Seasonal variations of reduced sulfur species in a stratified seawater lake (Rogoznica Lake, Croatia); Evidence for organic carriers of reactive sulfur

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By voltammetry, we measured total reduced sulfur species (RSS), as well as a non-volatile fraction (i.e. not gas-stripped at pH ~2) in a seasonally stratified, saline lake over a one year period. In the upper, oxic waters, total and non-volatile RSS are equal within uncertainty; they display little vertical or seasonal variation from winter to late summer, implying no direct link to concurrent photosynthesis. Both fractions rise sharply when stratification breaks down in autumn. Based on decay rate, RSS during mixing events is attributed mainly to dissolved S_8 from oxidation of sulfide and decomposition of inorganic polysulfides that formed below the pycnocline. At other times, limited variations of RSS exclude hydrophobic and volatile S_8 as a major species. During stratification periods, oxic-water RSS (averaging 8.7 nM) appears to be associated with organic macromolecules, perhaps as adsorbed S_8 or covalently bound RS_n^- or RS_nR'. Below the pycnocline, total RSS is dominated by ≤ 5 mM S^{-II}, present as $H_2S + HS^-$ and as inorganic polysulfides ($H_xS_n^{x-2}$); metal-bound S^{-II} (chiefly thiomolybdates) must be $\leq 1\%$ of total RSS. Less abundant non-volatile RSS is attributed to dissolved zero-valent sulfur (S^0) in inorganic polysulfides. Assuming that organic S^0 species are negligible in deep waters, the equilibrium distribution of all inorganic polysulfide ions is calculated; S_5^{2-} is found to predominate. We propose that the anoxic waters act as a zero-valent sulfur reactor, creating S^0-containing, dissolved organic macromolecules that are dispersed through the lake by mixing events, explaining subsequent RSS in oxic waters. Voltammetrically determined RSS in oxic natural waters are often described as 'sulfide' or 'metal complexed sulfide', implying an oxidation state of S^{-II}; we conclude that RSS in oxic Rogoznica Lake waters is mainly S^0. Largely overlooked in previous studies, dissolved S_8 is likely to be toxic and may have contributed to mass mortality in this lake during a mixing event in 1997.

Trace elements and Nd-Hf isotopes for 10 rock standards

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Measurement of reference materials is a necessity to validate analytical protocols and to compare data produced in different laboratories. However, the number of published analyses is relatively limited as shown in the GEOREM database. Here we present trace element and Nd-Hf isotopic analyses for a diversity of reference materials ranging from peridotites to lake sediments.

We measured 10 rock standards; 5 are relatively well known igneous rocks (BHVO-2, BE-N, RGM-1, AGV-1 and UB-N) and 5 are sediments (JSd-1, JSd-2, JSd-3 and JLk-1 from the Geological Survey of Japan and LKSD-1 from the NRCanada) whose trace element and isotopic compositions are not well constrained. At least 4 duplicate analyses were done for the 38 trace elements and at least 2 for Hf and Nd isotopic compositions.

The digestion method for basaltic rocks consists in an acid attack (5:1 HF-HNO_3) in Teflon beakers for 5 days at 120°C, while sediments were first treated with HNO_3 to oxidize the organic matter and then dissolved in Parr bombs (5:1 HF-$HClO_4$) for 1 week at 135°C.

Trace element contents are measured using an Agilent 7500ce, a dilution factor of 5000 and an internal standard (Be-Ge-In-Tm-Bi) to correct for drift during measurement. Calibration of the signal is based on the values published by Eggins (Chem Geol 1997) for the rock standard BR. Our measurements agree with published values when data are available and the reproducibility is better than 5 % except for some of the sediments .

Nd and Hf were isolated using the procedures published by Carpentier *et al.* (EPSL 2008) and Chauvel and Blichert-Toft (EPSL 2001) and isotopic ratios were measured on the Nu instrument at ENS Lyon. Results are normalized using the average value obtained for the Nd and Hf standards during the measuring session. Our results for BE-N, BHVO-2, RGM-1 and AGV-1 are similar to published values and other data are presented in Table 1.

	$^{143}Nd/^{144}Nd$	2σ	$^{176}Hf/^{177}Hf$	2σ
JLk-1	0.512142	7	0.282676	9
JSd-1	0.512571	8	0.282750	27
JSd-2	0.512627	9	0.282893	13
JSd-3	0.511976	26	0.282599	13
LKSd-1	0.512180	10	0.282393	9

Table 1: Hf and Nd isotopic compositions of geostandards.