

SUBJECT CATEGORIES FOR GODDARD JOURNAL

(To be used for classifying all NASA publications, journal articles, and other papers for inclusion in the Goddard Journal.)

Part A - Space Sciences

- A 1. Astronomy and Astrophysics
- A 2. Celestial Mechanics and Geodesy
- A 3. Solar Physics
- A 4. Ionosphere and Radio Physics
- A 5. Fields and Particles
- A 6. Planetology
- A 7. Planetary Atmospheres
- A 8. General (subjects not clearly belonging in any of categories 1-7)

Part B - Space Technology

- B 1. Projects and Programs
- B 2. Space Dynamics and Control Systems
- B 3. Spacecraft and Subsystems
- B 4. Vehicle Technology
- B 5. Sounding Rockets
- B 6. Sensors
- B 7. General Electronics
- B 8. Environmental Testing
- B 9. Tracking Systems
- B 10. General (subjects not clearly belonging in any of categories 1-9)

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 2.00

Microfiche (MF) .50

FACILITY FORM 802

N66-22177

(ACCESSION NUMBER)

(THRU)

(PAGES)

(CODE)

(NASA CR OR TMX OR AD NUMBER)

(CATEGORY)

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, Massachusetts

Abstract:

22177

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: SiO_2 , 75.5 - 80.6; Al_2O_3 , 9.62 - 12.64; TiO_2 , 0.268 - 0.460; Fe_2O_3 , 0.12 - 0.31; FeO , 1.42 - 2.36; MgO , 1.13 - 2.50; CaO , 1.46 - 3.71; Na_2O , 0.31 - 0.67; K_2O , 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 densities and refractive index values range from 2.3312 to 2.3718 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 observed variations in composition are largely due to fractional volatilization. The wide range of Rb/Sr ratios in conjunction with the uniformity of the Sr isotopic composition supports this theory.

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

auth

Available to NIST only
[Redacted]

ACKNOWLEDGEMENTS

This research was sponsored by the NASA Research Grant No. Nsg 222-61. 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 SiO_2 and Al_2O_3 were performed in the Geochemistry Laboratory, Goddard Space Flight Center, NASA, Greenbelt, Maryland. 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. In general, tektites are recognizable as such by their chemical compositions. 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 and to discuss theories of origin of the moldavites in the light of this data. Seventeen moldavites from the Bohemian "strewn field" and six 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 indices and ~~specific~~ ^{densities} ~~gravities~~ of the 23 tektites were also determined.

Previous chemical analyses of moldavites have been reported by Barnes (1940), Schnetzler and Pinson (1963, 1964a, 1964b), and Bouska and Payondra (1964).

Further details concerning all aspects of this work have been given by Philpotts (1965).

ANALYTICAL TECHNIQUES

Refractive Index and Density Determinations

Refractive index values for the 23 moldavites were obtained on powders by the immersion oil method. Most powders gave a range of refractive indices 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 ± 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 gm/cm^3 . The precision and accuracy of the density 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, Na₂O, K₂O, TiO₂ and P₂O₅ were determined by the rapid silicate procedures of Shapiro and Brannock (1956) as 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_2O_5 were made because the method proved unreliable at the low concentrations found in the moldavite samples. For the same reason, determinations of MnO, H_2O and CO_2 were not undertaken.

X-ray Fluorescence

It was decided to determine SiO_2 and Al_2O_3 by X-ray fluorescence techniques because of the number of determinations required to obtain a reliable SiO_2 value, and because of the frequently anomalous Al_2O_3 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 (i.e. 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 $K K_{\alpha}$ radiation of each sample was rapidly scanned (1 degree per minute) from 40° to 42° , 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); the mean difference between the two sets of results was 0.04% K. It was next decided to analyze for Al_2O_3 . A tungsten target and a gypsum crystal were used. Unfortunately only a few samples could be run because of other demands upon the X-ray unit at the time.

The Al_2O_3 determinations were continued on a General Electric, vacuum, X-ray unit in the Geochemistry Laboratory at the Goddard Space Flight Center. 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 Al_2O_3 determinations. Three sets of 100 second counts were taken at a background setting and on the AlK_α peak. This corresponded to a total of about 7500 counts on the background and 75,000 counts on the AlK_α peak for each sample. Moldavites previously analyzed for Al_2O_3 spectrophotometrically were used as standards. 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 SiK_α peak. This corresponded to a total of about 3000 counts on each of the backgrounds and about 90,000 counts on the SiK_α 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 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 RbK_α peak, and the SrK_α 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).

Table 1

Analyses of G-1 and W-1

G-1	Accepted Value	\bar{x}	n	σ	W-1	Accepted Value	\bar{x}	n	σ
SiO ₂	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 ₂ O	3.32	3.31	6	0.04		2.07	2.13	6	0.07
K ₂ O	5.45	5.53	6	0.07		0.64	0.55	6	0.01
TiO ₂	0.26	0.24	6	0.007		1.07	1.08	6	0.008
FeO	0.98	0.98	9	0.01		8.74	8.52	6	0.11
Fe ₂ O ₃	0.87	0.85				1.41	1.46		

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

n is the number of weighings

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

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 accuracy of the X-ray fluorescence determinations of SiO_2 and Al_2O_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 Al_2O_3 in the four standard moldavites was less than 0.1% Al_2O_3 . The average difference between the spectrophotometric and the X-ray fluorescence values for SiO_2 in the five standards was 0.5% 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 Fe₂O₃ determinations are not independent. A conservative estimate of the overall precision ($C = \frac{\sigma}{x} (100)$) of the analyses is as follows:

SiO₂, ±1%; Al₂O₃, ±3%; TiO₂, ±3%; MgO, ±5%; CaO, ±4%; Na₂O, ±15%; K₂O, ±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~~^{density} 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, are given. The contents of Rb and Sr in parts per million, are also reported. The results of the P_2O_5 analyses are not given because these analyses proved to be of poor quality; the 15 samples analyzed for P_2O_5 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_2 , 75.5 - 80.6; Al_2O_3 , 9.62 - 12.64; TiO_2 , 0.268 - 0.460; Fe_2O_3 , 0.12 - 0.31; FeO, 1.42 - 2.36; MgO, 1.13 - 2.50; CaO, 1.46 - 3.71; Na_2O , 0.31 - 0.67; K_2O , 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; Bouska and Povondra, 1964) with the exception of one K_2O analysis and four Rb analyses. The K_2O analyses all fall in the upper region of the range reported in the literature. The ~~specific gravity~~^{density} and refractive index values of the 23 moldavites range from 2.3312 to 2.3718 gm/cm³ and from 1.486 to 1.495, respectively.

Table 2

Analytical Results

	T 5296a Lhenice	T 5296b Lhenice	T 5296c Lhenice	T 5296d Lhenice	T 5296e Lhenice	T 5296f Lhenice	T 5309 Lhenice	T 5310 Lhenice
SiO ₂	79.2	77.3	76.7	75.7*	78.4	75.5	79.6	78.5*
Al ₂ O ₃	10.93	10.89	11.28	11.04	10.76	11.12	10.73	10.54
TiO ₂	0.307	0.336	0.331	0.314	0.303	0.313	0.300	0.294
Fe ₂ O ₃	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
MnO	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 ₂ O	0.51	0.51	0.63	0.45	0.45	0.48	0.37	0.41
K ₂ O	3.64	3.74	3.71	3.44	3.66	3.68	3.48	3.62
Total	99.79	99.72	99.36	98.77	100.71	98.48	100.80	99.25
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
Rb/Sr	1.11	0.94	1.01	0.86	0.92	0.97	0.95	1.00
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)

	T 5311		T 5312		T 5313		T 5314		T 5315		T 5316		T 5317		T 5318	
	Dolní	Chrástany	Habri		Habri		Slavce		Vrabce		Vrabce		Kročlov		Koroseky	
SiO ₂	178.6		77.6	78.4	80.6*	77.0	79.55	77.1*	78.4							
Al ₂ O ₃	10.77		11.13	10.30	10.09	10.28	9.94	10.43	10.11							
TiO ₂	0.307		0.331	0.300	0.295	0.287	0.286	0.285	0.268							
Fe ₂ O ₃	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 ₂ O	0.42		0.51	0.45	0.45	0.35	0.50	0.31	0.38							
K ₂ 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							
Rb/Sr	1.03		0.96	0.97	1.12	0.88	1.07	0.82	0.92							
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 Nechov	T 5320 Slavice	T 5321 Kozichovice	T 5322 Slavetice	T 5323 Dukovany	T 5324 Dukovany	T 5325 Dukovany
SiO ₂	80.3	79.8	80.2	79.4*	78.8	76.7*	80.0
Al ₂ O ₃	9.62	11.04	11.02	11.24	10.99	12.64	11.43
TiO ₂	0.284	0.402	0.337	0.364	0.326	0.460	0.361
Fe ₂ O ₃	0.20	0.26	0.14	0.16	0.17	0.28	
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 ₂ O	0.42	0.60	0.53	0.53	0.39	0.67	0.58
K ₂ 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
Rb/Sr	1.13	1.10	1.02	1.04	0.83	1.20	1.11
R.I.	1.489	1.490	1.487	1.489	1.491	1.492	1.489
Sp. G.	2.3414	2.3474	2.3353	2.3588	2.3484	2.3609	2.3372

Table 2 continued

* spectrophotometric determination of 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.

Note: The weights and shapes of the samples, and the results of each duplicate analysis may be found elsewhere (Philpotts, 1965).

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: SiO_2 , $\pm 2\%$; Al_2O_3 , $\pm 4\%$; TiO_2 , $\pm 13\%$; total Fe as FeO, $\pm 13\%$; MgO, $\pm 23\%$; CaO, $\pm 29\%$; Na_2O , $\pm 19\%$; K_2O , $\pm 4\%$; 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 SiO_2 , Al_2O_3 , TiO_2 , FeO and Na_2O , and lower average contents of MgO, CaO, and Sr, than the Bohemian tektites. The ^{densities} ~~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 TiO_2 contents with low and relatively constant CaO, MgO, and Sr, whereas the Bohemian samples have high and variable alkaline earth contents with low and constant FeO and 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". Considerable differences in chemical composition were found between tektites from the same localities. This is not surprising in view of the facts that moldavites of all colours occur in most localities (Paul and Bouska, 1963), and that tektites from Habri 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 degree of significance are presented for various pairs of constituents. The alkalis show positive correlations amongst themselves, as do the alkaline earths. Na_2O and Rb are inversely correlated with the alkaline earths. SiO_2 shows negative correlations of various significances with the alkaline earths, Al_2O_3 , refractive index and ^{density} ~~specific gravity~~. FeO (actually total Fe as FeO) has significant positive correlations with TiO_2 and with Na_2O .

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 almost all constituents with SiO_2 , concluded that the australite parent material consisted of a mixture of 75% homogeneous shale and 25% quartz. Such a mixture is not suggested by the moldavite data because SiO_2 is not inversely correlated with the alkalis or with FeO. In fact, the nonlinear correlations of certain pairs of constituents (e.g. CaO-FeO, Figure 1; Na_2O -FeO) cannot be explained in terms of any two-phase mixing process,

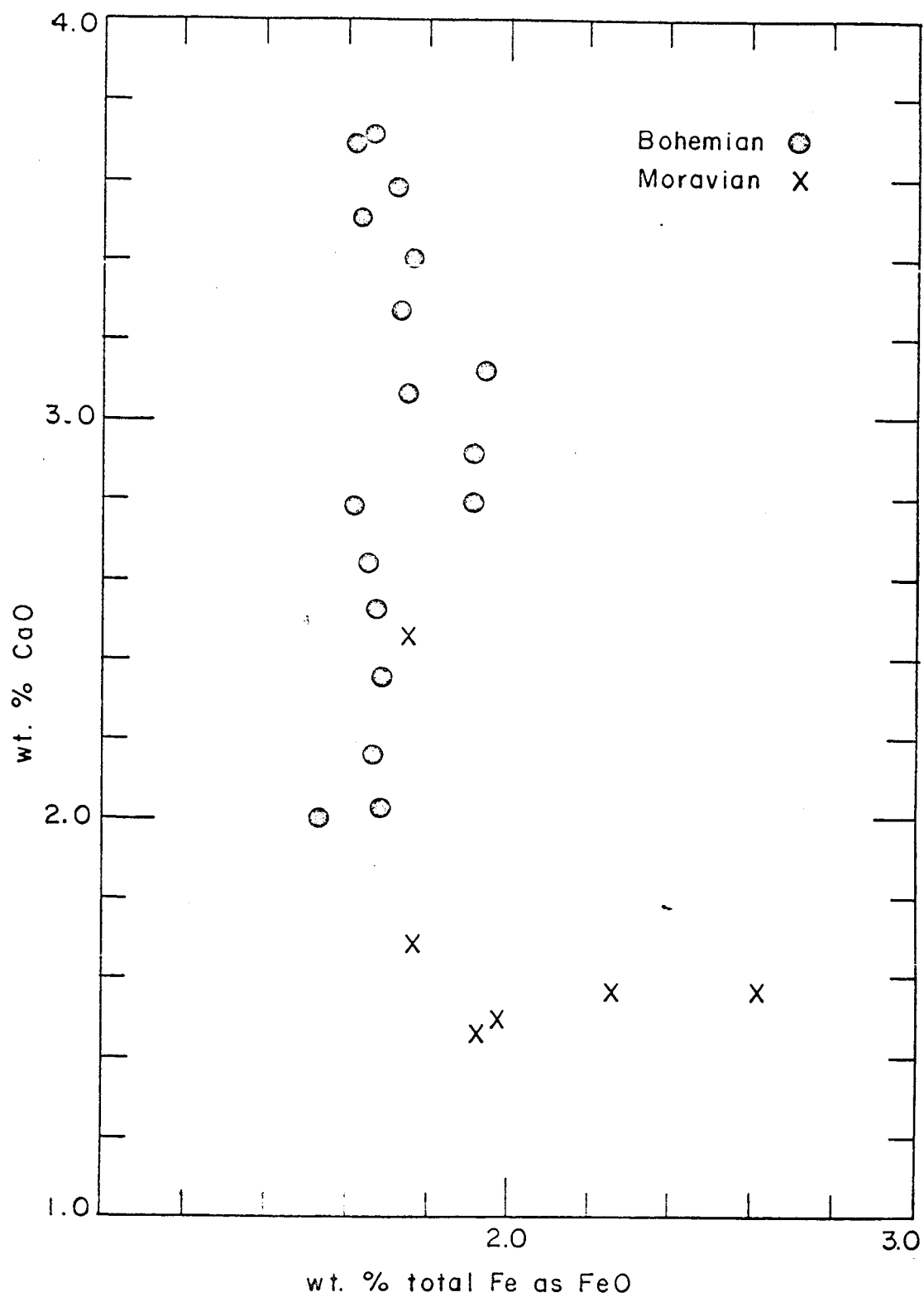


Fig. 1 CaO vs. FeO for 23 moldavites.

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 ₂ O-K ₂ O	+0.96	<1%	+0.63	<1%	+0.47	<5%
Na ₂ O-Rb	+0.99	<0.1	+0.61	<1	+0.73	<0.1
K ₂ 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 ₂ -Al ₂ O ₃	Not. sig.		-0.65	<1	-	- *
SiO ₂ -MgO	-0.93	<5"	-0.83	0.1	-0.88	<0.1 [^]
FeO ^x -TiO ₂	+0.99	<0.1	+0.85	<0.1	+0.96	<0.1
FeO ^x -Na ₂ O	+0.83	<5	+0.70	<1	+0.79	<0.1
Na ₂ O-MgO	-0.91	1	not sig.		-0.53	1
Na ₂ O-CaO	-0.83	<5	not sig.		0.64	<0.1
Rb-CaO	-0.83	<5	-0.73	<0.1	-	- *
Rb-Sr	-0.90	<5	-0.50	<1	-0.61	<1

* combined data not applicable

" n 5

^ n 22

x Total Fe as FeO

' n 16

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 extraterrestrial 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, some of the alkalis have positive correlations with SiO_2 , and iron is positively correlated with the alkaline earths and with Al_2O_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 SiO_2 phase. The presence of lechatelierite is of interest because melts of moldavite composition would presumably lie within the SiO_2 field and differentiation would occur by SiO_2 phase separation. Products of this SiO_2 subtraction would exhibit inverse correlations of all constituents with 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 μ 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 fractional volatilization. Many investigators (e.g. Cohen, 1960; Lovering, 1960; Lowman, 1962; Greenland and Lovering, 1962; Chao, 1963) have appealed to fractional volatilization in order to account for various features of the chemical compositions of tektites. Other evidence of extensive changes of composition by ^{fractional} selective volatilization is the apparent discrepancy between the U-Pb and Rb-Sr ages (Schnetzler and Pinson, 1964b).

Experimental data concerning ^{fractional} selective volatilization are meager. Experiments by Lovering (1960), Friedman et al (1960), and Walter and Carron (1964), and optical spectrographic studies (Ahrens and Taylor, 1961) on silicate materials have indicated the following order of volatility under most of the experimental conditions, from most to least volatile: Alkalies > Si, Fe > Al, alkaline earths. It therefore seems probably that ^{fractional} selective volatilization of tektite material would reduce the concentrations of alkalies 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 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 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). This situation cannot have long existed. Within the last 30 m.y. either Rb and Sr have been fractionated or Sr has been isotopically homogenized. It seems most probable that the change was effected during the thermal event dated by the K-A age. The parent material might have been homogeneous, chemically and isotopically, or homogenization could have occurred during the thermal event. The survival of the lechatelierite inclusions leads us to favor a homogeneous parent. In either case, the range of Rb/Sr ratios is best explained in terms of fractional volatilization.

It is assumed that the Rb/Sr ratio decreased with increasing temperature and duration of heating. Bohemian tektites with lower Rb/Sr ratios have lower SiO_2 , Na_2O , and Rb contents, and higher alkaline earth contents. Al_2O_3 , TiO_2 , FeO , and K_2O do not vary appreciably with decreasing Rb/Sr. Moravian tektites with lower Rb/Sr ratios have lower SiO_2 , 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 SiO_2 and higher Al_2O_3 than the other 5 Moravian samples. If the assumptions made concerning fractional volatilization are valid, then 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% K_2O and this indicates that Na_2O was more volatile than K_2O . 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: Na_2O , Rb, K_2O , SiO_2 , Al_2O_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 (Fig. 1, Fig. 4).

It is difficult to account for the relationships among the chemical constituents of moldavites by means other than fractional volatilization. This process might have masked preexisting variations. The authors feel, however, that such initial variations would involve the addition

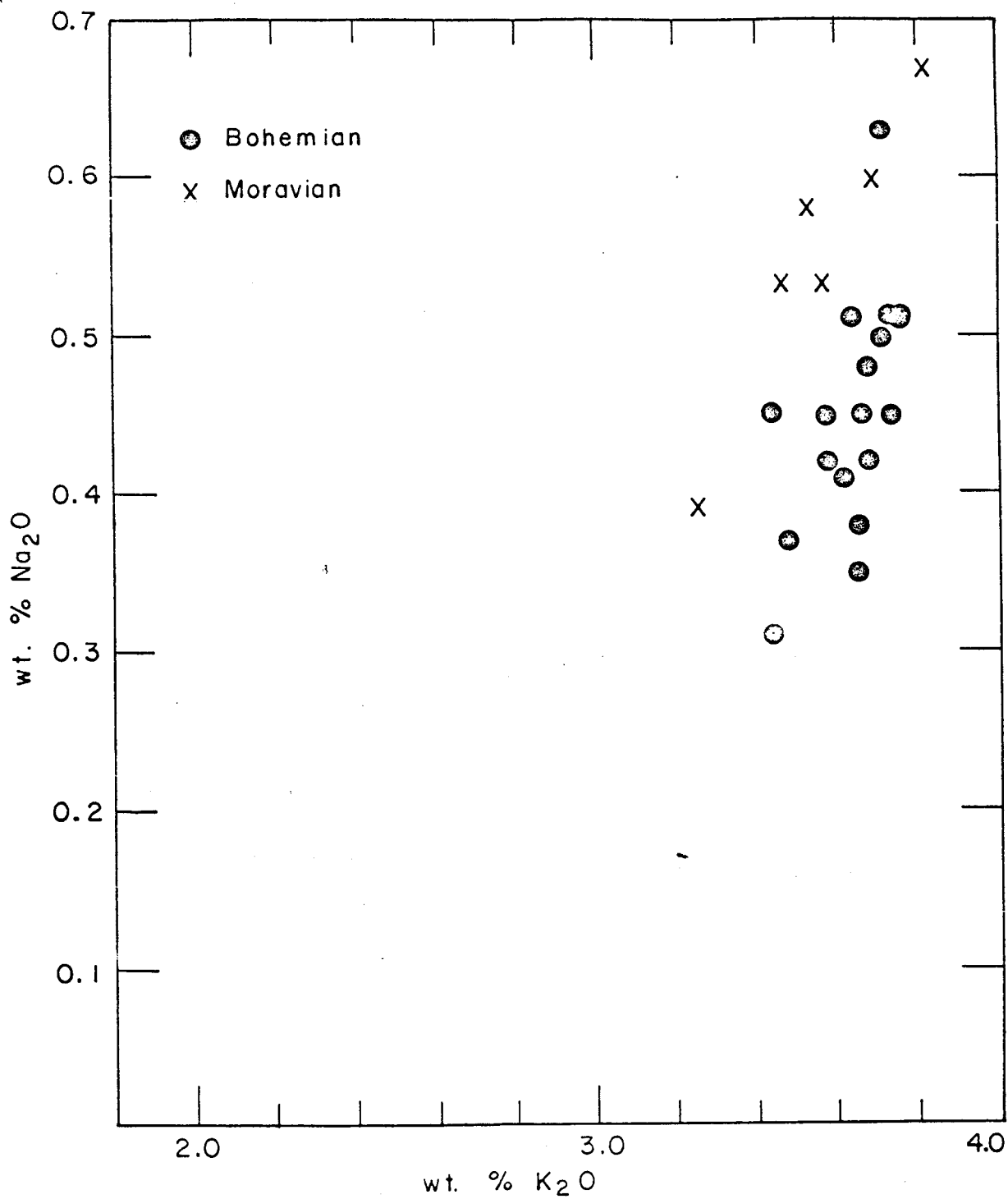


Fig. 2 Na_2O vs. K_2O for 23 moldavites

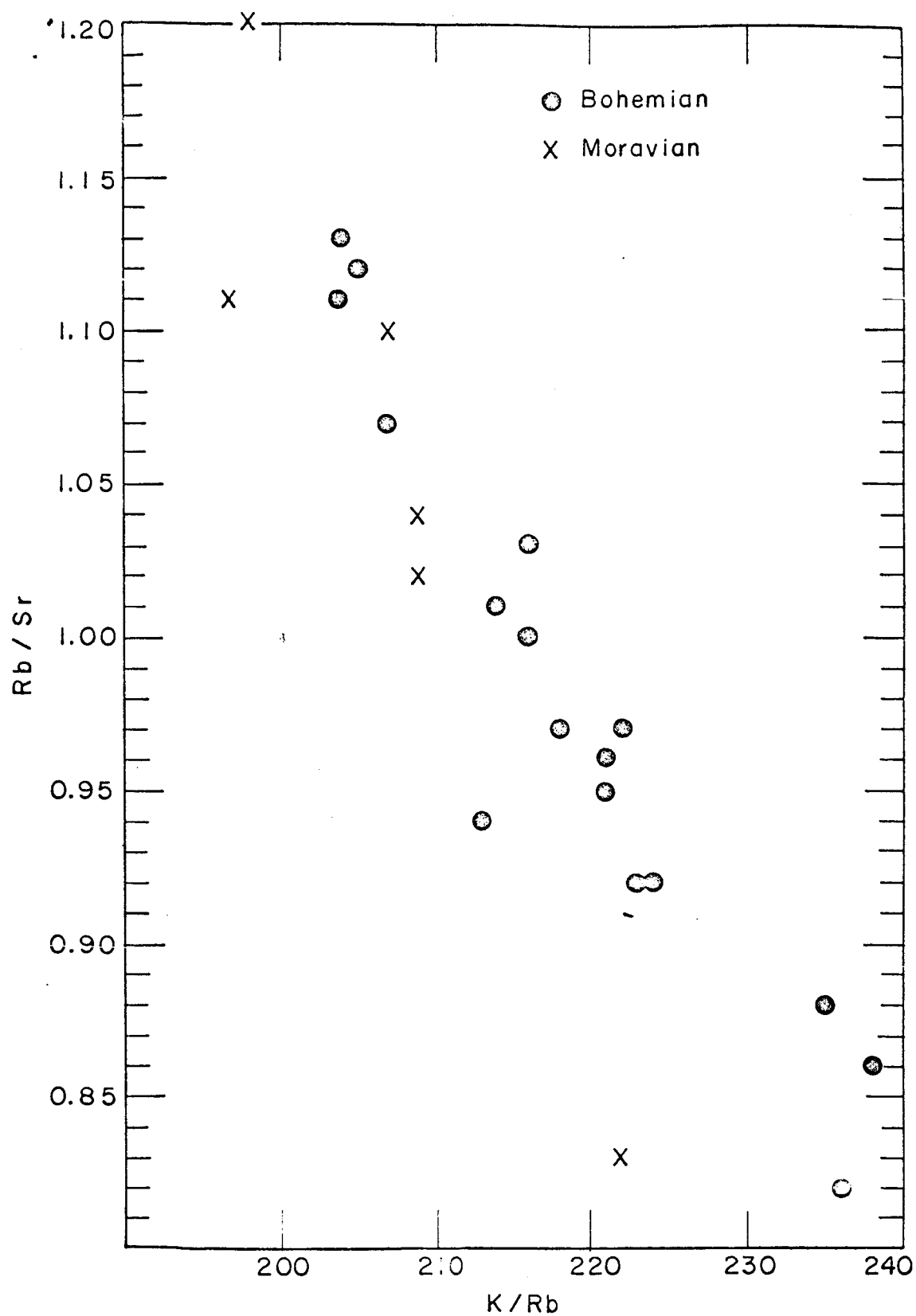


Fig. 3 Rb/Sr vs. K/Rb for 23 moldavites

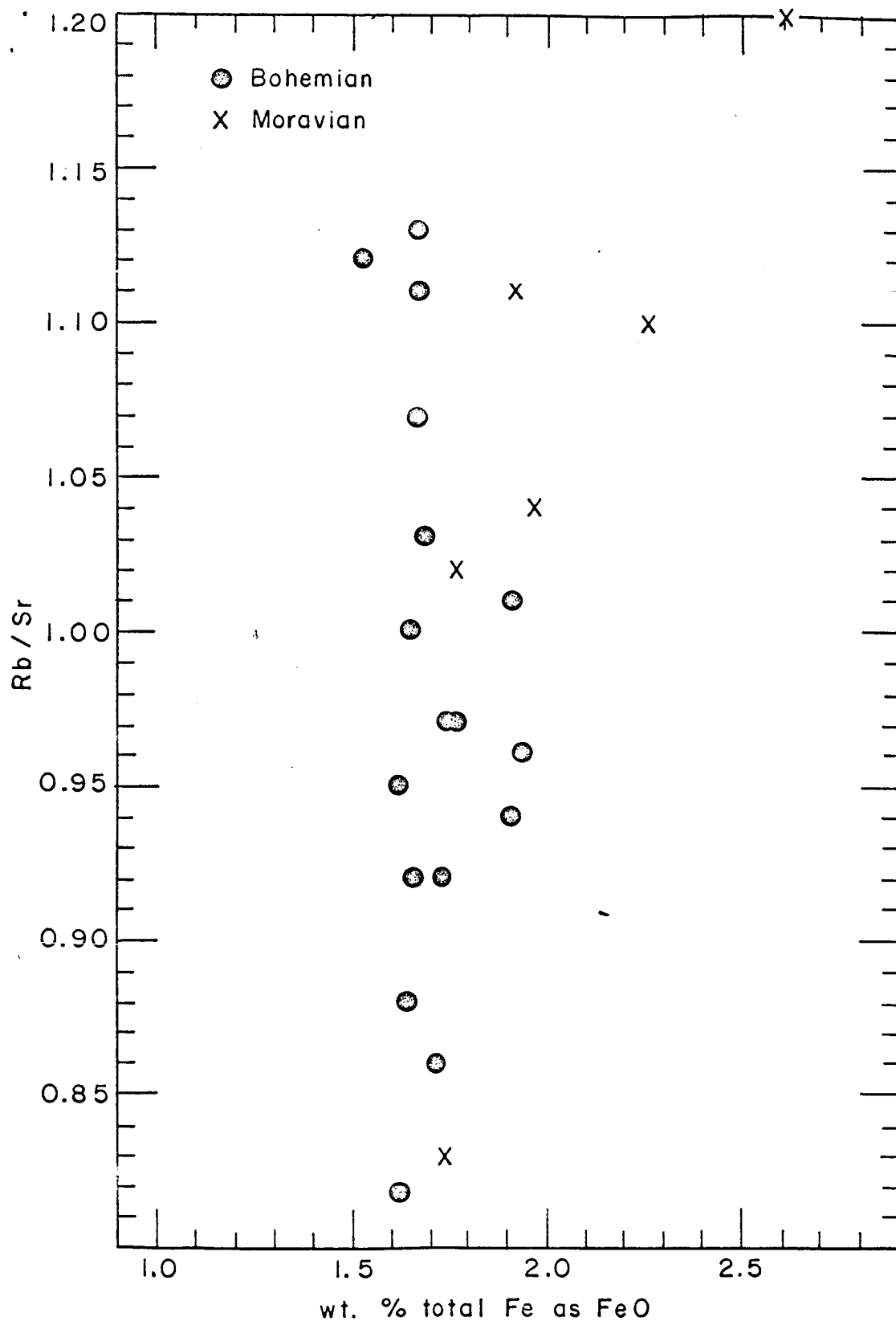


FIG. 4 Rb/Sr vs. FeO for 23 moldavites.

or subtraction of SiO_2 . The inverse correlations of the alkalis and alkaline earths in moldavites suggests that variations of 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 glassy matrix containing a few phenocrysts of a pure SiO_2 phase. Differences between the Bohemian and the Moravian tektites probably reflect different histories during the thermal event.

Fractional volatilization may have affected the compositions of tektites from other geographical groups. A brief discussion of possible volatilization effects in australites has been presented elsewhere (Philpotts and Pinson, 1965).

Four major tektite groups are generally recognized, namely North American, Czechoslovakian, Ivory Coast, and South East Asian. The probability of fusing terrestrial material that is similar to tektites in chemical composition, oxygen isotopic composition (Taylor and Epstein, 1962, 1963) and strontium isotopic composition (Schnetzler and Pinson, 1964b, 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 of the same age it could be fortuitous but this is unlikely in view of the similarity of ages of other tektite groups and various impactites (Fleischer, et al, 1965). 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 (Gentner et al, 1964), but they would also seem to have the same Rb-Sr age as rocks in that part of Africa (Schnetzer et al, 1965).

The interpretation of the moldavite data in terms of fractional volatilization throws no further light on the problem of terrestrial or lunar origin of tektites, although it does necessitate some modification in the explanation of the Rb-Sr ages of tektites. The oxygen isotope data indicate that acid igneous rocks are the only possible terrestrial parent-material for tektites (Taylor and Epstein, 1962, 1963). Such rocks, however, do not have contents of the rare earths similar to those possessed by tektites (Haskin and Gehl, 1963). This might be construed as evidence of the extra-terrestrial origin of tektites. However, the overall similarity in chemical composition, including the rare earths, of tektites and the "crustal average" indicates terrestrial

origin (Taylor and Sachs, 1964). In view of the conflicting evidence, however, it would seem that if tektites are of terrestrial origin then some fundamental point would so far seem to have been overlooked.

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 indices and bulk ^{densities} ~~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 SiO_2 , Al_2O_3 , TiO_2 , FeO and Na_2O , 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 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 TiO_2 . The overall similarity between tektites from the two groups suggests that a common origin is highly probably. 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 fractional 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 fractional volatilization process. The data indicate the following order of volatility from most to least volatile: Na_2O , Rb, K_2O , SiO_2 , Al_2O_3 , Sr, MgO and CaO.

The efficacy of the proposed fractional volatilization process might be demonstrated if (1) the occurrence of coesite (Walter, 1965) or the diffusion gradient around lechatelierite inclusions or any other indicator of thermal history could be related to bulk composition of tektites, (2) U-Pb or Rb-Sr ages of tektites from a specific geographic group were found to be the same as the K-A or fission track ages, or (3) the observed variations in chemical composition were duplicated by experimental volatilization studies.

It is concluded that if tektites are of terrestrial origin then some fundamental point would so far seem to have been overlooked.

REFERENCES

- Adams, E. W. and Huffaker, R. M. (1964) Aerodynamic analysis of the tektite problem. Geochim. et Cosmochim. Acta 28, 881-892.
- Ahrens, I. 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.
- Bouska, 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 Bouska, 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.
- Fleischer, R. L., Price, P. B. and Walker, R. M. (1965) On the simultaneous origin of tektites and other natural glasses. Geochim. et Cosmochim. Acta 29, 161-166.

- 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 Glaser. 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.
- Haskin, Larry and Gehl, Mary A. (1963) Rare-earth elements in tektites. Science 139 (3560), 1056-1058.
- 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.
- Philpotts, J. A. (1965) The chemical composition and origin of moldavites. Ph.D. Thesis, Dept. of Geol. and Geophys., M.I.T., Cambridge, Mass.
- Philpotts, J. A. and Pinson, W. H. Jr. (1965) Origin of australites. Submitted to Geochim. et Cosmochim. Acta.
- Pinson, W. H. Jr., Philpotts, J. A. and Schnetzler, C. C. (1965) K/Rb ratios in tektites, 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, Trans. Amer. Geophys. Un. 46, 118. (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., Pinson, W. H. Jr. and Fairbairn, H. W. (1965) Rb-Sr analyses of two Ivory Coast tektites, Trans. Amer. Geophys. Un. 46, 118 (Abstract).
- Shapiro, L. (1960) A spectrophotometric method for the determination of FeO in rocks. U.S.G.S. Prof. Paper 400B, 496-497.
- Shapiro, L. and Brannock, W. W. (1956) Rapid analysis of silicate rocks. U.S.G.S. Bull. 1036-C.
- 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 O^{18}/O^{16} 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. (1962) The chemical composition of australites, Geochim. et Cosmochim. Acta 26, 685-722.
- 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. 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. (1965) Coesite discovered in tektites, Science 147 (3661), 1029-1032.
- Walter, L. S. and Carron, M. K. (1964) Vapor pressure and vapor fractionation of silicate melts of tektite composition. Geochim. et Cosmochim. Acta 28, 927-951

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.