Geophysical Research Letters

RESEARCH LETTER
10.1029/2024GL113874

Distribution and Cycling of Siderophores in the Eastern North and Tropical Pacific Oceans

Jingxuan Li[1,2], Lydia Babcock-Adams[1,3], Matthew R. McIlvin[1], and Daniel J. Repeta[1]

[1]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA, USA, [2]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA, [3]Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA

Jingxuan Li and Lydia Babcock-Adams are co-first authors.
Jingxuan Li and Lydia Babcock-Adams contributed equally to this work.

Abstract Most iron (Fe) dissolved in seawater is complexed to organic ligands of unknown composition. Here we investigate the distribution of siderophores, small organic compounds synthesized by microbes to bind environmental Fe and facilitate its transport into the cell. Siderophores help relieve Fe-stress and enhance microbial production under Fe-deficient conditions. Siderophores were found at all stations sampled across a section of the eastern North and Tropical Pacific Oceans visited by the GEOTRACES GP15 expedition. In surface waters of the chronically Fe-limited North Pacific Subpolar Gyre, Fe-marinobactin and Fe-amphibactin siderophore concentrations reached 66 pM and accounted for up to 80% of dissolved Fe. Ferrioxamine/ferrichrome-like siderophores, including ferricrocin, were abundant near the Alaskan coast. Metal-free and Al-siderophores were also abundant across the section indicating rapid and active Fe-siderophore uptake. Fe-acquisition via siderophores is a common strategy for microbes inhabiting the upper ocean and likely supplies a large fraction of bioavailable-Fe in Fe-deficient regions.

Plain Language Summary Under conditions of iron (Fe) deficiency some bacteria synthesize siderophores, small organic compounds that when released into the environment bind Fe and enhance its uptake by microbes. Siderophores have been well studied in laboratory cultures, but their presence in seawater has only recently been confirmed. Therefore, the distribution of siderophores in the ocean remains largely unknown. In this study we investigated the distribution of siderophores across a section of the eastern North and Tropical Pacific Oceans sampled by the US GEOTRACES GP15 expedition. The section bisects two large oligotrophic gyres, two chronically Fe-limited regions, and a region influenced by the Alaskan coast and margin. Siderophores are found in all 33 stations we sampled, and in some samples the concentration of siderophores exceeded the concentration of dissolved Fe. Overall, Fe-siderophore complexes were a significant portion of dissolved Fe in the upper ocean and their distribution highlighted regions of the ocean where the microbial community is Fe-deficient.

Key Points:

- Microbial iron acquisition by siderophores is common in the upper 500 m of the eastern North and Tropical Pacific Oceans
- High concentrations of metal-free and Al-siderophores indicate rapid cycling of siderophores
- Marinobactins and amphibactins were the two most common families of siderophores in the eastern North and Tropical Pacific Oceans

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:
D. J. Repeta,
drepeta@whoi.edu

Citation:
Li, J., Babcock-Adams, L., McIlvin, M. R., & Repeta, D. J. (2025). Distribution and cycling of siderophores in the eastern North and Tropical Pacific Oceans. *Geophysical Research Letters*, *52*, e2024GL113874. https://doi.org/10.1029/2024GL113874

Received 22 NOV 2024
Accepted 3 JAN 2025

1. Introduction

Across large regions of the surface ocean, the essential micronutrient iron (Fe) limits the growth of microbes, including phytoplankton (Boyd et al., 2007; de Baar et al., 1990; Martin & Fitzwater, 1988; Price et al., 1994) and heterotrophic bacteria (Cochlan, 2001; Kirchman et al., 2000; Oliver et al., 2004; Pakulski et al., 1996). In seawater ~99% of dissolved Fe (DFe) is complexed to organic ligands (Rue & Bruland, 1995; van den Berg, 1995). These ligands are a heterogeneous mix of compounds with different Fe binding groups that exhibit a range of binding strengths (Gledhill & Buck, 2012). A fraction of the very strong Fe binding ligands are siderophores, small metabolites synthesized by microbes to facilitate Fe uptake (Hider & Kong, 2010).

Siderophores are produced by heterotrophic bacteria, especially gammaproteobacteria, including marine strains of *Vibrio*, *Alteromonas*, and *Marinobacter* (Martinez et al., 2003). In phytoplankton, siderophores are synthesized by a marine strain of *Synechococcus* cyanobacteria (Ito & Butler, 2005; Wilhelm & Trick, 1994). Siderophore synthesis has not been demonstrated in eukaryotic phytoplankton (Hopkinson & Morel, 2009). However, acquisition of Fe from siderophores is not limited to microbes capable of de novo synthesis. Many bacteria that do not synthesize siderophores nevertheless have siderophore transporters that are able to access siderophore bound Fe (Griffin et al., 2004; Kramer et al., 2020; Moeck & Coulton, 1998). At least some eukaryotic phytoplankton are able to assimilate Fe bound to exogenous siderophores by cell surface reduction of Fe (III) to Fe (II) (Shaked et al., 2005), endocytosis (Kazamia et al., 2018), or combination of these two mechanisms (Coale et al., 2019).

Iron acquisition via the siderophore pathway has been well studied in laboratory cultures from a number of different perspectives, but their presence in seawater has only recently been confirmed (Boiteau et al., 2013, 2016; Mawji et al., 2008; McCormack et al., 2003). To date, at least two major classes of siderophores have been found in seawater, including the hydrophilic ferrioxamines, which have a peptidic Fe-binding group, and the amphiphilic amphibactins, marinobactins, and synechobactins, which have different peptidic Fe-binding groups linked to suites of saturated and unsaturated fatty acids. Ferrioxamines have stability constants that are two orders of magnitude greater than amphibactins (Bundy et al., 2018), and it has been postulated that ferrioxamines are produced to extract Fe from minerals present in dust (Basu et al., 2019; Kessler et al., 2020; Mawji et al., 2008) and suspended particulate matter (Li et al., 2024). In contrast, amphiphilic siderophores are likely produced to promote Fe uptake and mitigate Fe-limitation, consistent with their presence in Fe-deficient regions, including the euphotic zone of low Fe upwelling regions (Boiteau et al., 2016, 2019), as well as in the mesopelagic of oligotrophic gyres (Bundy et al., 2018; Li et al., 2024).

The US GEOTRACES Pacific Meridional Transect cruise (GP15) extending from 56°N to 20°S along 156°W (Figure S1 in Supporting Information S1) was designed to survey the distribution of trace elements and their isotopes across a large section of the eastern Pacific Ocean. The cruise track bisects two large oligotrophic gyres (North and South Pacific Subtropical Gyres), two chronically Fe-limited regions (North Pacific Subpolar Gyre and Equatorial Pacific (EP)), and a region near the Alaskan margin heavily influenced by coastal, shelf, and slope processes. Here we report the distribution of siderophores across the GP15 section. Although siderophores have been identified in a growing number of studies in different regions of the Atlantic and Pacific Oceans (Boiteau et al., 2016, 2019; Bundy et al., 2018; Gledhill et al., 2022; Mawji et al., 2008; McCormack et al., 2003; Park et al., 2023), the GP15 section allowed us to make measurements across a large and continuous region of the ocean in parallel to concurrent measurements of DFe. We found siderophores to be present at all stations across the section. Their concentrations and composition changed markedly between samples with potential consequences for the Fe cycling across the region.

2. Methods

Detailed methods are provided in Li et al. (2024). Briefly, seawater was collected using a trace metal clean (GTC) rosette/Go-Flo bottle sampler and filtered through 0.2 μm PES filters into 4 L polycarbonate bottles. Each sample was then pumped through a solid phase extraction column (SPE, Agilent ENV) previously activated with methanol (MeOH). The SPE columns were frozen immediately after sample collection and returned to the laboratory for processing.

SPE columns were washed with ultra-high purity water to reduce salts, and siderophores eluted with MeOH. Ga-desferrioxamine E was added as a recovery standard and the extract concentrated to ∼500 μL by vacuum centrifugation. A 100 μL aliquot of the sample was mixed with 100 μL of water, and immediately analyzed by liquid chromatography-mass spectrometry using a C18 column eluted with a linear gradient of 95/5 (v/v) A/B (5 mM ammonium formate (aq)/5 mM methanolic ammonium formate) to 5/95 (v/v) A/B over 80 min at 10 μL/min. The eluent was supplemented post-column with 35 μL/min water and the flow directed into a Thermo Scientific iCAP Q ICPMS. The detector response for ^{56}Fe was calibrated with Fe-ferrichrome. Al-siderophores were quantified by normalizing peak areas by the detector response for Fe/Al in a calibration solution of 10 ppb ^{56}Fe and 10 ppb ^{27}Al in 5% nitric acid. Siderophores were identified by LC-electrospray ionization (ESI)-MS. Data were aligned with ICPMS data using a Ga-desferrioxamine E internal standard and interrogated using mass search algorithms to find co-eluting pairs of ions with a mass difference of 1.995 D ($\Delta D = {}^{56}Fe - {}^{54}Fe$) and an intensity ratio of 15.7, the crustal abundance ratio of ^{56}Fe to ^{54}Fe.

3. Results

3.1. Fe-Siderophores in GP15

Siderophores were found at all 33 stations we sampled along the GP15 cruise track. Concentrations of Fe-siderophores ranged from <0.5 to 68 pM, and were highest at 400 m of Station 25 (Figure 1). Indeed, high concentrations of Fe-siderophore are a feature at the upper mesopelagic (200–500 m) across the entire section, suggesting microbial Fe-limitation in the twilight zone of the eastern Pacific Ocean (Li et al., 2024).

10.1029/2024GL113874

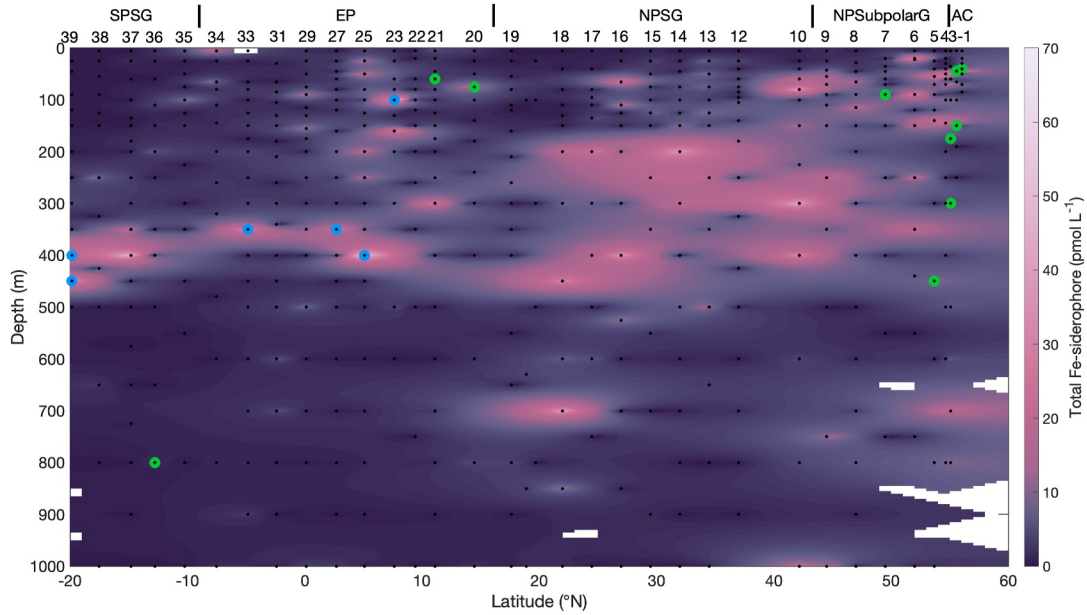

Figure 1. Distribution of Fe-siderophores between the surface and 1,000 m across the GP15 cruise track from 56°N to 20°S along 152°W. Samples with ferrioxamine and ferrichrome-like polar siderophores (green circles) were common in Stations 1–3 near the Alaskan Shelf and Slope, and in near surface waters around 10°N. Unidentified siderophores of mid-polarity (blue circles) were abundant in some samples south of 10°N. Sampling regions are adopted from Chmiel et al. (2022) and abbreviated as Alaskan Coast (AC), North Pacific Subpolar Gyre (NPSubpolarG), North Pacific Subtropical Gyre (NPSG), Equatorial Pacific (EP), and South Pacific Subtropical Gyre (SPSG).

Siderophore concentrations in surface waters ranged from <0.5 to 66 pM and were highest at 20 m of Station 6 in the chronically Fe-limited North Pacific Subpolar Gyre. Indeed, siderophore concentrations between 0 and 100 m of this region averaged 8.3 ± 13.5 pM, higher than the Alaskan Coast (AC) (5.9 ± 7.5 pM), North Pacific Subtropical Gyre (3.8 ± 7.9 pM), EP (4.9 ± 9.1 pM), and South Pacific Subtropical Gyre (SPSG) (1.0 ± 2.6 pM, Figure 1). Occasionally we measured significant concentrations of Fe-siderophores deeper than 500 m, for example, at Station 18, 700 m, the Fe-siderophore concentration was 52 pM, but generally (in 130 of 155 samples) Fe-siderophore concentrations in the deep sea (>500 m) were <5 pM.

Broadly, three classes of siderophores or metallophores, distinguished by their chromatographic properties, were present in the samples (Figure 2). One class included ferrioxamine and ferrichrome-like polar siderophores with chromatographic retention times of 30–50 min. These siderophores were only occasionally found and were most common in samples from Station 1–3, the region most strongly influenced by the continental shelf and slope of Alaska. We noted that the 40–44 m depth interval of Stations 1–2 had a high concentration of a single polar siderophore that we identified as ferricrocin (Figures S3 and S4 in Supporting Information S1). Ferricrocin has been previously isolated from fungi where it acts to facilitate Fe uptake and storage (Matzanke et al., 1988; Prabhu et al., 1996). With two exceptions (Station 5, 450 m and Station 36, 800 m) ferrioxamine and ferrichrome-like siderophores were only found in samples collected from <300 m depth.

In samples collected between Stations 23–39 we observed relatively high concentrations (up to 41 pM) of a moderately less polar class of Fe-metallophores that elute between 50 and 70 min on our chromatographic system (Figure 1). These metallophores are likely siderophores, but due to the high background of other co-eluting organic compounds we were unable to assign corresponding molecular ions, elemental formula, or compare these metallophores to siderophores described in public databases.

Finally, the most common siderophores found across the section were suites of nonpolar amphiphilic marinobactins and amphibactins with chromatographic retention times of 65–90 min. For marinobactins, we found Marinobactins A-E along with four previously undescribed homologs (Figure S2 and Table S1 in Supporting Information S1) that occurred in moderate to low abundance. In some samples the marinobactin distribution was dominated by a single homolog. For example, Marinobactin B contributed 93% of the total marinobactin at

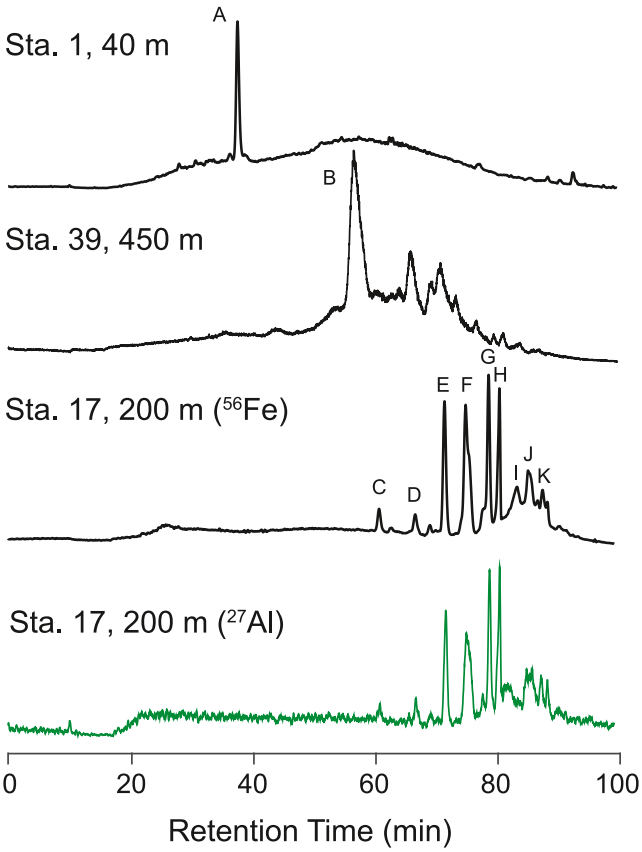

Figure 2. Siderophores in the US GEOTRACES GP15 section. Polar siderophores eluting between 30 and 50 min including ferricrocin (peak A) and other ferrioxamine and ferrichrome-like siderophores were common in stations near the Alaskan margin (Station 1, black trace, top), while in the upper mesopelagic waters of the section between 20°S and 10°N, unidentified siderophores (peak B) of mid-polarity eluting between 50 and 70 min were abundant (Station 39, black trace, middle). In the mesopelagic across the section, and in surface waters of the subpolar gyre and northern edge of the equatorial upwelling region, marinobactins and amphibactins were abundant (Station 17, peaks C-K; black trace, bottom). In addition to Fe-siderophores Al-siderophores were also common (green trace). Peak identifications are given in Table S1 in Supporting Information S1.

Station 3, 500 m, while Marinobactin D contributed 93% of the total marinobactin at Station 1, 20 m. In contrast, at Station 6, 350 m, Marinobactins A, B, C and D were all relatively abundant (11%, 64%, 14%, and 7% respectively). Amphibactins were less common and less abundant in our samples than marinobactins. Amphibactins appeared most frequently at 80–300 m in the North Pacific Subpolar and Subtropical Gyres between Station 7 and Station 17 (Figure S1 in Supporting Information S1). However, at a few stations we measured amphibactins in surface (5–25 m) and mesopelagic (300–600 m) samples. In contrast to marinobactions, amphibactins always occurred as complex mixtures of >10 homologs (Figure S2 in Supporting Information S1).

3.2. Metal-Free and Al-Siderophores in GP15

In addition to Fe-siderophores, we also found siderophores in their metal-free forms. We analyzed 18 samples collected between 20 and 700 m at 9 stations and found metal-free siderophores in 16 samples. Concentrations of metal-free siderophores ranged between 0.4 and 92 pM and on average accounted for 31% of the total siderophore concentration. In GP15 samples the distribution of metal-free siderophores closely tracked the distribution of Fe-siderophores (Figure 3).

Siderophores bound to aluminum were common and relatively abundant at nearly all stations at which Fe-siderophores were detected. For most Fe-marinobactins, Fe-amphibactins, and some Fe-ferrioxamine-like polar siderophores we found co-eluting Al-siderophore analogs (Figure 2). High concentrations of Al-siderophores, up to 57 pM, were found in surface waters of the North Pacific Subpolar Gyre. In the upper mesopelagic (200–500 m) of the North Pacific Subpolar and Subtropical Gyres between 20°N and 50°N, Al-siderophores were also abundant (Figure 4), although concentrations were generally lower (<16 pM) than in surface waters. Surprisingly, the concentrations of Al-siderophores were much lower (<4 pM) in the EP and SPSG even though in many samples from this region concentrations of Fe-siderophores remained high (up to 68 pM). The concentration of total siderophores (the sum of Fe-, Al-, and metal-free siderophores in the GP-15 samples ranged from <0.5 to 215 pM. Again, the highest concentration of total siderophores was found at 20 m of Station 6 including 66 pM Fe-siderophore, 57 pM Al-siderophore, and 92 pM metal-free siderophore.

4. Discussion

4.1. Fe-Siderophores as a Fraction of DFe

One striking feature of the GP15 section was the high concentration of siderophores and their contribution to the DFe pool. Early studies suggested that siderophore concentrations in surface waters were typically 0–20 pM (Boiteau et al., 2016, 2019; Bundy et al., 2018; Mawji et al., 2008), and therefore accounted for only a small fraction of DFe. Our results and the recent study by Park et al. (2023) show that Fe-siderophore concentration can approach 100 pM, similar to concentrations of DFe in low Fe environments. At Station 6, 20 m, of the North Pacific Subpolar Gyre, Fe-siderophore concentration reached 66 pM, accounting for ~80% of DFe (83 pM, Sieber et al., 2024). Siderophores can represent a major fraction of DFe.

4.2. Metal-Free and Al-Siderophores Indicate Rapid Cycling of Siderophores by Microbes

In addition to Fe-siderophores, we found metal-free siderophores contributed ~30% of the total siderophores in our samples (Figure 3). These results are similar to those in surface waters of the Eastern Tropical Pacific Ocean, where metal-free siderophores represented 40%–65% of total siderophores measured (Boiteau et al., 2016). When

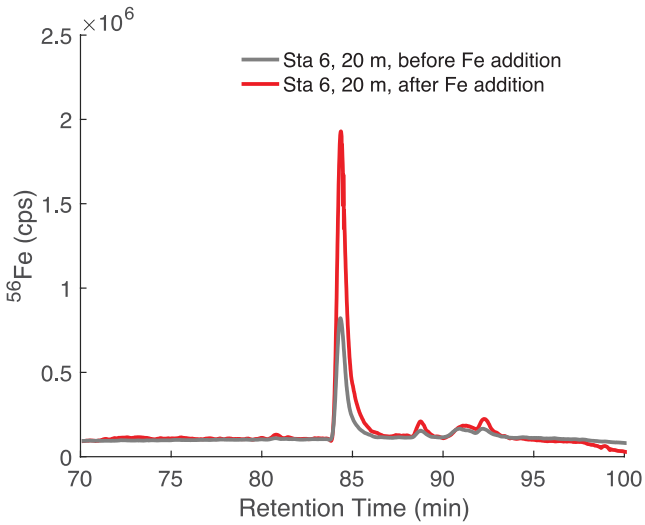

Figure 3. LC-ICPMS analysis of siderophores at 20 m of Station 6. The ^{56}Fe chromatogram plots ^{56}Fe abundance in counts per second (cps) as a function of chromatographic retention time. Fe-marinobactins present in the sample appear as peaks in the chromatogram (gray trace). After analysis, addition of $^{56}FeCl_3$ to the remaining sample allows metal-free siderophores to bind Fe. Subsequent LC-ICPMS analysis yields the total Fe- and metal-free siderophore in the sample (red trace).

environmental concentrations of bioavailable Fe are insufficient to meet cellular Fe demand some microbes synthesize siderophores to facilitate Fe uptake. After synthesis, metal-free siderophores are released into the environment where they take up Fe from weaker ligands. Isotope exchange experiments show that Fe binding by metal-free siderophores occurs quickly, suggesting the lifetime in seawater on the order of at most a few days (Boiteau & Repeta, 2022). Therefore, the presence of metal-free siderophores in GP15 samples at both surface and the upper mesopelagic indicates fast production and uptake of siderophores via the siderophore Fe acquisition pathway.

The relative contribution of metal-free siderophores to total siderophores was highest in surface waters of the North Pacific Subpolar Gyre, a region characterized by low DFe concentrations and high Nitrate:DFe ratios throughout the water column (Li et al., 2024). The high concentration of metal-free siderophores in surface waters of the North Pacific Subpolar Gyre reflects the severe Fe-stress of heterotrophic bacteria and the fast turnover of siderophores. The large fraction of DFe contributed by Fe-siderophores at some sites may force phytoplankton to acquire Fe from siderophores (Maldonado & Price, 1999).

Some siderophores form stable complexes with a suite of trace metals including Al (Schalk et al., 2011), which has seawater concentrations in the low nM range (Menzel Barraqueta et al., 2020), similar to Fe. Al-siderophores have not been previously found in environmental samples. However, Gledhill and colleagues found Al-ferrioxamines and Al-amphibactins in nutrient (glucose, ammonia, and phosphate) amended seawater in which Fe bioavailability had been reduced by the addition of ethylene diamine-*N*,*N*′-diacetic acid (Gledhill et al., 2004), suggesting that under conditions of severe Fe-stress and high siderophore production, Al-complexation could occur.

Our analyses of GP15 samples demonstrates that Al-siderophores are common in the ocean. For most Fe-siderophores we found co-eluting Al-siderophore analogs (Figure 2). High concentrations of Al-siderophores,

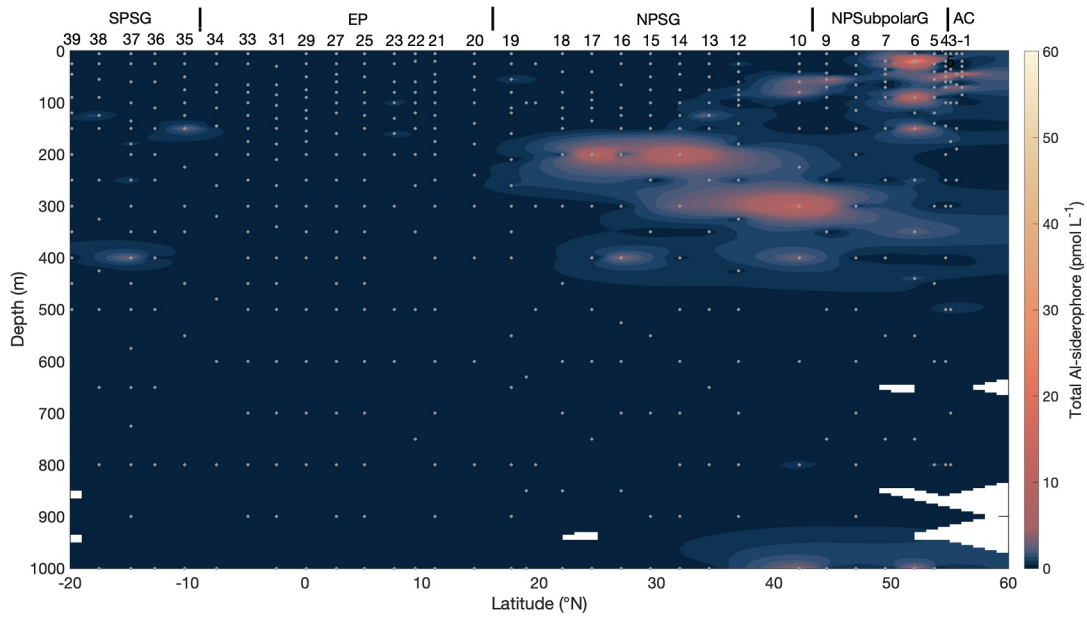

Figure 4. Distribution of Al-siderophores between the surface and 1,000 m across the GP15 cruise track from 56°N to 20°S along 152°W. Sample locations appear as gray dots overlayed on the plot of Al-siderophore concentration. Sampling region abbreviations are given in Figure 1.

up to 57 pM, comparable to the maximum concentration of Fe-siderophores (66 pM), were found in surface waters of the North Pacific Subpolar Gyre. Between 20°N and 50°N Al-siderophores were also abundant in the upper mesopelagic (Figure 4). South of 20°N we found much lower concentrations of Al-siderophores (<4 pM) even though concentrations of Fe-siderophores remain high (up to 68 pM). Below 200 m the ratio of Fe-siderophore/Al-siderophore was three times higher in the southern half of the GP15 section (<20°N) compared to the northern half of the section (>20°N).

The discovery of Al-siderophores in GP15 samples led us to suspect that there might also be Al-siderophores in other regions of the ocean. Upon reexamination of the mass spectral data collected in the Eastern Tropical Pacific Ocean (GP16, Boiteau et al., 2016), we found Al-siderophores including Al-Amphibactin D and Al-Siderophore 959. Therefore, Al-siderophores were also present in GP16 samples. While in many cases the distribution of Al-siderophores matched the distribution of Fe-siderophores (Figure 2) we noted that in some samples complexation with Al appeared to display some selectivity such that the distribution of Fe-siderophores was different than the distribution of Al-siderophores. In these samples the ratio of Fe-siderophore to Al-siderophore changed across the suite of siderophores present.

The accumulation of Al-siderophores in GP15 and GP16 samples, changes in the Fe-siderophore/Al-siderophore ratio, and differences in the distribution of Fe- and Al-siderophores within a sample are all likely driven by temporal differences in the production of siderophores, the competition between Fe and Al for metal-free siderophores (Li et al., 2024), and differences in siderophore uptake and processing by heterotrophic bacteria. Although siderophores bind Fe more strongly than Al, the relative rates of complexation are not known, and will depend in part on the concentration and distribution of competing Fe- and Al-ligands present in seawater. Bacteria can assimilate Al-siderophores through Ton-B dependent siderophore transporters (Greenwald et al., 2008; Hu & Boyer, 1996) however it is not known if the Al-siderophore complex is demetalated and the siderophore excreted back into the environment. If Al-siderophores cannot be demetalated, Al-siderophores represent a "dead-end" to the siderophore cycle and as such an inefficiency in the siderophore Fe-acquisition pathway.

4.3. Siderophores as Indicators of Fe Bioavailability

A wide variety of siderophores have now been identified in seawater, including amphibactins, ferrioxamines, marinobactins, petrobactins, synechobactins, and ferrichrome-like siderophores (i.e., ferricrocin) (Boiteau et al., 2016, 2019; Bundy et al., 2018; Gledhill et al., 2022; Manck et al., 2022; Mawji et al., 2008; Park et al., 2023). These siderophores are synthesized by different microbes, have different biosynthetic pathways, chemical properties (structures, Fe-binding constants, hydrophobicity, etc.) and may differ in the details of their uptake and cycling. It has been postulated that due to the very high Fe-binding constants and hydrophilicity of ferrioxamines and ferrichrome-like siderophores, microbes use these siderophores to acquire Fe from particulate matter (Akafia et al., 2014; Basu et al., 2019; Kessler et al., 2020; Mawji et al., 2008). Consistent with this hypothesis we found ferricrocin to be particularly abundant in samples collected near the AC (Stations 1–3). At the time of sample collection, the delivery of atmospheric dust to the eastern Pacific Ocean was at its annual minimum (Marsay et al., 2022), consistent with the near absence of ferrioxamines/ferrichrome-like siderophores in samples across the remainder of the section. This contrasts to the high concentrations of ferrioxamines found across a section from 40°N to 30°S of the mid Atlantic Ocean (Mawji et al., 2008), an area characterized by high dust inputs.

Marinobactins were the most common and most abundant siderophores across the GP15 section, and along with the closely related amphibactin family of siderophores occurred in surface waters of the chronically Fe-limited North Pacific Subpolar Gyre and EP, and throughout the mesopelagic. The reasons why these two families of siderophores were so common in the GP15 samples are unknown, however we noted that siderophore concentration and distribution often changed rapidly over even very small depth and spatial scales. For example, at Station 1, 20 m Marinobactins A and D represented 7% and 93% of the total siderophores, while at 30 m the abundance of these two siderophores reversed at 78% and 21%, respectively. At 40 m marinobactins were nearly undetectable, with ferricrocin contributing 98% of the siderophores at that depth. Such rapid changes in siderophore distribution were not uncommon in the GP15 samples. Assuming microbes optimize Fe uptake through the type and amount of siderophores they produce, the large fluctuations in siderophore composition in the GP15 samples likely point to equally significant changes in Fe bioavailability over small spatial and depth scales.

5. Conclusions

Siderophores are synthesized by microbes under conditions of Fe-stress, when the uptake of Fe by other acquisition pathways is not able to match cellular Fe demand. We found siderophores at all stations in the GP15 section, particularly in chronically Fe-limited surface waters of the subpolar gyre and the northern edge of the equatorial upwelling region, two areas characterized by low DFe concentrations but high concentrations of nitrate and phosphate. Siderophores were also abundant in the upper mesopelagic across the entire section. The marinobactin family of amphiphilic siderophores were the most common siderophores found across the section, with polar ferrioxamine/ferrichrome-like siderophores, including the fungal siderophore ferricrocin, particularly abundant in samples influenced by the Alaskan shelf and slope, and an unidentified group of siderophores abundant in upper mesopelagic south of ∼10°N. Microbial acquisition of Fe through siderophores is common in the eastern North and Tropical Pacific Oceans.

In addition to Fe-siderophores, metal-free and Al-siderophores were also common across the section. In a few samples collected from the subpolar gyre, Fe-siderophores represented a large fraction of DFe and concentrations of total siderophores (Fe + Al + metal free) equaled or exceeded concentrations of DFe. Metal-free siderophores are excreted by microbes but rapidly bind Fe or Al, so their presence in samples is assumed to be transitory and reflective of the rapid cycling of siderophores in the environment. A short half-life for siderophores in seawater is further supported by differences in the distribution of Fe- and Al-siderophores in many samples. The high concentrations and likely rapid cycling of siderophores in many GP15 samples, suggests that siderophores could support a large fraction of microbial Fe demand in chronically Fe-limited regions of the subpolar gyre and equatorial upwelling areas as well as the upper mesopelagic region.

Data Availability Statement

Siderophore concentration data for the GP15 transect are publicly available in Zenodo (Repeta, 2025). Other data in this paper are publicly available in Zenodo (Li & Repeta, 2025).

Acknowledgments
We thank Phoebe Lam, Karen Casciotti, Greg Cutter, Brent Summers, and Laramie Jensen for their organization, assistance and support of the GP15 expedition. Funding for this work was provided by National Science Foundation Chemical Oceanography Program (NSF Awards OCE-1736280 and OCE-2045223 to D.J.R).

References

Akafia, M. M., Harrington, J. M., Bargar, J. R., & Duckworth, O. W. (2014). Metal oxyhydroxide dissolution as promoted by structurally diverse siderophores and oxalate. *Geochimica et Cosmochimica Acta*, *141*, 258–269. https://doi.org/10.1016/j.gca.2014.06.024

Basu, S., Gledhill, M., de Beer, D., Prabhu Matondkar, S. G., & Shaked, Y. (2019). Colonies of marine cyanobacteria Trichodesmium interact with associated bacteria to acquire iron from dust. *Communications Biology*, *2*(1), 284. https://doi.org/10.1038/s42003-019-0534-z

Boiteau, R. M., Fitzsimmons, J. N., Repeta, D. J., & Boyle, E. A. (2013). Detection of iron ligands in seawater and marine cyanobacteria cultures by high-performance liquid chromatography–inductively coupled plasma-mass spectrometry. *Analytical Chemistry*, *85*(9), 4357–4362. https://doi.org/10.1021/ac3034568

Boiteau, R. M., Mende, D. R., Hawco, N. J., McIlvin, M. R., Fitzsimmons, J. N., Saito, M. A., et al. (2016). Siderophore-based microbial adaptations to iron scarcity across the eastern Pacific Ocean. *Proceedings of the National Academy of Sciences of the United States of America*, *113*(50), 14237–14242. https://doi.org/10.1073/pnas.1608594113

Boiteau, R. M., & Repeta, D. J. (2022). Slow kinetics of iron binding to marine ligands in seawater measured by isotope exchange liquid chromatography–inductively coupled plasma mass spectrometry. *Environmental Science & Technology*, *56*(6), 3770–3779. https://doi.org/10.1021/acs.est.1c06922

Boiteau, R. M., Till, C. P., Coale, T. H., Fitzsimmons, J. N., Bruland, K. W., & Repeta, D. J. (2019). Patterns of iron and siderophore distributions across the California Current System. *Limnology & Oceanography*, *64*(1), 376–389. https://doi.org/10.1002/lno.11046

Boyd, P. W., Jickells, T., Law, C. S., Blain, S., Boyle, E. A., Buesseler, K. O., et al. (2007). Mesoscale iron enrichment experiments 1993-2005: Synthesis and future directions. *Science*, *315*(5812), 612–617. https://doi.org/10.1126/science.1131669

Bundy, R. M., Boiteau, R. M., McLean, C., Turk-Kubo, K. A., McIlvin, M. R., Saito, M. A., et al. (2018). Distinct siderophores contribute to iron cycling in the mesopelagic at station ALOHA. *Frontiers in Marine Science*, *5*, 61. https://doi.org/10.3389/fmars.2018.00061

Chmiel, R., Lanning, N., Laubach, A., Lee, J. M., Fitzsimmons, J., Hatta, M., et al. (2022). Major processes of the dissolved cobalt cycle in the North and equatorial Pacific Ocean. *Biogeosciences*, *19*(9), 2365–2395. https://doi.org/10.5194/bg-19-2365-2022

Coale, T. H., Moosburner, M., Horák, A., Oborník, M., Barbeau, K. A., & Allen, A. E. (2019). Reduction-dependent siderophore assimilation in a model pennate diatom. *Proceedings of the National Academy of Sciences of the United States of America*, *116*(47), 23609–23617.

Cochlan, W. P. (2001). The heterotrophic bacterial response during a mesoscale iron enrichment experiment (IronEx II) in the eastern equatorial Pacific Ocean. *Limnology & Oceanography*, *46*(2), 428–435. https://doi.org/10.4319/lo.2001.46.2.0428

de Baar, H. J., Buma, A. G., Nolting, R. F., Cadée, G. C., Jacques, G., & Tréguer, P. J. (1990). On iron limitation of the southern ocean: Experimental observations in the Weddell and Scotia Seas. *Marine Ecology Progress Series*, *65*, 105–122. https://doi.org/10.3354/meps065105

Gledhill, M., & Buck, K. N. (2012). The organic complexation of iron in the marine environment: A review. *Frontiers in Microbiology*, *3*, 69. https://doi.org/10.3389/fmicb.2012.00069

Gledhill, M., McCormack, P., Ussher, S., Achterberg, E. P., Mantoura, R. F. C., & Worsfold, P. J. (2004). Production of siderophore type chelates by mixed bacterioplankton populations in nutrient enriched seawater incubations. *Marine Chemistry*, *88*(1–2), 75–83. https://doi.org/10.1016/j.marchem.2004.03.003

Gledhill, M., Zhu, K., Rusiecka, D., & Achterberg, E. P. (2022). Competitive interactions between microbial siderophores and humic-like binding sites in European shelf sea waters. *Frontiers in Marine Science*, *9*, 855009. https://doi.org/10.3389/fmars.2022.855009

Greenwald, J., Zeder-Lutz, G., Hagege, A., Celia, H., & Pattus, F. (2008). The metal dependence of pyoverdine interactions with its outer membrane receptor FpvA. *Journal of Bacteriology*, *190*(20), 6548–6558. https://doi.org/10.1128/jb.00784-08

Griffin, A. S., West, S. A., & Buckling, A. (2004). Cooperation and competition in pathogenic bacteria. *Nature*, *430*(7003), 1024–1027. https://doi.org/10.1038/nature02744

Hider, R. C., & Kong, X. (2010). Chemistry and biology of siderophores. *Natural Product Reports*, *27*(5), 637–657. https://doi.org/10.1039/b906679a

Hopkinson, B. M., & Morel, F. M. (2009). The role of siderophores in iron acquisition by photosynthetic marine microorganisms. *Biometals*, *22*(4), 659–669. https://doi.org/10.1007/s10534-009-9235-2

Hu, X., & Boyer, G. L. (1996). Siderophore-mediated aluminum uptake by Bacillus megaterium ATCC 19213. *Applied and Environmental Microbiology*, *62*(11), 4044–4048. https://doi.org/10.1128/aem.62.11.4044-4048.1996

Ito, Y., & Butler, A. (2005). Structure of synechobactins, new siderophores of the marine cyanobacterium Synechococcus sp. PCC 7002. *Limnology & Oceanography*, *50*(6), 1918–1923. https://doi.org/10.4319/lo.2005.50.6.1918

Kazamia, E., Sutak, R., Paz-Yepes, J., Dorrell, R. G., Vieira, F. R. J., Mach, J., et al. (2018). Endocytosis-mediated siderophore uptake as a strategy for Fe acquisition in diatoms. *Science Advances*, *4*(5), eaar4536. https://doi.org/10.1126/sciadv.aar4536

Kessler, N., Kraemer, S. M., Shaked, Y., & Schenkeveld, W. D. (2020). Investigation of siderophore-promoted and reductive dissolution of dust in marine microenvironments such as Trichodesmium colonies. *Frontiers in Marine Science*, *7*, 45. https://doi.org/10.3389/fmars.2020.00045

Kirchman, D. L., Meon, B., Cottrell, M. T., Hutchins, D. A., Weeks, D., & Bruland, K. W. (2000). Carbon versus iron limitation of bacterial growth in the California upwelling regime. *Limnology & Oceanography*, *45*(8), 1681–1688. https://doi.org/10.4319/lo.2000.45.8.1681

Kramer, J., Özkaya, Ö., & Kümmerli, R. (2020). Bacterial siderophores in community and host interactions. *Nature Reviews Microbiology*, *18*(3), 152–163. https://doi.org/10.1038/s41579-019-0284-4

Li, J., Babcock-Adams, L., Boiteau, R. M., McIlvin, M. R., Manck, L. E., Sieber, M., et al. (2024). Microbial iron limitation in the ocean's twilight zone. *Nature*, *633*(8031), 823–827. https://doi.org/10.1038/s41586-024-07905-z

Li, J., & Repeta, D. (2025). Distribution and cycling of siderophores in the North and tropical east Pacific Oceans [Dataset]. *Zenodo*. https://doi.org/10.5281/zenodo.14646115

Maldonado, M. T., & Price, N. M. (1999). Utilization of iron bound to strong organic ligands by plankton communities in the subarctic Pacific Ocean. *Deep Sea Research Part II: Topical Studies in Oceanography*, *46*(11–12), 2447–2473. https://doi.org/10.1016/s0967-0645(99)00071-5

Manck, L. E., Park, J., Tully, B. J., Poire, A. M., Bundy, R. M., Dupont, C. L., & Barbeau, K. A. (2022). Petrobactin, a siderophore produced by Alteromonas, mediates community iron acquisition in the global ocean. *The ISME Journal*, *16*(2), 358–369. https://doi.org/10.1038/s41396-021-01065-y

Marsay, C. M., Kadko, D., Landing, W. M., & Buck, C. S. (2022). Bulk aerosol trace element concentrations and deposition fluxes during the US GEOTRACES GP15 Pacific Meridional Transect. *Global Biogeochemical Cycles*, *36*(2), e2021GB007122. https://doi.org/10.1029/2021GB007122

Martin, J. H., & Fitzwater, S. E. (1988). Iron deficiency limits phytoplankton growth in the north-east Pacific subarctic. *Nature*, *331*(6154), 341–343. https://doi.org/10.1038/331341a0

Martinez, J. S., Carter-Franklin, J. N., Mann, E. L., Martin, J. D., Haygood, M. G., & Butler, A. (2003). Structure and membrane affinity of a suite of amphiphilic siderophores produced by a marine bacterium. *Proceedings of the National Academy of Sciences of the United States of America*, *100*(7), 3754–3759. https://doi.org/10.1073/pnas.0637444100

Matzanke, B. F., Bill, E., Trautwein, A. X., & Winkelmann, G. (1988). Ferricrocin functions as the main intracellular iron-storage compound in mycelia of Neurospora crassa. *Biology of Metals*, *1*, 18–25. https://doi.org/10.1007/bf01128013

Mawji, E., Gledhill, M., Milton, J. A., Tarran, G. A., Ussher, S., Thompson, A., et al. (2008). Hydroxamate siderophores: Occurrence and importance in the Atlantic Ocean. *Environmental Science & Technology*, *42*(23), 8675–8680. https://doi.org/10.1021/es801884r

McCormack, P., Worsfold, P. J., & Gledhill, M. (2003). Separation and detection of siderophores produced by marine bacterioplankton using high-performance liquid chromatography with electrospray ionization mass spectrometry. *Analytical Chemistry*, *75*(11), 2647–2652. https://doi.org/10.1021/ac0340105

Menzel Barraqueta, J. L., Samanta, S., Achterberg, E. P., Bowie, A. R., Croot, P., Cloete, R., et al. (2020). A first global oceanic compilation of observational dissolved aluminum data with regional statistical data treatment. *Frontiers in Marine Science*, *7*, 468. https://doi.org/10.3389/fmars.2020.00468

Moeck, G. S., & Coulton, J. W. (1998). TonB-dependent iron acquisition: Mechanisms of siderophore-mediated active transport. *Molecular Microbiology*, *28*(4), 675–681. https://doi.org/10.1046/j.1365-2958.1998.00817.x

Oliver, J. L., Barber, R. T., Smith Jr, W. O., & Ducklow, H. W. (2004). The heterotrophic bacterial response during the Southern Ocean iron experiment (SOFeX). *Limnology & Oceanography*, *49*(6), 2129–2140. https://doi.org/10.4319/lo.2004.49.6.2129

Pakulski, J., Coffin, R., Kelley, C., Holder, S., Downer, R., Aas, P., et al. (1996). Iron stimulation of Antarctic bacteria. *Nature (London)*, *383*(6596), 133–134. https://doi.org/10.1038/383133b0

Park, J., Durham, B. P., Key, R. S., Groussman, R. D., Bartolek, Z., Pinedo-Gonzalez, P., et al. (2023). Siderophore production and utilization by marine bacteria in the North Pacific Ocean. *Limnology & Oceanography*, *68*(7), 1636–1653. https://doi.org/10.1002/lno.12373

Prabhu, V., Biolchini, P. F., & Boyer, G. L. (1996). Detection and identification of ferricrocin produced by ectendomycorrhizal fungi in the genus Wilcoxina. *Biometals*, *9*(3), 229–234. https://doi.org/10.1007/bf00817920

Price, N. M., Ahner, B. A., & Morel, F. M. (1994). The equatorial Pacific Ocean: Grazer-controlled phytoplankton populations in an iron-limited ecosystem 1. *Limnology & Oceanography*, *39*(3), 520–534. https://doi.org/10.4319/lo.1994.39.3.0520

Repeta, D. (2025). GP15 iron ligands in seawater [Dataset]. *Zenodo*. https://doi.org/10.5281/zenodo.14948599

Rue, E. L., & Bruland, K. W. (1995). Complexation of iron (III) by natural organic ligands in the Central North Pacific as determined by a new competitive ligand equilibration/adsorptive cathodic stripping voltammetric method. *Marine Chemistry*, *50*(1–4), 117–138. https://doi.org/10.1016/0304-4203(95)00031-l

Schalk, I. J., Hannauer, M., & Braud, A. (2011). New roles for bacterial siderophores in metal transport and tolerance. *Environmental Microbiology*, *13*(11), 2844–2854. https://doi.org/10.1111/j.1462-2920.2011.02556.x

Shaked, Y., Kustka, A. B., & Morel, F. M. (2005). A general kinetic model for iron acquisition by eukaryotic phytoplankton. *Limnology & Oceanography*, *50*(3), 872–882. https://doi.org/10.4319/lo.2005.50.3.0872

Sieber, M., Lanning, N., Steffen, J., Bian, X., Yang, S. C., Lee, J., et al. (2024). Long distance transport of subsurface sediment-derived iron from Asian to Alaskan margins in the North Pacific Ocean. *Geophysical Research Letters*, *51*(20), e2024GL110836. https://doi.org/10.1029/2024gl110836

van den Berg, C. M. (1995). Evidence for organic complexation of iron in seawater. *Marine Chemistry*, *50*(1–4), 139–157. https://doi.org/10.1016/0304-4203(95)00032-m

Wilhelm, S. W., & Trick, C. G. (1994). Iron-limited growth of cyanobacteria: Multiple siderophore production is a common response. *Limnology & Oceanography*, *39*(8), 1979–1984. https://doi.org/10.4319/lo.1994.39.8.1979