THE ROLE OF GALIC ACID AND OCEAN ACIDIFICATION IN THE REDOX CHEMISTRY OF IRON IN SEAWATER

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Abstract: The biogeochemistry of iron (Fe) is affected by ocean acidification, both in terms of redox and complexation reactions. Accordingly, it is directly linked with ecosystems because Fe is an essential trace metal for microorganisms. Within the pool of organic ligands present in the ocean, polyphenols are exudated by marine microalgae and can complex Fe(III) and reduce it to Fe(II) in seawater (SW).
Among all the polyphenols, Gallic Acid (GA; 3,4,5-trihydroxy benzoic acid) has been studied in terms of oxidation and reduction of Fe in natural seawater. The presence of GA decreased the oxidation rate of Fe(II) in SW, ($[Fe(II)]_0$=25 nM, Fe:GA ratio from 1:1 to 1:4), increasing the permanence of Fe(II) in solution with increasing GA concentration. The decrease in Fe(II) oxidation rate is related to the Fe(III) reduction in the presence of GA. In this sense, Fe(III) is reduced to Fe(II) in a pH-dependent process, in both SW and NaCl-$NaHCO_3$. The Fe(III) reduction rate increased with pH, with a slope of 0.46 ± 0.03 in NaCl-$NaHCO_3$ and 0.91 ± 0.14 in SW. The addition of the major ions of SW, such as Ca^{2+} and Mg^{2+}, to the NaCl-$NaHCO_3$ solution showed a decrease in the Fe(III) reduction rate in the presence of Ca^{2+} and in the pH range 7.0-8.0. When the studies were carried out with different GA concentrations, the Fe(III) reduction increased with the GA levels. Accordingly, at pH = 7.0, an increase in the Fe(III) reduction rate was observed over the entire range of Fe:GA ratios studied (from 1: 2 to 1:20; [GA]=50-500 nM). At pH = 8.0, Fe(II) was only detected at ratios from 1:3 to 1:10, because the Fe(II)-FZ_3 was not observed by the interference of GA peaks under that experimental conditions.
This study shows that the presence of GA significantly increases the residence time of Fe(II) in SW due to the reduction of Fe(III) to Fe(II) and it has to be considered in the Fe biogeochemical cycles.

Key words: Gallic acid, Iron, Complexation, Redox, Seawater, Ocean acidification

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