

**DIAMOND NANOGRAINS IN CARBON SOOT: DOES THE CHEMISTRY OF EXTRACTED DIAMONDS DEPEND ON THE PROPERTIES OF PRISTINE SOOT?** A. P. Koscheev<sup>1</sup>, N. V. Zaripov<sup>1</sup>, U. Ott<sup>2</sup>, <sup>1</sup>Karpov Institute of Physical Chemistry, Vorontsovo Pole 10, 105064, Moscow, Russia, (koscheev@cc.nifhi.ac.ru), <sup>2</sup>Max-Planck-Institut für Chemie, Becherweg 27, D-55128 Mainz, Germany.

**Introduction:** Main efforts in the study of presolar diamond nanograins have been directed towards the isotopic analysis of trace elements (primarily, noble gases) [1] trapped inside the grains and the results allow to draw conclusions regarding stellar nucleosynthesis [1,2]. The surface chemistry of interstellar diamonds has been studied to much lesser extent, in spite of the fact that, due to the small size of diamond grains (2-4 nm) and their large surface to volume ratio, the surface species can represent a substantial part of grain material. Information about surface chemistry of diamond grains is important for the following reasons. First, the possibility exists that at least some extraterrestrial surface features of nanodiamonds may have survived [3]. If so, diamond grains with different history may reveal different surface chemistry. Second, surface species on diamond nanograins may be responsible for some of the IR absorption features observed in spectra of the interstellar medium [4,5] and it is necessary to know the relation between surface chemistry and optical properties of nanodiamonds.

The severe acidic treatments used usually to extract nanodiamond grains from meteorites were shown to modify surface properties analyzed by IR spectroscopy [6-9]. However, the fine details of IR spectra of diamonds extracted by the identical procedures from two different meteorites were not the identical [8]. In our previous work we have applied the same chemical treatment to the synthetic nanodiamonds extracted from detonation soot by different methods and the results indicated that a relation exists between the surface chemistry of nanodiamonds before and after treatment [10,11].

In the work presented here, we applied this approach to different types of untreated diamond containing soot which may be considered in some sense as analog of carbon material formed during explosion of stars. Such a study may help to understand if the different populations of diamonds (synthesized in different environments) can be distinguished by their surface chemistry after the extraction.

**Experimental:** We used two different types of diamond containing carbon soot produced by detonation of explosives in different scientific centers. According to the information of the producers the soot sample labeled CH7-ST was obtained by detonation of explosives in ice, the sample K2-ST – in carbon dioxide. Nanodiamonds chemically extracted from the soot have the same mean size of ~4 nm (estimated from the shape of X-ray diffraction lines) independent of the types of soot.

To extract nanodiamonds the pristine soot samples were treated by the same chemical procedure developed recently to separate meteoritic diamonds [12] including: 1) two steps of microwave digestion in HCl/HNO<sub>3</sub> and HNO<sub>3</sub>/HF mixtures; 2) washing in AlCl<sub>3</sub> solution; 3) washing in HCl solution; 4) colloidal separation in H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>; 5) drying. The surface chemistry of the samples both before and after chemical treatment was studied by means of thermodesorption mass spectrometry (TDMS) sensitive to the structure and abundance of different surface species in nanodiamonds [10,11,13]. Mass spectra of volatiles were measured by

quadrupole mass spectrometry in the mass range 2-100 amu during linear heating (15 °C/min) of the sample (~1.5 mg) up to 1100 °C in vacuum under permanent evacuation.

**Results and Discussion:** TDMS study of as received soot samples showed release of H<sub>2</sub>O, CO<sub>2</sub> and CO as main components (Fig. 1). In addition some hydrocarbons were released in the temperature range 200-500°C. H<sub>2</sub> and HCN started to be released at high temperature above 900°C.

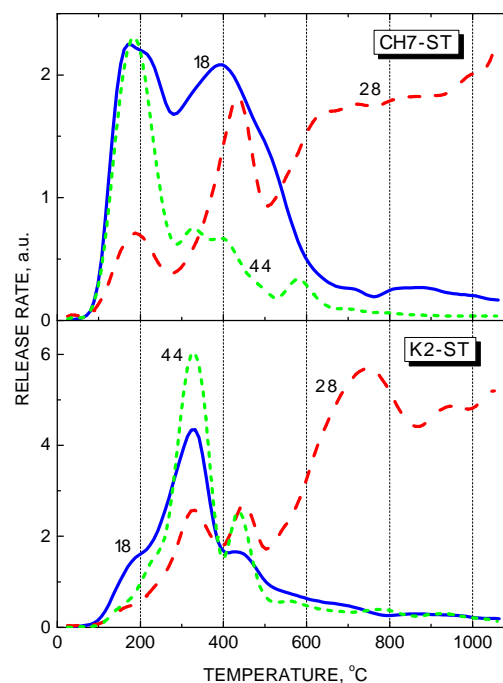


Fig. 1. TDMS profiles of H<sub>2</sub>O (m/e=18), CO (m/e=28) and CO<sub>2</sub> (m/e=44) for pristine carbon soot of different types.

Both the rates of release and the shapes of the temperature profiles of different components depended strongly on the type of the soot. As a rule TDMS profiles consisted of several peaks and shoulders (Fig. 1) accounting for the decomposition of different surface species on the soot grains. The positions and the intensities of these peaks are quite different for different soot samples. The total amount of volatiles released during pyrolysis of surface compounds on the surface of sample K2-ST is higher than in the case of CH7-ST.

The results indicate that the structure and the composition of surface species formed in diamond-containing soot during detonation synthesis strongly depend on conditions during the explosion. As detonation soot is a mixture of nanoparticles of diamond and nondiamond carbon [14], it is impossible to determine the surface properties of pristine diamond grains. However, it is reasonable to suggest that the surface chemistry of nanodiamonds in the soot depends on the synthesis conditions as well.

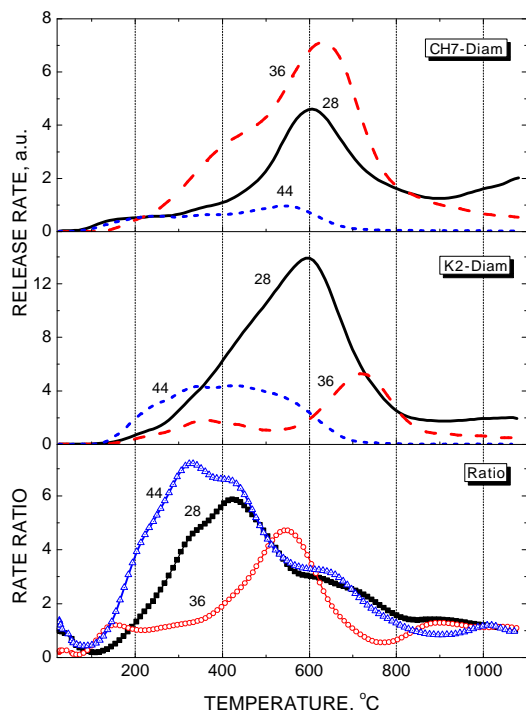


Fig. 2. The effect of chemical treatment on the TDMS patterns of CO ( $m/e=28$ ),  $\text{CO}_2$  ( $m/e=44$ ) and HCl ( $m/e=36$ ) release for nanodiamonds CH7-Diam and K2-Diam extracted from detonation soot CH7-ST and K2-ST, respectively.

The TDMS profiles for extracted nanodiamonds were modified substantially compared to the case of pristine soot (Fig. 2). The main components released from nanodiamonds were CO (500-700°C) and  $\text{CO}_2$  (200-600°C) both arising due to decomposition of surface oxide groups, and HCl (bimodal at 400-700°C) caused by contamination of the surface by chlorine during chemical extraction. The results indicate the pronounced difference between surface chemistry of different nanodiamonds illustrated by the ratio curves (“K2-Diam to CH7-Diam” for CO and  $\text{CO}_2$  and “CH7-Diam to K2-Diam” for HCl in the lower part of Fig. 2) between release rates of every component. The whole amount of released  $\text{CO}_x$  is higher in the case of K2-Diam in accordance with the data for pristine soot (Fig. 1). In contrast, the abundance of chlorine-containing species is highest for CH7-Diam. These results are in agreement with our previous data on chemically treated nanodiamonds CH7 and K2 [10,11]. What is more important, the shapes of ratio curves, consisting of several peaks and shoulders, indicate that the relative abundances of different surface oxide groups (carboxylic anhydride, lactone, carbonyl) decomposed at different temperatures are not identical for the two types of extracted diamonds. The same is valid for the chlorine-containing groups.

The obtained results give strong evidence that the final chemical state of extracted nanodiamond grains depends on the type of raw soot, which in turn differs according to the details of detonation synthesis. The detonation conditions can influence both the shape [15] and the structure of the

shell [16] of diamond grains. The chemical activity of diamond surfaces in various environments, on the other hand, depends on its atomic structure [17,18]. One could suggest therefore that surface “crystal” structure can be the primary factor affecting the chemical reactivity of nanodiamond surface towards environments (both during synthesis and extraction).

**Conclusions:** Our results strongly indicate that the details of detonation synthesis of diamond-containing carbon soot affect the surface chemistry of extracted nanodiamonds. In other words, the diamond grains retain a “chemical” memory on their origin even after extraction procedure. We are in the process of comparing details of the surface properties of presolar diamonds extracted by the same procedure from different meteorites.

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**References:** [1] Huss G. R. and Lewis R. S. (1994) *Meteoritics*, 29, 791-810. [2] Ott U. (1993) *Nature*, 364, 25-33. [3] Lewis R. S. et al. (1989) *Nature*, 339, 117-121. [4] Allamandola L. et al. (1993) *Science*, 260, 64-66. [5] Guillois O. et al. (1999) *Ap. J.*, 521, L133-L136. [6] Mutschke H. et al. (1995) *Ap. J.*, 454, L157-L160. [7] Hill H. G. M. et al. (1997) *MAPS*, 32, 713-718. [8] Braatz A. et al. (2000) *MAPS*, 35, 75-84. [9] Andersen A. C. (1998) *A&A*, 330, 1080-1090. [10] Koscheev A. P. et al. (2003) *LPSC XXXIV*, Abstract #1287. [11] Koscheev A. P. et al. (2003) *MAPS*, 38, A85. [12] Merchel S. et al. (2003) *GCA*, 67, 4949-4960. [13] Koscheev A. P. et al. (1998) *MAPS*, A88. [14] Kuznetsov V. L. et al. (1994) *Carbon*, 32, 873-882. [15] Chen P. et al. (2003) *Carbon*, 41, 2093-2099. [16] Iakoubovskii K. et al. (2000) *Diam. Relat. Mater.*, 9, 861-865. [17] Cheng C.-L. et al. (1997) *Phys. Rev. Lett.*, 78, 3713-3716. [18] De Theije F. K. et al. (2000) *Diam. Relat. Mater.*, 9, 929-934.