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The organic matter effect on Fe(II) oxidation kinetics within coastal seawater

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Iron is an essential nutrient that limits primary productivity in up to 30% of the world's ocean. Redox and complexation reactions control its solubility and therefore the fraction of dissolved and bioavailable iron. The iron (II) oxidation kinetic process was studied at 25 stations in coastal seawater of the Macaronesia region (around Cape Verde, the Canary Islands and Madeira). Laboratory experiments were carried out to study the pseudo-first-order oxidation rate constant (k', min^{-1}) over a range of pH (7.8-8.1) and temperature (T; 10-25ºC). Measured k' varied from the calculated k' (k'_{cal}) at the same T, pH and salinity (S) at most stations. Measured iron (II) half-life times ($t_{1/2}=ln2/k'$; min) at the 25 stations ranged from 1.8-3.5 min (mean 1.9±0.8 min) and for all but two stations were lower than the theoretically calculated $t_{1/2}$ of 3.2±0.2 min. The biogeochemical context was considered by analysing nutrients and variables associated with the organic matter spectral properties (CDOM and FDOM). A multilinear regression model indicated that k' can be described (R=0.921, SEE=0.064 for pH=8 and T=25ºC) from a linear combination of three organic variables.

$$k'^{OM} = k'_{cal} - 0.11 * TDN + 29.9 * b_{DOM} + 33.4 * C1_{humic}$$

where TDN is the total dissolved nitrogen, b_{DOM} is the spectral peak obtained from coloured DOM analysis when protein-like or tyrosine-like components are present and $C1_{humic}$ is the component associated with humic-like compounds obtained from the parallel factor analysis (PARAFAC) of the fluorescent DOM. Experimentally, k' and k'^{OM} provide the net result between the compounds that accelerate the process and those that slow it down. Results show that compounds with nitrogen in their structures mainly explain the observed k' increase for most of the samples, although other components could also present a relevant role.