

BEHAVIOR OF LOW-ENERGY IMPLANTED XE AND KR IN NANODIAMONDS AND OTHER NANOCARBONS: EXPERIMENTS, MODELING AND COSMOCHEMICAL IMPLICATIONS.

A. A. Shiryayev¹, A. L. Trigub², K. O. Kvashnina³, V. L. Bukhovets¹, A. V. Fisenko⁴, L. F. Semjonova⁴, A. B. Verkhovskiy⁵, A. L. Vasiliev², A. A. Averin¹, ¹Frumkin Institute of Physical chemistry and electrochemistry RAS, Moscow, Russia, shiryayev@phyche.ac.ru, ²NRC “Kurchatov Institute”, Moscow, Russia, ³ESRF, Grenoble, France, ⁴Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia, ⁵The Open University, UK.

Introduction: The nature of the main host for noble gases (NG) in meteorites – the Q-phase – remains elusive. Most studies suggest its carbonaceous composition, but structure and mechanism(s) of noble gases entrapment are still debatable. Simple adsorption fails to reproduce isotopic patterns of the Q-gases and ionization of the gaseous species appears to be important, thus implying possibility of low-energy ion implantation (e.g., [1]).

Using advanced chemical separation methods we extracted carbonaceous fractions highly enriched in Q-noble gases from Saratov L4 meteorite. Examination of these samples using multiwavelength Raman spectroscopy, high resolution TEM and static mass-spectrometry [2] strongly suggest that curved and rectilinear bi- and few-layers graphene stacks serve as a plausible carrier of the noble gases (NG). Somewhat unexpectedly, on step oxidation the gases are released in two distinct steps with maxima at approx. 350 and 500 °C. Structural studies of the Q-rich sample oxidized at 475 °C indicate survival of the few-layers graphenes at these conditions. Complex dependency of the noble gases' retention on details of chemical treatment of the Acid-resistant residue is also observed.

Results: Low energy ion implantation is, perhaps, the most plausible mechanism of introduction of noble gases into various types of nanocarbons in astrophysical environments. Two sets of nanodiamonds with well defined grain sizes (5 and 40 nm), nanocrystalline diamond film, graphite, and several types of sp²-nanocarbons were implanted using Kr/Xe plasma with energies up to 1500 eV and immediately packed. As a reference Xe adsorbed on zeolite and porous carbon was measured. Since high ion fluences may lead to complete disruption of a nanoparticle due to overheating (e.g., [3]) we had to limit our experiments to fluxes less than 5x10¹⁵ ions/cm². At ROBL beamline (ESRF) XANES spectra at Kr and Xe K-edges were measured in fluorescence mode using a dedicated grazing incidence holder to address only very thin implanted layer (the implantation depth is 1-3 nanometers). The experiments are complemented by quantum chemistry calculations.

Clear differences in the XANES region are observed for various types of nanocarbons. The XANES spectra of Xe implanted into nanodiamonds generally support our model [2], which shows that the most stable atomic configuration of this impurity in a nanodiamond grain is its complex with a vacancy, i.e. Xe-V defect. In graphite-like structures the most plausible trap for the implanted noble gases is the space between graphene sheets. However, since radii of Xe and Kr are larger than the interlayer spacing, puckering of the sheets should occur. Formation of the buldge appears to be energetically unfavorable for thick stacks due to interlayer interaction, thus explaining why graphite is often devoid of the noble gases. However, thermal stability of implanted ions of noble gases remains poorly explained: experiments show that significant fraction of the gases survive heating up to 500 °C [2], whereas models suggest rapid diffusion at these temperatures.

Interestingly, Xe environment in nanocrystalline diamond film resembles that in graphite. The most plausible explanation of this behaviour lies in complex structure of these nanocrystalline films, which consists of diamond grains enveloped into graphite-like shells.

References: [1] Fukunaga K. and Matsuda. J. (1997) *Geochemical Journal* 31(5):263-273. [2] Fisenko A. V. et al. (2018) *Meteoritics & Planetary Science* (in press). [3] Shiryayev A. A. (2018) *Scientific reports*, 8:5099.