

*Global Biogeochemical Cycles*

Supporting Information for

**Influence of changes in pH and temperature on the distribution of apparent iron solubility in the ocean**

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Table S1. All parameters applied in this study for the calculations of apparent iron solubility at ambient seawater conditions, using an ion paring-organic matter (NICA-Donnan) model (Liu and Millero, 1999; Lodeiro et al., 2020; Milne et al., 2001; Zhu et al., 2021).

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| The ion paring-organic matter (NICA-Donnan) model descriptions for both the formation of Fe hydroxide and proton/Fe(III) binding to organic matter |
| (1) The NICA-Donnan model |
| Proton binding constants (Lodeiro et al., 2020; Milne et al., 2001) | b=0.57, p1=0.59, p2=0.70;Q(max, H+,DOM1)=2.52, logkH+,DOM1=2.34, nH+,DOM1=0.66;Q(max, H+,DOM2)=0.80, logkH+,DOM2=8.6, nH+,DOM2=0.76 |
| Fe(III) NICA constants (Zhu et al., 2021) | logkFe(III), DOM1=2.94, nFe(III), DOM1=0.32;logkFe(III), DOM2=9.6, nFe(III), DOM2=0.30 |
| (2) The solubility constants of Fe hydroxide (i.e. assumed as fresh ferrihydrite in this study) (Liu and Millero, 1999) |
| logKso= 3.2 | ΔHr= -100.4 kJ mol-1 |

Table S2. We omitted dissolved Fe profiles that were strongly influenced by source signatures from e.g. hydrothermal vents, atmospheric dust and suboxic sediment inputs in both ocean basins, including the West Atlantic Ocean transect (GA02), Subtropical North Atlantic transect (GA06) and Southeast Pacific Ocean transect (GP16) (Fitzsimmons et al., 2017; Resing et al., 2015; Rijkenberg et al., 2014).

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| Depth (m) | West Atlantic Ocean transect (GA02) | Subtropical North Atlantic Ocean transect (GA06) | Southeast Pacific Ocean transect (GP16) |
| Locations (longitude or latitude) |
| <100(removed stations, according to the criteria that mean dFe exceeds 0.5 nM) | ~7-10 ºN (0-50m);~20 ºN (0-50m) | ~16-20 ºW (20-100m) | ~77-80 ºW (20-100m) |
| ~100-1000(removed stations, according to the criteria that mean dFe exceeds 0.8 nM) | ~30-40 ºS (150-250m);~0 ºN (200-250m);~10 ºN (300-800m) | ~16-20 ºW (100-1000m) | ~96 ºW (~250m);~77-84 ºW (100-1000m)  |
| >1000(removed stations, according to the criteria that mean dFe exceeds 0.8 nM) | ~5 ºS (~2500m) | ~16-20 ºW (1000-6000m) | ~109-132 ºW (~2500-3000m);~77-80 ºW (1000-6000m) |

References

Fitzsimmons, J. N., John, S. G., Marsay, C. M., Hoffman, C. L., Nicholas, S. L., Toner, B. M., German, C. R., and Sherrell, R. M. (2017), Iron persistence in a distal hydrothermal plume supported by dissolved-particulate exchange, *Nat Geosci*, *10*, 195-201. <https://doi.org/10.1038/Ngeo2900>

Liu, X., and Millero, F. J. (1999), The solubility of iron hydroxide in sodium chloride solutions, *Geochim Cosmochim Ac*, *63*(19-20), 3487-3497. [https://doi.org/10.1016/S0016-7037(99)00270-7](https://doi.org/10.1016/S0016-7037%2899%2900270-7)

Lodeiro, P., Rey-Castro, C., David, C., Achterberg, E. P., Puy, J., and Gledhill, M. (2020), Acid-base properties of dissolved organic matter extracted from the marine environment, *Sci Total Environ*, *729*. <https://doi.org/10.1016/j.scitotenv.2020.138437>

Milne, C. J., Kinniburgh, D. G., and Tipping, E. (2001), Generic NICA-Donnan Model Parameters for Proton Binding by Humic Substances, *Environ Sci Technol*, *35*(10), 2049-2059. <https://doi.org/10.1021/es000123j>

Resing, J. A., Sedwick, P. N., German, C. R., Jenkins, W. J., Moffett, J. W., Sohst, B. M., and Tagliabue, A. (2015), Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean, *Nature*, *523*(7559), 200-U140. <https://doi.org/10.1038/nature14577>

Rijkenberg, M. J. A., Middag, R., Laan, P., Gerringa, L. J. A., Van Aken, H. M., Schoemann, V., De Jong, J. T. M., and De Baar, H. J. W. (2014), The Distribution of Dissolved Iron in the West Atlantic Ocean, *Plos One*, *9*(6). <https://doi.org/10.1371/journal.pone.0101323>

Zhu, K., Hopwood, M. J., Groenenberg, J. E., Engel, A., Achterberg, E. P., and Gledhill, M. (2021), Influence of pH and Dissolved Organic Matter on Iron Speciation and Apparent Iron Solubility in the Peruvian Shelf and Slope Region, *Environ Sci Technol*, *55*(13), 9372-9383. <https://doi.org/10.1021/acs.est.1c02477>