From biomass to glassy carbon and carbynes: evidence of possible meteorite impact shock coalification and carbonization

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Introduction: Coalification defines the process in which vegetable matter like wood and peat becomes converted into coal of increasingly higher rank with anthracite, and in some cases graphite, as the final product, and that in geology leads to the formation of coal deposits. Simulation of natural coalification has been performed in the laboratory, and industrial coalification from biomass within hours is known as hydrothermal carbonization. Here, we present observations that suggest the possibility of a much shorter coalification in a natural environment by a kind of shock metamorphism in a meteorite impact event. Shock metamorphism of organic matter has so far been addressed only very subordinately (e. g., [1]).

Observations: The Holocene Chiemgau impact event is considered to have produced a large meteorite crater strewn field in southeast Bavaria, Germany ([2], and ref. therein). The impact is documented by abundant impact melt rocks and various glasses, shock-metamorphic effects like planar deformation features (PDFs) and diaplectic glass, geophysical anomalies and ejecta deposits, and 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, hapkeite and xifengite, and various carbides like, e.g., moissanite SiC. From dating archeological objects the impact must have happened more than 2500 years BP in the Bronze Age/Celtic era.

In the Chiemgau area in part very peculiar carbonaceous matter has abundantly been found both embedded in impact ejecta horizonts and as surficial finds, and most remarkable a suite of increasing coalification could be established. The suite begins with pure and relativly fresh wood, branches and twigs, sharply broken into small fragments and splinters and embedded as in part densely packed components in diamictite layers that are interpreted as impact ejecta. The most common carbon matter is charcoal more or less regularly intermixed in polymictic impact breccias. A second class of carbonaceous matter comprises dense, very hard black glassy fragments up to the size of a few centimeters. Between charcoal and glassy carbon, a broad variety of carbonaceous fragments is observed that obviously reflects intermediates in a series from wood/charcoal to glassy carbon. We observe: a monomictic charcoal breccia composed of finely grinded and firmly caked charcoal particles; crumbly however hard, very dense and partially glass-like carbonaceous matter with a few intermixed charcoal particles; pieces that combine merging charcoal and glassy carbon; stratified and very tough glassy carbon reminding of primary wood fiber, and, on a millimeter scale, alternately stratified and glassy carbon; centimeter-sized pieces of a strongly vesicular glassy carbon matter regularly interspersed with mostly platy carbon particles with remnants of wooden structure (Fig. 1A, B); pieces of this vesicular carbon matter with inclusions of wood particles, glass fragments and glass bubbles; polymictic breccias of wood and charcoal-like fragments and carbonate particles in the vesicular glassy carbon matter (Fig. 1, C); a very dense and hard glassy carbon piece with trapped fossil skeletons of various diatoms, and algae-like structures in magnetite-rich aggregates (Fig. 1, D).

Charcoal has regularly preserved the typical cellular structure but is no longer flammable and frequently seen only in the form of fossilized imprints on the glassy carbon matter. The diatoms-containing glassy carbon has ben studied under the SEM (Fig. 2), revealing a composition of the matrix of mostly C and O and traces of Na, S, Fe, Si, Al. K, Cl and Ca. For comparison, the EDX

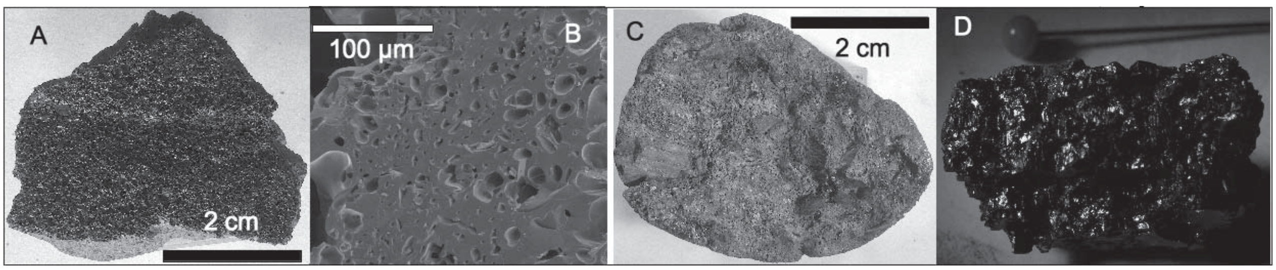

Fig. 1. A: Strongly vesicular carbon matter and SEM image of the dense matrix; C: polymictic carbonaceous breccia; D: glassy carbon with diatoms and algae-like structures (see Fig. 2)

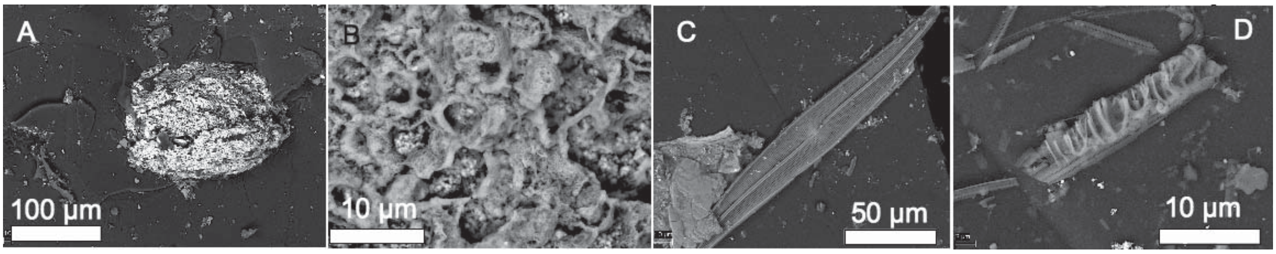

Fig. 2. Dense glassy carbon matter (see Fig. 1D) containing magnetite-rich inclusions (A) with algae-like structures (B), and diatoms (C, D) that are in part strongly fractured

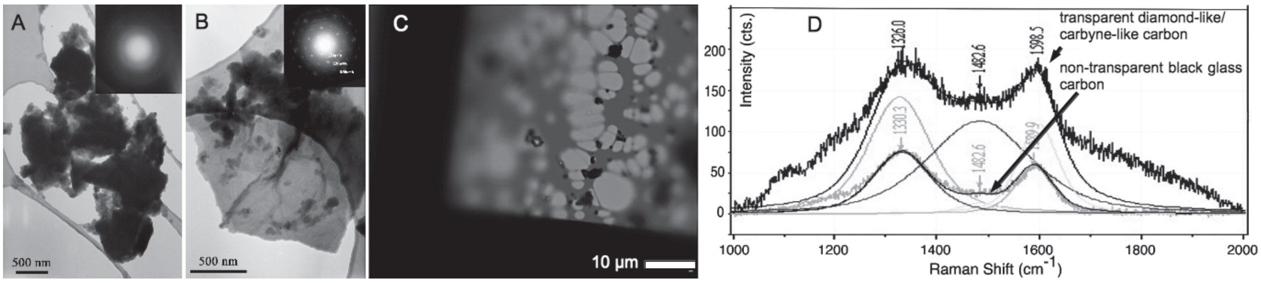

Fig. 3. A, B: TEM BF and SAED patterns of carbon particles from the sample in Fig. 1B. A: amorphous. B: co-oriented mono-crystalline slightly textured б- and в-carbynes. C: DLC or carbyne-like carbon submicrometer-sized optically transparent inclusions within the glassy carbon matrix. Reflected light. D: Raman spectra of the carbon matter.

analysis for another glassy carbon piece reveals mostly carbon, a high amount of oxygen (up to 25 wt. %), small amounts of Al, Si and Ca, and traces of Na, Mg, S, Cl, K and Fe, that is very similar in composition. Raman spectra of the sample show greatly disordered elemental carbon mostly in an amorphous state.

The special group of the strongly vesicular carbonaceous matter widely distributed in the impact strewn field (Fig. 1, A, B, Fig. 3) has more intensively been analyzed by a complex of high resolution Raman spectroscopy, X-Ray diffraction, electron scanning and atomic force microscopy, transmission electron microscopy and differential thermal analysis [3]. AFM data show various structures - from almost amorphous with rare globular inclusions up to fully nano-globular structure.

TEM shows irregular, flattened particles with triangular shape and nanosized globular elements (Fig. 3, A, 3, B). Particles occur as both well ordered and absolutely amorphous matter as seen by electron diffraction (SAED). From SAED patterns (Fig. 3, B) the crystalline variety is monocrystalline carbon - carbyne, most preferably the б-carbyne modification. In a single case в-carbyne was met together with б-carbyne in coherently connected structure (Fig. 3, B). Submicrometer-sized optically transparent inclusions prove to be diamond-like carbon and/or carbyne-like carbon (Fig. 3, C) Raman spectra of which are seen in Fig. 3, D. Their in part octahedron morphology (Fig. 3, C) may point to pseudomorphs after diamond as a result of recrystallization.

Discussion. The observations of the various carbonaceous finds strongly suggest they belong to a certain process of coalification beginning with vegetation mostly in the form of wood, passing the stage of charcoal, and ending with the dense glassy carbon. Even higher stages of coalification are documented by the occurrence of carbynes and diamond-like/carbyne-like carbon. From Whittaker's phase diagram (e. g., [4]), about 4–6 GPa and 2.500–4.000 K PT conditions of carbyne formation can be deduced. Also the DLC/carbyne-like carbon formed under high temperatures [5] possiby as pseudomorphs after diamond. This high PT carbon matter does not correspond to any known natural earth material with regard to the full complex of data [6]. An industrial production whether intentionally or accidentially does not make sense.

Summarizing the observations, the find of carbon matter in various modifications up to highest stages of an obvious coalification in young, Holocene geologic environs excludes any long-term processes known from coal deposit formation. Glass-like carbon has been shown to evolving from cellulose by thermal decomposition at 1.000–3.200 °C [7, 8], but the question remains how such a process could have run in nature. In the present case, it doesn't need much imagination to reasonably explain the exotic carbon matter to have originated from the Chiemgau Holocene impact event. From computer simulations a roughly 1.000 m sized impactor is suggested to have been a low-density disintegrated, loosely bound asteroid or a disintegrated comet to account for the extensive strewn field. The incoming cosmic projectile must have encountered a densely arborous landscape also hosting large areas of bogs and peat deposits. This giant reservoir of organic matter exposed to impact shock and explosion could have been the source for the observed coalification, although the most part of the vegetation probably simply burned. For the time being it is largely unresolved what happened in detail. The intriguing matter with indication of extreme PT conditions may speak in favor of an immediate shock transformation from organic matter to high-rank carbon. This is substantiated by wood and charcoal fragments in direct contact with dense glassy and high-PT carbon allotropes. In shocked rocks, the coexistence of strongly shocked minerals and minerals largely unaffected is a common observation and may be explained by the strongly nonlinear process of shock propagation. This may apply also to the observation that algae aggregates and diatom skeletons could have survived the formation of the glassy carbon.

Conclusion: The observations of high-PT carbon allotropes in direct contact with organic matter suggest a special type of shock effect in nature that may be observed also with older impacts.

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