

WHAT WE DO TO METEORITIC NANODIAMONDS WHEN WE HEAT THEM. E. Marosits¹, T. L. Daulton², Ch. Sudek¹, U. Ott¹, ¹Max-Planck-Institut für Chemie, Abteilung Geochemie, Becherweg 27, D-55128 Mainz, Germany (marosits@mpch-mainz.mpg.de), ²Department of Physics and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130, USA.

Introduction: Primitive meteorites contain a variety of presolar grains that are identified by their anomalous isotopic compositions (for recent reviews see [1,2]). Most types (e.g., SiC, graphite) are up to several micrometers in size, which allows the isotopic study of single grains. Nanodiamond, the most abundant type, however, is much smaller (average 2.6 nm; [3]). Since their “bulk” ¹²C/¹³C ratio is rather normal [4], it is often concluded that the major part should be of local rather than presolar origin. Some fraction, however, must be connected to anomalous noble gas components for which formation during a supernova explosion (e.g., [5]) is indicated.

Microscopic investigations on synthetic terrestrial nanodiamonds using HR-TEM show differences in their microstructure that depend on the formation mechanism [6]. Detonation diamonds (e.g., [7]) grow under anisotropic conditions; as a result they frequently show planar twin microstructures. CVD diamonds (e.g., [8]), on the other hand, show features indicating isotropic formation, like a large number of startwins [9]. From comparing the features of the various synthetic nanodiamonds with those of meteoritic ones it has been concluded that most of the latter were formed under isotropic conditions, similar to the low pressure CVD diamonds [6]. Note, however, the absence of the core exciton in XANES studies on meteoritic nanodiamonds [10], a feature that has been observed in studies on CVD diamonds of similar size [11].

Diamond is an unstable form of carbon under standard conditions. As a result of heating under low pressure diamond suffers morphological changes and is expected to transform into a nanodiamond-graphite core-shell structure [12]. Annealing of detonation diamonds produces onion-like carbon, where the temperature from which on noticeable transformation takes place is a function of the size of the particles. Diamond particles less than 2 nm in size convert rapidly at T ~1420 K [13].

Experimental: Expanding on work begun earlier [14], we investigated the alteration in annealed meteoritic nanodiamond samples with and without additional chemical treatment. For this we isolated nanodiamonds from acid dissolution residues of the primitive carbonaceous chondrites Allende and Murchison, following the procedure of [15]. Three sets of diamonds from each meteorite were annealed in vacuum at different temperatures (600, 800, 1000 °C). This was followed

by treatment with perchloric acid for several days in an attempt to remove the heating products, i.e. onions and amorphous carbon.

We studied all samples using high resolution transmission electron microscopy. The dry samples were ultrasonically suspended in a 1:1 mixture of isopropanol and H₂O. Between 1 and 5 μl of the suspension were deposited on 3 mm Cu grids coated with holey a-C film and dried at 85 °C in an oven.

Weight changes: Weight losses due to heating are similar for both Murchison (M) and Allende (A) nanodiamonds and as expected increase with temperature (600°C: M~16%, A~15%, 800°C: M~23%, A~20%, 1000°C: M~26%, A~22%). Additional weight loss, increasing in the same order was observed after the perchloric acid treatment of the heated samples.

HR-TEM studies: In the “pristine” samples (i.e. diamond residues) we found – as expected – almost only diamonds (Fig. 1).

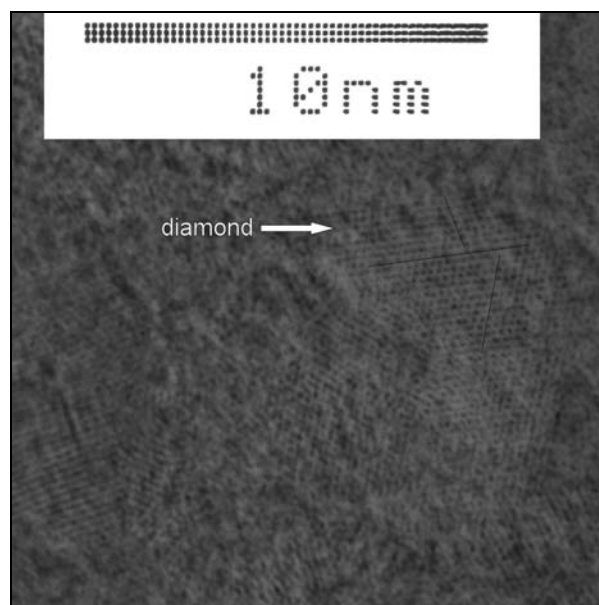


Figure 1: Nanodiamonds from Murchison (original residue).

Annealed samples. The annealed samples presented a problem because the diamonds tightly stuck together, and we did not succeed in efficient disaggregation by ultrasonication. Therefore we studied only the thinner rims of the aggregates. In all cases we found unaltered diamonds, smaller and bigger onion structures with one or more concentric rings, and amorphous carbon (Fig. 2). We also found some graphitic structures.

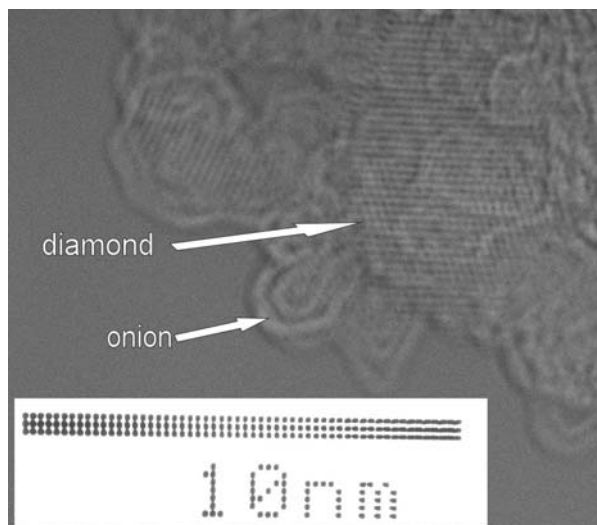


Figure 2: Onions and nanodiamonds in the annealed (1000 °C) nanodiamond sample from Allende.

Annealed and chemically treated samples. Our TEM investigations show that the chemical treatment had not been effective in removing the carbonaceous non-diamond phases. Apparently we partly destroyed the small onions, but on the other hand the treatment may have resulted in formation of some very large ones, some carbon tubes and significant amounts of amorphous carbon (Fig. 3).

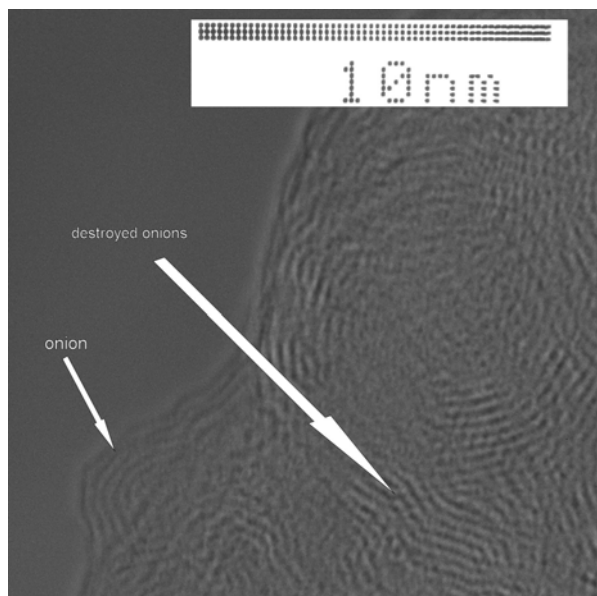


Figure 3: Onion-like structures in the annealed and chemically treated nanodiamond sample from Allende (1000°C).

In all samples we found remaining unaltered diamonds (Fig.4), but we did not find any diamonds with graphitic or onion-like shell as predicted by [12].

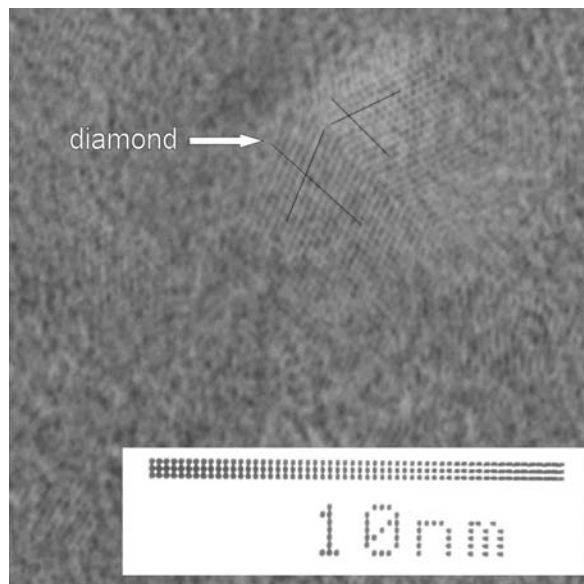


Figure 4: Nanodiamond in the annealed (1000 °C) and chemically treated nanodiamond sample from Murchison.

Implications and noble gases: Our TEM observations show that observable transformation of meteoritic diamond occurs at temperatures as low as 600 °C, which differs from the observations of [13], but agrees with our previous result [14]. Ultimately the aim of our investigations is to correlate the observed changes with the release of noble gases, and noble gas analyses of the annealed plus chemically treated samples are under way at this time. First results indicate that the residues still contain abundant noble gases of the HL type, with concentrations similar to those of the original diamond residues. Detailed mass balance calculations will be possible after completion of the measurements.

Acknowledgements: We thank S. Herrmann for help with the annealing and for performing the noble gas analyses.

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