Micro- and nano-diamond particles in carbon spherules found in soil samples

Z. Yang[1*], D. Schryvers[1], W. Rösler[2], N. Tarcea[3], J. Popp[3]

1. EMAT, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium
2. Institute for Pre- and Early History, University of Mainz, Schillerstrasse 11, D-55116 Mainz, Germany
3. Institute of Physical Chemistry, University of Jena, Helmholtzweg 4, D-07743, Jena, Germany
* now at College of Materials Science and Engineering, Hunan University, Changsha, Ch-410082, China

nick.schryvers@ua.ac.be
Keywords: diamond, nanoparticles, microflakes, impact

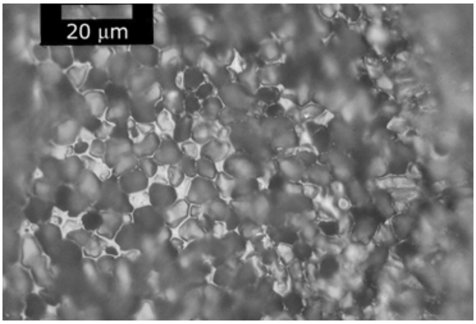
Carbonaceous spherules of millimeter size diameter and found in the upper soils throughout Europe are investigated by TEM, including SAED, HRTEM and EELS, and Raman spectroscopy. The spherules consist primarily of carbon and have an open cell-like internal structure. Most of the carbon appears in an amorphous state, but different morphologies of nano- and microdiamond particles have also been discovered including flake shapes. The latter observation, together with the original findings of some of these spherules in crater-like structures in the landscape and including severely deformed rocks with some spherules being embedded in the fused crust of excavated rocks, points towards unique conditions of origin for these spherules and particles, possibly exogenic [1].

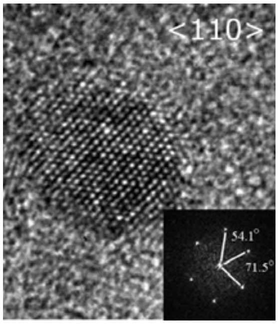
Optical microscopy and SEM reveal mainly cenospheres exhibiting foam-, sponge-, or cell-like internal structures with cell sizes approximately ranging from 10 to 40 micron, as shown in Figure 1. Elemental analyses using EDX show a high portion of C but also considerable amounts of O and no heavy elements. The matrix of the spherules consists of amorphous carbon, with in many cases embedded monocrystalline nanoparticles or defected polycrystalline nanograins, an example of the first shown in Figure 2. Diffraction rings correspond with an fcc-based structure with a lattice parameter of 0.360 nm ($a_{diamond}$ = 0.356 nm). The appearance of the 200 ring, extinct for the perfect diamond structure, can be attributed to the existence of multiple lattice defects in the nanograins or a deviation from the perfect diamond lattice in the nanoparticles. In some specimens, micrometer-sized, flake-shaped diamonds could be identified inside the cell-like structures: an example is shown in Figure 3 together with a set of SAED patterns revealing diamond extinctions in the expected positions. In Figure 4 the characteristic diamond ELNES shape of the C K-edge obtained from such a microflake is shown (the small π^* edge originates from amorphous C surface material) together with the plasmon peak at 33 eV, the latter shifting to 24 eV for the nanoparticles. The existence of micrometer sized diamonds in some particles was supported by the observation of the characteristic sharp diamond band at 1332.3 cm^{-1} in Raman spectroscopy, as shown in Figure 5 [2].

S. Richter, A. Schwedt (Eds.): EMC 2008, Vol. 2: Materials Science, pp. 833–834,
DOI: 10.1007/978-3-540-85226-1_417,

1. V. Hoffmann, W. Rösler, A. Patzelt, B. Raeymaekers, P. Van Espen, Meteoritics & Planetary Science **40** (2005) A69
2. Z.Q. Yang, J. Verbeeck, D. Schryvers, N. Tarcea, J. Popp and W. Rösler, (2008) (in press) doi:10.1016/j.diamond.2008.01.104

3. We kindly acknowledge support of the GOA project on EELS of the University of Antwerp

1.) 



2.)

Figure 1. SEM showing foam-like structure in the interior of the spherules.
Figure 2. Monocrystalline diamond nanoparticle viewed along <110> cubic zone.

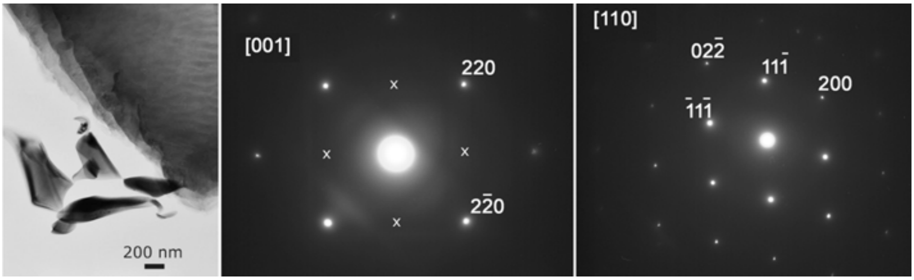
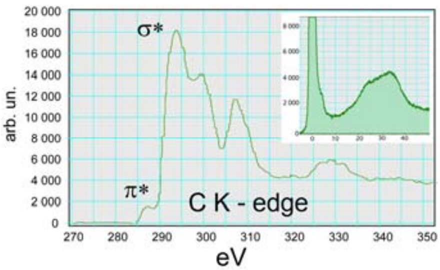
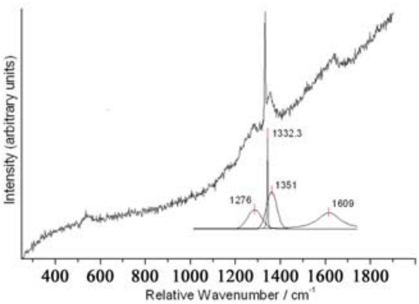
3.) 

Figure 3. Several diamond microflakes alongside amorphous carbon support together with some SAED patterns with extinctions indicated by crosses in [001] zone.

4.) 



5.)

Figure 4. C K-edge ELNES revealing characteristic diamond σ* shape plus plasmon peak at 33 eV in inset.
Figure 5. Raman spectrum with diamond peak at 1332.3 cm^{-1}.