GRAPHITIZATION OF THE METEORITIC NANODIAMONDS ACCORDING TO KINETICS OF Xe-HL RELEASE. A. V. Fisenko and L. F. Semjonova, Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Moscow, 119991 Russia (anat@chgnet.ru).

Introduction: During pyrolyses of the meteoritic nanodiamonds the high-temperature release of the noble gases (basically, the HL and P6 components) occurs mainly in a result of the diamond graphitisation. It follows from coincidence of maximum releasing temperatures of Ar and Xe [1]. We have calculated the parameters of graphitisation process of the meteoric nanodiamonds on basis of release kinetics of HL component xenon (Xe-HL) during stepped pyrolysis.

Calculations and data: Graphitisation process of the nanodiamond grains proceeds in a direction from surface to the centre (e.g., [2]) and therefore the speed of this process can be expressed as follows:

\[(R_i - R_{i+1})/t = A \exp(-E/kT)\]

(1),

where \(R_i\) and \(R_{i+1}\) are the radius of grains before and after heating at temperature \(T\) (in K) during time \(t\), accordingly, \(A\) and \(E\) – the preexponential factor and activation energy, accordingly, \(k\) – Boltzmann constant.

We calculated the \(R_i\) and \(R_{i+1}\) values on basis of the kinetics of \(^{132}\text{Xe}-\text{HL}\) release during stepped pyrolysis of the diamonds samples. At these calculations were accepted that (a) the average size of the grains containing the Xe-HL equal to \(R_0\), and (b) averaged on all these grains the radial distribution of the \(^{132}\text{Xe}-\text{HL}\) is uniform. Under these conditions the \((R_i - R_{i+1})\) value is equal:

\[(R_i - R_{i+1}) = R_0((N_r/N_0)^{1/3} - (N_{r+1}/N_0)^{1/3})\]

(2),

where \(N_0\) is initial content of the \(^{132}\text{Xe}-\text{HL}\) in sample, \(N_r\) and \(N_{r+1}\) are the \(^{132}\text{Xe}-\text{HL}\) contents before and after heating at temperature \(T\), accordingly. Having substituted (2) in (1) and take the logarithm, we shall receive following expression:

\[\ln((N_r/N_0)^{1/3} - (N_{r+1}/N_0)^{1/3}) = \ln(At/R_0) - E/kT\]

(3)

Parameters of linear dependence of \(\ln((N_r/N_0)^{1/3} - (N_{r+1}/N_0)^{1/3})\) from \(1/T\) allow to define the activation energy and \(A/R_0\) value of graphitisation process of the nanodiamonds – carrier phase of the HL component noble gases.

Values of \(E\) and \(A/R_0\) have been defined on the bases of release kinetics of \(^{132}\text{Xe}-\text{HL}\) according to data for bulk diamonds of various meteorites [1], and also for the fine-and coarse-grained fractions (DE2 and DE9, accordingly) of Efremovka nanodiamonds [3]. Note that the Ta foils were used in [1], whereas the Pt foils – in [3]. Values of \(E\) and \(A/R_0\) have been calculated also for four aliquots of carbonado diamonds (sample № 90717), using \(^4\text{He}\) contents according to data in [4]. The average size of grains of three carbonado aliquots (designated further as \(a, b, c\)) is equal 2 \(\mu\)m, and of fourth \((d)\) – 5 \(\mu\)m. At stepped pyrolysis of \(a\) and \(b\) aliquots the Al foils were used, and for \(c\) and \(d\) aliquots – the Pt foils.

Results and discussion: The Arrhenius plots for all diamonds samples are identical on structure and they are similar to plot, e.g., for meteorite Indarch nanodiamonds (Fig. 1).

Basic feature of these plots is that for any of samples all the pyrolysis data not is in agreement with one linear dependence (e.g., Fig. 1). Therefore at calculations of \(E\) and \(A/R_0\) for the diamond samples we only used a high-temperature interval (designated further as \(T(h)\)) in which the greatest amount of gas is released and data correspond to linear dependence. For meteoritic diamond samples the \(^{132}\text{Xe}-\text{HL}\) contents in interval of \(T(h)\) vary from 70 up to 90 \%. For carbonado samples the fraction of the \(^4\text{He}\) in interval of \(T(h)\) depends essentially on type of foil: for Al it is equal about 67 \%, whereas for Pt – about 97 \%.
The calculated values of \( \ln(A/R_o) \) and \( E \) are shown on Fig. 2 for all diamonds samples.

![Graph showing the dependence of \( \ln(A/R_o) \) on \( E \).]

**Fig. 2.** Dependence of \( \ln(A/R_o) \) from \( E \). Notation: MND – bulk meteoritic nanodiamonds; FDE – fractions of the Efremovka nanodiamonds; UDD – detonation nanodiamond; Carb – carbonado diamonds; Al, Or and In – Allende, Orgueil and Indarch diamonds, accordingly.

On Fig. 2 the \( \ln(A/R_o) \) and \( E \) are shown also for detonation diamond (UDD) according to data in [2]. The average size of UDD grains is equal 4.7 nm and the graphitic crucible was used during stepped pyrolysis. According to data in Fig. 2, we can see (1) the values of \( E \) and \( \ln(A/R_o) \) for meteoric nanodiamonds are less than those for other diamond samples, and (2) the linear dependence there is with high factor of correlation for all diamonds samples irrespective of their nature, except for DE2.

On the basis of different values of \( \ln(A/R_o) \) and \( E \) for carbonado diamonds aliquots (Fig. 2) it follows that the grains size and the presence of chemical elements interacting with carbon of the diamond are the factors, influencing on parameters of graphitization diamond process. Additional factor for the meteoric nanodiamonds can be the distinctions of morphology and(or) of defects of a superficial layer of the diamond grains, caused by different conditions of the metamorphism of meteorites parental bodies..

For meteoric nanodiamonds samples, the deviations of starting and final pyrolyses data from linear dependence in interval of \( T(h) \) on Arrhenius plot are caused by different factors. At starting stages this is the result of Xe-HL releasing due to thermal dissociation of the functional groups on a surface of grains, whereas on final – the result of infringement of layer-by-layer graphitization process. Formation of the functional groups on a surface of grains basically during chemical etching explains the Xe-HL release from Indarch nanodiamonds at temperatures of pyrolysis below 700 °C (Fig. 1), i.e. below temperature of thermal metamorphism of this meteorite [5].

During pyrolysis of the meteoritic nanodiamonds more high-temperature the release of xenon than Xe-HL is observed for P6 component xenon (Xe-P6) [1]. Xe-P6 isotopic composition is abnormal, but in less degree than of Xe-HL, or it is near normal. It is supposed that HL and P6 gases are contained in different on thermostability of diamond grains [1]. However, if the gases of HL and P6 components are released in result of the layer-by-layer graphitization of the diamond grains then perhaps that HL and P6 components is one component, in which the isotopic composition of gases depends on their localization in diamond grains. Namely, the central area of large grains are contains the gases corresponding to the P6 component, while other areas, as well as the fine grains content the HL component. Such heterogeneity of the grains in Xe isotopic composition can be caused by a radial gradient in content of the captured isotopes of Te. Radioactive precursors of \(^{132}\)Xe and \(^{134}\)Xe (\(^{132}\)Te and \(^{134}\)Te) have more long \( T_{1/2} \), than other isotopes of Te. Therefore the capture of \(^{132}\)Te and \(^{134}\)Te (e.g., in the form of carbides) by growing grains of diamond in a greater degree than other isotopes of Te and their subsequent decay in situ will lead to shift of Xe isotopic composition to Xe-P6. Note that linear dependence in interval of \( T(h) \) at using of (HL+P6)-Xe sum is kept, but the values of \( \ln(A/R_o) \) and \( E \) slightly are increased.

**Conclusion:** The values of the activation energy and normalized to average radius of grains the preexponential factor of graphitization process of the meteoritic nanodiamonds with HL component gases are in intervals (9.6-36.0) kcal/mol and (0.001-15.2) s\(^{-1}\), accordingly. These intervals are basically result of various conditions of thermal metamorphism of meteorites parent bodies. At layer-by-layer graphitization of the diamond grains heterogenous radial distribution of Xe radioactive precursors in grains can be the essential factor for the interpretation of the Xe-HL and the Xe-P6 origins.