

Sediments as the redox paleo-record

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Introduction:

Reconstructing the chemistry of past Earth's atmosphere and ocean and their redox states has gained enormous attention recently. Ocean sediments provide geochemical records through much of Earth's history. Reconstructing past environmental conditions from such archives depends on the quality of data that can be extracted from these records. The reliability of identifying good indicators of specific environmental conditions (so-called "proxies"), and the processes controlling sequestration from the aqueous phase into the sediments, are key points in the "reconstruction chain". The enrichment of several redox-sensitive trace elements, as well as their isotopic composition in (anoxic) sediments, have previously shown to carry important information about the mechanism of their removal and the prevailing redox conditions within the water column at the time of sediment deposition. Yet, to fully capitalize the potential of these emerging redox-sensitive proxies in reconstructing Earths' past oxygenation state, a thorough understanding of these proxies' geochemistry in modern environments is mandatory.

Also, the research (as well as the "science behind" those) planned within the project "Geochemistry and redox proxy's signature under the diverse environmental conditions: towards a better understanding of the past redox" (project acronym: REDOX) founded by the Croatian Science Foundation (IP-2018-01-7813) will be presented.

Methods:

The results within this work are obtained using high cutting edge techniques and instruments including anion exchange chromatographic separation of molybdenum and uranium from the sample matrix as well as the MC-ICP-MS isotope analysis.

Results: The isotopic composition of molybdenum and uranium (⁹⁸Mo and ²³⁸U - as well as their abundance) of recent anoxic sediments will be presented. The working principle of molybdenum and uranium isotopic system as the redox proxies will be discussed.

Discussion: Coupled Mo-U abundances have successfully been applied as paleo-redox proxies [1]. An extension of this approach to the isotope systems of the two elements has enormous potential, as

shown recently Bura-Nakić et al., (2018) [2]. This potential is currently limited by the lack of understanding of the processes by which Mo and U isotopes are fractionated in intermediate situations. For example, it became clear only recently that $\delta^{238}\text{U}$ values recorded in hypoxic sediments are highly variable, ranging from values characteristic for open oceans (-0.4‰) to up to 0.4‰ (e.g. [3])

Hypoxic sediments, in the above context, are sediments where reducing conditions prevail as a result of oxygen exhaustion, due to high primary productivity and organic matter fluxes.

Recently, isotopic composition of the carbonates was suggested as a novel proxy in order to assess the $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ of an ancient ocean. However, study of Mo and U isotopic composition of the modern Bahamian carbonate sediments revealed alteration of global $\delta^{98}\text{Mo}$ and $\delta^{238}\text{U}$ carbonate signatures by the localized diagenetic processes within the sediments [4]; [5]. The REDOX aims at a better understanding of the geochemistry of selected redox proxies (Mo, U, V and Re) under a range of critical environmental redox conditions.

Combining these proxies will provide an improved framework for interpreting and reconstructing the ancient redox conditions within the atmosphere and the ocean.

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References:

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