

# JGR Biogeosciences

## RESEARCH ARTICLE

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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

### Supporting Information:

- Supporting Information S1

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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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**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 cofactor for zinc (Zn) in photosynthetic carbon fixation pathways of 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 the 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 network centrality values when specifically considering sulfur (S)-containing species. Cadmium and Zn 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, were 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 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 (Dey et al., 2007; Holm et al., 1996; Hosseinzadeh & 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 two spheres became so intertwined. The transition metal cadmium (Cd) is toxic to many biological systems (Das et al., 1997; Flick et al., 1971). Exposure to Cd results in the breakdown of cellular phospholipid bilayers due to production of hydrogen peroxide (Khan et al., 2013), and Cd directly damages DNA making the metal a potent carcinogen (Coogan et al., 1992; Giaginis et al., 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 DNA nucleotide biosynthesis enzyme aspartate transcar-

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bamoylase (Rosenbusch & Weber, 1971). Carbonic anhydrase (CA) catalyzes the conversion of  $\text{CO}_2$  and  $\text{HCO}_3^-$  in photosynthetic organisms to fix carbon (Badger & Price, 1994; Meldrum & Roughton, 1933; Wilbur & Anderson, 1948), and in marine diatoms Cd is known to be used as an alternative cofactor to Zn in the CA enzyme (Lane & Morel, 2000; Park et al., 2007; Price & Morel, 1990). 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 ( $\sim 0.1\text{--}0.5$  nmol  $[\text{Cd}^{2+}]/\text{kg}$  seawater) and increasing concentrations in deeper waters ( $\sim 1.0$  nmol  $[\text{Cd}^{2+}]/\text{kg}$  seawater; Boyle et al., 1976). The concentration of Cd in seawater is below the level of Cd toxicity response in the marine diatom *Thalassiosira nordenskiöldii* (Wang & Wang, 2008), and the gradient of Cd in marine waters is impacted by light penetration, the ability of phytoplankton to sustain photosynthesis at depth, nonspecific uptake of Cd, and Cd homeostasis in microbial cells (Horner et al., 2013).

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). Volcanoes are the largest source of natural Cd emissions to the atmosphere, followed by biogenic sources, aeolian transport, terrestrial biomass burning, and sea-salt spray (Cullen & Maldonado, 2013; Nriagu, 1989). The specific environmental factors that influence Cd deposition and cycling vary greatly depending on the local ecosystem (Barrow et al., 1989; Bruemmer et al., 1988; Gerth & Brümmer, 1983; Kelly et al., 2001; Lock & Janssen, 2003; Yee & Fein, 2001). Within freshwater ecosystems, for example, Cd's availability and toxicity depends on the element's speciation with organic matter, concentration and characteristics of dissolved organic carbon, pH, and cations in solution (Sigg & Behra, 2005). By contrast, in more saline waters, cationic interactions increase Cd mobility and solubility (Duce et al., 1991). Finally, when Cd interacts with soils and minerals, factors such as redox potential, pH, and organic ion presence influence its bioavailability (Lock & 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 strong impact on the formation of an equilibration cycle between soil runoff and water cycling.

Various mechanisms of biological pathways involving Cd have been well documented (Beyersmann & Hechtenberg, 1997; Lane et al., 2005; Lane & Morel, 2000; Park et al., 2007; Rosenbusch & Weber, 1971; 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. (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 & Goldberg, 1971; Callender, 2003; Cullen & Maldonado, 2013).

Network analysis has emerged as a powerful technique to investigate mineral evolution and mineral ecology (Hazen et al., 2019; Hystad et al., 2019; Morrison et al., 2017). 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. For example, bipartite network analysis has recently been applied to understand redox evolution of cobalt and vanadium and their bioavailability in the Archean ocean (Moore et al., 2018, 2020). Here, we examine the mineral records and mineral chemistry networks of Cd and Zn to examine and compare the chemistry and location of potentially weatherable Cd and Zn mineral sources over different periods of Earth history. We specifically examine the time periods relevant to the emergence of marine diatoms and the utilization of Cd as a cofactor in the CA enzyme.

## 2. Methods

### 2.1. Mineral Chemistry Network Analysis

Bipartite network analysis of Cd and Zn mineral chemistry was performed using the R package dragon (Spielman & Moore, 2020). 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  $\geq 0.2$ . We selected the time range of  $\geq 2.7$  Ga because only one Cd mineral has a maximum (i.e., oldest) known age of  $\geq 2.8$  Ga (greenockite). We selected the time range of  $\geq 0.6$  Ga as it is positioned at the beginning of an increase in all preserved mineral localities, including Cd mineral and Zn mineral localities ([Golden et al., 2019] <https://rruff.info/evolution/>). Finally, we selected the time range of  $\geq 0.2$  Ga as this period approximately coincides with the oldest known evidence for the presence of diatoms, the only organisms known to use the alternative Cd-CA protein (Alterio et al., 2015; Falkowski & Knoll, 2007; Kooistra & Medlin, 1996; Sims et al., 2006).

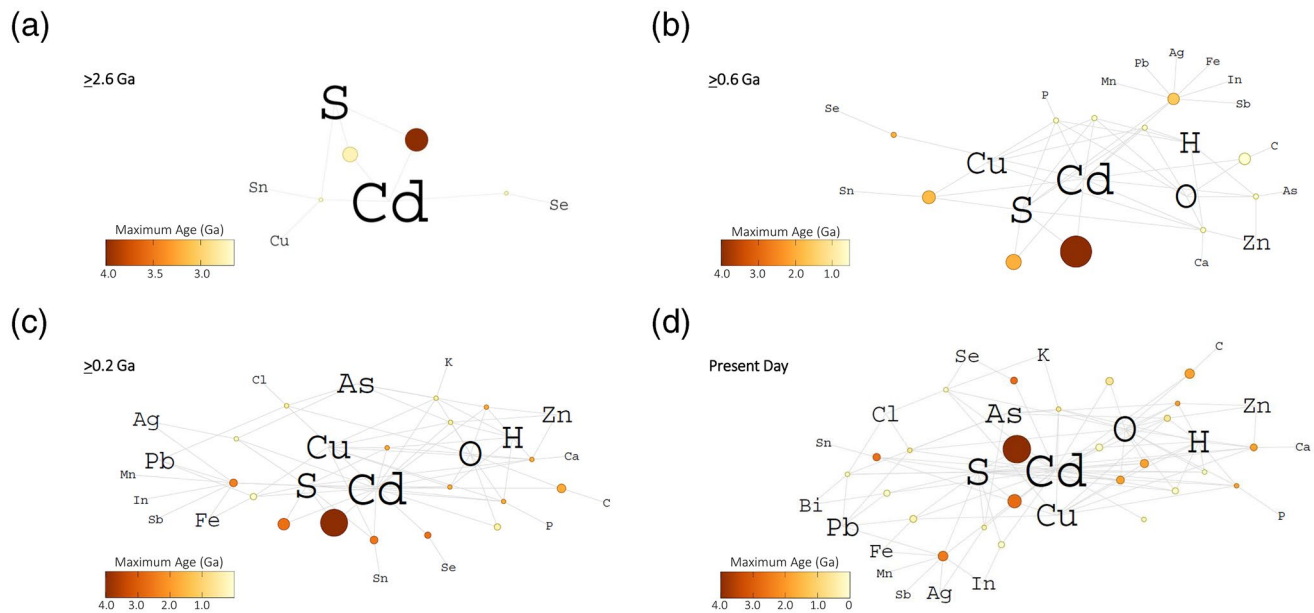
We performed Louvain community detection cluster analysis (Blondel et al., 2008) using dragon to identify associations between minerals and elements in the Cd and Zn combined mineral chemistry network. We specifically applied the Louvain community detection method for this study because it optimizes modularity when identifying network node communities (Blondel et al., 2008). The Louvain method is a greedy optimization method and is similar to the network community detection method developed by Clauset et al. (2004).

Mineral data were compiled for analysis from the Mineral Evolution Database (MED; [Golden et al., 2019] <https://rruff.info/evolution/>; Accessed February 3, 2020). The process of assembling, sorting and downloading mineral data from the MED is described in detail for carbon minerals by (Morrison et al., 2020). The data included 25 Cd mineral species, 307 Cd mineral localities, 255 Zn mineral species, and 10,837 Zn mineral localities (Cd and Zn minerals in Table S2). 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), cataloged in the MED ([Golden et al., 2019] <https://rruff.info/evolution/>). Minerals with the same Mindat locality ID number are defined as co-located. 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/>. 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 (Rapp & Watson, 1995; Taylor & McLennan, 1995) and potential age bias in some data from the MED. The maximum known mineral ages and associated references of Archean and Proterozoic Cd minerals are given in Table S1. Additionally, we performed a Position-Specific Iterative-Basic Local Alignment Search Tool (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).

### 3. Results

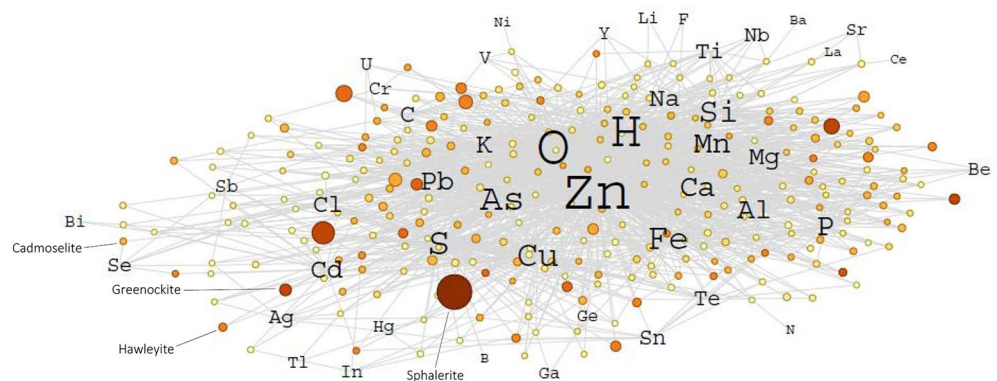
Evolving mineral chemistry bipartite networks can be used to examine the relationships between minerals and the chemical elements in their ideal chemical formulas through deep time (Spielman & Moore, 2020). Figure 1 represents the evolution of Cd mineral chemistry bipartite networks from the oldest known samples into modern day, clearly illustrating the limited mineral chemistry network expansion prior to 0.6 Ga for all minerals, including Cd, and the subsequent dramatic expansion after 0.6 Ga ([Golden et al., 2019; Hazen et al., 2019; Spielman & Moore, 2020]; <https://rruff.info/evolution/>, Accessed February 3, 2020). Sulfur is the most common mineral-forming element in Cd minerals based the number of Cd minerals that contain S and the number of localities at which S-containing Cd minerals occur 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. Additionally, 8 of the 11 Cd minerals with maximum known ages that are older than 1.8 Ga contain 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, coinciding with a general increase in mineral record preservation leading to the present day.

While Cd and Zn have the same outer shell electron configuration and similar chemical properties, Zn is much more abundant than Cd in the Earth's crust (Zn = 65.5 ppm; Cd = 0.102 ppm; [Cullen &



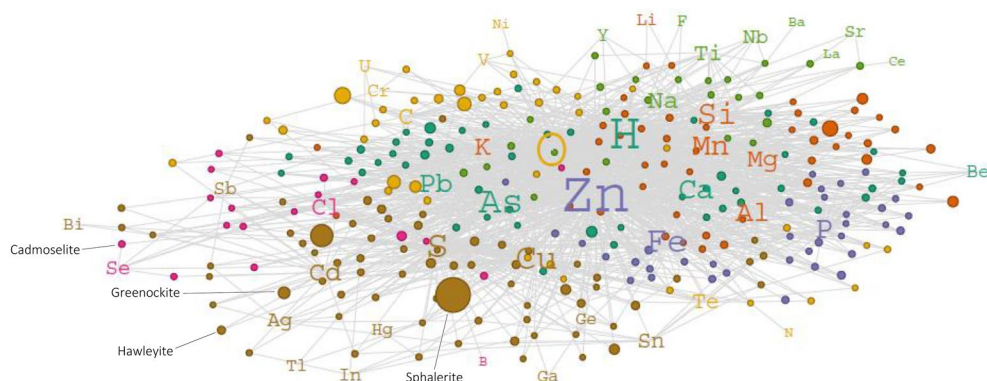
**Figure 1.** Expanding bipartite mineral chemistry networks depicting all known Cd minerals and their constituent elements at specific time periods ([Golden et al., 2019] <https://ruff.info/evolution/>). (a) All Cd minerals with maximum known ages  $\geq 2.7$  billion years ago (Ga); (b)  $\geq 0.6$  Ga; (c)  $\geq 0.2$  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 & Moore, 2020). Cd, cadmium; S, sulfur.

Maldonado, 2013; Rudnick & Gao, 2003; Wedepohl, 1995]). The mineral record further shows that Zn forms a larger number of minerals with a wider range of elements than does Cd (Figure 2). In particular, O and H form minerals with Zn much more commonly than they do 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 are 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



**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. Cd, cadmium; Zn, zinc.



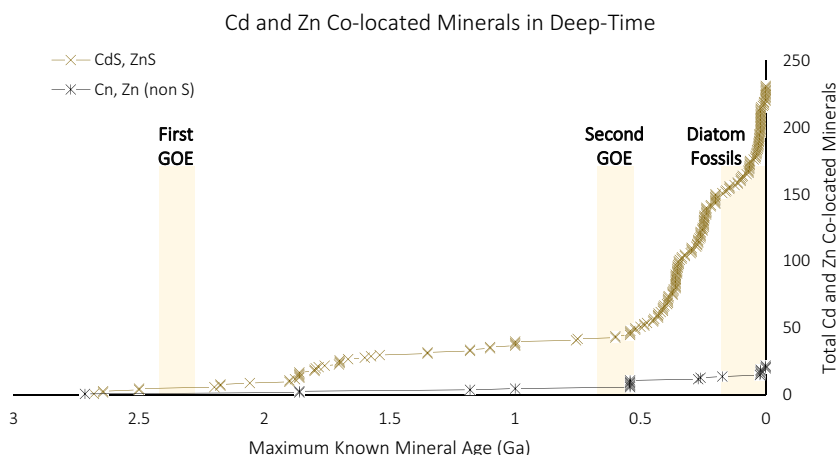


**Figure 3.** Cd and Zn bipartite mineral chemistry network at present day containing all known Zn and Cd minerals and their constituent elements. Mineral nodes and element nodes are colored by Louvain community detection clusters (Blondel et al., 2008). Mineral are sized by number of localities, and element nodes are sized by number of network edges. Cd, cadmium; Zn, zinc. Key: brown = cluster 1; pink = cluster 2; purple = cluster 3; teal = cluster 4; gold = cluster 5; green = cluster 6; dark orange = cluster 7.

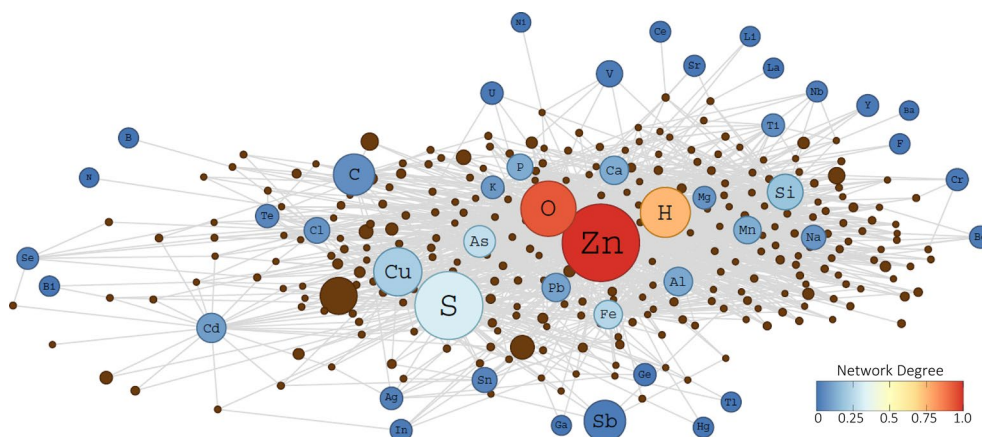
S still comprise the majority of all known Zn mineral localities (62%). Similarly to Cd and greenockite, the Zn sulfide mineral sphalerite is found at by far the largest number of known localities (>4,500 localities).

In the present day Cd-Zn combined network, based on Louvain community detection analysis, 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 elements that commonly form minerals with 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 with which Zn and O each form minerals, 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), suggesting 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



**Figure 4.** Total number of localities that S-containing Cd minerals and S-containing Zn minerals co-occur at (brown "X" symbols), and total number of localities that non-S-containing Cd minerals and non-S-containing Zn minerals co-occur at (black "cross-X" symbols) through geologic time. First GOE = Great Oxidation Event (Farquhar et al., 2000; Farquhar & Wing, 2003); Second GOE (Canfield et al., 2007; Fike et al., 2006; Sahoo et al., 2012); Oldest diatom fossils (Falkowski & Knoll, 2007; Kooistra & Medlin, 1996; Sims et al., 2006). Cd, cadmium; S, sulfur; Zn, zinc.



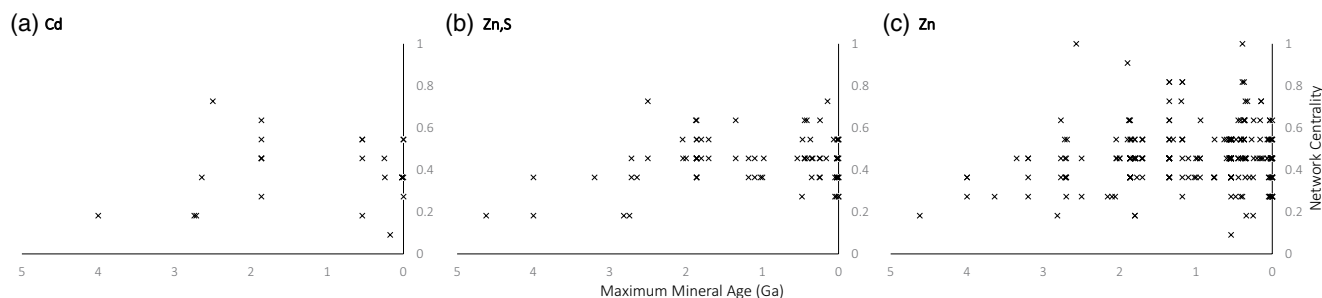
**Figure 5.** Cadmium and Zn bipartite mineral chemistry network containing all known Zn and Cd minerals and their constituent elements. Mineral nodes (brown) are sized by number of localities. Element nodes are sized by total number of mineral localities that each element occurs at in either a Cd or Zn mineral. Element nodes are colored by network degree: the number of network lines (i.e., edges) connected to each element (e.g., the number of Cd or Zn mineral species that each element occurs in). Cd, cadmium; Zn, zinc.

from 0.6 Ga to present day (Figure 4). While there are more O-containing Zn mineral species (i.e., higher network degree centrality) than there are S-containing Zn mineral species, S-containing Zn minerals occur at more localities than do O-containing Zn minerals. We also observe this trend for S-containing Cd minerals (Figure 5). Furthermore, the distributions of network degree centrality values are smaller and more similar between Cd minerals and S-containing Zn minerals as compared to the larger distribution of network centrality values for all other Zn minerals (Figure 6), illustrating the chemical similarities and, therefore, propensity toward 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

Although the mineral chemistry of Cd throughout Earth's history is less extensive than that of many other transition metals, Cd's chemical associations and mineral formation with S (Figures 1–3) are important to Cd geochemical cycling (Saito et al., 2003). Cadmium sulfides readily precipitate under acidic and alkaline conditions (Milligan, 1934; Rittner & Schulman, 1943) and are known to be highly weatherable (Bertine & Goldberg, 1971; Callender, 2003; Cullen & Maldonado, 2013). Weathered Cd sulfides or trace amounts of Cd associated with S in basalt therefore represent a potential source of dissolved Cd to the environment, particularly given the relative abundance of S-containing Cd minerals compared to all other Cd minerals



**Figure 6.** Plot of network centrality values for each mineral node in the combined Cd and Zn network by maximum mineral age in billions of years (Ga). Cd, cadmium; S, sulfur; Zn, zinc.

(Figure 1). Conversely, Zn is roughly 650 times more abundant than is Cd in the Earth's crust (Cullen & Maldonado, 2013; Rudnick & Gao, 2003; Wedepohl, 1995). This stark difference contributes to a substantially higher abundance of Zn mineral species compared to Cd mineral species, as well as the occurrence of Zn minerals at many more localities than Cd minerals ([Golden et al., 2019] <https://rruff.info/evolution/>). However, similar to S-containing Cd minerals, the high relative abundance of S-containing Zn mineral localities compared to all other Zn minerals (Figures 2 and 3), and the high weatherability of Zn sulfides (Robson et al., 2014; Stanton, 2005), 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. Approximately 64% of Cd mineral species contain S, while only 25% of Zn mineral species 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 physical and chemical conditions in seawater (Al-Farawati & van den Berg, 1999; Cutter et al., 1999; Luther et al., 1996; Zhang & Millero, 1994). Furthermore, bioinorganic chemical modeling work by Saito et al. (2003) determined that dissolved concentrations of Cd and Zn were much lower in both the ferro-sulfidic Archean ocean (Shen et al., 2001) and the sulfidic Proterozoic ocean (Canfield, 1998; Poulton et al., 2004) compared to the modern oxic ocean. The biological 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 how Cd availability allowed the element to be a replacement cofactor for Zn in CA of diatoms, and support the biogeochemical links between Cd and Zn described in Saito et al. (2003) by characterizing chemical associations of the two elements.

The high number of localities for S-containing Cd minerals and S-containing Zn minerals compared to non-S-containing Cd and Zn minerals, and the closer overlapping range of network degree centrality values and shared elements 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 and 6). Our results suggest 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 (Al-Farawati & van den Berg, 1999; Cutter et al., 1999; Luther et al., 1996; Zhang & Millero, 1994), would result in simultaneous weathering and availability of Cd and Zn to the environment. Co-weathering of S-containing Cd and Zn minerals would provide a direct source of Cd to marine diatoms if Zn were depleted, moreso than if Cd were weathered from a distant separate source that was not directly linked to the Zn source through aqueous/marine transport. The mutual mineral chemistry properties (Figures 3, 5 and 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. (2003).

Similar chemical and physical properties of Cd and Zn additionally underscore the various geochemical links between the two elements. Cadmium and Zn are both group 12 elements in the periodic table with similar electron configuration, and both elements predominantly occur in the  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  redox states (Nriagu, 1980). The surface coatings of Zn sulfides commonly contain Cd, and certain Zn silicates and carbonates can contain up to 1.25% concentration of Cd (Cullen & Maldonado, 2013; Fleischer et al., 1974; Gong et al., 1977; Nriagu, 1980). The Zn sulfide 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). Indeed, Cd was first isolated and discovered as a trace metal impurity in Zn carbonates (Cullen & Maldonado, 2013), further demonstrating the connection between these two elements. 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 beyond only the weathering of co-located Cd- and Zn-containing minerals and basalts.

The comparable mineral chemistry and common co-occurrence of Cd and Zn may also have contributed to the similar biological usage Cd and Zn in the CA enzymes of certain marine diatoms. By catalyzing the conversion of  $\text{CO}_2$  and  $\text{HCO}_3^-$  in photosynthetic organisms to fix carbon, CA represents an important enzyme

in the global carbon cycle (Badger & Price, 1994; Meldrum & Roughton, 1933; Wilbur & Anderson, 1948). Zinc is a crucial cofactor in the function of CA, 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 (Lane et al., 2005; Lane & Morel, 2000; Park et al., 2007; Price & Morel, 1990; 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). Studies have also 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 ( $\zeta$ -CA) which has an overall unique structure surrounding the metal cofactor ion (i.e., Zn or Cd; Alterio et al., 2012; Amata et al., 2011; Xu et al., 2008). In contrast, Zn CA occurs in a wide range of taxa from microbes to plants (Pinter & 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  $\zeta$ -CA is  $\beta$ -CA, such that both enzymes have two cysteine residues and one histidine residue that bind either Zn or Cd (Supuran, 2016; Xu et al., 2008). The evolutionary history of CAs remains an open question, largely due to the limited known occurrences of  $\zeta$ -CA. Indeed,  $\beta$ -CA has been found in largely photosynthetic plants and algae, while  $\zeta$ -CA appears, potentially, specific to marine diatoms (Amata et al., 2011; Moroney et al., 2001; Sültemeyer, 1998). However, the highly similar structures between  $\zeta$ -CA and  $\beta$ -CA, coupled with their distinct phylogenetic distributions, suggests an ancient evolutionary divergence.

Despite the structural similarities between  $\zeta$ -CA and  $\beta$ -CA, organisms that synthesize  $\beta$ -CA do not use Cd as an alternative cofactor to Zn (Day & Franklin, 1946; Rowlett, 2010) as  $\beta$ -CA synthesizing organisms are not able incorporate Cd into the CA active site without exhibiting a normal toxic cellular response to Cd exposure. Phytochelatins (PCs) are crucial proteins found in  $\zeta$ -CA synthesizing organisms that actively 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 et al., 1995; Lee et al., 1996; Wu et al., 2016). Phytochelatin synthase proteins are activated by the presence of Cd and other potentially toxic ions (e.g., Arsenic, As; [Schmöger et al., 2000; Uraguchi et al., 2017]) 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 et al., 1985, 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 (Falkowski & Knoll, 2007; Kooistra & Medlin, 1996; Sims et al., 2006), which dates to after the oxygenation of the oceans (Canfield, 1998; Scott et al., 2008) and the subsequent increase in Zn and Cd bioavailability in ocean waters (Saito et al., 2003). Phanerozoic continental weathering was also enhanced by the colonization of land by terrestrial plants (Bernier, 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 (Armbrust, 2009; Furnas, 1990; 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  $\zeta$ -CA and PCs involved in Cd utilization.

## 5. 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 CA. 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 capability of diatoms to use Cd as a cofactor in CA, during a stage of Earth history characterized by dramatic change in the geosphere and biosphere, enhanced 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.

## Data Availability Statement

Data presented in this manuscript can be accessed from the MED ([Golden et al., 2019]; <https://rruff.info/evolution/>).

## Conflict of Interest

There are no financial conflicts of interest for any author of this study.

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