

Geochemical characterization of moldavites from a new locality, the Cheb Basin, Czech Republic

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Abstract—Twenty-three moldavites from a new locality, the Cheb Basin in Western Bohemia, were analyzed by instrumental neutron activation analysis for 45 major and trace elements. Detailed comparison of the Cheb Basin moldavites with moldavites from other substrewn fields in both major and trace element composition shows that the Cheb Basin is a separate substrewn field. The geochemical data obtained are discussed with respect to the source materials and processes leading to formation of moldavites. The data show that three groups of Cheb Basin moldavites exist. Ten samples of group 1 are characterized by the lowest content of Al, Fe, Na, and other elements representing phyllosilicate minerals, and by high Ca + Mg contents related probably to carbonates. They resemble the “poisonous green” moldavites, a subgroup of the Southern Bohemian moldavites. Seven samples of group 2 and 6 samples of group 3 are similar to typical moldavites of the Southern Bohemian substrewn field. These two groups differ from each other mainly in Al contents; with higher contents of Al and the elements associated with phyllosilicate minerals (namely Ba and Sr), group 3 also resembles the Moravian moldavites. Significant positive correlations between K, Ca, Mg, and Mn found in group 2 of the Cheb Basin moldavites and the enrichment in these elements observed generally in all moldavites, as well as other facts, e.g., high K/Na and K/Rb ratios and the reduced conditions during formation of moldavites, have been attributed to possible contribution to the moldavite source materials of the ash produced by burning of vegetation and soil organic matter present at the pre-impact area.

INTRODUCTION

Moldavites were found for the first time in 1786 in gravels from the Vltava River (Moldau in German) in the surroundings of the town Týn nad Vltavou (Thein) in Southern Bohemia. Professor Mayer, the discoverer of these peculiar green stones, described them as chrysolites (Mayer 1787). Later, in 1836, the term moldavite was introduced, and in 1891 the Czech term “vltavín” was first used for them (Bouška 1994). In Moravia (the eastern part of the Czech Republic), first moldavites were found in 1880. Since 1914, moldavites have been found also in northern Austria, in the Horn area, for example near the towns of Radessen and Altenburg (Suess 1914; Koeberl et al. 1988), and since 1967 also in Germany in the Lusatia region, northeast of Dresden (Rost et al. 1979; Lange 1996; Störr and Lange 1992)—see map in Fig. 1. The most recent estimates of the original total mass of moldavites reach up

to 10⁹ kg, from which only 10⁷ kg has been preserved until today (Trnka and Houzar 2002).

Similar natural glasses—products of impact melting—were found later also in other places in the world, e.g., in Australia (1844) and in southeast Asia (1879). Suess (1900) published the first extensive monograph about these glasses. He introduced a new term for them—tektites. In the 1930s, tektites were discovered also in the USA (bediasites and georgianites) and at the Ivory Coast, Africa (ivorites). Despite the extensive literature on tektites and impact melts (recently reviewed by, e.g., Dressler and Reimold [2001]), the monographs by Rost (1972) and Bouška (1992, 1994) represent still the most comprehensive reviews of moldavites. Although dealing with moldavites from Lusatia only, the publication by Lange (1995) that provides a thorough characterization of this moldavite group cannot be omitted from this elite list. Of the most recent papers, a review by Trnka and Houzar (2002) and a paper by Engelhardt et al. (2005) should be mentioned.

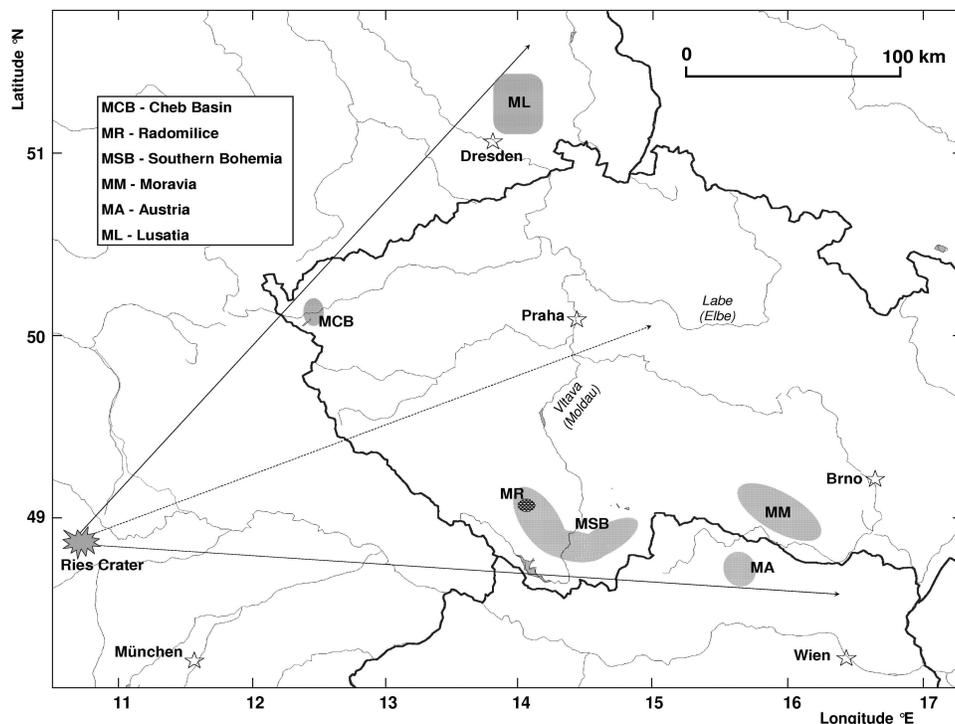


Fig. 1. Map of the Central European tektite strewn field and the Ries parent crater. The arrows define the current outer limits and axis of symmetry of the strewn field.

In 1993 and 1994, seven moldavites were found on the shore of the Jesenice water reservoir on the Odrava river near Cheb in the western part of the Czech Republic (see Fig. 1, MCB). Brief characteristics of these moldavites, together with the geology of the moldavite-bearing gravels from this locality, were described by Bouška et al. (1995). To date, several thousand moldavites have been found in this region, mostly in a gravel-pit near Dřenice village (T. Zuckermann, Tekaz, Ltd., Cheb, personal communication, 2006).

The present study is aimed at geochemical characterization of moldavites from this relatively new locality and their comparison with moldavites from other parts of the Central European tektite strewn field.

EXPERIMENTAL

Sample Preparation

Twenty-three small moldavites with masses of 0.7–2.5 g, randomly selected from the collection of about thousand samples from the Tekaz gravel pit provided by Dr. T. Zuckermann (director of the company), were taken for elemental analysis. These samples are gemmologically without value; their color varies from light green (sometimes with a blue tint) to bottle green. For comparison, the photograph in Fig. 2 shows moldavites from Southern Bohemia and from the Cheb Basin, whereby the latter ones typically have coarse sculpture. Samples

were carefully crushed in a hydraulic press with a die made of hardened steel. Crushing yielded chips with grain sizes less than 2 mm. The following masses of moldavites were taken for analysis using instrumental neutron activation analysis (INAA):

- Approximately 100 mg for short-time activation with epithermal and fast neutrons (in a Cd-box). These samples were also analyzed after one week of decay by short-time activation with thermal neutrons.
- Approximately 300 mg for long-time activation with thermal neutrons.

Samples were heat-sealed into disk-shaped capsules (diameter 25 mm) made of high-purity polyethylene foils pre-cleaned in hot dilute HNO_3 .

Standards and Monitors

Three synthetic multi-element standards (MES) for 17 elements, prepared by pipetting of 50 μL aliquots from stock solutions, and a single-element standard of high-purity Si prepared by weighing were used for short-time INAA as described previously (Řanda et al. 2005). Nine MES containing 46 elements (Řanda et al. 1978, 2003) were used for long-time INAA. The neutron dose for short-time INAA was determined using Au monitors (1 μg Au) prepared by pipetting as MES; for the long-time INAA, the neutron flux gradient along the axis of an irradiation can containing 23 samples and 9 MES was determined using 7 monitors made of an Fe-Co-Mo alloy foil (~60 mg).



Fig. 2. Photograph of typical samples of moldavites from the Cheb Basin (right) and moldavites from Southern Bohemia (left). Fineness of their sculpture is a primary distinguishing characteristic of these two groups of moldavites.

Neutron Irradiation and Counting

Irradiations were carried out in the nuclear reactor LVR-15 of the Nuclear Research Institute Řež, plc., which is operated at 9 MW. For the long-time INAA, a column-shaped packet containing samples, MES and monitors was irradiated in a water-cooled Al can for 3 hr in a channel located at the periphery of the reactor core with neutron fluence rates of 8×10^{13} and 2×10^{13} $\text{n cm}^{-2} \text{s}^{-1}$ for thermal and fast neutrons, respectively. For the short-time INAA, irradiation was carried out using a pneumatic tube system with a 3 s transport time in a channel with neutron fluence rates of 3×10^{13} , 8×10^{12} and 4.6×10^{12} $\text{n cm}^{-2} \text{s}^{-1}$ for thermal, epithermal and fast neutrons, respectively. For determination of U and Si (via the reaction $^{29}\text{Si}(\text{n,p})^{29}\text{Al}$) using INAA with epithermal and fast neutrons, respectively, irradiation in a cylindrical Cd-box with a wall thickness of 1 mm was used. Just before irradiation, a Cd-box with a sample and Au monitor was cooled down in liquid nitrogen (Řanda et al. 2005). Gamma spectrometric measurements were carried out using two types of HPGe detectors:

- a coaxial detector with a relative efficiency of 23%, and a FWHM resolution of 1.8 keV for the 1332.5 keV photons of ^{60}Co ,
- a planar detector with a thickness of 13 mm, active area of 200 mm^2 , and a FWHM resolution of 500 eV for the 122.06 keV photons of ^{57}Co ; this detector is indispensable for determination of elements producing radionuclides with analytical gamma lines only in the low-energy range of 50–250 keV (Ce, Nd, Sm, Gd, Tm, Lu, and U).

The times of irradiation (t_i), decay (t_d), and counting (t_c) used were as follows:

- a) for the short-time epithermal/fast INAA, $t_i-t_d-t_c = 1-15-15$ min;
- b) for the short-time thermal INAA, $t_i-t_d-t_c = 1-13-13$ min;
- c) for the long-time INAA, $t_i = 3$ hours, $t_d-t_c = 4$ d and 20 min for the first count, $t_d-t_c = 10$ d and 1 h for the second count, $t_d-t_c = 1$ month and 2 h for the third count, $t_d-t_c = 3$ months and 10 h for the last count using the planar detector.

RESULTS AND DISCUSSION

Results of INAA of the selected 23 moldavites are given in Table 1. Epithermal/fast short-time INAA was used for determination of Si, K, V, Ba and U, short-time thermal INAA for elements Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Ba and Dy, and long-time INAA for other elements including the majority of trace elements—Na, K, Ca, Sc, Cr, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Zr, Ag, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Tm, Yb, Lu, Hf, Ta, W, Ir, Au, Th, and U. Simultaneously with moldavites, the reference standard USGS granodiorite GSP-1 was analyzed for quality control purposes. The values determined are compared with certified values in Table 1. Values for Al, Mg, and Na were corrected for contributions arising from the interference (n,p) and (n, α) nuclear reactions involving Si, Al, and Mg. Similarly, for the determination of Zr (^{95}Zr), La (^{140}La), Ce (^{141}Ce), and Nd (^{147}Nd) concentrations, contributions from uranium fission were taken into account.

Table 1. Results of INAA of moldavites from the Cheb Basin locality and reference rock USGS granodiorite GSP-1 (element contents in $\mu\text{g g}^{-1}$ or in wt%, where % noted).

Sample MCB no.	1	2	3	4	5	6	7	8	9	10	11	12	13	Unc. % ^a
Na%	0.415	0.212	0.360	0.350	0.310	0.407	0.221	0.200	0.433	0.578	0.520	0.190	0.224	2
Mg%	1.24	1.71	0.99	1.07	1.06	1.02	1.62	1.83	1.32	1.72	1.56	1.96	1.63	4
Al%	4.80	4.62	5.02	5.11	4.88	5.52	4.64	4.40	5.51	6.05	6.04	4.21	4.60	2
Si%	37.5	37.2	37.8	37.2	37.8	37.8	36.8	37.1	36.4	35.0	35.4	36.9	36.5	3
Cl	<95	<37	<100	<74	<62	<107	<71	<85	<96	<91	<91	<68	<114	–
K%	1.89	2.63	2.44	2.54	2.56	2.24	2.70	2.82	2.35	3.20	2.92	2.40	3.15	3
Ca%	1.93	2.90	1.50	1.81	1.96	1.62	2.80	3.15	2.10	2.93	2.36	2.73	3.55	3
Sc	4.94	3.60	5.10	5.16	4.83	6.13	3.91	3.76	5.91	5.49	5.72	3.41	3.96	2
Ti%	0.194	0.140	0.197	0.202	0.170	0.234	0.157	0.145	0.236	0.214	0.265	0.139	0.150	5
V	26.7	23.1	24.3	24.2	25.2	22.2	23.9	25.3	25.8	32.1	28.6	18.6	30.9	4
Cr	18.1	16.8	19.2	20.2	20.0	20.1	18.4	19.0	21.1	20.1	20.1	16.0	21.3	2
Mn	664	822	600	722	760	568	760	1000	740	1117	960	1137	746	2
Fe%	1.09	0.917	1.11	1.15	1.08	1.29	0.995	0.920	1.30	1.36	1.32	0.745	1.07	2
Co	4.59	4.03	3.92	4.60	4.73	4.72	4.33	4.64	4.90	4.79	3.94	4.64	4.79	2
Ni	<15	8.6	<13	<13	<15	<16	11	<13	<14	<14	<15	12	<16	10
Cu	<9	<6	<8	<7	<8	<9	<8	<8	<9	<10	<10	<8	<9	–
Zn	82.9	21.0	76.0	70.4	67.6	93.8	23.1	166	92.5	57.1	96.6	153	70.1	2
As	<0.6	<0.4	<0.5	<0.5	<0.5	<0.6	<0.6	<0.5	<0.6	0.89	<0.7	<0.5	<0.6	23
Br	<0.8	<0.5	<0.6	<0.6	<0.7	<0.7	<0.7	<0.6	<0.7	<0.8	<0.8	<0.6	<0.6	–
Rb	78.8	108	103	107	106	95.3	115	118	96.3	125	112	104	127	2
Sr	146	109	134	150	163	189	117	81	202	194	195	116	109	7
Zr	230	206	265	275	297	326	232	258	268	298	274	276	220	4
Ag	<0.3	<0.1	<0.3	<0.3	<0.3	<0.3	<0.1	<0.3	<0.3	<0.3	<0.3	<0.1	<0.3	–
Sb	<0.06	0.047	<0.05	<0.05	<0.06	<0.06	0.034	0.110	<0.06	<0.06	0.480	0.058	0.100	2
Cs	12.4	11.9	17.3	18.1	17.6	15.5	12.6	14.7	15.0	16.5	16.0	13.0	14.3	2
Ba	905	605	975	950	980	1136	643	568	1128	1224	1065	530	622	3
La	28.6	22.3	30.2	30.7	31.0	34.8	23.5	23.1	33.4	38.5	34.0	24.2	22.7	2
Ce	53.7	41.8	58.5	59.7	60.7	69.1	44.6	45.2	64.1	72.3	62.4	47.4	43.3	2
Nd	23.3	18.4	25.5	26.9	26.9	31.4	19.4	19.7	28.7	31.5	27.4	20.1	19.5	2
Sm	4.45	3.65	4.98	5.14	5.18	5.82	3.95	3.80	5.25	5.92	5.27	3.95	3.69	2
Eu	0.870	0.758	1.02	1.00	0.993	1.17	0.791	0.748	1.04	1.09	1.05	0.769	0.749	2
Gd	3.36	2.96	3.98	3.82	4.12	4.59	3.24	3.32	4.12	4.36	4.03	3.36	3.20	4
Tb	0.490	0.438	0.538	0.580	0.570	0.640	0.454	0.445	0.536	0.654	0.573	0.480	0.453	3
Dy	3.0	4.3	4.2	4.0	4.2	4.4	3.2	3.4	4.1	4.6	4.3	3.5	4.4	7
Ho	0.64	0.49	0.54	0.74	0.72	0.66	0.64	0.53	0.58	0.90	0.60	0.61	0.67	15
Tm	0.238	0.243	0.285	0.323	0.330	0.345	0.230	0.275	0.314	0.374	0.318	0.274	0.24	4
Yb	1.37	1.25	1.50	1.60	1.72	1.67	1.37	1.32	1.56	1.81	1.53	1.40	1.28	2
Lu	0.20	0.20	0.24	0.26	0.27	0.25	0.21	0.23	0.26	0.27	0.24	0.21	0.20	3
Hf	5.75	4.95	6.10	6.22	6.60	7.03	5.33	6.03	6.29	7.09	6.07	6.24	4.79	2
Ta	0.496	0.467	0.535	0.540	0.554	0.619	0.495	0.497	0.605	0.621	0.567	0.467	0.502	2
W	<0.9	<0.6	<0.7	<0.7	<0.8	<0.9	<0.8	<0.8	<0.8	<1.0	<1.0	<0.7	<0.8	–
Ir							<0.0009							–
Th	11.7	8.35	12.4	12.5	12.5	14.5	9.07	8.88	14.3	15.7	13.6	9.29	8.64	2
U	3.0	2.4	2.9	3.3	3.5	3.2	2.7	3.7	3.2	3.4	2.8	3.7	3.2	4

Table 1. *Continued.* Results of INAA of moldavites from the Cheb Basin locality and reference rock USGS granodiorite GSP-1 (element contents in $\mu\text{g g}^{-1}$ or in wt%, where % noted).

Sample MCB no.	USGS GSP-1																			
	14	15	16	17	18	19	20	21	22	23	23	22	21	20	19	18	17	16	15	14
Na%	0.180	0.382	0.223	0.211	0.244	0.592	0.447	0.411	0.168	0.433	2	0.168	0.411	0.447	0.592	0.244	0.211	0.223	0.382	0.180
Mg%	1.80	1.17	1.55	1.76	1.62	1.36	1.40	1.05	1.68	1.49	3	1.68	1.05	1.40	1.36	1.62	1.76	1.55	1.17	1.80
Al%	4.23	4.63	4.59	4.42	4.38	5.56	5.88	5.06	4.12	4.63	2	4.12	5.06	5.88	5.56	4.38	4.42	4.59	4.63	4.23
Si%	37.3	37.0	36.7	36.8	36.3	36.0	36.1	37.5	37.6	36.6	3	37.6	37.5	36.1	36.0	36.3	36.8	36.7	37.0	37.3
Cl	<99	<90	<66	<59	<78	<100	<110	<74	<75	<105	–	<75	<74	<110	<100	<78	<59	<66	<90	<99
K%	2.57	2.91	2.73	2.86	3.13	2.66	2.10	2.39	2.31	3.09	3	2.31	2.39	2.10	2.66	3.13	2.86	2.73	2.91	2.57
Ca%	3.25	2.24	2.80	2.90	3.31	2.12	2.29	1.59	2.73	2.87	3	2.73	1.59	2.29	2.12	3.31	2.90	2.80	2.24	3.25
Sc	2.98	4.28	3.76	3.74	3.49	5.49	6.94	5.37	3.18	4.36	2	3.18	5.37	6.94	5.49	3.49	3.74	3.76	4.28	2.98
Ti%	0.119	0.171	0.139	0.133	0.118	0.231	0.269	0.222	0.120	0.153	5	0.120	0.222	0.269	0.231	0.118	0.133	0.139	0.171	0.119
V	17.7	28.8	23.5	22.4	27.4	27.2	31.6	26.0	17.2	27.9	3	17.2	26.0	31.6	27.2	27.4	22.4	23.5	28.8	17.7
Cr	12.9	22.0	18.2	18.0	19.8	17.2	23.8	21.5	13.3	22.8	2	13.3	21.5	23.8	17.2	19.8	18.0	18.2	22.0	12.9
Mn	1240	979	710	915	807	826	709	623	1082	1235	2	1082	623	709	826	807	915	710	979	1240
Fe%	0.687	1.12	0.952	0.920	0.952	1.33	1.49	1.21	0.683	1.16	2	0.683	1.21	1.49	1.33	0.952	0.920	0.952	1.12	0.687
Co	3.60	4.96	4.30	4.48	4.17	4.41	5.51	4.54	4.12	5.47	2	4.12	4.54	5.51	4.41	4.17	4.48	4.30	4.96	3.60
Ni	<13	<16	<12	11	17	<15	<21	<8	<11	<19	20	<11	<8	<21	<15	17	11	<12	<16	<13
Cu	<7	<11	<7	<8	<9	<12	<14	<11	<8	<15	–	<8	<11	<14	<12	<9	<8	<7	<11	<7
Zn	39.4	40.6	19.8	59.0	23.7	6.60	69.7	78.9	63.4	43.6	2	63.4	78.9	69.7	6.60	23.7	59.0	19.8	40.6	39.4
As	<0.5	<0.7	<0.4	0.4	<0.5	<0.7	<0.8	<0.6	<0.4	<0.7	30	<0.4	<0.6	<0.8	<0.7	<0.5	0.4	<0.4	<0.7	<0.5
Br	<0.6	<0.8	<0.5	<0.6	<0.6	<0.8	<1	<0.7	<0.5	<1	–	<0.5	<0.7	<1	<0.8	<0.6	<0.6	<0.5	<0.8	<0.6
Rb	102	125	109	116	122	104	90.8	97.9	94.8	123	2	94.8	97.9	90.8	104	122	116	109	125	102
Sr	96	135	100	126	117	203	187	152	87	170	7	87	152	187	203	117	126	100	135	96
Zr	269	230	219	235	208	269	277	263	289	270	5	289	263	277	269	208	235	219	230	269
Ag	<0.2	<0.3	<0.2	<0.1	<0.3	<0.3	<0.4	<0.2	<0.2	<0.4	–	<0.2	<0.3	<0.4	<0.3	<0.3	<0.1	<0.2	<0.3	<0.2
Sb	3.8	0.17	<0.05	0.067	<0.06	<0.06	<0.07	0.048	<0.05	0.13	15	<0.05	0.048	<0.07	<0.06	<0.06	0.067	<0.05	0.17	3.8
Cs	11.1	24.3	12.0	13.4	13.1	13.5	14.2	17.8	11.3	20.1	2	11.3	17.8	14.2	13.5	13.1	13.4	12.0	24.3	11.1
Ba	617	994	612	594	668	1260	1079	1026	577	1043	3	577	1026	1079	1260	668	594	612	994	617
La	24.4	26.5	22.5	22.5	22.2	33.3	34.7	30.6	24.5	28.8	2	24.5	30.6	34.7	33.3	22.2	22.5	22.5	26.5	24.4
Ce	46.5	51.5	42.3	42.8	40.8	63.8	66.0	58.5	47.1	56.1	2	47.1	58.5	66.0	63.8	40.8	42.8	42.3	51.5	46.5
Nd	21.3	20.8	18.2	18.6	17.2	26.6	28.3	26.9	20.2	24.9	2	20.2	26.9	28.3	26.6	17.2	18.6	18.2	20.8	21.3
Sm	4.12	4.28	3.60	3.70	3.56	5.14	5.38	4.84	4.00	4.61	2	4.00	4.84	5.38	5.14	3.56	3.70	3.60	4.28	4.12
Eu	0.791	0.832	0.749	0.796	0.776	1.026	1.061	0.970	0.779	0.878	2	0.779	0.970	1.061	1.026	0.776	0.796	0.749	0.832	0.791
Gd	3.30	3.38	2.89	3.23	2.92	3.94	4.17	3.81	3.19	3.63	4	3.19	3.81	4.17	3.94	2.92	3.23	2.89	3.38	3.30
Tb	0.475	0.498	0.436	0.441	0.416	0.580	0.590	0.528	0.460	0.511	3	0.460	0.528	0.590	0.580	0.416	0.441	0.436	0.498	0.475
Dy	3.3	4.1	3.1	3.0	3.1	4.1	4.2	4.0	3.1	3.8	7	3.1	4.0	4.2	4.1	3.1	3.0	3.1	4.1	3.3
Ho	0.69	0.47	0.53	0.48	0.46	0.55	0.78	0.65	0.62	0.53	15	0.62	0.65	0.78	0.55	0.46	0.48	0.53	0.47	0.69
Tm	0.280	0.280	0.262	0.263	0.272	0.300	0.358	0.305	0.215	0.286	4	0.215	0.305	0.358	0.300	0.272	0.263	0.262	0.280	0.280
Yb	1.42	1.34	1.26	1.29	1.34	1.45	1.61	1.45	1.43	1.50	3	1.43	1.45	1.61	1.45	1.29	1.29	1.26	1.34	1.42
Lu	0.22	0.21	0.20	0.21	0.38	0.23	0.24	0.23	0.23	0.24	3	0.23	0.23	0.24	0.23	0.38	0.21	0.20	0.21	0.22
Hf	6.17	4.54	4.86	5.26	4.59	5.49	6.47	5.60	6.42	5.14	2	6.42	5.60	6.47	5.49	4.59	5.26	4.86	4.54	6.17
Ta	0.433	0.515	0.476	0.483	0.445	0.591	0.640	0.546	0.448	0.570	2	0.448	0.546	0.640	0.591	0.445	0.483	0.476	0.515	0.433
W	<0.7	1.2	<0.6	<0.7	<0.8	<1	<1	<0.9	<0.6	<1	25	<0.6	<0.9	<1	<1	<0.8	<0.7	<0.6	1.2	<0.7
Ir						<0.0009					–									
Th	9.51	10.7	8.18	8.43	8.06	13.8	14.0	12.5	9.37	11.7	2	9.37	12.5	14.0	13.8	8.06	8.43	8.18	10.7	9.51
U	3.0	3.5	2.6	2.9	2.3	2.3	3.1	2.9	3.3	3.5	3	3.3	2.9	3.1	2.3	2.3	2.9	2.6	3.5	3.0

^aIn italics are given combined uncertainties (in rel.%) based on counting statistics and an additional uncertainty estimated at 2% (fluctuation of neutron flux, difference between counting geometry of samples and standards, accuracy of standard concentration); coverage factor $k = 1$. ^bGovindaraju 1994. ^cCalculated from total Fe given as Fe_2O_3 .

Correlation analysis based on major and most of the trace elements is presented in Table 2. Correlations between selected elements are also illustrated by Fig. 3. Based on these correlations, the set of 23 moldavites can be divided into three geochemically different groups. Group 1 consists of the samples MCB 2, 7, 8, 12–14, 16–18, and 22, group 2 of the samples MCB 1, 3–5, 15, 21, and 23, and group 3 consists of the samples 6, 9–11, 19, and 20. Average values of the major oxides for these three groups of the Cheb Basin moldavites (MCB), together with values for moldavites from other substrewn fields, i.e., Radomilice (MR), Southern Bohemia (MSB) with a subgroup of the so-called “poisonous green” moldavites (MPG) (Bouška et al. 1990), Moravia (MM), Austria (MA) and Lusatia (ML) are presented in Table 3. Similarly, values for trace elements excluding the rare earth elements (REE) are given in Table 4. The values for the REE are given in Table 5 and the chondrite normalized REE patterns in the individual groups are depicted in Fig. 4.

The division of the studied samples has been based mainly on the Si/Al and Ca/Mg (Figs. 3a and 3d, respectively) ratios. The three groups differ from each other in Al contents, increasing in the order group 1 < group 2 < group 3. Silicon content in group 1 and group 2 is similar, whereas it is lower and more variable in group 3. The correlation between Si and Al is generally negative in the whole set with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios decreasing in the order group 1 > group 2 > group 3 (cf. Fig. 3a and Table 3). The division into three groups based on the Al content is yet more pronounced in a correlation between Al and the elements associated predominantly with Al in phyllosilicate minerals, such as Na, the REE, Ti, Cr, Fe, Sr, Ba, Ta and Th, etc. (see Table 2, and Figs. 3b and 3c for Ti and Ba, respectively, as illustrative examples of these correlations). Contents of these elements are significantly higher in group 2 and especially in group 3, not only compared to group 1, but also in comparison with other moldavites. The classification into the three groups is possible also on the basis of Ca, Mg and Mn contents (Figs. 3d–f), although this does not allow such a good distinction as the Al contents. With the highest CaO + MgO content, group 1 moldavites resemble the MPG moldavites. In the set of 23 MCB samples studied, the MPG-like samples make up more than 40%, in contrast to MSB with only ~2% of the “poisonous green” moldavites. Group 2 and group 3 samples are similar to typical MSB moldavites. With higher contents of Al, Na, Fe and of the majority of trace elements including the REE, group 3 data resemble also those of MM moldavites. However, they do not have the extremely low CaO + MgO content of MM (cf. Table 3). Barium and Sr contents in group 3 are the highest of all moldavites. All three groups have similar CaO/MgO ratios; however, two samples of group 1, MCB 13 and MCB 18, have somewhat higher values of the CaO/MgO ratio (1.84 and 1.72, respectively), resembling the rare subgroup of MPG, the so-called “HCa/Mg” moldavites, with a ratio of about 2 (Delano et al. 1988; Bouška et al. 1990). Within the individual groups, Mg is strongly

correlated with Mn in agreement with the data by Delano et al. 1988 (see Fig. 3e). The MgO/MnO ratios vary in the order group 1 > group 3 > group 2. As for the correlation between Mn and Fe, no correlations exist in group 2 and group 3, and in group 1 it is negative, as obvious from Fig. 3f. Contents of Na and K and their ratios provide also interesting information. Group 1 is characterized by an extremely high K/Na ratio given mainly by the lowest Na content of all three groups and generally higher K content. As already mentioned above, Na is strongly correlated with Al for the whole set (see Table 2). However, a possible correlation between K and Al, if at all, can be observed only within the individual groups (see Fig. 3g and Table 2). Similar patterns as that observed for K versus Al can be observed for the relations between Ca and Al (Fig. 3h), and between Mn and Al (Fig. 3i). Hence, in agreement with these correlations, K, Ca, Mg, and Mn are significantly positively correlated in group 2 and group 3, contrary to group 1 (see again Figs. 3d, 3e, 3j, and 3k). Potassium is highly correlated with Rb with a similar K/Rb ratio (230–260) in all MCB samples, which is significantly correlated with the K content (see Fig. 3l).

Source Materials of Moldavites

At present, the Ries crater is accepted without question as the parent impact structure to moldavites, above all due to a perfect coincidence of their ages, recently constrained to $\sim 14.3 \pm 0.2$ Ma (Laurenci et al. 2003; Buchner et al. 2003). Several facts support that the parent source materials were purely of terrestrial origin, e.g., the chondrite normalized REE patterns, contents of trace elements, and a high K/Na ratio in moldavites, which is similar to the ratio for soils originating from the Earth's crust (e.g., Bouška 1968; Bouška et al. 1973; Delano et al. 1988). The uppermost layer of pre-impact sedimentary rocks in the Ries region dated to the Middle Miocene, the so-called Upper Freshwater Molasse (Obere Süßwassermolasse, OSM), has frequently been suggested as a source material (e.g., Luft 1983; Engelhardt et al. 1987, 2005).

As documented by numerous papers (most recently, e.g., Engelhardt et al. [2005]), despite the close similarity of the chemical composition in terms of the major oxide contents (SiO_2 , $\text{Al}_2\text{O}_3 + \text{FeO}$, $\text{MgO} + \text{CaO}$) of moldavites with the sand samples collected from the surface and drill holes in the vicinity of the Ries impact structure (data for these samples plotted together with the MCB data in some of the graphs of Fig. 3), there are some significant differences in both major and trace element contents, which can be hardly assigned solely to the variability of sands or later influence of weathering processes. Some elements were enriched (e.g., K, Rb, Cs, Ba, and Sr), other elements were depleted (e.g., As, Br, Ga, P, Sb, Fe, Co, Ti, Cr, Se, Ta) in moldavites during the processes related to their formation, indicating that these processes must have involved chemical differentiation (e.g.,

Table 2. Correlation matrix for the elemental composition of the Cheb Basin moldavites (Pearson product-moment correlation coefficient, $r \times 100$).

	Na	Mg	Al	Si	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Zn	Rb	Sr	Zr	Cs	Ba	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Tm	Yb	Lu	Hf	Ta	Th					
Na	-																																						
Mg	-47	-																																					
Al	87	-40	-																																				
Si	-50	-40	-54	-																																			
K	-2	39	-8	-54	-																																		
Ca	-52	88	-47	-37	62	-																																	
Sc	83	-62	91	-27	-33	-68	-																																
Ti	84	-55	93	-33	-32	-66	97	-																															
V	65	-23	61	-61	37	-2	56	52	-																														
Cr	52	-48	51	-28	19	-28	64	55	81	-																													
Mn	-15	68	-31	-30	43	59	-49	-43	-21	-36	-																												
Fe	89	-54	92	-46	-3	-50	94	90	77	77	-41	-																											
Co	30	-20	24	-16	-1	-10	43	29	52	74	-2	48	-																										
Zn	-8	8	2	15	-27	-14	13	17	-12	7	6	-4	23	-																									
Rb	-12	36	-16	-43	97	59	-36	-36	35	25	40	-7	9	-19	-																								
Sr	91	-48	88	-44	-11	-54	88	86	53	54	-21	89	38	-3	-19	-																							
Zr	41	-28	46	5	-30	-45	50	47	-13	2	12	31	20	39	-32	51	-																						
Cs	45	-56	26	1	26	-41	35	31	45	67	1	45	49	7	36	38	21	-																					
Ba	95	-65	85	-30	-11	-65	87	85	56	56	-24	89	35	-8	-18	93	53	55	-																				
La	89	-52	91	-33	-22	-62	90	88	45	44	-19	84	31	12	-29	91	71	38	93	-																			
Ce	86	-56	87	-25	-25	-65	89	87	41	44	-19	82	35	15	-30	90	76	42	93	99	-																		
Nd	82	-57	85	-19	-26	-65	88	85	36	43	-22	79	33	18	-32	87	78	39	90	98	99	-																	
Sm	83	-58	87	-21	-25	-66	88	85	36	42	-21	79	29	14	-30	87	77	41	91	99	99	99	-																
Eu	82	-63	89	-19	-27	-71	92	88	36	44	-35	82	23	11	-32	89	71	37	90	96	97	98	-																
Gd	75	-55	83	-16	-24	-64	87	83	33	44	-23	76	33	26	-27	85	81	41	86	95	97	97	98	-															
Tb	80	-52	85	-24	-19	-61	84	81	36	39	-17	76	30	13	-23	84	79	41	87	96	97	96	98	95	96	-													
Dy	60	-41	70	-25	12	-35	64	64	52	52	-20	68	27	6	13	62	40	51	66	67	68	68	68	67	70	71	-												
Ho	32	-11	49	-20	-19	-15	44	41	22	11	-1	35	24	15	-22	36	58	-1	36	59	58	61	60	50	56	65	38	-											
Tm	68	-38	79	-35	-2	-42	77	71	43	51	-10	73	38	17	-5	76	66	42	76	85	85	86	84	86	84	86	87	65	56	-									
Yb	62	-43	70	-15	-19	-50	70	64	23	30	-3	59	33	19	-22	72	86	35	73	88	90	91	92	85	91	92	59	74	83	-									
Lu	54	-42	61	-14	-4	-44	61	53	21	33	-2	52	27	21	-8	64	79	40	67	78	80	82	82	78	83	79	53	54	80	90	-								
Hf	30	-16	47	5	-45	-39	48	46	-16	-10	3	24	8	49	-47	40	89	-5	38	66	69	71	71	65	74	71	31	71	61	83	73	-							
Ta	84	-50	89	-37	-11	-52	93	87	59	67	-27	93	56	11	-14	90	59	44	89	91	92	90	89	89	90	87	72	46	82	77	70	49	-						
Th	89	-56	89	-28	-25	-65	90	88	43	44	-20	83	32	13	-31	91	71	41	94	99	99	98	99	96	95	95	67	56	82	87	78	65	91	-					
U	-5	0	-9	17	-5	-4	2	-3	18	38	-6	56	67	8	-1	50	44	4	15	22	22	23	20	6	27	23	15	34	23	40	36	45	17	18	-				

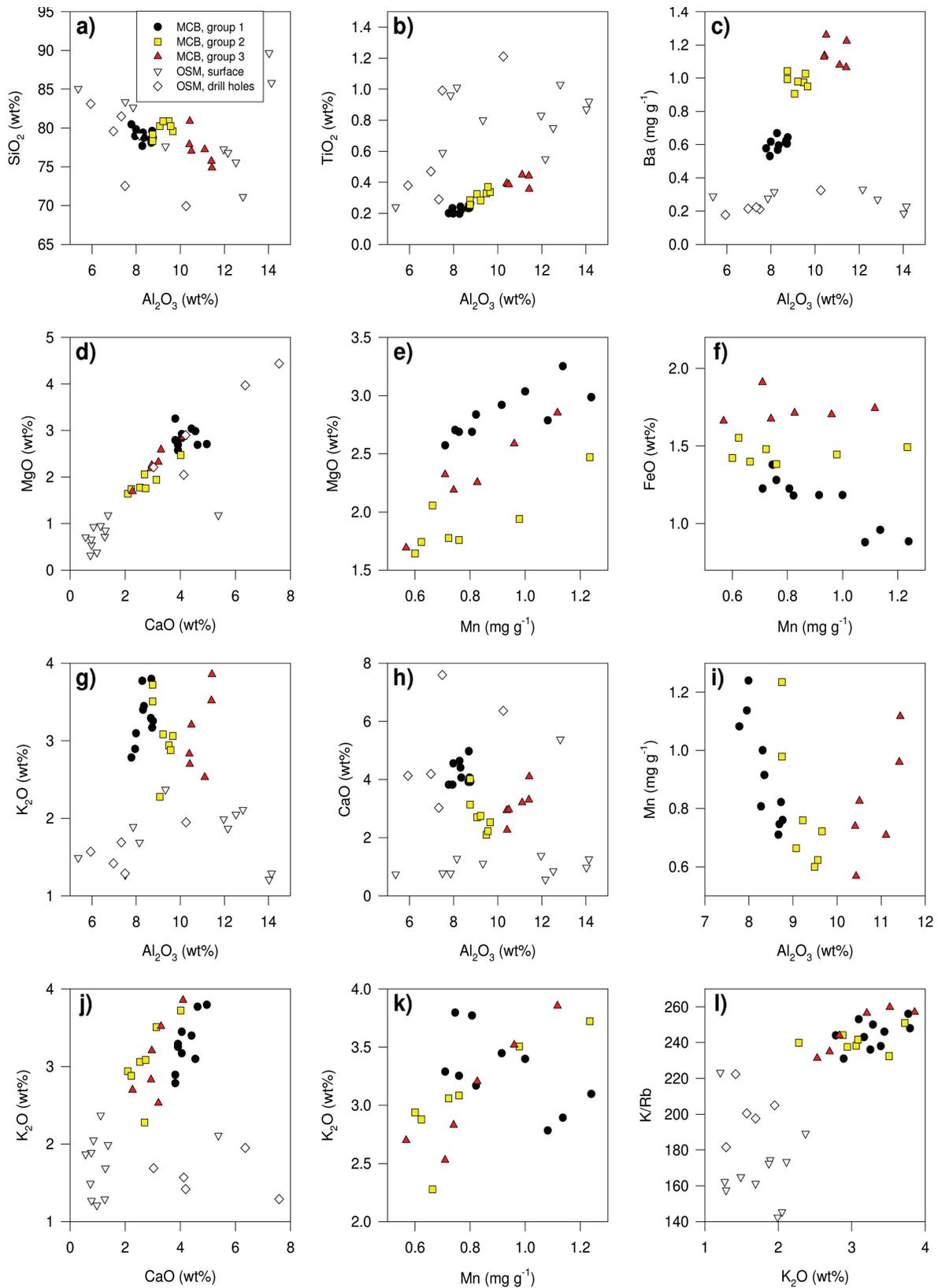


Fig. 3. Correlation between selected elements in moldavites from the Cheb Basin and the Obere Süßwassermolasse (OSM) sediments (data taken from Engelhardt et al. 2005): a) Si versus Al; b) Ti versus Al; c) Ba versus Al; d) Mg versus Ca; e) Mg versus Mn; f) Fe versus Mn; g) K versus Al; h) Ca versus Al; i) Mn versus Al; j) K versus Ca; k) K versus Mn; l) K/Rb versus K.

Table 3. Comparison of chemical composition of moldavites from the Cheb Basin with moldavites from other substrewn fields (average wt% from *n* samples, or dimensionless ratio).

Reference	Strewn field ^a							
	MCB		MPG	MR	MSB	MM	ML	MA
Oxide	This work ^b		Bouška et al. (1990)	Bouška (1992)	Bouška (1992)	Bouška (1992)	Lange (1996)	Koerberl et al. (1998)
	Group 1 (<i>n</i> = 10)	Group 2 (<i>n</i> = 7)	Group 3 (<i>n</i> = 6)	<i>n</i> = 13	<i>n</i> = 93	<i>n</i> = 45	<i>n</i> = 15	<i>n</i> = 7
SiO ₂	79.0 ± 0.8	79.9 ± 0.9	77.3 ± 2.1	83.2	80.0	79.3	79.3	79.7
TiO ₂	0.23 ± 0.02	0.31 ± 0.04	0.40 ± 0.04	0.30	0.33	0.40	0.34	0.30
Al ₂ O ₃	8.35 ± 0.36	9.21 ± 0.37	10.9 ± 0.5	8.04	9.95	10.86	10.5	9.81
FeO tot.	1.14 ± 0.17	1.45 ± 0.06	1.73 ± 0.09	1.35	1.81	2.18	1.84	1.54
MnO	0.12 ± 0.02	0.10 ± 0.03	0.11 ± 0.03	0.08	0.08	0.07	0.06	0.06
MgO	2.85 ± 0.20	1.91 ± 0.28	2.32 ± 0.39	1.89	1.97	1.31	1.75	1.72
CaO	4.21 ± 0.40	2.78 ± 0.64	3.13 ± 0.60	2.28	2.71	1.43	2.00	2.41
Na ₂ O	0.28 ± 0.03	0.51 ± 0.06	0.67 ± 0.11	0.29	0.46	0.54	0.47	0.39
K ₂ O	3.29 ± 0.33	3.07 ± 0.47	3.11 ± 0.51	2.41	3.38	3.39	3.46	3.49
Total	99.5	99.2	99.6	99.8	100.7	99.4	99.7	99.5
CaO + MgO	7.06	4.69	5.45	4.17	4.68	2.74	3.75	4.13
Ratio								
SiO ₂ /Al ₂ O ₃	9.46	8.68	7.09	10.4	8.04	7.30	7.55	8.12
CaO/MgO	1.48	1.46	1.35	1.21	1.38	1.09	1.14	1.40
MgO/MnO	23.8	19.1	21.1	23.6	24.6	18.7	29.2	28.7
K ₂ O/Na ₂ O	11.8	6.02	4.64	8.31	7.43	6.28	7.36	8.95
K ₂ O/CaO	0.78	1.10	0.99	1.06	1.25	2.37	1.73	1.45
Al ₂ O ₃ /CaO	1.98	3.31	3.48	3.53	3.67	7.59	5.25	4.07

^aMCB—Cheb Basin, MPG—“poisonous green” moldavites, MR—Radomilice, MSB—Southern Bohemia, MM—Moravia, ML—Lusatia, MA—Austria.

^bSample standard deviation (1s) is given.

Table 4. Trace element (excluding the REE) contents in moldavites from the Cheb Basin and comparison with moldavites from other substrewn fields (average $\mu\text{g g}^{-1}$ from n samples).

Strewn field ^a		MPG	MR	MSB	MM	ML	MA		
Reference	MCB		Bouška et al. (1990)	Bouška (1992) Řanda (1989)	Bouška (1992) Řanda (1989)	Řanda (1989)	Lange (1995)	Koeberl et al. (1988)	
	Group 1 ($n = 10$)	Group 2 ($n = 7$)	Group 3 ($n = 6$)	$n = 13$	$n = 93$	$n = 45$	$n = 1$	$n = 10$	$n = 5$
Sc	3.58 ± 0.32	4.86 ± 0.41	5.95 ± 0.55	4.32	4.91	6.23	4.65	5.3	5.14
V	23.0 ± 4.3	26.2 ± 1.8	27.9 ± 3.7	—	—	—	—	—	—
Cr	17.4 ± 2.7	20.5 ± 1.6	20.4 ± 2.1	20.7	24.3	29.6	30.5	33.3	30.5
Mn	922 ± 184	798 ± 230	820 ± 195	—	—	—	—	382	531
Co	4.31 ± 0.35	4.69 ± 0.47	4.66 ± 0.57	4.5	4.7	5.6	6.09	6.57	6.32
Ni	11.9 ± 3.1	<19	<21	—	31.3	23.1	30	27.6	18
Zn	63.9 ± 53.8	65.7 ± 16.9	69.4 ± 34.5	31.7	26.7	32.0	20	13.0	14
As	<0.4–0.4	<0.7	<0.6–0.89	<0.6–0.89	0.39	—	0.5	—	0.15
Rb	112 ± 10	106 ± 16	104 ± 13	103	120	141	121	121	148
Sr	106 ± 14	150 ± 13	195 ± 7	133.6	129.7	118.6	175	125	135
Zr	241 ± 30	261 ± 24	285 ± 23	333	339	363	300	211	253
Sb	0.60 ± 1.41	0.12 ± 0.06	<0.06–0.48	0.16	0.15	0.24	0.41	0.086	0.7
Cs	12.7 ± 1.2	18.2 ± 3.6	15.1 ± 1.1	12.5	13.1	13.9	10.8	13.2	15.1
Ba	604 ± 39	982 ± 46	1149 ± 78	602	733	789	743	754	668
Hf	5.46 ± 0.69	5.71 ± 0.70	6.41 ± 0.60	6.0	5.7	7.0	6.44	6.59	6.72
Ta	0.47 ± 0.02	0.54 ± 0.02	0.61 ± 0.03	0.64	0.64	0.79	0.64	0.775	0.76
Ir	<0.0009	<0.0009	<0.0011	<0.0011	—	—	<0.01	—	<0.001
Th	8.78 ± 0.52	12.0 ± 0.7	14.3 ± 0.8	9.78	10.1	12.0	10.6	11.8	11.1
U	2.98 ± 0.50	3.23 ± 0.29	3.00 ± 0.39	3.39	2.67	2.65	3.6	2.77	2.49

^aMCB—Cheb Basin, MPG—“poisonous green” moldavites, MR—Radomilice, MSB—southern Bohemia, MM—Moravia, ML—Lusatia, MA—Austria.

^bSample standard deviation (1 σ) is given.

Table 5. REE abundances in moldavites from the Cheb Basin and comparison with moldavites from other substrewn fields (average $\mu\text{g g}^{-1}$ from n samples).

Reference	Strewn field ^a		MPG	MR	MSB	MM	ML	MA	
	Group 1 ($n = 10$)	Group 2 ($n = 7$)	Bouška et al. (1990)	Bouška (1992) Řanda (1989)	Bouška (1992) Řanda (1989)	Bouška (1992) Řanda (1989)	Řanda (1989)	Lange (1995)	
Element	Group 1 ($n = 10$)	Group 2 ($n = 7$)	Group 3 ($n = 6$)	$n = 13$	$n = 93$	$n = 45$	$n = 1$	$n = 10$	$n = 5$
La	23.2 ± 0.9	29.5 ± 1.6	34.8 ± 1.9	25.8	26.2	31.6	26.0	30.4	26.6
Ce	44.2 ± 2.3	57.0 ± 3.4	66.3 ± 3.7	55.9	56.2	68.3	57.9	60.7	60.6
Nd	19.3 ± 1.2	25.0 ± 2.3	29.0 ± 2.0	25.3	25.7	30.6	27.0	25.2	27.2
Sm	3.8 ± 0.2	4.78 ± 0.35	5.46 ± 0.33	4.28	4.39	5.35	5.2	5.62	5.07
Eu	0.77 ± 0.02	0.94 ± 0.08	1.07 ± 0.05	0.85	0.91	1.05	0.80	0.80	0.98
Gd	3.16 ± 0.17	3.73 ± 0.29	4.20 ± 0.24	4.7	5.2	5.6	4.8	5.5	4.24
Tb	0.45 ± 0.02	0.53 ± 0.03	0.60 ± 0.04	0.50	0.52	0.60	0.45	0.67	0.73
Dy	3.44 ± 0.50	3.90 ± 0.42	4.28 ± 0.19	—	—	—	—	—	4.13
Ho	0.57 ± 0.08	0.61 ± 0.10	0.68 ± 0.14	0.78	0.84	1.02	1.0	$0.52 (n=1)$	0.85
Tm	0.26 ± 0.02	0.29 ± 0.03	0.33 ± 0.03	0.27	0.28	0.34	0.26	0.27	0.36
Yb	1.33 ± 0.07	1.50 ± 0.13	1.61 ± 0.12	1.49	1.59	1.85	1.65	1.92	2.16
Lu	0.23 ± 0.05	0.24 ± 0.03	0.25 ± 0.01	0.24	0.26	0.32	0.23	0.31	0.31

^aMCB—Cheb Basin, MPG—“poisonous green” moldavites, MR—Radomilice, MSB—southern Bohemia, MM—Moravia, ML—Lusatia, MA—Austria.

^bSample standard deviation (1s) is given.

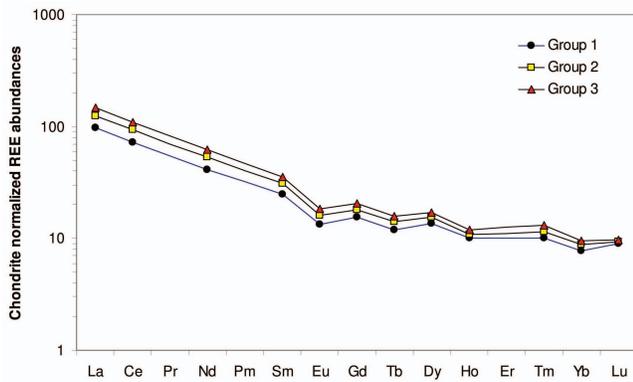


Fig. 4. Chondrite (C1) normalized average REE pattern for the three groups of the Cheb Basin moldavites (data for chondrites taken from Sun and McDonough 1989).

Engelhardt et al. 2005; Trnka and Houzar 2002). Fractional vaporization as a mechanism of differentiation has been suggested already by several authors (Konta 1972; Konta and Mráz 1975; Engelhardt et al. 1987). However, this model contradicts the enrichment of moldavites in the volatile elements K, Rb, and Cs (Engelhardt et al. 2005) and a significant correlation between volatile alkali elements Na, K, and Rb and refractory elements Sr, Mg, Al, and Ti (Delano and Lindsley 1982; Delano et al. 1988). Engelhardt et al. (2005) noticed that the ratios of average abundances of 28 elements in moldavites to their average abundances in OSM sands are significantly correlated with their ionic radii. They have proposed a theory for the formation of moldavites as early condensates from plasma generated at the impact from the source materials, in which large ions were preferentially trapped (see below for further discussion of this theory).

From a poor correlation between Fe and Mn in moldavites, Delano et al. (1988) suggested that these elements were in different valence states in the pre-impact source materials (i.e., Fe^{III} and Mn^{II}). When both elements occur in the same valence state (2+) in geological samples, they are usually highly correlated, which is not the case in moldavites. In moldavites, Fe^{II} predominates over Fe^{III} (Fe^{III}/ΣFe ratio is 0.13 in MM, 0.17 in MSB, 0.25 in MR according to Trnka and Houzar [2002]; a value of 0.06 for a MSB moldavite from Jankov was reported by Dunlap et al. [1998]), although in the parent source material (clays) the oxidized state Fe^{III} must have been present. Delano et al. (1988) pointed out also the consistently lower TiO₂/Al₂O₃ ratios in moldavites compared to the OSM sediments indicating that other, non-carbonate components, in addition to OSM, must have contributed to the source materials. According to, e.g., Spears and Kanaris-Sotiriou (1976), the TiO₂/Al₂O₃ ratio in sediments is directly proportional to the quartz/clay mineral ratio. Based on statistical analysis (R-mode factor analysis) of a large set of analytical data for all elements determined in

moldavites, Delano et al. (1988) assigned three main types of the sand-dominated sediments: fine quartz sands, clay and clayey soil, and carbonates of Ca and Mg.

Quartz, clays and carbonates as the only moldavite source materials do not explain sufficiently the high K/Na ratios found in moldavites and the positive correlations of K with Ca, Mg, and Mn discussed above for the MCB data. Although Na is leached off by rain water and K is retained due to sorption (ion exchange) of K⁺ on clays and soil organic matter, as follows from a negative correlation of K with the main clay components (Si, Al) and majority of trace elements associated with clays (Sc, REE, Zr, Hf, Th, etc.), another source material must have contributed to the extremely high content of K in moldavites. This is supported also by the K/Rb ratios, which are systematically higher in moldavites (200–260) than in OSM sediments (174—sands from surface, 201—sands from drill holes, 152—clays from surface; averages calculated for the data of Engelhardt et al. [2005]) and are positively correlated with K content (see Fig. 3). Possibly, and as discussed in the following section, K originating from burned organic matter (trees, shrubs) should be considered as an indispensable component of the moldavite source material. Vascular plants are characterized by a strong enrichment of K over Na and Rb, as well as high contents of Ca, Mg, and Mn as the major ash constituents. Based on several literature sources (Misra et al. 1993; Lioudakis et al. 2005; Kabata-Pendias and Pendias 2001) and our unpublished experimental data, we can present typical concentration ranges of these elements in ash (in wt%): Na 0.1–2.3, K 4–18, Rb 0.005–0.01, Mg 2–10, Ca 15–37, Mn 0.1–4. Assuming an impact area of about 2 × 10⁶ m² (see the next section) and the surface density of dendromass (both living and dead including substrate) estimated at 10⁶ kg per hectare (10⁴ m²), the total organic mass possibly contributing to the precursor materials for the tektites could have been 2 × 10⁸ kg which corresponds to 6 × 10⁶ kg of ash assuming an average wood ash yield of 3 wt% (Lioudakis et al. 2005). This is a conservative estimate based on the data available for the oldest virgin forest in Southern Bohemia (Vrška et al. 2001); at the warm and humid climate of the Middle Miocene ages with the mixed mesophytic forests characterized by a great variety of species dominated by Laureaceae and Mastixioideae species and giant Gymnosperm trees (Mai 1995), these values could be much higher.

From the above discussion, we have attempted to roughly estimate proportions of the individual components of the source materials for moldavites. We suggest that these materials were soils composed of quartz, fine-grained (~10⁻² mm) clay minerals such as hydromicas (e.g., illite), Ca and Mg carbonates, and organic matter including both soil organic matter and biomass. If we consider Al as the characteristic and determining component of clays, then with an average content of Al₂O₃ in illites of 25 wt% (Vejsada et al. 2005), the Al₂O₃ content of about 9 wt% in moldavites

corresponds to ~36% clay component. Assuming a typical SiO₂ content of 50 wt% in the considered clay, about 18% of moldavite matter is covered by SiO₂ from phyllosilicates. Thus, with the typical SiO₂ content in moldavites >78 wt%, the quartz component can be estimated at >60%. The rest (<4%) is contributed mainly by the carbonates and the ash produced from the total organic matter. The above estimated proportion of ash in the moldavite source materials corresponds roughly with the differences of K/Rb ratios in moldavites and OSM sediments.

Significant differences in abundance of the individual components of the source material can be observed not only between moldavite samples from the separate substrewn fields, but also within one group. As shown by the analytical data presented and commented in the previous section, within the MCB moldavites differentiation is quite pronounced.

The Zr/Hf ratio is virtually the same for all samples, about 45, which is typical for zircon. An accessory component of heavy minerals (zircon, rutile, etc.) at a 10⁻² % level was probably present in the source materials. Practically no occurrence of Ir (at sub-ng g⁻¹ level) and a very low Ni content in moldavites (see, e.g., Tables 1 and 4; Řanda 1989; Koeberl et al. 1988) provide evidence that moldavites were not contaminated by extraterrestrial matter derived from the impactor.

In comparison with moldavites from the other substrewn fields, group 1 has the lowest content of Al₂O₃, FeO and other major and trace elements, such as Na, Sc, Ti, Cr, Sr, Ba, REE, Ta, and Th, similar to the MR moldavites. This indicates that the clay component was lowest in the source materials of both groups. While in MR the lower clay component corresponds with a significantly higher quartz component compared to other moldavites, in MCB group 1 the SiO₂ content is similar to other moldavites, whereas the higher CaO + MgO (and MnO) contents similar to the MPG moldavites point to a significant presence of Mg/Ca/Mn carbonates and/or ash in their source materials. The lack of any correlation between Mg and Ca in group 1 could be assigned to a non-uniform source carbonate component (e.g., dolomite, dolomitic limestone, limestone, marly limestone) and/or various mixing ratios between carbonate and ash indicated by a great span of K₂O values and the highest K₂O/Na₂O ratio of all moldavites.

Group 2, with an intermediate content of Al₂O₃ as well as of all elements associated with phyllosilicates, with the highest SiO₂ and the lowest CaO + MgO contents, may represent a group of moldavites with the most pronounced signature of the ash component. Although the effect of the ash component is difficult to distinguish from the association of K, Ca, Mg, and Mn with clay, the significant positive correlations within this group of elements and simultaneously their negative correlation with Al₂O₃ indicates that the enhanced levels of K, Ca, Mg, and Mn could be attributed to the ash component. Association of these elements with carbonates can be excluded because of the minor contents of K and Mn in all common

carbonates (Bowen 1979; Govindaraju 1994). When we calculate roughly the differences between the lowest and the highest levels of K, Ca, Mg, and Mn found in the MCB moldavites (wt%: K ~1, Ca ~2.1, Mg ~1, Mn ~0.06) and compare them with the above given typical values for ash, we can see that the ratios between the elements are similar and the highest contents of the elements allow to estimate the ash contribution in the source materials at up to 10%.

The source materials for group 3 moldavites characterized by the highest contents of Al₂O₃ (and associated elements) and the lowest SiO₂ contents of all known moldavites were no doubt dominated by the clay component. Contrary to group 2, the moderate correlations of K, Ca, Mg, and Mn with Al₂O₃ are generally positive. The rather high Ba contents correspond well with the higher cation exchange selectivity of clays for Ba²⁺ over Ca²⁺ and Mg²⁺ (Pichtel et al. 2000), although a preferential association with ash at lower Al₂O₃ levels is also probable due to common accumulation of Ba in plants (according to Kabata-Pendias and Pendias [2001], Ba concentrations >1 wt% have been reported in different trees and shrubs).

Processes Leading to Formation of Moldavites

First studies attempting to reconstruct the Ries impact and the related ejection mechanics of moldavites appeared already in the 1960s (Vand 1962; David 1966). Later, several theoretical energy-scaling law models were developed providing estimates of the amount of melt and vapor produced upon an impact by shock compression and release (O'Keefe and Ahrens 1977, 1994; Cintala and Grieve 1994; Pierazzo et al. 1997; Koeberl 1994). The most advanced 3D hydrocode modeling allows for simulation of oblique impacts (Pierazzo and Melosh 2000). Numerical modeling of the Ries-Steinheim impact and formation of the moldavite strewn field using detailed geological, petrographic, geochemical, and geographical constraints was performed by Stöffler et al. (2002); a series of 3-D hydrocode simulations was followed by separate modeling of the motion of tektites through the atmosphere.

The hydrocode simulation does not answer directly the geochemical aspects of formation of tektites. Recently, Engelhardt et al. (2005) presented a hypothesis of formation of moldavites as condensates from vaporized OSM sands (see also the previous section). To explain the chemical differentiation in moldavites, they proposed formation of a highly dissociated phase, a plasma containing free ions. The small-scale inhomogeneities of moldavites including schlieren and lechatelierite were interpreted as relics of chemically different precursors accumulated to larger bodies at temperature too low for mixing and shaped under conditions of laminar flow and compressional stress. In our opinion, this theory is questionable. Numerous deviations in the proposed correlation between the OSM sands/moldavites

distribution of elements and their ionic radii, as well as the existing correlations in moldavite samples (alkali and alkali earth elements versus Al) have been underrated. The theory has been contradicted also by several other well known facts. Although Engelhardt et al. (2005), similarly to, e.g., Delano and Lindsley (1982), reject the differentiation by selective vaporization as it is contradicted by the fact that significant losses of volatile species do not occur, their theory has been based mainly on the vaporization-condensation processes. The proposed mechanism of formation of larger moldavite bodies by coalescence of small condensed primary units during their transport ignores not only the particle size distribution assumed by the latest models of tektite production (e.g., Stöffler et al. 2002), but also basic mechanical and ballistic principles. By coalescing in an expanding cloud the particles would gradually lose their initial kinetic energy, which contradicts the fact that larger moldavites occur more distant from the Ries crater—cf. MM and MSB moldavites (Bouška 1994; Trnka and Houzar 2002). It is improbable that such a mechanism would produce bodies reaching the original size (before corrosion) of moldavites. Finally, the mechanism is inconsistent with the existence of bubbles found in moldavites, the properties (composition and pressure of gas inside the bubbles) of which have also been used to reconstruct the thermal and flight history of moldavites (e.g., Dolgov et al. 1969; Trnka and Houzar 2002).

The latest simulations of the Ries-Steinheim impact (Stöffler et al. 2002) provide convincing results, whereby the calculated distribution of moldavites is only slightly different from the known distribution. However, there are several aspects which have been ignored or neglected by the hydrocode models, namely processes of atmospheric heating and radiation emitted during the flight of the large cosmic body. Although sophisticated numerical modeling would be required to solve appropriate state or radiation transfer equations (Nemtschinov et al. 1994), we have attempted, in a first approximation, to outline the so far neglected early processes together with their effect on formation and geochemistry of moldavites. We have started from these facts:

- The Ries crater is the parent crater of moldavites.
- The geochemical constraints on the moldavite source materials demand contributions from terrestrial sedimentary rocks, namely quartz sands, clays and Ca/Mg carbonates.
- There is none or insignificant contamination of moldavites by extraterrestrial matter of the impactor.
- The distance of the moldavite substrewn fields from the source crater ranges from ~200 km (MCB) to 450 km (MM).
- There is negligible content of water in moldavites, usually <0.01 wt%.
- There are abundant signs of atmospheric ablation, as well as for intense and short heating followed by cooling (presence of lechatelierites, imperfectly melted grains of SiO₂).

- Strong friction was involved during melting of source materials (schlieren, form of elongated lechatelierites, layering of the moldavite glass).
- Conditions during the impact processes were reduced (predominance of Fe^{II} in moldavites v. Fe^{III} in clays, reducing gasses H₂, CO, H₂S in bubbles present in tektites).
- High K/Na ratios are found in moldavites.

According to Stöffler et al. (2002), the Ries event was part of the impact of a binary asteroid consisting of two bodies, one with 1.5 km diameter producing the Ries crater with a diameter of 25 km (although, a smaller body, 300–500 m, has been suggested in previous studies, e.g., Řanda 1989), the other one with 0.15 km diameter producing the Steinheim crater with a diameter of 4 km, situated 42 km southwest of the Ries crater.

When we assume that the Ries crater was produced by an impactor with a diameter of 1.5 km, the corresponding mass of such an impacting body with spherical or similar shape is 6.4×10^{12} kg (the density for a chondrite is about 3.6×10^3 kg m⁻³). The kinetic energy corresponding to a velocity of 20 km s⁻¹ (for a body with a retrograde orbit up to 70 km s⁻¹) can be estimated at 1.3×10^{21} J, corresponding to 3×10^8 kt TNT. An impactor with such a large diameter acts as a piston (in contrast to small bodies or space vehicles, where atmospheric gasses escape from the front to edges) and imparts its velocity (20 km s⁻¹) to air molecules, at its front. From the general gas law it follows that the temperature of the plasma at the projectile front would be 4.5×10^5 K (Řanda 1989). Although the plasma does not correspond to an ideal gas, the temperature will reach extreme values. Emitted radiation is proportionate to T⁴ according to the Stefan-Boltzmann law, and for the impactor's front area of $\sim 2 \times 10^6$ m², an impact angle of 30° (the best case scenario for tektite production, Stöffler et al. 2002) and the mass of pressurized atmospheric gasses about 3.5×10^{10} kg, it is possible to estimate the radiation energy released within the last hundreds of meters of flight at 10^{15} J, equivalent to 250 kt TNT. The total kinetic energy of the gasses (plasma) in the front wave can be estimated at 7×10^{18} J, equivalent to 1.7×10^6 kt TNT. The energy of the glowing plasma is partially spent for dissociation of molecules of nitrogen (main component of the atmosphere) and mainly for ionization of nitrogen atoms; however, this spent energy is subsequently released due to recombination of ions during the stage of adiabatic expansion and cooling of the recoiled plasma. Although the kinetic energy of the plasma corresponds to only less than 1% of the impactor's kinetic energy, the energy contained in the gas mass, and thus also the energy emitted, reach enormous values, even in the case that a part of the plasma generated in front of the projectile escapes at the sides of the impactor. The immediately pre-impact thermal conditions must have been similar to conditions of a nuclear explosion in air.

As discussed in the previous section, it is highly probable

that a substantial mass of organic matter, such as trees and other plants, as well as soil organic matter, occurred at the impact site and in its vicinity, which must have been ignited and immediately burned under the above extreme conditions (Nemtschinov et al. 1994). The burned organic carbon reacted with water and atmospheric gasses resulting in CO and H₂. This possibility is supported by the composition of the gas trapped in bubbles inside moldavites, where the gasses CO₂, H₂, CO, and H₂S predominate (Dolgov et al. 1969; Bouška 1992). Together with depletion in oxygen consumed for burning, the presence of the reduction gasses led to strongly reduced conditions explaining, e.g., the predominance of Fe^{II} over Fe^{III} in moldavites, which can be hardly caused solely by the inherently reducing nature of the isentropic cooling path (Sheffer and Melosh 2005; Sheffer et al. 2006). Further, due to the energy emitted by the glowing plasma, just before a transversal impact of the body, surface layers of the sandy-clay sediments in the epicenter of the future crater were intensively pre-heated or even partially melted. Melting could be promoted if substantial amounts of K₂CO₃ and CaCO₃ were produced from the burned organic matter and acted as flux agents.

Before contact of the impactor with the surface, a shock wave of the glowing plasma with a pressure reaching 10¹–10² GPa caused complete melting and partly also vaporization of surface sediments, followed by their ejection with a velocity estimated at up to 10 km s⁻¹ to the upper atmospheric layers (>50 km) in direction of the trajectory of the impacting body, without contamination of the melt—future moldavites—by meteoritic matter (Pierazzo and Melosh 2000; Stöffler et al. 2002). During this process, volatile components such as water (including that which was chemically bound), chlorides, N, S, B, P, As, etc., were evaporated. It cannot be excluded that volatile carbonyls of Cr, Fe, Ni were formed in the presence of CO under these extreme P-T conditions. This would explain why contents of these components are depleted. Recoiled plasma picking up the moldavites was quickly decompressed and due to an adiabatic process also quickly cooled (>70 K s⁻¹, cooling rate inside tektites was about ten times lower—Trnka and Houzar 2002). During the first parts of a second after the contact of the impactor with the surface, these processes resulted in expanding the plasma carrying moldavites in a cone space centered around the recoil trajectory. That is why the fan of known substrewn fields extends to about 60° (75° according to the hydrocode simulation by Stöffler et al. 2002). Many facts, such as the relatively homogeneous composition of the moldavite glass with the presence of incompletely melted grains of SiO₂—lechatelierites—show that the temperature of the melt could have been between 1200 and 2000°C, and the heating process was very short. Although no microtektites associated with the Ries impact have been found, likely due to their complete loss by weathering, they must have been formed by condensation and spraying of vapors and melt, respectively, produced from the source material.

An explosion of the impactor in the deeper bedrock producing the crater with impact glasses and suevite breccias followed, at a time when the moldavites had already flown away beyond the reach of this explosion. We maintain that the partially different composition of moldavites from the different parts of the Central European strewn field is given by variable contents of the essential mineral components of the sedimentary source materials. Considering that the contact area is relatively small, in the order of 10⁶ m², it seems logical to assume that these differences in composition were mainly in vertical direction. The geochemical differences between moldavites from the individual substrewn fields could be attributed also to the development of the impact process. The MCB moldavites situated closest to the Ries crater may have been produced from the uppermost organic-rich soil layer at initial stages, the ML and MM moldavites, which are most distant from the Ries crater, originated subsequently from deeper clay-rich sediment layers depleted in organic matter.

CONCLUSIONS

In 1993, a new moldavite locality was discovered in the Cheb Basin in Western Bohemia, Czech Republic, where several thousand moldavites have been found so far. Twenty-three samples of moldavites from this locality were analyzed by INAA for their abundances of 45 major and trace elements, and the results are compared with compositions of moldavites from other parts of the Central European tektite strewn field, i.e., Southern Bohemia and its substrewn field Radomilice, Moravia, Austria, and Lusatia.

On the basis of these INAA results and correlation analysis, the new data set must be split into three different groups. Ten samples of group 1 are characterized by a comparatively higher sum of CaO + MgO and the lowest FeO content of all moldavites, and resemble the “poisonous green” subgroup of the Southern Bohemia moldavites. Carbonates must have significantly contributed to the source materials of these moldavites. Thirteen samples of group 2 and group 3 are similar to typical moldavites from Southern Bohemia, however, with higher contents of the elements associated with phyllosilicate (clay) minerals (namely Ba and Sr), group 3 resembles also the Moravian moldavites. Group 2 may represent samples with the most pronounced signature of the ash component due to significant positive correlations between K, Ca, Mg, and Mn. These elements are, on the other hand, negatively correlated with aluminum. However, the high ratios K/Na and K/Rb found in the other two groups as well as in all other moldavites support a component of the burned organic matter also in their source materials. Variation in composition of moldavites from the different substrewn fields as well as differentiation within the Cheb Basin group is discussed on the basis of variable contents of the essential mineral components of their source materials—quartz, clay minerals, Ca and Mg carbonates, and ash produced from burned organic matter.

We assume that the formation of moldavites by impact shock processes as recently simulated by hydrocode modeling was preceded by early processes including atmospheric heating and radiation emitted during the flight of the impactor. These processes must have led to burning of vegetation and partial melting of surface materials at the impact site. This participation of burned organic matter from the impact site in the formation of moldavites, a factor contributing to their composition, has so far not been considered. This factor could, among others, contribute to reduced conditions during the formation of moldavites.

From the data presented, we can conclude that the Cheb Basin represents an individual substrewn field, and that no two groups of moldavites from different substrewn fields are identical. From the wide fan of moldavite occurrences to individual substrewn fields situated at different distances from the Ries crater (Fig. 1), it is highly probable that in the future new localities bearing moldavites will be discovered within other areas of occurrence of Middle/Upper Miocene gravels in the Czech Republic.

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