



Rhenium geochemistry in hypoxic and euxinic marine lakes of the Eastern Adriatic Sea

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Rhenium (Re) is known as one of the rarest elements at Earth's surface. Re enrichment in sediments deposited beneath anoxic and sulfidic water columns can be few orders of magnitude greater in comparison to the average crustal concentration of Re. The exact mechanism of Re transformation and transport from dissolved phase in oxic environments to anoxic sediments is still poorly understood. The hypothesis of Re enrichment involves the reduction of perrhenate to an insoluble Re(IV) product within the sediment-water interface or progressive thiolation of perrhenate anion that leads to the formation of particle-reactive thioperrhenates. Like molybdenum (Mo) and uranium (U), the analysis of vanadium (V) and Re enrichment covariations within anoxic sediments may also be potentially used as an important paleoredox tool. To broaden our understanding of Re geochemistry in hypoxic and euxinic marine lakes, we have performed sampling of seawater and sediments in two marine lakes in the Eastern Adriatic Sea (Small Lake on the Island of Mljet and Dragon Eye Lake near the town of Rogoznica). Samples were collected in April 2020 and November 2020 at the Small Lake, while those in the Dragon Eye were collected in July 2020. Seawater profiles were collected from the surface to near-bottom layer. Sediments were sampled using core-sampler and cut in 2-cm layers under nitrogen atmosphere. Porewater was separated from the sediment by centrifugation and filtered under nitrogen atmosphere. Re in sediments was determined using ID-ICP-MS following acid digestion, matrix substitution, and preconcentration on Dowex resin. Re in seawater and porewater was determined using ID-ICP-MS after preconcentration on Dowex resin. Multi-elemental analyses in waters and sediments were also performed to obtain insights into Re behavior in these compartments. The first results for the Small Lake (April sampling) showed that Re concentration in seawater is rather uniform (about 8 ng/L). Further on, Re concentrations in sediments were increasing with depth (from 3.5 to 9.7 ng/g), while the corresponding Re concentrations in porewater were decreasing (from 4.6 to 1.8 ng/L). Principal component analyses showed different behavior of Re in porewaters and sediments when compared to other redox sensitive elements. In sediments, Re was highly correlated with Mo and U, and usually without correlations with Mn or Fe. On the contrary, Re in porewaters was highly correlated to Mn and Fe, and negatively correlated with Mo and U. Regarding correlations between Re in V: in cores in which Re was negatively correlated with V in porewater, there were no significant correlations in sediments, and vice versa. Re in porewaters did not show correlations with sulfide. These first results indicate

different geochemistry of Re in hypoxic and euxinic marine lakes when compared to Mo, U, and V. The appropriate data analysis will be evaluated following the analysis of other samples.