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 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)
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:

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: SiO₂, 75.5 - 80.6; Al₂O₃, 9.62 - 12.64; TiO₂, 0.258 - 0.460; Fe₂O₃, 0.12 - 0.31; FeO, 1.42 - 2.36; MgO, 1.13 - 2.50; CaO, 1.46 - 3.71; Na₂O, 0.31 - 0.67; K₂O, 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/cm³ 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.
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)-1331, 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$_2$O$_3$ 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 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 ±0.001 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$_2$O, K$_2$O, TiO$_2$ and P$_2$O$_5$ 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_α
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$_2$O$_3$. 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$_2$O$_3$ 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$_2$O$_3$ determinations. Three sets of 100 second counts were taken at a background setting and on the AlK$_\alpha$ peak. This corresponded to a total of about 7500 counts on the background and 75,000 counts on the AlK$_\alpha$ peak for each sample. Moldavites previously analyzed for Al$_2$O$_3$ 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$_\alpha$ peak. This corresponded to a total of about 3000 counts on each of the backgrounds and about 90,000 counts on the 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 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$_\alpha$ peak, and the 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).
Table 1
Analyses of G-1 and W-1

<table>
<thead>
<tr>
<th></th>
<th>G-1</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Accepted</td>
<td>̄x</td>
<td>n</td>
<td>σ</td>
<td></td>
<td>̄x</td>
<td>n</td>
<td>σ</td>
<td></td>
<td>̄x</td>
<td>n</td>
<td>σ</td>
<td></td>
<td>̄x</td>
<td>n</td>
<td>σ</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Value</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>72.41</td>
<td>72.32</td>
<td>6</td>
<td>0.55</td>
<td></td>
<td>10.01</td>
<td>9.94</td>
<td>6</td>
<td>0.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Fe as FeO</td>
<td>1.76</td>
<td>1.74</td>
<td>6</td>
<td>0.04</td>
<td></td>
<td>6.62</td>
<td>6.47</td>
<td>6</td>
<td>0.12</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.41</td>
<td>0.26</td>
<td>6</td>
<td>0.07</td>
<td></td>
<td>2.07</td>
<td>2.13</td>
<td>6</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>1.39</td>
<td>1.41</td>
<td>6</td>
<td>0.10</td>
<td></td>
<td>10.96</td>
<td>10.88</td>
<td>6</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.32</td>
<td>3.31</td>
<td>6</td>
<td>0.04</td>
<td></td>
<td>0.64</td>
<td>0.55</td>
<td>6</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>5.45</td>
<td>5.53</td>
<td>6</td>
<td>0.07</td>
<td></td>
<td>1.07</td>
<td>1.08</td>
<td>6</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.26</td>
<td>0.24</td>
<td>6</td>
<td>0.007</td>
<td></td>
<td>8.74</td>
<td>8.62</td>
<td>6</td>
<td>0.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>0.98</td>
<td>0.98</td>
<td>9</td>
<td>0.01</td>
<td></td>
<td>1.41</td>
<td>1.46</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.87</td>
<td>0.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

̄x is the average value from this work

n is the number of weighings

σ = \sqrt{\frac{(x - ̄x)^2}{n - 1}} , 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 $\text{SiO}_2$ 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 four 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 five standards was 0.5% $\text{SiO}_2$.

The Rb X-ray fluorescence analyses of the moldavites have a precision (c) of about ±2%; the Sr X-ray analyses have a precision of about ±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 ±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 \( \sigma = \frac{\sigma}{x} (100) \) of the analyses is as follows:

- SiO₂, ±1%;
- Al₂O₃, ±3%;
- TiO₂, ±3%;
- MgO, ±5%;
- CaO, ±4%;
- Na₂O, ±5%;
- 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 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 P2O5 analyses are not given because these analyses proved to be of poor quality; the 15 samples analyzed for P2O5 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: SiO2, 75.5 - 80.6; Al2O3, 9.62 - 12.64; TiO2, 0.268 - 0.460; Fe2O3, 0.12 - 0.31; FeO, 1.42 - 2.36; MgO, 1.13 - 2.50; CaO, 1.46 - 3.71; Na2O, 0.31 - 0.67; K2O, 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 K2O analysis and four Rb analyses. The K2O 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/cm3 and from 1.486 to 1.495, respectively.
<table>
<thead>
<tr>
<th>Analytical Results</th>
<th>T 5296a</th>
<th>T 5296b</th>
<th>T 5296c</th>
<th>T 5296d</th>
<th>T 5296e</th>
<th>T 5296f</th>
<th>T 5309</th>
<th>T 5310</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>79.2</td>
<td>77.3</td>
<td>76.7</td>
<td>75.5</td>
<td>75.5</td>
<td>78.4</td>
<td>78.5</td>
<td>78.5</td>
</tr>
<tr>
<td>A12O3</td>
<td>10.93</td>
<td>11.28</td>
<td>11.04</td>
<td>10.76</td>
<td>10.76</td>
<td>10.76</td>
<td>10.54</td>
<td>10.54</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.307</td>
<td>0.336</td>
<td>0.314</td>
<td>0.303</td>
<td>0.314</td>
<td>0.303</td>
<td>0.300</td>
<td>0.300</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>0.16</td>
<td>0.20</td>
<td>0.12</td>
<td>0.29</td>
<td>0.12</td>
<td>0.18</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>FeO</td>
<td>1.54</td>
<td>1.63</td>
<td>1.73</td>
<td>1.47</td>
<td>1.62</td>
<td>1.50</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td>MgO</td>
<td>2.09</td>
<td>2.09</td>
<td>2.19</td>
<td>2.50</td>
<td>2.13</td>
<td>2.20</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td>CaO</td>
<td>3.64</td>
<td>3.71</td>
<td>3.74</td>
<td>3.66</td>
<td>3.66</td>
<td>3.71</td>
<td>3.74</td>
<td>3.74</td>
</tr>
<tr>
<td>Na2O</td>
<td>0.51</td>
<td>0.51</td>
<td>0.63</td>
<td>0.45</td>
<td>0.63</td>
<td>0.45</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>K2O</td>
<td>3.64</td>
<td>3.64</td>
<td>3.64</td>
<td>3.66</td>
<td>3.66</td>
<td>3.66</td>
<td>3.74</td>
<td>3.74</td>
</tr>
<tr>
<td>Total Fe as FeO</td>
<td>1.68</td>
<td>1.91</td>
<td>1.91</td>
<td>1.72</td>
<td>1.73</td>
<td>1.73</td>
<td>1.76</td>
<td>1.76</td>
</tr>
<tr>
<td>Rb ppm</td>
<td>148</td>
<td>146</td>
<td>144</td>
<td>120</td>
<td>136</td>
<td>120</td>
<td>139</td>
<td>139</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>133</td>
<td>156</td>
<td>156</td>
<td>156</td>
<td>156</td>
<td>156</td>
<td>138</td>
<td>138</td>
</tr>
<tr>
<td>Rb/Sr</td>
<td>1.11</td>
<td>0.94</td>
<td>1.01</td>
<td>0.86</td>
<td>0.92</td>
<td>0.86</td>
<td>0.95</td>
<td>0.95</td>
</tr>
<tr>
<td>R.I.</td>
<td>1.486</td>
<td>1.491</td>
<td>1.491</td>
<td>1.495</td>
<td>1.492</td>
<td>1.495</td>
<td>1.492</td>
<td>1.492</td>
</tr>
<tr>
<td>Sp. G.</td>
<td>2.3350</td>
<td>2.3521</td>
<td>2.3521</td>
<td>2.3718</td>
<td>2.3635</td>
<td>2.3635</td>
<td>2.3493</td>
<td>2.3493</td>
</tr>
</tbody>
</table>
Table 2 (Continued)

<table>
<thead>
<tr>
<th></th>
<th>T 5311 Dolni Chrastany</th>
<th>T 5312 Habri</th>
<th>T 5313 Habri</th>
<th>T 5314 Slavce</th>
<th>T 5315 Vrabc</th>
<th>T 5316 Vrabc</th>
<th>T 5317 Kroolov</th>
<th>T 5318 Koroseky</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>78.6</td>
<td>77.6</td>
<td>78.4</td>
<td>80.6*</td>
<td>77.0</td>
<td>79.55</td>
<td>77.1*</td>
<td>78.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>10.77</td>
<td>11.13</td>
<td>10.30</td>
<td>10.09</td>
<td>10.28</td>
<td>9.94</td>
<td>10.43</td>
<td>10.11</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.307</td>
<td>0.331</td>
<td>0.300</td>
<td>0.295</td>
<td>0.287</td>
<td>0.286</td>
<td>0.285</td>
<td>0.268</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.26</td>
<td>0.21</td>
<td>0.13</td>
<td>0.12</td>
<td>0.16</td>
<td>0.13</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>FeO</td>
<td>1.46</td>
<td>1.75</td>
<td>1.63</td>
<td>1.42</td>
<td>1.49</td>
<td>1.55</td>
<td>1.49</td>
<td>1.50</td>
</tr>
<tr>
<td>MgO</td>
<td>1.66</td>
<td>2.10</td>
<td>1.90</td>
<td>1.38</td>
<td>2.19</td>
<td>1.63</td>
<td>2.33</td>
<td>2.12</td>
</tr>
<tr>
<td>CaO</td>
<td>2.35</td>
<td>3.12</td>
<td>3.07</td>
<td>2.00</td>
<td>3.50</td>
<td>2.16</td>
<td>3.69</td>
<td>3.71</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.42</td>
<td>0.51</td>
<td>0.45</td>
<td>0.45</td>
<td>0.35</td>
<td>0.50</td>
<td>0.31</td>
<td>0.38</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.59</td>
<td>3.75</td>
<td>3.74</td>
<td>3.58</td>
<td>3.65</td>
<td>3.71</td>
<td>3.44</td>
<td>3.65</td>
</tr>
<tr>
<td>Total</td>
<td>99.42</td>
<td>100.50</td>
<td>99.92</td>
<td>99.94</td>
<td>98.91</td>
<td>99.46</td>
<td>99.22</td>
<td>100.32</td>
</tr>
<tr>
<td>Total Fe as FeO</td>
<td>1.69</td>
<td>1.94</td>
<td>1.75</td>
<td>1.53</td>
<td>1.63</td>
<td>1.67</td>
<td>1.62</td>
<td>1.66</td>
</tr>
<tr>
<td>Rb ppm</td>
<td>138</td>
<td>141</td>
<td>140</td>
<td>145</td>
<td>129</td>
<td>149</td>
<td>121^</td>
<td>135</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>134</td>
<td>146</td>
<td>144</td>
<td>130</td>
<td>147</td>
<td>139</td>
<td>147</td>
<td>147</td>
</tr>
<tr>
<td>Rb/Sr</td>
<td>1.03</td>
<td>0.96</td>
<td>0.97</td>
<td>1.12</td>
<td>0.88</td>
<td>1.07</td>
<td>0.82</td>
<td>0.92</td>
</tr>
<tr>
<td>R.I.</td>
<td>1.491</td>
<td>1.495</td>
<td>1.494</td>
<td>1.488</td>
<td>1.493</td>
<td>1.489</td>
<td>1.494</td>
<td>1.493</td>
</tr>
<tr>
<td>Sp. G.</td>
<td>2.3440</td>
<td>2.3647</td>
<td>2.3708</td>
<td>2.3312</td>
<td>2.3653</td>
<td>2.3413</td>
<td>2.3681</td>
<td>2.3644</td>
</tr>
</tbody>
</table>
Table 2 (Continued)

<table>
<thead>
<tr>
<th></th>
<th>T 5319 Nechov</th>
<th>T 5320 Slavice</th>
<th>T 5321 Kozichovice</th>
<th>T 5322 Slaveticé</th>
<th>T 5323 Dukovany</th>
<th>T 5324 Dukovany</th>
<th>T 5325 Dukovany</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>80.3</td>
<td>79.8</td>
<td>80.2</td>
<td>79.4*</td>
<td>78.8</td>
<td>76.7*</td>
<td>80.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.62</td>
<td>11.04</td>
<td>11.02</td>
<td>11.24</td>
<td>10.99</td>
<td>12.64</td>
<td>11.43</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.284</td>
<td>0.402</td>
<td>0.337</td>
<td>0.364</td>
<td>0.326</td>
<td>0.460</td>
<td>0.361</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.20</td>
<td>0.26</td>
<td>0.14</td>
<td>0.16</td>
<td>0.17</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>1.49</td>
<td>2.03</td>
<td>1.164</td>
<td>1.83</td>
<td>1.60</td>
<td>2.36</td>
<td>1.71</td>
</tr>
<tr>
<td>MgO</td>
<td>1.57</td>
<td>1.24</td>
<td>1.25</td>
<td>1.33</td>
<td>1.61</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>2.52</td>
<td>1.57</td>
<td>1.68</td>
<td>1.50</td>
<td>2.46</td>
<td>1.57</td>
<td>1.46</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.42</td>
<td>0.60</td>
<td>0.53</td>
<td>0.53</td>
<td>0.39</td>
<td>0.57</td>
<td>0.58</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.68</td>
<td>3.69</td>
<td>3.47</td>
<td>3.57</td>
<td>3.26</td>
<td>3.81</td>
<td>3.53</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.08</strong></td>
<td><strong>100.63</strong></td>
<td><strong>100.27</strong></td>
<td><strong>99.92</strong></td>
<td><strong>99.61</strong></td>
<td><strong>99.64</strong></td>
<td><strong>100.43</strong></td>
</tr>
<tr>
<td><strong>Total Fe as FeO</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb ppm</td>
<td>150</td>
<td>148</td>
<td>138</td>
<td>142</td>
<td>122</td>
<td>160*</td>
<td>149</td>
</tr>
<tr>
<td>Sr ppm</td>
<td>133</td>
<td>134</td>
<td>135</td>
<td>137</td>
<td>146</td>
<td>133*</td>
<td>134</td>
</tr>
<tr>
<td>Rb/Sr</td>
<td>1.13</td>
<td>1.10</td>
<td>1.02</td>
<td>1.04</td>
<td>0.83</td>
<td>1.20</td>
<td>1.11</td>
</tr>
<tr>
<td>R.I.</td>
<td>1.489</td>
<td>1.490</td>
<td>1.487</td>
<td>1.489</td>
<td>1.491</td>
<td>1.492</td>
<td>1.489</td>
</tr>
<tr>
<td>Sp. G.</td>
<td>2.3414</td>
<td>2.3474</td>
<td>2.3353</td>
<td>2.3388</td>
<td>2.3484</td>
<td>2.3609</td>
<td>2.3372</td>
</tr>
</tbody>
</table>
Table 2 continued

* spectrophotometric determination of SiO₂

^ mass spectrometric isotope dilution analysis by Professors


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: SiO₂, ±2%; Al₂O₃, ±4%; TiO₂, ±13%; total Fe as FeO, ±13%; MgO, ±23%; CaO, ±29%; Na₂O, ±19%; K₂O, ±4%; Rb, ±7%; Sr, ±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 SiO₂, Al₂O₃, TiO₂, FeO and Na₂O, and lower average contents of MgO, 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 TiO₂ 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 TiO₂. 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 (Faul 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. Na₂O and Rb are inversely correlated with the alkaline earths. SiO₂ shows negative correlations of various significances with the alkaline earths, Al₂O₃, refractive index and specific gravity. FeO (actually total Fe as FeO) has significant positive correlations with TiO₂ and with Na₂O.

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 SiO₂, 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 SiO₂ 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; Na₂O-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.

<table>
<thead>
<tr>
<th></th>
<th>Moravia</th>
<th></th>
<th>Bohemia</th>
<th></th>
<th>Combined data</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>r</td>
<td>significance</td>
<td>r</td>
<td>significance</td>
<td>r</td>
<td>significance</td>
</tr>
<tr>
<td>Na$_2$O - K$_2$O</td>
<td>+0.96</td>
<td>&lt;1%</td>
<td>+0.63</td>
<td>&lt;1%</td>
<td>+0.47</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>Na$_2$O - Rb</td>
<td>+0.99</td>
<td>&lt;0.1</td>
<td>+0.61</td>
<td>&lt;1</td>
<td>+0.73</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>K$_2$O - Rb</td>
<td>+0.94</td>
<td>&lt;1</td>
<td>+0.75</td>
<td>&lt;0.1</td>
<td>+0.72</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>MgO - CaO</td>
<td>+0.91</td>
<td>1</td>
<td>+0.61</td>
<td>&lt;0.1</td>
<td>+0.96</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>MgO - Sr</td>
<td>+0.98</td>
<td>&lt;0.1</td>
<td>+0.72</td>
<td>&lt;0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CaO - Sr</td>
<td>+0.91</td>
<td>1</td>
<td>+0.56</td>
<td>&lt;5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$ - Al$_2$O$_3$</td>
<td>Not. sig.</td>
<td></td>
<td>-0.65</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiO$_2$ - MgO</td>
<td>-0.93</td>
<td>&lt;5&quot;</td>
<td>-0.83</td>
<td>0.1</td>
<td>-0.88</td>
<td>&lt;0.1&lt;&quot;</td>
</tr>
<tr>
<td>FeO$^x$ - TiO$_2$</td>
<td>+0.99</td>
<td>&lt;0.1</td>
<td>+0.85</td>
<td>&lt;0.1</td>
<td>+0.96</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>FeO$^x$ - Na$_2$O</td>
<td>+0.83</td>
<td>&lt;5</td>
<td>+0.70</td>
<td>&lt;1</td>
<td>+0.79</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Na$_2$O - MgO</td>
<td>-0.91</td>
<td>not sig.</td>
<td>-0.53</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_2$O - CaO</td>
<td>-0.83</td>
<td>&lt;5</td>
<td>not sig.</td>
<td></td>
<td>0.64</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Rb - CaO</td>
<td>-0.83</td>
<td>&lt;5</td>
<td>-0.73</td>
<td>&lt;0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rb - Sr</td>
<td>-0.90</td>
<td>&lt;5</td>
<td>-0.50</td>
<td></td>
<td>-0.61</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

* 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 SiO₂, and iron is positively correlated with the alkaline earths and with Al₂O₃. 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 SiO₂ phase. The presence of lechatelierite is of interest because melts of moldavite composition would presumably lie within the SiO₂ field and differentiation would occur by SiO₂ phase separation. Products of this SiO₂ subtraction would exhibit inverse correlations of all constituents with SiO₂. 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 100µ 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 selective volatilization is the apparent discrepancy between the U-Pb and Rb-Sr ages (Schnetzler and Pinson, 1964b).

Experimental data concerning 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: Alkalis > Si, Fe > Al, alkaline earths. It therefore seems probably 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 SiO₂ 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 SiO₂). 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 Sr⁸⁷/Sr⁸⁶ 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 SiO₂, Na₂O, and Rb contents, and higher alkaline earth contents. Al₂O₃, TiO₂, FeO, and K₂O do not vary appreciably with decreasing Rb/Sr. Moravian tektites with lower Rb/Sr ratios have lower SiO₂, TiO₂, 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 SiO₂ and higher Al₂O₃ 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% K₂O and this indicates that Na₂O was more volatile than K₂O. 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: Na₂O, Rb, K₂O, SiO₂, Al₂O₃, 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 Na₂O vs. K₂O 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 SiO₂. The inverse correlations of the alkalis and alkaline earths in moldavites suggests that variations of SiO₂ 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 SiO₂ 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 (Schneckler 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 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 SiO₂, Al₂O₃, TiO₂, FeO and Na₂O, 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 TiO₂ 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 TiO₂. 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 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: Na₂O, Rb, K₂O, SiO₂, Al₂O₃, 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


Silicate sample preparation for light element analysis by X-ray

Chapter 6, 137-142, Univ. of Chicago Press, Chicago.