

ON THE RELEASE MECHANISM OF Xe-P3 DURING STEPPED AND ISOTHERMAL PYROLYSIS OF ORGUEIL METEORITE NANODIAMONDS. A. V. Fisenko¹, A. B. Verchovsky² and L. F. Semjonova¹, ¹Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, 19 Kosygin st., Moscow 119991, Russia (anat@chgnnet.ru), ²Department of Physical Sciences, Open University, Walton Hall, Milton Keynes MK7 6AA, UK.

Introduction. In the meteoritic nanodiamonds there are two main noble gas components, P3 and HL [1]. P3 noble gases are isotopically similar to solar and release during pyrolysis mostly up to 800°C while HL are significantly different from solar isotopic composition and released in the range from 1100 to 1500°C [1]. If for the HL gases there is a consensus regarding the release process as a result of graphitisation of nanodiamonds at high temperature [1] then the process of the P3 gases release remains much less understood. We have performed the analysis of the release kinetics of Xe-P3 during stepped and isothermal pyrolysis of the coarse-grained fractions of Orgueil nanodiamonds in order to shed more light on this problem.

Experimental. The separation of the Orgueil colloidal nanodiamonds into seven grain-size fractions have been performed by sedimentation method under various conditions of the centrifugation [2]. We have analysed three of them, designated as OD-11, OD-16 and OD-15, which are supposed to be the most coarse-grained.

Isotopic compositions and concentrations of C, N, Ar and Xe have been analysed by a combination of pyrolysis and subsequent combustion using Finesse instrument [3]. Pyrolysis of the samples has been carried out from 300 to 800°C with 100 increment and release time on each step of about 150 min, except for the first step, which was shorter (30-100 min). We also used the results of isothermal pyrolysis of the OD-11 fraction aliquot (designated as OD-11B) at 400°C [4]. The number of steps at this temperature in this experiment was equal to eight and the duration of heating on the steps was from 31 until 220 minutes.

Results and discussion. Some of the results of analyses of the fractions are shown in Table 1. For calculations of the relative abundance of Xe-P3 and -HL, we ignored Xe-P6.

Table 1.

Fraction	¹³² Xe, 10 ⁻⁸ cm ³ /g	¹³⁶ Xe/ ¹³² Xe	¹³² Xe-P3/ ¹³² Xe-HL	¹³² Xe-P3*, %
OD-7	52.1	0.443 (3)	1.95 (7)	84.4 (1.1)
OD-11	127.9	0.369 (3)	5.61 (34)	85.5 (9)
OD-11B	140	0.407 (2)	3.10 (9)	85.1 (1.0)
OD-16	222.4	0.349 (2)	9.0 (1.0)	88.8 (5)
OD-15	362.5	0.332 (2)	16.7 (1.6)	89.2 (3)
Orgueil [1]	49.79	0.4202 (11)	2.54 (4)	84.4 (1)

* The part of Xe-P3, which was released up to 800°C in this work and up to 865°C in [1]. One sigma uncertainties are shown in parentheses.

The Xe concentration and the Xe-P3/Xe-HL ratio for the fractions are higher than for the bulk Orgueil nanodiamonds (fraction OD-7 and data from [1]). These results are additional arguments that the fractions are coarser than the bulk nanodiamonds.

Xe-P3 diffusion with single activation energy. We investigated the diffusion process of the Xe-P3 release suggesting that it is determined by the mechanism of the first order chemical reaction.

For the calculations of the activation energy (E) and frequency factor (ν_0) of this process we used the linear dependence of these parameters in a following kind [5]:

$$\ln \ln(N_0/N_r) = \ln(\nu_0 t) - E/kT, \quad (1)$$

where N_0 is the initial concentration of Xe-P3, N_r is the concentration of Xe-P3 after heating during time t , k - Boltzmann constant and T - temperature of heating (in K). The N_0 has been supposed to be equal to the total amount of Xe-P3 released up to 800°C. The Arrhenius plot for Xe-P3 released during pyrolysis of the coarse-grained fractions of Orgueil nanodiamonds are shown in Fig. 1.

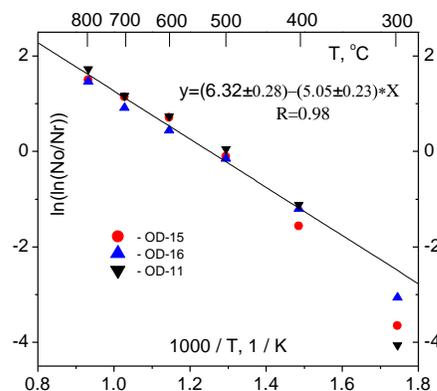


Figure 1.

Since the release time at 300°C was shorter than for the other steps, we ignored the 300°C step. According to parameters of linear dependence for three fractions, the activation energy and the frequency factor are equal to (10.0 ± 0.5) kcal/mol and $(0.062^{+0.020}_{-0.015})$ s⁻¹, correspondingly.

Using the values of E and ν_0 , we have calculated from the equation (1) how much of the initial Xe-P3 can be preserved in the nanodiamonds during parent body metamorphism. For this purpose, we accepted the metamorphism temperature for Orgueil was equal to 100°C [6]. The results of the calculations indicate that all Xe-P3 should be lost for two years. Such a short time of the Xe-P3 loss is not compatible with the much longer time scale of the thermal metamorphism of the meteorites parent bodies. Thus, the diffusion with single activation energy is not the right physical model for this case. This conclusion follows also from consideration of the data for the isothermal pyrolysis, using equation (1) as follows:

$$\ln \ln(N_0/N_r) = (\ln(\nu_0) - E/kT) + \ln(t) \quad (2)$$

As can be seen, during the diffusion with single activation energy at const T the slope of the line on the plot $\ln \ln(N_0/N_r)$ vs $\ln(t)$ must be equal to unity. However, the data for the isothermal pyrolysis of the OD-11B fraction at 400 °C form a line with the slope that is significantly less than one (Fig. 2).

Thus, it is obvious that the Xe-P3 diffusion with single activation energy does not fit the experimental observations and must be rejected.

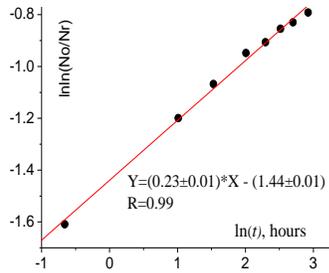


Figure 2. The results of isothermal pyrolysis of the OD-11B fraction at 400°C.

Xe-P3 diffusion with spectrum of activation energies.

In this case, we assume that the release curve of Xe-P3 is a result of a superposition of a number of the Xe-P3 release peaks at different temperatures. For simplicity, we assumed that all peaks have a Gaussian form. Seven peaks of the Xe-P3 release with corresponding relative abundances have been chosen for the model calculations (Fig. 3).

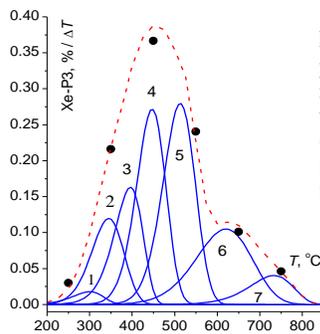


Figure 3. The assumed peaks of the Xe-P3 release. Dash line fits the experimental data (black points representing average for the fractions analysed).

For each peak the values of E and v_0 have been calculated (Table 2) using the equation (1) and the Gaussian function for definition of Nr values depending on temperature.

Peaks	E , kcal/mol	v_0 , s ⁻¹	%
1	18.3	1270	1.7
2	21.3	4425	11.4
3	28.5	295 × 10 ³	14.0
4	32.3	89 × 10 ⁴	23.6
5	35.0	725 × 10 ³	26.6
6	26.3	297	17.4
7	41.4	120 × 10 ³	5.3

Table 2. The model-calculated diffusion parameters of Xe-P3 release and relative abundance of the Xe-P3 in the peaks.

Calculation of the Xe-P3 losses according to the model with a spectrum of activation energies has shown that the main part of the Xe-P3 is retained at 100°C even during tens of thousand years (Fig. 4).

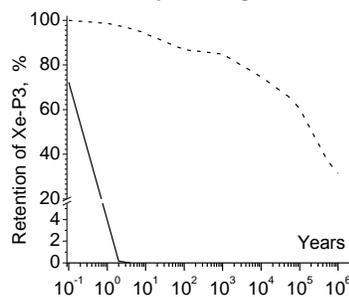


Figure 4. The solid line is for the model with single activation energy; the dashed line is for the polymodal Xe-P3 release.

Thus, the model with a spectrum of desorption parameters appears to describe the Xe-P3 release from nanodiamonds adequately enough.

An important question is what causes the appearance of such an energetically complex Xe-P3 distribution within the nanodiamond grains?

One possibility is based on assumption that the P3 gases are located in a separate population of the diamond grains, which are significantly damaged by the radiation [7]. Therefore the kinetics of Xe-P3 release depends on the kinetics of annealing of defects. For example, the spectrum of activation energies of helium release is observed for radioactive minerals the lattice of which is damaged by radiation produced as a result of radioactive decay of U and Th [8]. There is an experimental evidence showing that the higher the implantation dose of implanted noble gases the lower their release temperature [7]. In the implantation experiments by Koscheev et al. [9] the low temperature release of implanted noble gases also can be a result of radiation damages caused by implantation (i.e. the low temperature traps which are assumed by these authors are a consequence of significant structural damages of the grains by radiation).

Other possibility is based on assumption that the P3 gases are trapped by the graphite-like mantle of the diamond grains [1, 10]. This mantle could be formed by a radiation-induced reactions on the cold diamond surfaces [1] or by thermal effect [11]. Variable sp²/sp³ hybridisation ratio in the mantle and modification of this mantle as a result of closing of the traps containing the Xe-P3 could lead to a spectrum of activation energies of the Xe-P3 release during pyrolysis.

Conclusions. The diffusion process of the first order chemical reaction can describe release kinetics of the main fraction of Xe-P3 from meteoritic nanodiamonds during stepped or isothermal pyrolysis. However, in the framework of this model a good agreement between the calculated and observed retention of Xe-P3 during parent body thermal metamorphism can only be achieved if there is spectrum of the activation energy of Xe-P3 release. Most likely, the energetically complex Xe-P3 distribution in the meteoritic nanodiamonds is caused by the structural damages of the diamond grains or their mantles. These damages have probably a radiation or thermal origins.

References: [1] Huss G.R. and Lewis R.S. (1994) *Meteoritics*, 29, 791-810. [2] Fisenko A.V. and Semjonova L.F. (2008) *LPS XXXIX*, Abstract # 1078. [3] Verchovsky A.B. et al. (1997) *Meteoritics & Planet. Sci.*, 32, A131. [4] Fisenko A.V. et al. (2013) *Geochem. Intern.*, 51, 1-12. [5] Anufriev G.S. (2010) *Phys. Stat. Sol.* 52, 2058-2062. [6] Huss G.R. and Lewis R.S. (1994) *Meteoritics*, 29, 811-829. [7] Verchovsky A.B. et al. (2000) *Goldschmidt 2000, Oxford, Cambridge Publications 2000*. Abstract # 1050. [8] Shukolyukov Yu.A. (1970) *Uranium nuclides fission in nature*. Atomizdat, Moscow, USSR. 270p. [9] Koscheev A.P. et al. (2001) *Nature*, 412, 615-617. [10] Fisenko A.V. and Semjonova L.F. (2010) *Geochem. Intern.*, 46, 1177-1184. [11] Braatz A. et al. (1999) *Meteoritics & Planet. Sci.*, 34, A16.

Acknowledgements - This work was supported by RFBR (grant # 12-05-00208a).