

THE STUDY OF KINETICS OF C, N AND Xe RELEASE DURING ISOTHERMAL PYROLYSIS AND SUBSEQUENT OXIDATION OF NANODIAMONDS FROM ORGUEIL. A. V. Fisenko¹, A. B. Verchovsky² and L. F. Semjonova¹, ¹Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, 19 Kosygin st., Moscow 117975, Russia (anat@chgnnet.ru), ²PSSRI, Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

Introduction. Analysis of grain-sizes fractions of meteoritic nanodiamonds is a perspective direction in cosmochemistry [1-3]. Here we present results on kinetics of release of C, N and Xe under different conditions during pyrolysis of two aliquots from intermediate in grain size fraction of nanodiamonds from meteorite Orgueil (CI). An isothermal pyrolysis which preceded step oxidation has been applied to one of the nanodiamond aliquot for the first time [4].

Experimental. Two aliquots designated as OD11-A and OD11-B from an intermediate in grain size fraction OD11 separated from meteorite Orgueil (CI) [5] are used for the study. Analysis of OD11-A has been performed by step pyrolysis from 300 to 800°C with 100°C increment and duration at each step of about 150 minutes. For OD11-B a multi-step isothermal pyrolysis has been applied in an interval from 400 to 800°C. The number of steps at each temperature varied from 4 to 10 with the total duration of 15-37 hours. The total duration of the isothermal pyrolysis experiment was about 130 hours. After pyrolysis both aliquots have been oxidized in the temperature range from 300 to 1000°C. The content and isotopic composition of C, N and Xe has been measured on our complex of mass spectrometers, Finesse, which allows to measure all these elements simultaneously [6, 7].

Results and Discussion. The fractions of C, N and Xe released during pyrolysis of OD11-A are equal (in %) to 12, 13 and 73, accordingly, whereas for OD11-B – 19, 50 and 67, correspondingly. The most important features of C, N and Xe release kinetics are summarized as following: 1. The rate of C, N and Xe release during isothermal pyrolysis decreases with time (Fig. 1). 2. The cumulative yields of C during pyrolysis for both aliquots are equal for all temperatures bellow 800°C (Fig. 2a). The difference in the C yield at 800°C (11.8% vs. 18.5%) is caused by a partial oxidation of OD11-B by oxygen released from quartz. This process depends on duration of pyrolysis at 800°C. Since the yield of carbon during pyrolysis does not exceed 20% of the total (Fig. 2a) most of it seems to be surface-correlated. The dependences of cumulative yields of C on temperature during oxidation almost coincide for both aliquots (Fig. 3a). 3. Release of N during pyrolysis strongly depends on duration of heating (Fig. 2b) that can be considered as an argument in favour of diffusion as the most important mechanism of its release. Release of N from OD11-B during oxidation is shifted to a high-

temperature range compared to OD11-A (Fig. 3b). The aliquot OD11-B is characterized by low N/C ratios at the beginning of oxidation (Fig. 3c). 4. The fraction of Xe-P3 released during pyrolysis does not depend on experimental conditions and for both aliquots is equal to about 85% (Fig. 2c). Consequently, it is the temperature of heating that is the major factor of Xe-P3 release. It can be due to, for instance, diffusion governed by mechanism of first-order reaction or destruction of its carrier by non oxidizing mechanism. 5. Only 12% of total C is released during pyrolysis when almost all Xe-P3 is released from aliquots (Fig. 5). The prolonged heating of OD11-B at 800°C does not result in additional release of Xe-P3 but does result in additional release of C. 6. Xe released by oxidation has different isotopic composition in OD11-A and OD11-B aliquots (Fig. 6a) that obviously is due to a different distribution of Xe-P3 after pyrolysis. Since cumulative yields of C on T during oxidation are almost identical in the aliquots (Fig. 3a) then the Xe-P3 carrier should represent a small fraction of the total carbon of the aliquots. This conclusion is in conflict with that made earlier [8] according to which P3 carrier is the most abundant diamond population.

Interpretation of N isotopic composition (Fig. 4a) has been made assuming that it consists of two components: N_h with $\delta^{15}N \approx 0$ and N_l with $\delta^{15}N \approx -350$. The amount of N_l released by pyrolysis from OD11-A is significantly lower than from OD11-B: about 10 and 45% respectively. For N_h this difference is considerably smaller but its fraction is much higher than for N_l : 43 and 72% for OD11-A and OD11-B, correspondingly. The biggest difference between the aliquots is observed in the kinetics of N_h released by oxidation (Fig. 4b).

The observed particularities in the kinetics of N released by pyrolysis and oxidation can be explained the following way: 1. The main fraction of N is located in the extended defects of nanodiamonds [11]. 2. N_h is located in at least two populations of nanodiamonds, while N_l only in one of them [10]. Concentration of N_h sharply decreases from grain surface to its centre whereas N_l has an opposite distribution that seems to be caused by the processes of the diamond formation. 3. The diamond grains with higher N_l concentration (due to fluctuations in N content in nanograins) are destroyed preferentially during exposure to heat [12].

The decrease of Xe-P3 release rate observed during pyrolysis of OD11-B and the small fraction of the total C associated with it can be explained by the

surface location of Xe-P3 [13, 14]. Alternatively Xe-P3 can be located in a separate diamond population with high concentration of defects caused by radiation [15]. In this case Xe-P3 has to have been implanted into grains of the population.

Conclusions. 1. The surface of meteoritic nanodiamonds contains different O bearing radicals dissociation temperature of which (leading to formation of CO/CO₂) has a wide temperature range (up to 800°C). 2. Concentration of nitrogen (N_h) with δ¹⁵N=0 sharply decreases from grain surface to its centre whereas nitrogen (N_i) with δ¹⁵N=-350 has an opposite distribution. The most probably N_i has been trapped into diamond during its growths but N_h could have been implanted at low energy. The diamond grains of the population with N_i have probably grown fast that provided preservation of N mainly in extended defects.

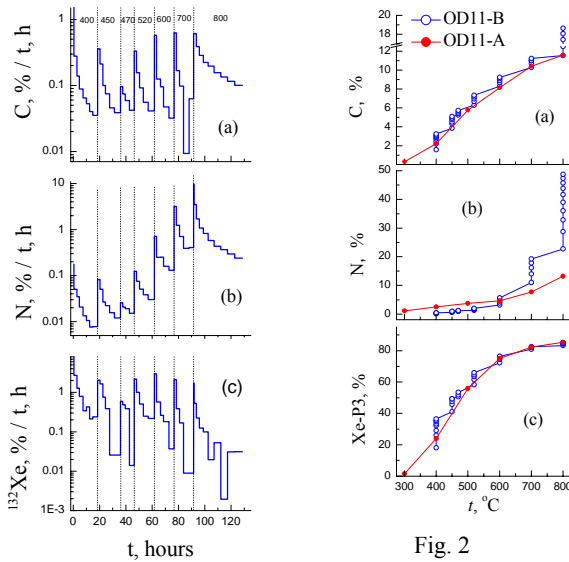


Fig. 1

Fig. 2

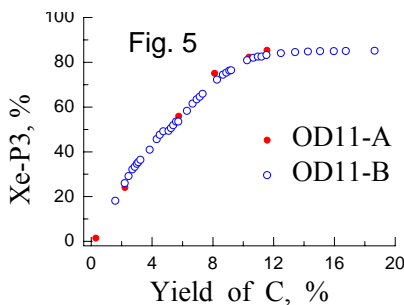


Fig. 5

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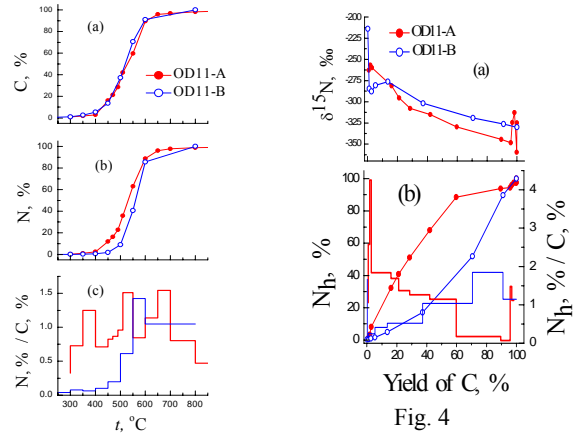


Fig. 3

Fig. 4

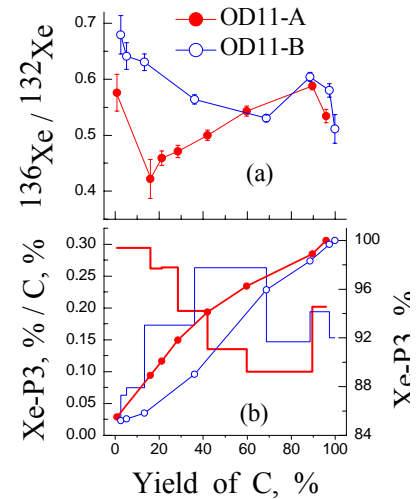


Fig. 6

3. Independently of the nature of Xe-P3 carrier, its fraction represents a small part of the total nanodiamonds.

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