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 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]).

The Holocene Chiemgau impact event is considered to have produced a large meteorite crater strewn field in southeast Bavaria, Germany ([2], and ref. therein; Fig. 1). 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.

Fig. 1. Location map for the Chiemgau impact meteorite crater strewn field.

Observations and analyses

General. - In the Chiemgau area in part very peculiar carbonaceous matter has abundantly been found both embedded in impact ejecta horizons 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 (Fig. 2 A). The most common carbon matter is charcoal more or less regularly intermixed in polymictic impact breccias (Fig. 2 B). A second class of carbonaceous matter comprises dense, very hard black glassy fragments up to the size of a few centimeters (Fig. 2 F). 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.

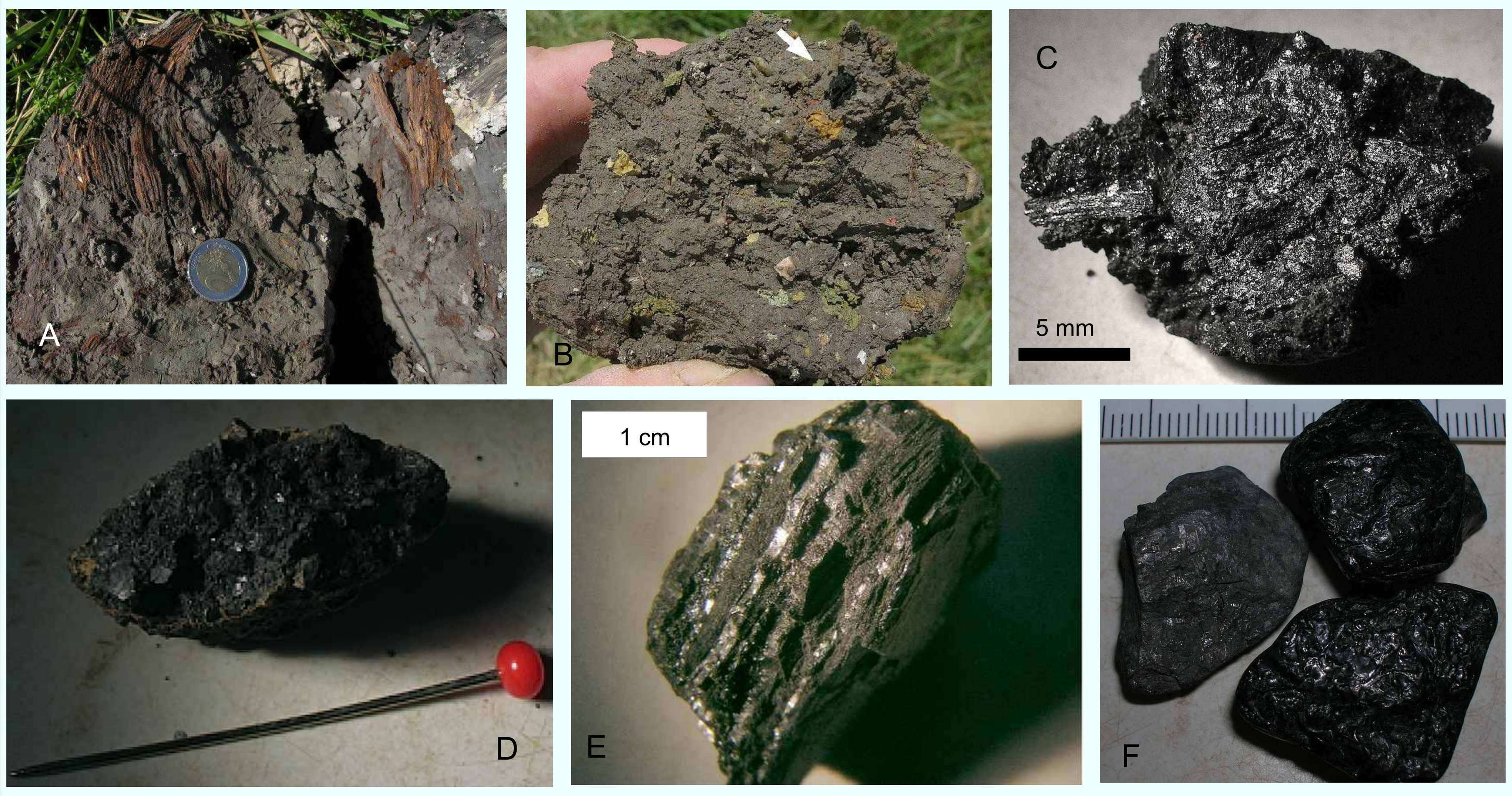
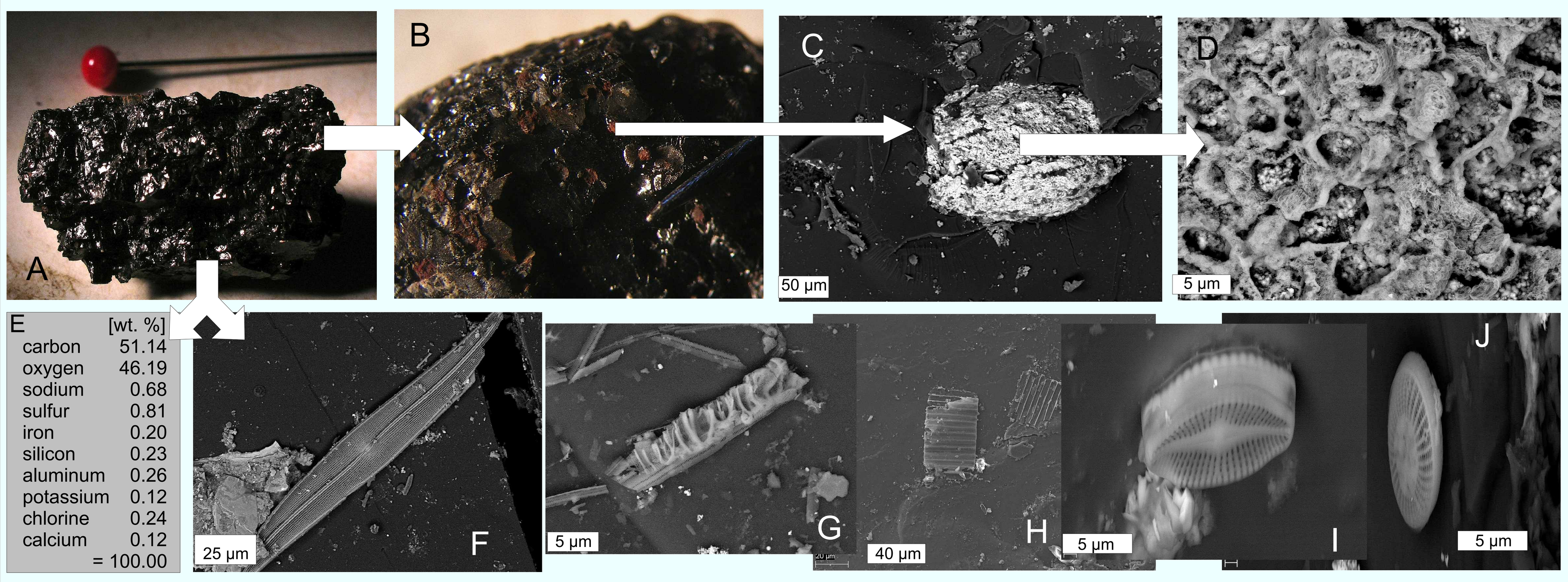


Fig. 2. Observations from the Chiemgau impact strewn field. A: fractured wood particles in a polymictic impact breccia. B: charcoal particles (arrow) in a polymictic impact breccia. C: monomictic glassy charcoal breccia. D: breccia of crumbly glassy carbon particles with intermixed charcoal pieces. E: alternately finely stratified and dense glassy carbon. F: pieces of massive glassy carbon and dense charcoal imprints on massiv glassy carbon (left piece).

We observe: -- a monomictic charcoal breccia composed of finely grinded and firmly caked charcoal particles (Fig. 2 C). The charcoal has got a glassy appearance and is no longer flammable. -- crumbly however hard, very dense and partially glass-like carbonaceous matter with a few intermixed charcoal particles (Fig. 2 D) -- 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 (Fig. 2 E). 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. An EDX analysis for a glassy carbon piece reveals mostly carbon (>70 wt. %), 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. Raman spectra of the sample show greatly disordered elemental carbon mostly in an amorphous state.

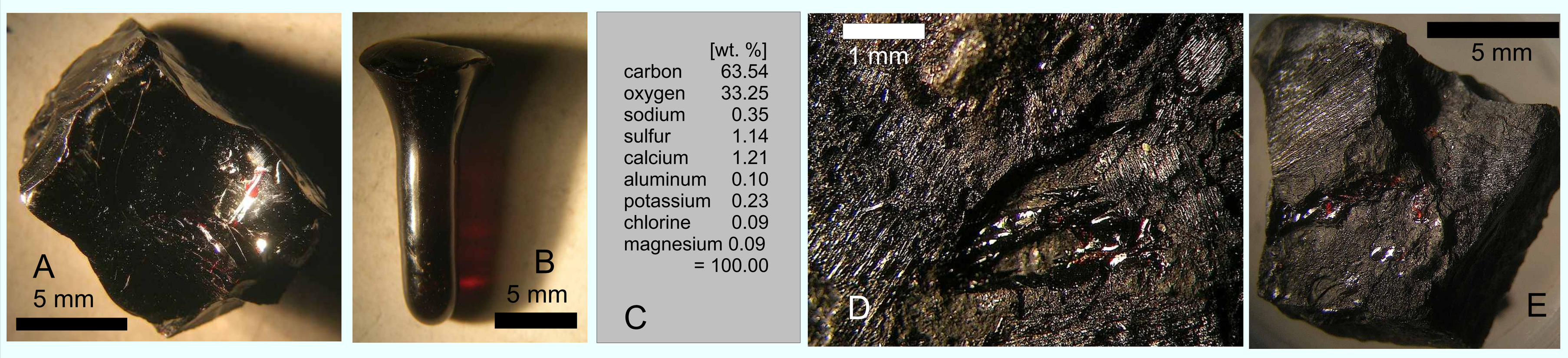
Glassy carbon with diatoms and cyanobacteria. - A moderately magnetic very dense and hard glassy carbon piece has been found near Lake Chiemsee (Fig. 3 A) that contains rust-red aggregates (Fig. 3 B, C). Under the SEM the aggregates reveal coccoid cyanobacteria (Fig. 3 D), and the EDX analysis shows up to 16 wt. % Fe which, as magnetite Fe_3O_4, probably is responsible of the magnetization of the sample. SEM images of the black glassy matrix show trapped fossil skeletons of various diatoms (Figs. 3 F – J). An EDX element analysis (Fig. 3 E) lists carbon and oxygen as making up more than 97 wt. %.



E	[wt. %]
carbon	51.14
oxygen	46.19
sodium	0.68
sulfur	0.81
iron	0.20
silicon	0.23
aluminum	0.26
potassium	0.12
chlorine	0.24
calcium	0.12
	= 100.00

Fig. 3. Glassy carbon piece (A) with rust-red aggregates (B). C: SEM image of an iron-rich aggregate implemented in the glassy carbon matrix. D: SEM image of the inclusion in (C) exhibiting coccoid cyanobacteria. E: Chemical analysis of the black glassy matrix. F-J: Various diatom skeletons embedded in the black glassy matrix.

Transparent red glassy carbon. - Transparent red glassy carbon has been found as fractured and drop-shaped pieces in the field west of Lake Chiemsee (Fig. 4 A, B) and as tiny particles interspersed in charcoal-bearing black glassy carbon (Fig. D, E). The chemical composition as analyzed for a larger particle is similar to that of the black glassy carbon again revealing a c. 97 wt. % carbon-oxygen content.



C	[wt. %]
carbon	63.54
oxygen	33.25
sodium	0.35
sulfur	1.14
calcium	1.21
aluminum	0.10
potassium	0.23
chlorine	0.09
magnesium	0.09
	= 100.00

Fig. 4. Transparent red glassy carbon with conchoidal fracture (A), drop-shaped (B) and as tiny inclusions in charcoal-bearing black glassy carbon (D, E). C: Chemical analysis of a particle of the red glassy material.

Pumice-like carbon matter (chiemite). - A very characteristic carbon matter from the Chiemgau area that for reasons of a clear definition and according to the type locality has been termed *chiemite*, has been analyzed in greater detail. The highly porous blackish material (Fig. 5 A-C) found as pebbles and cobbles in the field has a glassy to metallic luster on freshly crushed surfaces. The material is unknown from any industrial or other anthropogenic processes and thus appears to have a natural origin.

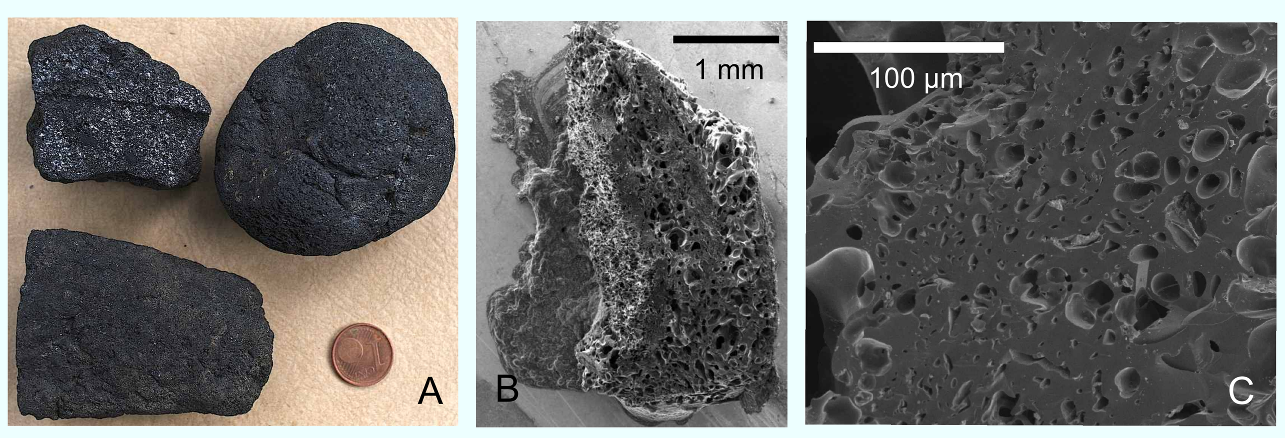


Fig. 5. A: Typical chiemite cobbles from the field; upper left sawed face. B: SEM image of a freshly broken chiemite cobble. C: SEM image of the porous chiemite matrix;

Observations and analyses, cont.

Four samples were studied [3, 4] 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). X-ray fluorescence spectroscopy (XRF) and δ13 isotopic data add to the studies. For comparison, other poorly structured carbon substances – shungite (Shunga deposit, Russia), glass-like carbon (SU-2000) and coal (Severnaya mine, Russia) - were studied.

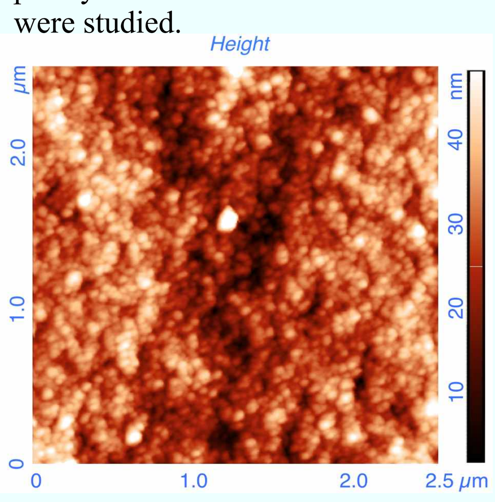


Fig. 6. AFM data of chiemite with globular structure.

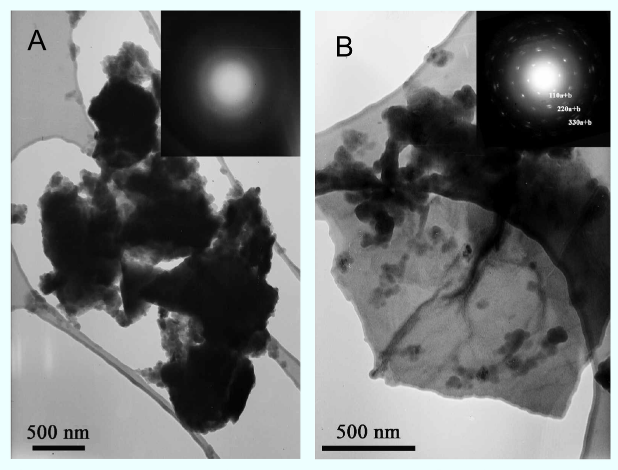


Fig. 7. TEM BF and SAED patterns of carbon particles from a chiemite sample. A: amorphous. B: co-oriented mono-crystalline slightly textured α- and β-carbynes.

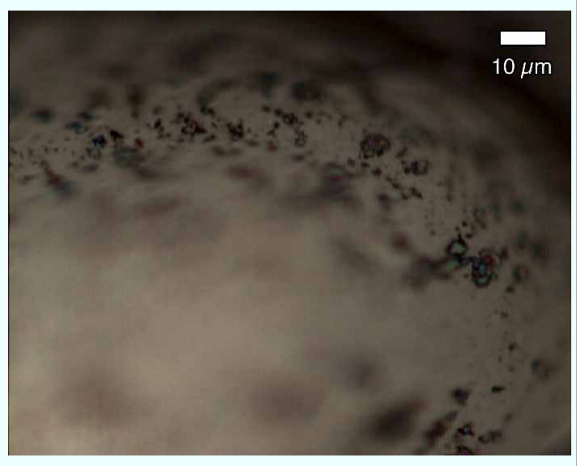


Fig.8. Chiemite: submicrometer-sized optically transparent inclusions within the glass-like carbon matrix. Reflected light.

XRF reveals about 90 % pure C. The remaining constituents show a concentration on Si, Al and Fe, subordinately on S. Minor contents concern Ti, Mn, Mg, Ca, K, P, Sr.

AFM data show various structures - from almost amorphous with rare globular inclusions up to fully nano-globular structure (Fig. 6). TEM shows irregular, flattened particles with triangular shape and nanosized globular elements (Fig. 7 A, B). Particles occur as both well ordered and absolutely amorphous matter as seen by electron diffraction (SAED). From SAED patterns (Fig. 7 B) the crystalline variety is mono-crystalline carbon - carbyne, most preferably the α-carbyne modification. In a single case β-carbyne was met together with α-carbyne in coherently connected structure (Fig. 8 B). Submicrometer-sized optically transparent inclusions prove to be diamond-like carbon and/or carbyne-like carbon (Fig. 7) Raman spectra of which are seen in Fig. 9. Their in part octahedron morphology (Fig. 8) may point to pseudomorphs after diamond as a result of recrystallization.

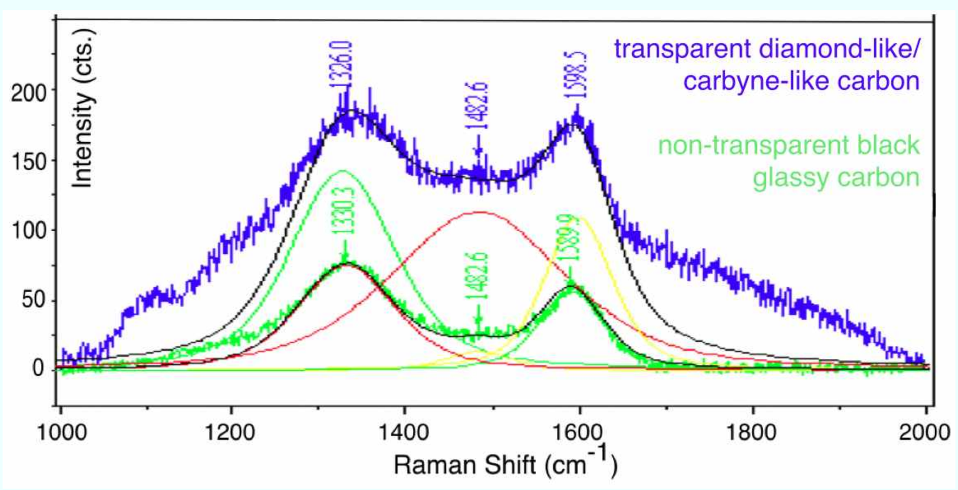


Fig. 9. Raman spectra of a chiemite sample.

Chiemite special features - In most cases the chiemite matrix as described is interspersed with black glassy mostly platy particles that obviously represent former wooden matter (Fig. 10 A). In a few cases relatively fresh wood fragments are embedded in the chiemite matrix (Fig. 10 B).

Chiemite has been found as a crust on a sandstone cobble from the shore of Lake Chiemsee (Fig. 11 A). Frequently, chiemite appears as to form pseudomorphic after pieces of wood (Fig. 11 B). Often, pieces of chiemite show flow texture and surfaces similar to ropy lava (Fig. 10 1). Fig. 11 D shows a sample of chiemite forming together with the "fossilized" wooden particles a real breccia. Transitions from chiemite to massive glassy carbon are also observed.

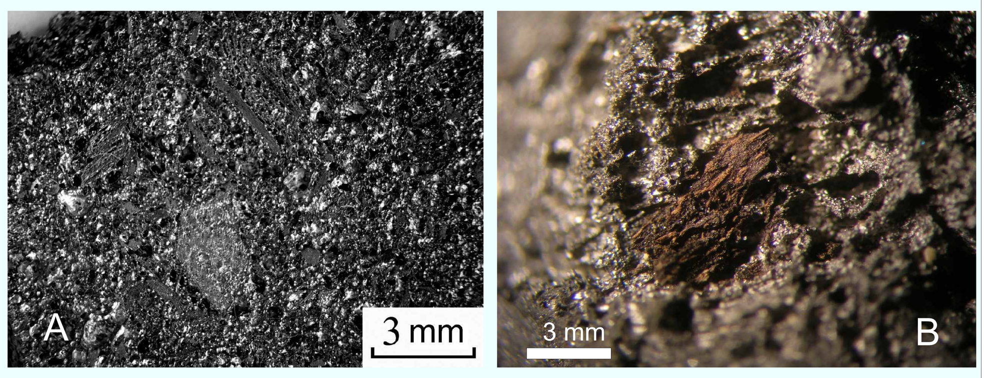


Fig. 10. A: Chiemite with platy inclusions exhibiting fossil wooden structure.; B: wood particle embedded in chiemite.

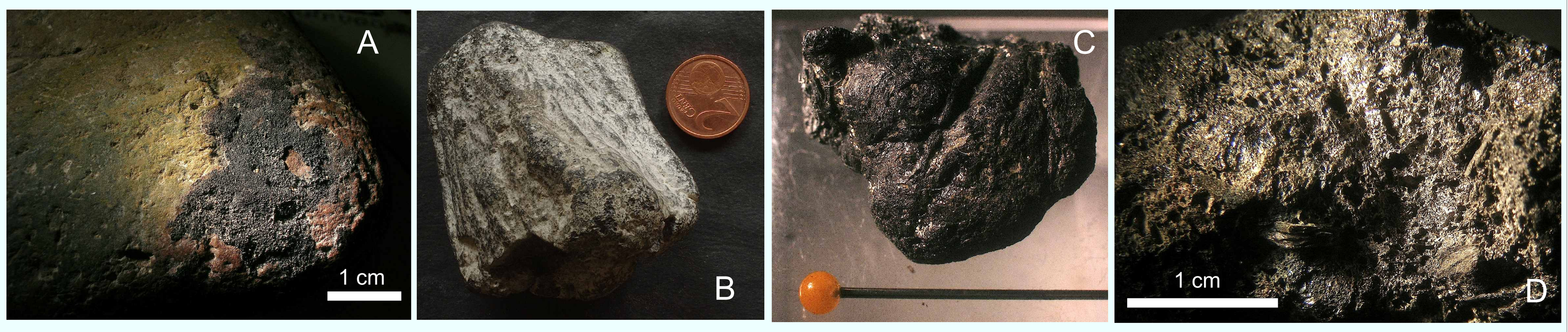


Fig. 11. Chiemite as a crust on a sandstone cobble (A), pseudomorphic after wood (B), exhibiting flow texture (C), and forming a carbonaceous breccia (D).

Discussion

The observations of the various carbonaceous finds strongly suggest they belong to a certain process of coalification/carbonization 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., [5]), 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 [6] possibly 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 [7]. An industrial production whether intentionally or accidentally does not make sense.

Summarizing the observations, the find of carbon matter in various modifications up to highest stages of an obvious coalification/carbonization 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 [8, 9], but the question remains how such a process could have run in nature. In the present case, we suggest 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 of roughly 60 km x 30 km. The incoming cosmic projectile must have encountered a densely arboreous 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. 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 aggregates of cyanobacteria and diatom skeletons could have survived the formation of the glassy carbon. Moreover, the occurrence of wood mostly fragmented to very small pieces and "fossilized" to glassy carbon, and the formation of carbonaceous breccias speaks in favor of a highly energetic process as is expected for a meteorite impact.

For the time being it is largely unresolved what happened in detail. This concerns both the general, probably shock-induced process of carbonization/coalification and quite specific metamorphisms. It is unresolved how the chiemite could have formed pseudomorphic after wood fragments frequently exhibiting the typical shape of tree branches and bark. Here, a relation to phytofulgurites, a new type of fulgurites that have originated from a lightning stroke on a haycock with resulting anthraxolite-like matter pseudomorphic after grass stems [10], appears to be an interesting starting point for further studies, particularly with regard to similar PT conditions during lightning strokes and meteorite impact. The formation of the transparent red glassy carbon matter is likewise enigmatic. Because of drop-shaped particles (Fig. 4) a vague idea considers resin as the source material particularly in view of the tiny particles embedded within "fossilized" wood/charcoal (Fig. 4). The elemental analysis is similar to that of the massive glassy carbon (Figs. 3, 4) with a high amount of O in addition to C. This corresponds roughly with the percentage C, O content of firewood (≈ 50 % C, 43 % O) but differs markedly from the chiemite composition with about 90 % C. Although carbonaceous pieces of massive glassy carbon in contact with porous, pumice-like glassy chiemite have been found, both are basically forming distinct groups pointing to different processes of carbonization/coalification and a subsequent mixing of the various components, wood and charcoal included. This is not untypical for impact processes when rocks of quite different shock stages are mixed together in the various phases of impact cratering to form conspicuous impact breccias and impact melt rocks.

Conclusions

The observations of peculiar carbonization/coalification in the Chiemgau impact meteorite crater strewn field cannot reasonably be ascribed to industrial or any other anthropogenic activities. Natural carbonization processes like wildfires cannot explain the manifold findings as described in the *Observation and analyses* chapter. The 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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