Comment on bg-2021-134
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Community comment on "Comparing CLE-AdCSV applications using SA and TAC to determine the Fe-binding characteristics of model ligands in seawater" by Loes J. A. Gerringa et al., Biogeosciences Discuss., https://doi.org/10.5194/bg-2021-134-CC1, 2021

This is an interesting manuscript and a welcome addition to this field, however in reading through its conclusions regarding the underestimation of the model ligand concentrations it is apparent that some key aspects have been overlooked in the analysis to date.

- Independent determination of ligand concentration

For many of the siderophore ligands the purity of commercial sources is not 100% and for desferrioxamine B it is typically 90-95% depending on the manufacturer and lot/batch number. Earlier works also suggested that some siderophores were not stable in solution as they were easily degraded, though other studies have shown that solutions can be stable for days to weeks (Hayes et al., 1994). It is important then to obtain an independent determination of the model ligand concentration, rather than simply assume 100% and using the mass weighed out initially. This is frequently done using ASV in clean KCl or NaCl solutions and titrating with Cu, as then there should be no interferences. In the current work there is no information on how the ligand concentration was assayed prior to analysis.

- Composition of seawater used in this study:

The paper states that a range of leftover samples were used in this study, though there is no information on their salinity or potential for having other metals which may complex the model ligands under the experimental conditions. For example Cu and V may also be present in seawater at significant concentrations to chelate DTPA, siderophores and fulvic/humic acids thus resulting in lower than expected ligand concentrations when titrated with iron. The question then is, which metals could be present under these conditions to outcompete iron for the model ligands tested? This also is a reminder that all measurements done in natural waters are conditional measurements and this applies to the ligand concentration as well as the stability constant.

- Phytic acid is not a strong iron chelator under seawater conditions:

While the earlier study on Phytic acid by Witter et al. (2000) suggested that this ligand
was capable of chelating Fe(III) in seawater, subsequent work suggests this isn’t the case. Indeed calculations based on thermodynamic data (Crea et al., 2008; Torres et al., 2005) suggest that no significant complexes would be formed under seawater conditions. Voltammetric studies (Marolt and Pihlar, 2015) do indicate that both Fe(III) and Fe(II) complexes are formed however though they are very weak. Ultrafiltration studies (Schlosser and Croot, 2008) also indicate that the conditional binding constants in seawater for Phytic acid are significantly lower than that reported in the kinetic titrations of Witter et al. (2000). While Purawatt et al. (2007) using FFF found that Phytic acid reacts with Fe(III) to form colloidal material. These results suggest that Phytic acid is not a strong iron chelator (Luther et al., 2021) and the results reported in the current manuscript should be reinterpreted along those lines.

Lastly a recent paper (Sanvito and Monticelli, 2021) has suggested that pH buffering is not required for measurements such as this though despite earlier works indicating that it is a critical parameter. One aspect where all speciation work could be improved, and the current work should be no exception, is to include the relevant information on the pH scale (Dickson et al., 2016) being used (NBS, total, seawater, free) to describe the system, along with temperature and salinity (ionic strength) to fully describe the experimental system.

References:


