250-Ma old nature carbon nanostructuring materials and nanotubes in inrusive rocks

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Numerous studies of the synthesis of carbon nanostructuring materials were conducted after publication [1] (1952 year), and [2] (1991 year), and it was thought after that the nanotubes can be obtained only by artificial means in the laboratory. However, studies of graphite-like globules (size - 2 ÷ 10 mm) from leykogabbro with age of 250 million years have shown the possibility of formation of carbon nanotubes in magmatic processes.

Analytical procedures include following steps: 1) acid decomposition of silicate rocks, 2) selection of graphite particles under a microscope, 3) study of morphology and composition using a scanning microscope, and 4) identification of the C-C bond (Raman microscopy) and carbon isotopic composition.

'Anatomy' of globule (from the edge to the center) is as follows: 1) the thin layer of carbon film (graphene?), 2) outer shell, made of a porous carbon material with thickness of ~ 20μm (turbostatic graphite), 3) the inside of the shell is covered by 'forest' of carbon microtubes; 4) the length of the microtubes – 0.2-0.3 mm, diameter - 1-5μm (Fig. 1, left part); 5) multi-walled carbon nanotubes 'growing' from the microtubes (Fig.1, right part). Temperature of the carbon nanostructuring material formation (Raman spectroscopy) ranges from 650 to 470°C. $\delta^{13}C$ values of different forms vary from -16 to -12‰. In general, the data, obtained in this study, have shown that nano- and microtubes were formed in gaseous environment (from CO^2) through the molecular dynamic mechanism.

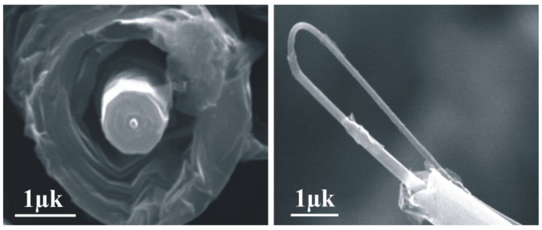

Figure 1: left - section of the carbon microtube, right – nanotube growing from microtube.

[1] Radushkevich *et al.* (1952) *J. of Phys. Chem.* **26**, 88–95. [2] Lijima (1991) *Nature* **354**, 56–58.

Stable isotope composition and volume of Early Archaean oceans

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Oxygen and hydrogen isotope compositions of seawater are controlled by volatile fluxes between mantle, lithospheric (oceanic and continental crust) and atmospheric reservoirs. Throughout geologic time oxygen was likely conserved within these Earth system reservoirs, but hydrogen was not, as it can escape to space [1]. Hydrogen isotope ratios of serpentinites from the ~3.8Ga Isua Supracrustal Belt in West Greenland are between -53 and -99‰; the highest values are in antigorite ± lizardite serpentinites from a low-strain lithologic domain where hydrothermal reaction of Archaean seawater with oceanic crust at elevated temperatures was geochemically preserved, indicating that the $\delta D_{SEAWATER}$ was at most 25 ± 5‰ lower than modern VSMOW. We propose that the progressive increase in $\delta D_{SEAWATER}$ since this time is due to preferential uptake of hydrogen in continent-forming minerals and to hydrogen escape via biogenic methanogenesis [2]. Mass balance considerations within the Earth system places a cumulative upper limit on elemental hydrogen loss to space of ~$1.8x10^{22}$mol elemental hydrogen H, constraining maximum Archaean atmospheric methane levels at ~3.8Ga to <500ppmv (depending on the volume of continents present at that time), and the mass of Early Archaean oceans to ~109 to 126% of present day oceans. Oxygen isotope analyses from these Isua serpentinites ($\delta^{18}O$ = +0.1 to 5.6‰ relative to VSMOW) indicate that early Archaean $\delta^{18}O_{SEAWATER}$ similar to modern oceans. Our observations suggest that the low-$\delta^{18}O$ values of Precambrian sedimentary cherts and carbonates are not a consequence of isotope variability of seawater or extreme ocean temperatures [3, 4], but rather are due to isotopic exchange with shallow hydrothermal fluids on the ocean floor or during diagenesis [5].

[1] Lécuyer *et al.* (1998) *Chem. Geol.* **145**, 249–261. [2] Catling *et al.* (2001) *Science* **293**, 839–843. [3] Hren *et al.* (2009) *Nature* **462**, 205–208. [4] Jaffrés *et al.* (2007) *Earth-Science Reviews* **83**, 83–122. [5] Blake *et al.* (2010) *Nature* **464**, 1029–1032.