

**ISOTHERMAL LOW-TEMPERATURE COMBUSTION OF NANODIAMONDS FROM ORGUEIL: RELEASE OF Xe-P3 BY VOLUME DIFFUSION.** A. B. Verchovsky<sup>1</sup>, A. V. Fisenko<sup>2</sup> and L. F. Semjonova<sup>2</sup>, <sup>1</sup>PSSRI, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (a.verchovsky@open.ac.uk) <sup>2</sup>Vernadsky Institute of Geochemistry and Analytical Chemistry RAS, 19 Kosygin st., Moscow 117975, Russia.

**Introduction:** The bimodal release pattern of noble gases (and in particular Xe) from meteoritic nanodiamonds remains a subject of debate. The difference in the release temperatures between the low-temperature Xe-P3 and the high-temperature Xe-HL (and P6) is huge – almost 1000° [1]. The first idea to explain such difference suggested [1] that the low-temperature Xe-P3 is sited in the poor crystalline diamond surface layer with non diamond sp<sup>2</sup> structure, while Xe-HL is located in the proper sp<sup>3</sup> diamond structure and can be released only as a result of graphitization at high temperature. The scenario corresponding to this case suggests that Xe-P3 is surface-trapped component and Xe-HL – implanted. A different explanation has come from separation of nanodiamonds into grain-size fractions which demonstrated a strong correlation between concentrations of both Xe-P3 and HL and grain size of nanodiamonds: the higher the grain-size, the higher the concentration of Xe [2]. When concentrations of Xe-P3 are changed by 3 orders of magnitude, concentrations of Xe-HL are different only by factor of 3, so that P3-Xe/HL-Xe ratio varies significantly on grain size being higher in the coarser fractions [3]. The observations have been explained as a result of ion implantation of P3 and HL noble gases at which the ion ranges are comparable with the size of diamond grains [2]. This scenario supposes that in order to explain the bimodal release it is necessary to suggest that HL and P3 components are located in different populations with similar grain sizes but distinct thermal properties. And of course Xe-P3 in this case is not surface correlated. However, if Xe-P3 and HL are located in different populations then the last statement is true only if population with Xe-P3 is dominated in the mixture. Otherwise, if it is a minor component, the dependence of Xe-P3 concentration on grain size remains uncertain because of normalization to the total amount of diamonds. And in principal it can be surface-correlated and not implanted. Another explanation of the bimodal release has been suggested on the basis of the experimental noble gas implantation into synthetic nanodiamonds [4]. Release pattern of an implanted noble gas mixture in a single event demonstrated a striking similarity with bimodal release of noble gases from meteoritic nanodiamonds. The scenario which would fit the experimental data suggests that the HL noble gases have been implanted first at relatively high temperature so that the low-temperature peak was annealed. P3 gases have been implanted later

when the temperature of diamonds dropped and therefore both peaks were preserved. The P3 and HL noble gases can be located in the same or different populations but in any case the scenario suggests that the high-temperature release is also dominated by Xe-P3, and consequently Xe-HL must be a minor component with extremely anomalous isotopic composition [5]. This scenario has some problems. First of all, it is not clear why noble gases implanted into nanodiamonds in a single event have bimodal release. Whether it is a fundamental property of nanodiamonds to have two different types of defects to be released at such different temperatures or the defects are formed during irradiation? Secondly, it is possible that the bimodal release is an artifact due to implantation into a thick target so that noble gases penetrated deeper than into one layer of the diamonds target. As has been shown earlier [6], the release temperature of implanted noble gases is controlled mostly by the total radiation dose which would be different for the different layers. And therefore bimodal release can be explained by such an effect. Thirdly, a simple consideration of Xe isotopic compositions and Ar/Xe element ratios on the three-isotope plot for nanodiamonds with different Xe-P3/Xe-HL mixing ratios suggests that <sup>136</sup>Xe/<sup>132</sup>Xe in the pure Xe-HL component is close to the maximum observed - ~0.7 [7] i.e. it is not extremely anomalous.

In order to shed more light on the problem of the bimodal release of noble gases from meteoritic nanodiamonds we decided to make a long-term oxidation experiment at relatively low constant temperature.

**Experimental:** A fraction of nanodiamonds separated from Orgueil with grain size a little bit higher than average have been used for the experiment. For the isotope measurements we used our multi-element analyzer Finesse. C, N, Ar and Xe isotope were analyzed in each step. The experiment has been conducted at 400°C with step time ~1h and constant oxygen pressure at each step. 40 steps have been done at that temperature, then 10 more at 450°C in order to release almost all Xe-P3.

**Results:** As can be seen from Figure 1, release of Xe-HL and P3 are significantly different from each other in the combustion steps. In contrast to Xe-HL which release is mostly controlled by amounts of combusted C (Xe-HL/C ratio is only slightly variable), Xe-P3 seems to be released almost independently of carbon.

More than 80% of Xe-P3 is released when ~40% of C is oxidised. This roughly corresponds to the surface sited atoms of carbon. Thus, this observation can be considered as indication of surface location of Xe-P3. Such idea is accepted in [8]. However, it is very difficult to explain extremely sharp increase of Xe-P3 concentration with increasing grain size within this hypothesis.

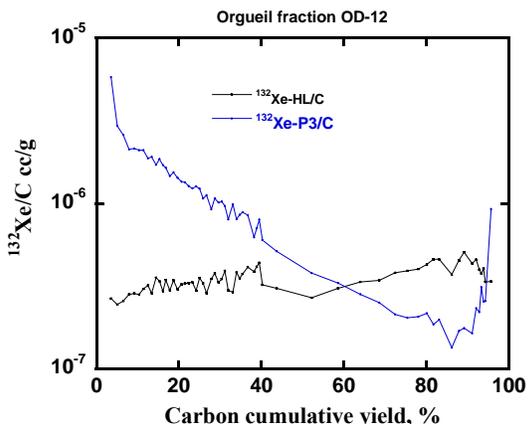


Figure 1. Release of Xe components.

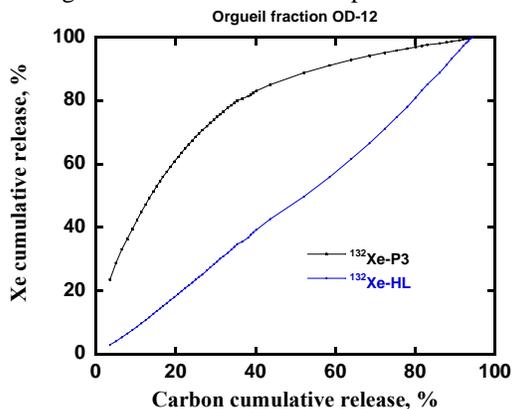


Figure 2. Carbon and Xe release.

**Discussion:** In order to identify the mechanism by which Xe-P3 is released we decided to use Fick's law applied for spherical grains:

$$Q = Q_0 \cdot \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left( \frac{1}{n^2} e^{-\pi^2 \cdot n^2 \cdot \tau} \right)$$

where  $Q_0$  and  $Q$  – initial concentration and concentration left in the grains after heating for certain amount of time correspondingly, and  $\tau = Dt/R^2$  – factor Fourier;  $D$  – diffusion coefficient,  $t$  – time and  $R$  – grain radius. If release of Xe follows the volume diffusion law, then  $\tau$  is linear function of  $t$  at constant  $D$  (temperature). In the case of desorption from the surface layer the process would rather follow the 1<sup>st</sup> order reaction and  $\tau$  is not linear function of  $t$ . In Figure 3 the values of  $\tau$  found from the above equation for each time-step are

plotted against time for the steps at 400°C. As can be seen the experimental data form a well defined linear dependence indicating that the physical process controlled the release of Xe from the nanodiamond grains is volume diffusion (AVF suggests that Xe-P3 can be released by volume diffusion from the graphite-like sp<sup>2</sup> surface layer). Oxidation does not seem to affect very much grain radius since at the end of Xe release at 400°C only the very surface layer is destroyed.

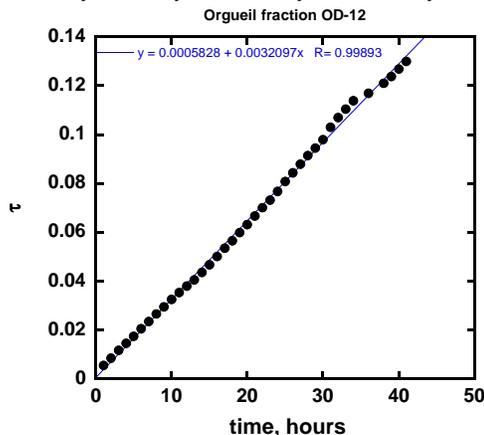


Figure 3. Dependence of factor Fourier on time.

Thus, the results allow to conclude that Xe-P3 is distributed within the nanodiamond grains as a volume-correlated component. The most likely process of its trapping is ion implantation. In order to explain the relatively low (compared to Xe-HL) release temperature of Xe-P3 we have to suggest that it is located in a separate population in which diffusion of Xe occurs faster than in the population containing Xe-HL. The reason for that could be different radiation history of the populations since experimental data suggest that the higher the radiation dose the higher the diffusion rate of implanted species [6].

We plan to apply isothermal heating without oxidation to the same sample and also analyse fractions with different grain size in order to confirm the volume diffusion mechanism of Xe-P3 release from nanodiamonds.

**References** [1] Huss G. R and Lewis R. S. (1994) *Meteoritics* 29, 791; [2] Verchovsky A. B. et al. (1998) *Science*, 281, 1165; [3] Fisenko A. V. et al. (2004) *Geochim. Int.* 42, 708; [4] Koscheev A.P. et al. (2001) *Nature* 412, 615; [5] Huss G.R., Ott U., Koscheev A.P. (2008) *Met. Plan. Sci.* 43. 1811; [6] Verchovsky A. B. et al. (2000) *Goldschmidt 2000, J. Conf. Abstracts* 5, No 2, abstr. # 1050; [7] Fisenko A. V. et al (2010) *LPSC XLI*, abstr. # 2008; [8] Fisenko A. V. and Semjonova L. F. (2010) *Geochim. Int.* 48, 1177.