



Nitrogen isotopes in shungites

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Shungites are a unique type of carbonaceous rocks (with reduced carbon contents of 1-100%) whose origin remains uncertain; both biological (1) and non biological (2) hypotheses have been put forward. Although rare in a general sense they have been found in the Eastern part of the Baltic Shield in the Onega Lake region, Karelia (age $\sim 2 \times 10^9$ years), where they are distributed across a wide region of about 9000 km² with an estimated carbon abundance of $\sim 2.5 \times 10^{11}$ tonnes (1,3 and references therein). This represents the largest organic material accumulation on the Earth during Paleoproterozoic time. In trying to access the origin of the organic material note that the total range of $\delta^{15}\text{N}$ for the reduced carbon in shungites varies from -17‰ to -46‰. The $\delta^{15}\text{N}$ is strongly grouped by locality and has a bimodal distribution with median values at -27 and -37‰ (1). It has been suggested (1) this variation/bimodality reflects diagenetic as well as metamorphic alterations of the primary organic carbon, isotopically light and heavy carbon requiring different fractionation processes. The former would involve thermal maturation of kerogen, with release of hydrocarbons gases (e.g. methane) or liquids (petroleum) with the latter would be associated with oxidation/equilibration of the residual carbon with CO₂-rich fluid and concomitant large (>80%) loss of carbon (1). However if this latter process was initiated by regional (greenschist facies) metamorphism then it is not clear why the carbon isotopic composition of shungites is grouped by locality. Those shungites with the highest (almost 100%) carbon contents have a lustrous appearance, resembling a highly metamorphosed coal (anthracite) and occur in veins that indicates their allochthonous nature. It has been proposed (1) that they represent metamorphose bitumen (i.e. pyrobitumen) migrated from deeper layers of shungite rocks.

In his study we investigated the nitrogen isotopic compositions of a number of shun-

gite samples in order to shed more light on their origins. As one of the key elements in biological cycle, nitrogen can be used for understanding the nature of organic carbon in shungites and to reconstruct environmental conditions of their formation.

The samples we analysed represent different types of shungite rocks both primary, sedimentary rocks and migrated lustrous samples, with a range of carbon contents (from <1% to 98%) and isotopic compositions ($\delta^{13}\text{C}$ = -20‰, to -40‰). We analysed nitrogen and carbon isotopic compositions simultaneously using static mass spectrometry and stepped combustion (4).

The results indicate that two nitrogen components are present in the samples. One is closely associated with carbon (i.e. accompanies the carbon release during stepped combustion in the range 500-700°C), has $\delta^{15}\text{N}$ of -0 to -5‰, and N/C of 0.001 to 0.007. The other is released at higher temperature (600-1000°C), has isotopically heavier nitrogen ($\delta^{15}\text{N}$ of +5 to +15‰) and is not obviously associated with carbon.

As things stand we do not yet have a good explanation for the high-temperature, isotopically heavy nitrogen, however, it might be associated with potassium-bearing minerals in which NH_3 replaces K; further experiments are needed to constrain the nature of this material. In contrast, the low-temperature nitrogen is obviously connected with the major organic constituent of shungites, apparently of a biological nature. Curiously, the nitrogen isotopic composition is not what would have been expected for metamorphosed organic material of proterozoic origin (5). A possible explanation is that the nitrogen records a rather specific origin for the organic component, perhaps an anaerobic environment (6).

Pyrolysis-gas chromatography-mass spectrometry of the shungites, we performed in the study, also indicates their biological nature and suggests an algal origin.

Referenses: 1. V. A. Melezhik et al, 1999, *Earth-Science Review* 47, 1; 2. P. T. Buseck et al., 1997, *Canadian Min.* 35, 3136; 3. V. A. Melezhik et al., 2004, *Ore Geol. Rev.* 24, 135; 4. A. B. Verchovsky et al., 1997, *Met. Planet. Sci.* 32, 131; 5. V. Beaumont and F. Robert, 1999, *Precambr. Res.* 96, 63; 6. D. L. Pinti and K. Hashizume, 2001, *Precambr. Res.* 105, 85.