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

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Introduction: Unusual carbonaceous matter (from now on UCM) in the form of mostly centimeter-sized lumps and cobbles has been sampled in the southeast Bavarian Alpine Foreland (Fig. 1). It is a highly porous blackish material with a glassy luster on freshly crushed surfaces. In some cases aerodynamically shaped cobbles (like some volcanic bombs) can be sampled. The material is unknown from any industrial or other anthropogenic processes and thus appears to have a natural origin, which is underlined by findings on a small island in the large Lake Chiemsee and at some altitude in the pre-Alps mountains. In one case, the UCM occurs as a crust on an Alpine fluvio-glacial sandstone cobble from the Lake Chiemsee shore. Here we report on preliminary results of a detailed analysis of this strange matter pointing to a process of formation that in part may have a cosmogenic component.

Fig. 1. Typical UCM cobbles (centimeter scale) and SEM image of the porous UCM matter

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: From *SEM and MPA analysis*, the porous (pores sized between 1 and 250 µm, Fig. 1) and almost pure glass-like black carbon contains traces of O, S, Si, Al but no N. Few particles of aluminosilicate inclusions (sized up to 20 µm x 2 µm) were identified as well as submicrometer-sized inclusions with a complex composition of Ca, Cl, O, Mn, Cr, Fe, Na, Al, Si, and P. The most interesting inclusions were micrometer-sized Ag particles dispersed through the carbon matter and presented by aggregates of small 200-600 nm grains (Fig. 2).

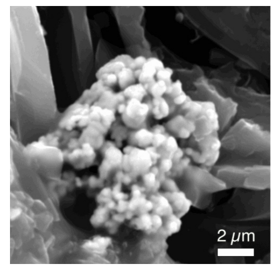

Fig. 2. SEM: Aggregate of Ag grains in the UCM matrix.

Atomic force microscopy. AFM data show various structures - from almost amorphous with rare globular inclusions up to fully nano-globular structure. Compared to synthetic glass-like carbon and shungite the UCM globular structures are essentially smaller. The AFM electric properties (of the most purely structured UCM) show similar average and maximum conductivity but differ significantly with regard to the low density of very small locally focused spots of conductivity on the UCM dispersion map.

X-ray diffractometry. Also XRD shows similarities between glass-like carbon/shungite and the UCM concerning wide peak positions, but differences exist for FWHM which depends on the size of the diffracting regions. The data for the UCM reveal different and smaller diffracting regions.

Transmission electron microscopy. Two UCM specimens with essentially different ordering were studied by TEM. The carbon particles are characterized by different morphology including irregular, flattened particles with triangular shape and nanosized globular elements (Fig. 3). Particles occur as both well ordered and absolutely amorphous matter as seen by electron diffraction (SAED). From SAED patterns (Fig. 3B) the crystalline variety for both specimens 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. 3B). Interestingly, not any graphite particles were met among the crystalline material.

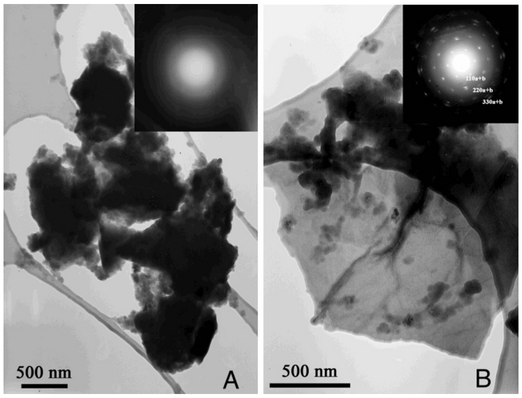

Fig. 3. TEM BF and SAED patterns of carbon particles from a UCM sample. A: amorphous. B: co-oriented mono-crystalline slightly textured α- and β-carbynes.

Differential thermal analysis. 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. Some parameters prove to be higher than for all standard materials.

Raman spectroscopy. The RS data are characterized by poor however varied patterning - from almost completely amorphous up to sp^2 structuring similar to glass-like carbon or onion-like carbon (Fig. 4). 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].

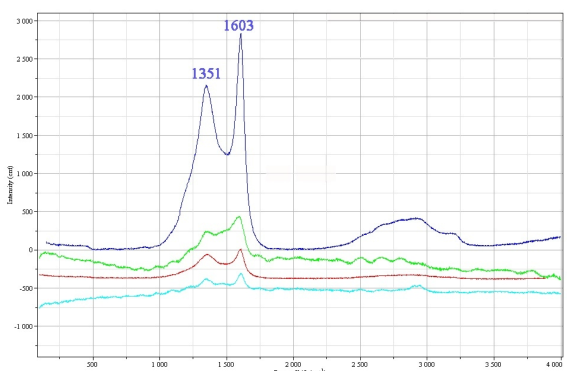

Fig.4. Raman spectra of UCM sample #2010-4.

Discussion: The studied carbon matter generally has poor ordering of different level. The poorly ordered carbon matter co-exists with high ordering monocrystalline α-carbyne. During carbon matter 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. As deduced from Whittaker's phase diagram [3, 4], PT conditions of carbyne formation were about 4-6 GPa and 2,500-4,000 K. The absence of graphite points to temperatures too high for its formation. The presence of probable carbon glass within the UCM as seen from RS suggests that temperatures could have attained even 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]. Also, an industrial production whether intentionally or accidentially does not make sense.

Conclusions: The observational data with the strange compositon of the UCM point to a cosmic, meteoritic or impact component, or both. The high pressures and temperatures required for carbyne formation can be supplied by impact shock, and the conditions of carbyne formation have repeatedly been discussed in relation to shock compression and meteorite impact [4, 6-9]. We therefore conclude that the UCM formed in relation with a meteorite impact event and point to the proposed so-called Chiemgau impact, that produced a large crater strewn field only a few thousand years ago [10, 11]. The UCM occurrence seems to be restricted to this strewn field. Details of the formation process remain unclear for the time being, but the rich vegetation in the impact target area could have been the basis of the carbon formation. This may be supported by other finds of various carbonaceous matter that led to the model of a short-term shock coalification [12]. On the other hand, 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.

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