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Key Points:

- Particles in the water column of the Ross Sea have an average Mn oxidation state of <3, and lack detectable Mn oxides
- Soluble Mn(III)-L complexes compose up to 100% of the dissolved Mn pool, with highest concentrations in surface waters and ice
- Cobalt profiles do not exhibit scavenging behavior, and Co uptake rates are low to nondetectable, indicating an absence of scavenging to particles within the waters

Supporting Information:

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

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Inhibited Manganese Oxide Formation Hinders Cobalt Scavenging in the Ross Sea

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Abstract The Southern Ocean plays a critical role in regulating global uptake of atmospheric CO₂. Trace elements like iron (Fe), cobalt (Co), and manganese (Mn) have been shown to modulate this primary productivity. Despite limited data, the vertical profiles for Mn, Fe, and Co in the Ross Sea show no evidence of scavenging, as typically observed in oceanic sites. This was previously attributed to low-particle abundance and/or by mixing rates exceeding scavenging rates. Scavenging of some trace metals such as cobalt (Co) is thought to be largely governed by Mn (oxyhydr)oxides, assumed to be the main component of particulate Mn (pMn). However, our data show that pMn has an average oxidation state below 3 and with nondetectable Mn oxides. In addition, soluble Co profiles show no evidence of scavenging and Co uptake measurements show little Co uptake in the euphotic zone and low/no scavenging at depth. Instead, high concentrations of dissolved Mn (dMn, up to 90 nM), which is primarily complexed as Mn(III)-L (up to 100%), are observed. Average dMn concentrations (10 ± 14 nM) are highest in bottom and surface waters. Manganese sources may include sediments and sea-ice melt, as elevated dMn was measured in sea ice (12 nM) compared to its surrounding waters (3 nM), and sea ice dMn was 97% Mn(III)-L. We contend that the lack of Co scavenging in the Ross Sea is due to a unique Mn redox cycle that favors the stabilization of Mn(III)-complexes at the expense of Mn oxide particle formation.

Plain Language Summary Manganese (Mn) oxides were nondetectable in the particulate phase in the Ross Sea, but abundant soluble Mn in the form of Mn(III)-L complexes was measured throughout the basin. This unique redox speciation for Mn helps to explain the lack of scavenging in the Ross Sea and may indicate that soluble Mn plays an important role in primary productivity by modulating the cycles of other elements of the Southern Ocean.

1. Introduction

Phytoplankton productivity in the Southern Ocean is an important sink for CO₂ (Arrigo, Robinson, et al., 1999) and accounts for 5%–10% of total global oceanic primary production (Arrigo et al., 2008; Moore & Abbott, 2000). While the Southern Ocean is generally considered to be iron (Fe) and light-limited (Alderkamp et al., 2019; Martin et al., 1990; Mitchell et al., 1991; Strzepek et al., 2019), there is increasing interest in the influence of additional trace elements such as cobalt (Co) and manganese (Mn) on primary productivity (Bertrand et al., 2007; Buma et al., 1991; Coale & Bruland, 1990; Noble et al., 2013). The cycling and bioavailability of these elements are controlled by chemical speciation, including element coordination, and oxidation state. In most water columns, Fe is maintained in the soluble phase via complexation to organic ligands (e.g., Bundy et al., 2018; Hassler et al., 2017; Rue & Bruland, 1995), and in the Southern Ocean, many of these ligands are thought to be biologically produced as siderophores or saccharides (Hassler et al., 2011; Maldonado et al., 2005). Thus, the complexation of Fe is inherently linked to biological activity and cycling. Recent work has shown that the Southern Ocean may be co-limited by other trace elements, notably, soluble Mn (Pausch et al., 2019; Wu et al., 2019), but little is known regarding how Mn speciation affects its biogeochemistry in the Southern Ocean.

Soluble Mn composes both hexaaqua Mn(II) and Mn(III)-ligand (L) complexes, while particulate Mn (pMn) consists of both oxidized Mn(III/IV) (oxyhydr)oxides and (ad)sorbed Mn(II) and Mn(III) complexes. While soluble Mn also forms strong complexes with organic ligands, including siderophores (Luther et al., 2015),

Figure 1. Station map, indicating the study region (top) along the western coast of the Ross Sea, as well as the specific site locations (below). Red symbols indicate Mn-# stations, and yellow symbols are Cobalamin and Iron Co-Limitation of Phytoplankton Species (CICLOPS) stations used for Co uptake rates (CICLOPS 20 and 22) as well as the ice sampling site (CICLOPS 77).

studies examining Mn complexation have been limited to coastal systems (Oldham et al., 2015; Oldham, Miller, et al., 2017; Oldham, Miller, et al., 2020; Oldham, Mucci, et al., 2017; Oldham, Tebo, et al., 2017; Trouwborst et al., 2006), and sediments (Madison et al., 2013; Oldham, Mucci, et al., 2017). In these previous studies that speciated dMn, Mn(III)-L complexes were found to compose a predominant fraction of the dissolved pool. The ligands comprising these Mn(III) complexes include humics in some environments. As metal-humic complexes precipitate when acidified, previous field Mn measurements where Mn(III)-humics were present and where samples were acidified for sample preservation likely underestimated soluble Mn concentrations (Oldham, Miller, et al., 2017; Oldham, Mucci, et al., 2017). While the Ross Sea is coastal, it receives lower fluxes of dissolved metals and organic matter input compared to other coastal systems with more terrestrial biota. Thus, from a trace element perspective it shares some similarities with an open ocean system, except for its explosive productivity in the summer months. In the limited studies that have investigated total dissolved Mn in the Southern Ocean, the chemistry of Mn is reported as atypical, with a nutrient-type dissolved profile (Sedwick et al., 2000) instead of scavenged-nutrient hybrid-type profile, as in most other oceanic sites. Noble et al. (2013) reported higher dMn concentrations (~ 5 nM) under sea ice compared to the open ocean but very low pMn (~ 0.04 nM), whereas open ocean systems typically have concentrations of 0.1–3 nM pMn (e.g., Lee et al., 2018).

The distribution of pMn is often invoked as an important control on the scavenging of other trace elements like iron, cobalt, nickel, and zinc (Means et al., 1978; Murray, 1975; Saito et al., 2004; Tonkin et al., 2004; Yamagata & Iwashima, 1963). This behavior is based on observations that Mn oxidation to Mn(III/IV) oxides is an important process that scavenges other metals by co-precipitation or adsorption. For example, dissolved Co (dCo) can be co-oxidized along with Mn(II) and incorporated into Mn oxides (Murray et al., 2007), resulting in dCo profiles exhibiting scavenging with depth below the euphotic zone (Hawco et al., 2018; Moffett & Ho, 1996). However, in the Southern Ocean dCo profiles have been found to reflect little to no scavenging, maintaining a nutrient-profile vertical structure (Noble et al. 2013; Saito et al. 2010). It has been hypothesized that the absence of scavenging could be due to low rates of Mn oxide formation, but the underpinning constraints on precipitation are unknown. Indeed, the speciation of dMn and pMn within Southern Ocean waters has not been interrogated, precluding the ability to fully interpret the dynamics of Mn and associated trace elements, such as Co.

Here, we characterize the dissolved and solid-phase speciation of Mn in the Ross Sea to reveal a unique Mn redox cycle with important implications for the cycling and distribution of Co. In addition, we present measurements of soluble Mn speciation in sea ice to make inferences on the source and fate of Mn during redox cycling in the Ross Sea. We also include soluble Co speciation and Co uptake measurements from two stations. The Co measurements shed further light on Mn as a key constraint on trace element distributions and trace element nutrient uptake in the Southern Ocean.

2. Materials and Methods

2.1. Sampling

Ten stations in the Ross Sea polynya, including stations in the western Ross Sea and Terra Nova Bay (map Figure 1; Table S1), were sampled during the NBP-1801 expedition aboard the RV/IB *N.B. Palmer* from February to March 2018 as part of the CICLOPS (Cobalamin and Iron Co-Limitation of Phytoplankton Species) expedition. Station numbers for Mn sampling were less frequent than expedition stations and were numbered according to their distance from shore, corresponding to expedition stations as described in Table S1

(stations Mn-1 to Mn-10). Measurements were made for soluble phase Mn speciation using a 12-bottle (Niskin-X bottles) trace metal clean CTD (conductivity, temperature, and depth) rosette sampling system equipped with SeaBird equipment for salinity, temperature, dissolved oxygen, conductivity, and fluorometry. Sampling depths were selected based on the down-cast profile of salinity, fluorescence and dissolved oxygen. For most stations, 8 depths were selected for soluble Mn speciation. Upon retrieval, Niskin bottles were transported with gloved hands to a trace metal clean van and sampled into acid-washed 1 L PTFE bottles. Bottles were triple rinsed before filling and were overflowed to prevent oxygen contamination. The seawater was immediately filtered in the main laboratory through 0.2 μm PES Millipore filters using acid washed Savillex vacuum-filtration rigs. One 10 mL volume of filtrate was immediately amended with 1 μM hydroxylamine hydrochloride for total dMn (over 10 times excess predicted total dMn concentration), and one volume was immediately analyzed for soluble Mn(II) + Mn(III)-L_w (see Section 2.2). The filter was immediately amended with a 0.1% solution of leucoberberlin blue (LBB) dye and kept in the refrigerator until analysis (Section 2.2).

One sea ice station (nearest to CICLOPS station 77, Figure 1, Table S1) was sampled by Zodiac for sea ice and surrounding water. Water was collected using a trace-metal clean “toothbrush” shaped pole: A plastic wrapped pole with an acid washed rectangular polypropylene container attached with Nylon cable ties. Sea ice, brine and surrounding seawater were separately “scooped” into 5 L acid washed PTFE bottles. These were double-bagged and transported into the trace metal room aboard the ship. The seawater and brine were immediately filtered, and the sea ice was thawed in the dark and then filtered through a 0.2 μm acid-washed Supor (polyestersulfone) filter. The filtrate was immediately analyzed for soluble Mn speciation.

Filter samples ($>0.2 \mu\text{m}$) were also collected using in situ pumps (McLane Research Laboratories) at three stations: One near the continent (station Mn-1), one 20 km from the continent (station Mn-5), and one in the open water of the polynya which extends into Terra Nova Bay (station Mn-9). Over 200 L (up to 1150 L, exact volumes in Table S3) of seawater was collected at 4, 3, and 6 depths from each respective site, targeting the aphotic zone. Filtration was size fractionated, and the fraction represented in this study is the 0.2–3.0 μm size fraction, onto Supor 0.2 μm filters. Filters were sliced in a clean room and frozen immediately for later analysis at the Stanford Synchrotron Radiation Lightsource (SSRL, Section 2.3).

One terrestrial sample from McMurdo station was taken next to the dock by scooping surface dirt into a new 15 mL falcon tube. This sample was kept in the freezer for later analysis at SSRL.

Dissolved cobalt (dCo) samples (sites 2, 9, and CICLOPS station 20) were collected using the same rosette system described above. Niskin-X bottles were pressurized at sea with high purity N₂ gas in a trace metal clean van under positive pressure, allowing samples to be filtered with an acid-washed 0.2 μm Supor membrane filter (polyestersulfone; Pall Corporation, 142 mm diameter) within 3 h of recovery. Samples for dCo analysis were stored in 60 mL low-density polyethylene bottles that had been soaked for ~1 week in Citranox, an acidic detergent, rinsed with Milli-Q water, soaked for ~2 weeks in 10% trace metal grade HCl, and rinsed with dilute HCl in Milli-Q water ($>0.1\%$ HCl). Bottles were rinsed 3 times prior to filling, and dissolved Co samples were stored in double sealed bags at 4°C until analysis. Samples for the radiotracer incubation experiment were dispensed directly into polycarbonate bottles, rinsed with filtered trace metal clean seawater for radiotracer incubation experiments. Bottles were prepared prior by detergent and acid leaching and rinsing (0.1% citranox, 10% HCL, pH2 filtered water).

2.2. Shipboard Mn Speciation and Concentrations

Speciation of soluble Mn(II) and Mn(III)-L was carried out using the spectrophotometric competitive ligand assay first described by Madison et al. (2011) and modified for low-level analysis by Oldham, Miller, et al. (2017). In brief, a meso-soluble porphyrin ligand α , β , γ , δ -tetrakis (4-carboxyphenyl) porphine (T(4-CP)P) is added to the sample, complexes Mn(II), and rapidly oxidizes to form Mn(III)-T(4-CP)P in the presence of oxygen. This complex is quantified spectrophotometrically at 468 nm. For complete determination of Mn speciation, a separate sample aliquot is completely reduced to Mn(II) by addition of hydroxylamine and quantified similarly. The difference in these two parallel measurements permits determination of total Mn, Mn(II) and strongly bound Mn(III)-L by difference (Oldham, Miller, et al., 2017).

Filtered samples were analyzed immediately for Mn speciation shipboard using UV/Vis spectrophotometry. One aliquot of sample was amended with 1 μ M hydroxylamine and allowed to react overnight at 4°C before analysis (total dissolved Mn [dMn]). A second aliquot was analyzed immediately; the unreduced fraction represents Mn(II), but as the reaction proceeds for over an hour, it is likely that this fraction also contained some weakly bound Mn(III)-L complexes (Mn(III)-L_w), so our reported Mn(III)-L is a conservative estimate. Samples were added to a solution containing T(4-CP)P, CdCl₂ (which complexes T(4-CP)P, opening its ring structure), and imidazole tetraborate buffer (pH = 8.2) at a 1:12 dilution factor to avoid chloride interference (Madison et al., 2011). The samples were then heated for 60 min in a 90°C hot water bath, cooled to room temperature, then injected by syringe into the spectrophotometric setup. The analytical setup uses a 100 cm liquid waveguide capillary cell (World Precision Instruments) coupled with an Ocean Optics UV/Vis spectrophotometer in which a mini deuterium halogen light source (DT-Mini-2-GS) is coupled with a USB2000+ fiber optic spectrometer, controlled with SpectraSuite software. The Mn(III)-T(4-CP)P complex is measured at its absorbance maximum against appropriate reagent blanks. The detection limit for this method is 0.5 nM.

Filters were amended with 2 mL of 0.0032% leucoberbelin blue dye (LBB, 65% diluted, Sigma-Aldrich) in 1% acetic acid, as in Altman (1972). The dye color, formed upon oxidation by particulate manganese oxide (MnOx), was measured in a 1 cm cuvette, as well as a 100 cm cell at 624 nm using the Ocean Optics spectrophotometric set-up described above. A calibration curve was generated using potassium permanganate (KMnO₄). Calibration values were corrected for the stoichiometric difference for reaction between LBB and permanganate and MnOx. Specifically, 2.5 times more Mn(IV) is required than Mn(VII) to oxidize an equivalent amount of LBB, since Mn(VII) oxidizes 5 LBB molecules compared to 2 LBB molecules for Mn(IV). In a 100-cm pathlength cell, the limit of detection is 2.7 nM (270 nM in a 1 cm cell).

2.3. Synchrotron-Based Solid-Phase Mn Speciation

Frozen filter samples were sliced into strips and 10 strips were stacked and affixed to aluminum holders and sealed with gas impermeable Mylar tape. Manganese K-edge X-ray absorption near edge structure (XANES) spectra were collected on beamline 11-2 at the SSRL using a Si(220) monochromator ($\phi = 90$) and analyzed as described in detail previously (Learman et al., 2011; Santelli et al., 2011). Spectra were collected using a liquid N₂ cryostat to avoid beam-damage or alteration of samples during spectra collection. Fluorescence data were collected with a 100-element Ge solid-state detector array with soller slits and Cr filters. Transmission and fluorescence spectra were collected (three to five scans per sample) from -200 to $+500$ eV around the Mn K-edge (6,539 eV). All XANES spectra were collected with an internal Mn(0) foil standard (6,539.00 eV) to correct the sample spectra energy for any drift and/or fluctuations in the incoming X-rays. Additional checks on the beam stability were conducted by measuring a KMnO₄ standard (6,543.34 eV) in the sample chamber. Data analysis of sample spectra was performed using the SIXPACK software program (Webb, 2005). The absorption edge of the Mn K-edge XANES spectra was used to quantify the average oxidation state in samples by comparing the inflection point of the absorption edge to that of reference standards. The inflection point for Mn(II), Mn(III), Mn(IV) was defined for the three model compounds MnCl₂, MnOOH (feitknechtite), and δ -MnO₂ (average oxidation state ~ 3.9), respectively. Similar results were obtained via linear combination fitting over the data range 6,540–6,600 eV as conducted previously (Bargar et al., 2005; Learman et al., 2011; Santelli et al., 2011; Tang et al., 2013).

2.4. Dissolved Co Speciation

dCo was analyzed by cathodic stripping voltammetry (CSV) using Metrohm 663 VA and μ AutolabIII systems with a hanging mercury drop working electrode using reagent concentrations of 0.77 mM dimethylglyoxime (Sigma Aldrich), 5 mM EPPS (Sigma Aldrich), and 0.225 M sodium nitrite (Merck), as originally described by Saito and Moffett (2001) with later modification (Hawco et al., 2016; Saito et al., 2010). Measurement occurred shipboard within 3 weeks of sample collection. For total dCo analysis, filtered seawater samples were UV-irradiated for one hour (Metrohm 705 UV Digester) prior to CSV analysis to destroy natural ligand-bound cobalt complexes. To measure the concentration of labile dCo, the fraction of dCo not bound by strong organic ligands, no UV-irradiation was performed.

2.5. Shipboard Cobalt Radiotracer Incubation Experiments and Assimilation Rates

The shipboard radiotracer incubation experiments were carried out using acid-washed 250 mL polycarbonate bottles filled with seawater from the trace metal rosette, same as the dCo samples. The incubation bottles were double-bagged and transported in sealed containers from the trace metal van to the radiochemical van for processing. The bottles were placed in a positive-pressure, trace metal environment constructed with a laminar flow hood and plastic sheeting to minimize trace-metal contamination. Each incubation bottle was spiked with a 0.1 pM tracer-level concentration of $^{57}\text{CoCl}_2$. On average, deep water in Antarctic seas has ~ 50 pM total dCo, so this radiotracer spike was at the tracer-level to not inflate measured in situ uptake rates. The bottles were sealed and placed into a flow-through, UV-transparent plexiglass on-deck incubator, with neutral density light screens that shaded the incubator to 20% ambient surface irradiance, and allowed to incubate for 24 h. The samples were then vacuum-filtered onto 0.2 μm pore-size Supor filters and transferred in petri dishes for counting. The biomass captured on the 0.2 μm filter represents the total community (phytoplankton and bacterioplankton biomass) and its associated ^{57}Co assimilation. In this study, we focus on radiotracer uptake rates for CICLOPS station 20, in the Ross Sea, taken 2 weeks prior to our Mn samples. CICLOPS station 22 in Terra Nova Bay was also sampled, these data are presented in the supporting information (Figure S1).

The radiochemical incubation samples were measured on a Canberra Germanium Gamma detector to measure gamma particles emitted from the $^{57}\text{CoCl}_2$ on filtered biomass. Samples were either measured on a detector on board (model GC2518) or on land (model GL2020), until they were below 5% error for surface samples and below 10% error for deeper samples due to their lower counts. The counts per minute at 122 keV (^{57}Co peak) were corrected for decay between sample collection and measurements dates and normalized to a percent uptake per day (accounting for the 0.1 pM of radiotracer added), which was calculated by dividing the activity on each filter by the total activity added to each incubation bottle. The percent Co uptake rate represents the fraction of ^{57}Co radiotracer that was captured on the 0.2 μm filter after the 24-h incubation, normalized to 1 L, indicating uptake into cells. Cobalt uptake rate measurements were made by multiplying the percent uptake per day by the total dissolved Co concentration, representing an upper bound on the in situ uptake rates, following methods in Saito et al. (2010).

3. Results

3.1. Soluble Mn and Water Column Properties

All sites across our 10 station transect have a salinity minimum ($S_p < 34.5$) in the top 50 m of the water column (Figure 2d), presumably due to the melting of sea ice and surface glacial runoff. In the top 100 m of the water column, the fluorescence maximum (Figure 2e)—which is highest between 20 and 40 m depth—coincides with the disappearance of measurable irradiance (PAR becomes nondetectable at 30–50 m, Table S2). Surface salinity (Figure 2b) shows a salinity minimum at stations Mn-2, Mn-5, and Mn-6 ($S_p < 34.2$).

The total dMn in surface waters, which was mostly Mn(III) (Figure 2c, % Mn(III)) has a maximum at the salinity minimum (>90 nM dMn, stations Mn-2, Mn-5 and Mn-6) and a minimum at stations 1 and 7, where surface salinity is higher ($S_p < 34.2$). Looking at the total dMn with depth across our transect (Figure 2f), we see that several stations have a maximum in surface waters (upper 100 m) and a less pronounced maximum in bottom waters (>400 m; dMn ~ 10 –15 nM). In midwaters (100–400 m), dMn is generally >5 nM, with measurements as low as 0.2 nM. In surface waters, where dMn is high, it is mostly in the form of Mn(III)-L (80%–95%; Figure 2g). The dMn is particularly high at the salinity minimum of stations Mn-2, Mn-5, and Mn-6. In the bottom water dMn maximum below 515 m depth, dMn is $<50\%$ Mn(III)-L, mostly reduced as Mn(II). Interestingly, the fluorescence at station Mn-4 exhibits a minimum which corresponds to the highest values of dMn.

Soluble Mn speciation, along with salinity, fluorescence and temperature, was compared at four different sites (Figure 3 and Table S2) (Mn-1) a high salinity, coastal site (Mn-2) a low-salinity site (Mn-8) a shallow off-coast site, and (Mn-9) an “off-transect” site. Each site has a unique Mn speciation profile, albeit with some similarities—namely, relatively high Mn(III)-L concentration in surface water, a subsurface dMn minimum which corresponds to the fluorescence maximum, and a bottom water maximum (except at station Mn-2). At station Mn-1, dissolved Mn ranges from ~ 6 –14 nM, and most of the dMn is Mn(II) (67%–100%). There is a small

Figure 2. Map of study region in the western Ross Sea, including stations Mn-1 to Mn-10, with transect highlighted (a). (b) Surface salinity. (c) Surface Mn(III)-L as percent of total dissolved Mn. (d) Salinity for the Section through the stations outlined in (a). (e) Calibrated fluorescence for the same Section. (f) Total dissolved Mn. (g) Mn(III)-L in nM.

subsurface dMn maximum here, which occurs at the same depth as the fluorescence minimum. Station Mn-2, which is close to station Mn-1 but has lower surface salinity, has much higher dMn (~8–93 nM dMn), and this dMn is almost entirely in the form of Mn(III)-L complexes in the top 30 m of the water column (81%–95% Mn(III)-L). At this site, we do not see the subsurface maximum of dMn that was observed at station Mn-1. Stations Mn-8 and Mn-9 do have small subsurface dMn maxima at the same depth as the fluorescence decreases. At both of these offshore sites, we observe high dMn in bottom waters, mostly as Mn(III)-L, in contrast to stations Mn-1 and Mn-2 where dMn in bottom waters was mostly Mn(II). Another interesting feature is the increase of dMn corresponding to a decrease in fluorescence at stations Mn-1, Mn-8, and Mn-9. Station Mn-2, which has the highest dMn observed in this study (93 nM), also has the lowest fluorescence and salinity in surface waters, which is presumed to reflect the influence of sea ice or glacial ice meltwater

3.2. Sea Ice Mn

The speciation of soluble Mn was examined at an ice station (CICLOPS station 77; 74°51.759'S, 165°45.768'E) including an ice sample, slush sample and surrounding seawater. The dMn is significantly higher in the ice (12.2 nM) than surrounding water (3.0 nM), and mostly in the form of Mn(III)-L complexes (97% in ice; Table 1).

Figure 3. Vertical profiles of soluble Mn (a) and water column parameters (b) are displayed for four Mn stations (shown on map). At station Mn-2 and Mn-9, the speciation of soluble Co is also given (c). Note that the depth axes change for each profile, and that at station Mn-2, the [dMn] axis is also different.

3.3. Particulate Mn

Although a significant fraction of the dissolved Mn measured in the Ross Sea is oxidized in the form of Mn(III)-L complexes, the same cannot be said for the solid-phase Mn ($>0.2 \mu\text{m}$). In fact, XANES spectra for the particles have a peak absorption energy at 6,552.5 eV, which is consistent with more reduced manganese (Figure 4, Table S3). If the particles were composed primarily of oxides, the average oxidation state would be ≥ 3 reflected by a shift in the XANES spectra to higher energies with a peak at $\sim 6,555$ eV. A linear relationship exists between the energy of the inflection point of the absorption edge (i.e., binding energy of the core 1s electron) and the oxidation state (inset Figure 4). By constraining this relationship using known reference standards, the average oxidation state of the particles from three stations (Mn-1, Mn-5, and Mn-9) and terrestrial material collected at McMurdo Station on Ross Island ranges from 2.13 to 2.84 (inset Figure 4, Table S3. Over

Table 1
Dissolved Mn Speciation and Concentrations Taken From Ice Sample at CICLOPS Station 77

Sample	Mn(II) nM	Mn(T) (nM)	% Mn(III)-L	Salinity
Surrounding water	0.6 ± 0.12	3.03 ± 0.2	80.06	34.24
Ice	0.37 ± 0.88	12.17 ± 0.35	96.96	12.02
Melted Ice	0.96 ± 0.64	9.81 ± 0.35	90.17	33.95

Figure 4. Mn K-edge X-ray absorption near edge structure (XANES) spectra of particles in comparison to reference standards for Mn(II) (as MnCl_2), Mn(III) (as feitknechtite, MnOOH) and Mn(IV) (as $\delta\text{-MnO}_2$). The plot shows four representative XANES spectra of particles collected at four depths (20, 40, 60, and 162 m) at station 1 (Mn-1). The dotted vertical lines show the peak absorbance positions for Mn(II), Mn(III), and Mn(IV) illustrating that the spectra for the particles are composed of primarily reduced Mn species. Binding energy of the core 1s electron, defined as the inflection point of the absorption edge, versus oxidation state plotted in the inset show that the average oxidation state of the particles at several depths from stations 1 (Mn-1), 5 (Mn-5), and 9 (Mn-9) and McMurdo soil are less than 3. The inflection point values and corresponding oxidation states as a function of station and depth are tabulated in Table S3.

50 filter samples from all depths were also analyzed for Mn oxides using the LBB method, but Mn concentrations were nondetectable (<0.01 nM).

3.4. Dissolved Co Measurements and Co Uptake

The speciation of dCo from stations Mn-2 and Mn-9 are included in Figure 3, with the labile fraction representing free and weakly bound Co and the total fraction representing all measured dCo, both free and ligand-bound. Dissolved Co concentrations were found to be lowest in surface waters where Co is utilized by phytoplankton as a nutrient (15 pM average) and highest near the seafloor of station Mn-9 (54 pM). Station Mn-2 showed a slight scavenging signal at depth with a loss of only 8 pM dCo over the bottom 600 m, likely due to nepheloid layer scavenging as observed in the North Atlantic (Noble et al., 2017). At all three sites, there is a dCo maximum due to remineralization at ~ 100 m and a small dCo minimum at ~ 200 m, which corresponds to a slight decrease in total dMn at the same stations. Labile dCo was only detected below ~ 100 m, likely because it is quickly consumed at the surface as a nutrient. In general, Co uptake rates were highest in the euphotic zone, corresponding to phytoplankton growth, and decreased at depth.

The uptake of Co was measured using ^{57}Co at CICLOPS station 20, in the Ross Sea (Figure 5, Table S1). This station, even with relatively low fluorescence, had its highest Co uptake rates in the euphotic zone at 0.21 pM day^{-1} with the chlorophyll maximum at 30 m depth, but dropped off to very low rates of $0.015\text{--}0.043$ pM day^{-1} in the subsurface. Total Co for this profile decreases below the fluorescence maximum and increases with depth, the invert of what we would expect for a scavenged profile. We note that at another station within Terra Nova Bay, with particularly high biomass, Co uptake rates were higher in the surface, reaching 2.64 pM day^{-1} (Figure S1), but had similarly low Co uptake rates in the subsurface ranging $0.048\text{--}0.012$ pM day^{-1} at 100 and 400 m, respectively.

4. Discussion

The dominant component of the dissolved Mn pool in this study was Mn(III)-L complexes (up to 100% of total dMn), and concentrations were higher than in previous Ross Sea work (Sedwick et al., 2000). In previous studies examining dMn in the Ross Sea, dMn concentrations were $0.5\text{--}4$ nM (Gerringa et al., 2020; Noble et al., 2013; Sedwick et al., 2000), slightly higher than open ocean concentrations of $0.1\text{--}2$ nM (e.g., Landing & Bruland, 1987). These previous Ross Sea values are significantly lower than the dMn measurements from this study, which range from 0.2 to 94 nM, and average 10 ± 14 nM. This discrepancy may be due in part to the acidification step in previous work, which can miss humic-type Mn(III)-L complexes (Oldham, Miller, et al., 2017; Oldham, Mucci, et al., 2017). In fact, high concentrations of dMn in surface waters is a feature of the dMn profile at all sites (Figure 2), and these surface measurements are predominantly in the form of Mn(III)-L complexes. Photoreduction of Mn oxide phases has long been known to enhance dMn in surface waters (Sunda and Huntsman, 1988, 1994), which certainly plays a role in maintaining Mn in the soluble phase in the austral summer of the Ross Sea. However, most of this surface dMn is in the form of Mn(I-II)-L—an oxidized form of Mn—and yet we do not detect MnOx. Thus, oxidation is occurring in surface waters, but Mn oxides are not being formed or not persisting. As the oxidation of Mn(II) to Mn(IV) occurs via a two-step electron transfer process (Luther, 2005), three possibilities could explain our observations: (1) there is a mechanism for oxidation of Mn(II) to Mn(III) but not Mn(III) to Mn(IV) occurring in surface waters; (2) the rate of Mn oxide photoreduction exceeds the oxidation rate of the Mn(III) to Mn(IV) step but not the Mn(II) to Mn(III) step; and/or (3) the oxidation of Mn(II) to Mn(IV) does not go to completion because the Mn(III)-L complex formed upon oxidation of Mn(II) is too strong to be oxidized and/or is resistant to photoreduction. We expect Mn-organic complexes to form at sites with organic matter in excess of

Figure 5. Vertical profiles of Co uptake measured using ^{57}Co radiotracer incubation experiments, total dissolved Co and fluorescence from CICLOPS station 20.

metal concentration, and so there must be sufficient Mn(III)-complexing ligands in this system to account for high Mn(III)-L. It has been shown that Fe(III) is mostly complexed in the Ross Sea (Gerringa et al., 2019) and since Mn(III) complexes to the same ligands as Fe(III) with similar or greater conditional stability constants (Luther et al., 2015), it follows that Mn(III) should also be mostly complexed.

The high dMn at the surface may suggest that dMn enters this system from sea ice melt and/or dust. Indeed, measurements from our ice station confirm that dMn is elevated in fresh sea ice (12 nM compared to 3 nM in surrounding waters, Table S3). This sampling campaign occurred during the formation of the Ross Sea polynya, and we observed several episodes of ice formation and break-up; therefore, the higher dMn at some stations (e.g., station Mn-2) may correspond to ice processes, but as sea ice distribution changes dramatically on the order of hours in the Ross Sea, this source is difficult to point to definitively. The dMn we measure in sea ice is mostly in the form of Mn(III)-L complexes, the origins of which are currently unknown. There are four potential sources for Mn in sea ice, pack ice in this case: dust deposition, lateral advection, sediment entrainment, and incorporation of complexed metals. Because dust deposition is known to be low in the Southern Ocean (Cassar et al., 2007), it is more likely that sediments or metal incorporation dominate. We do note that although most of the Antarctic Continent is ice-covered, the Dry Valleys, not far from the Ross Sea, could act as a source of dust to these waters and ice (Gao et al., 2013). Most of the open polynya sea ice is first year ice, providing a time constraint on these processes. It has been shown that high dissolved iron (dFe) concentrations in Antarctic Sea (1–2 orders of magnitude higher in ice than in surrounding seawater) can trigger ice-edge phytoplankton blooms (de Jong et al., 2013; DiTullio & Smith, 1997; DiTullio et al., 2000; Grotti et al., 2005; Lannuzel et al., 2007, 2008; Sedwick & DiTullio, 1997; van der Merwe et al., 2009, 2011). Once the ligands are metal-saturated, scavenging onto particles controls the amount of dissolved metals contained in sea ice. This may also be the case for Mn, which forms similar organic complexes to Fe (Luther et al., 2015). Though ice is a possible source, as our ice concentrations are 12 nM and our highest surface measurement is 94 nM, there are likely many sources contributing to high dissolved Mn.

Reduced, soluble Mn(II) dominated the dMn at a few depths at some stations, notably in bottom waters. The high Mn(II) in bottom waters suggests that Mn fluxes from sediments, and that the Mn is composed of Mn(II) and not Mn(III)-L. Indeed, Middag et al. (2013) indicate that the

flux of Mn from the continental margin of the Weddell Sea is twice as high as dust inputs. Furthermore, dMn is highest over the continental margin in the Drake passage (Middag et al., 2012) indicating a strong sedimentary source. The only sediment flux study examining the speciation of dissolved Mn was previously conducted in the St. Lawrence Estuary (Oldham, Miller, et al., 2017), which also showed that only Mn(II) [and not Mn(III)-L] fluxed from the sediments. This may be because Mn(III)-L complexes are used up as oxidants in the sediments and/or that the rates of sediment flux exceed oxidation rates in the top of sediments and overlying waters. The sediments of the western Ross Sea are shallow (average 600 m) compared to the rest of the Southern Ocean, and troughs are dominated by diatomaceous oozes rich in organic matter where anaerobic heterotrophy and subsequent sediment diagenesis is likely fairly active (Smith et al., 2006), supporting a relatively high flux of reduced Mn. Furthermore, the central Ross Sea polynya sediments receive high *Phaeocystis* deposition (Grebmeier et al., 2003) that can trigger sediment diagenesis and subsequent Mn(II) fluxes if Mn(II) is being incorporated by *Phaeocystis*. Wu et al. (2019) indicated that Mn was co-limiting with Fe in *Phaeocystis* from the McMurdo Sound, which suggests Mn may indeed accumulate via

this pathway in the sediments. Uptake of Mn and co-limitation has been observed in the Southern Ocean (Browning et al., 2014; Middag et al., 2011, 2013; Wu et al., 2019), and our data do show lower dMn along the fluorescence maximum (Figure 2). Furthermore, lower concentrations of macronutrients in surface waters (Table S2) indicate that uptake of Mn in the water column corresponds to higher primary productivity at this depth.

We performed bioassay experiments in Terra Nova Bay during January and February 2018 that revealed significant impacts of iron and Vitamin B12 co-limitation on phytoplankton biomass and photosynthetic parameters (DiTullio, unpublished). The phytoplankton community structure at the time was mainly a mixture of diatoms and *Phaeocystis antarctica*. Iron limitation in diatoms has been shown to increase reactive oxygen species that results in a higher cellular requirement for Mn to activate superoxide dismutase (SOD) synthesis to combat oxidative stress (Peers & Price, 2004). Hence, it is possible that Fe-limitation in our study area triggered microbial production of metal binding ligands to increase Mn-L uptake for Mn-SOD synthesis. In a recent study, significant interactive effects of Fe, Mn and B12 were observed on the growth of laboratory populations of *P. antarctica* (Wu et al., 2019). This study observed that the cobalamin dependent enzyme MetH was upregulated under conditions of low Fe and high Mn but not under low Fe and low Mn levels (Wu et al., 2019). Hence, the availability of Mn may play an important, but unresolved, role on Southern Ocean microbial populations that are co-limited by iron and Vitamin B12. This role is influenced by the speciation of Mn, which we find to be unique in the Ross Sea.

Interestingly, we find that the average oxidation state of the Mn-bearing particles collected at three stations within the Ross Sea is < 3 (Figure 4, Table S3). These findings indicate that pMn at these stations is predominantly composed of the reduced species Mn(II), which is likely present in association with biomass, as species (ad)sorbed to other mineral phases, or in the form of a primary mineral (e.g., silicate-bound Mn in dust or glacial flour). Total pMn has previously been measured below the ice in the Ross Sea at concentrations of 0.1–0.3 nM (Noble et al., 2013). Thus, while traditionally it is expected that pMn is predominantly in the form of a Mn(III/IV) oxide below the photic zone, we surprisingly find no evidence for Mn oxide particles in the Ross Sea based on spectroscopic analyses (Figure 4). Further, the LBB dye assay was attempted on over 50 samples from a variety of depths, and at all sites and depths, values were nondetectable even in a 100-cm-long pathlength cell, with a detection limit of 0.01 nM. Based on these lines of evidence, there are negligible concentrations or no Mn oxides in the water column of the Ross Sea.

The majority of Mn oxides in seawater are presumed to form via indirect or direct activity of microbes, particularly bacteria (Hansel et al., 2017; Tebo et al., 2005). Microbial assemblages in the Ross Sea are known to be quite different compared to other oceanic basins. Notably, several phytoplankton functional groups are absent or near-absent in the Ross Sea including coccolithophorids, cyanobacteria, chlorophytes and prochlorophytes (Smith et al., 2006b). The absence of Mn oxide particles may be the result of an absence of specific bacterial assemblages, or low/no activity of Mn-oxidizing enzymes. However, the processes (e.g., extracellular superoxide production) and proteins (e.g., multicopper oxidases) responsible for direct and indirect microbial Mn oxidation are taxonomically widespread and not regulated by Mn (Hansel, 2017). Moreover, Mn(II)-oxidizing bacteria have been isolated from a range of marine environments, including for instance Arctic sediments (Xuezheng et al., 2008) and seamounts (Templeton et al., 2005). In fact, Mn(II)-oxidizing microbes are widespread regardless of nutrient conditions, temperature and Mn concentration. Thus, it is likely that Mn oxidizers are present within the waters but that they are either not oxidizing Mn(II) or the conditions are not conducive to Mn oxide formation.

It is likely that the surrounding biogeochemical conditions do not promote the formation of Mn oxides. This may be a consequence of, for example, slow oxidation kinetics and/or rapid recycling of Mn between Mn(II) and Mn(III)-L, inhibiting the formation of Mn oxides. For instance, temperature is a key factor in the kinetics of the oxidation of Mn(II) to Mn oxides (Tebo & Emerson, 1985) with rates half as fast at 4°C than at 18°C (Lee & Fisher, 1993). Thus, the rate of Mn oxide formation may simply be slower than the residence time. Nonetheless, a two electron transfer is considered in the two aforementioned studies, and yet we do not know the kinetics of the Mn(III) to Mn(IV) electron transfer step and the impact of temperature on Mn(III) oxidation rates is not yet known. Alternatively, reactions between the reactive oxygen species (ROS) superoxide ($O_2^{\cdot -}$) and hydrogen peroxide (H_2O_2) can cycle Mn between Mn(II) and Mn(III). While superoxide oxidizes Mn(II) to Mn(III) (Hansard et al., 2011; Learman et al., 2011), hydrogen peroxide re-

duces some Mn(III)-L complexes, leading to the (re)generation of Mn(II) (Archibald & Fridovich, 1981; Learman et al., 2013). Despite limited data, there is evidence of high rates of H_2O_2 formation within surface waters of Antarctica (Yocis et al., 2000). Furthermore, an important phytoplankton in the Ross Sea is the haptophyte group, dominated by *P. antarctica*, which has been shown to produce high levels of superoxide (Sutherland et al., 2019), which could then dismutate to H_2O_2 or perhaps even oxidize Mn(II) to Mn(III). Interestingly, it has also been shown that *P. antarctica* colonies can concentrate soluble Mn up to 58 times that of the surrounding media (Davidson & Marchant, 1987), which may have implications for the lack of Mn oxide particles but abundant soluble Mn in the Ross Sea and for the life cycle of colonial *P. antarctica*. Thus, another possible explanation for the absence of Mn oxides is that soluble Mn is being taken up faster than it is oxidized to Mn(IV).

Perhaps the most significant implication of undetectable and thus presumably absent Mn oxides in the Ross Sea is the consequent lack of scavenging efficiency in the particulate phase. Manganese oxides are known to be important scavengers of many trace elements (Goldberg et al., 1954), including Co which has been demonstrated to be co-oxidized with Mn (Lee et al., 1994). The absence of Mn oxides here may explain previously anomalous nutrient-type profiles in the Ross Sea for elements like Co (Noble et al., 2013) and to an extent, Fe and other hybrid-type elements (Marsay et al., 2017; Saito et al., 2010). The distribution of these scavenged and hybrid-type elements is thought to be affected by (ad)sorption and oxidation on Mn oxide particles (Lee & Tebo, 1994; Tebo et al., 1984). Previous studies have suggested that low Mn concentrations may be responsible for the lack of scavenging in the Southern Ocean (Fitzwater et al., 2000; Marsay et al., 2017; Noble et al., 2013), but in the Ross Sea we see abundant dMn, yet no Mn oxides. Thus, the absence of Co scavenging could be better attributed to a lack of Mn oxides.

Of the three dCo profiles included here, station Mn-9 and CICLOPS station 20 show no observable scavenging signals and an increase in concentration with depth (Figure 3). In contrast, station Mn-2 displays a slight dCo loss, which may be attributable to deeper nepheloid scavenging processes as seen in the North Atlantic (Figure 3). The labile fractions also have a very similar profile shape to dMn(II). Further, ^{57}Co uptake rates in the Ross Sea were particularly low below 200 m throughout the Ross Sea with average rates of 0.036 pM d^{-1} , almost 20-fold less than surface waters (Figure 5). Comparison of the kinetics for biotic microbial oxidation have shown that Mn oxidation is $\sim 7\text{--}10$ times faster than Co oxidation within productive coastal waters (Moffett & Ho, 1996). As a first approximation, using these rates, if this deep Co uptake is conservatively attributed solely to Mn co-oxidation rather than passive adsorption or sinking phytoplankton or bacterial uptake, then Mn oxidation rates would be $0.25\text{--}0.36 \text{ pM d}^{-1}$, resulting in a Mn residence time of over 90 years when using a deep inventory of 12 nM. These processes are far longer than the annual deep mixing of the Ross Sea and are consistent with prior findings that Co scavenging is limited in the Ross Sea (Noble et al., 2013). The lack of Mn and Co scavenging in this region is unusual and may be due to the stability provided by abundant Mn(III)-L complexes, which in turn may be abundant because of enhanced Mn assimilation and Mn(III)-ligand production by phytoplankton growing under regional iron limitation.

5. Conclusions

The chemical speciation of elements governs their fate and cycling in the ocean because speciation controls the fundamental chemical properties of an element. We show that pMn in the Ross Sea is not in the form of an oxide, but instead is present primarily as Mn(II) likely associated in large part with biomass. This result in turn impacts the profiles of other elements that are atypical in the Ross Sea, notably soluble Co, which does not show evidence of scavenging. The measurements of Mn(III)-L but absence of Mn(III/IV) oxides in the Ross Sea suggest a partial redox cycle for Mn, where Mn(II) is oxidized to Mn(III), but that the oxidation pathways responsible for Mn oxide formation are not occurring here (or at least not occurring rapidly enough). These data provide important insights into the cycling of Mn in the Southern Ocean, as well as the cycling of elements that are controlled by the cycling and speciation of Mn. The Ross Sea may present a unique microbial ecosystem, with low or no bacterial Mn oxidation, warranting future exploration into the ecology of Mn oxidizers in the Ross Sea. As the bioavailability of many trace elements is impacted by scavenging onto Mn oxide particles, the lack of Mn oxide particles observed here has a cascading impact on micronutrient cycling in the Ross Sea and similar systems. These results further highlight that an improved

understanding of the redox cycle of Mn in the Southern Ocean requires better constraints on the rates of Mn oxidation reactions and fluxes from external sources within the region.

Data Availability Statement

This data are publicly available through the Biological and Chemical Oceanography Data Management Office (BCO-DMO) as data set version 2020 (<https://doi.org/10.26008/1912/bco-dmo.850300.1>).

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