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Reconstruction of early Palaeoproterozoic sulfur cycling: sulfur isotope analysis of Shungite bearing rocks

Denise Meister (1), Harald Strauss (1), and Martin J. Whitehouse (2)

(1) Westfälische Wilhelms-Universität Münster, Institut für Geologie und Paläontologie, Lehrstuhl für Historische und Regionale Geologie, Münster, Germany (dmeis_01@uni-muenster.de), (2) Swedish Museum of Natural History, Box 50007, SE-104 05 Stockholm, Sweden

Early Earth's ocean - atmosphere system experienced fundamental global perturbations during the early Paleoproterozoic including the Great Oxidation Event (GOE, 2.3 Ga) [1] and the unprecedented accumulation of organic matter during the Shunga event ∼2.05 billion years ago [2]. Under the auspices of the International Continental Drilling Program (ICDP) three drillcores were obtained from the Karelian Zaonega Formation, Onega Paleobasin, NW Russia. The volcano-sedimentary succession was deposited under low-energy, non-euxinic depositional conditions and underwent greenschist facies metamorphism during the Svecofennian Orogeny at 1.8 Ga. Organic matter occurs in the form of petrified hydrocarbons (termed Shungite [3]) represented by residual kerogen and migrated pyrobitumen, the latter mobilized as a consequence of metamorphic processes [4]. The great abundance of sedimentary sulfides within this succession provides ample evidence for microbially driven turnover of sulfate.

Ore microscopy reveals the presence of sulfides with highly variable morphologies and substantial differences can be identified with respect to the timing of sulfide formation ranging from early diagenetic, framboidal like to late diagenetic pyrite in cross cutting veins.

Analyses of total sulfur (TS), total carbon (TC) and total inorganic carbon (TIC) abundances in bulk rock samples have been conducted. Sedimentary rocks with high TS values usually (but not always) show an enrichment in the total organic carbon (TOC). Interbedded are rocks with a high TIC/TC ratio.

Stable sulfur isotope data where obtained via sequential extraction [5], and they reveal highly variable δ^{34}S values of the chromium reducible fraction (pyrite) ranging between -21.7 to +33.9‰. Results are consistent with bacterial sulfate reduction, but different conditions for microbial sulfur cycling must have prevailed. Although no clear correlation between δ^{34}S and TOC or TIC contents are discernible, samples displaying the highest TOC values show preferentially more negative δ^{34}S signals (-13.0 and -17.2‰ VCDT). Up-section an overall shift to more positive δ^{34}S is discernible, which can be interpreted as a change towards a limited sulfate supply and subsequently, successively heavier δ^{34}S signatures of the residue. A positive correlation between δ^{34}S and total sulfur content (R^2=0.81) in the uppermost massive organic matter rich rocks could be observed, whereas the deeper ones show negative signatures (-13.0‰ to -17.5‰ VCDT) with relatively constant TS values around 2 wt.%.

In situ isotopic measurements on a single grain scale have been conducted on the NordSim ion probe facility in Stockholm and yielded a substantial range in δ^{34}S between -40.10 and +84.76‰ VCDT. Δ^{33}S values vary between +0.53‰ to -0.81‰, suggestive of mass independent fractionation (MIF). This is commonly accepted as a sign for an oxygen free atmosphere [6]. The slight mass independent fractionation signature in Δ^{33}S of up to -0.81‰ in the conglomerates and of -0.63‰ in greywacke could reflect the inheritance of an older sulfur isotope signature produced in the pre-GOE atmosphere.

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[1] Holland, H.D. (1999). When did the Earth's atmosphere become oxic? The Geochemical News 100: 20-22.

[2] Hannah, J.L. (2008). Re-Os geochronology of a 2.05 Ga fossil oil field near Shunga, Karelia, NW Russia. Abstract, 33rd International Geological Congress, Oslo, 2008, 6-14 August.

[3] Melezhik, V.A.; Fallick, A.E.; Medvedev, P.V.; Makarikhin, V.V. (1999). Extreme $^{13}C_{carb}$ enrichment in ca. 2.0 Ga magnesite-stromatolite-dolomite-'red beds' association in a global context: A case for the world-wide signal enhanced by a local environment. Earth-Science Reviews 48: 71–120.

[4] Strauss, H.; Melezhik, V.A.; Lepland, A.; Fallik, A.E.;.Hanski, E.J.; Filippov, M.M.; Deines, Y.E.; Illing, C.J.;

Črne, A.E.; Brasier, A.T. (2013). Enhanced accumulation of organic matter: The Shunga Event. In: Reading the archive of Earth's oxygenation, Vol.3: 1195-1273.

[5] Poulten, S.W. & Canfield, D.E. (2005). Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. Chemical Geology 214: 209-221.

[6] Farquhar, J.; Bao, H.; Thiemens, M. (2000). Atmospheric influence of Earth's earliest sulphur cycle. Science 289: 756-758.