# ENIGMATIC POORLY STRUCTURED CARBON SUBSTANCES FROM THE ALPINE FORELAND, SOUTHEAST GERMANY: EVIDENCE OF A COSMIC RELATION


Tatyana G. Shumilova
Sergey I. Isaenko
Boris A. Makeev
Institute of Geology, Komi SC, Russian Academy of Sciences, Pervomayskaya st. 54, Syktyvkar, 167982 Russia, shumilova@geo.komisc.ru

Kord Ernstson
Faculty of Philosophy I, University of Würzburg, D-97074 Würzburg, Germany, kernstson@ernstson.de

Andreas Neumair
Michael A. Rappenglück
Institute for Interdisciplinary Studies, D-82205 Gilching, Germany, mr@infis.org


## Abstract


Unusual carbonaceous matter (UCM) from the Alpine Foreland in Southeast Germany has been investigated by various analytical methods. Poorly ordered carbon matter co-exists with high-ordering monocrystalline α-carbyne and contains submicrometer-sized inclusions of complex composition. The required very high temperatures and pressures for carbyne formation point to a shock event which is considered to have been the recently proposed Holocene Chiemgau impact event with the formation of an extended meteorite crater strewn field. A contribution of an extraterrestrial component cannot be excluded. The material is suggested to represent a new type of a carbon impactite.


## The material


The highly porous blackish material (Fig. 2) found as pebbles and cobbles in the field in a limited region in Southeast Bavaria (Fig. 1) has a glassy luster on freshly crushed surfaces. In some cases aerodynamically shaped cobbles can be sampled. Physically the material differs by its significantly varying electrical conductivity and magnetization. The material is unknown from any industrial or other anthropogenic processes and thus appears to have a natural origin.

Fig. 1. Location map for the sampled carbonaceous matter.

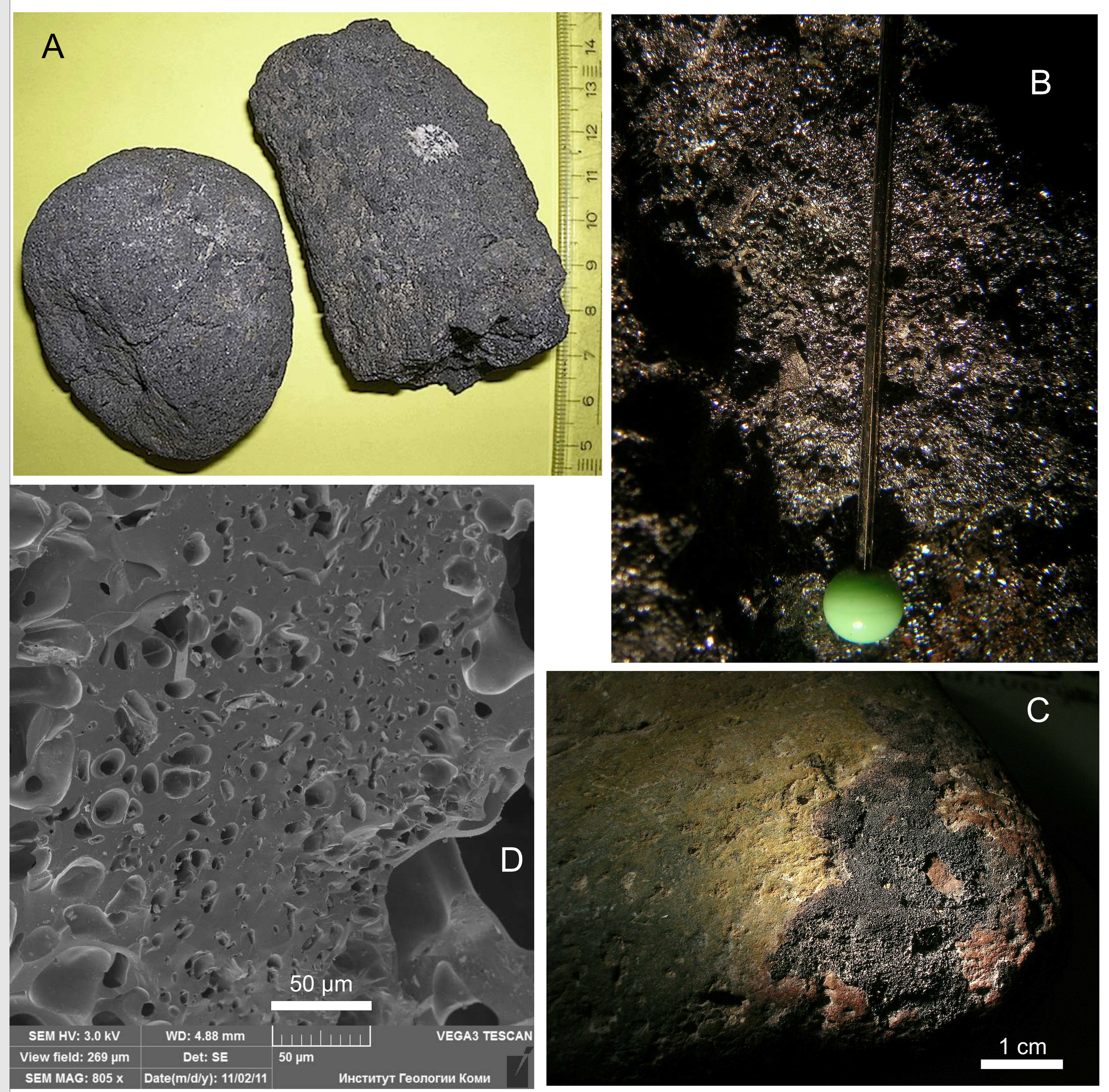



Fig. 2. A: Typical UCM cobbles from the field; cm scale. B: A freshly broken UCM cobble. C: Crust of UCM on a sandstone cobble. D: SEM image of the porous UCM.

## Methods

Four samples were studied by optical, atomic force microscopy (AFM, microscope NT-MDT), scanning electron microscopy (SEM) and microprobe analysis (MPA) (VEGA 3 TESCAN with EDX spectrometer), transmission electron microscopy (TEM Tesla BS-500), Raman spectroscopy (RS, high resolution LabRam HR 800), X-ray diffraction (XRD, Shimadzu XRD 6000) and differential thermal analysis (DTA, Shimadzu DTG 60). For comparison, other poorly structured carbon substances – shungite (Shunga deposit, Russia), glass-like carbon (SU-2000) and coal (Severnaya mine, Russia) - were studied.

## Results

### SEM and microprobe analysis

The porous (pores sized between 1 and 250 $\mu$m, Fig. 2D) and almost pure glass-like black carbon contains traces of O, S, Si, Al, but no N, as well as submicrometer-sized inclusions with a complex composition of Ca, Cl, O, Mn, Cr, Fe, Na, Al, Si, and P. Micrometer-sized Ag particles dispersed through the carbon matter are presented by aggregates of small 200-600 nm grains (Fig. 3).

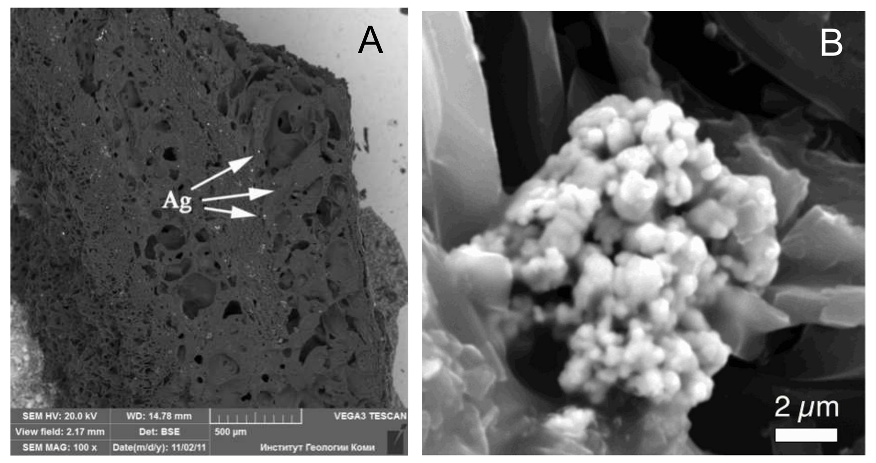
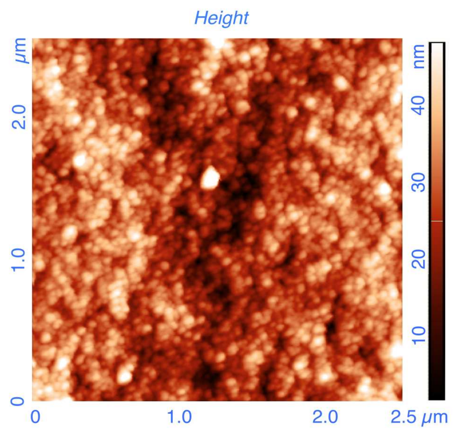



Fig. 3. SEM: Micrometer-sized aggregates (A) of silver grains (B) in the UCM matrix.

### Atomic force microscopy, AFM




AFM data show various structures - from almost amorphous with rare globular inclusions up to fully nano-globular structure (Fig. 4). The AFM electric properties reveal low density of very small locally focused spots of conductivity on the UCM dispersion map.

Fig. 4. AFM data of UCM with globular structure.

### X-ray diffractometry, XRD

From XRD the UCM resembles glass-like carbon/shungite concerning wide peak positions. Differences exist for FWHM, the UCM revealing different and smaller diffracting regions.

### Transmission electron microscopy, TEM

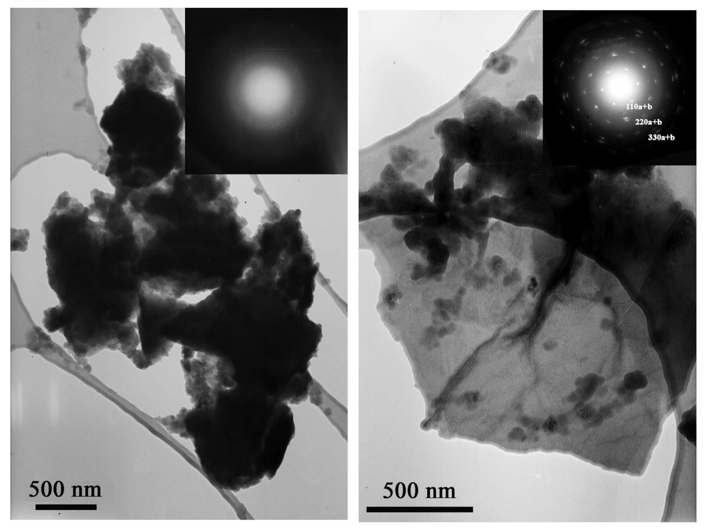



Fig. 5. TEM BF and SAED patterns of carbon particles from a UCM sample. A: amorphous. B: co-oriented mono-crystalline slightly textured α- and β-carbynes.

The carbon particles have different morphology including irregular, flattened particles with triangular shape and nanosized globular elements (Fig. 5). Particles occur as both well ordered and absolutely amorphous matter as seen by electron diffraction (SAED). From SAED patterns (Fig. 5B) the crystalline variety is monocrystalline carbon - carbyne [1], most preferably the α-carbyne modification. In a single case β-carbyne was met together with α-carbyne in coherently connected structure (Fig. 5B). Not any graphite particles were met among the crystalline material.

### Differential thermal analysis, DTA

DTA of the UCM analysis shows largely varying properties from sample to sample. On the whole, the thermal data are significantly higher than for coal kerogene and resemble more those of the glass-like and shungite carbon.

### Raman spectroscopy, RS

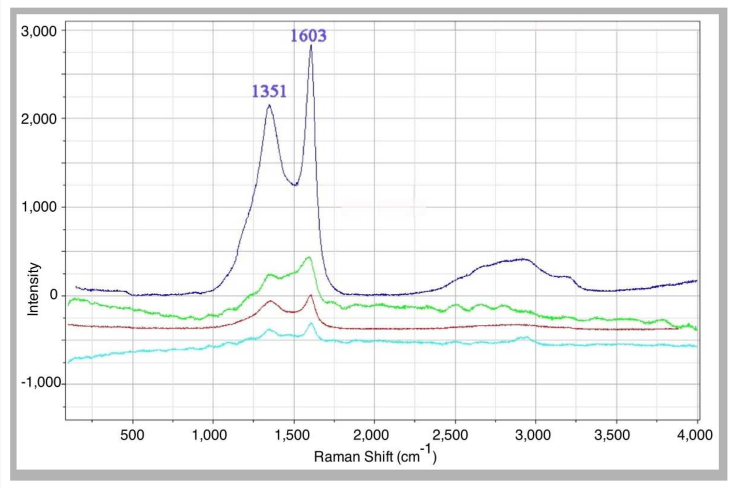



Fig. 6. Raman spectra of a UCM sample

The RS data show poor however varied patterning - from almost completely amorphous up to $sp^2$ structuring similar to glass-like carbon or onion-like carbon (Fig. 6). We observe very wide D and G bands of $sp^2$ carbon with a weak poorly resolved second order. The analyzed RS poor structuring is similar to some of the varieties of primitive meteorites [2].

## Discussion and relations

### Basic properties

Poorly ordered carbon matter co-exists with high ordering monocrystalline α-carbyne. During formation an intense gas phase developed, which explains the strongly porous texture of the UCM. Among the inclusions are noble Ag particles as fine-grained aggregates.

From Whittaker's phase diagram [3, 4], about 4-6 GPa and 2,500-4,000 K PT conditions of carbyne formation were deduced. Graphite did not form because of too high temperatures. Probable carbon glass within the UCM as seen from RS suggests temperatures as high as 3,800-4,000 K. At these temperatures and on fast decompression, two phases (carbyne and carbon glass) with possible partial sublimation into the gas phase could have occurred.

The carbon matter does not correspond to any known natural earth material with regard to the full complex of data [5]. An industrial production whether intentionally or accidentially does not make sense.

### Carbon allotropes in impact structures

The UCM points to a cosmic, meteoritic or impact component, or both. Carbon allotropes are known from meteorites and impact rocks, and terrestrial impact craters show evidence of all four carbon allotropes as are diamond, graphite, fullerenes and carbynes [6]. The high pressures and temperatures required for carbyne formation can be supplied by impact shock, and the conditions of carbyne (and the mineral chaoite) formation have repeatedly been discussed in relation to shock compression and meteorite impact [4, 7-10]. Hence, it is very probable that the UCM formed in relation with a meteorite impact event, and we point to the proposed Chiemgau impact event in Southeast Germany.

### The Chiemgau impact and meteorite crater strewn field

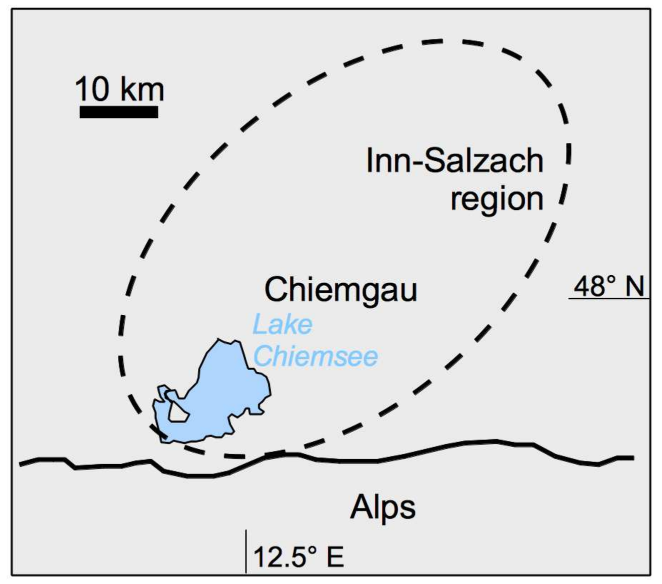



Fig. 7. Location map of the Chiemgau impact elliptically shaped strewn field (see Fig. 1).

The Chiemgau strewn field [11] dated to the Bronze Age/Celtic era comprises more than 80 mostly rimmed craters scattered in a region of about 60 km length and ca. 30 km width in the very South-East of Germany (Fig. 7, Fig. 1). The crater diameters range between a few meters and a few hundred meters, among them Lake Tüttensee, the hitherto established largest crater of the strewn field with a rim-to-rim diameter of about 600 m and an extensive ejecta blanket. Geologically, the craters occur in Pleistocene moraine and fluvio-glacial sediments.

The craters and surrounding areas are featuring heavy deformations of the Quaternary cobbles and boulders, abundant fused rock material (impact melt rocks and various glasses), shock-metamorphic effects, and geophysical anomalies [11]. The impact is substantiated by the abundant occurrence of metallic, glass and carbon spherules, accretionary lapilli, and of strange matter in the form of iron silicides like gupeiite, xifengite and probably hapkeite, and various carbides like, e.g., moissanite SiC [12]. The impactor is suggested to have been a roughly 1,000 m sized low-density disintegrated, loosely bound asteroid or a disintegrated comet in order to account for the extensive strewn field [11].

With regard to the UCM matter so far restricted to finds in the Chiemgau crater strewn field, the abundant occurrence of carbon spherules in the same area is intriguing. They contain fullerene-like structures and nanodiamonds that point to an impact-related origin [13].

### Short-term shock coalification – a possible relation with the UCM occurrence

Parallel to the uncovering of the strange iron silicides from the subsoil, the abundant finds of carbonaceous particles of strongly varying composition including, among others, brecciated charcoal, glass-like carbon containing fossilized organic matter and graphite-like substances also attracted attention leading to the model of a short-term coalification by immediate impact shock transformation from organic matter to high-rank carbon [14]. A possible relation with the carbyne carrying UCM from the Chiemgau impact area is standing to reason.

## Conclusions

The strange compositon of the UCM carrying the C carbyne allotrop suggests very high pressures and temperatures on formation.

UCM formed in a meteorite impact event and is closely related with the Chiemgau impact that produced a large crater strewn field only a few thousand years ago. The UCM occurrence seems to be restricted to this strewn field.

Details of the formation process remain unclear for the time being. The rich vegetation in the impact target area with extended forests and bogs could have been the basis of the carbon formation which is supported by abundant other finds of various and in part strange carbonaceous matter.

A meteoritic carbon contribution of the impactor that is assumed to have been a comet or a low-density "rubble pile" asteroid [11] cannot be excluded. Although silver is rare in meteorites, the nanometer-sized Ag particles in the UCM are possibly of cosmic origin.

We suggest that the UCM constitutes a new carbon impactite possibly existing elsewhere in similar formation.


### *Acknowledgements*

We thank V.A. Radaev, S.S. Shevchuk, M.V. Gorbunov and G.N. Modyanova for analytical support. A. Litwin was the first to draw attention to the strange matter.


## References


[1] Kudryavtsev, Yu.P. et al. (1997) Chemistry and Physics of carbon, 1997, Marchel Dekker, Inc. New York etc., 2-70. [2] Busemann, H. et al. (2007) *Meteoritics & Planet. Sci.*, 42, 1387-1416. [3] Whittaker, A.G. (1978) *Science*, 200, 763. [4] Lamperti, A. and Ossi, P.M. (2003), *Chemical Physics Letters*, 376, 662-665. [5] Shumilova, T.G. (2003) *Mineralogy of native carbon*. Ekaterinburg: UB RAS Press (in Russian). [6] Gilmour, I. (1998) Geological Society, London, Special Publications January 1, 1998, v. 140, p. 205-216 [7] Goresy, A. and Donney, G. (1968) *Science*, 161, 363-366. [8] Yamada, K. et al. (1991) Naturwissenschaften, 78, 450-452. [9] Gilmour. I. (1998) *Geol. Soc. London Spec. Publ.*, 140, 205-216. [10] Zhuk, A.Z. et al. (2000) *Doklady Physics*, 45, 14-17. [11] Ernstson, K. et al. (2010), *J. Siberian Federal Univ., Engineering. & Technology*, 2010, 3/1, 72-103. [12] Hiltl, M. et al. (2011), *LPSC XXXXII*, Abstract #1391. [13] Yang Z.Q. et al. (2008) Diamond Related Materials, 17, 937- 943. [14] Ernstson, K. et al. (2010) http://impact-structures.com/news/coalificationcomp.pdf.