LECHATELIERITE IN MOLDAVITE TEKTITES: NEW ANALYSES OF COMPOSITION. Martin Molnár¹, Stanislav Šlang², Karel Ventura³. Kord Ernstson⁴. Resselovo nám. 76, Chrudim 537 01, Czech Republic (molnar@ego93.com) ²Center of Materials and Nanotechnologies, University of Pardubice, 532 10 Pardubice, Czech Republic, stanislav.slang@upce.cz ³Faculty of Chemical Technology, University of Pardubice, 530 02 Pardubice, Czech Republic, karel.ventura@upce.cz. ⁴University of Würzburg, D-97074 Würzburg, Deutschland (kernstson@ernstson.de)

Introduction: Moldavites are tektites with a beautiful, mostly green discoloration and a very pronounced sculpture (Fig.1), which have been studied many times e.g. [1-3]).



Fig. 1. Moldavites from Besednice analyzed in this study. Scale bar 1 cm.

According to the most probable theory, they were formed 14.5 million years ago together with the Ries crater meteorite impact in Germany. They belong to the mid-European tektite strewn field and fell mostly in Bohemia. The prominent sculpture is considered the result of acidic waters in the ground having etched away the more alkaline parts of the moldavite and left lechatelierite inclusions as sharp edges and peaks. Originally, the curious pitting and wrinkles on the surfaces were compared to meteorite regmaglypts and the moldavites ascribed to a cosmic, meteorite origin (F.E. Suess 1900). Lechatelierite is amorphous SiO₂ silica glass and commonly forms at very high temperatures in lightning strike fulgurites and as a result of shock metamorphism during meteorite impact cratering. Authors [4, 5] state that it is 99% SiO₂based. A comparison reveals (Tab. 1):

	Refractive index	Density (g/cm ³)	Softening point (°C)		
pure SiO ₂ glass (1)	1,46	2,23	1610		
Lechatelierite (2)	1,462	2,2	1175		
Moldavite (3)	1,48 – 1,54	2,3 - 2,51	1295 – 1325		

Tab.1. Selected physical properties of pure SiO₂ glass, lechatelierite and moldavite. Sources [5-7].

While refractive index and density are very close to each other, the main difference lies in the temperatures of the softening point, which differs by more than 400 °C. This led to the question what is it that reduces the melting point so rigidly and increases acid resistance.

The conclusion from the present comparison is clear. Lechatelierite from moldavite is not a pure ${\rm SiO_2}$ glass. Here we report on experimental investigations that pursue this question and lead to new findings of the lechatelierite composition.

Experiments and Results: Experiments 1 and 2 - the boron question. The question of lowering the melting point and acid resistance led to the possibility of adding boron. The experiment 1 on a moldavite plate etched in 15%-HF to expose the lechatelierite was performed by laser ablation spectrometry and showed B₂O₃ concentration of >1%. In experiment 2, 38 g of lechatelierite fragments were then separated from 482 g of pure moldavite, and after the boron content remained high (Tab. 2), the remaining carbon was washed away. The analysis in Tab. 3 shows remaining low boron content, which is obviously bound to the carbon of the moldavites [8].

Concentration in mg/kg								
Li	В	Rb	Sr	Zr	Ce	Ba	Но	Bi
7.5±2.6	17066±1147	16.3±4.3	27.7±5.8	270±2	17.2±1.6	80±28	0.23±0.02	02:42±00:56

Tab. 2. Multi-element analysis of isolated lechatelierite, contaminated by carbon.

l	Konzentration in mg/kg											
	Mg	Ca	Na	K	Al	Li	В	Ti	Sr	Rb	La	Ce
	3710	790	706	7172	16792	8,3	134	1221	60	45,9	19,5	25,2

Tab. 3. Multi-element analysis of isolated lechatelierite after carbon separation.

Experiment 3 - EDS analysis of lechatelierite and embedding moldavite matter. In the SEM image of Fig. 2 measuring points and areas for EDS analyses have been marked, and the results for comparison are shown in Tab 4.

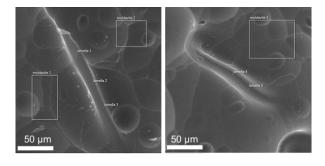


Fig. 2. SEM image of a carbon-coated moldavite specimen with marked measuring points in the area of the lamellae and the surrounding material.

The results show that the composition of the lamellae differs significantly from the surrounding moldavite. The moldavite material consists of

SiO₂with traces of Al, Mg, Na, K, Ca, Fe and in places a small amount of Ti. In the area of the lamellae the content of accompanying elements is significantly lower (close to the quantitative error limit of this method. Particularly significant in comparison is the high silicon content with an average Si:O ratio of 1.2 (0.42 in moldavite).

	Lech at.%	Mold. at.%
<u> </u>	Lecii at.76	moru. at.76
0	44.58	64.10
Na		0.22
Mg	0.20	1.30
ΑI	0.52	3.54
Si	54.08	27.08
K	0.27	1.66
Ca	0.20	1.54
Ti		0.06
Fe	0.17	0.56

Tab. 4. Results of the elementary EDS analysis of the carbon-coated moldavite specimen, mean values. Lech = Lechatelierite lamellae, 6 samples; Mold = moldavite material, 5 samples.

Experiment 4 - the condensation beaker method and the SiO question. A fireclay graphite beaker was filled with 20 g of concentrate of lechatelierite, which close together with an identical empty beaker was heated in a maximum sealed electric furnace for 1 hour to a temperature of 1670 °C (Fig. 3). After spontaneous cooling until the next day, the previously empty cup was lined with a white felted mass (Fig. 3), which was analyzed in the SEM (LYRA 3, Tescan) (Fig. 4)

For comparison we carried out a blind test with 20 g gravelly SiO₂ sand from the Střeleč quarry and with exactly the same experimental procedure of heating and cooling. After removal of the empty beaker, it did not even contain traces of a felt mass (Fig. 3).



Fig. 3. Condensation beaker after the lechatelierite experi-ment (left), condensation beaker after the Střeleč sand experiment (center), and experimental arrangement of the beakers in the CLASIC furnace (right).

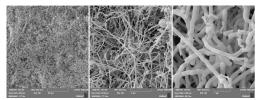


Fig. 4. SEM images of the felted material in increasing magnification.

Discussion: The experiments no. 1 and no. 2 excluded basic concentrations of light elements in lechatelierite, i.e. lithium, boron and beryllium. An interesting secondary finding was the fact that carbon inclusions in the moldavite contain up to 1.7% boron.

Experiment no. 3 showed that lechatelierite consists mainly of silicon and oxygen atoms. The molecular ratio of these elements is close to 1:1, which could indicate the presence of silicon monoxide (SiO). Silicon monoxide [e.g., 6] is a diatomic molecule in the gaseous state. It is the most common silicon oxide in space [7]. In the terrestrial environment, silicon monoxide forms a polymer (SiO)n, where n can be 2, 3, 4 or 5. The polymer forms closed circular structures. It is self-igniting and reacts with water. The melting point is 1,702 °C and the boiling point 1,880 °C. Due to the stability of lechatelierite it is therefore unlikely that it consists only of SiO glass. The ratio of Si:O = 1:1 can also be obtained by mixing silicon with silicon dioxide. This mixture reacts above 1,650 °C to form silicon monoxide SiO, which is volatile This was confirmed by our condensation beaker method, where at a temperature of 1,670 °C gaseous SiO escaped from the lechatelierite concentrate and condensed in the other beaker and oxidized to the characteristic SiO₂ fibers (Fig. 4). A blind test with pure SiO₂ under the same conditions proved that it is not substantially volatile and does not produce felted fibers in the accompanying beaker.

Conclusions: We suggest that lechatelierite consists of a mixture of SiO₂ glasses and Si glass (pure silicon). We attribute to this mixture the excellent acid resistance and, thanks to the eutectic of Si, SiO, the strongly reduced softening point of 1.175 °C of lechatelierite.

References: [1] Skála, R. et al (2016) J. Geosciences, 61, 171-191. [2] V. Bouška, V. (1994) Moldavites. The Czech Tektites. Stylizace, Prag. [3] Trnka, M. and Houzar, S. (2002). Bulletin of the Czech Geological Survey, 77, 283–302. [4] Kučera, J. and Knobloch, V. (1982) Radiochemical and Radioanalytical Letters, 54, 197-208. [5] Řanda, Z. et al. (2008) Meteoritics & Planetary Science, 43, 461–477. [6] Hohl, A. (2003) Untersuchungen zur Struktur von amorphem Siliziummonoxid. PhD thesis (in German), Darmstadt, Technical University. [7] Jutzi, P. and Schubert, U. (2003) Silicon chemistry: from the atom to extended systems. Wiley-VCH.