendus Acad. Sc. Paris, Groupe 9, t.258, 1569 - 1571.
- Varsavsky C. M. (1958) Dynamical limits on a lunar origin for tektites. Geochim. et Cosmochim. Acta 14, 291.



- Verbeek R. D. M. (1897) Glaskogels van Billiton Jarrb. Minjiv. Ned. -Ooost - Ind. 20, 235.
- Volborth A. (1963) X-ray spectrographic determination of all major oxides in igneous rocks and precision and accuracy of a direct pelletizing method. Nevada Bur. of Mines Rept. 6, 1 - 72.
- Walter L. S. and Carron M. K. (1964) Vapor pressure and vapor fractionation of silicate melts of tektite composition. Geochim. et Cosmochim. Acta 28, 937 - 951.
- Welday E. E., Baird A. K., McIntyre D. B. and Madlem K.W. (1964) Silicate sample preparation for light element analysis by x-ray spectrography. Amer. Min. 49, 889 - 903.
- Zahringer J. (1963) Isotopes in tektites. Tektites (Ed. J. O'Keefe) Chapter 6, 137 - 149, Univ. of Chicago Press, Chicago.

## BIOGRAPHY

The author was born on May 22, 1940, in Patchway, England. His early years were spent in Filton, Cheltenham, Oldhurst, and Llandough. The author first attended school at James Gillespie, Edinburgh. Following the war, he lived in Copenhagen, Denmark, for a year. His education was continued at XIV School, Bristol. In 1949, he emigrated to Canada with his family. He attended Ashbury College, Ottawa, for a year, and then continued his schooling at Lower Canada College, Montreal. He received his Junior Matriculation in 1955 and his Senior Matriculation a year later.

In 1956, the author entered McGill University in Montreal. He received the B.Sc. degree with Honours in Physics and Geology in 1959 and was awarded the Logan Gold Medal. He received the M.Sc. degree in Geology in 1961. He was awarded a staff scholarship, 1958-59, the Mobil Oil Scholarship, 1958-59, and the Quebec Department of Mines Scholarship, 1959-61. He instructed a laboratory course in General Geology from 1959 to 1961 and did library research for a course in Earth Physics, 1959-60. During the summers of 1957-61, the author was engaged in geological and geophysical field work in Canada, with the Quebec Department of Mines, the Geological Survey of Canada, and the Johns Manville Company.

The author entered the Massachusetts Institute of

Technology in 1961 as a candidate for the Ph.D. degree. He was teaching assistant in Petrography from 1961-63. He was awarded the Quebec Department of Mines Scholarship in 1961-62. He was a research assistant in geochemistry from 1963-65. During the summer of 1962 he was employed as a Science Counsellor at the Wesleyan Science Centre, Wesleyan University, Middletown, Connecticut.

In August, 1963, the author married Miss Reiko P. Tanaka of Montreal. In October, 1964, a daughter, Jamie Kyoko, was born. In April the author plans to join the Theoretical Division, Goddard Space Flight Centre, N.A.S.A., Greenbelt, Maryland, where he will continue research in the field of cosmochemistry.