

## LECHATELIERITE-BEARING MICROSPHERULES FROM SEMICOKE HILL (KIVIÕLI, ESTONIA): CONTRIBUTION TO THE CONTAMINATION PROBLEM OF NATURAL MICROTEKTITES

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*During the course of the last hundred years, microscopic magnetite and glassy spherules of different genesis (extraterrestrial, volcanic, industrial, biogenic, diagenic, explosive, etc.) have often been found in various geological formations. Alongside classical geological methods, research into extraterrestrial and explosive spherules can provide valuable information and facilitates stratigraphical correlations over large areas. Several authors have recently stressed that studies on cosmic- and impact-related microspherules may seriously be hampered by outcrop- and laboratory contamination. Fly-ash particles and steel slags resembling iron-rich cosmic spheres are the most frequently invoked industrial contaminants. In contrast, little attention has been paid to glassy spherules of industrial origin that might resemble microtektites. Our finding of lechatelierite inclusions in obvious industrial provenance might cast serious doubts of the validity of the classical « Lechatelierite Criterion » as a test for impact glasses.*

### Introduction

Natural microtektites are small glass droplets derived from melting and quenching of terrestrial rocks during hypervelocity meteorite impacts on the Earth (see [1] and refs. therein). Most of these natural glass droplets occur in the form of microspherules ranging in size from 1mm to a few tens of micrometers (Fig. 1). In Kaali area (Island of Saaremaa, Estonia) both magnetite-silicate and silicate spherules were identified [2]. Silicate spherules are

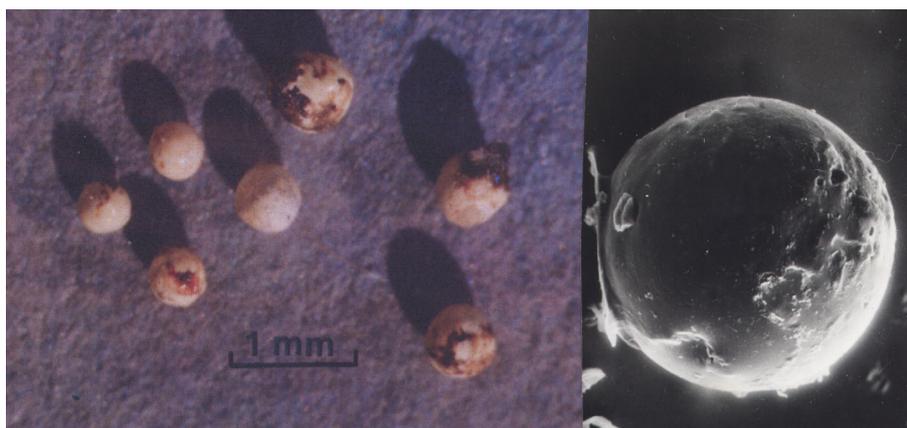
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primarily drop-like or rounded well-shaped, white, grey or light-beige to dark-brown globules. They have smooth lustrous surfaces and are sometimes hollow. The chemical composition of glassy microimpactites is diverse, being controlled by the mineralogy of the target rocks. Some spherules consist mainly of silica and calcium, others from calcium and iron, and a third set of silica with a small quantity of calcium. They contain specific for iron meteorites admixture of iron and nickel, sometimes also cobalt and several other elements. In some spherules Ni is practically absent, but in some pieces it is present in extremely high concentrations, almost equal to those of iron. Clear relationships between the morphology and chemical composition were not discovered.

However, a variety of industrial processes also may produce broadly similar glassy microspheres, and there still are risks in mistaking man-made products for natural microtektites. Moreover, industrial spherules may contaminate the natural glasses, both at the outcrop and during laboratory treatments [3–5].

In several papers we have demonstrated that investigation of impact spherules is a promising method for the correlation of Quaternary deposits and a good tool to estimate the age of impact craters [2, 6, 7]. To test the contamination potential we documented the occurrence of glassy microspherules resembling microtektites in solid residues of oil-shale retorting (semicoke heaps) in north-eastern Estonia near the town of Kiviõli. Surprisingly, these spherules exhibit conspicuous inclusions of lechatelierite (pure  $\text{SiO}_2$  glass). Such inclusions were previously considered typical of natural tektites and microtektites, in which they are believed to derive from shock-induced melting of quartz grains from the impacted rocks [8, 9]. Admittedly, lechatelierite inclusions have been taken as a criterion to distinguish natural glasses related to impacts from most common industrial glasses.



*Fig. 1.* Typical glassy spherules from the Piila Mire at a depth of 3.00 – 3.10 m accumulated during the Kaali impact.

## **Estonian oil shale deposit and shale oil processing**

World oil shales vary widely in their content and composition of organic compounds – kerogen. Presently there is no unanimously accepted limits of sapropelic organic matter percentage for oil shales. The lower limit varies from 5 to 10% and the upper limit from 60 to 70%. It is difficult to find two analogous oil shales, mainly because of their extremely variable deposition conditions as well as postsedimentation alterations. The Estonian kukersite oil shale seams contain organic matter, carbonate and clastic materials in various proportions. The carbonate material consists mainly of pore-filling micritic carbonate mud together with a variable content of fine to coarse skeletal debris. The carbonate content (mainly calcite) ranges in different kukersite seams from 20 to 70% and the organic matter content from 10–15 to 50–60%. The clastic matrix is composed mainly of silt-size quartz and illite, the minor clastic minerals are feldspars and chlorite, pyrite is a rather common authigenic mineral. The organic matter represents a mixture of high-molecular polyfunctional organic compounds, the real structure of which is yet a subject of studies.

At present oil shale is used for electricity generation in power plants, shale oil production and in small amounts also for cement production. Since the 1960s, Estonia has been the greatest oil-shale producer and consumer in the world. Up to 1960, the main oil shale consumers were the Kohtla-Järve and Kiviõli shale oil plants and the railway. Fine oil shale was used as a fuel at local power stations. Later large power stations using oil shale were launched in Narva – Balti Thermal Power Station in 1966 and Eesti Thermal Power Station in 1973. This altered the structure of oil shale consumption: about 80% of mined oil shale was used for producing energy. Oil shale production reached its peak in 1980, when 31.3 million tonnes was mined.

The total oil resource in the Estonian deposit amounts to 985.7 million tonnes [10]. Presently shale oil is mainly used for producing fuel oil, and small amounts go to the production of calcined petroleum coke and road asphalt. Also phenols, resins, glues, impregnators, tanning agents, mastic, and other products are produced. The composition of crude shale oil is distinguished by a high content of oxygen compounds in addition to aliphatic and aromatic hydrocarbons. During the last decades, two methods were used for shale oil processing. The Galoter or TSK-140 process with solid heat carrier in which poorer fine oil shale is used has lower environmental impacts but the technology needs improvement. The Kiviter process (vertical retorts with internal heating, some 1000 t oil shale per day) with the use of enriched oil shale ensures 15–17% oil yield. Unfortunately, large amounts of organic matter get lost with harmful semicoke, which accumulates in large waste piles (Fig. 2).



Fig. 2. Kiviõli semicoke pile in May 2001. Photo by A. Käärd.

### Sampling and description of semicoke spherules

The samples were taken from the top of the Kiviõli semicoke hill: a large heap towering over hundred meters above the surface (Fig. 2). The semicoke appears as blackish, coarse gravel sand (grain size: ca. 50 mm-10 microns) of high intergranular porosity. It mainly consists of fragments of carbonaceous matter, compound fragments (involving silt-sized admixtures of quartz-, phyllosilicate- and carbon- particles), broken carbonate fossil remnants, calcite and dolomite rhomboedrons, and detrital grains of quartz and feldspars (Fig. 3).

Oil shale semicoke is classified in Estonian and European Union waste lists as hazardous waste since it contains tarry and bituminous substances. Its chemical composition strongly resembles the composition of raw oil shale and contains high amounts (mg/kg) of Ca (about 250 000), Mg (9800–12 000), Fe (25 000–27 000), Al (12 000–16 000), K (7300–8800) and Na (990–1100), in less amounts Mn (190–230), Pb (39–45), As (about 10), Ba (44–54), Cr (16–18), Cu (7–10), Zn (12–13), Ni (16–17), Mo (3,9–4,5), Se (up to 9) and other elements [11].

The spherule content in the semicoke is comparatively high: over 5 spherules per gram after removal of the largest fragments. We found both opaque (Fe-oxide-) and transparent (silicate-) spherules (size range: 50–200 microns). Leaving aside the opaque spherules, and part of the transparent

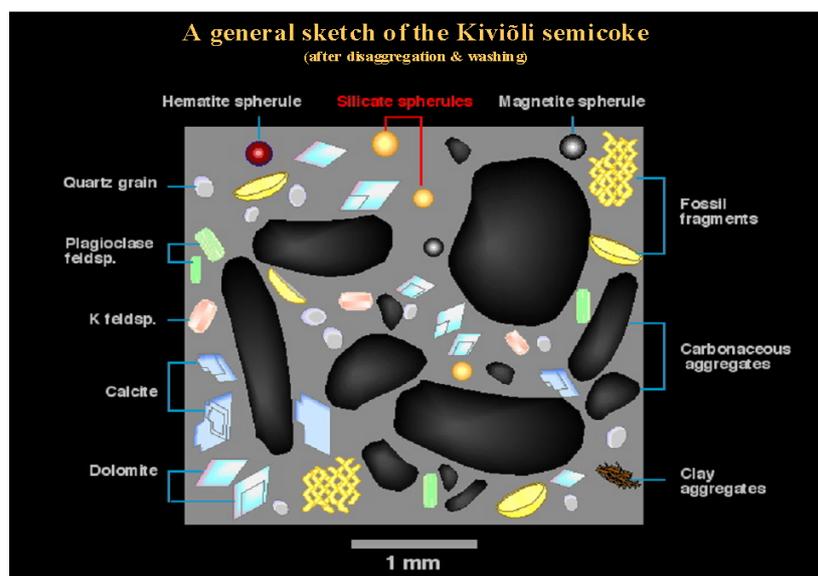


Fig. 3. A general sketch of the Kiviõli semicoke.

ones (rare colourless spherules of Si-rich silicate glass), we focused here on the dominant type: faint yellow spherules of Ca-Al silicate glass, thereafter quoted as the “Kiviõli spherules”.

Most of these spherules broadly resemble microtektites, although some may be distinguished readily by their higher content in gas vesicles. Hollow spheres are infrequent, in contrast to silicate coenospheres commonly found in fly ashes from coal power plants [12]. The main glassy component of the “Kiviõli spherules” falls within the compositional range of melilites, more precisely K-rich- Na-poor- melilites (see Table).

The salient feature of the Kiviõli spherules, however, is the general occurrence of unmixed silica remnants (5–15 microns). These can appear in all intermediate conditions, from unmelted quartz grains adhering to the surface of the spherules to rounded patches of completely melted silica (now lechatelierite). The same situation can be seen in section, from full quartz- to pure lechatelierite- inclusions (intermediate stages show lechatelierite embedding some relictual quartz). These observations are readily confirmed under electron probe: in stark contrast to the quartz remains, the lechatelierite glass is

Table. Faint yellow glas, from 71 selected WDS analyses. Camebax SX100. FeOT = Tot. Fe as FeO. Melilite range (wt%) from data in [13]

	Mean wt%	St. Dev.	Melilite Range		Mean wt%	St. Dev.	Melilite Range
SiO <sub>2</sub>	41.76	2.57	(44.1–37.8)	MgO	3.50	1.52	(9.43–3.12)
TiO <sub>2</sub>	0.66	0.33	(0.66–0.00)	CaO	32.2	5.07	(34.9–29.8)
Al <sub>2</sub> O <sub>3</sub>	11.30	1.53	(12.9–5.02)	Na <sub>2</sub> O	0.14	0.08	(5.27–2.83)
FeOT	4.98	1.82	(7.95–0.98)	K <sub>2</sub> O	2.86	1.07	(1.72-tr.)

deeply damaged under focussed electron-beam, even at moderate conditions (10 nA, 15 kV). In figures 4–6 we can see different types of spherules from the semicoke: Fig. 4 – most typical Kiviõli silicate spherule, Fig. 5 – a more evolved one, and Fig. 6 – a complicated spherule with semicoke fill.

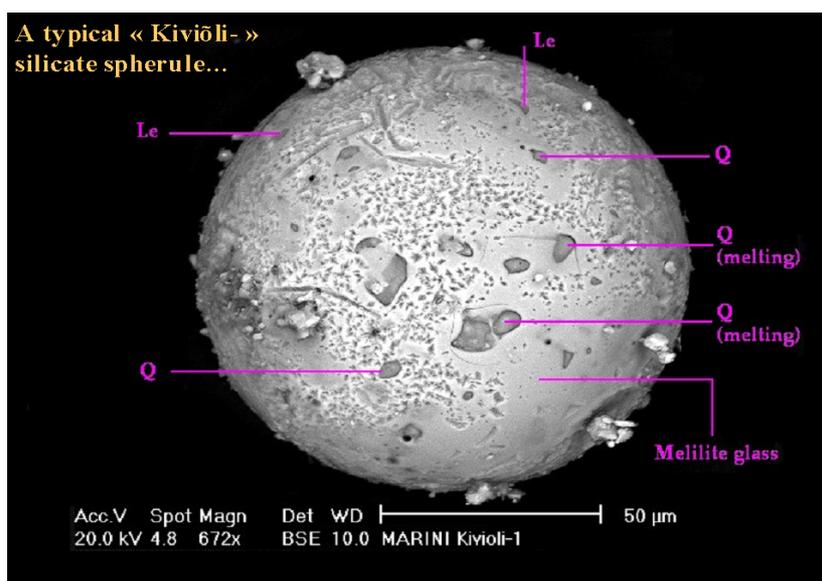


Fig. 4. A typical Kiviõli silicate spherule is well rounded. Photo by F. Marini.

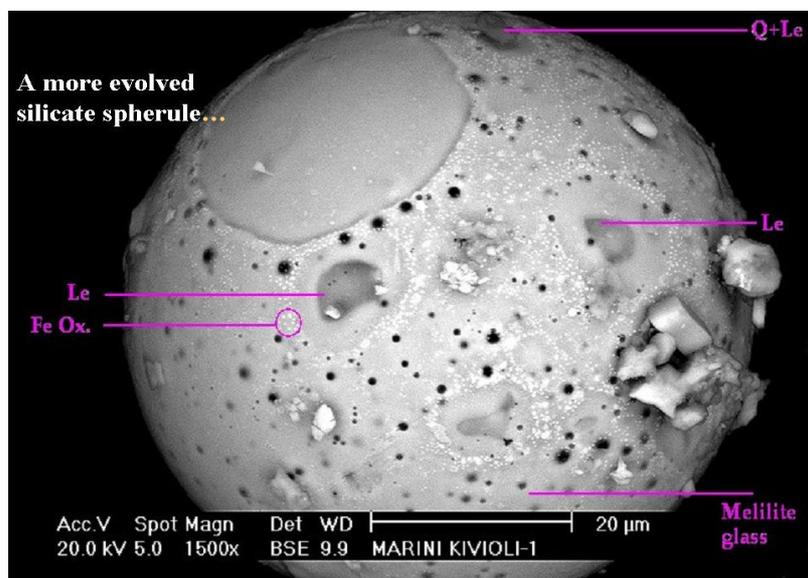


Fig. 5. A more evolved silicate spherule from Kiviõli semicoke, rich in lechatelierite inclusions. Photo by F. Marini.

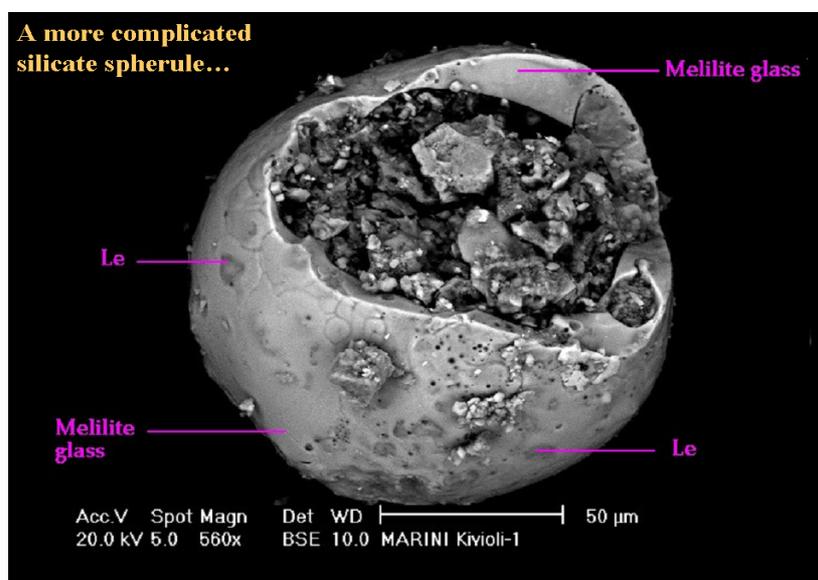


Fig. 6. A more complicated silicate spherule with melilite glass and semicoke fill.  
Photo by F. Marini.

## Discussion

A complete understanding of the origin of the “Kiviõli spherules” and their lechatelierite inclusions must base on further precise thermodynamic investigations of the melting and cooling processes. As a preliminary draft, we propose the following scenario: the observed glassy components – hence their parent melts – are fairly close in composition to the bulk of the semicoke (as reported in [14]). During oil shale retorting, the shale is heated in absence of oxygen to the temperature at which kerogen is decomposed or pyrolysed. Thermal destruction of kukersite begins at 170–180 °C, at the temperature 350–400 °C the organic substance of kukersite is converted into semi-liquid state, called thermobitumen. The rate of kerogen (thermobitumen) decomposition is the highest at retort temperature of 480–520 °C, at which kerogen converts into oil, gas and residual carbon. The last stage of retorting is short heating at 900–1000 °C, which is primarily aimed to burn off the coke (organic) residue [15].

But it seems that the melts derive from much later self-ignition of the residual organic matter, inside the semicoke heap (mean content: 4–6 wt% of organic carbon). This may result in spots of high temperature some 1400 degrees, leading to local and partial melting of the porous aggregate of particles which form the semicoke pile. Surface tension would produce spherules when droplets of such melts are expelled into the pores of the semicoke and then driven suspended in hot gas ascending through this porous medium. Rapid cooling of this gas outside the burning spots would

congeal the spherules to the glassy state. This scenario also would explain why glassy spherules can be found between semicoke components which seemingly escaped any high temperature transformation (i.e., carbonate fossil remains, calcite and dolomite rhomboedrons).

## Conclusion

Our finding of lechatelierite inclusions in glass spherules of obvious industrial provenance might cast serious doubts on the validity of the classical “Lechatelierite Criterion” as a test for impact glasses. This stresses the need to take into account a wider set of indicators from the spherule-bearing samples (i.e., occurrence of shocked materials, diagnostic minerals, and chemical anomalies) when evaluating the impact derivation of glassy spherules of unknown origin.

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