April 2024

Iron Isotope Transformations in Saanich Inlet

Claire Onak
University of South Florida

Iron Isotope Transformations in Saanich Inlet

by

Claire Onak

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
College of Marine Science
University of South Florida

Major Professor: Tim M. Conway, Ph.D.
Amelia E. Shevenell, Ph.D.
Jay T. Cullen, Ph.D.

Date of Approval:
March 21, 2024

Keywords: isotopic fractionation, redox chemistry, oxidative precipitation, anoxic basin

DEDICATION

In memory of my father, Douglas. Thank you for your unwavering support, advice, and jokes.

You are in every thought and hope and dream.

ACKNOWLEDGMENTS

I would like to extend my deepest gratitude to the MarMITE lab group: Tim, Zach, Hannah, and Dylan. You have all provided impeccable laboratory training, writing feedback, and camaraderie. My overwhelmingly positive experience in graduate school is in large part due to your assistance and enthusiasm. I would also like to thank my undergraduate advisor at Lake Superior State University, Dr. Derek Wright, for encouraging me to pursue additional research opportunities and a graduate level education.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Iron (Fe) is required for many biogeochemical processes, with Fe bioavailability and chemistry being controlled by redox reactions that transform Fe between oxidation states and dissolved and particulate phases. In oxic seawater, Fe is present in the Fe(III) oxidation state, mainly as Fe oxyhydroxides. Under anoxic marine conditions, such as margin sediments under oxygen minimum zones or restricted basins with anoxic bottom water, Fe(III) is reduced to Fe(II), which is highly soluble and can be present at high concentrations ([Fe]). Fe isotope ratios (δ^{56}Fe relative to IRMM-14) can be used to characterize Fe redox transformations, constrain Fe sources of Fe to the ocean, and understand Fe biogeochemical cycling. In addition, Fe isotopes recorded in Precambrian sediments may aid in tracking the oxygenation of the Earth. A time series of dissolved [Fe] and δ^{56}Fe was measured in Saanich Inlet, a fjord with seasonally restricted bottom water circulation and a redox gradient between oxic and anoxic water which is disrupted during annual renewal events. Results show a consistent δ^{56}Fe of approximately -0.3‰ throughout the water column in the renewal season (Oct- Nov 2016) with layers of remnant older water containing high [Fe] and light δ^{56}Fe. During the rest of the time series (Dec 2017- Apr 2017), a strong stratification develops, separating an oxic, Fe-depleted surface layer ([Fe]= 5-30 nmol kg^{-1}; δ^{56}Fe ≈ -0.3‰) which overlays an anoxic and sulfidic layer with high [Fe] and light δ^{56}Fe ([Fe]= 30-500 nmol kg^{-1}; δ^{56}Fe ≈ -1‰). Below this, a slight increase in δ^{56}Fe with depth may be linked to Fe-sulfide interactions. Stratified profiles show a consistent increase in δ^{56}Fe from anoxic to oxic water, likely corresponding with oxidative precipitation, consistent with a dominance of kinetic effects during

the precipitation of Fe(III) minerals. This work supports the need to consider both kinetic and equilibrium fractionations in order to accurately interpret ‘paleo’ Fe isotope records when considering the early redox evolution of the Earth’s oceans.

CHAPTER ONE: INTRODUCTION

1.1 Fe Abundance, Chemistry, and Importance

Iron (Fe) is one of the most abundant elements on Earth, accounting for approximately one-third of the planet's composition by mass (Morgan & Anders, 1980) and 6% of the crust, where it is the fourth most abundant element (Frey & Reed, 2012). Despite this abundance, dissolved Fe (dFe) is typically present at very low concentrations ([Fe] < 1 nmol kg^{-1}) in the ocean (Landing & Bruland, 1987; Schlitzer, 2021) due to the low solubility of Fe(III) (< 0.1 nmol kg^{-1}) in oxic seawater near pH 8 (Byrne & Kester, 1976; Liu & Millero, 2002), and removal from the water column via biological uptake and scavenging by sinking particles (Johnson et al., 1997). Low [Fe] limit the use of Fe as a vital micronutrient in oceanic surface waters, as it is required for processes such as photosynthesis, respiration, nitrogen fixation, and chlorophyll synthesis (Twining & Baines, 2013; van Noort & Wallace, 1965).

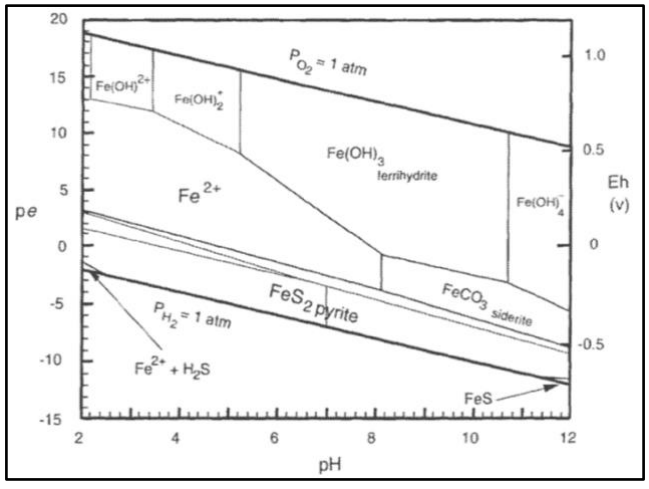

Figure 1. pe/pH stability diagram assuming ferrihydrite as the ferric oxide phase. Redox potential (Eh) and electron activity (pe) on the y-axes express the tendency of a species to be reduced or oxidized. At a given pe and pH (x-axis), the thermodynamiccally stable phase of Fe predominates (Drever, 1997).

Fe chemistry in marine environments is influenced by reduction and oxidation (redox) reactions between reduced (ferrous) Fe^{2+} or Fe(II) and oxidized (ferric) Fe^{3+} or Fe(III) oxidation states, via a gain or loss of electrons. In oxygenated seawater (pH ~8), Fe^{3+} is the thermodynamically stable form (Stumm & Morgan, 1995) and is

hydrolyzed to form insoluble ferric hydroxides ($Fe(OH)_3$) (Fig. 1, pg. 1) (Drever, 1997; Hem & Cropper, 1962). The extent of the complexation of hydrolyzed metals (such as Fe) with hydroxide is strongly dependent on temperature and pH (Byrne et al., 1988). In addition, more than 99% of dFe^{3+} in seawater is thought to be complexed with natural organic ligands (Gledhill & van den Berg, 1994; Rue & Bruland, 1995) which increases the effective Fe(III) solubility near pH 8 (Kuma et al., 1996; Liu & Millero, 2002). However, in waters at low pH (< 5) and under reducing conditions (Eh < 0.3), the more soluble Fe(II) can be present at high concentrations (μ-mM) (Drever, 1997). Fe solubility is related to the different size fractions of Fe in seawater, which are operationally defined by passage through filter pores. These include particulate Fe (pFe > 0.2 μm), dissolved Fe (dFe < 0.2 μm), soluble Fe (sFe <0.02 μm), and colloidal Fe (cFe = dFe – sFe or 0.02 μm < cFe < 0.2 μm) (Fitzsimmons & Boyle, 2014).

Under steady state, Fe residence time (the average length of time Fe remains in a reservoir, e.g., the ocean) is equal to the Fe inventory in the reservoir divided by the flux of Fe into or out of the reservoir (Eq. 1) (Black et al., 2020). Estimates of marine Fe residence times vary from 5 to more than 500 years in different observational studies and model outputs depending on the Fe sources included in calculations of residence time (Tagliabue et al., 2016). Residence time also depends on the speciation and form of dissolved Fe, whether as free ions (Fe^{2+} or Fe^{3+}), organically complexed, or colloidal. The most recent estimates have calculated Fe residence time to between 10 and 100 days for Fe in the upper 250 m of the water column (Black et al., 2020).

$$\tau = \frac{inventory}{inputs\ or\ outputs} \quad (1)$$

In remote regions of the surface ocean (away from sources), the short residence time and low solubility limit of Fe means that [Fe] are often less than 0.1 nmol kg^{-1}, which can limit phytoplankton growth in surface ocean regions otherwise rich in macronutrients (phosphate,

nitrate, and silicate) (Martin & Fitzwater, 1988). These regions are termed high-nutrient low-chlorophyll (HNLC) regions, make up ~30% of the global surface ocean, and are found in the eastern equatorial Pacific, subarctic North Pacific, and the Southern Ocean. (Kohfeld & Ridgwell, 2009; Tyrrell et al., 2005; Watson et al., 2000). Early Fe addition experiments in HNLC areas led John Martin to develop his "Iron Hypothesis", which sought to explain the regular 80-100 ppmv fluctuations in atmospheric carbon dioxide levels (pCO_2) on glacial-interglacial cycles (~100,000 years) through enhanced carbon uptake and export due to a relief of oceanic Fe deficiency in HNLC regions caused by elevated dust supply during glacial periods (Martin, 1990; Sigman & Boyle, 2000). More recently, other processes have been invoked as more important in driving glacial-interglacial shifts in pCO_2 (R. Anderson et al., 2009; Kohfeld & Ridgwell, 2009; Sigman et al., 2010). However, studies still suggest a role for changes in the delivery of Fe-bearing dust in influencing pCO_2 on both glacial and millennial timescales, as evidenced by the correlation between changes in nitrate consumption and fluxes in Fe burial and productivity proxies in marine sediments (Martínez-García et al., 2014; Röthlisberger et al., 2004; Ziegler et al., 2013). Such studies demonstrate the utility of Fe in understanding large-scale changes in the ocean-atmosphere system throughout Earth's history, but this level of understanding was not reached without overcoming obstacles preventing accurate Fe measurement.

1.2 Measurement of Dissolved Fe in Seawater

Given the low [Fe] in seawater and ubiquity on ships and in lab environments, Fe was difficult to measure without contaminating samples prior to the development of clean sampling and analytical techniques in the 1970s, which allowed for the precise and accurate measurements of trace metals in seawater (Bruland et al., 1979; Patterson & Settle, 1976). The 1970s

Geochemical Ocean Sections Study (GEOSECS) was a transformative early effort in the field of chemical oceanography to characterize global marine biogeochemical cycles through study of the distribution of "chemical, isotopic, and radiochemical tracers in the sea" (Broecker & Peng, 1982), but the limitations of the time meant that it was not possible to measure most trace metals accurately (Middag et al., 2023). Additional advances in clean techniques and sample handling led to the first reliable measurements of cadmium (Cd) and zinc (Zn) in the late 1970s, followed by Fe in the 1980s (Boyle et al., 1976; Bruland et al., 1978; Gordon et al., 1982; Landing & Bruland, 1987). These early studies revealed low [Fe] in surface waters (< 0.1 nmol kg^{-1}), greater [Fe] at depth (0.5-1 nmol kg^{-1}), and higher [Fe] in low-oxygen waters (up to 6.6 nmol kg^{-1}) (Landing & Bruland, 1987; Martin, 1990). By 1997, Fe was considered a 'hybrid' type element, with its distribution dominated by surface Fe addition from dust, biological uptake and regeneration, scavenging, and buffering from a 'constant' ligand concentration at depth (K. Johnson et al., 1997; Sedwick et al., 2005).

Early Fe studies greatly transformed our understanding of marine Fe distributions, yet, by the early 2000s, only 25 profiles of dFe were measured to 2,000 m throughout the ocean, leaving many questions on Fe and its biogeochemical cycling unanswered (R. Anderson et al., 2014). More recently, the need to accelerate research on trace metals and paleoceanographic geochemical proxies became evident, leading to the establishment of the international GEOTRACES program, which was inspired by GEOSECS, and had the purpose of quantifying fluxes of trace elements and their isotopes (TEIs) at ocean boundaries and identifying processes that redistribute TEIs throughout the global ocean (R. Anderson et al., 2014). GEOTRACES has led to a large expansion of TEI measurements, which has improved our understanding of the marine Fe cycle, especially the role of external sources of Fe such as sediments (Conway & Middag, In press).

1.3 Fe Sources

One of the main goals of GEOTRACES is to elucidate the fluxes of TEIs at ocean interfaces with the atmosphere, freshwater, continental margins, and midocean ridges (R. Anderson, 2020). The first conceptual and numerical models of controls on [Fe] included the assumption that the main source of Fe to the ocean was the atmospheric transport of Fe-rich, terrigenous dust to surface water (K. Johnson et al., 1997). A large amount of desert dust (and thus Fe in mineral aerosols) originates in North African deserts (Ginoux et al., 2012), and is largely transported to and deposited in the North Atlantic Ocean, but can also reach North and South America and as far north as Scandinavia (Goudie & Middleton, 2001). Dust deposited in the Southern Ocean largely originates in South America and Australia (Albani et al., 2012), and the North Pacific receives Asian mineral dust originating in the deserts of Mongolia, Kazakhstan, and China (Tan et al., 2017). The atmospheric input of Fe mainly originates in the continental crust, but anthropogenic aerosols are increasingly being recognized as important Fe sources and include aerosols generated by fossil fuel and biomass burning and incinerator use (e.g. Luo et al., 2008; Mahowald et al., 2009).

The GEOTRACES program has challenged the paradigm of the atmospheric flux as the dominant Fe source through additional Fe measurements that have improved the characterization of the marine Fe cycle and revealed the transfer of Fe between seawater and interfaces like marine sediments and hydrothermal vents (Tagliabue et al., 2014). Fe(III) oxide minerals in anoxic marine sediments undergo reductive dissolution (RD), producing a flux of dFe(II) that can be transported from sediments to the water column, thereby acting as a source of bioavailable Fe to the ocean (Elrod et al., 2004; Vosteen et al., 2022). Benthic fluxes of dFe show a strong relationship with oxidized organic carbon, and thus, marine sedimentary Fe fluxes are enhanced on highly

productive continental margins (Elrod et al., 2004) and from sediments under oxygen-deficient bottom water (Severmann et al., 2010) as the resuspension of sediments mobilizes both dissolved and colloidal Fe to waters directly above sediments (Homoky et al., 2021). Subsequently, when upwelling water flows over resuspended Fe-rich sediments, Fe-rich water is upwelled to the surface, where it can fuel the high productivity often observed in upwelling systems (K. Johnson et al., 1999). While marine sediments (especially those low in oxygen) were recognized as an importance Fe source in early studies of the Fe cycle (K. Johnson et al., 1999; Landing & Bruland, 1987), it was not until the GEOTRACES era when ocean sections were able to show long distance transport of Fe from sediment margins into the open ocean (Conway & John, 2014; Schlitzer, 2021).

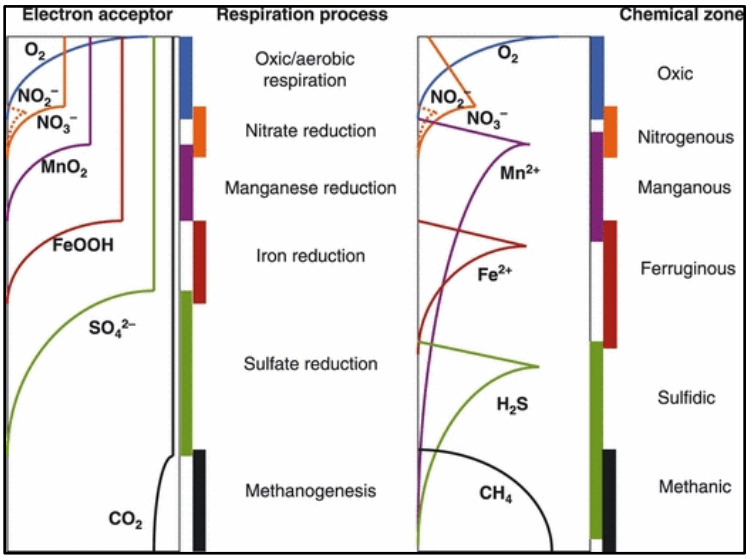

Figure 2. The classic redox sequence of electron acceptors. Left- the depth distribution of electron acceptors and corresponding respiration processes used in sedimentary organic matter oxidation. Right- chemical zones which accompany processes on the left (Canfield and Thamdrup, 2009).

Marine sediments are transformed through diagenesis, which refers to physical and chemical processes that transform marine sediments into sedimentary rock. Changes occurring from the sediment-water interface to depths of a few hundred meters (where sediment pore spaces are continuously filled with water) are considered "early diagenesis", which includes the process of microbial oxidation of organic matter (Berner, 1980). Microbial oxidation of organic matter proceeds through a sequence of coupled redox reactions which utilize oxidants as terminal electron acceptors (Fig. 2) (McKinney &

Conway, 1957). With increasing depth through the sediment column, organic matter (the reductant) is consumed in a specific order of electron acceptors based on the thermodynamics of the processes and the energy yielded to organisms in the order of: aerobic respiration (oxygen = O_2), nitrate (NO_3^-), manganese (Mn), Fe, and sulfate (SO_4^{3-}) reduction, and methanogenesis (Canfield & Thamdrup, 2009; Froelich et al., 1979; Roberts, 2015). Fe reduction during organic matter oxidation can generate large concentrations of dFe(II) (μ-mmol kg^{-1}) in low-oxygen sediments, which can escape to overlying water (especially in oxygen-depleted water) (Severmann et al., 2006; Homoky et al., 2011). The enrichment of reduced and soluble Fe(II) in sediment porewater and bottom water is driven by dissimilatory iron reduction (DIR) by bacteria (or reductive dissolution=RD) (Homoky et al., 2009) which involves the microbial reduction of the Fe(III) minerals buried in sediments below the redox boundary (Reyes et al., 2016). RD is coupled with organic carbon oxidation, and as such, is observed in shallow porewaters in sediments where organic carbon fluxes and oxygen consumption are high (Rapp et al., 2020). While RD is thought to dominate as an Fe production mechanism on shallow shelves where total organic carbon (TOC) accumulation is high and oxygen is low, non-reductive dissolution (NRD, or colloid production from the weathering of lithogenic material) has been suggested to drive sedimentary Fe(III) release in oxic sediments in the deep ocean (Homoky et al., 2021). Horizontal advection from sediments in shelf and slope settings can also provide both dissolved Fe(II), colloidal Fe(III) (Sanial et al., 2018), and particulate Fe (Lam et al., 2018) to the water column. The production of dissolved Fe^{2+} on shelves/slopes, the advection of this Fe(II) through low oxygen regions, and the eventual diffusion upward and precipitation of particulate Fe (which returns to deep sediments) is known as the “shelf to basin shuttle” (e.g., the Black Sea (Severmann et al., 2008)).

TEI exchange also occurs in hydrothermal settings as seawater percolates through the ocean crust along the 60,000 km submarine volcanic mountain range that is the MOR system (Toner et al., 2012). In hydrothermal settings, seawater is heated, becomes buoyant upon exceeding 400°C, rises to the seafloor as vent fluids, and is discharged back into the ocean as hydrothermal 'plumes'. Vent fluids and hydrothermal plumes can be enriched or depleted in certain elements relative to ambient seawater (Holland & Turekian, 2011). For example, [Fe] in vent fluids are typically on the μmol kg^{-1} level (Schmidt et al., 2017), with lower [Fe] of approximately 50-150 nmol kg^{-1} measured in plumes above vent sites (Conway and John, 2014; Jenkins et al., 2020; Wang et al., 2023). Hydrothermal Fe inputs were previously thought to be quantitatively precipitated from vent fluids and deposited on the seafloor soon after being discharged, and thus were considered a negligible source of Fe, but more recent investigations have demonstrated that hydrothermal Fe can travel thousands of kilometers from its vent source (Conway & John, 2014; Fitzsimmons et al., 2014; Resing et al., 2015; Saito et al., 2013). This is the result of the stabilization of hydrothermal Fe by organic ligands, which may sustain a significant flux of Fe to the deep ocean, as described by the Leaky Vent Hypothesis (Fitzsimmons et al., 2016; Toner et al., 2012). Large [dFe] anomalies associated with hydrothermal venting have now been observed in the Atlantic (Conway and John, 2014; Hatta et al., 2015; Saito et al., 2013), Pacific (Boyle et al., 2005; J. Wu et al., 2011; Resing et al., 2015; Fitzsimmons et al., 2014; 2017), Southern (Klunder et al., 2011), Indian (Moffett & German, 2020; Nishioka et al., 2013), and Arctic (Klunder et al., 2012; Rijkenberg et al., 2018), ocean basins, largely as part of GEOTRACES surveys.

Fe can also enter the ocean via riverine inputs. The dissolved products of the continental weathering of silicate rocks enter rivers, and subsequently the ocean, where coastal surface waters can have 3-5 orders of magnitude greater [Fe] (μ-mmol kg^{-1}) compared to the open ocean

(Gaillardet et al., 2013; Krachler et al., 2005; Wetz et al., 2006). However, rivers are thought to only account for around 3% of the Fe delivered to the ocean annually (Raiswell & Canfield, 2012) due to Fe removal in estuaries (Boyle et al., 1974). In estuaries, colloidal Fe oxyhydroxides form as river water mixes with seawater and subsequently coagulate into large particles that settle out of solution in a process known as flocculation. Up to 95% of Fe can be removed from solution in the estuarine mixing zone (Boyle et al., 1977; Nowostawska et al., 2008), therefore, most of the dissolved river input of Fe becomes trapped within estuaries and is not a significant source of bioavailable Fe to the ocean. Exceptions to this include the Congo River, which provides a large offshore Fe flux more than 1,000 km from the river's outflow, which may influence phytoplankton production in the South Atlantic Gyre (Vieira et al., 2020). Similarly, the Amazon River delivers a large quantity of metals in river water, including approximately 34 x 10^6 tons of Fe (Poitrasson et al., 2014), with dissolved [Fe] reaching 25x levels normally present in the western tropical Atlantic (even after flocculation in estuaries) (Subramaniam et al., 2008). Similarly, TEI cycling in the Arctic is strongly influenced by Arctic river inputs (Charette et al., 2020).

Fe can also be released from glaciers, which occurs with loss during downstream transport, likely due to precipitation of Fe oxyhydroxides (Zhang et al., 2015). Additionally, the direct injection of Fe from melting ice as basal melt driven overturning circulation within ice shelf cavities transports deep Fe to the surface, known as the 'meltwater pump' (Dinniman et al., 2020). Recently, the addition of Fe in basal melting has been found to be smaller than previously thought, with much reworking and processing of dissolved Fe within ice-cavities (Tian et al., 2023). Furthermore, icebergs can accumulate dust aerosols or sediments from continental shelves as they drift, which can contribute bioavailable Fe once icebergs are transported to remote polar regions (Raiswell et al., 2006, 2008; K. L. Smith et al., 2007). In some areas, such as Antarctic shelves,

coastal polynyas (areas of open water that would normally be expected to be ice covered) have higher productivity than nearby ice-covered waters (Arrigo & van Dijken, 2003; Arrigo et al., 2008), likely due to continental shelf waters enriched in Fe from sediments (Fitzwater et al., 2000). Fe has also been shown to be transported long distances into the open Southern Ocean from the Antarctic Peninsula and Weddell Seas, where it may influence primary productivity (Sieber et al., 2021).

Undoubtedly, Fe in marine environments originates from a variety of settings and undergoes diverse physical and chemical transformations with transit to and throughout the ocean. Thus, the study of Fe in seawater requires a keen understanding of the differences in Fe chemistry between different Fe sources and sinks, which can be improved through the study of isotopic abundances.

1.4 Stable Fe Isotopes

To distinguish between different Fe sources and better understand Fe biogeochemical cycling, we measure the four stable isotopes of Fe (with respective abundances): ^{54}Fe (5.80%), ^{56}Fe (91.72%), ^{57}Fe (2.20%), and ^{58}Fe (0.28%) which show mass-dependent isotopic variations in nature (Conway et al., 2013; Poitrasson, 2011). Isotopic data are typically reported in "delta notation" as a ratio of the two most abundant Fe isotopes (^{56}Fe and ^{54}Fe) in a sample relative to the same ratio in a standard (IRMM-14), expressed in parts per thousand or per mil (‰) (Eq. 2, pg. 11) (C. Johnson et al., 2020). Most stable Fe isotope literature is reported relative to the IRMM-14 standard, therefore, on the IRMM-14 scale, the δ^{56}Fe value of the average of igneous rocks (which is approximately equal to that of the upper continental crust) is +0.09‰ (Beard et al., 2003; C. Johnson et al., 2020). δ^{56}Fe greater than +0.09‰ is isotopically heavy and contains more of the

heavy isotope (^{56}Fe) than the crust, and $\delta^{56}Fe$ less than +0.09‰ is isotopically light and contains more of the light isotope (^{54}Fe) than the crust (Fitzsimmons & Conway, 2023).

$$\delta^{56}Fe = \left(\frac{^{56}Fe/^{54}Fe_{sample}}{^{56}Fe/^{54}Fe_{IRMM-014}} - 1 \right) \times 1{,}000 \quad (2)$$

Low-temperature geochemical and biological processes are known to drive the fractionation of Fe isotope ratios, with a range of ~8-9‰ (Fig 3;(C. Johnson et al., 2020; Wang et al., 2023)). As with all stable isotope systems, fractionation can be driven by equilibrium or kinetic processes. Equilibrium fractionation involves the redistribution of isotopes among different compounds when a reaction is at equilibrium (the forward and reverse reaction rates are the same), and results in the preferential accumulation of the heavier isotope in the compound with a higher oxidation state (Kendall & Caldwell, 1998). The largest Fe isotope fractionation values are associated with redox reactions between Fe(II) and Fe(III) species. For example, the fractionation associated with the abiotic or bio-mediated oxidation of dFe^{2+} to dFe^{3+} is an equilibrium isotope fractionation, with an Fe isotope fractionation factor ($\Delta^{56}Fe_{product\text{-}reactant} = \delta^{56}Fe_{product} - \delta^{56}Fe_{reactant} = \delta^{56}Fe_{Fe3+} - \delta^{56}Fe_{Fe2+}$) around +3‰, meaning dFe^{2+} is 3‰ lighter than dFe^{3+} in equilibrated solutions at 22°C (C. Johnson et al., 2002; Welch et al., 2003). The magnitude of this fractionation can also depend on the specific Fe(III) mineral formed upon precipitation,

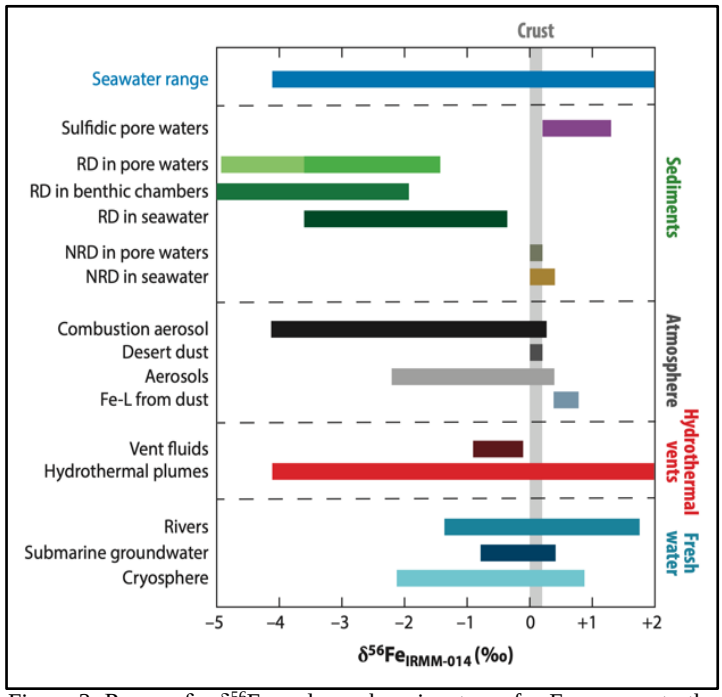

Figure 3. Ranges for $\delta^{56}Fe$ end-member signatures for Fe sources to the ocean (Conway and Fitzsimmons, 2023).

with equilibrium of dFe^{2+} with ferrihydrite being +3‰ at 25°C while goethite is only +1‰, even though both are Fe(III)oxides (Fitzsimmons & Conway, 2023; Wu et al., 2011).

Following equilibrium redox fractionation, Fe isotopic composition can be modified by kinetic effects, which are often associated with fast or unidirectional processes (e.g., precipitation and photosynthesis), and result in light isotopes diffusing faster than heavier isotopes, and thus, products preferentially incorporating the light isotope relative to the reactant (Dauphas et al., 2017; Sharp, 2007). For example, rapid (24 hour) hematite (Fe_2O_3) precipitation from Fe(III) (as $[Fe^{III}(H_2O)_6]^{3+}$ results in a kinetic isotope fractionation of $+1.32\pm0.12$‰, with the precipitate preferentially incorporating light isotopes, whereas longer-term incubation experiments reduce the fractionation between Fe and hematite over time (Skulan et al., 2002). Similarly, a +1‰ fractionation reflecting kinetic isotope effects has been measured during the rapid abiotic oxidation and precipitation of dFe(II) to isotopically heavier ferrihydrite, leaving remnant dFe^{2+} isotopically lighter (Bullen et al., 2001). Additionally, equilibrium and kinetic effects can combine, such as those described by a two-step reaction model (Beard & Johnson, 2004), in which a 3‰ fractionation during Fe(II)-Fe(III) oxidation (Fe(III) is heavier) (Welch et al., 2003) is followed by a 2‰ fractionation associated with a kinetic reaction during precipitation (Fe(III)(s) is lighter) (Skulan et al., 2002), which can produce an overall fractionation of approximately 1‰ (Fe(III)(s) is heavier). This could be due to a series of equilibrium and/or kinetic effects that combine during microbial Fe redox reactions which produce less fractionation than one would expect from a single-step process (Anbar, 2004).

In sediments (or anoxic aqueous systems), redox-driven Fe isotope fractionation is observed when organic matter is oxidized via DIR by microbes using Fe oxides as an electron acceptor during the classic redox sequence (Fig. 2, pg. 6). This occurs as particulate Fe(III) is

reduced to dissolved Fe(II) by microbial activity and released into pore waters (Beard et al., 1999; Homoky et al., 2009; Severmann et al., 2010). This flux is characterized by an isotopically light signature (-3.5 to -1.5‰) driven by equilibrium fractionation, which can subsequently be transferred to both oxic and anoxic bottom water (Hunt et al., 2022; John et al., 2012; Severmann et al., 2006) where it may undergo further fractionation.

Prior to the year 2000, the analysis of Fe isotopes was performed using thermal ionization mass spectrometry (TIMS) (Götz & Heumann, 1988; Walczyk, 1997), however, this method did not produce data with sufficient reproducibility to detect natural mass fractionation (Anbar, 2004; Dixon et al., 1993). Since then, developments in analytical technology, such as the adoption of multiple collector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) to measure Fe isotopic composition, have greatly improved analytical precision (Belshaw et al., 2000). Use of the isotopic 'double spike' technique has yielded even greater precision and provided the first evidence of mass-dependent Fe isotope fractionation in nature (Beard & Johnson, 1999). Since 2007, improved clean sampling and analysis practices and advances in MC-ICP-MS have allowed for increasingly precise and accurate measurements of the isotopic composition of metals in seawater. Modern isotopic analysis now allows for measurement with the precision and accuracy required to resolve oceanic variability (<0.1‰ Conway et al., 2021), providing Fe isotopic composition values with uncertainties in the range of 0.03-0.05‰ (Johnson et al., 2020). A precision of 0.02-0.2‰ can presently be obtained in seawater (depending largely on concentration), as compared to natural variability in the ocean ranging from 1-5‰ (Fig. 3, pg. 11 & Fig. 4, pg. 14) (Conway et al., 2013; Lacan et al., 2010).

These advances allowed for the first seawater measurements of dissolved $\delta^{56}Fe$ in coastal environments (de Jong et al., 2007), followed by the first measurements of dissolved $\delta^{56}Fe$ in the

open ocean (Lacan et al., 2008). Subsequently, improved techniques for Fe chemical separation and purification, a reduced sample volume requirement (John & Adkins, 2010), and better detection limits and blank corrections have allowed for δ^{56}Fe measurement even in Fe depleted HNLC regions, given sufficient volume (~20L; Lacan et al., 2010). Improved measurement of δ^{56}Fe and other metal isotope ratios in seawater is also due to the adoption of ion-exchange resins during sample processing (e.g. Hitachi Nobias PA-1), which bind with transition metals in a sample, and allow for trace metal clean extraction and purification for isotopic analysis with MC-ICP-MS (Conway et al., 2013; Rolison et al., 2018). The improvement in the accuracy of analytical techniques has allowed for an increase in data and publications on trace metal isotope compositions throughout the ocean, as seen in the expansion of Fe isotope measurements, which at the onset of the GEOTRACES field program consisted of just 37 data for dissolved Fe isotopic composition, and 10 years later (2020), increased to 1,718: a 46 fold increase (Conway et al., 2021).

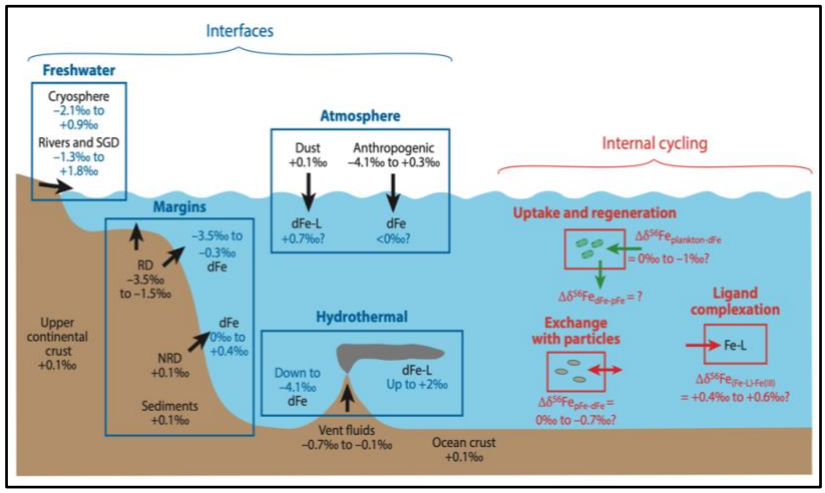

Figure 4. δ^{56}Fe values associated with major interfaces and cycling. Left- δ^{56}Fe for Fe fluxes at the four ocean interfaces. Right- Δ for internal Fe cycling (Fitzsimmons and Conway, 2023).

Each Fe source can be described by a range of δ^{56}Fe values (Fig. 4). Dust Fe tends to share the isotopically homogenous composition of crustal igneous rocks, a δ^{56}Fe value of ca. +0.1‰, which provides a baseline for comparison with other isotopic variations (Beard et al., 2003; Poitrasson, 2006).

RD in sediments produces Fe(II) with δ^{56}Fe values between -3.5 and -1.5‰ which are driven by equilibrium redox fractionation (Fitzsimmons & Conway, 2023). Subsequent oxidation

of Fe(II) has traditionally been assumed to similarly be dominated by equilibrium fractionation, which would drive the remnant dFe even lighter, such as that seen in porewaters and benthic chamber experiments (Severmann et al., 2006, 2010). However, studies in the Black Sea (Rolison et al., 2018), Baltic Sea (Staubwasser et al., 2013), Benguela upwelling system (Hunt et al., 2022), and Californian Margin (John et al., 2012) water columns suggest that kinetic isotope effects during precipitation can instead drive the remnant dFe isotopically heavier. In contrast, NRD produces relatively unfractionated or heavy Fe, as observed in oxygenated sediment porewaters in the open ocean with δ^{56}Fe values of +0.37‰ near Papua New Guinea (Radic et al., 2011), +0.22‰ for pore waters from the Cape margin in South Africa (Homoky et al., 2013), and +0.1‰ for NRD-derived colloids in the South Atlantic (Homoky et al., 2021).

Fe in rivers is more complex, with δ^{56}Fe varying from −1.34‰ to +1.78‰ (Fitzsimmons & Conway, 2023). Arctic rivers have δ^{56}Fe values between -0.1 and +1.6‰ in small, organic-rich rivers (Escoube et al., 2015), whereas values in the Mun River in Thailand range from -1.34 to +0.48‰ (Han et al., 2021), and in the Congo River from +0.07 to +0.33‰ (Hunt et al., 2022).

Hydrothermal δ^{56}Fe values depend on the host rock, with Fe in vent fluids from the ultramafic mantle (approximately -0.23 to -0.12‰) being isotopically heavier than Fe from basalts (-0.7 to -0.25‰) (Nasemann et al., 2018; Rouxel et al., 2008, 2016). As vent fluids mix with seawater in hydrothermal plumes, there is additional isotopic fractionation during Fe sulfide precipitation ($\Delta^{56}Fe_{dFe2+\text{-}FeS}$ = +0.6‰) (Bennett et al., 2009), oxidation ($\Delta^{56}Fe_{dFe3+\text{-}dFe2+}$ = +3.01‰) (Welch et al., 2003), and Fe oxide precipitation, which may leave residual dFe^{2+} as light as -7‰ (Wang et al., 2023).

The characterization of the isotopic composition of the various Fe sources continues to improve our understanding of Fe biogeochemical cycling in the global ocean, however, there have

been relatively fewer efforts to characterize the changes in Fe isotopic composition associated with redox changes. Fe isotope fractionation across aquatic redox boundaries and with temporal redox changes is poorly constrained, therefore, additional inquiry is needed to clarify how $\delta^{56}Fe$ values are affected by a change in redox conditions. Insight gained from such a study would not only improve interpretations of Fe isotope measurements in the modern ocean but may also aid in interpretation of isotopic signatures recorded in the rock record, which may provide a window into the conditions of the Precambrian Ocean.

1.5 Earth's Oxygen Evolution

Before ~2.3 billion years ago (Ga), the Earth's atmosphere and ocean were nearly devoid of oxygen. A shift from anoxic to oxic conditions occurred ca. 2.4-2.1 Ga in a stepwise transition known as the Great Oxidation Event (GOE) (Canfield, 2004; Holland, 2002, 2006; Lyons et al., 2014). Two models propose different timings for this transition: the Cloud-Walker-Kasting-Holland (C-W-K-H) model suggests that oxygen was very low before ca. 2.3 Ga, and the partial pressure of oxygen (pO_2) subsequently increased dramatically between ca. 2.25 and 2.05 Ga, but the Dimroth-Kimberley-Ohmoto model alternatively suggests that atmospheric pO_2 was nearly constant since ca. 4 Ga (Holland, 1999; Ohmoto, 1997). The mechanism through which the atmosphere and ocean became oxygenated has also been debated. A change in the redox state of volcanic gases and/or hydrothermal inputs may have triggered a change in the oxidation state of the atmosphere (Holland, 2002; Kasting et al., 1993). Alternatively (or in addition), Earth's oxygenation may have resulted from the onset of oxygenic photosynthesis with the evolution and radiation of oxygenic cyanobacteria, which is likely occurred ca. 3.7 - 2.2 Ga (Kopp et al., 2005; Rosing & Frei, 2004; Waldbauer et al., 2009). More precise timing of the GOE 2.33 Ga has been

suggested and may have featured rapid oxygenation (within 1-10 million years) as evidenced by sulfur isotopes which indicate that the transition followed a climate perturbation (Luo et al., 2016).

One way to better understand the timing of Earth's oxygenation is by studying banded iron formations (BIFs) which are marine deposits consisting of alternating Fe-rich (Fe oxides) and silica-rich (chert) layers (Katsuta et al., 2012) with a limited occurrence in time (around 3.8-1.8 Ga and 750 Ma) (A. J. B. Smith, 2015). Initial BIF deposition ended ca. 1.8 Ga, which is interpreted to indicate the oxygenation of the deep ocean (Holland, 1999), which would have resulted in the production of Fe^{3+}, which forms insoluble Fe-oxyhydroxides that are unable to form BIFs (Anbar & Knoll, 2002). The molybdenum (Mo) isotopic record also suggests expanded seafloor anoxia in the mid-Proterozoic ocean, which may have persisted after Earth's atmospheric oxygenation during the GOE (Arnold et al., 2004).

Fe isotopes have also been used to determine changes in the marine Fe reservoir and atmospheric oxygen availability over time (Fan et al., 2014; Planavsky et al., 2012; Rouxel et al., 2005). For example, a 1.3‰ fractionation associated with microbial DIR (Beard et al., 1999) and a similar fractionation reported in BIFs (1.25‰) suggested that isotopic variations reflect biogenic DIR and production of Fe^{2+} (Beard & Johnson, 1999). Otherwise, elevated δ^{56}Fe values in the marine sediment record are generally associated with lower Fe(II) oxidation rates in a ferruginous ocean, whereas δ^{56}Fe values near zero are associated with oxic conditions (Fan et al., 2014). These interpretations rely on the use of modern anoxic systems as analogues to the conditions of the ancient ocean and a knowledge of the isotopic fractionations associated with redox processes. Thus, a better understanding of modern processes that cause δ^{56}Fe variations associated with redox transformations would improve interpretation of isotope records in Proterozoic and Archean Fe deposits (Kunzmann et al., 2017). Further inquiry into Fe isotopes in modern anoxic basins that

act as analogues to past ocean conditions may improve our understanding of the evolution of oxygenation and Fe cycling over time, and improve predictions of changes in the Fe cycle in a future ocean that is expected to be increasingly deoxygenated due to inputs of nutrients from agriculture, sewage, and fossil fuel use, and lower oxygen solubility in a warmer ocean (Breitburg et al., 2018).

1.6 Fe Isotopes at Redox Boundaries

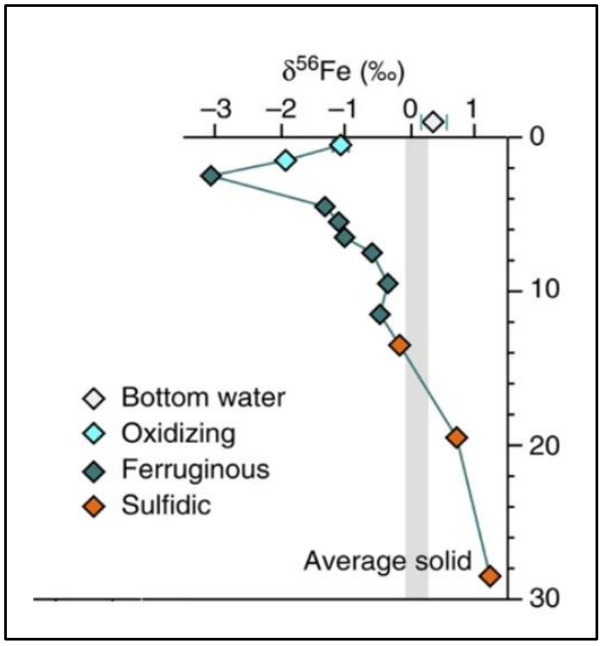

Figure 5. A down-core distribution of $\delta^{56}Fe$ in Cape Margin sediments. Different chemical zones are characterized by unique isotopic signatures, with light Fe associated with Fe(III) reduction (Homoky et al., 2013).

A transition from oxidizing to reducing conditions in sediments or the water column can influence the oxidation state, speciation, concentration, and isotopic composition of redox-sensitive metals (Drever, 1997). In sediment porewaters, $\delta^{56}Fe$ changes are observed across redox boundaries (transitions between oxic and anoxic layers) (Fig. 5), with light Fe produced in the reducing ferruginous zone reflecting equilibrium isotope fractionation during Fe reduction (-1.5 to -2‰; Homoky et al., 2009; Severmann et al., 2006; Severmann et al., 2010). This is consistent with laboratory experiments that demonstrate isotopic fractionation during microbial DIR of ferrihydrite, goethite, and hematite (Fe(III) minerals) which produces Fe(II) that is isotopically lighter by 1-3‰ (Beard et al., 1999; Crosby et al., 2005). As sedimentary Fe(II) diffuses up across the oxic-anoxic interface and oxidizes to Fe(III), $\delta^{56}Fe$ values are driven even lighter (to -3.5 to -5‰) by further fractionation

likely due to Fe(II)-Fe(III) equilibrium effects during oxidation (Homoky et al., 2013; Severmann et al., 2010), leaving the precipitated ferrihydrite 3.2‰ heavier (Wu et al., 2011).

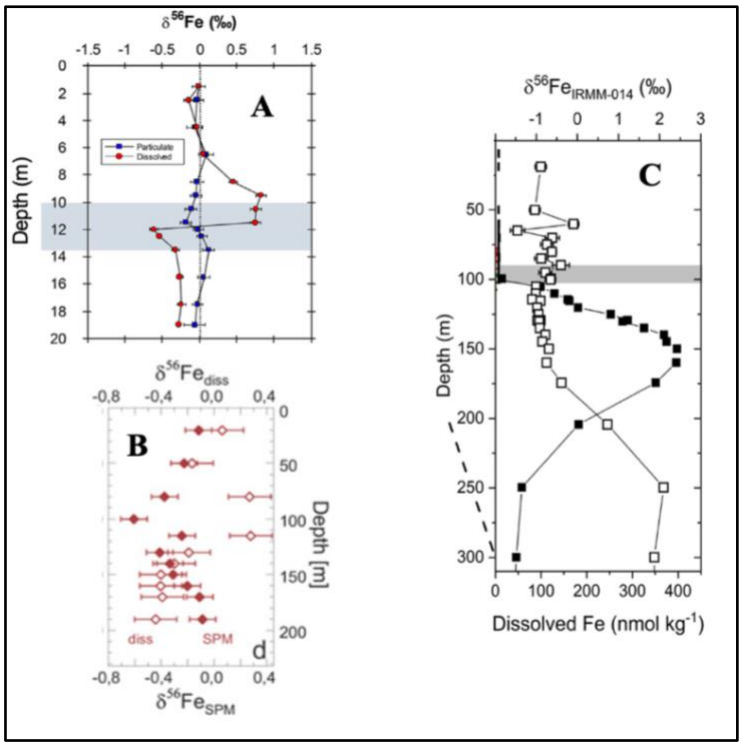

Figure 6. $\delta^{56}Fe$ changes across redox boundaries. A- Lake Cadagno (Ellwood et al., 2019), B- the EGB of the Baltic Sea (Staubwasser et al., 2013), and C- the Black Sea (Rolison et al., 2018).

In anoxic basins and sediments that release Fe(II) via RD and diffusion, such as the San Pedro and Santa Barbara basins on the California margin, a light Fe flux is observed from anoxic sediments ($\delta^{56}Fe$ = -3.5 to -1.8‰) (John et al., 2012). Here, however, as oxygen increases higher in the water column, [Fe] decreases and $\delta^{56}Fe$ become isotopically heavier, a trend that is against expectations for equilibrium-dominated fractionation during oxidative precipitation (John et al., 2012; Staubwasser et al., 2013). Similar $\delta^{56}Fe$ shifts are observed the anoxic Lake Cadagno, the Baltic and Black Seas, and the Benguela upwelling system (Fig. 6) (Ellwood et al., 2019; Hunt et al., 2022; Rolison et al., 2018; Staubwasser et al., 2013). In the redox-stratified freshwater Lake Cadagno, a ca. 1.4‰ increase is coincident with a 10-fold [Fe] decrease from anoxic to oxic water (Fig. 6A) (Ellwood et al., 2019). In the Baltic, the lightest $\delta^{56}Fe$ values are found in anoxic waters (-0.4 to -0.5‰; Fig. 6B), with a 0.7‰ increase to ca. +0.3‰ above the redox boundary (Staubwasser et al., 2013). In the Black Sea, a relatively smaller $\delta^{56}Fe$ increase from ca. -1‰ in anoxic water to ca. -0.7‰ in oxic water is observed (Fig. 6C). The $\delta^{56}Fe$ trends observed in these basins are attributed to a two-step model

of Fe(II)-Fe(III) oxidation followed by the precipitation of Fe(III) minerals as Fe(II) diffuses up from anoxic water, where a kinetic isotope fractionation during Fe precipitation is suspected to dominate the fractionation, leaving remnant dFe(III) isotopically heavier (δ^{56}Fe ca. +0.7 to +1‰) (John et al., 2012; Rolison et al., 2018; Staubwasser et al., 2013). This effect has been observed within an oxic water column, such as in the Benguela upwelling system (Hunt et al., 2022), and at the oxic-anoxic interface, such as in the Baltic (Staubwasser et al., 2013). This value is similar to the -0.8 to -0.9‰ fractionation determined for abiotic oxidative precipitation in lab studies at pH > 5 (Bullen et al., 2001).

Fe oxide precipitation is not the only mineral formation process capable of fractionating Fe isotopes, as δ^{56}Fe changes are also associated with Fe sulfide precipitation. As mentioned previously, the δ^{56}Fe in the Black Sea is ca. -0.7‰ immediately above the redoxcline and decreases to the δ^{56}Fe minimum (ca. -1‰) near the [Fe] maximum (ca. 440 nmol kg^{-1} near 105-150 m) (Fig. 6C, pg. 19). Below the δ^{56}Fe minimum, δ^{56}Fe increases to ca. +2‰ in euxinic deep water, coincident with an order of magnitude [Fe] decrease (Rolison et al., 2018). This shift is also attributed to a kinetic isotope effect during Fe sulfide precipitation as the redox sequence proceeds with depth (Fig. 2, pg. 6), with the use of SO_4^{3-} as an electron acceptor, resulting in the production of H_2S. In the Black Sea, the removal of dFe to isotopically light Fe sulfide particles (FeS_2) was modelled to occur with a fractionation factor between Fe(II) and FeS_2 of +2.75‰, leaving the dissolved Fe isotopically heavy (Rolison et al., 2018). A similar pattern is seen in δ^{56}Fe profiles in sediment porewaters, with a δ^{56}Fe increase from -3 to +1.2‰ in Cape Basin sediments moving downward from ferruginous to sulfidic zones (Fig. 5, pg. 18) (Homoky et al., 2013). Similarly, δ^{56}Fe values in Lac Pavin are light from RD at 60 m and become heavier with depth as [H_2S]

increases, consistent with fractionation associated with Fe sulfide precipitation in euxinic water (Busigny et al., 2014).

Accordingly, there is complexity in interpreting $\delta^{56}Fe$ in both modern and past redox environments, with oxide and sulfide formation likely playing competing roles at different stages of the redox sequence. There is disagreement over the role of equilibrium and kinetic processes (and even the direction of the fractionation) in driving fractionation across redox boundaries. Overall, the isotopic fractionation of specific redox processes and the processes that dominate Fe isotope fractionation in modern redox settings remain poorly quantified and understood, challenging the use of this parameter for interpreting modern Fe biogeochemistry and past ocean conditions. Such inconsistencies inspire further study into how different redox processes and environments fractionate Fe isotopes.

Of special interest is how $\delta^{56}Fe$ values change as conditions shift between oxidizing, reducing, and sulfidic throughout the water column, and over time as the redox environment is transformed, which is the focus of the present study that aimed to better characterize Fe isotopes in a modern, redox-stratified environment. Improved characterization of Fe isotopic composition across redox boundaries will elucidate Fe isotope fractionation associated with Fe redox transformations, and thus improve interpretations of $\delta^{56}Fe$ measurements throughout the ocean. In addition, redox transformations associated with the oxygenation of the Earth may be better understood through additional $\delta^{56}Fe$ investigations, allowing for more accurate interpretation of $\delta^{56}Fe$ signatures preserved in sedimentary rocks. Case studies of modern redox-stratified settings can be used as analogues to the chemistry of the anoxic and Fe-rich Precambrian ocean that likely dominated Earth's history (Poulton & Canfield, 2011). Elucidating Fe redox chemistry may also

help improve predictions of changes in the Fe cycle with redox changes associated with anthropogenic deoxygenation of the ocean.

A case study of Fe isotopes across a redox boundary was carried out in the classically studied Saanich Inlet as part of a time series exercise in which dynamic redox stratification in the inlet's water column allowed for investigation of Fe isotopes across the redox boundary and over time as the redox environment is modified with changes in circulation. There are presently very few detailed case studies of changes in Fe isotope composition across redox transitions in marine environments, and no previous time series studies focusing on changes in isotopic composition with temporal redox changes. This study aimed to fill these knowledge gaps by clarifying mechanisms of Fe isotope fractionation and Fe redox cycling in Saanich Inlet.

1.7 Saanich Inlet

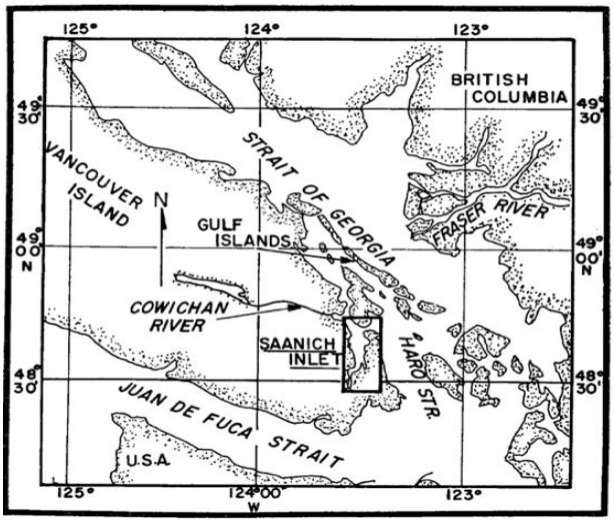

Figure 7. The location of Saanich Inlet within the Salish Sea (Herlinveaux, 1962).

Saanich Inlet is a seasonally stratified fjord on southeastern Vancouver Island in British Columbia, Canada (Fig. 7). The inlet is 24 km long, with a maximum depth of ~240 m. A 75 m depth sill at the mouth of the inlet (Fig. 8C, pg. 23) restricts the circulation of water between the inlet and the Georgia and Haro Strait regions, resulting in the isolation of water below sill depth (Herlinveaux, 1962; Morford et al., 2001). Saanich is unique among British Columbia inlets in that it has negligible freshwater input at the head (a small discharge of ~0.85 m^3/sec from the Goldstream River, Fig. 8B, pg. 23). Most freshwater input to Saanich originates

in the Cowichan River, ~3 miles north of the fjord (maximum discharge in the winter) and the Fraser River on mainland British Columbia, northeast of the mouth of the fjord (maximum discharge in the summer) (Fig. 7, pg. 22) (Herlinveaux, 1962).

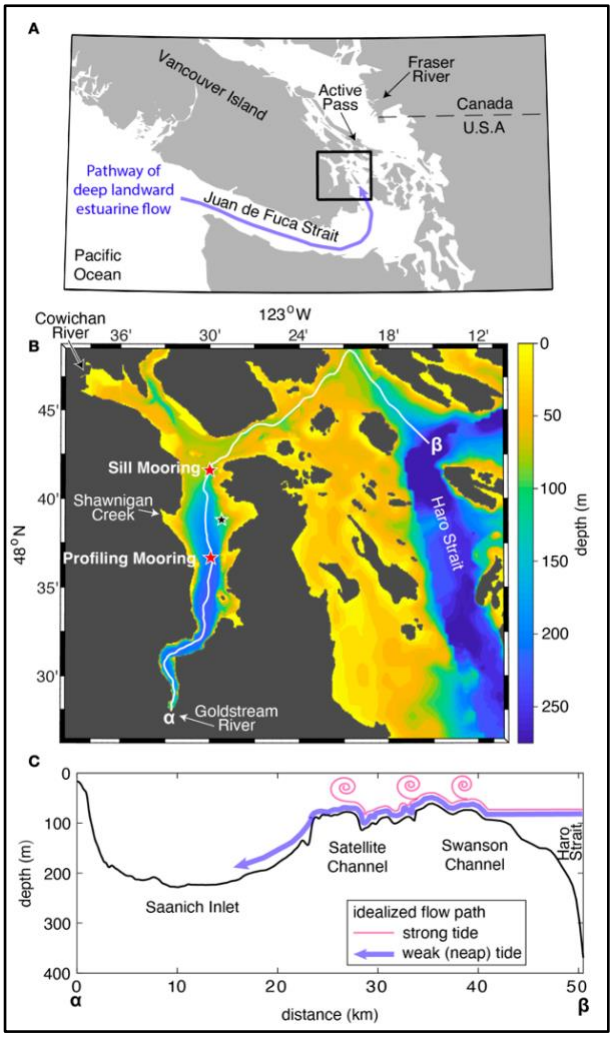

Figure 8. Saanich Inlet geography and renewal mechanism. A- a map of Saanich Inlet (black box) within the Salish Sea, with the landward flow through the Juan de Fuca Strait indicated by the purple line. B- A map of Saanich Inlet and Haro Strait displayed with a colored depth gradient, demonstrating the deeper inlet and strait water (blue) separated by a shallow region (yellow). C- A cross section of the inlet drawn from α to β on the map in Fig. 8B contrasting the two different circulation regimes: a stratified (strong tide) water column, and a water column that experiences renewals (weak tide) (Soetaert et al., 2022).

Saanich circulation is influenced by the broader estuarine circulation in the Salish Sea (encompassing the Haro Strait, the Strait of Georgia, the Strait of Juan de Fuca, and Puget Sound) which is dominated by winter precipitation and summer snowmelt. A deep inflow of dense, oxygen-depleted shelf water into the Juan de Fuca Strait flows over sills in southern Strait of Georgia (typically in the fall), and mixes with the warm, fresh surface plume from the Fraser River (which is larger in summer due to snowmelt), forming an intermediate water mass. This circulation produces a landward transport of dense, salty water in the lower water column, and a seaward transport of fresher surface water in the upper water column (Fig. 8A) (Masson, 2002, 2006; Thomson, 1994; Waldichuk, 1957). The intermediate water mass forms near the San Juan Islands and has a maximum seasonal salinity and density for the region, which gradually displaces deep water in the Georgia/Haro Straits throughout

the spring/summer (J. J. Anderson & Devol, 1973; Waldichuk, 1957). In fall, when freshwater contributions to strait waters are lowest and during periods of low tidal mixing, water in Haro Strait above the sill become more dense than inlet water below the sill, and flows into Saanich, delivers oxygen-rich water, and displaces water initially in the Inlet (Fig. 8C, pg. 23) (Herlinveaux, 1962; Manning et al., 2010; Hamme et al., 2015). These renewal events occur regularly during summer and fall, resulting in more dynamic redox conditions than other anoxic basins, such as the Black and Baltic Seas, which experience oxygenated renewal events once a decade or less (Rolison et al., 2018; Staubwasser et al., 2013).

High Saanich surface productivity results in a high oxygen demand in deeper water due to the microbial respiration of sinking organic matter (Timothy & Soon, 2001). Oxygen consumption through respiration combines with restricted circulation to produce anoxic conditions ($[O_2] < 15$ μmol kg^{-1}) at depths below approximately 100 m, which persist from around December to August of most years until seasonal renewal events displace isolated deep water with dense, oxygenated water in the late summer/early fall (J. J. Anderson & Devol, 1973). After oxygen depletion and the

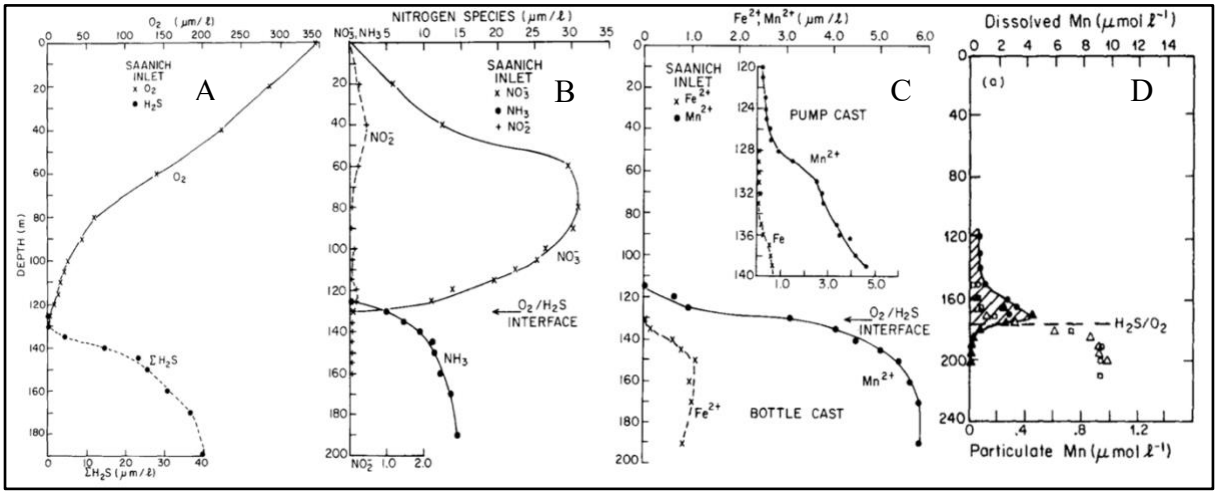

Figure 9. Distribution of electron acceptors in the late 1970s Saanich water column. The classic redox sequence is observed with depth as each oxidant is consumed in organic matter respiration. A- $[O_2]$ decreases from the surface to ~130 m, below which H_2S accumulation begins. B- Nitrogen species distribution showing a $[NO_3]$ peak at mid-depths, with the NH_3 increase beginning below the O_2/H_2S interface. C- Fe^{2+} & Mn^{2+} profiles show increases in anoxic water. D- Particulate (shaded region) and dMn distribution. The Mn-enriched particulate layer lies above the O_2/H_2S interface and is attributed to biologically enhanced oxidation of Mn^{2+} diffusing from anoxic water (Emerson et al., 1979; Jacobs & Emerson, 1982).

onset of anoxia, organic matter oxidation continues through the redox sequence, with the reduction of NO_3^-, Mn, Fe, and SO_4^{3-} resulting in elevated Mn, Fe and H_2S in bottom waters (Fig. 9, pg. 24) (Emerson 1987; Jacobs and Emerson 1982). During the stratified season, oxic water (above ca. 100 m) is separated from sulfidic water by a region displaying a distribution of parameters associated with the classic redox sequence of electron acceptors (Emerson et al., 1979). Saanich Inlet sediments are characterized as jet black in color, anaerobic, laminated, and sulfide-rich, as determined by two cores (1033 and 1034) from the Ocean Discovery Program (Blais-Stevens et al., 2001).

The Saanich Inlet Redox Experiment (SaanDox) aimed to sample the inlet on a fortnightly basis to investigate how transitions between oxic and sulfidic conditions influence various biogeochemical parameters in the Saanich water column through measurements from autonomous sensors at moorings through Ocean Networks Canada (ONC) and a series of cruises to sample the water column, which both occurred at approximately the same location in the central inlet (Fig. 10, pg. 26) (Hamme et al., 2017). The moorings provided high-resolution [O_2] measurements, revealing the occurrence of several renewal events during July-October 2016, followed by a return to stratified water column conditions (Fig. 11, pg. 34) (Soetaert et al., 2022). The SaanDox project helped to better characterize renewal events, revealing a complex layering of water masses produced by intrusions of oxygen-rich water, with different proportions of new, oxic water layered within old, anoxic water as a result of density differences. It was also found that renewal events likely condition the inlet for subsequent renewals (Soetaert et al., 2022). This improved understanding of the renewal mechanism and its influence on Saanich redox conditions, combined with other geochemical measurements from the SaanDox project (e.g., H_2S, NOx, and other

metals) provided a basis for interpreting [Fe] and δ^{56}Fe measurements across the varying redox conditions throughout the time series.

1.8 Purpose of this Study

The dynamic redox conditions in the Saanich Inlet water column provided an excellent location to study redox processes, especially those which affect Fe and its isotopes (e.g., fractionation associated with redox interfaces and oxidation or precipitation). Distributions of redox sensitive trace metals such as Fe and Mn have been previously investigated in the Saanich Inlet water column and sediments (Binqiu et al., 1987; Emerson et al., 1979; German & Elderfield, 1990). Prior to this study, there were no data for redox-sensitive trace element isotope systems in Saanich, with the exception of uranium (Holmden et al., 2015).

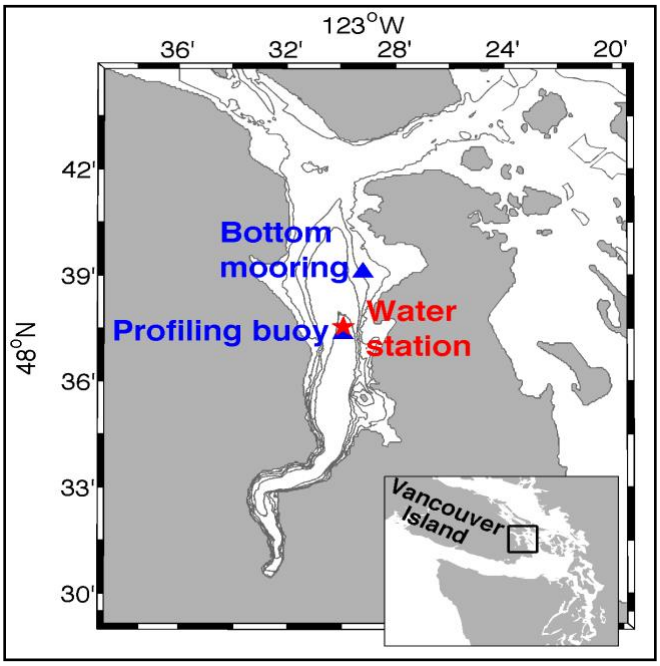

Figure 10. Saanich sampling locations. A map of Saanich Inlet showing the locations of the sampling station (red star) for the SaanDox project CTD casts, and the ONC profiling buoy and bottom mooring (blue triangles) (Hamme et al., 2017).

The SaanDox project, which included the collection of water column profiles for various parameters, provided an ideal sample set to investigate Fe redox cycling. The purpose of this study was to characterize Fe isotope fractionation across the Saanich redox boundary and changes in [Fe] and δ^{56}Fe with renewal events. This allowed for the calculation of fractionation factors across the redox interface and with renewal events. SaanDox cruises provided 13 water column profiles (124 individual samples) for this study, collected biweekly from the central inlet during October 2016- April 2017 (Fig. 10), which included the October renewal event

and the establishment of stable anoxic conditions through the winter. This project sought to answer several research questions:

1. How does δ^{56}Fe change across the redox boundary in Saanich Inlet? What isotopic fractionation factor(s) describe the variability above and below the [Fe] maximum?
2. Which processes (e.g., oxidation, precipitation) dominate Fe isotope fractionation during Fe removal from the dissolved phase?
3. How (and why) does δ^{56}Fe change throughout the water column during renewal events? What fractionation factors describe the change?

This study was proposed with the aim of performing the first Fe isotope measurements in Saanich Inlet in order to clarify fractionation factors associated with oxidative precipitation at redox interfaces and improve the interpretation of the large amount of Fe isotope data published in recent years (Conway et al., 2021). Redox effects on Fe isotope dynamics are generally poorly quantified, challenging the use of Fe isotopes to understand past and modern marine Fe redox cycling. For example, there is disagreement in the literature about the magnitude and direction of fractionation factors upon oxidative loss of Fe in the ocean. This study also aimed to better characterize the redox chemistry of metals in anoxic environments, which may prove useful in the future, as ocean deoxygenation continues to expand (Breitburg et al., 2018), and may elucidate the implications of this expanded anoxia on the Fe cycle and, thus, primary production and carbon sequestration. Lastly, my results may also improve the interpretation of Fe isotopes in the ancient sediment record, as the redox state of the Earth and its ocean transformed over time.

1.9 Hypotheses

Based on preliminary measurements of oxygen, Fe, and H_2S concentrations in the Saanich Inlet water column and previous studies in redox-stratified systems, three hypotheses were proposed to explain how Fe isotopes may be fractionated in the Saanich water column:

H1: $\delta^{56}Fe$ values will be low in low-[O_2], high-[Fe] conditions at depth, where equilibrium fractionation dominates RD from the respiration of sinking organic matter in the water column or in sediments, producing light dFe(II) in, or released to, the water column (Severmann et al., 2006).

H2: $\delta^{56}Fe$ values will increase moving up across the redox boundary as Fe precipitates and kinetic isotopic effects dominate, as seen in the Baltic Sea and the San Pedro Basin (John et al., 2012; Staubwasser et al., 2013); and may also be heavier above the redox boundary due to strong Fe-binding ligands that leave the solution isotopically heavy (Lotfi-Kalahroodi et al., 2021).

H3: $\delta^{56}Fe$ values will increase with transition to euxinic water at depth (when H_2S is elevated), where the loss of Fe from the dissolved phase occurs due to pyrite formation.

CHAPTER TWO: METHODS AND VALIDATION

2.1 Sample Collection (SaanDox)

Seawater samples were collected as part of the Saanich Inlet Redox Experiment (SaanDox) led by Roberta Hamme of the University of Victoria. Samples for [Fe] and $\delta^{56}Fe$ were collected approximately every 10 m from 60- 200 m onboard the R/V John Strickland from the central inlet (48° 37.53'N, 123° 29.91'W (Fig. 10, pg. 26) approximately every two weeks from October 4, 2016, through April 27, 2017. On each cruise, approximately 10 1L samples were collected using a 6-Niskin external closure rosette (Hamme et al., 2017) following trace metal procedures adapted from GEOTRACES protocols (Cutter et al., 2010). Following collection, the samples were filtered using 0.2 μm Pall Acropak capsule filters into acid-cleaned LDPE bottles and acidified shipboard to pH 2 with concentrated ultrapure HCl. The samples were stored acidified for 6 years before analysis, and thus all metals remained dissolved before processing. 13 profiles including 124 1L samples were available for dissolved [Fe] and $\delta^{56}Fe$ analysis at the University of South Florida. Supporting data for salinity, temperature, conductivity, depth, H_2S, nutrients, etc., were available to aid in interpretation of Fe measurements.

2.2 Sample Processing (USF)

Sample processing was carried out in an ISO 6 (Class ~10,000) clean laboratory in an ISO-5 filtered laminar flow bench using trace-metal clean techniques, including the wearing of clean suits, sleeves, hats, and vinyl and polyethylene gloves to reduce metal contamination from

handling. All water used in sample processing was 18.2 Ω-cm (ultrapure; UPW; Milli-Q) from a Barnstead Genpure System, and all reagents were ultrapure grade or double-distilled from trace metal grade using Savillex stills. Plastic bottles and beakers used were LDPE or PFA Teflon cleaned using trace-metal procedures by soaking in 1% Citrad detergent overnight and room temperature HCl for one week (LDPE) or hot nitric acid (HNO_3) (PFA) overnight, with extensive rising with UPW between steps (Conway et al., 2013). Procedural blanks were checked and minimized prior to processing. 1 L samples were subsampled for dFe extraction and purification following established methods (Conway et al., 2013; Sieber et al., 2019):

1. A ^{57}Fe–^{58}Fe double-spike was added to samples in a 1:2 sample: spike ratio, based on previous [Fe] measurements (Cullen & Meyer, 2020). (^{57}Fe and ^{58}Fe are used in the double spike because they have the lowest natural abundances of Fe isotopes, which allows for optimal beam intensity (Lacan et al., 2010)).
2. 10 mmol L^{-1} hydrogen peroxide (H_2O_2) was added to oxidize all Fe to Fe(III). Samples were left for at least 24 hours to allow the double-spike to equilibrate with the natural Fe in the sample.
3. Nobias PA-1 chelating resin beads were added to the sample to extract trace metals from seawater, followed by shaking on an orbital shaker table for at least 2 hours.
4. The sample was filtered through a 47 mm PFA Savillex Filter Rig with a 5 μm pore size Nucleopore polycarbonate filter to collect the resin and trace metals bound to it.
5. Metals were eluted from the resin using 3M HNO_3.
6. Samples were dried down at 180°C, refluxed with concentrated HNO_3 and 10 mmol L^{-1} H_2O_2 to dissolve organics, and dried down again.

7. Samples were taken up in 200 μL 7M HCL + 0.001 H_2O_2 and added to 20 μL PTFE micro-columns filled with AG-MP1 resin for purification by anion exchange chromatography.
8. Major cations, Cr, Cu, and Ni were eluted with 7M HCl + 0.001 H_2O_2.
9. Fe was eluted with 1M HCl.
10. Samples were dried down and redissolved in 1 mL 2% HNO_3 for MC-ICPMS analysis.

2.3 Fe Isotope Analysis (USF)

Fe isotope analyses were performed on a Thermo Neptune MC-ICP-MS in the Tampa Bay Plasma Facility at the University of South Florida. Samples were introduced using a Teflon® PFA (perfluoro alkoxy) nebulizer with a flow rate of ~100 μL/min via an ESI Apex-Omega desolvator, with a Pt Jet Sampler and Al skimmer cone (Hunt et al., 2022). The ^{57}Fe–^{58}Fe double-spike technique was used to correct for instrumental mass bias (Siebert et al., 2001). [Fe] were calculated using isotope dilution, the amount of spike added, and the weight of the seawater aliquot. Samples were typically analyzed in groups of 5, bracketed by IRMM-14 double-spike mixtures, with δ^{56}Fe values expressed relative to the average of these zero-standard mixtures. The procedural blank for my work was assessed at 0.96$\pm$0.14 ng Fe (n=5), which corresponded to less than 2% of sample concentrations. Accuracy and precision of seawater δ^{56}Fe measurements were assessed through long-term repeat measurements of an Fe reference solution (NIST 3126a) which is measured once with each group of 5 samples. The long-term mean δ^{56}Fe and 2SD for the NIST-3126a standards is +0.36$\pm$0.06‰ (n=524; runs=37) (Hunt et al., 2022), with the δ^{56}Fe consistent with other published measurements (Conway et al., 2013). As such, a conservative estimate of external precision on δ^{56}Fe at USF is typically considered to be 0.06‰, and error on [Fe] is considered to be 2% (Conway et al., 2013). For samples where the internal 2SE of analysis is greater than the

external precision of 0.06‰, the 2SE is taken to be a better representation of uncertainty and is used in figures.

2.4 Method Validation

While using long term statistics of a secondary pure standard solution provides an estimate of external precision, the most robust approach for assessing full external precision is to carry out multiple (ideally >30) full extractions and analyses of each sample. Typically, however, the low dissolved [Fe] in seawater (and thus large volume requirements) preclude multiple analyses. In the case of anoxic (and Fe-rich) water, such as the deep Saanich Inlet, however, just ~5-10 mL of sample is needed for analysis, and so a 1 L sample permits multiple analyses.

Accordingly, I assessed the precision and accuracy of the method by carrying out repeated (30-40x per sample) extractions and measurements of a 160 m sample from Saanich Inlet (collected on 15 March 2017) chosen to reflect stable anoxic bottom water, and a 150 m anoxic Black Sea reference sample (obtained from a 2013 Dutch-led Intercalibration exercise) for which [Fe] and δ^{56}Fe values were previously determined (Rolison et al., 2018). Both samples allowed the precision of the method to be established, while comparison of the [Fe] and δ^{56}Fe values obtained for the Black Sea sample with values from other labs provide evidence of accuracy. (The full replicate results of these analyses are in Table 1, pg. 33).

The mean δ^{56}Fe ($\pm$ 2SD) values obtained for the Black Sea reference material and the Saanich 160 m sample in this study were -0.80$\pm$0.06‰ and -0.80$\pm$0.07‰ respectively (with n=40 for both). The 2SD of these samples (+0.06 and +0.07‰) are effectively equivalent to that of the long term NIST standard (+0.06), supporting the use of that as a good estimate of external precision. The mean value of -0.80‰ obtained for the Black Sea reference sample agrees with

previous measurements of -0.79±0.03‰ (Rolison et al., 2018), -0.82±0.03‰ (Wang et al., 2023), and -0.80±0.05‰ (Conway and John, pers. comm.), demonstrating the accuracy of my dataset. For [Fe] (n=30; the first 10 replicates are not included in both cases due to a poorly calibrated pipette leading to less accurate concentrations), both samples had a 1SD of ~2% (equivalent to stated precision in (Conway et al., 2013)) with the Saanich [Fe] = 262 nmol kg^{-1} and the Black Sea [Fe] = 359 nmol kg^{-1} (comparable (within 4-10%) of previous measurements of 330, 381 and 375 nmol kg^{-1} in previous studies cited above).

Table 1. Results of the Black Sea Fe GEOTRACES intercomparison exercise. Replicate analyses allowed for the assessment of precision and accuracy of methods used in this study.

	δ^{56}Fe (‰)	2SD	[Fe] (nmol kg^{-1})	n
This study	-0.80	0.06	359	40 (30 for [Fe])
Rolison et al., 2018	-0.79	0.03	375	6
Wang et al., 2023	-0.82	0.04	382	1
T. Conway, pers. comm.	-0.80	0.05	375	2

CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Oxygen, Nitrate, Manganese, and Hydrogen Sulfide in Saanich Inlet

CTD casts conducted at 48° 37.53'N, 123° 29.91'W (Fig. 10, pg. 26) as part of the SaanDox project provided concentration measurements for oxygen ([O_2]: data processed by J. Sorensen, R. Hamme, and J. Klymak), nitrate ([NO_3^-]: analyzed in the Varela lab at the University of Victoria by K. Giesbrecht and S. Wyatt), and hydrogen sulfide ([H_2S]: analyzed by E. Raftery). These data are used in figures and interpretations. At the time of writing, [Mn] data are not available for the time series.

In winter and spring, water in the central inlet was stratified and anoxic ([O_2] < 15 µmol kg^{-1}) below ca. 100 m. Four renewal events occurred during summer and fall of 2016, indicated by elevated [O_2] below 100 m (July, August, September, and October; Fig. 11) (Soetaert et al., 2022).

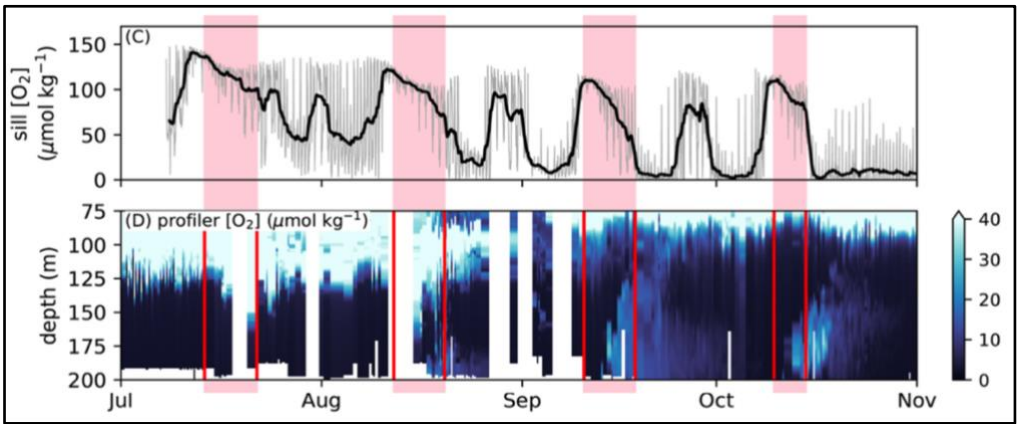

Figure 11. [O_2] changes during the renewal season. [O_2] at the sill mooring (Top) and the profiling mooring (bottom) demonstrate the timing of the four summer and fall 2016 renewal events (Soetaert et al., 2022).

The July renewal increased [O_2] above 150 m from ca. 5 to 25 µmol kg^{-1}, with the water column below remaining anoxic. In the September renewal, oxygen-rich water initially arrived

near 130 m during 9-12 Sept, then around 160 m during 13-15 Sept (Soetaert et al., 2022). Following this renewal period, water became cooler and less oxygenated, suggesting lateral mixing with older, anoxic water (Hamme et al., 2015; Soetaert et al., 2022). The October renewal first experiences elevated oxygen below ~130 m on 11 Oct, followed by changes above 130 m by 18 Oct, with water below decreasing in oxygen, again likely due to lateral mixing with older, anoxic water (Soetaert et al., 2022). From early November on, anoxia is assumed to persist at depths greater than ca. 100 m.

3.2 Overview of [Fe] and δ^{56}Fe in Saanich Inlet

Consistent with earlier studies of Saanich (Emerson et al., 1979; Jacobs & Emerson, 1982) (Fig. 9, pg. 24) the majority of the time series shows an oxygen stratified water column with a mostly consistent pattern over time for [NO_3], [H_2S], [Fe] (and δ^{56}Fe) with descent through the water column (Figs. 13-16, pgs. 38-43; Table 2, pg. 61). This pattern corresponds to the classic redox sequence seen in sediments and the Black Sea, in which anoxic conditions below the oxic zone are associated with the progression of biological respiration pathways in the order of the reduction of NO_3^-, Mn, Fe, and SO_4^{3-}, with the full progression of these pathways encompassing the redoxcline (Canfield & Thamdrup, 2009; Lewis & Landing, 1991; Rolison et al., 2018). Eventually, this sequence reaches methanogenesis, which occurs in Saanich surface sediments (Whiticar & Elvert, 2001). For this study, the top of the Saanich redoxcline is defined as beginning at the lowest point in the water column with appreciable [O_2] (> ca. 15 μmol kg^{-1}) around 75-100 m and extending to just below the depth of the first abrupt [H_2S] increase or [Fe] maximum around 130 m. Anoxic water is defined as the first depth where [O_2] < 15 μmol kg^{-1}. The pronounced redoxcline is absent in fall profiles, which are influenced by renewal events, but as winter

progresses the oxic-anoxic interface and the redoxcline increase in depth through the time series (Figs. 13-16, pgs. 38-43).

Throughout the time series, [Fe] vary between ca. 4 and 530 nmol kg^{-1} and $\delta^{56}Fe$ vary between ca. -1.2 and +0.7‰. In oxic water, [Fe] are low (< ca. 20 nmol kg^{-1}), and $\delta^{56}Fe$ are typically ca. -0.3‰. In anoxic water, [Fe] are high (> 200 nmol kg^{-1}) and isotopically lighter $\delta^{56}Fe$ (ca. -1‰). In the winter and spring stratified profiles (15 Dec- 27 Apr), $\delta^{56}Fe$ become slightly heavier in the sulfidic region (> ca. 5 nmol kg^{-1}) below the [Fe] maxima. The stratified water column provides the opportunity to investigate Fe isotope fractionation across a stable redoxcline, and the renewal season water column provides the opportunity to see how this changes with the addition of oxic water. To further investigate changes in Fe redox cycling across the redoxcline and with renewal events, [O_2], [NO_3], [H_2S], [Fe], and $\delta^{56}Fe$ depth profiles can be grouped together based on general trends of their distributions (Figs. 13-16). I begin with a description of profiles during the October renewal event (Section 3.3), followed by the November post-renewal profiles (Section 3.4), and finally the stratified water column that is established in winter through spring (15 Dec- 27 Apr) and subdivided by the oxic-anoxic interface (Sections 3.5-3.6).

3.3 October 2016 Renewal Event

Summer and fall of 2016 experienced four renewal events (July, August, September, and October), as observed in autonomous observations from ONC moorings located in the central inlet, which provided measurements of salinity, temperature, conductivity, pressure, and oxygen, reproduced from (Soetaert et al., 2022) (Fig. 12, pg. 37). While this mooring time series characterizes the full summer and fall 2016 renewal season with multiple renewal events, the first

SaanDox Fe profile was collected on 4 Oct 2016, and so only the effects of the October renewal on Fe and $\delta^{56}Fe$ can be considered in detail in this study.

Following the 9-18 Sept renewal and a return to pre-renewal conditions (Soetaert et al., 2022), the 4 Oct water column is O_2 stratified (Fig. 12 & Fig. 13, pg. 38), with the oxic-anoxic boundary at 100 m. [NO_3^-] in the oxic layer is ca. 20 µmol L^{-1}, decreases through the redoxcline, and increases to ~12 µmol L^{-1} at 160 m. [H_2S] is <1 µmol L^{-1} throughout the water column. [Fe] was less than 8 nmol kg^{-1}, with an isolated area of high [Fe] at 130 m (113.62 nmol kg^{-1}). $\delta^{56}Fe$ varied slightly between -0.44 and -0.16‰, shifting lighter between 110 and 130 m to -1.05‰ (a 0.6‰ decrease) corresponding with the [Fe] maximum. The distribution of O_2, NO_3^-, and Fe suggest a return to anoxic water at depth following the September renewal from oxygen utilization, but high NO3$^-$ and low Fe suggest that denitrification and Fe reduction had yet to begin. The isolated peaks in H_2S, Fe and $\delta^{56}Fe$ likely indicate a layer of older pre-renewal anoxic water, consistent with previous findings that renewals produces a complex series of interlaying of water masses (Soetaert et al., 2022).

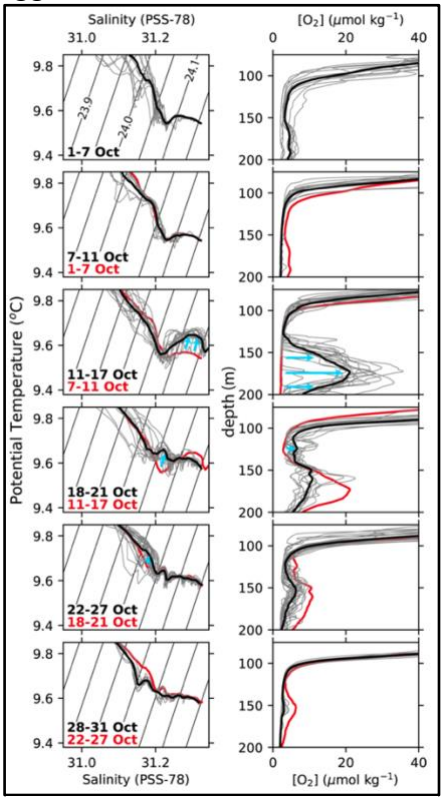

Figure 12. Saanich [O_2] mooring profiles during the October 2016 renewal event. Black lines represent temperature and salinity (left) and [O_2] (right) on date indicated in black font. Red lines represent the previous profile for the sake of comparison (Soetaert et al., 2022).

The October renewal occurred during 11-17 Oct, with the arrival of new water indicated by an increase in [O_2] below 130 m (Fig. 12, pg. 36 & Fig. 13, pg. 38). On 18 Oct, [O_2] at 75 m was greater than the same depth on 4 Oct (77 compared to 23 µmol kg^{-1}). [O_2] then decreased to less than 2 µmol kg^{-1}, below the oxic-anoxic boundary (100 m), and increased between 140 and 170 m (up to ~ 30 µmol kg^{-1}),

demonstrating the lingering effects of the 11 Oct renewal and the start of a return to pre-renewal low O_2 conditions, likely due to lateral mixing with older water (Soetaert et al., 2022). The 18 Oct profile was also characterized by high [NO_3] (26 µmol L^{-1}) in the oxic layer, which decreased (< 9 µmol L^{-1}) below the oxic-anoxic boundary, and increased between 140 and 170 m (up to ~13 µmol L^{-1}) in the oxic layer, which may reflect NO_3^- delivery within renewal waters, or the production of NO_3^- in deeper waters during organic matter respiration.

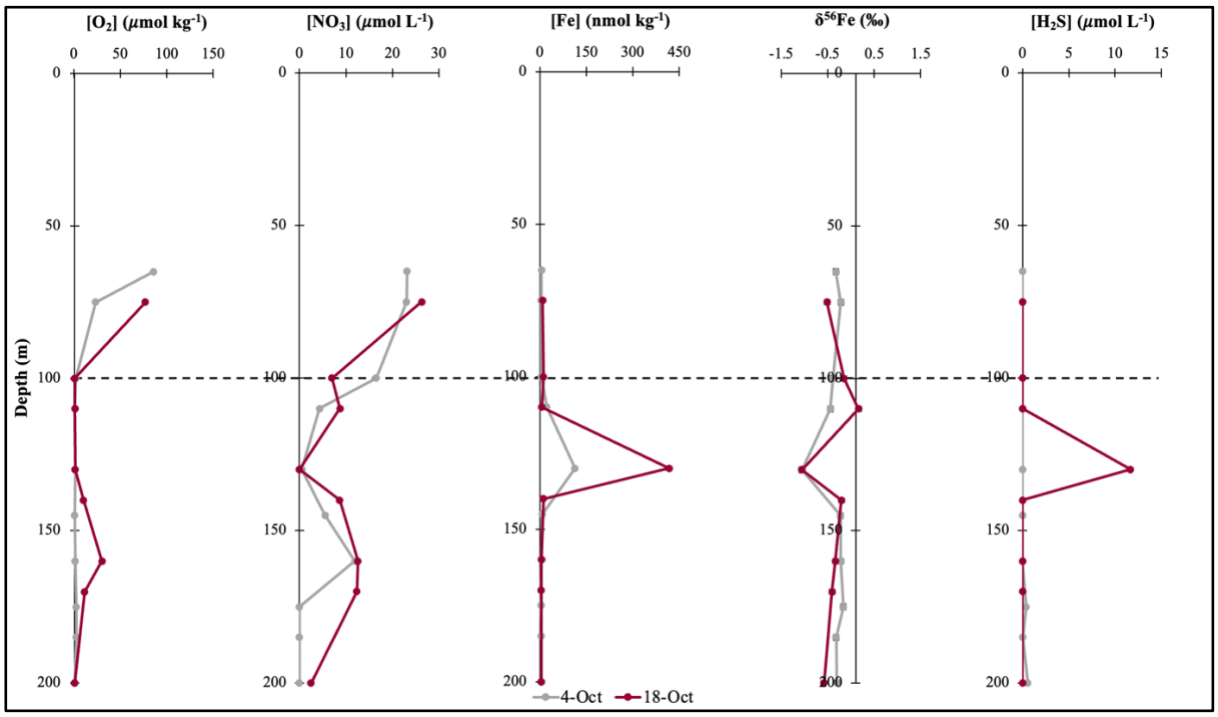

Figure 13. SaanDox time series profiles during the renewal season (4 & 18 Oct 2016). CTD [O_2] (courtesy of Roberta Hamme), [NO_3] (measured by Karina Giesbrecht & Shea Wyatt), and [H_2S] (measured by Erinn Raftery) were previously determined. [Fe] and δ^{56}Fe were determined for this study. Uncertainty on δ^{56}Fe is typically ~0.06‰. The horizontal dashed line separates oxic from anoxic (<15 µmol kg^{-1}) water.

H_2S, Fe, and δ^{56}Fe profiles show a homogeneous distribution throughout the water column, except for an anomaly in each parameter at 130 m for both October profiles (not H_2S on 4 Oct). Throughout the 18 Oct profile, [H_2S] was below the detection limit, [Fe] was less than ca. 12 nmol kg^{-1}, and δ^{56}Fe varied between -0.6 and -0.2‰. At 130 m, however, [H_2S] was ca. 12 µmol L^{-1}, [Fe] was ca. 400 nmol kg^{-1}, and δ^{56}Fe was -1.06‰. Like the 4 Oct profile, this pattern

can be interpreted as reflecting post-renewal conditions when Fe reduction had yet to occur in deep water, with a similar anomaly at 130 m likely reflecting a layer of remnant anoxic water.

By 28-31 Oct, mooring data showed that [O_2] had returned to early October conditions, with a sharp transition between oxic and anoxic waters around 100 m (Fig. 12, pg. 37) (Soetaert et al., 2022). The 4 and 18 Oct profiles can be considered to reflect a water column just before a renewal event and during the renewal recovery period, respectively (Hamme et al., 2015).

3.4 2016 Post-Renewal Water Column

November Saanich profiles reflect a time of transition as the water column recovered from the disruption of renewal events and began to transition back to a reliably stratified water column demonstrating the classic redox sequence. On 1 Nov (Fig. 14, pg. 40), [O_2] in the oxic water column was ca. 97 μmol kg^{-1} and decreased across the oxic-anoxic boundary between 85 and 100 m, below which waters were anoxic ([O_2] < 3 μmol kg^{-1}). [NO_3] was high (> 20 μmol L^{-1}) above the oxic-anoxic boundary, decreased in low oxygen water, and, like October profiles, increased (up to ~10 μmol L^{-1}) between 150 and 160 m. [H_2S] remained less than 0.1 μmol L^{-1} throughout the profile. [Fe] was consistently low (<10 nmol kg^{-1}), with a lack of any clear [Fe] maximum seen in other profiles in the time series. The $\delta^{56}Fe$ was between ca. -0.4 and +0.2‰ throughout the profile, similar to the October profiles, but with a slight mid-depth maximum from 110 to 120 m (+0.18 and +0.15‰, respectively). Again, this profile likely reflects a period of oxygen depletion in deep water, when NO_3^- is still present and Fe(III) reduction (and production of Fe(II)) had yet to occur.

On 15 Nov (Fig. 14, pg. 40), the redoxcline was more developed, with [O_2] ca. 3 μmol kg^{-1} below 75 m (anoxic water by 90 m, which was shallower than on 1 Nov). [NO_3^-] was high (> 20

μmol L^{-1}) above the redoxcline and generally decreased with depth, except for an elevated area (6 μmol L^{-1}) at 160 m, the same depth as the isolated high [NO_3^-] on 1 Nov. This represents a decline in [NO_3^-] at this depth from 1 Nov, suggesting a greater degree of denitrification by this time. [H_2S] was below detection limits, except at 120 and 190 m, where it was 0.14 and 1.05 μmol L^{-1}, respectively. Like the October profiles, [Fe] were less than 10 nmol kg^{-1}, with an [Fe] maximum (16.13 nmol kg^{-1}) at 130 m (the same depth as the October profiles maxima). δ^{56}Fe ranged between -0.55 and +0.70‰, with lightest values at the [Fe] maximum (-0.55 ‰), and a large shift from 120 to 130 m as [Fe] increased (a 1.25‰ decrease), comparable to the shift observed on 18 Oct (a 1.06‰ decrease coincident with a rapid [Fe] increase). Above this (100-110 m), there was a small interval of near-crustal δ^{56}Fe (0 to +0.2‰). Taken together, the November profiles reflect a continuing recovery from renewal events, with any resolvable Fe reduction yet to have occured.

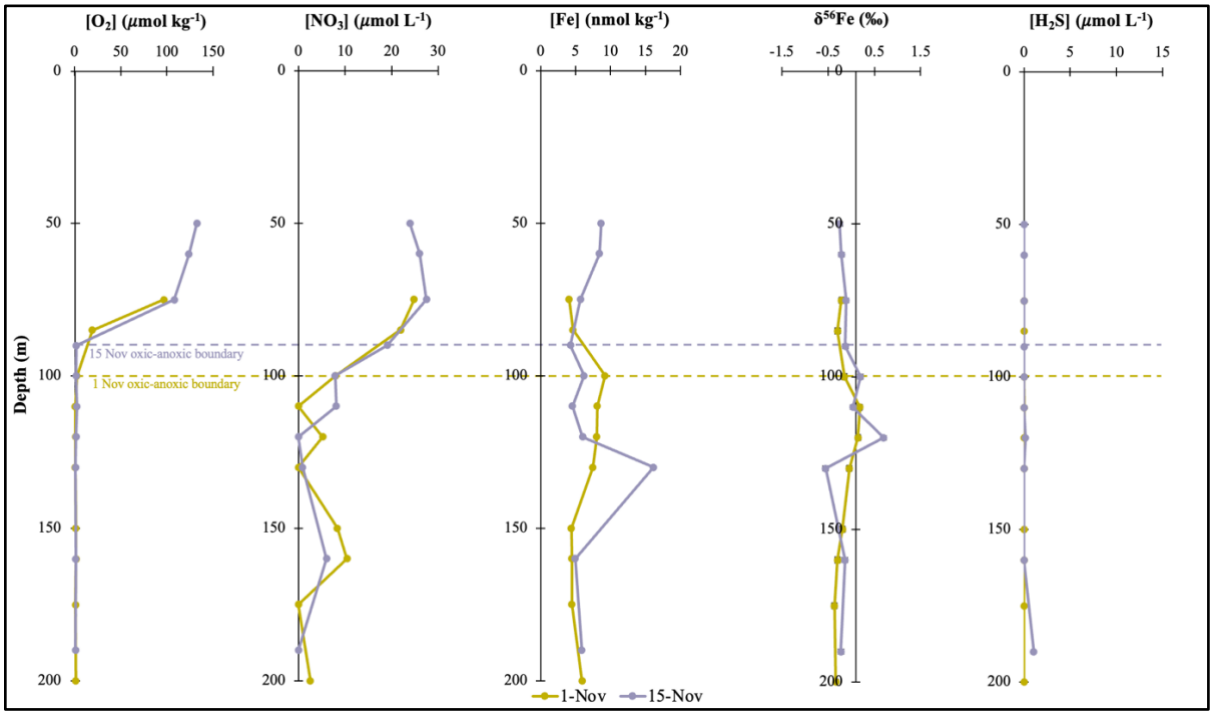

Figure 14. SaanDox time series profiles after the renewal season (1 & 15 Nov 2016). Same as in Fig. 13. The horizontal dashed lines separate oxic from anoxic (<15 μmol kg^{-1}) water, corresponding to the color of each profile.

3.5 2016-17 Winter Stratification

The winter profiles (15 Dec; 4, 17, & 31 Jan) (Fig. 15, pg. 42) were characterized by water column stratification and the restoration of the redox sequence after the renewal season. A clear redoxcline was observed between 75 and 130 m, which deepened over time. The oxic-anoxic boundary for these profiles was between 75 and 100 m, progressively deepening with each subsequent profile. Anoxia was present at 90 m on 15 Nov and 15 Dec, and at 100 m for 31 Jan, with [O_2] consistently less than 6 μmol kg^{-1} below 90-100 m. [NO_3^-] was high (> 11 μmol L^{-1}) above the redoxcline, decreased within the redoxcline, and reached 0 below the redoxcline, indicative of all NO_3^- being consumed in deep water by denitrification by this point. [H_2S] was 0 above the redoxcline and consistently increased at the bottom of the redoxcline below the oxy- and nitri- clines, with elevated levels (ca. 4-10 μmol L^{-1}) around 110 m, with [H_2S] maxima (ca. 10-13 μmol L^{-1}) occurring in the deepest sample (nearest to the sediments for 4 & 17 Jan). [Fe] were low (< 30 nmol kg^{-1}) above the redoxcline, with a consistent [Fe] gradient (ferricline) between ca. 90 and 130 m, which deepened slightly over time, and an [Fe] maxima of 227-371 nmol kg^{-1}. For all four profiles, the [Fe] maximum and $\delta^{56}Fe$ minimum occur at 110 m. The [Fe] increase generally occurs at similar depths as the [H_2S] increase near the bottom of the redoxcline. In all profiles, $\delta^{56}Fe$ decreased from ca. -0.2 to +0.1‰ in surface waters to ca. -1‰ near the [Fe] maxima (100-110 m). 15 Dec and 4 Jan showed a unidirectional transition to light values below 90 m, while in earlier profiles, there was more variability as [Fe] increased and $\delta^{56}Fe$ values just above the interface (80-100 m) gradually became heavier throughout the time series. Below the [Fe] maxima, [Fe] decreased and became slightly heavier (a 0.1-0.2‰ increase) in the deepest waters (below 130 m), a trend observed in all profiles with high [H_2S].

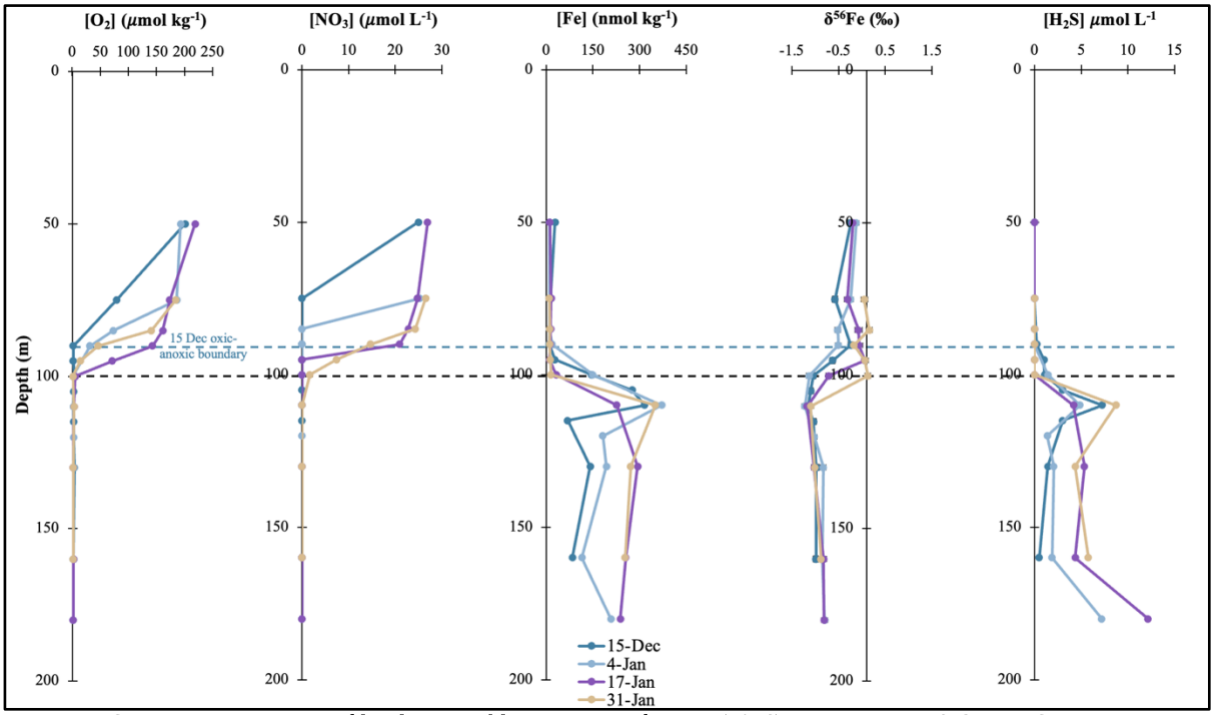

Figure 15. SaanDox time series profiles during stable winter stratification (2016). 15 Dec; 4, 17, & 31 Jan. Same as in Figs. 13 & 14. The blue horizontal dashed line (top) is the oxic-anoxic boundary for 15 Dec. The black horizontal dashed line (bottom) is the oxic-anoxic boundary for the January profiles.

3.6 2017 Spring Stratification

The spring stratified profiles (15 Feb; 1, 15, and 29 Mar; and 27 Apr (Fig. 16, pg. 43) had similar patterns as the winter stratified profiles, with a consistent redoxcline between 100 and 130 m. [O_2] was high (> 200 μmol kg^{-1}) above the redoxcline, decreased similarly between 90 and 105 m, reached anoxic conditions at 105 m, and was consistently less than 3 μmol kg^{-1} below this. Notably, the depth of anoxic waters was slightly deeper in this season than in winter (105 vs 90-100 m). [NO_3] ca. 20 μmol L^{-1} above the redoxcline gradually decreased and reached 0 by 130 m. [H_2S] remained ca. 0 until consistently increasing around 130 m, with concentrations below the redoxcline ranging between 5 and 14 μmol L^{-1}. [Fe] were less than 20 nmol kg^{-1} in oxic waters, increased across the ferricline which was deeper (ca. 100-130 m) than for the winter stratified profiles, and reached [Fe] maxima at 130 m (except for 27 Apr, which reached a maximum [Fe]

for the entire time series at 160 m at 527.4 nmol kg^{-1}). [Fe] then decreased below the maximum for all March profiles (a 4-223 nmol kg^{-1} decrease). $\delta^{56}Fe$ ranged from -0.4 to 0.0‰ in oxic waters, with the heaviest values just above the ferricline. Downwards across the ferricline, $\delta^{56}Fe$ shifts to ca. -1‰ at the [Fe] maxima, below which $\delta^{56}Fe$ becomes slightly heavier (ca. -0.8‰). Like the winter stratified profiles, $\delta^{56}Fe$ varies throughout the oxic-anoxic boundary between relatively heavy and light values before shifting to the $\delta^{56}Fe$ minimum for each profile. On 29 Mar and 27 Apr, the top of the ferricline has an elevated $\delta^{56}Fe$ value (ca. +0.3‰), corresponding with a 1.2-1.5‰ shift across ca. 20 m from the $\delta^{56}Fe$ minimum. Notably, these heavy values were heavier than in the oxic waters above.

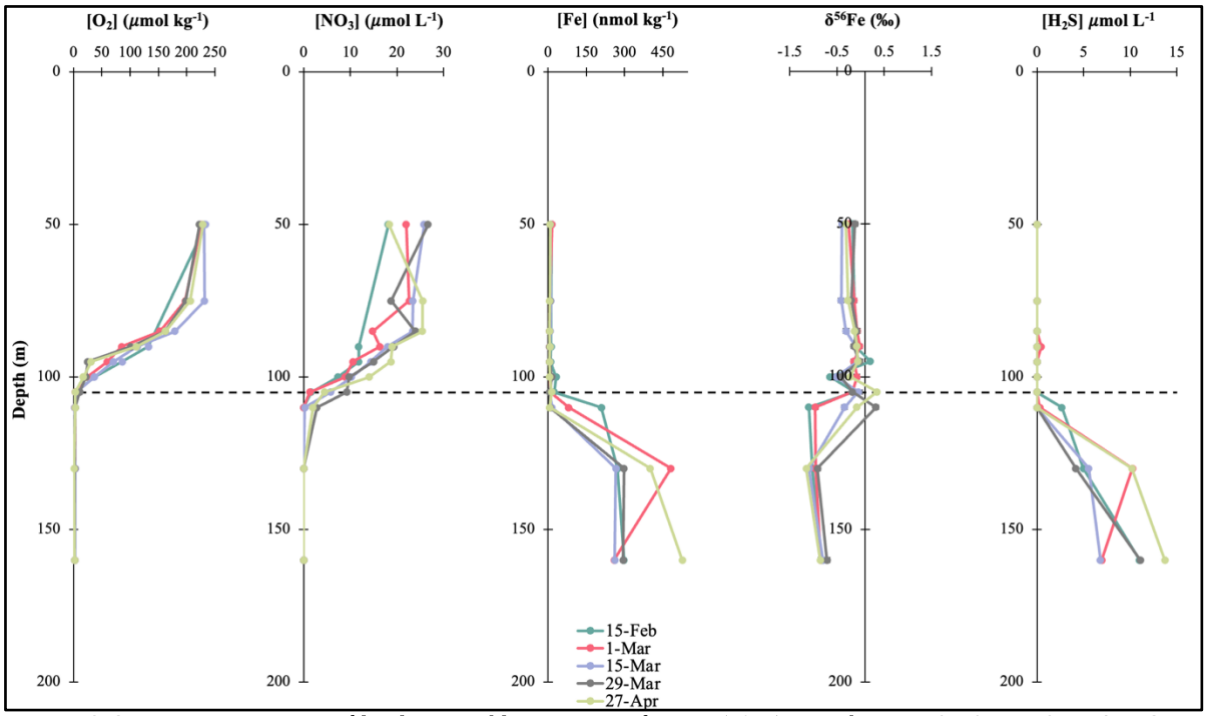

Figure 16. SaanDox time series profiles during stable spring stratification (2017). 15 Feb; 1, 15, & 29 Mar; & 27 Apr. Same as in Figs. 13 - 15. The black horizontal dashed line is the oxic-anoxic boundary.

3.7 SaanDox Data Summary

Overall, the SaanDox time series shows a progression from the renewal season when [Fe] was low (with isolated pockets of old, high [Fe] water), to the gradual re-establishment of anoxic and then euxinic waters, where Fe(III) was used as an electron accepter and dissolved Fe(II) was produced (Fig. 17). By winter, a relatively stable redox sequence is evident, with the oxycline and ferricline both increasing in depth over the course of the winter. The depth of the [Fe] maxima reached in April 2017 corresponds to the depth of the remaining high [Fe] water in the 2016 renewal events. In the following section, I will discuss how these systematic changes in [Fe] and δ^{56}Fe can provide insight into fractionation factors and the processes driving them.

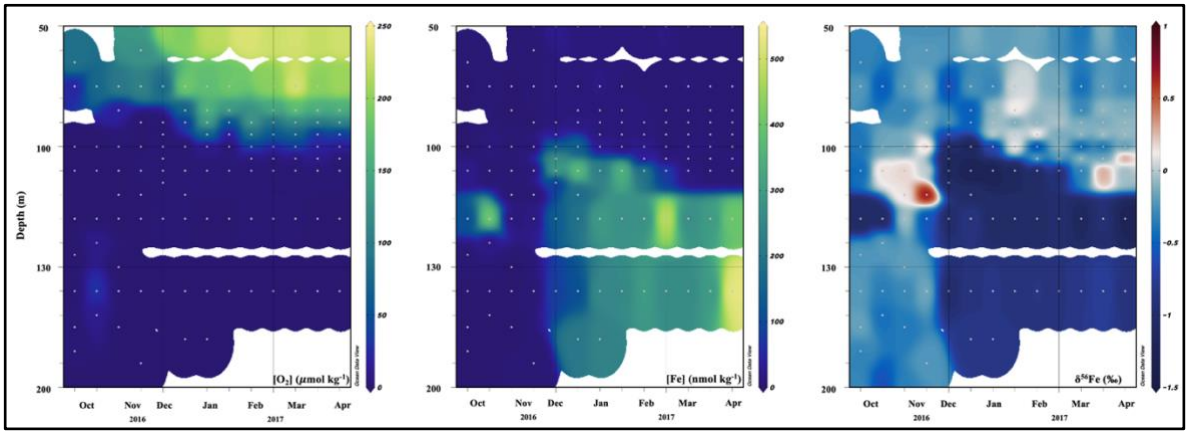

Figure 17. SaanDox time series summary for [O_2], [Fe], & δ^{56}Fe. [Fe] are high (up to 530 nmol kg^{-1}) in anoxic water (< 15 μmol kg^{-1}). δ^{56}Fe were generally lighter in anoxic water. The boundary between oxic, Fe-depleted and ~ -0.3‰ surface water and anoxic bottom water deepened throughout the time series.

3.8 Discussion

The following is a discussion of the extent to which several processes drive variations in [Fe] and δ^{56}Fe profiles in Saanich Inlet. These include Fe redox cycling, Fe sulfide formation, and renewal events. I conclude with an assessment of the utility of my δ^{56}Fe measurements for paleoredox applications.

3.8.1 Fe Isotope Fractionation at the Redoxcline

The $\delta^{56}Fe$ minimum in the each of the stratified Saanich profiles (15 Dec- 27 Apr) (mean -1.10‰, SD 0.10, and range from -1.22 to -0.91‰) typically occurred at or near the [Fe] maximum for a given profile, and was overlain by water with heavier $\delta^{56}Fe$, higher [O_2], and lower [Fe]. This pattern can be investigated first by considering the production of isotopically light $\delta^{56}Fe$ associated with the reduction of Fe(III), followed by fractionation from oxidation that upwards across the redoxcline.

The Saanich water column displayed the idealized distribution of electron acceptors used in organic matter respiration (Millero, 2013). In this scheme, the fjord's highly productive surface water results in a flux of organic matter (the electron donor) which sinks throughout the water column and is decomposed by aerobic respiration in the presence of O_2 (the electron acceptor), which is consumed. Denitrification occurs after aerobic respiration, producing a [NO_3^-] maximum near 80 m, followed by MnO_2 reduction that occurs below the O_2/H_2S interface, as suggested by previous observations of a [dMn] maximum near 180 m (Jacobs & Emerson, 1982). Subsequently, NO_3^- is reduced to NH_4^+, and Fe(III) oxyhydroxides are reduced to dFe(II), which occurs at or very near the O_2/H_2S interface and 10-40 m deeper in the water column than the depth of Mn cycling (Jacobs & Emerson, 1982). Lastly, SO_4^{3-} is used as an electron acceptor, resulting in sulfate reduction and H_2S production, followed by methanogenesis, the latter of which happens in surface sediments (Whiticar & Elvert, 2001).

Microbial DIR of Fe(III) minerals is associated with the production of isotopically light Fe, as seen in anoxic sediment porewaters on the Amazon River shelf region (ca. -1.3‰ (Bergquist & Boyle, 2006)) and the Cape margin (-3 to -0.3‰) (Homoky et al., 2013). DIR is also suggested to produce the ca. -1.2‰ value seen at the oxic-anoxic interface in the Lake Nyos water column

(Teutsch et al., 2009). The production of light Fe is also supported by experimental results which demonstrate DIR of Fe(III) minerals to produce light dFe(II) ($\delta^{56}Fe$ = -3 to -1‰) (Beard et al., 1999; Crosby et al., 2007). DIR and dissolution are often associated with a high supply of organic matter (Lovley, 1991). Thus, given the high supply of organic matter to the fjord's oxic-anoxic interface, and the correspondence with similar sedimentary, water column, and experimental results, I suggest that the $\delta^{56}Fe$ ca. -1‰ in anoxic and Fe-rich water below the oxic-anoxic boundary observed in all 9 stratified profiles is consistent with DIR of sinking Fe(III) minerals and the production of dFe(II) that is isotopically lighter than the initial Fe(III) mineral. Another possibility is a contribution to the Fe maxima from advection of DIR-derived Fe from lateral sediments. However, lateral advection of Fe(II) from sediments is likely limited by the steep sides of the fjord, unlike the stratified Black Sea, which is thought to receive a greater Fe contribution from sediments on a broader continental shelf (Severmann et al., 2008).

Overall, this finding supports Hypothesis 1, which predicted isotopically light Fe production in anoxic water due to the equilibrium fractionation during DIR of sinking organic matter. Previous calculations of redox potential in Saanich indicate that the Fe(III) oxyhydroxide-Fe(II) redox couple approaches or is at equilibrium in anoxic water (Emerson et al., 1979; German & Elderfield, 1990). Between the coexisting reduced and oxidized phases, Fe isotopes are exchanged until the system reaches equilibrium, with fractionation of isotopes between phases dependent on the strength of the Fe bonds (Dauphas et al., 2017; Urey, 1947). Experimental culture studies show a 1.3‰ fractionation with bacterial DIR of ferrihydrite, leaving the dFe(II) product isotopically lighter (Beard et al., 1999). Similarly, bacterial oxidation of Fe(II) to Fe(III) oxyhydroxide results in a 1.5‰ fractionation, with dFe(II) being isotopically lighter (Croal et al., 2004). The -1‰ fractionation reported here is smaller than a -3‰ equilibrium fractionation

reported between reactive Fe(II) and Fe(III) pools which coexist during DIR (Crosby et al., 2005). However, the exact size of this fractionation likely depends on factors such as temperature, the mineral in equilibrium with dissolved Fe, and the role of different microbes (Welch et al., 2003), with the -1‰ reported here in agreement with a number of observational studies, including the Black Sea (Rolison et al., 2018) and porewater examples (Fitzsimmons & Conway, 2023).

Water above the $\delta^{56}Fe$ minima in Saanich stratified profiles is consistently ca. 0.5-1.5‰ heavier, with relatively higher [O_2] and lower [Fe] (with some variability in depth), which may be explained by Fe cycling at the redoxcline. Transformations of Fe at the oxic-anoxic interface are observed in fresh and marine water columns, at the sediment-water interface, and within sediments (Stumm & Morgan, 1995). If typical redox processes are occurring at the Saanich redox interface, we can assume a clear boundary between oxidizing and reducing conditions, a supply of oxidized particulate material to the boundary, and transport processes (i.e., eddy diffusivity) near the boundary, all of which result in Fe redox cycling across the boundary as described by Davison (1993) (Fig. 18):

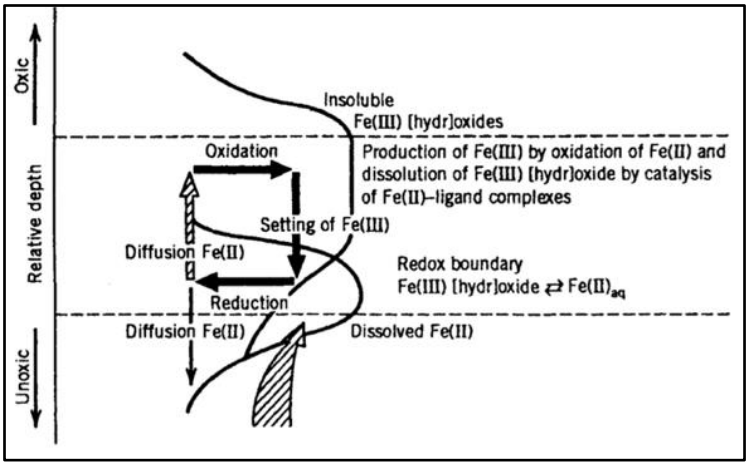

Figure 18. Fe redox cycling. The idealized redox cycling of Fe across the oxic-anoxic boundary in a sediment or water column (Davison, 1993).

1. Oxidized particulate material sinks from the surface to the redox boundary.
2. Fe(III)(s) is reduced to dFe(II).
3. dFe(II) diffuses upwards.
4. dFe(II) enters oxic water where it is oxidized back to Fe(III)(s).
5. Fe(III)(s) particles sink and are reduced in anoxic water (or carried to sediments), thereby completing the redox cycle.

The stratified profiles generally demonstrated a consistent shift in $\delta^{56}Fe$ from ca. -1‰ near 130 m to ca. -0.5 to +0.5‰ near 100 m, corresponding with a decrease in [Fe] and increase in [O_2] (Figs. 15 & 16, pgs. 42-43). I interpret this overall shift toward heavier $\delta^{56}Fe$ above the [Fe] maxima/$\delta^{56}Fe$ minima to reflect fractionation associated with oxidative precipitation, which occurs as dFe(II) diffuses up across the [Fe] gradient into oxic water and precipitates as Fe(III) oxyhydroxide. Although particles were not analyzed in this study, previous work has suggested a particulate Mn maximum just above the oxic-anoxic interface, which may promote precipitation and scavenging of Fe (Jacobs & Emerson, 1982). Oxidative precipitation and the associated change in $\delta^{56}Fe$ can be described in a two-step model (Beard & Johnson, 2004). First, the oxidation of dFe(II) to dFe(III) leaves dFe(III) 3‰ heavier when the species are at isotopic equilibrium (Eq. 3) (C. Johnson et al., 2020; Welch et al., 2003). Subsequently, the precipitation of Fe(III) oxyhydroxides can result in a kinetic isotope effect (Eq. 4) (Skulan et al., 2002).

$$4Fe^{2+} + O_2 + 8OH^- + 2H_2O \rightleftharpoons 4Fe^{3+} + 12OH^- \quad (3)$$

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \quad (4)$$

It is likely that as dFe(II) in Saanich diffused up in the water column, it encountered oxic water and was oxidized and precipitated to Fe(III) oxyhydroxides, with $\delta^{56}Fe$ mediated by a predominantly kinetic isotope effect that enriched the precipitate in light isotopes, thus leaving the water column ca. 0.5-1.5‰ heavier. This effect can be modelled using closed-system Rayleigh fractionation (Ripperger & Rehkämper, 2007) which shows that the winter and spring stratified profiles can be reasonably well described by a fractionation with an α of 0.99955 to 0.99980 (Eqs. 5-6 & Fig. 19, pg. 49).

$$\delta^{56}Fe_{seawater} = \delta^{56}Fe_{seawater,0} + 1{,}000 \times (\alpha - 1) \times \ln(F) \quad (5)$$

$$F = \frac{[Fe]}{[Fe]_{initial}} \quad \alpha = \frac{R_{particles}}{R_{seawater}} \quad R = {}^{56}Fe/{}^{54}Fe \quad (6)$$

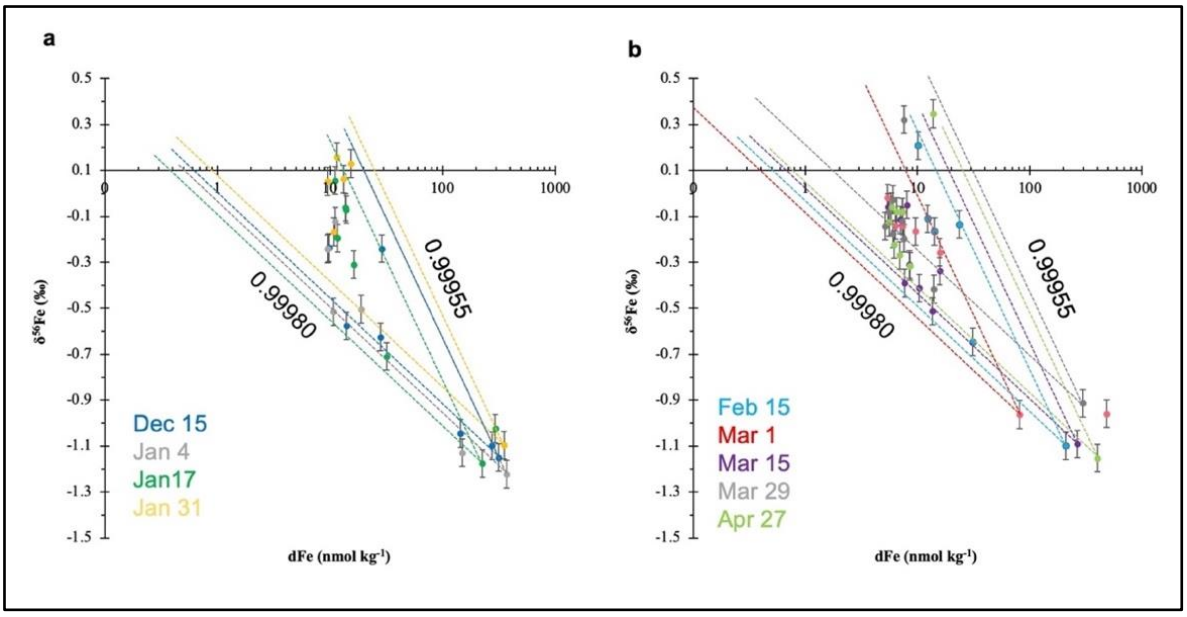

Figure 19. Fe isotope systematics for Saanich winter (a) & spring (b) stratified profiles. α lines representing Rayleigh fractionation factors drawn from the δ^{56}Fe minimum for each profile to demonstrate the change resulting from oxidative precipitation of dFe(II). Only samples from above this depth are shown to exclude samples below which may be influenced by sulfide loss.

The ability to describe the data with a small range of α values typically points to the dominance of a single kinetic fractionation, although the range of possible α values observed and the lack of a direct transition across the oxic-anoxic interface suggest the possibility of multiple oxidation-reduction steps and may also be complicated by the formation of different Fe minerals, the role of Mn in oxidizing Fe (Davison, 1993; Ellwood et al., 2019), and the possible effect of FeS precipitation where [H_2S] is sufficient. This closed-system model also assumes no additional Fe sources or loss processes, such as surface addition or biological uptake. However, the top 50 m of the water column was not included in this study, which should minimize these effects. Another complexity to establishing fractionation factors from field data over laboratory experiments is the fact that the operational definition of [Fe] by its nature includes nanoparticles and colloids (which likely include Fe(III) precipitates) as well as a range of 'dissolved' species, and so the δ^{56}Fe does not represent only the dissolved Fe(II) or Fe(III) species present. Generally, however, the Saanich

redox transition can be described by a kinetic fractionation (α between 0.99955 and 0.99980) that leaves the dissolved Fe relatively heavier, not lighter as would be expected from equilibrium-dominated experiments (Bullen et al., 2001). Additionally, the α values modelled here are similar to the best fit α of 0.9995 reported for oxidation of soluble Fe(II) in low-Fe, oxic porewaters in the South Atlantic (Homoky et al., 2021).

The $\delta^{56}Fe$ increase in Saanich associated with the oxidative precipitation of dFe(II) across the redoxcline suggests the dominance of a kinetic isotope effect, similar to that reported in the Eastern Gotland Basin (EGB) in the Baltic Sea, a similarly stratified basin with restricted and anoxic bottom water (Staubwasser et al., 2013). Here, $\delta^{56}Fe$ increases from a minimum ca. -0.4‰ in the ferruginous zone (depths of decreasing or no O_2, steep [Fe] gradient, and RD of Fe-oxyhydroxides (Staubwasser et al., 2013)) to heavier values above, attributed to dFe(II) oxidative precipitation at the oxic-anoxic interface which preferentially incorporates light Fe isotopes into the final Fe(III) precipitate, leaving the residual dFe(II) above the redox boundary isotopically heavier (Staubwasser et al., 2013). A similar $\delta^{56}Fe$ trend is reported in the Black Sea where there is a $\delta^{56}Fe$ minimum ca. -1‰ in the ferruginous zone overlain by relatively heavier values above (-0.88 to -0.61‰) (Rolison et al., 2018). $\delta^{56}Fe$ also increases upward across the water column oxic-anoxic boundary in Lake Cadagno (-0.61‰ to +0.75‰) coincident with a ten-fold [Fe] decrease across 0.5 m, associated with oxidative precipitation as dFe(II) diffuses up, and influenced by anoxygenic phototrophic bacteria which may influence the overall fractionation factor by modifying relative reaction rates of Fe(II) oxidation and Fe(III) precipitation (Ellwood et al., 2019). Similarly, in the San Pedro basin, oxidative precipitation of dFe(II) is dominated by a kinetic isotope effect which imparts a -0.8‰ fractionation factor between dFe(II) and Fe(III)(s), with preferential precipitation of lighter Fe isotopes as Fe(III) is removed to the particulate phase

(John et al., 2012).This is also reported on the anoxic Benguela shelf where $\delta^{56}Fe$ becomes heavier as [Fe] decreases, also attributed to kinetic isotope fractionation during precipitation (Hunt et al., 2022). Thus, I conclude that the positive $\delta^{56}Fe$ trend upwards from the [Fe] maxima and into oxic water in Saanich stratified profiles is consistent with kinetic isotope effects dominating fractionation associated with dFe(II) oxidative precipitation. This confirms Hypothesis 2, in which $\delta^{56}Fe$ was anticipated to increase through Fe precipitation above the oxic-anoxic boundary.

Typically, during oxidative precipitation at equilibrium, Fe(III)(s) is expected to be enriched in heavy isotopes, thus leaving residual dFe lighter (Bullen et al., 2001). However, the natural systems described above demonstrated the opposite, with oxidation and precipitation of Fe to leaving residual Fe isotopically heavier consistent with the dominance of kinetic effects on isotopic fractionation, in which either the oxidation step proceeds to completion prior to precipitation (John et al., 2012) and/or the rate constant for precipitation is larger than that for back-reduction of dFe(III) (Staubwasser et al., 2013). In either case, the Fe(II)-Fe(III) equilibrium no longer dominates fractionation, and instead kinetic effects during precipitation control the eventual $\delta^{56}Fe$ of the remnant dissolved phase. In situations such as the Benguela Upwelling and the San Pedro Basin, where a very low $\delta^{56}Fe$ is preserved into oxic bottom waters, and then more-significantly fractionated (-3 to -1‰), quantitative oxidation seems likely. In the Baltic Sea and Saanich, where there is a large [Fe] gradient and a more muted change in $\delta^{56}Fe$ (smaller fractionation factor), a faster rate constant for precipitation compared to the back reaction may be more likely (Staubwasser et al., 2013). Additionally, the exact fractionation factor depends on the specific Fe(III) minerals involved. Further, organic-complexation of the remnant dissolved Fe(III) could play a role in driving remnant Fe isotopically-heavier, with strong Fe-binding ligands thought to preferentially bind heavier isotopes (Dideriksen et al., 2008).

3.8.2 Fe Isotope Fractionation Associated with Sulfide Formation

Studies of other anoxic basins demonstrate similar overall shifts in $\delta^{56}Fe$, [H_2S], and [Fe] in anoxic water, as those seen in Saanich, all of which have been attributed to the formation of Fe sulfide minerals. For example, the Black Sea demonstrates a more than 3‰ $\delta^{56}Fe$ gradient corresponding with a two orders of magnitude decrease in [Fe], resulting in bottom water (>200 m) with [H_2S] exceeding 400 μmol kg^{-1} and heavy $\delta^{56}Fe$ (> +2‰) (Fig. 20,) (Rolison et al., 2018). Here, the formation of Fe sulfides is suggested to be the main driver of Fe removal and $\delta^{56}Fe$ increase in the euxinic layer as light Fe isotopes are preferentially lost from solution with a kinetic fractionation, with pyrite thought to be the dominant form of Fe sulfide precipitating in the water column (Landing & Lewis, 1991; Lewis & Landing, 1991; Rolison et al., 2018). The +2.75‰ fractionation factor between dFe(II) and FeS_2 (residual dFe(II) is 2.75‰ heavier) inferred for the Black Sea and attributed to syngenetic pyrite formation (Rolison et al., 2018) is similar to the fractionation factor experimentally determined for pyrite precipitation (ca. +3.1‰) which is suggested to be controlled by a unidirectional kinetic process (Guilbaud et al., 2011). Similarly, Lake Cadagno demonstrates an increase in $\delta^{56}Fe$ at the bottom of the water column corresponding with a ca. 100 uM [H_2S] increase and a ca. 0.3 uM [Fe] decrease (Ellwood et al., 2019), with Fe sulfide formation suggested to occur at the depth where $\delta^{56}Fe$ and

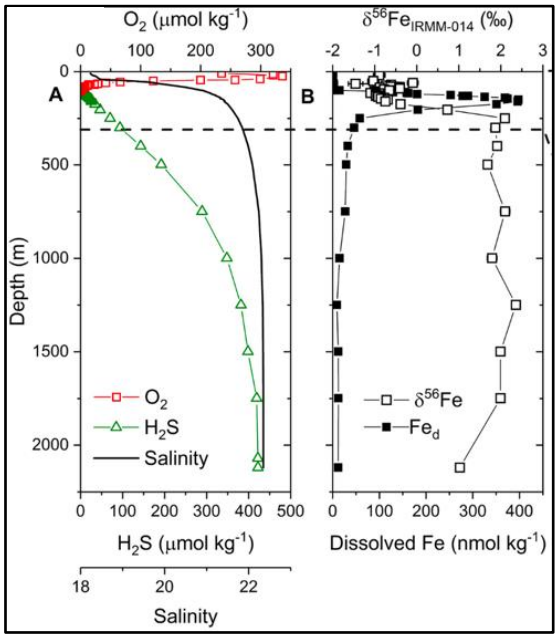

Figure 20. [O_2], [H_2S], salinity, [Fe], & $\delta^{56}Fe$ in the Black Sea. The large positive $\delta^{56}Fe$ shift in sulfidic deep water is interpreted to reflect isotopic fractionation associated with pyrite formation (Rolison et al., 2018).

[H_2S] increase (Canfield et al., 2010). Kinetic and equilibrium models of $\delta^{56}Fe$ measurements in Lake Cadagno produce fractionation values of around -0.3‰, which is smaller than in the Black Sea, but similar to the equilibrium fractionation factor of -0.3‰ between dFe(II) and mackinawite (FeS), a precursor to pyrite (Wu et al., 2012).

The interpretation of isotopic fractionation factors associated with Fe sulfide formation is complicated by the convoluted mechanism of pyrite precipitation, which occurs through different pathways which may impart unique fractionations with a large range of $\delta^{56}Fe$ associated with pyrite formation (-4 to +4‰) (Mansor & Fantle, 2019; Rolison et al., 2018). Pyrite formation involves slow pyrite nucleation followed by faster crystal growth, with dissolution of a precursor mineral leading to the formation of an intermediate aqueous Fe sulfide complex, and reaction with H_2S or polysulfide to form pyrite (Rickard & Luther, 2007; Rolison et al., 2018). The small, yet consistent increase in $\delta^{56}Fe$ below the [Fe] maxima among Saanich stratified profiles may point to Fe sulfide formation occurring in the anoxic water column where H_2S is present, especially considering the corresponding [Fe] decrease across the same region, which may suggest removal of dFe from the water column and into the Fe sulfide mineral.

Saanich Inlet sediments are jet black, indicating the presence of iron sulfides (Murray et al., 1978). All 9 stratified profiles were characterized by Fe- and H_2S- rich water in the anoxic water column, hypothetically allowing for the reaction of dFe(II) with H_2S to form Fe sulfides. If a similar mechanism of pyrite formation occured in Saanich as that in the Black Sea, pyrite precipitation in the water column would preferentially remove light Fe isotopes from solution, leaving the water column enriched in heavier isotopes (Rolison et al., 2018). There was indeed a small, but consistent enrichment in relatively heavy Fe in the sulfidic bottom water of the stratified Saanich profiles. Each of the stratified profiles increase from ca. -1‰ near the [Fe] maximum for

the given profile to -0.98 – -0.72‰ for the deepest samples (160- 180 m) (typically a $\delta^{56}Fe$ increase of 0.11- 0.37‰), which generally coincided with an increase in [H_2S], and a decrease in [Fe]. This difference is smaller than the 2.75‰ fractionation for pyrite formation in the Black Sea, but closer to the fractionation factor of 0.3‰ between dFe(II) and mackinawite experimentally determined (Wu et al., 2012), and that attributed to the $\delta^{56}Fe$ trend in Lake Cadagno, suggesting that the $\delta^{56}Fe$ trend in Saanich may reflect mackinawite formation rather than pyrite formation, especially as the Lake Cadagno study was interpreted to reflect mackinawite as the main FeS formed in the presence of sulfate reducing bacteria (Ellwood et al., 2019), which would be consistent with the active production of H_2S in the anoxic waters of Saanich. However, as the change in [Fe] with depth varied through the time series (with little concomitant change in $\delta^{56}Fe$), the decline in Fe cannot be modelled by a simple closed system Rayleigh fractionation. Further, H_2S never reached as high of concentrations as in the Black Sea or Lake Cadagno. However, the presence of micro-particulate or colloidal sulfide minerals might act to obscure a simple fractionation between dissolved and particulate phase.

In summary, the consistent increase in $\delta^{56}Fe$ in sulfidic Saanich deep water may reflect the formation of Fe sulfides, especially as [Fe] also decreased, suggesting a potential removal to FeS(s), though evidence for this is less clear and equivocal than in other basins with elevated [H_2S]. However, given the intricacies of isotopic fractionation associated with pyrite formation and a lack of particulate samples, this cannot be concluded with certainty. Overall, Hypothesis 3 correctly predicted heavier $\delta^{56}Fe$ values in sulfidic water, however whether this can be attributed to pyrite formation remains unclear. It is also possible that a flux of heavier Fe from sediments or reduction of different Fe minerals in the water column with slightly different reduction fractionation factors could contribute to this change. Additional characterization of Fe sulfide minerals in Saanich

sediments and measurement of $\delta^{56}Fe$ of particulate Fe in sediments and the water column may provide more insight on this matter.

3.8.3 Fe Isotope Fractionation Associated with Renewal Events

During the renewal season (4 and 18 Oct 2016), the $\delta^{56}Fe$ profiles were moderately homogenous (ca. -0.3‰) under low [Fe] conditions throughout the water column, except for deviations at an isolated depth (130 m) (Fig. 13, pg. 38). The $\delta^{56}Fe$ minima for both profiles were sandwiched between regions of isotopically heavier water above and below: above the $\delta^{56}Fe$ minima, $\delta^{56}Fe$ increased by 1.49‰ (4 Oct) and 1.22‰ (18 Oct), and below the $\delta^{56}Fe$ minima, $\delta^{56}Fe$ increased by 0.82‰ (4 Oct) and 0.86 ‰ (18 Oct). The $\delta^{56}Fe$ minima were both associated with [Fe] maxima, which were similarly sandwiched between low [Fe] (<25 nmol kg^{-1}) above and below.

The October profiles both reflect a water column recovering from the September renewal season, which introduced new water first closer to the surface, followed by a subsequent intrusion of new water near the bottom of the water column. As oxic water entered Saanich and mixed with anoxic water, any Fe(II) was likely oxidized and precipitated, leaving the water column Fe depleted and isotopically heavier than the $\delta^{56}Fe$ minima. The "sandwich" of high [Fe] and light $\delta^{56}Fe$ between relatively lower [Fe] and heavier $\delta^{56}Fe$ corresponds well with the layering effect described by Soetaert et al. (2022) in which Saanich contains layers of water masses, each containing different proportions of old and new water due to density differences. Thus, the isolated region of both October profiles reflects remnant water column characteristics for that depth (130 m) and was underlain by a layer of new water introduced during renewal events which delivered oxygen below the oxic-anoxic boundary, which was then slowly consumed. Each profile seems to have captured

a water column returning to normal stratified conditions, with high [NO_3^-] below the oxic-anoxic boundary suggesting that respiration had not yet consumed all O_2 and NO_3^- introduced in the renewal before reaching the point of DIR, as indicated by the low [Fe] and elevated $\delta^{56}Fe$ remaining in deep water in both cases.

In both profiles, the transition in $\delta^{56}Fe$ from the older remnant water to the surrounding low-Fe water was in the positive direction (-1.05‰ to -0.44 and -0.23 for 4 Oct and -1.06 to -0.20 and +0.16‰ for 18 Oct) suggesting the influence of oxidative precipitation that left remnant dFe(II) isotopically heavier, similar to the $\delta^{56}Fe$ trend seen in stratified profiles with transition into the oxic upper water column (Figs. 15 & 16, pgs. 21-43). The question then is, do the transitions between the high Fe pocket and surrounding water reflect a transition between two unconnected layers, or is there indeed fractionation at each interface? Evidence for such a kinetic fractionation is found from 11 Oct, where the +0.16±0.06 and -0.20±0.06 ‰ are heavier than the next samples (-0.15±0.06 and -0.34±0.06 respectively), something that must involve a fractionation compared to background. Further, the transition both above and below the high Fe water in both profiles can be well described by α of 0.9997 (4 Oct) and 0.99962 (18 Oct), comparing well with the fractionation factors calculated across the stable redoxcline (0.99955-0.99980; Fig 19, pg. 49), suggesting a similar effect.

The November profiles generally show lower [Fe], but the 15 Nov profile shows a more muted [Fe] maxima at 130 m (16 nmol kg^{-1}) with isotopically light Fe (-0.55‰). Interestingly, like the October profiles, apparent fractionation in water below can be modelled by an α of 0.99965; however, the shift from -0.55‰ to +0.70‰ from 130 to 120 m would require a much larger α of 0.9988. Such a large α could indicate a different fractionation process, such as quantitative oxidation followed by precipitation, rather than a mix of oxidation and precipitation as inferred for

the lower [Fe] conditions of the San Pedro basin compared to the Baltic Sea (Staubwasser et al., 2013). However, this observation is only based on one data point, which while has no obvious analytical concerns, could still be an anomaly.

3.8.4 Fe Isotopes as a Paleoredox Proxy

The change in Earth's oxidation state associated with oxygenation of the atmosphere ca. 2.3 Ga during the GOE (Holland, 2006) is assumed to have significantly altered Fe redox chemistry and isotopic composition. $\delta^{56}Fe$ measurements of marine sediments indicate as such, with $\delta^{56}Fe$ of Fe sulfides in black shales being generally isotopically light $\delta^{56}Fe$ (-3.5 to +0.5‰) before 2.3 Ga and the rise of atmospheric O_2, (Fig. 21, pg. 58) which may reflect DIR (Rouxel et al., 2005) which utilized photochemically generated Fe(III), which was likely an important electron acceptor for microbial respiration during the Archean (Cairns-Smith et al., 1992; Vargas et al., 1998). Planavsky et al., (2012) suggest that pre-GOE deposits record the partial oxidation of Fe(II) under low-Fe conditions (whereas near quantitative oxidation is inferred in younger deposits), which led to deposition of Fe formations and Fe-rich sediments enriched in heavy isotopes in the deep ocean, leaving isotopically light Fe to precipitate as Fe sulfides on continental margins, as reflected in pyrites in black shales (Rouxel et al., 2005). However, the origin of this negative $\delta^{56}Fe$ signature in Archean pyrite remains disputed (Rolison et al., 2018).

Light $\delta^{56}Fe$ values disappeared as atmospheric O_2 increased, leading to heavier $\delta^{56}Fe$ (-0.3 to +1.2‰) which persisted through ca. 1.7 Ga, and is interpreted to reflect oxidation in the early Paleoproterozoic (Rouxel et al., 2005). The disappearance of light $\delta^{56}Fe$ in the black shale record ca. 2.3 Ga corresponds with the disappearance of BIFs (BIFs eventually return around 2.1 Ga (Isley & Abbott, 1999)). The increase in atmospheric oxygen ca. 2.3 Ga led to oxidative weathering and

thus sulfate delivery to the ocean, which allowed for Fe sulfide formation, which may have interrupted BIF deposition (Canfield, 1998). Thus, the heavier $\delta^{56}Fe$ values after the GOE may indicate an increased influence of sulfide precipitation in a redox-stratified ocean (Rouxel et al., 2006).

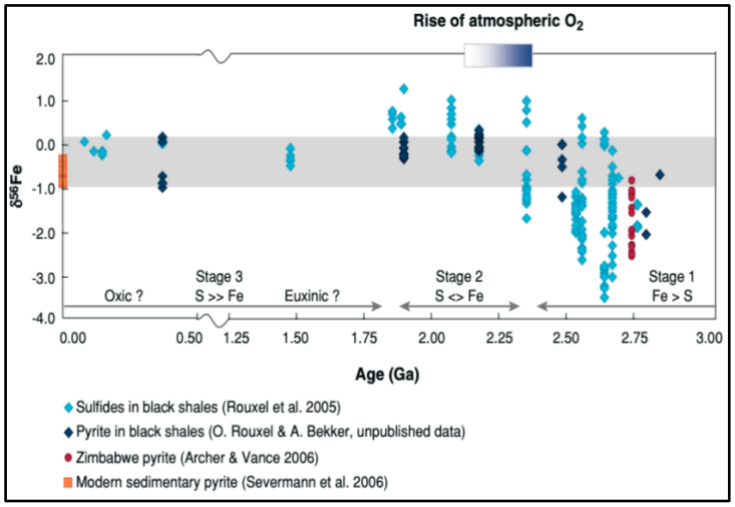

Figure 21. $\delta^{56}Fe$ vs. sample age for pyrite. Anbar & Rouxel (2007) divide the ancient marine Fe cycle into three stages based on trends in $\delta^{56}Fe$. Stage 1 is characterized by lighter values, which increase to more crustal/heavy values in stage 2 and 3.

The $\delta^{56}Fe$ measurements in this study demonstrate isotopic fractionation in a water column that transitions between oxic, anoxic, and euxinic conditions. Similarities between the chemistry of the Saanich Inlet anoxic water column and that of the anoxic, Fe-rich, pre-GOE ocean (Poulton & Canfield, 2011) make Saanich a useful analogue to Precambrian ocean conditions, and water column $\delta^{56}Fe$ measurements presented here likely reflect similar fractionation that occurred during this time. Importantly, my results contribute to the marine literature which show that kinetic fractionations may be more important in driving residual oceanic $\delta^{56}Fe$ than previously assumed in earlier paleo studies (Beard & Johnson, 1999). Thus, while DIR may generate very low $\delta^{56}Fe$ in as reported in Archean Fe deposits, the subsequent $\delta^{56}Fe$ transformations upon precipitation/deposition and further reaction of Fe in ancient sediments remains unclear, with the accuracy of the assumption of sedimentary $\delta^{56}Fe$ acting a passive recorder of seawater conditions (Rolison et al., 2018) remaining somewhat ambiguous.

Overall, my $\delta^{56}Fe$ measurements have contributed to our understanding of isotopic fractionation associated with redox changes by demonstrating the importance of including both equilibrium and kinetic fractionation factors in interpretations of the sedimentary rock record, and thus may inform future studies seeking to further constrain the meaning of $\delta^{56}Fe$ in Archean Fe deposits and how it may record marine redox changes associated with atmospheric oxygenation.

3.9 Conclusions

A time series of dissolved [Fe] and $\delta^{56}Fe$ from October 2016 through April 2017 in Saanich Inlet was presented. Saanich is a redox stratified fjord with dynamic redox conditions which have made it a classically studied anoxic basin. In summer and fall, the inlet is flushed with dense water which is a product of estuarine circulation in the Salish Sea. Such renewal events deliver oxygen-rich water to the inlet, disrupting the typical stratification between the oxygenated upper water column and anoxic water below, which provides a unique setting in which to explore redox sensitive trace metals like Fe. During the renewal season (Oct- Nov), [Fe] and $\delta^{56}Fe$ profiles demonstrated a layering of renewal water with anoxic water, with a consistent $\delta^{56}Fe$ ca. -0.3‰ background surrounding layers of isotopically light (-1‰) high [Fe] water. Following the renewal season, stratification of the water column was established (Dec- April), with oxic, Fe-depleted surface water separated from anoxic, Fe-rich deep water. Anoxic water had $\delta^{56}Fe$ minima (-1‰) associated with [Fe] maxima, attributed to equilibrium redox fractionation associated with the reduction of Fe during microbial respiration of organic matter. An upward increase in $\delta^{56}Fe$ and a decrease in [Fe] up across the oxic-anoxic boundary suggests fractionation associated with the oxidative precipitation of Fe(II) as Fe diffuses upward across the boundary, whereas an increase in $\delta^{56}Fe$ below the $\delta^{56}Fe$ minimum corresponding with an increase in [H_2S] may reflect

fractionation associated with Fe sulfide formation. In Saanich, fractionation during oxidative precipitation appears to be dominated by kinetic effects during precipitation and can be modelled by closed system Rayleigh fractionation with an a of 0.99955 to 0.9998, similar to findings from other modern marine anoxic basins. Overall, my results indicate the importance of considering both equilibrium and kinetic isotope effects in interpretation of $\delta^{56}Fe$ measurements and changes throughout both the modern global ocean and in the past marine sediment record for an understanding of the Earth's redox changes through time. Additional inquiry in similar anoxic basins, measurement of particulate $\delta^{56}Fe$, and precipitation/mixing experiments would help to further improve interpretation of isotopic fractionation associated with Fe redox transformations.

Table 2. O_2, NO_3^-, Fe, and H_2S concentrations and $\delta^{56}Fe$ for the SaanDox time series.

	Depth (m)	**[O_2] μmol kg^{-1}**	**[NO_3^-] μmol kg^{-1}**	**[Fe] nmol kg^{-1}**	**δ^{56}Fe (‰)**	**2SE**	**[H_2S] μmol L^{-1}**
Oct 4 2016	65	85.67	23.13	5.13	-0.33	0.05	0
	75	23.49	23.03	4.13	-0.22	0.04	0
	100	2.1	16.48	4.05	-0.39	0.04	0
	110	1.24	4.29	22.04	-0.44	0.06	0
	130	1.69	0.5	113.62	-1.05	0.02	0
	145	1.11	5.51	7.79	-0.23	0.03	0.1
	160	1.47	11.92	4.06	-0.21	0.04	0
	175	2.87	0	3.77	-0.16	0.05	0.39
	185	2.64	0	4.47	-0.32	0.05	0.03
	200	1.27	0	4.98	-0.30	0.05	0.56
Oct 18 2016	75	76.97	26.31	8.74	-0.51	0.03	0
	100	1.11	6.99	11.51	-0.15	0.03	0
	110	1.13	8.68	5.87	0.16	0.04	0
	130	1.65	0	416.96	-1.06	0.04	11.67
	140	10.4	8.64	11.44	-0.20	0.03	0
	160	30.25	12.59	5.04	-0.34	0.04	0
	170	11.55	12.35	4.27	-0.41	0.05	0
	200	1.09	2.49	3.96	-0.58	0.04	0
Nov 1 2016	75	96.57	24.84	4.06	-0.21	0.04	0
	85	19.39	21.9	4.64	-0.30	0.05	0
	100	2.76	7.97	9.21	-0.15	0.03	0
	110	0.78	0	8.10	0.18	0.04	0.04
	120	1.15	5.18	8.00	0.15	0.03	0
	130	0.9	0	7.47	-0.04	0.04	0
	150	1.6	8.31	4.38	-0.19	0.03	0
	160	1.72	10.38	4.48	-0.30	0.05	0
	175	1.04	0	4.47	-0.37	0.04	0.01
	200	1.33	2.52	5.94	-0.33	0.03	0

Table 2 (Continued)

	Depth (m)	$[O_2]$ μmol kg^{-1}	$[NO_3^-]$ μmol kg^{-1}	[Fe] nmol kg^{-1}	δ^{56}Fe (‰)	2SE	$[H_2S]$ μmol L^{-1}
Nov 15 2016	50	132.27	23.96	8.66	-0.25	0.06	0
	60	123.85	25.98	8.41	-0.21	0.03	0
	75	107.89	27.51	5.68	-0.11	0.04	0
	90	1.94	19.04	4.26	-0.13	0.04	0
	100	1.87	7.87	6.22	0.20	0.04	0
	110	2.54	8.11	4.57	0.03	0.05	0
	120	1.66	0	5.99	0.70	0.04	0.14
	130	1.12	0.84	16.13	-0.55	0.04	0
	160	1.54	6	4.94	-0.14	0.05	0
	190	1.25	0	5.88	-0.23	0.05	1.05
Dec 15 2016	50	201.39	24.95	28.89	-0.24	0.03	0
	75	78.99	0	13.96	-0.58	0.04	0
	90	1.91	0	9.75	-0.24	0.05	0.23
	95	1.71	0	28.15	-0.62	0.05	0.99
	100	3.68	0	144.84	-1.04	0.04	1.06
	105	3.06	0	276.25	-1.10	0.03	3
	110	2.5	0	316.58	-1.15	0.04	7.24
	115	2.52	0	68.78	-1.04	0.04	3
	130	3.8	0	141.79	-0.98	0.04	1.42
	160	2.32	0	84.38	-0.98	0.04	0.49
Jan 4 2017	50	192.96	0	11.13	-0.12	0.04	0
	75	186.11	25.17	9.53	-0.24	0.03	0
	85	73.27	0	10.73	-0.52	0.05	0
	90	31.87	0	18.90	-0.50	0.04	0
	100	1.5	0	149.55	-1.13	0.05	1.43
	110	2.8	0	371.28	-1.22	0.05	4.85
	120	2.29	0	182.05	-1.02	0.04	1.35
	130	2.47	0	193.46	-0.83	0.04	2.05
	160	1.96	0	114.32	-0.85	0.07	1.88
	180	1.95	0	208.32	-0.80	0.05	7.2

Table 2 (Continued)

	Depth (m)	[O_2] μmol kg^{-1}	[NO_3^-] μmol kg^{-1}	[Fe] nmol kg^{-1}	δ^{56}Fe (‰)	2SE	[H_2S] μmol L^{-1}
Jan 17 2017	50	218.83	26.89	11.70	-0.20	0.05	0
	75	173.65	24.74	16.23	-0.31	0.07	0
	85	161.55	22.79	13.94	-0.07	0.08	0
	90	143.15	20.96	13.78	-0.06	0.08	0
	95	71.44	0	11.05	0.06	0.05	0
	100	5.63	0	32.01	-0.71	0.05	0
	110	3.55	0	226.56	-1.18	0.04	4.17
	130	1.41	0	294.51	-1.02	0.04	5.34
	160	2.2	0	255.94	-0.82	0.05	4.35
	180	1.69	0	238.90	-0.81	0.05	12.17
Jan 31 2017	75	184.43	26.48	9.50	0.05	0.07	0
	85	140.93	24.3	11.54	0.16	0.07	0
	90	46.08	14.74	10.83	-0.17	0.06	0
	95	14.43	7.43	13.23	0.06	0.07	0
	100	1.4	1.66	15.29	0.13	0.07	0
	110	3.23	0	350.86	-1.10	0.04	8.71
	130	2.12	0	271.39	-1.02	0.04	4.37
	160	1.9	0	254.04	-0.87	0.05	5.77
Feb 15 2017	50	233.37	18.14	14.13	-0.17	0.07	0
	90	132.34	11.83	12.24	-0.11	0.08	0
	95	85.77	11.79	10.11	0.21	0.04	0
	100	36.13	7.34	31.09	-0.65	0.05	0
	105	3.44	1.63	23.61	-0.14	0.07	0
	110	2.3	0	209.34	-1.10	0.04	2.68
	130	2.72	0	273.02	-1.02	0.04	4.96
	160	1.74	0	297.89	-0.83	0.02	10.98
Mar 1 2017	50	226.07	21.99	15.70	-0.26	0.05	0
	75	197.48	22.61	7.38	-0.14	0.04	0
	85	152.63	14.82	5.61	-0.07	0.03	0
	90	85.03	16.35	5.42	-0.02	0.04	0.46
	95	59.63	10.53	6.34	-0.14	0.03	0
	100	23.09	8.88	7.32	-0.08	0.03	0
	105	2.57	1.32	9.60	-0.17	0.04	0
	110	2.11	0	81.13	-0.96	0.03	0.29
	130	2.35	0	482.73	-0.96	0.05	10.24
	160	1.59	0	260.06	-0.85	0.04	6.96

Table 2 (Continued)

	Depth (m)	[O_2] μmol kg^{-1}	[NO_3^-] μmol kg^{-1}	[Fe] nmol kg^{-1}	δ^{56}Fe (‰)	2SE	[H_2S] μmol L^{-1}
Mar 15 2017	50	230.61	25.8	7.67	-0.39	0.04	0
	75	231.71	23.41	10.37	-0.41	0.05	0
	85	179.05	23.36	8.43	-0.31	0.04	0
	90	112.41	17.96	7.01	-0.12	0.04	0
	95	70.49	14.39	5.47	-0.06	0.04	0
	100	36.44	10.23	13.59	-0.51	0.05	0
	105	4.65	5.79	8.02	-0.05	0.09	0
	110	1.97	0.29	15.70	-0.34	0.04	0
	130	2.37	0	266.72	-1.09	0.05	5.53
	160	2.15	0	262.17	-0.80	0.04	6.79
Mar 29 2017	50	222.69	26.63	7.30	-0.12	0.05	0
	75	198.39	18.77	7.52	-0.20	0.07	0
	85	161.8	23.92	5.49	-0.08	0.03	0
	90	100.92	19.3	5.13	-0.14	0.05	0
	95	25.28	14.96	6.01	-0.03	0.07	0
	100	21.65	9.77	13.97	-0.42	0.06	0
	105	10.88	9.24	6.04	-0.18	0.05	0
	110	2.83	2.85	7.54	0.32	0.04	0
	130	1.74	0	297.72	-0.91	0.02	4.16
	160	1.59	0	294.49	-0.72	0.03	11.06
Apr 27 2017	50	228.71	18.32	8.56	-0.32	0.05	0
	75	206.52	25.5	6.94	-0.27	0.04	0
	85	162.62	25.45	5.60	-0.13	0.03	0
	90	111.2	18.99	7.24	-0.08	0.04	0
	95	30.78	18.7	5.84	-0.06	0.05	0
	100	17.28	14.01	6.20	-0.22	0.03	0
	105	2.69	4.44	13.76	0.35	0.03	0
	110	2.81	1.99	6.52	-0.08	0.04	0
	130	0.94	0	401.56	-1.15	0.03	10.18
	160	2	0	527.44	-0.86	0.03	13.69

REFERENCES

Albani, S., Mahowald, N. M., Delmonte, B., Maggi, V., & Winckler, G. (2012). Comparing modeled and observed changes in mineral dust transport and deposition to Antarctica between the Last Glacial Maximum and current climates. *Climate Dynamics*, *38*(9), 1731–1755. https://doi.org/10.1007/s00382-011-1139-5

Anderson, J. J., & Devol, A. H. (1973). Deep water renewal in Saanich Inlet, an intermittently anoxic basin. *Estuarine and Coastal Marine Science*, *1*(1), 1–10. https://doi.org/10.1016/0302-3524(73)90052-2

Anderson, R. (2020). GEOTRACES: Accelerating research on the marine biogeochemical cycles of trace elements and their isotopes. *Annual Review of Marine Science*, *12*(1), 49–85. https://doi.org/10.1146/annurev-marine-010318-095123

Anderson, R., Ali, S., Bradtmiller, L. I., Nielsen, S. H. H., Fleisher, M. Q., Anderson, B. E., & Burckle, L. H. (2009). Wind-Driven Upwelling in the Southern Ocean and the Deglacial Rise in Atmospheric CO2. *Science*, *323*(5920), 1443–1448. https://doi.org/10.1126/science.1167441

Anderson, R., Mawji, E., Cutter, G., Measures, C., & Jeandel, C. (2014). GEOTRACES: Changing the way we explore ocean chemistry. *Oceanography*, *27*, 50–61. https://doi.org/10.5670/oceanog.2014.07

Beard, B. L., & Johnson, C. M. (1999). High precision iron isotope measurements of terrestrial and lunar materials. *Geochimica et Cosmochimica Acta*, *63*(11), 1653–1660. https://doi.org/10.1016/S0016-7037(99)00089-7

Beard, B. L., & Johnson, C. M. (2004). Fe Isotope Variations in the Modern and Ancient Earth and Other Planetary Bodies. *Reviews in Mineralogy and Geochemistry*, *55*(1), 319–357. https://doi.org/10.2138/gsrmg.55.1.319

Beard, B. L., Johnson, C. M., Cox, L., Sun, H., Nealson, K. H., & Aguilar, C. (1999). Iron isotope biosignatures. *Science*, *285*(5435), 1889–1892. https://doi.org/10.1126/science.285.5435.1889

Beard, B. L., Johnson, C., Skulan, J., Nealson, K., Cox, L., & Sun, H. (2003). Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chemical Geology - CHEM GEOL*, *195*. https://doi.org/10.1016/S0009-2541(02)00390-X

Bennett, S. A., Rouxel, O., Schmidt, K., Garbe-Schönberg, D., Statham, P. J., & German, C. R. (2009). Iron isotope fractionation in a buoyant hydrothermal plume, 5°S Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta*, *73*(19), 5619–5634. https://doi.org/10.1016/j.gca.2009.06.027

Bergquist, B. A., & Boyle, E. A. (2006). Dissolved iron in the tropical and subtropical Atlantic Ocean. *Global Biogeochemical Cycles*, *20*(1). https://doi.org/10.1029/2005GB002505

Berner, R., A. (1980). *Early Diagenesis*. Princeton University Press; JSTOR. https://doi.org/10.2307/j.ctvx8b6p2

Binqiu, Z., Wong, C. S., & Johnson, W. K. (1987). Controlling mechanisms for the trace metals, (Cu, Zn, Cd, Fe, Co and Ni) in anoxic sea water in Saanich Inlet, British Columbia, Canada. *Chinese Journal of Oceanology and Limnology*, *5*(3), 193–204. https://doi.org/10.1007/BF02843983

Black, E. E., Kienast, S. S., Lemaitre, N., Lam, P. J., Anderson, R. F., Planquette, H., Planchon, F., & Buesseler, K. O. (2020). Ironing Out Fe Residence Time in the Dynamic Upper Ocean. *Global Biogeochemical Cycles*, *34*(9), e2020GB006592. https://doi.org/10.1029/2020GB006592

Blais-Stevens, A., Bornhold, B. D., Kemp, A., Dean, J. M., & Vaan, A. A. (2001). Overview of Late Quaternary stratigraphy in Saanich Inlet, British Columbia: Results of Ocean Drilling Program Leg 169S. *Marine Geology*, *174*, 3–20. https://doi.org/10.1016/S0025-3227(00)00139-0

Boyle, E. A., Sclater, F., & Edmond, J. M. (1976). On the marine geochemistry of cadmium. *Nature*, *263*(5572), 42–44. https://doi.org/10.1038/263042a0

Breitburg, D., Levin, L., Oschlies, A., Grégoire, M., Chavez, F., Conley, D., Garcon, V., Gilbert, D., Gutiérrez, D., Isensee, K., Jacinto, G., Limburg, K., Montes, I., Naqvi, S. W. A., Pitcher, G., Rabalais, N., Roman, M., Rose, K., Seibel, B., & Zhang, J. (2018). Declining oxygen in the global ocean and coastal waters. *Science (New York, N.Y.)*, *359*. https://doi.org/10.1126/science.aam7240

Broecker, W. S., & Peng, T.-H. (1982). *Tracers in the sea*. Published by Lamont-Doherty Geological Observatory, Columbia University.

Bruland, K. W., Franks, R. P., Knauer, G. A., & Martin, J. H. (1979). Sampling and analytical methods for the determination of copper, cadmium, zinc, and nickel at the nanogram per liter level in sea water. *Analytica Chimica Acta*, *105*, 233–245. https://doi.org/10.1016/S0003-2670(01)83754-5

Bruland, K. W., Knauer, G. A., & Martin, J. H. (1978). Cadmium in northeast Pacific waters 1. *Limnology and Oceanography*, *23*(4), 618–625. https://doi.org/10.4319/lo.1978.23.4.0618

Bullen, T. D., White, A. F., Childs, C. W., Vivit, D. V., & Schulz, M. S. (2001). Demonstration of significant abiotic iron isotope fractionation in nature. *Geology*, *29*(8), 699–702. https://doi.org/10.1130/0091-7613(2001)029<0699:DOSAII>2.0.CO;2

Byrne, R. H., & Kester, D. R. (1976). Solubility of hydrous ferric oxide and iron speciation in seawater. *Marine Chemistry*, *4*(3), 255–274. https://doi.org/10.1016/0304-4203(76)90012-8

Byrne, R. H., Kump, L. R., & Cantrell, K. J. (1988). The influence of temperature and pH on trace metal speciation in seawater. *Inorganic Marine Chemistry*, *25*(2), 163–181. https://doi.org/10.1016/0304-4203(88)90062-X

Cairns-Smith, A. G., Hall, A. J., & Russell, M. J. (1992). Mineral Theories of the Origin of Life and an Iron Sulfide Example. In N. G. Holm (Ed.), *Marine Hydrothermal Systems and the Origin of Life: Report of SCOR Working Group 91* (pp. 161–180). Springer Netherlands. https://doi.org/10.1007/978-94-011-2741-7_9

Canfield, D. E. (1998). A new model for Proterozoic ocean chemistry. *Nature*, *396*(6710), 450–453. https://doi.org/10.1038/24839

Canfield, D. E., Farquhar, J., & Zerkle, A. L. (2010). High isotope fractionations during sulfate reduction in a low-sulfate euxinic ocean analog. *Geology*, *38*(5), 415–418. Scopus. https://doi.org/10.1130/G30723.1

Canfield, D. E., & Thamdrup, B. (2009). Towards a consistent classification scheme for geochemical environments, or, why we wish the term 'suboxic' would go away. *Geobiology*, *7*(4), 385–392. https://doi.org/10.1111/j.1472-4669.2009.00214.x

Charette, M. A., Kipp, L. E., Jensen, L. T., Dabrowski, J. S., Whitmore, L. M., Fitzsimmons, J. N., Williford, T., Ulfsbo, A., Jones, E., Bundy, R. M., Vivancos, S. M., Pahnke, K., John, S. G., Xiang, Y., Hatta, M., Petrova, M. V., Heimbürger-Boavida, L.-E., Bauch, D., Newton, R., … Zhang, R. (2020). The Transpolar Drift as a Source of Riverine and Shelf-Derived Trace Elements to the Central Arctic Ocean. *Journal of Geophysical Research: Oceans*, *125*(5), e2019JC015920. https://doi.org/10.1029/2019JC015920

Conway, T. M., Horner, T. J., Plancherel, Y., & González, A. G. (2021). A decade of progress in understanding cycles of trace elements and their isotopes in the oceans. *Chemical Geology*, *580*, 120381. https://doi.org/10.1016/j.chemgeo.2021.120381

Conway, T. M., & John, S. G. (2014). Quantification of dissolved iron sources to the North Atlantic Ocean. *Nature*, *511*(7508), 212–215. https://doi.org/10.1038/nature13482

Conway, T. M., & Middag, R. (In press). Controls and distributions of trace elements in the ocean. In *Treatise on Geochemistry* (3rd edition).

Conway, T. M., Rosenberg, A. D., Adkins, J. F., & John, S. G. (2013). A new method for precise determination of iron, zinc and cadmium stable isotope ratios in seawater by double-spike mass spectrometry. *Analytica Chimica Acta*, *793*, 44–52. https://doi.org/10.1016/j.aca.2013.07.025

Croal, L. R., Johnson, C. M., Beard, B. L., & Newman, D. K. (2004). Iron isotope fractionation by Fe(II)-oxidizing photoautotrophic bacteria. *Geochimica et Cosmochimica Acta*, *68*(6), 1227–1242. https://doi.org/10.1016/j.gca.2003.09.011

Crosby, H. A., Johnson, C. M., Roden, E. E., & Beard, B. L. (2005). Coupled Fe(II)−Fe(III) electron and atom exchange as a mechanism for Fe isotope fractionation during dissimilatory iron oxide reduction. *Environmental Science & Technology*, *39*(17), 6698–6704. https://doi.org/10.1021/es0505346

Crosby, H. A., Roden, E. E., Johnson, C. M., & Beard, B. L. (2007). The mechanisms of iron isotope fractionation produced during dissimilatory Fe(III) reduction by Shewanella putrefaciens and Geobacter sulfurreducens. *Geobiology*, *5*(2), 169–189. https://doi.org/10.1111/j.1472-4669.2007.00103.x

Cullen, J., & Meyer, A. (2020). *Saanich Inlet Fe concentrations* [Personal Communication].

Cutter, G. A., Andersson, P., Codispoti, L. A., Croot, P. L., Franc'ois, R., Lohan, M. C., Obata, H., & Loeff, M. M. R. van der. (2010). *Sampling and Sample-handling Protocols for GEOTRACES Cruises*.

Dauphas, N., John, S. G., & Rouxel, O. (2017). Iron Isotope Systematics. *Reviews in Mineralogy and Geochemistry*, *82*(1), 415–510. https://doi.org/10.2138/rmg.2017.82.11

Davison, W. (1993). Iron and manganese in lakes. *Earth-Science Reviews*, *34*(2), 119–163. https://doi.org/10.1016/0012-8252(93)90029-7

Dideriksen, K., Baker, J. A., & Stipp, S. L. S. (2008). Equilibrium Fe isotope fractionation between inorganic aqueous Fe(III) and the siderophore complex, Fe(III)-desferrioxamine B. *Earth and Planetary Science Letters*, *269*(1), 280–290. https://doi.org/10.1016/j.epsl.2008.02.022

Dinniman, M. S., St-Laurent, P., Arrigo, K. R., Hofmann, E. E., & van Dijken, G. L. (2020). Analysis of Iron Sources in Antarctic Continental Shelf Waters. *Journal of Geophysical Research: Oceans*, *125*(5), e2019JC015736. https://doi.org/10.1029/2019JC015736

Drever, J. I. (1997). *The geochemistry of natural waters: Surface and groundwater environments* (3rd ed). Prentice Hall Upper Saddle River, N.J.; WorldCat.

Ellwood, M. J., Hassler, C., Moisset, S., Pascal, L., Danza, F., Peduzzi, S., Tonolla, M., & Vance, D. (2019). Iron isotope transformations in the meromictic Lake Cadagno. *Geochimica et Cosmochimica Acta*, *255*, 205–221. https://doi.org/10.1016/j.gca.2019.04.007

Elrod, V. A., Berelson, W. M., Coale, K. H., & Johnson, K. S. (2004). The flux of iron from continental shelf sediments: A missing source for global budgets. *Geophysical Research Letters*, *31*(12). https://doi.org/10.1029/2004GL020216

Emerson, S., Cranston, R. E., & Liss, P. S. (1979). Redox species in a reducing fjord: Equilibrium and kinetic considerations. *Deep Sea Research Part A. Oceanographic Research Papers*, *26*(8), 859–878. https://doi.org/10.1016/0198-0149(79)90101-8

Fitzsimmons, J. N., & Boyle, E. A. (2014). Assessment and comparison of Anopore and cross flow filtration methods for the determination of dissolved iron size fractionation into soluble and colloidal phases in seawater. *Limnology and Oceanography: Methods*, *12*(4), 246–263. https://doi.org/10.4319/lom.2014.12.246

Fitzsimmons, J. N., Boyle, E. A., & Jenkins, W. J. (2014). Distal transport of dissolved hydrothermal iron in the deep South Pacific Ocean. *Proceedings of the National Academy of Sciences*, *111*(47), 16654–16661. https://doi.org/10.1073/pnas.1418778111

Fitzsimmons, J. N., & Conway, T. M. (2023). Novel insights into marine iron biogeochemistry from iron isotopes. *Annual Review of Marine Science*, *15*(1), 383–406. https://doi.org/10.1146/annurev-marine-032822-103431

Fitzsimmons, J. N., Conway, T. M., Lee, J.-M., Kayser, R., Thyng, K. M., John, S. G., & Boyle, E. A. (2016). Dissolved iron and iron isotopes in the southeastern Pacific Ocean. *Global Biogeochemical Cycles*, *30*(10), 1372–1395. https://doi.org/10.1002/2015GB005357

Fitzwater, S. E., Johnson, K. S., Gordon, R. M., Coale, K. H., & Smith, W. O. (2000). Trace metal concentrations in the Ross Sea and their relationship with nutrients and phytoplankton growth. *Deep Sea Research Part II: Topical Studies in Oceanography*, *47*(15), 3159–3179. https://doi.org/10.1016/S0967-0645(00)00063-1

Frey, P. A., & Reed, G. H. (2012). The Ubiquity of Iron. *ACS Chemical Biology*, *7*(9), 1477–1481. https://doi.org/10.1021/cb300323q

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., & Maynard, V. (1979). Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: Suboxic diagenesis. *gca*, *43*(7), 1075–1090. https://doi.org/10.1016/0016-7037(79)90095-4

Gaillardet, J., Viers, J., & Dupre, B. (2013). Trace elements in river waters. In J. I. Drever (Ed.), *Surface and Groundwater Weathering and Soils* (pp. 225–272). Elsevier-Pergamon.

German, C. R., & Elderfield, H. (1990). Application of the Ce anomaly as a paleoredox indicator: The ground rules. *Paleoceanography*, *5*(5), 823–833. https://doi.org/10.1029/PA005i005p00823

Ginoux, P., Prospero, J. M., Gill, T. E., Hsu, N. C., & Zhao, M. (2012). Global-scale attribution of anthropogenic and natural dust sources and their emission rates based on MODIS Deep Blue aerosol products. *Reviews of Geophysics*, *50*(3). https://doi.org/10.1029/2012RG000388

Gledhill, M., & van den Berg, C. M. G. (1994). Determination of complexation of iron(III) with natural organic complexing ligands in seawater using cathodic stripping voltammetry. *Marine Chemistry*, *47*(1), 41–54. https://doi.org/10.1016/0304-4203(94)90012-4

Gordon, R. M., Martin, J. H., & Knauer, G. A. (1982). Iron in north-east Pacific waters. *Nature*, *299*(5884), 611–612. https://doi.org/10.1038/299611a0

Goudie, A. S., & Middleton, N. J. (2001). Saharan dust storms: Nature and consequences. *Earth-Science Reviews*, *56*(1), 179–204. https://doi.org/10.1016/S0012-8252(01)00067-8

Guilbaud, R., Butler Ian, B., & Ellam Rob, M. (2011). Abiotic Pyrite Formation Produces a Large Fe Isotope Fractionation. *Science*, *332*(6037), 1548–1551. https://doi.org/10.1126/science.1202924

Hamme, R. C., Berry, J. E., Klymak, J. M., & Denman, K. L. (2015). In situ O2 and N2 measurements detect deep-water renewal dynamics in seasonally-anoxic Saanich Inlet. *Continental Shelf Research*, *106*, 107–117. https://doi.org/10.1016/j.csr.2015.06.012

Hamme, R. C., Raftery, E. C., & Sorensen, J. V. (2017). *NSERC Cruise Report for the Saanich Inlet Redox Experiment (SaanDox): Program period 2016-2017* [Unpublished].

Hem, J. D., & Cropper, W. H. (1962). *Survey of ferrous-ferric chemical equilibria and redox potentials* (1459-A; Chemistry of Iron in Natural Water). U.S. Geological Survey.

Herlinveaux, R. H. (1962). Oceanography of Saanich Inlet in Vancouver Island, British Columbia. *Journal of the Fisheries Research Board of Canada*, *19*(1), 1–37. https://doi.org/10.1139/f62-001

Holland, H. D. (1999). When did the Earth's atmosphere become oxic? A reply. *The Geochemical News*, *100*, 20–21.

Holland, H. D. (2006). The oxygenation of the atmosphere and oceans. *Philosophical Transactions of the Royal Society of London. Series B, Biological Sciences*, *361*(1470), 903–915. PubMed. https://doi.org/10.1098/rstb.2006.1838

Holmden, C., Amini, M., & Francois, R. (2015). Uranium isotope fractionation in Saanich Inlet: A modern analog study of a paleoredox tracer. *Geochimica et Cosmochimica Acta*, *153*, 202–215. https://doi.org/10.1016/j.gca.2014.11.012

Homoky, W. B., Conway, T. M., John, S. G., König, D., Deng, F., Tagliabue, A., & Mills, R. A. (2021). Iron colloids dominate sedimentary supply to the ocean interior. *Proceedings of the National Academy of Sciences*, *118*(13), e2016078118. https://doi.org/10.1073/pnas.2016078118

Homoky, W. B., Hembury, D. J., Hepburn, L. E., Mills, R. A., Statham, P. J., Fones, G. R., & Palmer, M. R. (2011). Iron and manganese diagenesis in deep sea volcanogenic sediments and the origins of pore water colloids. *Geochimica et Cosmochimica Acta*, *75*(17), 5032–5048. https://doi.org/10.1016/j.gca.2011.06.019

Homoky, W. B., John, S. G., Conway, T. M., & Mills, R. A. (2013). Distinct iron isotopic signatures and supply from marine sediment dissolution. *Nature Communications*, *4*(1), 2143. https://doi.org/10.1038/ncomms3143

Homoky, W. B., Severmann, S., Mills, R. A., Statham, P. J., & Fones, G. R. (2009). Pore-fluid Fe isotopes reflect the extent of benthic Fe redox recycling: Evidence from continental shelf and deep-sea sediments. *Geology*, *37*(8), 751–754. https://doi.org/10.1130/G25731A.1

Hunt, H. R., Summers, B. A., Sieber, M., Krisch, S., Al-Hashem, A., Hopwood, M., Achterberg, E. P., & Conway, T. M. (2022). Distinguishing the influence of sediments, the Congo River, and water-mass mixing on the distribution of iron and its isotopes in the Southeast Atlantic Ocean. *Marine Chemistry*, *247*, 104181. https://doi.org/10.1016/j.marchem.2022.104181

Isley, A. E., & Abbott, D. H. (1999). Plume-related mafic volcanism and the deposition of banded iron formation. *Journal of Geophysical Research: Solid Earth*, *104*(B7), 15461–15477. https://doi.org/10.1029/1999JB900066

Jacobs, L., & Emerson, S. (1982). Trace metal solubility in an anoxic fjord. *Earth and Planetary Science Letters*, *60*(2), 237–252. https://doi.org/10.1016/0012-821X(82)90006-1

John, S. G., Mendez, J., Moffett, J., & Adkins, J. (2012). The flux of iron and iron isotopes from San Pedro Basin sediments. *Geochimica et Cosmochimica Acta*, *93*, 14–29. https://doi.org/10.1016/j.gca.2012.06.003

Johnson, C., Beard, B., & Weyer, S. (2020). *Iron Geochemistry: An Isotopic Perspective*. https://doi.org/10.1007/978-3-030-33828-2

Johnson, C., Skulan, J., Beard, B., Sun, H., Nealson, K., & Braterman, P. (2002). Isotopic fractionation between Fe(III) and Fe(II) in aqueous solutions. *Earth and Planetary Science Letters*, *195*, 141–153. https://doi.org/10.1016/S0012-821X(01)00581-7

Johnson, K., Chavez, F. P., & Friederich, G. E. (1999). Continental-shelf sediment as a primary source of iron for coastal phytoplankton. *Nature*, *398*(6729), 697–700. https://doi.org/10.1038/19511

Johnson, K., Gordon, R. M., & Coale, K. H. (1997). What controls dissolved iron concentrations in the world ocean? *Marine Chemistry*, *57*(3), 137–161. https://doi.org/10.1016/S0304-4203(97)00043-1

Katsuta, N., Shimizu, I., Helmstaedt, H., Takano, M., Kawakami, S., & Kumazawa, M. (2012). Major element distribution in Archean banded iron formation (BIF): Influence of metamorphic differentiation. *Journal of Metamorphic Geology*, *30*(5), 457–472. https://doi.org/10.1111/j.1525-1314.2012.00975.x

Kendall, C., & Caldwell, E. A. (1998). Fundamentals of Isotope Geochemistry. In C. Kendall & J. J. McDonnell (Eds.), *Isotope Tracers in Catchment Hydrology* (pp. 51–86). Elsevier Science.

Kohfeld, K., & Ridgwell, A. (2009). Glacial-interglacial variability in atmospheric CO2. In *Surface Ocean-Lower Atmosphere Processes* (p. 350 pp).

Krachler, R., Jirsa, F., & Ayromlou, S. (2005). Factors influencing the dissolved iron input by river water to the open ocean. *Biogeosciences*, *2*(4), 311–315. https://doi.org/10.5194/bg-2-311-2005

Kuma, K., Nishioka, J., & Matsunaga, K. (1996). Controls on iron(III) hydroxide solubility in seawater: The influence of pH and natural organic chelators. *Limnology and Oceanography*, *41*(3), 396–407. https://doi.org/10.4319/lo.1996.41.3.0396

Lacan, F., Radic, A., Labatut, M., Jeandel, C., Poitrasson, F., Sarthou, G., Pradoux, C., Chmeleff, J., & Freydier, R. (2010). High-Precision Determination of the Isotopic Composition of Dissolved Iron in Iron Depleted Seawater by Double Spike Multicollector-ICPMS. *Analytical Chemistry*, *82*(17), 7103–7111. https://doi.org/10.1021/ac1002504

Lam, P. J., Lee, J.-M., Heller, M. I., Mehic, S., Xiang, Y., & Bates, N. R. (2018). Size-fractionated distributions of suspended particle concentration and major phase composition from the U.S. GEOTRACES Eastern Pacific Zonal Transect (GP16). *Marine Chemistry*, *201*, 90–107. https://doi.org/10.1016/j.marchem.2017.08.013

Landing, W. M., & Bruland, K. W. (1987). The contrasting biogeochemistry of iron and manganese in the Pacific Ocean. *Geochimica et Cosmochimica Acta*, *51*(1), 29–43. https://doi.org/10.1016/0016-7037(87)90004-4

Landing, W. M., & Lewis, B. L. (1991). Thermodynamic Modeling of Trace Metal Speciation in the Black Sea. In E. İzdar & J. W. Murray (Eds.), *Black Sea Oceanography* (pp. 125–160). Springer Netherlands. https://doi.org/10.1007/978-94-011-2608-3_8

Lewis, B. L., & Landing, W. M. (1991). The biogeochemistry of manganese and iron in the Black Sea. *Black Sea Oceanography: Results from the 1988 Black Sea Expedition*, *38*, S773–S803. https://doi.org/10.1016/S0198-0149(10)80009-3

Liu, X., & Millero, F. J. (2002). The solubility of iron in seawater. *Marine Chemistry*, *77*(1), 43–54. https://doi.org/10.1016/S0304-4203(01)00074-3

Lotfi-Kalahroodi, E., Pierson-Wickmann, A.-C., Rouxel, O., Marsac, R., Bouhnik-Le Coz, M., Hanna, K., & Davranche, M. (2021). More than redox, biological organic ligands control iron isotope fractionation in the riparian wetland. *Scientific Reports*, *11*(1), 1933. https://doi.org/10.1038/s41598-021-81494-z

Lovley, D. R. (1991). Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiological Reviews*, *55*(2), 259–287. https://doi.org/10.1128/mr.55.2.259-287.1991

Luo, C., Mahowald, N., Bond, T., Chuang, P. Y., Artaxo, P., Siefert, R., Chen, Y., & Schauer, J. (2008). Combustion iron distribution and deposition. *Global Biogeochemical Cycles*, *22*(1). https://doi.org/10.1029/2007GB002964

Mahowald, N. M., Engelstaedter, S., Luo, C., Sealy, A., Artaxo, P., Benitez-Nelson, C., Bonnet, S., Chen, Y., Chuang, P. Y., Cohen, D. D., Dulac, F., Herut, B., Johansen, A. M., Kubilay, N., Losno, R., Maenhaut, W., Paytan, A., Prospero, J. M., Shank, L. M., & Siefert, R. L. (2009). Atmospheric Iron Deposition: Global Distribution, Variability, and Human Perturbations. *Annual Review of Marine Science*, *1*(1), 245–278. https://doi.org/10.1146/annurev.marine.010908.163727

Mansor, M., & Fantle, M. S. (2019). A novel framework for interpreting pyrite-based Fe isotope records of the past. *Geochimica et Cosmochimica Acta*, *253*, 39–62. https://doi.org/10.1016/j.gca.2019.03.017

Martin, J. H. (1990). Glacial-interglacial CO2 change: The Iron Hypothesis. *Paleoceanography*, *5*(1), 1–13. https://doi.org/10.1029/PA005i001p00001

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

Martínez-García, A., Sigman, D. M., Ren, H., Anderson, R. F., Straub, M., Hodell, D. A., Jaccard, S. L., Eglinton, T. I., & Haug, G. H. (2014). Iron Fertilization of the Subantarctic Ocean During the Last Ice Age. *Science*, *343*(6177), 1347–1350. https://doi.org/10.1126/science.1246848

Masson, D. (2002). Deep Water Renewal in the Strait of Georgia. *Estuarine, Coastal and Shelf Science*, *54*(1), 115–126. https://doi.org/10.1006/ecss.2001.0833

Masson, D. (2006). Seasonal Water Mass Analysis for the Straits of Juan de Fuca and Georgia. *Atmosphere-Ocean*, *44*(1), 1–15. https://doi.org/10.3137/ao.440101

McKinney, R. E., & Conway, R. A. (1957). Chemical Oxygen in Biological Waste Treatment. *Sewage and Industrial Wastes*, *29*(10), 1097–1106. JSTOR.

Middag, R., Zitoun, R., & Conway, T. (2023). Trace Metals. In J. Blasco & A. Tovar-Sánchez (Eds.), *Marine Analytical Chemistry* (pp. 103–198). Springer International Publishing. https://doi.org/10.1007/978-3-031-14486-8_3

Millero, F. J. (2013). *Chemical oceanography* (Fourth edition). Taylor & Francis Group.

Morford, J. L., Russell, A. D., & Emerson, S. (2001). Trace metal evidence for changes in the redox environment associated with the transition from terrigenous clay to diatomaceous sediment, Saanich Inlet, BC. *Marine Geology*, *174*(1), 355–369. https://doi.org/10.1016/S0025-3227(00)00160-2

Morgan, J. W., & Anders, E. (1980). Chemical composition of Earth, Venus, and Mercury. *Proceedings of the National Academy of Sciences*, *77*(12), 6973–6977. https://doi.org/10.1073/pnas.77.12.6973

Murray, J. W., Grundmanis, V., & Smethie, W. M. (1978). Interstitial water chemistry in the sediments of Saanich Inlet. *Geochimica et Cosmochimica Acta*, *42*(7), 1011–1026. https://doi.org/10.1016/0016-7037(78)90290-9

Nasemann, P., Gault-Ringold, M., Stirling, C. H., Koschinsky, A., & Sander, S. G. (2018). Processes affecting the isotopic composition of dissolved iron in hydrothermal plumes: A case study from the Vanuatu back-arc. *Chemical Geology*, *476*, 70–84. https://doi.org/10.1016/j.chemgeo.2017.11.005

Ohmoto, H. (1997). When did the Earth's atmosphere become oxic? *The Geochemical News*, *93*, 12–13, 26–27.

Patterson, C., C., & Settle, D., M. (1976). The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting, handling, and analysis. *Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis*, *1*, 321–351.

Planavsky, N., Rouxel, O. J., Bekker, A., Hofmann, A., Little, C. T. S., & Lyons, T. W. (2012). Iron isotope composition of some Archean and Proterozoic iron formations. *Geochimica et Cosmochimica Acta*, *80*, 158–169. https://doi.org/10.1016/j.gca.2011.12.001

Poitrasson, F. (2011). Iron Isotopes. In M. Gargaud, R. Amils, J. C. Quintanilla, H. J. (Jim) Cleaves, W. M. Irvine, D. L. Pinti, & M. Viso (Eds.), *Encyclopedia of Astrobiology* (pp. 852–855). Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-11274-4_811

Poulton, S. W., & Canfield, D. E. (2011). Ferruginous Conditions: A Dominant Feature of the Ocean through Earth's History. *Elements*, *7*(2), 107–112. https://doi.org/10.2113/gselements.7.2.107

Raiswell, R., Benning, L. G., Tranter, M., & Tulaczyk, S. (2008). Bioavailable iron in the Southern Ocean: The significance of the iceberg conveyor belt. *Geochemical Transactions*, *9*(1), 7. https://doi.org/10.1186/1467-4866-9-7

Raiswell, R., Tranter, M., Benning, L. G., Siegert, M., De'ath, R., Huybrechts, P., & Payne, T. (2006). Contributions from glacially derived sediment to the global iron (oxyhydr)oxide cycle: Implications for iron delivery to the oceans. *Geochimica et Cosmochimica Acta*, *70*(11), 2765–2780. https://doi.org/10.1016/j.gca.2005.12.027

Rapp, I., Schlosser, C., Browning, T. J., Wolf, F., Le Moigne, F. A. C., Gledhill, M., & Achterberg, E. P. (2020). El Niño-Driven Oxygenation Impacts Peruvian Shelf Iron Supply to the South Pacific Ocean. *Geophysical Research Letters*, *47*(7), e2019GL086631. https://doi.org/10.1029/2019GL086631

Resing, J. A., Sedwick, P. N., German, C. R., Jenkins, W. J., Moffett, J. W., Sohst, B. M., & Tagliabue, A. (2015). Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean. *Nature*, *523*(7559), 200–203. https://doi.org/10.1038/nature14577

Reyes, C., Dellwig, O., Dähnke, K., Gehre, M., Noriega-Ortega, B. E., Böttcher, M. E., Meister, P., & Friedrich, M. W. (2016). Bacterial communities potentially involved in iron-cycling in Baltic Sea and North Sea sediments revealed by pyrosequencing. *FEMS Microbiology Ecology*, *92*(4). https://doi.org/10.1093/femsec/fiw054

Rickard, D., & Luther, G. W. (2007). Chemistry of Iron Sulfides. *Chemical Reviews*, *107*(2), 514–562. https://doi.org/10.1021/cr0503658

Ripperger, S., & Rehkämper, M. (2007). Precise determination of cadmium isotope fractionation in seawater by double spike MC-ICPMS. *Geochimica et Cosmochimica Acta*, *71*(3), 631–642. https://doi.org/10.1016/j.gca.2006.10.005

Roberts, A. P. (2015). Magnetic mineral diagenesis. *Earth-Science Reviews*, *151*, 1–47. https://doi.org/10.1016/j.earscirev.2015.09.010

Rolison, J. M., Stirling, C. H., Middag, R., Gault-Ringold, M., George, E., & Rijkenberg, M. J. A. (2018). Iron isotope fractionation during pyrite formation in a sulfidic Precambrian ocean analogue. *Earth and Planetary Science Letters*, *488*, 1–13. https://doi.org/10.1016/j.epsl.2018.02.006

Röthlisberger, R., Bigler, M., Wolff, E. W., Joos, F., Monnin, E., & Hutterli, M. A. (2004). Ice core evidence for the extent of past atmospheric CO2 change due to iron fertilisation. *Geophysical Research Letters*, *31*(16). https://doi.org/10.1029/2004GL020338

Rouxel, O. J., Bekker, A., & Edwards, K. J. (2005). Iron isotope constraints on the Archean and Paleoproterozoic Ocean redox state. *Science*, *307*(5712), 1088–1091. https://doi.org/10.1126/science.1105692

Rouxel, O. J., Bekker, A., & Edwards, K. J. (2006). Response to Comment on "Iron Isotope Constraints on the Archean and Paleoproterozoic Ocean Redox State." *Science*, *311*(5758), 177–177. https://doi.org/10.1126/science.1118420

Rouxel, O. J., Shanks, W. C., Bach, W., & Edwards, K. J. (2008). Integrated Fe- and S-isotope study of seafloor hydrothermal vents at East Pacific Rise 9–10°N. *Chemical Geology*, *252*(3), 214–227. https://doi.org/10.1016/j.chemgeo.2008.03.009

Rouxel, O. J., Toner, B. M., Manganini, S. J., & German, C. R. (2016). Geochemistry and iron isotope systematics of hydrothermal plume fall-out at East Pacific Rise 9°50′N. *Chemical Geology*, *441*, 212–234. https://doi.org/10.1016/j.chemgeo.2016.08.027

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. *The Chemistry of Iron in Seawater and Its Interaction with Phytoplankton*, *50*(1), 117–138. https://doi.org/10.1016/0304-4203(95)00031-L

Saito, M. A., Noble, A. E., Tagliabue, A., Goepfert, T. J., Lamborg, C. H., & Jenkins, W. J. (2013). Slow-spreading submarine ridges in the South Atlantic as a significant oceanic iron source. *Nature Geoscience*, *6*(9), 775–779. https://doi.org/10.1038/ngeo1893

Sanial, V., Kipp, L. E., Henderson, P. B., van Beek, P., Reyss, J. L., Hammond, D. E., Hawco, N. J., Saito, M. A., Resing, J. A., Sedwick, P., Moore, W. S., & Charette, M. A. (2018). Radium-228 as a tracer of dissolved trace element inputs from the Peruvian continental margin. *Marine Chemistry*, *201*, 20–34. https://doi.org/10.1016/j.marchem.2017.05.008

Schlitzer, R. et al. (2021). *The GEOTRACES Intermediate Data Product 2021.* https://www.bodc.ac.uk/data/published_data_library/catalogue/10.5285/cf2d9ba9-d51d-3b7c-e053-8486abc0f5fd/

Schmidt, K., Garbe-Schönberg, D., Hannington, M. D., Anderson, M. O., Bühring, B., Haase, K., Haruel, C., Lupton, J., & Koschinsky, A. (2017). Boiling vapour-type fluids from the Nifonea vent field (New Hebrides Back-Arc, Vanuatu, SW Pacific): Geochemistry of an early-stage, post-eruptive hydrothermal system. *Geochimica et Cosmochimica Acta*, *207*, 185–209. https://doi.org/10.1016/j.gca.2017.03.016

Sedwick, P. N., Church, T. M., Bowie, A. R., Marsay, C. M., Ussher, S. J., Achilles, K. M., Lethaby, P. J., Johnson, R. J., Sarin, M. M., & McGillicuddy, D. J. (2005). Iron in the Sargasso Sea (Bermuda Atlantic Time-series Study region) during summer: Eolian imprint, spatiotemporal variability, and ecological implications. *Global Biogeochemical Cycles*, *19*(4). https://doi.org/10.1029/2004GB002445

Severmann, S., Johnson, C. M., Beard, B. L., & McManus, J. (2006). The effect of early diagenesis on the Fe isotope compositions of porewaters and authigenic minerals in continental margin sediments. *Geochimica et Cosmochimica Acta*, *70*(8), 2006–2022. https://doi.org/10.1016/j.gca.2006.01.007

Severmann, S., Lyons, T. W., Anbar, A., McManus, J., & Gordon, G. (2008). Modern iron isotope perspective on the benthic iron shuttle and the redox evolution of ancient oceans. *Geology*, *36*(6), 487–490. https://doi.org/10.1130/G24670A.1

Severmann, S., McManus, J., Berelson, W. M., & Hammond, D. E. (2010). The continental shelf benthic iron flux and its isotope composition. *Geochimica et Cosmochimica Acta*, *74*(14), 3984–4004. https://doi.org/10.1016/j.gca.2010.04.022

Sharp, Z. (2007). *Principles of stable isotope geochemistry*. Pearson/Prentice Hall; /z-wcorg/. http://catalog.hathitrust.org/api/volumes/oclc/62330665.html

Sieber, M., Conway, T. M., de Souza, G. F., Hassler, C. S., Ellwood, M. J., & Vance, D. (2021). Isotopic fingerprinting of biogeochemical processes and iron sources in the iron-limited surface Southern Ocean. *Earth and Planetary Science Letters*, *567*, 116967. https://doi.org/10.1016/j.epsl.2021.116967

Sieber, M., Conway, T. M., de Souza, G. F., Obata, H., Takano, S., Sohrin, Y., & Vance, D. (2019). Physical and biogeochemical controls on the distribution of dissolved cadmium and its isotopes in the Southwest Pacific Ocean. *Chemical Geology*, *511*, 494–509. https://doi.org/10.1016/j.chemgeo.2018.07.021

Siebert, C., Nägler, T. F., & Kramers, J. D. (2001). Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. *Geochemistry, Geophysics, Geosystems*, *2*(7). https://doi.org/10.1029/2000GC000124

Sigman, D. M., & Boyle, E. A. (2000). Glacial/interglacial variations in atmospheric carbon dioxide. *Nature*, *407*(6806), 859–869. https://doi.org/10.1038/35038000

Sigman, D. M., Hain, M. P., & Haug, G. H. (2010). The polar ocean and glacial cycles in atmospheric CO2 concentration. *Nature*, *466*(7302), 47–55. https://doi.org/10.1038/nature09149

Skulan, J. L., Beard, B. L., & Johnson, C. M. (2002). Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(III) and hematite. *Geochimica et Cosmochimica Acta*, *66*(17), 2995–3015. https://doi.org/10.1016/S0016-7037(02)00902-X

Smith, A. J. B. (2015). RESEARCH FOCUS: The life and times of banded iron formations. *Geology*, *43*(12), 1111–1112. https://doi.org/10.1130/focus122015.1

Smith, K. L., Robison, B. H., Helly, J. J., Kaufmann, R. S., Ruhl, H. A., Shaw, T. J., Twining, B. S., & Vernet, M. (2007). Free-Drifting Icebergs: Hot Spots of Chemical and Biological Enrichment in the Weddell Sea. *Science*, *317*(5837), 478–482. https://doi.org/10.1126/science.1142834

Soetaert, G., Hamme, R. C., & Raftery, E. (2022). Renewal of seasonally anoxic Saanich Inlet is temporally and spatially dynamic. *Frontiers*.

Staubwasser, M., Schoenberg, R., von Blanckenburg, F., Krüger, S., & Pohl, C. (2013). Isotope fractionation between dissolved and suspended particulate Fe in the oxic and anoxic water column of the Baltic Sea. *Biogeosciences*, *10*(1), 233–245. https://doi.org/10.5194/bg-10-233-2013

Stumm, W., & Morgan, J. J. (1995). *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. John Wiley & Sons, Incorporated. http://ebookcentral.proquest.com/lib/usf/detail.action?docID=1550541

Tagliabue, A., Aumont, O., DeAth, R., Dunne, J. P., Dutkiewicz, S., Galbraith, E., Misumi, K., Moore, J. K., Ridgwell, A., Sherman, E., Stock, C., Vichi, M., Völker, C., & Yool, A. (2016). How well do global ocean biogeochemistry models simulate dissolved iron distributions? *Global Biogeochemical Cycles*, *30*(2), 149–174. https://doi.org/10.1002/2015GB005289

Tan, S.-C., Li, J., Che, H., Chen, B., & Wang, H. (2017). Transport of East Asian dust storms to the marginal seas of China and the southern North Pacific in spring 2010. *Atmospheric Environment*, *148*, 316–328. https://doi.org/10.1016/j.atmosenv.2016.10.054

Teutsch, N., Schmid, M., Müller, B., Halliday, A., Bürgmann, H., & Wehrli, B. (2009). Large iron isotope fractionation at the oxic-anoxic boundary in Lake Nyos. *Earth and Planetary Science Letters*, *285*, 52–60. https://doi.org/10.1016/j.epsl.2009.05.044

Thomson, R., E. (1994). *Physical oceanography of the Strait of Georgia—Puget Sound—Juan de Fuca Strait System* (Canadian Technical Report of Fisheries and Aquatic Sciences 1948; Review of the Marine Environment and Biota of Strait of Georgia, Puget Sound, and Juan de Fuca Strait, pp. 36–100).

Tian, H.-A., van Manen, M., Bunnell, Z. B., Jung, J., Lee, S. H., Kim, T.-W., Reichart, G.-J., Conway, T. M., & Middag, R. (2023). Biogeochemistry of iron in coastal Antarctica: Isotopic insights for external sources and biological uptake in the Amundsen Sea polynyas. *Geochimica et Cosmochimica Acta*, *363*, 51–67. https://doi.org/10.1016/j.gca.2023.10.029

Timothy, D. A., & Soon, M. Y. S. (2001). Primary production and deep-water oxygen content of two British Columbian fjords. *Marine Chemistry*, *73*(1), 37–51. https://doi.org/10.1016/S0304-4203(00)00071-2

Toner, B. M., Marcus, M. A., Edwards, K. J., Rouxel, O., & German, C. R. (2012). Measuring the form of iron in hydrothermal plume particles. *Oceanography*, *25*(1), 209–212. JSTOR.

Twining, B. S., & Baines, S. B. (2013). The trace metal composition of marine phytoplankton. *Annual Review of Marine Science*, *5*(1), 191–215. https://doi.org/10.1146/annurev-marine-121211-172322

Tyrrell, T., Merico, A., Waniek, J. J., Wong, C. S., Metzl, N., & Whitney, F. (2005). Effect of seafloor depth on phytoplankton blooms in high-nitrate, low-chlorophyll (HNLC) regions. *Journal of Geophysical Research: Biogeosciences*, *110*(G2). https://doi.org/10.1029/2005JG000041

Urey, H. C. (1947). The thermodynamic properties of isotopic substances. *Journal of the Chemical Society (Resumed)*, *0*, 562–581. https://doi.org/10.1039/JR9470000562

van Noort, D., & Wallace, A. W. (1965). Iron: Chlorophyll and synthesis. *California Agriculture*, *19*, 4–5.

Vargas, M., Kashefi, K., Blunt-Harris, E. L., & Lovley, D. R. (1998). Microbiological evidence for Fe(III) reduction on early Earth. *Nature*, *395*(6697), 65–67. https://doi.org/10.1038/25720

Vosteen, P., Spiegel, T., Gledhill, M., Frank, M., Zabel, M., & Scholz, F. (2022). The Fate of Sedimentary Reactive Iron at the Land-Ocean Interface: A Case Study From the Amazon Shelf. *Geochemistry, Geophysics, Geosystems*, *23*(11), e2022GC010543. https://doi.org/10.1029/2022GC010543

Waldichuk, M. (1957). Physical oceanography of the Strait of Georgia, British Columbia. *Journal of the Fisheries Research Board of Canada*, *14*(3), 321–486.

Wang, W., Lough, A. J. M., Goring-Harford, H., Flanagan, O., González-Santana, D., Resing, J., Connelly, D., Lohan, M. C., Tagliabue, A., & James, R. H. (2023). Fractionation of iron and chromium isotopes in hydrothermal plumes from the northern Mid-Atlantic Ridge. *Earth and Planetary Science Letters*, *624*, 118468. https://doi.org/10.1016/j.epsl.2023.118468

Watson, A. J., Bakker, D. C. E., Ridgwell, A. J., Boyd, P. W., & Law, C. S. (2000). Effect of iron supply on Southern Ocean CO2 uptake and implications for glacial atmospheric CO2. *Nature*, *407*(6805), 730–733. https://doi.org/10.1038/35037561

Welch, S. A., Beard, B. L., Johnson, C. M., & Braterman, P. S. (2003). Kinetic and equilibrium Fe isotope fractionation between aqueous Fe(II) and Fe(III). *Geochimica et Cosmochimica Acta*, *67*(22), 4231–4250. https://doi.org/10.1016/S0016-7037(03)00266-7

Wetz, M. S., Hales, B., Chase, Z., Wheeler, P. A., & Whitney, M. M. (2006). Riverine input of macronutrients, iron, and organic matter to the coastal ocean off Oregon, U.S.A., during the winter. *Limnology and Oceanography*, *51*(5), 2221–2231. https://doi.org/10.4319/lo.2006.51.5.2221

Whiticar, M. J., & Elvert, M. E. (2001). Organic geochemistry of Saanich Inlet, BC, during the Holocene as revealed by Ocean Drilling Program Leg 169S. *Marine Geology*, *174*(1), 249–271. https://doi.org/10.1016/S0025-3227(00)00154-7

Wu, L., Beard, B. L., Roden, E. E., & Johnson, C. M. (2011). Stable iron isotope fractionation between aqueous Fe(II) and hydrous ferric oxide. *Environmental Science & Technology*, *45*(5), 1847–1852. https://doi.org/10.1021/es103171x

Wu, L., Druschel, G., Findlay, A., Beard, B. L., & Johnson, C. M. (2012). Experimental determination of iron isotope fractionations among Feaq2+–FeSaq–Mackinawite at low temperatures: Implications for the rock record. *Geochimica et Cosmochimica Acta*, *89*, 46–61. https://doi.org/10.1016/j.gca.2012.04.047

Ziegler, M., Diz, P., Hall, I. R., & Zahn, R. (2013). Millennial-scale changes in atmospheric CO2 levels linked to the Southern Ocean carbon isotope gradient and dust flux. *Nature Geoscience*, *6*(6), 457–461. https://doi.org/10.1038/ngeo1782

APPENDIX A: COPYRIGHT PERMISSION DOCUMENTS

JOHN WILEY AND SONS LICENSE
TERMS AND CONDITIONS

Mar 25, 2024

This Agreement between Ms. Claire Onak ("You") and John Wiley and Sons ("John Wiley and Sons") consists of your license details and the terms and conditions provided by John Wiley and Sons and Copyright Clearance Center.

License Number	5756021077675
License date	Mar 25, 2024
Licensed Content Publisher	John Wiley and Sons
Licensed Content Publication	Geobiology
Licensed Content Title	Towards a consistent classification scheme for geochemical environments, or, why we wish the term ‘suboxic’ would go away
Licensed Content Author	B. THAMDRUP, D. E. CANFIELD
Licensed Content Date	Aug 11, 2009
Licensed Content Volume	7

Licensed Content Issue	4
Licensed Content Pages	8
Type of use	Dissertation/Thesis
Requestor type	University/Academic
Format	Print and electronic
Portion	Figure/table
Number of figures/tables	1
Will you be translating?	No
Title of new work	Iron Isotope Transformations in Saanich Inlet
Institution name	University of South Florida
Expected presentation date	Apr 2024
Portions	Fig.1 on page 386
Requestor Location	Ms. Claire Onak 830 1st St S SAINT PETERSBURG, FL 33701

United States
Attn: Ms. Claire Onak

Publisher Tax ID EU826007151

Total 0.00 USD

Terms and Conditions

TERMS AND CONDITIONS

This copyrighted material is owned by or exclusively licensed to John Wiley & Sons, Inc. or one of its group companies (each a"Wiley Company") or handled on behalf of a society with which a Wiley Company has exclusive publishing rights in relation to a particular work (collectively "WILEY"). By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the billing and payment terms and conditions established by the Copyright Clearance Center Inc., ("CCC's Billing and Payment terms and conditions"), at the time that you opened your RightsLink account (these are available at any time at http://myaccount.copyright.com).

Terms and Conditions

- The materials you have requested permission to reproduce or reuse (the "Wiley Materials") are protected by copyright.
- You are hereby granted a personal, non-exclusive, non-sub licensable (on a stand-alone basis), non-transferable, worldwide, limited license to reproduce the Wiley Materials for the purpose specified in the licensing process. This license, **and any CONTENT (PDF or image file) purchased as part of your order,** is for a one-time use only and limited to any maximum distribution number specified in the license. The first instance of republication or reuse granted by this license must be completed within two years of the date of the grant of this license (although copies prepared before the end date may be distributed thereafter). The Wiley Materials shall not be used in any other manner or for any other purpose, beyond what is granted in the license. Permission is granted subject to an appropriate acknowledgement given to the author, title of the material/book/journal and the publisher. You shall also duplicate the copyright notice that appears in the Wiley publication in your use of the Wiley Material. Permission is also granted on the understanding that nowhere in the text is a previously published source acknowledged for all or part of this Wiley Material. Any third party content is expressly excluded from this permission.

- With respect to the Wiley Materials, all rights are reserved. Except as expressly granted by the terms of the license, no part of the Wiley Materials may be copied, modified, adapted (except for minor reformatting required by the new Publication), translated, reproduced, transferred or distributed, in any form or by any means, and no derivative works may be made based on the Wiley Materials without the prior permission of the respective copyright owner.**For STM Signatory Publishers clearing permission under the terms of the STM Permissions Guidelines only, the terms of the license are extended to include subsequent editions and for editions in other languages, provided such editions are for the work as a whole in situ and does not involve the separate exploitation of the permitted figures or extracts,** You may not alter, remove or suppress in any manner any copyright, trademark or other notices displayed by the Wiley Materials. You may not license, rent, sell, loan, lease, pledge, offer as security, transfer or assign the Wiley Materials on a stand-alone basis, or any of the rights granted to you hereunder to any other person.

- The Wiley Materials and all of the intellectual property rights therein shall at all times remain the exclusive property of John Wiley & Sons Inc, the Wiley Companies, or their respective licensors, and your interest therein is only that of having possession of and the right to reproduce the Wiley Materials pursuant to Section 2 herein during the continuance of this Agreement. You agree that you own no right, title or interest in or to the Wiley Materials or any of the intellectual property rights therein. You shall have no rights hereunder other than the license as provided for above in Section 2. No right, license or interest to any trademark, trade name, service mark or other branding ("Marks") of WILEY or its licensors is granted hereunder, and you agree that you shall not assert any such right, license or interest with respect thereto

- NEITHER WILEY NOR ITS LICENSORS MAKES ANY WARRANTY OR REPRESENTATION OF ANY KIND TO YOU OR ANY THIRD PARTY, EXPRESS, IMPLIED OR STATUTORY, WITH RESPECT TO THE MATERIALS OR THE ACCURACY OF ANY INFORMATION CONTAINED IN THE MATERIALS, INCLUDING, WITHOUT LIMITATION, ANY IMPLIED WARRANTY OF MERCHANTABILITY, ACCURACY, SATISFACTORY QUALITY, FITNESS FOR A PARTICULAR PURPOSE, USABILITY, INTEGRATION OR NON-INFRINGEMENT AND ALL SUCH WARRANTIES ARE HEREBY EXCLUDED BY WILEY AND ITS LICENSORS AND WAIVED BY YOU.

- WILEY shall have the right to terminate this Agreement immediately upon breach of this Agreement by you.

- You shall indemnify, defend and hold harmless WILEY, its Licensors and their respective directors, officers, agents and employees, from and against any actual or threatened claims, demands, causes of action or proceedings arising from any breach of this Agreement by you.

- IN NO EVENT SHALL WILEY OR ITS LICENSORS BE LIABLE TO YOU OR ANY OTHER PARTY OR ANY OTHER PERSON OR ENTITY FOR ANY SPECIAL, CONSEQUENTIAL, INCIDENTAL, INDIRECT, EXEMPLARY OR PUNITIVE DAMAGES, HOWEVER CAUSED, ARISING OUT OF OR IN CONNECTION WITH THE DOWNLOADING, PROVISIONING, VIEWING OR USE OF THE MATERIALS REGARDLESS OF THE FORM OF ACTION, WHETHER FOR BREACH OF CONTRACT, BREACH OF WARRANTY, TORT, NEGLIGENCE, INFRINGEMENT OR OTHERWISE (INCLUDING, WITHOUT LIMITATION, DAMAGES BASED ON LOSS OF PROFITS, DATA, FILES, USE, BUSINESS OPPORTUNITY OR CLAIMS OF THIRD PARTIES), AND WHETHER OR NOT THE PARTY HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. THIS LIMITATION SHALL APPLY NOTWITHSTANDING ANY FAILURE OF ESSENTIAL PURPOSE OF ANY LIMITED REMEDY PROVIDED HEREIN.

- Should any provision of this Agreement be held by a court of competent jurisdiction to be illegal, invalid, or unenforceable, that provision shall be deemed amended to achieve as nearly as possible the same economic effect as the original provision, and the legality, validity and enforceability of the remaining provisions of this Agreement shall not be affected or impaired thereby.

- The failure of either party to enforce any term or condition of this Agreement shall not constitute a waiver of either party's right to enforce each and every term and condition of this Agreement. No breach under this agreement shall be deemed waived or excused by either party unless such waiver or consent is in writing signed by the party granting such waiver or consent. The waiver by or consent of a party to a breach of any provision of this Agreement shall not operate or be construed as a waiver of or consent to any other or subsequent breach by such other party.

- This Agreement may not be assigned (including by operation of law or otherwise) by you without WILEY's prior written consent.

- Any fee required for this permission shall be non-refundable after thirty (30) days from receipt by the CCC.

- These terms and conditions together with CCC's Billing and Payment terms and conditions (which are incorporated herein) form the entire agreement between you and WILEY concerning this licensing transaction and (in the absence of fraud) supersedes all prior agreements and representations of the parties, oral or written. This Agreement may not be amended except in writing signed by both parties. This Agreement shall be binding upon and inure to the benefit of the parties' successors, legal representatives, and authorized assigns.

- In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall prevail.

- WILEY expressly reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

- This Agreement will be void if the Type of Use, Format, Circulation, or Requestor Type was misrepresented during the licensing process.

- This Agreement shall be governed by and construed in accordance with the laws of the State of New York, USA, without regards to such state's conflict of law rules. Any legal action, suit or proceeding arising out of or relating to these Terms and Conditions or the breach thereof shall be instituted in a court of competent jurisdiction in New York County in the State of New York in the United States of America and each party hereby consents and submits to the personal jurisdiction of such court, waives any objection to venue in such court and consents to service of process by registered or certified mail, return receipt requested, at the last known address of such party.

WILEY OPEN ACCESS TERMS AND CONDITIONS

Wiley Publishes Open Access Articles in fully Open Access Journals and in Subscription journals offering Online Open. Although most of the fully Open Access journals publish open access articles under the terms of the Creative Commons Attribution (CC BY) License only, the subscription journals and a few of the Open Access Journals offer a choice of Creative Commons Licenses. The license type is clearly identified on the article.

The Creative Commons Attribution License

The Creative Commons Attribution License (CC-BY) allows users to copy, distribute and transmit an article, adapt the article and make commercial use of the article. The CC-BY license permits commercial and non-

Creative Commons Attribution Non-Commercial License

The Creative Commons Attribution Non-Commercial (CC-BY-NC)License permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.(see below)

Creative Commons Attribution-Non-Commercial-NoDerivs License

The Creative Commons Attribution Non-Commercial-NoDerivs License (CC-BY-NC-ND) permits use, distribution and reproduction in any medium, provided the original work is properly cited, is not used for commercial purposes and no modifications or adaptations are made. (see below)

Novel Insights into Marine Iron Biogeochemistry from Iron Isotopes

Fitzsimmons, Jessica N.; Conway, Tim M. *Annual review of marine science*, 16 Jan 2023, Vol. 15, Issue 1, pages 383 - 406

ISSN: 19410611
DOI: 10.1146/annurev-marine-032822-103431
PMID: 36100217
Publisher: Annual Reviews

Language: English
Country: United States of America
URL: https://www.annualreviews.org/toc/marine/15/1

Less Details >

Abstract:

The micronutrient iron plays a major role in setting the magnitude and distribution of primary production across the global ocean. As such, an understanding of the sources, sinks, and internal cycling processes that drive the oceanic distribution of iron is key to unlocking iron's role in the global carbon cycle and climate, both today and in the geologic past. Iron isotopic analyses of seawater have emerged as a transformative tool for diagnosing iron sources to the ocean and tracing biogeochemical processes. In this review, we summarize the end-member isotope signatures of different iron source fluxes and highlight the novel insights into iron provenance gained using this tracer. We also review ways in which iron isotope fractionation might be used to understand internal oceanic cycling of iron, including speciation changes, biological uptake, and particle scavenging. We conclude with an overview of future research needed to expand the utilization of this cutting-edge tracer. Expected final online publication date for the Annual Review of Marine Science, Volume 15 is January 2023. Please see http://www.annualreviews.org/page/journal/pubdates for revised estimates.

CCC Marketplace

Order Number: 1465773
Order Date: 25 Mar 2024

Payment Information

Claire Onak
conak@usf.edu
Payment method: Invoice

Billing Address:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

+1 (906) 748-7232
conak@usf.edu

Customer Location:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

Order Details

1. Geochimica et cosmochimica acta

Billing Status: Open

Article: Iron isotope transformations in the meromictic Lake Cadagno

Order License ID	1465773-1	**Type of Use**	Republish in a thesis/dissertation
Order detail status	Completed		
ISSN	0016-7037	**Publisher**	PERGAMON
		Portion	Chart/graph/table/figure

0.00 USD
Republication Permission

LICENSED CONTENT

Publication Title	Geochimica et cosmochimica acta	**Rightsholder**	Elsevier Science & Technology Journals
Article Title	Iron isotope transformations in the meromictic Lake Cadagno	**Publication Type**	Journal
Author/Editor	GEOCHEMICAL SOCIETY., METEORITICAL SOCIETY.	**Start Page**	205
		End Page	221
Date	01/01/1950	**Volume**	255
Language	English, French, German		
Country	United Kingdom of Great Britain and Northern Ireland		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	United States
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language of publication
		Copies for the Disabled?	No
Format (select all that apply)	Print, Electronic	**Minor Editing Privileges?**	No
Who Will Republish the Content?	Academic institution	**Incidental Promotional Use?**	No
		Currency	USD
Duration of Use	Life of current edition		
Lifetime Unit Quantity	Up to 14,999		
Rights Requested	Main product		

NEW WORK DETAILS

Title	Iron Isotope Transformations in Saanich Inlet	**Institution Name**	University of South Florida
		Expected Presentation Date	2024-04-01
Instructor Name	Claire Onak		

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Claire Onak

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Fig. 3D. Iron isotope profiles	**Title of the Article / Chapter the Portion Is From**	Iron isotope transformations in the meromictic Lake Cadagno
Editor of Portion(s)	Ellwood, Michael J.; Hassler, Christel; Moisset, Sophie; Pascal, Ludovic; Danza, Francesco; Peduzzi, Sandro; Tonolla, Mauro; Vance, Derek	**Author of Portion(s)**	Ellwood, Michael J.; Hassler, Christel; Moisset, Sophie; Pascal, Ludovic; Danza, Francesco; Peduzzi, Sandro; Tonolla, Mauro; Vance, Derek
Volume / Edition	255	**Publication Date of Portion**	2019-06-15
Page or Page Range of Portion	205-221		

Elsevier Science & Technology Journals Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals, for which an author selects a user license permitting certain types of reuse without permission. Before proceeding please check if the article is Open Access on http://www.sciencedirect.com and refer to the user license for the individual article. Any reuse not included in the user license terms will require permission. You must always fully and appropriately credit the author and source. If any part of the material to be used (for example, figures) has appeared in the Elsevier publication for which you are seeking permission, with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder. Please contact permissions@elsevier.com with any queries.

Total Items: 1

Subtotal: 0.00 USD

Order Total: 0.00 USD

Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following

authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise,

CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c) (i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

Isotope fractionation between dissolved and suspended particulate Fe in the oxic and anoxic water column of the Baltic Sea

Staubwasser, M.; Schoenberg, R.; Von Blanckenburg, F.; Krüger, S.; ...More *Biogeosciences*, 15 Jan 2013, Vol. 10, Issue 1, pages 233 - 245

ISSN: 17264189
DOI: 10.5194/bg-10-233-2013
Publisher: Copernicus GmbH; COPERNICUS GMBH

Language: English
Country: Germany
URL: https://bg.copernicus.org/articles/10/233/2013/

CC BY 3.0 DEED

Attribution 3.0 Unported

Notice

This is an older version of this license. Compared to previous versions, the 4.0 versions of all CC licenses are more user-friendly and more internationally robust . If you are licensing your own work , we strongly recommend the use of the 4.0 license instead: CC BY 4.0 Deed | Attribution 4.0 International

Canonical URL : https://creativecommons.org/licenses/by/3.0/

See the legal code

You are free to:

Share — copy and redistribute the material in any medium or format for any purpose, even commercially.

Adapt — remix, transform, and build upon the material for any purpose, even commercially.

The licensor cannot revoke these freedoms as long as you follow the license terms.

Under the following terms:

Attribution — You must give appropriate credit , provide a link to the license, and indicate if changes were made . You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use.

No additional restrictions — You may not apply legal terms or technological measures that legally restrict others from doing anything the license permits.

Notices:

You do not have to comply with the license for elements of the material in the public domain or where your use is permitted by an applicable exception or limitation .

No warranties are given. The license may not give you all of the permissions necessary for your intended use. For example, other rights such as publicity, privacy, or moral rights may limit how you use the material.

CCC Marketplace

Order Number: 1465779
Order Date: 25 Mar 2024

Payment Information

Claire Onak
conak@usf.edu
Payment method: Invoice

Billing Address:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

+1 (906) 748-7232
conak@usf.edu

Customer Location:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

Order Details

1. Earth and planetary science letters

Billing Status: Open

Article: Iron isotope fractionation during pyrite formation in a sulfidic Precambrian ocean analogue

Order License ID	1465779-1	**Type of Use**	Republish in a thesis/dissertation
Order detail status	Completed		
ISSN	0012-821X	**Publisher**	ELSEVIER BV
		Portion	Chart/graph/table/figure

0.00 USD
Republication Permission

LICENSED CONTENT

Publication Title	Earth and planetary science letters	**Rightsholder**	Elsevier Science & Technology Journals
Article Title	Iron isotope fractionation during pyrite formation in a sulfidic Precambrian ocean analogue	**Publication Type**	Journal
		Start Page	1
		End Page	13
Date	01/01/1966	**Volume**	488
Language	English, French, German		
Country	Netherlands		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	United States
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language of publication
		Copies for the Disabled?	No
Format (select all that apply)	Print, Electronic	**Minor Editing Privileges?**	No
Who Will Republish the Content?	Academic institution	**Incidental Promotional Use?**	No
		Currency	USD
Duration of Use	Life of current edition		
Lifetime Unit Quantity	Up to 499		
Rights Requested	Main product		

NEW WORK DETAILS

Title	Iron Isotope Transformations in Saanich Inlet	**Institution Name**	University of South Florida
		Expected Presentation Date	2024-04-01

Instructor Name	Claire Onak

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Claire Onak

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Fig. 2D. Water column depth profiles of delta56Fe in the Black Sea.	**Title of the Article / Chapter the Portion Is From**	Iron isotope fractionation during pyrite formation in a sulfidic Precambrian ocean analogue
Editor of Portion(s)	Gault-Ringold, Melanie; George, Ejin; Middag, Rob; Rijkenberg, Micha J.A.; Rolison, John M.; Stirling, Claudine H.	**Author of Portion(s)**	Gault-Ringold, Melanie; George, Ejin; Middag, Rob; Rijkenberg, Micha J.A.; Rolison, John M.; Stirling, Claudine H.
Volume / Edition	488		
Page or Page Range of Portion	1-13	**Publication Date of Portion**	2018-04-01

Elsevier Science & Technology Journals Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals, for which an author selects a user license permitting certain types of reuse without permission. Before proceeding please check if the article is Open Access on http://www.sciencedirect.com and refer to the user license for the individual article. Any reuse not included in the user license terms will require permission. You must always fully and appropriately credit the author and source. If any part of the material to be used (for example, figures) has appeared in the Elsevier publication for which you are seeking permission, with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder. Please contact permissions@elsevier.com with any queries.

Total Items: 1

Subtotal: 0.00 USD

Order Total: 0.00 USD

Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such

discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is

terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is

used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

CCC Marketplace

Order Number: 1465786
Order Date: 25 Mar 2024

Payment Information

Claire Onak
conak@usf.edu
Payment method: Invoice

Billing Address:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

+1 (906) 748-7232
conak@usf.edu

Customer Location:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

Order Details

1. Journal of the Fisheries Research Board of Canada

Billing Status: Open

Article: Oceanography of Saanich Inlet in Vancouver Island, British Columbia

Order License ID	1465786-1	**Type of Use**	Republish in a thesis/dissertation
Order detail status	Completed		
ISSN	0015-296X	**Publisher**	Canadian Science Publishing
		Portion	Chart/graph/table/figure

0.00 USD
Republication Permission

LICENSED CONTENT

Publication Title	Journal of the Fisheries Research Board of Canada	**Rightsholder**	Canadian Science Publishing
		Publication Type	Journal
Article Title	Oceanography of Saanich Inlet in Vancouver Island, British Columbia	**Start Page**	1
		End Page	37
Author/Editor	FISHERIES RESEARCH BOARD OF CANADA.	**Issue**	1
		Volume	19
Date	01/01/1970		
Language	English		
Country	Canada		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	United States
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language of publication
		Copies for the Disabled?	No
Format (select all that apply)	Print, Electronic	**Minor Editing Privileges?**	No
Who Will Republish the Content?	Academic institution	**Incidental Promotional Use?**	No
		Currency	USD
Duration of Use	Life of current edition		
Lifetime Unit Quantity	Up to 499		
Rights Requested	Main product		

NEW WORK DETAILS

Title	Iron Isotope Transformations in Saanich Inlet	**Institution Name**	University of South Florida
		Expected Presentation Date	2024-04-01
Instructor Name	Claire Onak		

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Claire Onak

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Fig. 1. Saanich Inlet and neighboring regions.	**Title of the Article / Chapter the Portion Is From**	Oceanography of Saanich Inlet in Vancouver Island, British Columbia
Editor of Portion(s)	Herlinveaux, R. H.		
Volume / Edition	19	**Author of Portion(s)**	Herlinveaux, R. H.
Page or Page Range of Portion	1-37	**Issue, if Republishing an Article From a Serial**	1
		Publication Date of Portion	1962-01-01

Total Items: 1

Subtotal: 0.00 USD

Order Total: 0.00 USD

Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that

such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

Citation: Soetaert G, Hamme RC and Raftery E (2022) Renewal of seasonally anoxic Saanich Inlet is temporally and spatially dynamic. *Front. Mar. Sci.* 9:1001146. doi: 10.3389/fmars.2022.1001146

Received: 22 July 2022; **Accepted:** 15 September 2022;
Published: 11 October 2022.

Edited by:
Sudheesh Valliyodan, Central University of Kerala, India

Reviewed by:
Alyse K. Hawley, University of British Columbia, Canada
Mónica Torres-Beltrán, Autonomous University of Baja California, Mexico

***Correspondence:** Roberta C. Hamme, rhamme@uvic.ca

CCC Marketplace

Order Number: 1465793
Order Date: 25 Mar 2024

Payment Information

Claire Onak
conak@usf.edu
Payment method: Invoice

Billing Address:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

+1 (906) 748-7232
conak@usf.edu

Customer Location:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

Order Details

1. Deep-sea research. Part A, Oceanographic research papers

Billing Status: Open

Article: Redox species in a reducing fjord: equilibrium and kinetic considerations

Order License ID	1465793-1	**Type of Use**	Republish in a thesis/dissertation
Order detail status	Completed		
ISSN	0198-0149	**Publisher**	PERGAMON PRESS,
		Portion	Chart/graph/table/figure

0.00 USD
Republication Permission

LICENSED CONTENT

Publication Title	Deep-sea research. Part A, Oceanographic research papers	**Publication Type**	Journal
		Start Page	859
Article Title	Redox species in a reducing fjord: equilibrium and kinetic considerations	**End Page**	878
		Issue	8
Date	01/01/1979	**Volume**	26
Language	English		
Country	United Kingdom of Great Britain and Northern Ireland		
Rightsholder	Elsevier Science & Technology Journals		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	United States
Number of Charts / Graphs / Tables / Figures Requested	3	**Translation**	Original language of publication
		Copies for the Disabled?	No
Format (select all that apply)	Print, Electronic	**Minor Editing Privileges?**	No
Who Will Republish the Content?	Academic institution	**Incidental Promotional Use?**	No
		Currency	USD
Duration of Use	Life of current edition		
Lifetime Unit Quantity	Up to 499		
Rights Requested	Main product		

NEW WORK DETAILS

Title	Iron Isotope Transformations in Saanich Inlet	**Institution Name**	University of South Florida
		Expected Presentation Date	2024-04-01
Instructor Name	Claire Onak		

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Claire Onak

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Fig.1, Fig. 2, & Fig. 5	**Title of the Article / Chapter the Portion Is From**	Redox species in a reducing fjord: equilibrium and kinetic considerations
Editor of Portion(s)	Emerson, S.; Cranston, R.E.; Liss, P.S.	**Author of Portion(s)**	Emerson, S.; Cranston, R.E.; Liss, P.S.
Volume / Edition	26		
Page or Page Range of Portion	859-878	**Issue, if Republishing an Article From a Serial**	8
		Publication Date of Portion	1979-01-01

Elsevier Science & Technology Journals Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals, for which an author selects a user license permitting certain types of reuse without permission. Before proceeding please check if the article is Open Access on http://www.sciencedirect.com and refer to the user license for the individual article. Any reuse not included in the user license terms will require permission. You must always fully and appropriately credit the author and source. If any part of the material to be used (for example, figures) has appeared in the Elsevier publication for which you are seeking permission, with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder. Please contact permissions@elsevier.com with any queries.

Total Items: 1

Subtotal: 0.00 USD

Order Total: 0.00 USD

Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between

General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in

the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any

necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be

paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

CCC Marketplace

Order Number: 1465802
Order Date: 25 Mar 2024

Payment Information

Claire Onak
conak@usf.edu
Payment method: Invoice

Billing Address:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

+1 (906) 748-7232
conak@usf.edu

Customer Location:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

Order Details

1. Earth and planetary science letters

Billing Status: Open

Article: Trace metal solubility in an anoxic fjord

Order License ID	1465802-1	**Type of Use**	Republish in a thesis/dissertation
Order detail status	Completed	**Publisher**	ELSEVIER BV
ISSN	0012-821X	**Portion**	Chart/graph/table/figure

0.00 USD
Republication Permission

LICENSED CONTENT

Publication Title	Earth and planetary science letters	**Publication Type**	Journal
Article Title	Trace metal solubility in an anoxic fjord	**Start Page**	237
Date	01/01/1966	**End Page**	252
Language	English, French, German	**Issue**	2
Country	Netherlands	**Volume**	60
Rightsholder	Elsevier Science & Technology Journals		

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	United States
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language of publication
Format (select all that apply)	Print, Electronic	**Copies for the Disabled?**	No
Who Will Republish the Content?	Academic institution	**Minor Editing Privileges?**	No
Duration of Use	Life of current edition	**Incidental Promotional Use?**	No
Lifetime Unit Quantity	Up to 499	**Currency**	USD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Iron Isotope Transformations in Saanich Inlet	**Institution Name**	University of South Florida

Instructor Name	Claire Onak	**Expected Presentation Date**	2024-04-01

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Claire Onak

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Fig. 3	**Title of the Article / Chapter the Portion Is From**	Trace metal solubility in an anoxic fjord
Editor of Portion(s)	Jacobs, Lucinda; Emerson, Steven	**Author of Portion(s)**	Jacobs, Lucinda; Emerson, Steven
Volume / Edition	60	**Issue, if Republishing an Article From a Serial**	2
Page or Page Range of Portion	237-252	**Publication Date of Portion**	1982-01-01

Elsevier Science & Technology Journals Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals, for which an author selects a user license permitting certain types of reuse without permission. Before proceeding please check if the article is Open Access on http://www.sciencedirect.com and refer to the user license for the individual article. Any reuse not included in the user license terms will require permission. You must always fully and appropriately credit the author and source. If any part of the material to be used (for example, figures) has appeared in the Elsevier publication for which you are seeking permission, with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder. Please contact permissions@elsevier.com with any queries.

Total Items: 1

Subtotal: 0.00 USD

Order Total: 0.00 USD

Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot

reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)

(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022

CCC Marketplace

Order Number: 1465819
Order Date: 25 Mar 2024

Payment Information

Claire Onak
conak@usf.edu
Payment method: Invoice

Billing Address:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

+1 (906) 748-7232
conak@usf.edu

Customer Location:
Ms. Claire Onak
830 1st St S
Saint Petersburg, FL 33701
United States

Order Details

1. Annual review of earth and planetary sciences

Billing Status: Open

Article: Metal Stable Isotopes in Paleoceanography

Order License ID	1465819-1	**Type of Use**	Republish in a thesis/dissertation
Order detail status	Completed	**Publisher**	ANNUAL REVIEWS INC.
ISSN	1545-4495	**Portion**	Chart/graph/table/figure

0.00 USD
Republication Permission

LICENSED CONTENT

Publication Title	Annual review of earth and planetary sciences	**Publication Type**	e-Journal
Article Title	Metal Stable Isotopes in Paleoceanography	**Start Page**	717
Date	01/01/1973	**End Page**	746
Language	English	**Issue**	1
Country	United States of America	**Volume**	35
Rightsholder	Annual Reviews, Inc.	**URL**	http://arjournals.annualreviews.org/loi/earth

REQUEST DETAILS

Portion Type	Chart/graph/table/figure	**Distribution**	United States
Number of Charts / Graphs / Tables / Figures Requested	1	**Translation**	Original language of publication
Format (select all that apply)	Print, Electronic	**Copies for the Disabled?**	No
Who Will Republish the Content?	Academic institution	**Minor Editing Privileges?**	No
Duration of Use	Life of current edition	**Incidental Promotional Use?**	No
Lifetime Unit Quantity	Up to 499	**Currency**	USD
Rights Requested	Main product		

NEW WORK DETAILS

Title	Iron Isotope Transformations in Saanich Inlet	**Institution Name**	University of South Florida
		Expected Presentation Date	2024-04-01

Instructor Name	Claire Onak

ADDITIONAL DETAILS

The Requesting Person / Organization to Appear on the License	Claire Onak

REQUESTED CONTENT DETAILS

Title, Description or Numeric Reference of the Portion(s)	Figure 4. Plot of delta56Fe values versus sample age for pyrite in organic-rich marine sediments.	**Title of the Article / Chapter the Portion Is From**	Metal Stable Isotopes in Paleoceanography
		Author of Portion(s)	Anbar, Ariel D.; Rouxel, Olivier
Editor of Portion(s)	Anbar, Ariel D.; Rouxel, Olivier	**Issue, if Republishing an Article From a Serial**	1
Volume / Edition	35	**Publication Date of Portion**	2007-05-30
Page or Page Range of Portion	717-746		

Total Items: 1

Subtotal: 0.00 USD

Order Total: 0.00 USD

Marketplace Permissions General Terms and Conditions

The following terms and conditions ("General Terms"), together with any applicable Publisher Terms and Conditions, govern User's use of Works pursuant to the Licenses granted by Copyright Clearance Center, Inc. ("CCC") on behalf of the applicable Rightsholders of such Works through CCC's applicable Marketplace transactional licensing services (each, a "Service").

1) **Definitions.** For purposes of these General Terms, the following definitions apply:

"License" is the licensed use the User obtains via the Marketplace platform in a particular licensing transaction, as set forth in the Order Confirmation.

"Order Confirmation" is the confirmation CCC provides to the User at the conclusion of each Marketplace transaction. "Order Confirmation Terms" are additional terms set forth on specific Order Confirmations not set forth in the General Terms that can include terms applicable to a particular CCC transactional licensing service and/or any Rightsholder-specific terms.

"Rightsholder(s)" are the holders of copyright rights in the Works for which a User obtains licenses via the Marketplace platform, which are displayed on specific Order Confirmations.

"Terms" means the terms and conditions set forth in these General Terms and any additional Order Confirmation Terms collectively.

"User" or "you" is the person or entity making the use granted under the relevant License. Where the person accepting the Terms on behalf of a User is a freelancer or other third party who the User authorized to accept the General Terms on the User's behalf, such person shall be deemed jointly a User for purposes of such Terms.

"Work(s)" are the copyright protected works described in relevant Order Confirmations.

2) **Description of Service.** CCC's Marketplace enables Users to obtain Licenses to use one or more Works in accordance with all relevant Terms. CCC grants Licenses as an agent on behalf of the copyright rightsholder identified in the relevant Order Confirmation.

3) **Applicability of Terms.** The Terms govern User's use of Works in connection with the relevant License. In the event of any conflict between General Terms and Order Confirmation Terms, the latter shall govern. User acknowledges that Rightsholders have complete discretion whether to grant any permission, and whether to place any limitations on any grant, and that CCC has no right to supersede or to modify any such discretionary act by a Rightsholder.

4) **Representations; Acceptance.** By using the Service, User represents and warrants that User has been duly authorized by the User to accept, and hereby does accept, all Terms.

5) **Scope of License; Limitations and Obligations.** All Works and all rights therein, including copyright rights, remain the sole and exclusive property of the Rightsholder. The License provides only those rights expressly set forth in the terms and conveys no other rights in any Works

6) **General Payment Terms.** User may pay at time of checkout by credit card or choose to be invoiced. If the User chooses to be invoiced, the User shall: (i) remit payments in the manner identified on specific invoices, (ii) unless otherwise specifically stated in an Order Confirmation or separate

written agreement, Users shall remit payments upon receipt of the relevant invoice from CCC, either by delivery or notification of availability of the invoice via the Marketplace platform, and (iii) if the User does not pay the invoice within 30 days of receipt, the User may incur a service charge of 1.5% per month or the maximum rate allowed by applicable law, whichever is less. While User may exercise the rights in the License immediately upon receiving the Order Confirmation, the License is automatically revoked and is null and void, as if it had never been issued, if CCC does not receive complete payment on a timely basis.

7) **General Limits on Use.** Unless otherwise provided in the Order Confirmation, any grant of rights to User (i) involves only the rights set forth in the Terms and does not include subsequent or additional uses, (ii) is non-exclusive and non-transferable, and (iii) is subject to any and all limitations and restrictions (such as, but not limited to, limitations on duration of use or circulation) included in the Terms. Upon completion of the licensed use as set forth in the Order Confirmation, User shall either secure a new permission for further use of the Work(s) or immediately cease any new use of the Work(s) and shall render inaccessible (such as by deleting or by removing or severing links or other locators) any further copies of the Work. User may only make alterations to the Work if and as expressly set forth in the Order Confirmation. No Work may be used in any way that is unlawful, including without limitation if such use would violate applicable sanctions laws or regulations, would be defamatory, violate the rights of third parties (including such third parties' rights of copyright, privacy, publicity, or other tangible or intangible property), or is otherwise illegal, sexually explicit, or obscene. In addition, User may not conjoin a Work with any other material that may result in damage to the reputation of the Rightsholder. Any unlawful use will render any licenses hereunder null and void. User agrees to inform CCC if it becomes aware of any infringement of any rights in a Work and to cooperate with any reasonable request of CCC or the Rightsholder in connection therewith.

8) **Third Party Materials.** In the event that the material for which a License is sought includes third party materials (such as photographs, illustrations, graphs, inserts and similar materials) that are identified in such material as having been used by permission (or a similar indicator), User is responsible for identifying, and seeking separate licenses (under this Service, if available, or otherwise) for any of such third party materials; without a separate license, User may not use such third party materials via the License.

9) **Copyright Notice.** Use of proper copyright notice for a Work is required as a condition of any License granted under the Service. Unless otherwise provided in the Order Confirmation, a proper copyright notice will read substantially as follows: "Used with permission of [Rightsholder's name], from [Work's title, author, volume, edition number and year of copyright]; permission conveyed through Copyright Clearance Center, Inc." Such notice must be provided in a reasonably legible font size and must be placed either on a cover page or in another location that any person, upon gaining access to the material which is the subject of a permission, shall see, or in the case of republication Licenses, immediately adjacent to the Work as used (for example, as part of a by-line or footnote) or in the place where substantially all other credits or notices for the new work containing the republished Work are located. Failure to include the required notice results in loss to the Rightsholder and CCC, and the User shall be liable to pay liquidated damages for each such failure equal to twice the use fee specified in the Order Confirmation, in addition to the use fee itself and any other fees and charges specified.

10) **Indemnity.** User hereby indemnifies and agrees to defend the Rightsholder and CCC, and their respective employees and directors, against all claims, liability, damages, costs, and expenses, including legal fees and expenses, arising out of any use of a Work beyond the scope of the rights granted herein and in the Order Confirmation, or any use of a Work which has been altered in any unauthorized way by User, including claims of defamation or infringement of rights of copyright, publicity, privacy, or other tangible or intangible property.

11) **Limitation of Liability.** UNDER NO CIRCUMSTANCES WILL CCC OR THE RIGHTSHOLDER BE LIABLE FOR ANY DIRECT, INDIRECT, CONSEQUENTIAL, OR INCIDENTAL DAMAGES (INCLUDING WITHOUT LIMITATION DAMAGES FOR LOSS OF BUSINESS PROFITS OR INFORMATION, OR FOR BUSINESS INTERRUPTION) ARISING OUT OF THE USE OR INABILITY TO USE A WORK, EVEN IF ONE OR BOTH OF THEM HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES. In any event, the total liability of the Rightsholder and CCC (including their respective employees and directors) shall not exceed the total amount actually paid by User for the relevant License. User assumes full liability for the actions and omissions of its principals, employees, agents, affiliates, successors, and assigns.

12) **Limited Warranties.** THE WORK(S) AND RIGHT(S) ARE PROVIDED "AS IS." CCC HAS THE RIGHT TO GRANT TO USER THE RIGHTS GRANTED IN THE ORDER CONFIRMATION DOCUMENT. CCC AND THE RIGHTSHOLDER DISCLAIM ALL OTHER WARRANTIES RELATING TO THE WORK(S) AND RIGHT(S), EITHER EXPRESS OR IMPLIED, INCLUDING WITHOUT LIMITATION IMPLIED WARRANTIES OF MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE. ADDITIONAL RIGHTS MAY BE REQUIRED TO USE ILLUSTRATIONS, GRAPHS, PHOTOGRAPHS, ABSTRACTS, INSERTS, OR OTHER PORTIONS OF THE WORK (AS OPPOSED TO THE ENTIRE WORK) IN A MANNER CONTEMPLATED BY USER; USER UNDERSTANDS AND AGREES THAT NEITHER CCC NOR THE RIGHTSHOLDER MAY HAVE SUCH ADDITIONAL RIGHTS TO GRANT.

13) **Effect of Breach.** Any failure by User to pay any amount when due, or any use by User of a Work beyond the scope of the License set forth in the Order Confirmation and/or the Terms, shall be a material breach of such License. Any breach not cured within 10 days of written notice thereof shall result in immediate termination of such License without further notice. Any unauthorized (but licensable) use of a Work that is terminated immediately upon notice thereof may be liquidated by payment of the Rightsholder's ordinary license price therefor; any unauthorized (and unlicensable) use that is not terminated immediately for any reason (including, for example, because materials containing the Work cannot reasonably be recalled) will be subject to all remedies available at law or in equity, but in no event to a payment of less than three times the Rightsholder's ordinary license price for the most closely analogous licensable use plus Rightsholder's and/or CCC's costs and expenses incurred in collecting such payment.

14) **Additional Terms for Specific Products and Services.** If a User is making one of the uses described in this Section 14, the additional terms and conditions apply:

a) ***Print Uses of Academic Course Content and Materials (photocopies for academic coursepacks or classroom handouts).*** For photocopies

for academic coursepacks or classroom handouts the following additional terms apply:

i) The copies and anthologies created under this License may be made and assembled by faculty members individually or at their request by on-campus bookstores or copy centers, or by off-campus copy shops and other similar entities.

ii) No License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied) (ii) permit "publishing ventures" where any particular anthology would be systematically marketed at multiple institutions.

iii) Subject to any Publisher Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the academic pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to no more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular anthology, whether photocopied or electronic, at more than one institution of learning;

E) in the case of a photocopy permission, no materials may be entered into electronic memory by User except in order to produce an identical copy of a Work before or during the academic term (or analogous period) as to which any particular permission is granted. In the event that User shall choose to retain materials that are the subject of a photocopy permission in electronic memory for purposes of producing identical copies more than one day after such retention (but still within the scope of any permission granted), User must notify CCC of such fact in the applicable permission request and such retention shall constitute one copy actually sold for purposes of calculating permission fees due; and

F) any permission granted shall expire at the end of the class. No permission granted shall in any way include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied).

iv) Books and Records; Right to Audit. As to each permission granted under the academic pay-per-use Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any photocopies sold or by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this License for any reason.

b) ***Digital Pay-Per-Uses of Academic Course Content and Materials (e-coursepacks, electronic reserves, learning management systems, academic institution intranets).*** For uses in e-coursepacks, posts in electronic reserves, posts in learning management systems, or posts on academic institution intranets, the following additional terms apply:

i) The pay-per-uses subject to this Section 14(b) include:

A) **Posting e-reserves, course management systems, e-coursepacks for text-based content,** which grants authorizations to import requested material in electronic format, and allows electronic access to this material to members of a designated college or university class, under the direction of an instructor designated by the college or university, accessible only under appropriate electronic controls (e.g., password);

B) **Posting e-reserves, course management systems, e-coursepacks for material consisting of photographs or other still images not embedded in text,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorization: to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above, including any necessary resizing, reformatting or modification of the resolution of such requested material (provided that such modification does not alter the underlying editorial content or meaning of the requested material, and provided that the resulting modified content is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms), but not including any other form of manipulation, alteration or editing of the requested material;

C) **Posting e-reserves, course management systems, e-coursepacks or other academic distribution for audiovisual content,** which grants not only the authorizations described in Section 14(b)(i)(A) above, but also the following authorizations: (i) to include the requested material in course materials for use consistent with Section 14(b)(i)(A) above; (ii) to display and perform the requested material to such members of such class in the physical classroom or remotely by means of streaming media or other video formats; and (iii) to "clip" or reformat the requested material for purposes of time or content management or ease of delivery, provided that such "clipping" or reformatting does not alter the underlying editorial content or meaning of the requested material and that the

resulting material is used solely within the scope of, and in a manner consistent with, the particular authorization described in the Order Confirmation and the Terms. Unless expressly set forth in the relevant Order Conformation, the License does not authorize any other form of manipulation, alteration or editing of the requested material.

ii) Unless expressly set forth in the relevant Order Confirmation, no License granted shall in any way: (i) include any right by User to create a substantively non-identical copy of the Work or to edit or in any other way modify the Work (except by means of deleting material immediately preceding or following the entire portion of the Work copied or, in the case of Works subject to Sections 14(b)(1)(B) or (C) above, as described in such Sections) (ii) permit "publishing ventures" where any particular course materials would be systematically marketed at multiple institutions.

iii) Subject to any further limitations determined in the Rightsholder Terms (and notwithstanding any apparent contradiction in the Order Confirmation arising from data provided by User), any use authorized under the electronic course content pay-per-use service is limited as follows:

A) any License granted shall apply to only one class (bearing a unique identifier as assigned by the institution, and thereby including all sections or other subparts of the class) at one institution;

B) use is limited to not more than 25% of the text of a book or of the items in a published collection of essays, poems or articles;

C) use is limited to not more than the greater of (a) 25% of the text of an issue of a journal or other periodical or (b) two articles from such an issue;

D) no User may sell or distribute any particular materials, whether photocopied or electronic, at more than one institution of learning;

E) electronic access to material which is the subject of an electronic-use permission must be limited by means of electronic password, student identification or other control permitting access solely to students and instructors in the class;

F) User must ensure (through use of an electronic cover page or other appropriate means) that any person, upon gaining electronic access to the material, which is the subject of a permission, shall see:

- a proper copyright notice, identifying the Rightsholder in whose name CCC has granted permission,
- a statement to the effect that such copy was made pursuant to permission,
- a statement identifying the class to which the material applies and notifying the reader that the material has been made available electronically solely for use in the class, and
- a statement to the effect that the material may not be further distributed to any person outside the class, whether by copying or by transmission and whether electronically or in paper form, and User must also ensure that such cover page or other means will print out in the event that the person accessing the material chooses to print out the material or any part thereof.

G) any permission granted shall expire at the end of the class and, absent some other form of authorization, User is thereupon required to delete the applicable material from any electronic storage or to block electronic access to the applicable material.

iv) Uses of separate portions of a Work, even if they are to be included in the same course material or the same university or college class, require separate permissions under the electronic course content pay-per-use Service. Unless otherwise provided in the Order Confirmation, any grant of rights to User is limited to use completed no later than the end of the academic term (or analogous period) as to which any particular permission is granted.

v) Books and Records; Right to Audit. As to each permission granted under the electronic course content Service, User shall maintain for at least four full calendar years books and records sufficient for CCC to determine the numbers of copies made by User under such permission. CCC and any representatives it may designate shall have the right to audit such books and records at any time during User's ordinary business hours, upon two days' prior notice. If any such audit shall determine that User shall have underpaid for, or underreported, any electronic copies used by three percent (3%) or more, then User shall bear all the costs of any such audit; otherwise, CCC shall bear the costs of any such audit. Any amount determined by such audit to have been underpaid by User shall immediately be paid to CCC by User, together with interest thereon at the rate of 10% per annum from the date such amount was originally due. The provisions of this paragraph shall survive the termination of this license for any reason.

c) ***Pay-Per-Use Permissions for Certain Reproductions (Academic photocopies for library reserves and interlibrary loan reporting) (Non-academic internal/external business uses and commercial document delivery).*** The License expressly excludes the uses listed in Section (c)(i)-(v) below (which must be subject to separate license from the applicable Rightsholder) for: academic photocopies for library reserves and interlibrary loan reporting; and non-academic internal/external business uses and commercial document delivery.

i) electronic storage of any reproduction (whether in plain-text, PDF, or any other format) other than on a transitory basis;

ii) the input of Works or reproductions thereof into any computerized database;

iii) reproduction of an entire Work (cover-to-cover copying) except where the Work is a single article;

iv) reproduction for resale to anyone other than a specific customer of User;

v) republication in any different form. Please obtain authorizations for these uses through other CCC services or directly from the rightsholder.

Any license granted is further limited as set forth in any restrictions included in the Order Confirmation and/or in these Terms.

d) ***Electronic Reproductions in Online Environments (Non-Academic-email, intranet, internet and extranet).*** For "electronic reproductions", which generally includes e-mail use (including instant messaging or other electronic transmission to a defined group of recipients) or posting on an intranet, extranet or Intranet site (including any display or performance incidental thereto), the following additional terms apply:

i) Unless otherwise set forth in the Order Confirmation, the License is limited to use completed within 30 days for any use on the Internet, 60 days for any use on an intranet or extranet and one year for any other use, all as measured from the "republication date" as identified in the Order Confirmation, if any, and otherwise from the date of the Order Confirmation.

ii) User may not make or permit any alterations to the Work, unless expressly set forth in the Order Confirmation (after request by User and approval by Rightsholder); provided, however, that a Work consisting of photographs or other still images not embedded in text may, if necessary, be resized, reformatted or have its resolution modified without additional express permission, and a Work consisting of audiovisual content may, if necessary, be "clipped" or reformatted for purposes of time or content management or ease of delivery (provided that any such resizing, reformatting, resolution modification or "clipping" does not alter the underlying editorial content or meaning of the Work used, and that the resulting material is used solely within the scope of, and in a manner consistent with, the particular License described in the Order Confirmation and the Terms.

15) **Miscellaneous.**

a) User acknowledges that CCC may, from time to time, make changes or additions to the Service or to the Terms, and that Rightsholder may make changes or additions to the Rightsholder Terms. Such updated Terms will replace the prior terms and conditions in the order workflow and shall be effective as to any subsequent Licenses but shall not apply to Licenses already granted and paid for under a prior set of terms.

b) Use of User-related information collected through the Service is governed by CCC's privacy policy, available online at www.copyright.com/about/privacy-policy/.

c) The License is personal to User. Therefore, User may not assign or transfer to any other person (whether a natural person or an organization of any kind) the License or any rights granted thereunder; provided, however, that, where applicable, User may assign such License in its entirety on written notice to CCC in the event of a transfer of all or substantially all of User's rights in any new material which includes the Work(s) licensed under this Service.

d) No amendment or waiver of any Terms is binding unless set forth in writing and signed by the appropriate parties, including, where applicable, the Rightsholder. The Rightsholder and CCC hereby object to any terms contained in any writing prepared by or on behalf of the User or its principals, employees, agents or affiliates and purporting to govern or otherwise relate to the License described in the Order Confirmation, which terms are in any way inconsistent with any Terms set forth in the Order Confirmation, and/or in CCC's standard operating procedures, whether such writing is prepared prior to, simultaneously with or subsequent to the Order Confirmation, and whether such writing appears on a copy of the Order Confirmation or in a separate instrument.

e) The License described in the Order Confirmation shall be governed by and construed under the law of the State of New York, USA, without regard to the principles thereof of conflicts of law. Any case, controversy, suit, action, or proceeding arising out of, in connection with, or related to such License shall be brought, at CCC's sole discretion, in any federal or state court located in the County of New York, State of New York, USA, or in any federal or state court whose geographical jurisdiction covers the location of the Rightsholder set forth in the Order Confirmation. The parties expressly submit to the personal jurisdiction and venue of each such federal or state court.

Last updated October 2022