FIRST RESULTS OF ULTRASONIC PROCESSING OF THE METEORITIC NANODIAMONDS.
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Introduction. The meteoritic nanodiamonds (MND) are heterogeneous by the contents and isotopic compositions of carbon and impurities elements [e.g., 1-3]. This heterogeneity is caused by mixing of different populations of nanodiamond grains and by processes of impurity elements capture. One of possible ways of study the MND heterogeneity can be an ultrasonic processing. The idea behind is in the formation of the cavitations bubbles with relatively high P and T that could affect the diamond grains selectively. Here we present the first results of a ultrasonic effect on the Orgueil (CI) diamond-rich separate.

Experimental part. The bulk diamond-rich separate of Orgueil (designated further as OD7) has been treated ultrasonic (22 kHz) in a brass crucible during 3 hours in a solution of <0.1M HCl. Then the traces of brass have been removed by the HCl–HNO_3 (80 ^oC) treatment. After removing the acids the separate has been transferred to colloid. The following samples have been obtained as a result of centrifugation (1000g, 40 min) of the colloid: a suspension (OD7C) and a sediment (OD7D). The contents and isotope compositions of C, N and Xe in OD7C were measured using the multielement analyzer, Finesse [4], employing a combination of stepped pyrolysis from 300 to 800 ^oC and combustion from 300 to 1300 ^oC. The results for OD7C are given in the Table and in Figs. 1, 2. The unpublished data for OD7 and OD10 and the other grain-size fractions of Orgueil diamond-rich separate are also included. Note, the fraction OD10 was obtained from a suspension after centrifugation (13500g, 6h) of the colloidal solution of the Orgueil bulk diamond-rich separate OD7.

Discussion. The decrease of nitrogen concentration in the fractions OD7C and OD10 relative to OD7 is observed for both pyrolysis and oxidation (Table, Fig. 1a). The reduction of N for OD10 is caused by depletion of this fraction with coarse grains. According to the centrifugation conditions the fraction OD7C must be depleted by coarse grains relative to OD7 in lesser degree, than OD10. This is confirmed, in particular, by almost identical isotopic composition of the bulk Xe in OD7C and OD7 (Table) in view of the fact that Xe isotopic composition is a function of grain sizes [3]. At the same time the Xe isotopic composition in OD10 is significantly different from that in OD7 (Table). Therefore the losses of nitrogen in OD7C in a greater degree, than in OD10, are most likely caused by the ultrasonic processing. Reduction of the nitrogen concentrations during pyrolysis and oxidation of OD7C does not correlate with changes of its isotopic composition relatively to that in OD7 (Fig. 1b). The $\delta^{15}N$ value sharply decreases in the pyrolysis steps and in the first oxidation steps of OD7C (yield of C up to 35%) compared to OD7 (Fig. 1b). However in the further oxidation steps of OD7C (yield of C from 35 up to 82%) the $\delta^{15}N$ values almost coincide with those for OD7 (Fig. 1b). After release of 82% C the $\delta^{15}N$ in OD7C continues to decrease up to the last oxidation step whereas for OD7 and OD10 the $\delta^{15}N$ begins to increase (Fig. 1b). Hence, the ultrasonic processing and the subsequent centrifugation of OD7 have led to removal of a fraction of heavy nitrogen associated probably with the superficially functional groups and with high-temperature carrier phase(s) (e.g., Si_3N_4, SiC).

The above changes in nitrogen content and isotopic composition in OD7C suggest the following four components of nitrogen to be present in the sample OD7. One of them is the surface-connected nitrogen which associated, possibly, with the functional groups. The identical $\delta^{15}N$ values observed in OD7 and OD7C in the interval of 35-82% of C yield during oxidation suggests the following properties for the other two nitrogen components. These components should have a different N isotopic composition, but an identical efficiency of N preservation in the diamonds during ultrasonic processing. The both conditions are satisfied if these nitrogen components are volume-connected and located in different populations of the diamond grains. The fourth nitrogen component is enriched in the heavy isotope and should have a carrier phase(s) (e.g., Si_3N_4, SiC) which is destroyed by the ultrasonic or is separated after that from the diamond grains during the subsequent centrifugation.

The significant decrease of the Xe concentration in OD7C has almost not resulted in the changes of the $^{136}Xe/^{132}Xe$ and $^{134}Xe/^{132}Xe$ ratios, except for Xe in pyrolysis steps (Table). This possibly happened as a result of cavitation processes that led to the destruction of some diamond grains with Xe atoms, e.g., as a result of oxidation due to a local increase of temperature. At the same time, the $^{136}Xe/^{132}Xe$ ratio for Xe released during pyrolysis of OD7C is considerably deviated from the trend observed for the other grain-size fractions (Fig. 2). Obviously, the ratio of

$(^{136}Xe/^{132}Xe)_{pyr}$ for OD7C exceeds significantly that for the fractions with similar values of the $(^{136}Xe/^{132}Xe)_{total}$ ratio. This increase is caused, most likely, by losses of a fraction of Xe-P3 as a result of ultrasonic processing. Whether these losses are connected with the removal of Xe-P3 from the superficial layers of the diamond grains or with the destruction of grains with P3 component of noble gases only, remains an open question now.

The changes in the contents and isotopic compositions of N and Xe revealed after the ultrasonic processing of the grain separates are most likely caused by the formation of cavitations bubbles and their subsequent collapses. The gas in the bubbles contains oxygen and the collapse of them is accompanied by increasing of P and T. The complex influence of these factors leads to the depletion of the nitrogen content in the functional groups on the surface of the grains as well as N and other volume-connected impurities from the grain's interiors.

Conclusion. The ultrasonic processing of the diamond-rich separates from meteorites and the subsequent separation of them by the sedimentation method can be used for the analysis of the impurity elements heterogeneity in the meteoritic nanodiamonds.

References: [1] Huss G.R and Lewis R.S. (1994) *Meteoritics, 29,* 811–829. [2] Russell S.S. et al. (1996) *Meteoritics & Planet. Sci., 31,* 343–355. [3] Verchovsky et al. (1998) *Science 281,* 1165–1168. [4] Verchovsky et al. (2000) *Goldschmidt 2000,* Abstract #5(2). *This work was partly supported by RFBR grant 12-05-00208-a*

Table. Results of analysis of the diamond-rich separates of Orgueil meteorite

	$\delta^{13}C$, ‰	$\delta^{15}N$, ‰	100*N/C	$^{132}Xe/Cg$	$^{136}Xe/^{132}Xe$	$^{134}Xe/^{132}Xe$
			Pyrolysis up to 800 °C			
OD7	-30.5	-184.5	1.11	3.54E-06	0.326±0.003	0.385±0.003
OD7C	**-25.2**	**-248.3**	**0.56**	**2.38E-06**	**0.340±0.001**	**0.393±0.001**
OD10	-29.4	-202.8	0.81	2.32E-06	0.329±0.003	0.387±0.004
			Oxidation up to 1300 °C			
OD7	-34.9	-314.2	1.37	3.49E-07	0.603±0.005	0.564±0.005
OD7C	**-30.4**	**-320.6**	**0.97**	**2.32E-07**	**0.599±0.001**	**0.565±0.001**
OD10	-34.5	-335.5	1.26	3.64E-07	0.609±0.005	0.575±0.004
			Total			
OD7	-34.4	-301.6	1.34	7.17E-07	0.442±0.003	0.459±0.003
OD7C	**-29.7**	**-315**	**0.94**	**4.97E-07**	**0.447±0.001**	**0.464±0.001**
OD10	-33.8	-324.7	1.21	5.97E-07	0.477±0.003	0.486±0.003

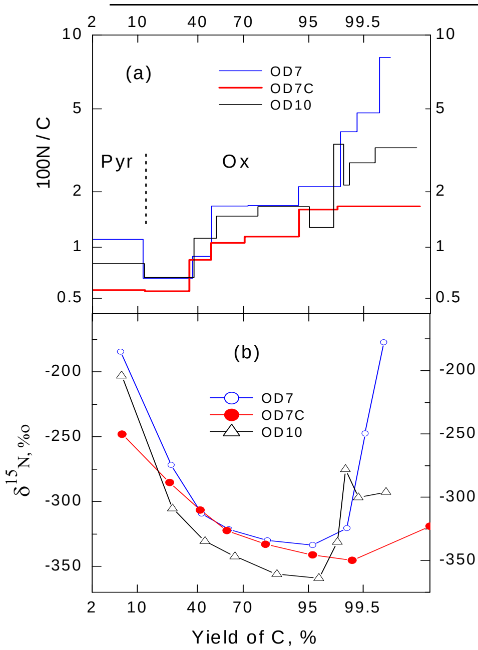

Fig. 1. Changes of concentration (a) and isotopic composition (b) of the nitrogen in the OD7C and OD10 fractions, and in the bulk diamond-rich separate (OD7).

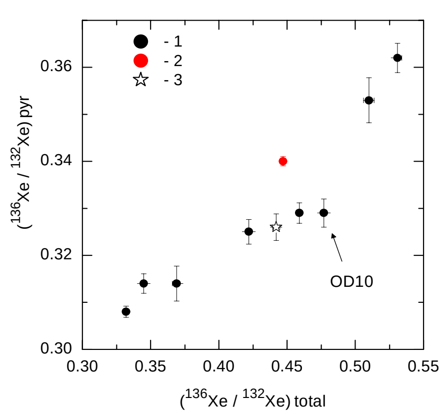

Fig. 2. Xe ratios in the various Orgueil diamond-rich fractions.
1 - grain-size fractions,
2 - the fraction after the ultrasonic processing (OD7C),
3 – bulk diamond-rich separate (OD7).