

## **Shunga Event: capturing early Palaeoproterozoic sulphur cycling in Karelia**

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The early Palaeoproterozoic marks an important time period in Earth history as a time of fundamental environmental changes like the accumulation of unprecedented amounts of autochthonous organic matter during the Shunga Event in the aftermath of the Lomagundi-Jatuli Event some 2 billion years ago. Samples from three drill cores (12A, 12B and 13A) through the Zaonega Formation (ZF), Onega Palaeobasin, NW Russia, were studied as part of the Fennoscandian Arctic Russia – Drilling Early Earth Project (FAR-DEEP) under the auspices of the International Continental Drilling Program (ICDP).

The Zaonega Formation comprises organic carbon-rich, rhythmically bedded, grey to black coloured sedimentary rocks deposited under low-energy, non-euxinic depositional conditions. The organic matter represents biological material, most likely of algal or bacterial nature [1]. Subsequently, the whole sequence underwent greenschist facies metamorphism during the Svecofennian Orogeny at 1.8 Ga, resulting in the mobilization and migration of hydrocarbons (termed as “Shungite”, V.A. Melezhik, pers. comm.) [2]. Abundant different species of sulphides, mainly iron sulphides show a variety of mineral habits.

In a first step, total carbon (TC), total sulphur (TS) and total inorganic carbon (TIC) contents have been measured on bulk rock samples. In the depth profile, intervals exhibiting elevated contents of both TOC and TS are discernible, but no general correlation could be detected. A set of samples shows high TOC (30.8-45.9 wt.%) coincident with low TS (0.58-2.57 wt.%) values. These likely reflect migrated bitumen.

Stable sulphur isotopes represent an important fingerprint in the rock record for tracing sulphur sources and prevailing reaction pathways. Available evidence points to more than one process of microbial sulphur cycling during and after deposition of the Shungite bearing rocks, based on highly variable  $\delta^{34}\text{S}$  values between -21.7 to +22.8 ‰ VCDT for drill cores 12A and 12B and between -6.4 to +14.8 ‰ VCDT for drill core 13A, measured on the chromium reducible sulphide fraction (pyrite). These isotopic signals are typical for bacterially mediated sulphate reduction (BSR) [3]. Both depth profiles clearly show a general positive shift up-section, which can be interpreted as an environmental change towards a limited sulphate supply and subsequently, successively heavier  $\delta^{34}\text{S}$  signatures in the residue. Heavier  $\delta^{34}\text{S}$  values in the gabbro and basalt in the lower part of the drill core 12B suggest a magmatic input of sulphur.

$\delta^{34}\text{S}$  values in conjunction with TOC or TIC contents show no clear correlation except for samples displaying the highest values for TOC, which show preferentially negative  $\delta^{34}\text{S}$  signals consistent with BSR (-13 and -17.2 ‰ VCDT). Very preliminary results in iron speciation support the assumption of sedimentation under euxinic marine conditions.

The abundant sulphides and their different generations point to a complex (dia)genetic history.

[1] Melezhik, V.A., Fallick, A.E., Filippov, M. M. Larsen, O. (1999a). Karelian shungite - an indication of 2.0-Ga-old metamorphosed oil-shale and generation of petroleum: geology, lithology and geochemistry. *Earth-Science Reviews* 47: 1-40.

[2] Melezhik, V.A., Fallick, A.E., Filippov, M.M., Lepland, A., Rychanchik, D.V., Deines, Y.E., Medvedev, P.V., Romashkin, A.E., Strauss, H. (2009). Petroleum surface oil seeps from a Palaeoproterozoic petrified giant oilfield. *Terra Nova* 21: 119–126.

[3] Habicht, K.S., Canfield, D.E., Rethmeier, J. (1998). Sulphur isotope fractionation during bacterial reduction and disproportionation of thiosulphate and sulfite. *Geochimica et Cosmochimica Acta* 62 (15): 2585-2595.