



## Sensitivity of trace element pyritization to pyrite oxidation processes

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Total trace elements concentration variability in marine sediments has been widely used as a proxy for redox conditions and marine paleoproductivity. However, partial extraction procedures reduce influences of detrital sedimentary fractions, and information on trace element geochemical partitioning can contribute to provide comprehensive evidences on elemental sensitivity to particular processes. The potential effect of sedimentary pyrite re-oxidative cycling on the degree of trace metal pyritization (DTMP) has not been previously evaluated. This study investigates this effect in 4 sediment cores from the continental shelf under the influence of a tropical upwelling system (Cabo Frio, Brazil). The relation of DTMP with stable isotope signals ( $\delta^{34}\text{S}_{CRS}$ ) of chromium reducible sulfur, which becomes lighter in response to intense pyrite re-oxidative cycling in the study area, suggests high (As, Cd and Mn), low (Cu and Zn) or negligible (Cr and Ni) re-oxidation influences. The oldest, pyrite-richer sediments provide an apparent threshold for intense pyrite re-oxidation, after which most trace elements (As, Cd, Zn and Mn) presented more accentuated pyritization. A middle shelf core presented negative correlations of reactive (HCl-soluble) Mn, Cu and Ni with pyrite iron, suggesting Mn oxide (and associated metals) depletion in reaction with pyrite. Results provided evidences for coupled influences from both aerobic and anaerobic oxidative processes on trace elements incorporation into pyrite. Pyrite  $\delta^{34}\text{S}$  signatures under the oxic bottom water from the study area were similar to those from euxinic sedimentary environments, suggesting that pyrite re-oxidative cycling can affect trace element susceptibility to be incorporated and preserved into pyrite in a wide range of sedimentary conditions. The evaluation of trace elements sensitivity to these processes can contribute to improve the use of multiple DTMP data (e.g., as paleoredox proxies). Considering that S re-oxidative cycling is ubiquitous in many sedimentary conditions, such coupled use of DTMP and  $\delta^{34}\text{S}_{CRS}$  proxies can be possibly applied to a large variety of sedimentary environments.