Marine Chemistry 173 (2015) 52–66

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Using the L* concept to explore controls on the relationship between paired ligand and dissolved iron concentrations in the ocean

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ARTICLE INFO

Article history:
Received 12 June 2014
Received in revised form 3 December 2014
Accepted 10 December 2014
Available online 13 December 2014

Keywords:
Iron biogeochemistry
Siderophores
Ligands
Particle remineralisation

ABSTRACT

Ligand (L) dynamics are inextricably linked to iron biogeochemistry, and their binding characteristics define much of the oceanic distributions of dissolved iron (DFe). Usually, L concentrations [L] are considered to be perennially in excess of [DFe] at any oceanic locale or point in time. Here we use the biogeochemical * concept to investigate whether distinct trends and patterns are evident for L* (the excess of [L] over [DFe]) across the two conventional ligand classes L1 and L2. The largest global datasets are available for L2* and point overwhelmingly to positive L2* values (but clearly establishing whether ligands in published studies are L2 versus L1 can be problematic). This trend is also apparent, for a more limited dataset, for L1*. Negative L2* values are mainly linked to high-iron waters (>2 nmol L^{-1}). Datasets from process studies, such as mesoscale iron-enrichments and shipboard particle remineralisation time-series, provide insights into the main drivers of L* in surface and subsurface waters, respectively. Multiple studies reveal rapid (days) microbial responses to iron-enrichment, with L1* increasing from negative to positive values. Deeper in the water column, particle remineralisation releases L2 concurrently with DFe but at higher concentrations (i.e. +L2*). We propose that +L1* is driven by opportunism within marine bacteria, but the magnitude of L1* is constrained by the energetic demands of producing siderophores, for example in response to episodic iron-enrichment, such that L1 is produced in slight excess only. In contrast, during subsurface particle solubilisation, +L2* values are probably driven by concurrent release of a larger excess of organic compounds (linked to major elements like C, which can act as L2) relative to trace amounts of DFe.

1. Introduction

The growing realization that the trace metal iron sets the primary productivity of ~50% of the surface waters of the global ocean (Moore et al., 2004) has quickened the development of the field of iron biogeochemistry (Boyd and Ellwood, 2010). Understanding the pivotal role that iron-binding ligands play in maintaining a highly particle-reactive metal in solution has been a key component in better understanding the functioning of the oceans' iron biogeochemical cycle (Johnson et al., 1997; Rue and Bruland, 1995; van den Berg, 1995; Gledhill and Buck, 2013). The ongoing GEOTRACES (www.geotraces.org/) global survey of trace elements and their isotopes is making a significant contribution in better understanding the distributions of trace metals in the ocean such as iron (Saito et al., 2013; Tagliabue et al., 2014a), and is supplementing the coverage provided by prior distributional datasets (Boye et al., 2001; Mawji et al., 2008) for both trace metals and ligands.

Despite the importance of ligands as complexing agents of trace metals, their provenance remains enigmatic (Gledhill and Buck, 2013). We presently still have only indirect evidence – co-incidence of high conditional stability constants between ligands and bacterial siderophores – that the most strongly binding ligands (conventionally described as L1) are most likely microbially-synthesised siderophores (Macrellis et al., 2001). For the weaker binding ligands (the so-called L2 class, Rue and Bruland, 1995), or 'Lx' ligand classes (Ibisanmi et al., 2011), a wider range of provenances, relative to L1, have been reported. Sources of weak ligands include: humics (Laglera and van den Berg, 2009), other organics (Stolpe et al., 2010), exo-polymeric substances (Hassler et al., 2011), and/or the products released during biogenic particle remineralisation (Boyd et al., 2010; Velasquez et al., unpublished manuscript) or grazing (Sato et al., 2007).

The increasing regional data coverage for both iron-binding ligands and dissolved iron (DFe) has revealed a wide range of concentrations for each (see synthesis in Gledhill and Buck, 2013), and often regional trends in excess ligand concentration (relative to DFe concentration) (Boye et al., 2003; Buck and Bruland, 2007; Wagener et al., 2008). This appears to be the case for each of the commonly cited nominal classes L1 and L2. It is now timely, given the GEOTRACES-mediated proliferation of datasets across the global ocean, on both DFe and iron-binding ligands, to more formally explore the relationship between each metal-ligand pair of these datasets using the biogeochemical convention L*.

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http://dx.doi.org/10.1016/j.marchem.2014.12.003
0304-4203/

The * convention has been used successfully to probe the drivers of, and the relationship between a range of biogeochemically coupled elements. These include major elements N and P (N* and P* Gruber and Sarmiento, 1997; Moore et al., 2009; Weber and Deutsch, 2010), or major and minor elements such as Fe and P (Fe* Parekh et al., 2005), and how this relationship varies, relative to Redfield molar stoichiometry, in space and time across the global ocean. For example, this biogeochemical * convention has provided valuable insights into how such stoichiometric signatures in nutrients can drive ecosystem dynamics, and moreover act as a powerful tracer of trends in physical circulation (Deutsch and Weber, 2012).

In this synthesis, our aim is to use the difference in concentrations between [L] and [DFe] from paired samples to probe how the term L* can be used to begin to address the following key questions about L dynamics in relation to those for trace metals, in this case Fe: Is L* relatively constant with depth and locale across the global ocean? Do we observe seasonal, regional or vertical gradients in L* (where there is sufficient data resolution)? We also assess whether L* provides an additional process-driven constraint on models (specifically using a new model by Volker and Tagliabue, 2015-in this issue) seeking to represent DFe and L. To conclude this analysis, we reappraise a series of previously published biogeochemical experimental manipulation studies to gain insights into the drivers and timescales (days) of L* dynamics.

2. Methods

Global trends in L*, for L1 (L1*) and L2 (L2*) ligand classes, were derived from a data compilation from published studies where data pairs of L1 and/or L2 and DFe concentrations were available. As far as the authors are aware this dataset represents a complete inventory of all relevant published studies, until mid 2013. The sources of the datasets are detailed in Appendix A. During the collation of these data pairs, it became evident that in some cases different methodologies for the analysis of DFe (Johnson et al., 2007) and/or windows of detection used to diagnose different ligand classes (Hunter and Boyd, 2007; Gledhill and Buck, 2013) had been used across the studies that comprise this dataset. Although it is desirable to have paired DFe/L datasets obtained using the same analytical techniques, and hence be directly comparable, for our subsequent analysis, this was deemed as beyond the scope of our study. For example, to employ only directly comparable data pairs we would have to surmount a range of problematic issues, such as how to cross-compare datasets in which the ligand data had been derived using different voltammetry techniques (discussed in Hunter and Boyd, 2007) and/or dissolved iron had been measured using different techniques. For example, some approaches such as chemiluminescence have been shown to provide higher estimates of dissolved iron (Johnson et al., 2007). In other cases, different definitions of the cutoffs for different ligand classes between studies may define them as L1 rather than L2 (this is illustrated in a comparison of the Buck and Bruland (2007) and Boyd et al. (2010) studies, both of which are heavily used in the present study). Thus, such methodological differences have been ignored for the datasets presented in Appendix A. However, we reiterate the plea made by Gledhill and Buck (2013) for better standardization of the operational cut-off between ligand classes, and for clearer reportage of such demarcations. The insights on ligand and iron dynamics provided from the global data compilation in the present study provide a further motivation for such standardization.

In the present study we define L1* as the difference between L1 and its paired dissolved iron concentration. L2* is also defined in this manner. Although the data compilation was dominated by L2, in a number

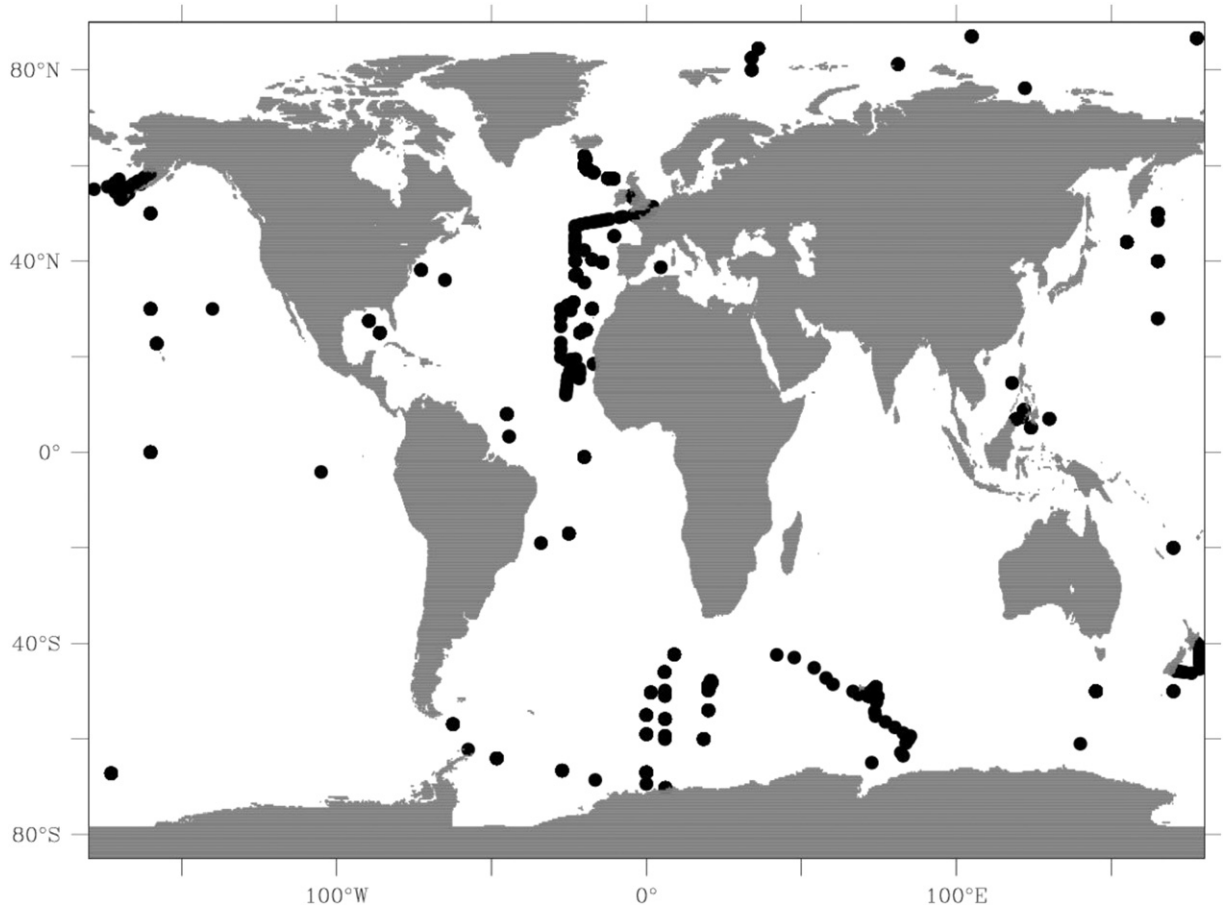

Fig. 1. Map of available data for dissolved iron and ligand pairs, at all depths, and for both ligand classes across the global ocean. The published sources for these datasets are presented in Appendix A.