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Geological factors impacted cadmium availability and use as an alternative cofactor for zinc in the carbon fixation pathways of marine diatoms

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Key Points:

- Cd and Zn share similar sulfide mineral chemistry and weatherability
- Sulfur-containing Cd minerals are often co-located with sulfur-containing Zn sulfide minerals
- Simultaneous weathering of sulfur-containing Cd and Zn minerals allows Cd to be a substitute for Zn in protein complexes during periods of Zn depletion

Abstract

Transition metal cofactors are crucial for many biological processes. Despite being primarily considered to be toxic, the transition metal cadmium (Cd) was discovered to be a substitute for zinc (Zn) in photosynthetic carbon fixation pathways in marine diatoms. However, it is not known how conditions in the geosphere impacted Cd availability and its incorporation as an alternative metal cofactor for phytoplankton. We employed mineral chemistry network analysis to investigate which geochemical factors may have influenced the availability of Cd and Zn during the putative time period that alternative Cd-based pathway evolved. Our results show that Zn minerals are more chemically diverse than are Cd minerals, but Zn- and Cd-containing minerals have similar mean electronegativities when specifically considering sulfur (S)-containing species. Cadmium and zinc sulfides are the most common Cd- and Zn-containing mineral species over the past 500 million years. In particular, the Cd and Zn sulfides, respectively greenockite and sphalerite, are highly abundant during this time period. Furthermore, S-containing Cd- and Zn minerals are commonly co-located in geologic time, allowing them to be weathered and transported to the ocean in tandem, rather than occurring from separate sources. We suggest that the simultaneous weathering of Cd and Zn sulfides allowed for Cd to be a bioavailable direct substitute for Zn in protein complexes during periods of Zn depletion. The biogeochemical cycles of Zn and Cd exemplify the importance of the coevolution of the geosphere and biosphere in shaping primary production in the modern ocean.

Plain Language Summary

Cadmium (Cd) is a toxic heavy metal in biology, but the element is also used as an alternative cofactor for zinc (Zn) in carbon fixation proteins of productive marine phytoplankton called diatoms. It is not known how a toxic metal became available for biological utilization during periods of diatom evolution. In this study we used network analysis of the chemistry of Cd and Zn minerals over billions of years of Earth history to better understand how these elements are related. Our results show that the chemistry of Zn minerals is much more diverse than for Cd minerals, but the two elements are similar in terms of their sulfur-containing mineral chemistry in geologic time. Cadmium sulfides are also commonly co-located with Zn sulfides, which are both highly weatherable. Simultaneous weathering of Cd and Zn sulfides make Cd a bioavailable substitute for Zn in protein complexes during periods of Zn depletion.

1. Introduction

Transition metals are crucial cofactors in many biological processes across the tree of life (Holm, Kennepohl, and Solomon 1996; Dey et al. 2007; Hosseinzadeh and Lu 2016). The evolving geosphere and biosphere impacted the availability of metal cofactors and emergence of metabolic pathways in geologic time (Dupont et al. 2006; Moore et al. 2017). Deep-time changes in the geosphere and biosphere provide insight into how the relationship between the two spheres became so intertwined. The transition metal cadmium (Cd) is toxic to many biological systems (Flick, Kraybill, and Dlmitroff 1971; Das, Samantaray, and Rout 1997). Exposure to Cd results in the production of hydrogen peroxide and the breakdown of cellular phospholipid bilayers (Khan et al. 2013), and Cd's ability to directly attack and damage DNA makes Cd a potent carcinogen (Coogan, Bare, and Waalkes 1992; Giaginis, Gatzidou, and Theocharis 2006).

Despite Cd's predominantly toxic effects, there are several known instances where Cd in fact participates beneficially in biological pathways. For example, Cd is able to substitute for zinc (Zn) at certain functional Zn-binding protein sites, such as the pyrimidine (a type of DNA nucleotide) biosynthesis enzyme aspartate transcarbamoylase (Rosenbusch and Weber 1971). Cd is also known to serve as an alternative cofactor in the Carbonic Anhydrase (CA) enzyme, which is involved in acquiring dissolved CO_2 for photosynthesis, of marine diatoms (Price and Morel 1990; Lane and Morel 2000; Park, Song, and Morel 2007). While Zn is a more energetically efficient CA cofactor, Cd can function as an effective substitute when Zn availability is low (Lane et al. 2005; Xu et al. 2008). Cadmium therefore possesses a micronutrient profile in marine systems with lower concentrations in surface waters (~0.1 to 0.5 nmol [Cd^{2+}]/kg seawater) and increasing concentrations in deeper waters (~1.0 nmol [Cd^{2+}]/kg seawater) (Boyle, Sclater, and Edmond 1976). The gradient of Cd is formed based on light penetration, how deep phytoplankton live, their ability to sustain photosynthesis, and nonspecific uptake and Cd homeostasis in microbial cells (Horner et al. 2013). The concentration of Cd in seawater is below the level of Cd toxicity responses in the marine diatom *Thalassiosira nordenskioeldii* (Wang and Wang 2008).

Basalt, on average, contains approximately 120 parts per billion (ppb) of Cd, and is a major source of Cd to the ocean due to weathering and the prevalence of basalt in oceanic crust (Yi et al. 2000). Hydrothermal fluids are also major sources of Cd to the ocean, with Cd concentrations up to 2 nM (Douville et al. 2002). Natural emission of Cd occurs primarily from volcanoes , followed by biogenic sources, aeolian transport, terrestrial biomass burning, and sea-salt spray (Jerome O. Nriagu 1989; Cullen and Maldonado 2013). Cadmium deposition and cycling varies across different environmental conditions (Kelly et al. 2001; Yee and Fein 2001), specifically among saltwater, freshwater, and soil environments (Gerth and Brümmer 1983; Bruemmer, Gerth, and Tiller 1988; Barrow, Gerth, and Brümmer 1989; Lock and Janssen 2003). Within freshwater ecosystems, Cd's availability and toxicity strictly depends on the element’s distributional speciation with organic matter due to concentration and characteristics of dissolved organic carbon, pH, and cations in solution (Sigg and Behra 2005). Upon transitioning into more saline waters, cationic interactions increase Cd mobility and solubility (Duce et al. 1991). When Cd interacts with soils and minerals, factors such as redox potential, pH, and organic ion presence influence its bioavailability (Lock and Janssen 2003). The wide range of interactions between Cd and the environment create a cascade of reactions that have varying impacts on the solubility and mobility of Cd in the environment. These processes therefore have a dramatic effect on the formation of an equilibration cycle between soil runoff and water cycling.

Various aspects of the biological pathways involving Cd have been well documented (Rosenbusch and Weber 1971; Beyersmann and Hechtenberg 1997; Lane and Morel 2000; Lane et al. 2005; Park, Song, and Morel 2007; Xu et al. 2008), but it is not fully known how the geosphere impacted the availability of Cd and evolution of associated biological pathways. Saito et al. (Saito, Sigman, and Morel 2003) showed that the dissolved concentrations of Cd in the ocean would have been altered by changing ocean chemistry at different stages of Earth history. Although oceanic basalt and hydrothermal vents are likely the main sources of Cd to the ocean (Yi et al. 2000), minerals are important for understanding the geochemistry and solubility of both Cd and Zn to the ocean from geological sources through weathering processes (Bertine and Goldberg 1971; Callender 2003; Cullen and Maldonado 2013). Here, we examine the mineral records of Cd and Zn in order to compare the chemistry and location of potentially weatherable Cd and Zn mineral sources to the environment at different periods of Earth history relevant to the emergence of marine diatoms and the utilization of Cd as a cofactor in carbonic anhydrase. This study considers Cd and Zn minerals to be those in which Cd and Zn are listed in the chemical formula, as defined by the International Mineralogical Association (IMA); lists of IMA-defined Cd and Zn minerals can be found at https://rruff.info/ima/.

2. Methods

2.1 Mineral chemistry network analysis

Network analysis has emerged as a powerful technique to investigate mineral evolution and mineral ecology (Morrison et al. 2017; Hystad, Morrison, and Hazen 2019; Hazen et al. 2019). Bipartite mineral chemistry network analysis includes two classes of nodes, minerals and chemical elements, with network edges connecting each mineral node to each one of its constituent element nodes. The bipartite network method has recently been applied to understand redox evolution of cobalt and vanadium and their bioavailability in the Archean ocean (Moore et al. 2018; 2020). Bipartite network analysis of Cd and Zn mineral chemistry was performed using the R package `dragon` (Spielman 2019). Specifically, we examined Cd's bipartite mineral chemistry network across the three time periods of $\geq$2.7 billion years ago (Ga), $\geq$0.6 Ga, and $\geq$0.2. The time range of $\geq$2.7 Ga was selected because only one Cd mineral has a maximum (i.e. oldest) known age of $\geq$2.8 Ga (greenockite). The time range of $\geq$0.6 Ga was selected as it is positioned at the beginning of an increase in preserved Cd mineral and Zn mineral localities [(Golden et al. 2019) http://rruff.info/evolution/]. The time range of $\geq$0.2 Ga was selected as this period approximately coincides with the oldest known evidence for the origin of diatoms (Kooistra and Medlin 1996; Sims, Mann, and Medlin 2006; Falkowski and Knoll 2007). Indeed, diatoms are the only organisms known to use the alternative Cd-CA protein (Alterio et al. 2015). We performed a PSI-BLAST search against the *nr* database (all non-redundant proteins sequences in NCBI) to identify any orthologous sequences to the known Cd-CA protein from the marine diatom *Thalassiosira weissflogii* (PDB ID 3BOB).

Louvain community detection cluster analysis (Blondel et al. 2008) was performed using `dragon` to identify associations between minerals and elements in the Cd and Zn combined mineral chemistry network. The Louvain community detection method was chosen for this study because of the algorithm's optimization of modularity for grouping network nodes by measuring the density of network edges inside of network communities to edges outside network communities (Blondel et al. 2008). The Louvain method is a greedy optimization method, and is similar to the network community detection method by Clauset et al. (Clauset, Newman, and Moore 2004). Mean mineral electronegativity is calculated as the unweighted average of each mineral's constituent element electronegativities.

Mineral data were compiled for analysis from the Mineral Evolution Database [(Golden et al. 2019) http://rruff.info/evolution/; Accessed June 19th, 2019]. Co-located Cd minerals and Zn minerals were identified by comparing Mindat locality ID numbers of Cd minerals and Zn minerals, including Cd minerals and Zn minerals that contain sulfur (S), catalogued in the Mineral Evolution Database [(Golden et al. 2019) http://rruff.info/evolution/]. Minerals with the same Mindat locality ID number are defined as co-located in this analysis.

3. Results

Evolving mineral chemistry bipartite networks can be used to examine the relationships between minerals and the chemical elements in their ideal chemical formulas through deep-time (Spielman 2019). Figure 1 represents the evolution of Cd mineral chemistry bipartite networks from the oldest known samples into modern day, clearly illustrating the limited mineral chemistry network expansion prior to 0.6 Ga and the subsequent dramatic expansion after 0.6 Ga [(Golden et al. 2019); http://rruff.info/evolution/, Accessed June 19th, 2019]. Sulfur is the most common element found to form as a major constituent in Cd minerals at all time periods of Cd mineralization, with 270 known localities and 16 minerals with Cd and S in their ideal chemical formula. Cadmium minerals containing S account for 92% of all dated Cd mineral localities in the MED, with 8 of the 11 Cd minerals with maximum known ages older than 1.8 Ga containing S. The Cd-sulfide greenockite, CdS, is the oldest known Cd mineral currently recorded in the MED (maximum age of 4.0 Ga) and has the most reported localities of all Cd minerals (196 localities). Hawleyite, CdS, has the second most localities at 30 but with a significantly younger maximum known age of 2.74 Ga. Oxygen is the second most common element known to form Cd minerals, with 14 minerals containing Cd and O in their ideal chemical formula and 41 known localities in the MED. Cadmoselite, CdSe, has the oldest maximum known age (2.72 Ga) among Cd minerals that do not contain S or O as an essential constituent. Arsenic, As, and lead, Pb, become more prominent mineral forming elements with Cd from 0.6 to 0.2 Ga as the number of Cd minerals and localities increases leading up to present day.

Cadmium and zinc both belong to periodic table group 12 (same outer shell electron configuration) and the two elements have similar chemical properties, but Zn is approximately 650 times more abundant than Cd in the Earth's crust [Zn = 65.5 ppm; Cd = 0.102 ppm; (Wedepohl 1995)] and forms a larger number of minerals with a wider range of elements than Cd (Figure 2). In particular, O and H form minerals with Zn much more commonly than with Cd: Zn forms nearly 16 times more minerals with O than Cd forms with O, with 89% of Zn minerals and 57% of Cd minerals containing O. Zinc forms nearly 18 times more minerals with H than Cd forms with H, with 72% of Zn minerals and 43% of Cd minerals containing H. Additionally, Zn minerals that contain O or H are found at many more localities (4,110 localities) than Cd minerals that contain O or H (41 localities). Zinc minerals that contain O and H also contain various other common mineral forming elements that do not form minerals with Cd (e.g. silicon, magnesium, sodium, titanium, etc.; Figure 2). Conversely, Zn forms only approximately 4 times more minerals with S than Cd forms with S, with only 25% of Zn minerals containing S while 64% of Cd minerals contain S. Despite the larger number of elements that form minerals with Zn than Cd, Zn minerals that contain sulfur still make up the majority of all known Zn mineral localities (62%). Similarly to Cd and greenockite, the Zn sulfide mineral sphalerite is found at by far the largest number of known localities (>4,500 localities).

Louvain community detection (Blondel et al. 2008) was used to identify mineral element associations between Cd, Zn, and their mineral forming elements, while accounting for the number of mineral localities. In the Cd-Zn combined network, Cd clusters with S, the abundant Cd sulfide minerals greenockite and hawleyite, the abundant Zn sulfide sphalerite, and other abundant Zn sulfides (Figure 3). Other common mineral-forming elements for both Cd and Zn include O, H, As, Fe, Cu, and Pb. Zinc and O each cluster separately given the wide range of other elements that Zn and O each form minerals with, but overall there is a great deal of mineral chemistry overlap between network clusters 3 (Zn cluster) and 5 (Oxygen cluster). Far less mineral chemistry overlap occurs between cluster 1 (Cd and S cluster) and other network clusters (Figure 3), showing that the main chemical similarities between Cd and Zn minerals exist among Cd and Zn minerals that contain S.

The number of co-located S-containing Cd and Zn minerals increases through geologic time, accounting for the vast majority (87%) of all co-located Cd and Zn minerals (Figure 4). Co-located non-S-containing Cd minerals and non-S-containing Zn minerals make up a much smaller portion of co-located Cd minerals and Zn minerals as illustrated in Figure 4. The majority (81%) of co-located Cd minerals and Zn minerals occur from 0.6 Ga to present day (Figure 4). Cd minerals have a narrower range of mean mineral electronegativity values than Zn minerals (Cd mean mineral electronegativity range = 1.97 to 2.565; Zn mean mineral electronegativity range = 1.61 to 2.7; pure Cd and Zn mean mineral electronegativities are not included), which coincides with the greater chemical diversity of Zn minerals compared to Cd minerals (Figure 5). Furthermore, minerals that contain both Zn and S also have a narrow range of mean mineral electronegativity values through geologic time (mean mineral electronegativity range of S-containing Zn minerals = 1.737 to 2.582) that is more similar to Cd minerals (Figure 6), illustrating the chemical similarities and, therefore, propensity towards similar weathering rates of Cd minerals and S-containing Zn minerals.

The PSI-BLAST search performed using the seed Cd-CA sequence from the marine diatom *Thalassiosira weissflogii* (PDB ID 3BOB) did not reveal any related sequences. Therefore, it is either possible that the Cd-CA is a lineage-specific evolutionary innovation in these diatom species, or further environmental metagenomics studies may reveal other species which also possess this protein.

4. Discussion

The mineral chemistry of Cd throughout Earth's history is less extensive compared to many other transition metals, however, the element's chemical associations and mineral formation with S (Figures 1-3) are important to Cd geochemical cycling (Saito, Sigman, and Morel 2003). Cadmium sulfides readily precipitate under acidic and alkaline conditions (Milligan 1934; Rittner and Schulman 1943), and are known to be highly weatherable (Bertine and Goldberg 1971; Callender 2003; Cullen and Maldonado 2013). Weathered Cd sulfides or trace amounts of Cd associated with S in basalt can therefore represent a potential source of Cd to the environment, particularly given the relative abundance of S-containing Cd minerals compared to all other Cd minerals (Figure 1). Conversely, Zn is roughly 650 times more abundant than Cd in the Earth's crust (Wedepohl 1995), which largely contributes to the existence of many more Zn mineral species than Cd mineral species, and the occurrence of Zn minerals at a much larger number of localities than Cd minerals [(Golden et al. 2019) http://rruff.info/evolution/]. However, similar to Cd, the high relative abundance of S-containing Zn mineral localities compared to all other Zn minerals (Figures 2, 3), and the high weatherability of Zn sulfides (Stanton 2005; Robson et al. 2014), indicate that Zn sulfides represent a potential source of Zn to the environment.

Despite the differences in mineral chemistry between Cd and Zn, the S-containing minerals and sulfide complexation of the two elements share certain characteristics in common. Approximately 64% of Cd mineral species contain S, while only 25% of Zn minerals contain S, resulting in Cd and S clustering together in the combined Cd-Zn mineral chemistry network (Figure 3). Multiple Zn and Cd sulfide compounds have comparable stability constants and display similar dissolved concentration fluctuations in response to changing conditions in seawater (Zhang and Millero 1994; Luther et al. 1996; Al-Farawati and van den Berg 1999; Cutter, S. Walsh, and Silva de Echols 1999). Furthermore, bioinorganic chemistry modelling work by Saito et al. (Saito, Sigman, and Morel 2003) demonstrated that dissolved concentrations of both Cd and Zn would have been significantly lower than present day in the ferro-sulfidic ocean of the Archean eon (Shen, Buick, and Canfield 2001), and even lower still in the sulfidic ocean of the Proterozoic eon (D. E. Canfield 1998; Poulton, Fralick, and Canfield 2004). The importance of late-evolving Zn-binding proteins in Eukaryotes, and the increased bioavailability Zn in oxygenated waters of the Phanerozoic eon indicate that Zn was a crucial cofactor in eukaryotic evolution (Dupont et al. 2006; 2010). Mineral chemistry can shed additional light on the biogeochemical links between Cd and Zn described in Saito et al. (Saito, Sigman, and Morel 2003) by characterizing chemical associations of the two elements.

The closer overlapping range of mean mineral electronegativity between Cd minerals and S-containing Zn minerals represents similar chemical attributes between Cd minerals and S-containing Zn minerals compared to all other non-S-containing Zn minerals (Figures 5, 6). Our results show that the common co-location of S-containing Cd and Zn minerals (Figure 4), in concert with the similar stability constants of Cd sulfides and Zn sulfides in seawater (Zhang and Millero 1994; Luther et al. 1996; Al-Farawati and van den Berg 1999; Cutter, S. Walsh, and Silva de Echols 1999), would result in simultaneous weathering and availability of Cd and Zn to the environment. Co-weathering of S-containing Cd and Zn minerals would result in a direct source of Cd to marine diatoms after Zn is depleted, and greater access to Cd as an alternative cofactor than if the element was weathered from a distant separate source that is not directly linked through aqueous/marine transport. The mutual mineral chemistry properties (Figures 3, 5, 6) and shared localities (Figure 4) of S-containing Cd and Zn minerals allow for weatherability and simultaneous transport of Cd and Zn to marine waters, thus supporting the biogeochemical link between the two elements described in Saito et al. (Saito, Sigman, and Morel 2003).

Similar chemical and physical properties of Cd and Zn underscore the various geochemical links between the two elements. Cadmium and zinc are both group 12 elements in the periodic table with similar electron configuration, and both elements predominantly occur in the Cd^{2+} and Zn^{2+} redox states (J. O. Nriagu 1980). Significant sources of Cd in Earth's crust occur as surface coatings with the abundant Zn sulfides sphalerite and wurtzite, and certain Zn silicates and carbonates can contain up to 1.25% concentration of Cd (Fleischer et al. 1974; Gong, Rose, and Suhr 1977; J. O. Nriagu 1980). Sphalerite generally contains 0.2 to 1.0 wt.% Cd, and in some cases Cd content in sphalerite can be as high 13.2 wt.% (Cook et al. 2009). Additionally, Cd was first isolated and identified as a trace metal impurity in Zn carbonates (Cullen and Maldonado 2013). Therefore, the weathering of trace amounts of Cd associated with Zn minerals, particularly the highly abundant mineral sphalerite, would be an additional simultaneous source of both Cd and Zn to the environment in addition to the weathering of co-located Cd- and Zn-containing minerals and basalts. Due to tectonic processes, there is a greater probability that older rocks and minerals will be subducted and lost to the mantle, resulting in greater preservation of younger minerals (Taylor and McLennan 1995; Rapp and Watson 1995) and potential age bias in some data from the Mineral Evolution Database. The maximum known mineral ages and associated references of Archean and Proterozoic Cd minerals are given in Supplementary Table S1.

The comparable mineral chemistry and common co-occurrence of Cd and Zn appear to be important in the shared biological functions of Cd and Zn in carbonic anhydrase (CA) as well. Carbonic anhydrase is a globally significant enzyme that catalyzes the interconversion of CO_2 and HCO_3^- in photosynthetic organisms to fix carbon (Meldrum and Roughton 1933; Wilbur and Anderson 1948; Badger and Price 1994). Zinc is a crucial cofactor in the function of carbonic anhydrase, but it has also been discovered that Cd can serve as an alternative metal cofactor in CA for marine diatoms when Zn is depleted in the environment (Price and Morel 1990; Lane and Morel 2000; Lane et al. 2005; Park, Song, and Morel 2007; Xu et al. 2008). Diatoms are highly productive primary producers that rapidly deplete nutrients in surface waters during blooms and influence global Zn biogeochemistry (Vance et al. 2017). It has also been shown that Zn may limit primary production in diatom dominated sub-arctic waters (Coale 1991; Crawford et al. 2003). Therefore, the weathering and availability of co-located S-containing Cd and Zn minerals, and trace Cd in Zn minerals, may support CA function and primary production by diatoms during Zn scarcity.

Although several classes of CA proteins exist, Cd is only found in one specific class of CA (ζ-CA) which has an overall unique amino acid residue structure surrounding the metal cofactor ion (i.e. Zn or Cd) (Xu et al. 2008; Amata et al. 2011; Alterio et al. 2012). In contrast, Zn carbonic anhydrase occurs in a wide range of taxa (Pinter and Stillman 2014; Supuran 2016). The diatoms that are known to use Cd during periods of Zn scarcity prefer Zn when it is available, due to the greater enzymatic efficiency and faster yield rate of inorganic carbon when using Zn as the metal cofactor (Lane et al. 2005; Xu et al. 2008). The only other class of CAs known to have a similar structure to ζ-CA is β-CA, such that both enzymes have 2 cysteine residues and 1 histidine residue that bind either Zn or Cd (Xu et al. 2008; Supuran 2016). The shared structures of ζ-CA and β-CA suggest an evolutionary link between the two protein classes, and may be a topic of evolutionary divergence given that β-CA synthesizing organisms are largely photosynthetic plants and algae, while ζ-CA synthesizing organisms are a specific group of marine diatoms (Sültemeyer 1998; Moroney, Bartlett, and Samuelsson 2001; Amata et al. 2011).

Despite the structural similarities between ζ-CA and β-CA, organisms that synthesize β-CA do not use Cd as an alternative cofactor to Zn (Day and Franklin 1946; Rowlett 2010). This is because β-CA synthesizing organisms exhibit a normal toxic response to Cd exposure. Phytochelatins (PC) are crucial proteins found in ζ-CA synthesizing organisms that serve to transport Cd ions to the CA complex for carbon fixation and inhibit the toxic shock response diatoms experience when taking in Cd ions, thus allowing Cd to be utilized in the CA metal cofactor site (Ahner, Kong, and Morel 1995; Lee, Ahner, and Morel 1996; Wu et al. 2016). Phytochelatin synthase proteins are activated by the presence of Cd and other potentially toxic ions [ex: Arsenic, As; (Uraguchi et al. 2017; Schmöger, Oven, and Grill 2000)], and the PC proteins themselves are composed from Glutathione (Cysteine, Glutamic acid, and Glycine), which function to form tight covalent bonds around the metallic ions (i.e. chelation) (Grill, Winnacker, and Zenk 1985; Grill et al. 1989). The evolution of PC proteins was thus crucial for the utilization of Cd by diatoms when Zn is unavailable in the environment.

The oldest known diatom fossils are approximately 180 million years old (Kooistra and Medlin 1996; Sims, Mann, and Medlin 2006; Falkowski and Knoll 2007), which occurs after the oxygenation of the oceans (D. E. Canfield 1998; Scott et al. 2008) and subsequent increase in Zn and Cd bioavailability in ocean waters (Saito, Sigman, and Morel 2003). Phanerozoic continental weathering was also enhanced by the colonization of land by terrestrial plants (Berner 1992), which could have impacted the mobilization of co-located S-containing Cd and Zn minerals (Figure 4) to coastal waters. Given that diatoms are known to be highly productive primary producers that quickly use up available dissolved nutrients (Furnas 1990; Armbrust 2009; Mahadevan et al. 2012), the availability of Cd from weathered S-containing minerals following rapid Zn depletion by highly productive diatom blooms may have influenced the evolution of ζ-CA and PCs involved in Cd utilization.

6. Conclusions

Despite the limited mineral chemistry of Cd, the relative abundance of highly weatherable S-containing Cd minerals compared to other Cd minerals, and the co-location of S-containing Cd and Zn minerals were likely contributing factors in the availability and utilization of Cd as an alternative cofactor to Zn in carbonic anhydrase. Zinc forms minerals with a wider range of elements than Cd, but the shared S-containing mineral chemistry, solubility, and localities of the two metals enhanced their biogeochemical link. The ability of diatoms to use Cd as a cofactor in carbonic anhydrase during a period of dramatic change in the geosphere and biosphere, supported carbon fixation by diatoms during periods of Zn scarcity. Alterations to the biogeochemical cycles of Zn and Cd exemplify the importance of the coevolution of the geosphere and biosphere in shaping primary production in the modern ocean.

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Figure Captions

Figure 1. Expanding bipartite mineral chemistry networks depicting all known Cd minerals and their constituent elements at specific time periods [(Golden et al. 2019) http://rruff.info/evolution/]. (**a**) All Cd minerals with maximum known ages ≥2.7 billion years ago (Ga); (**b**) ≥0.6 Ga; (**c**) ≥0.2 Ga; (**d**) Present day. Mineral nodes are represented by circles (color represents maximum known mineral ages). Element nodes are represented by their chemical symbols. Mineral nodes have network connections (referred to as "edges"; edges are unweighted) to each of their constituent elements. For example, greenockite (CdS) has network edges connected to Cd and S. Mineral nodes are sized by number of known localities, and element nodes are sized by number of network edges (i.e., the number of minerals which contain that element). Networks were created using the `dragon` R package (Spielman 2019).

Figure 2. Cd and Zn bipartite mineral chemistry network at present day containing all known Zn and Cd minerals and their constituent elements. Mineral nodes are sized by number of localities and colored by maximum known age. Element nodes are sized by number of network edges.

Figure 3. Cd and Zn bipartite mineral chemistry network at present day containing all known Zn and Cd minerals and their constituent elements. Mineral nodes and element nodes are colored by Louvain community detection clusters (Blondel et al. 2008). Mineral are sized by number of localities and element nodes are sized by number of network edges.

Figure 4: Total number of localities that S-containing Cd minerals and S-containing Zn minerals co-occur at (brown triangles), and total number of localities that non-S-containing Cd minerals

and non-S-containing Zn minerals co-occur at (black squares) through geologic time. First GOE = Great Oxidation Event (Farquhar, Bao, and Thiemens 2000; Farquhar and Wing 2003); Second GOE (Fike et al. 2006; Don E. Canfield, Poulton, and Narbonne 2007; Sahoo et al. 2012); Oldest diatom fossils (Kooistra and Medlin 1996; Sims, Mann, and Medlin 2006; Falkowski and Knoll 2007).

Figure 5. Cadmium and zinc bipartite mineral chemistry networks at present day containing all known Zn and Cd minerals and their constituent elements. Mineral nodes are sized by number of localities and colored by mean element electronegativity. Element nodes are sized by number of network edges. (**a**) Cadmium minerals and their constituent elements are highlighted. (**b**) Zinc minerals and their constituent elements are highlighted.

Figure 6. Plot of mean mineral electronegativity by maximum mineral age in billions of years (Ga) for (**a**) minerals that contain Cd; (**b**) minerals that contain both Zn and S; and (**c**) minerals that contain Zn. Mean mineral electronegativity is calculated as an unweighted average of each mineral's constituent element electronegativities.