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Trace metal diagenesis in sulfidic sediments: Insights from Chesapeake Bay

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ABSTRACT

Sediments were recovered from the mid-bay portion of the Chesapeake Bay when bottom water conditions were sulfidic. Metal concentrations (Fe, Mn, Ba, V, Ni, Cu, Co, Cd, Mo, U, and Re) were determined in both pore waters and solid phase samples, which were determined using total and nitric acid digestion (EPA 3051a) methods. V, Cr, and Ni were preferentially retained in pore waters even under sulfidic conditions that would normally result in authigenic accumulation, likely due to complexation with dissolved organic matter (DOM). Mo was efficiently removed from pore waters in the zone in which FeS phases and polysulfides are available. Re was not delivered to the sediments through the Mn/Fe shuttle, so that its diffusive flux into sediments solely depends on the extent of reducing conditions.

A non-steady state oxygenation event was recorded in the solid phase, with coincident solid phase enrichments in Fe, Mn, Ni, Cu and Co. Deeper enrichments in U and Mo likely reflect remobilization from the relict Fe and Mn peaks, downward diffusion into more reducing conditions, and subsequent immobilization. The absence of peaks in solid phase Re, Cr and Cd was indicative of their lack of association with Mn and Fe oxides and/or resistance of their respective authigenic phases to oxidation on these seasonal to yearly timescales. Relative changes within the solid phase profiles were captured using the acid digestion method for Fe, Ni and Co, and acid digestion concentrations were within 90% of the total concentration for Mn and Cu. The presence of excess pore water sulfide may have promoted the removal of trace metals from the detrital fraction resulting in the formation of authigenic sulfides that might become mobile during oxygenation events.

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1. Introduction

Trace metals in sediments have been used to elucidate past changes in sedimentary reducing conditions (e.g., Calvert and Pedersen, 1993; Crusius et al., 1996; Piper and Isaacs, 1996; Zheng et al., 2000; Tribouillard et al., 2006; Algeo and Lyons, 2006), water column or bottom water oxygen (Zheng et al., 2000; Adelson et al., 2001; Scholz et al., 2011), bottom water sulfide (Zheng et al., 2000; Scott and Lyons, 2012), and anthropogenic influences (Adelson et al., 2001; Böning et al., 2004). In addition to metal concentrations or enrichment factors, investigations have interpreted the sediment record using metal/metal ratios (Crusius et al., 1996; Böning et al., 2004), metal concentrations in specific mineral phases, such as pyrite (Chappaz et al., 2014; Gregory et al., 2015), and isotopic fractionation (Von Allmen et al., 2010; Ellis et al., 2002; Frei et al., 2009; Scheiderich et al., 2010).

Literature describing trace metal geochemistry under present day conditions has been critical for making correct interpretations of past trace metal records (e.g., Beck et al., 2008; Scholz and Neumann, 2007; Dellwig et al., 2002; Shaw et al., 1990). The analysis of a suite of trace metals over a range of depositional environments was presented for sediments from the California Borderland to develop a comprehensive understanding of trace metal diagenesis (Shaw et al., 1990). This seminal publication provided a framework for interpreting trace metal pore water profiles and understanding authigenic accumulation within the context of a range of bottom water oxygen and sediment reducing conditions. The most reducing site, the Santa Monica Basin, had bottom water $[O_2] < 5 \mu M$ and sufficient reducible Fe (oxyhydr)oxides (referred to as Fe oxides) to both consume produced pore water sulfide and maintain pore water Fe concentrations in excess of $100 \mu M$ (Shaw et al., 1990). Shaw et al. further used a hydroxylamine hydrochloride leach method to operationally define the trace metals associated with reducible Mn and Fe oxides (Chester and Hughes, 1967), which was ideal for the relatively oxic conditions in the California Borderland Basins.

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To optimize our interpretation of past changes in sedimentary metal signatures, we must have a clear understanding of metal diagenesis extending to the sulfidic conditions responsible for authigenically accumulating so many different trace metals. Literature has focused on trace metal accumulation in sediments that are dominated by sulfate reduction and effectively remove all pore water Fe in the precipitation of FeS and FeS₂. However, these publications have tended to focus on solid phase profiles to determine authigenic accumulation (e.g., Jacobs et al., 1987; François, 1988; Crusius et al., 1996; Adelson et al., 2001; Dolor et al., 2012; Helz and Adelson, 2013). Fewer publications have included both pore water and solid phase profiles to provide a complementary description of trace metal diagenesis and to augment our understanding of authigenic accumulation in marine areas with sulfidic bottom and/or pore waters (e.g., Scholz et al., 2013). We seek to extend the work of Shaw et al. (1990) to the sulfidic environment of Chesapeake Bay, where we present an analysis of Fe, Mn, Ba, V, Ni, Cu, Co, Cd, Mo, U and Re in sediments. In addition to pore water (all elements) and total solid phase concentrations (Al, Fe, Mn, Ba, V, Ni, Cu, and Co), we also present a solid phase acid digestion fraction to elucidate the portion of trace metals that accumulate in sulfidic and/or carbonate phases (all elements, EPA 3051a; Link et al., 1998). The simultaneous investigation of a large number of trace metals from the same sediment cores allows for the immediate comparison of both diagenetic mobility and authigenic accumulation.

2. Background

There have been several recent papers that have included reviews of trace metal geochemistry (e.g., Tribouillard et al., 2006; Morford et al., 2005, 2009; Beck et al., 2008; Scholz et al., 2011; Swanner et al., 2014; Ingri et al., 2014; Huang et al., 2015); therefore, only brief reviews are included below.

2.1. Mn and Fe

Both Mn(IV) and Fe(III) exist as oxides under oxic conditions in marine waters. Both are used as oxidants in the oxidation of organic matter in a predictable order after the use of oxygen, producing pore water Mn(II), and after nitrate, producing pore water Fe(II); both of the aqueous ions can diffuse upwards to be reoxidized or down into more reducing sediments (e.g., Froelich et al., 1979). The reoxidation of Mn(II) is often slower than reoxidation of Fe(II), resulting in Mn(II) diffusion into overlying waters but an Fe cycle that is often restricted to sediments. Upon downward diffusion into sediments replete with sulfide, amorphous FeS and poorly ordered mackinawite result in measurable acid volatile sulfides (AVS, see Schoonen, 2004 and references therein). The formation of pyrite (FeS₂) is dependent on the amount of reactive Fe oxides in sediments relative to the amount of available hydrogen sulfide produced during sulfate reduction, and is further dependent on the particular mechanism of FeS₂ formation (e.g., Rickard, 1997; Rickard and Luther, 1997; Schoonen, 2004; Rickard and Luther, 2007). In sediments replete with pore water sulfide and limited in reactive Fe oxides, pore water Fe(II) can be completely exhausted in the precipitation of iron sulfides (e.g., Canfield, 1989). Mn(II) often precipitates in sediments as a carbonate (Jakobsen and Postma, 1989; Böttcher, 1998), leaving little pore water Mn available for incorporation into FeS₂. However, in sediments replete with pore water sulfide and high pore water Mn/Fe ratios, Mn can be found in the pyrite fraction (Morse and Luther, 1999). The reductive dissolution of Fe(III) and Mn(IV) oxides also liberates adsorbed trace metals to pore waters (see below), which can then diffuse up into overlying waters or down into sediments where conditions may be conducive for accumulation in the solid phase.

2.2. Cd, Ni, Co, and Cu

Cd is released to pore waters during organic matter diagenesis and accumulates in sediments (e.g., Rosenthal et al., 1995). Morse and Luther (1999) predicted the precipitation of CdS by determining that its relatively fast water exchange rate would allow for displacement by sulfide, which is the first step in metal sulfide precipitation. As CdS precipitation kinetics are faster than the precipitation of Fe monosulfide phases then Cd²⁺ is removed from pore waters upon the appearance of pore water H₂S, precluding its incorporation into FeS phases (Morse and Luther, 1999). The literature supports the precipitation of CdS (Framson and Leckie, 1978; Pedersen et al., 1989; Griffin et al., 1989), and solid phase Cd concentrations increase with increasing AVS, lending further support to authigenic Cd precipitation as CdS (Gobeil et al., 1997).

Both Ni and Co are associated with release during organic matter oxidation (Westerlund et al., 1986; Saito et al., 2002; Fones et al., 2004), adsorption to Mn and occasionally Fe oxides, and subsequent release during Mn and Fe reduction (Heggie and Lewis, 1984; Shaw et al., 1990; Fones et al., 2004; Tankere-Muller et al., 2007; Santos-Echeandia et al., 2009; Stockdale et al., 2010; Wu et al., 2011; Pradit et al., 2013; Ingri et al., 2014; Swanner et al., 2014). Data suggest lower water exchange rates for Ni and Co would result in sufficiently high pore water concentrations to allow for adsorption onto or co-precipitation with FeS solid phases (Morse and Luther, 1999), which has been observed with sequential extractions for Ni (Griffin et al., 1989). However, there has been some data that suggests the formation of distinct sulfides rather than co-precipitation (Huerta-Diaz et al., 1998; Gao et al., 2009; Frohne et al., 2011).

Cu is also released during organic matter oxidation (Shaw et al., 1990; Tankere-Muller et al., 2007; Scholz and Neumann, 2007; Santos-Echeandia et al., 2009). Under oxic conditions, the adsorption to Mn oxides allows for the subsequent Cu release to pore waters during Mn(IV) reduction and remobilization to pore waters (Fones et al., 2004; Ingri et al., 2014). There are a wide variety of Cu sulfide and Cu-Fe sulfide phases that can form and coexist (Morse and Luther, 1999), which can complicate understanding Cu inclusion in pyrite-containing sediments. Under sulfidic conditions sediment profiles tend to show decreasing Cu pore water concentrations and increasing solid phase Cu associated with solid FeS (Huerta-Diaz et al., 1998; Gao et al., 2009).

2.3. V, and Cr, and Ba

In oxygenated waters, V is found as vanadate (HVO₄²⁻ or H₂VO₄⁻), which adsorbs to both Mn and Fe oxides (e.g., Takematsu et al., 1985; Trefry and Metz, 1989), and is summarily released during Mn and Fe oxide reduction and mobilization to pore waters (Shaw et al., 1990; Emerson and Husted, 1991; Morford and Emerson, 1999; Morford et al., 2005; Wang and Sañudo-Wilhelmy, 2009; Scholz et al., 2011). Pore water V concentrations have also been seen to increase during organic matter oxidation (Shaw et al., 1990; Beck et al., 2008; Santos-Echeandia et al., 2009). Under more reducing conditions, V(V) is reduced to V(IV), which more easily complexes with organic or inorganic ligands while also being more surface reactive relative to vanadate. This dual ability of V(IV) can result in pore water V concentrations that remain high even under reducing conditions, presumably due to the ability of V(IV)O₂⁺ to complex with dissolved organic matter leading to a preference for remaining in the aqueous phase (Cheshire et al., 1977; Beck et al., 2008; Santos-Echeandia et al., 2009; O'Connor et al., 2015). Upon further reduction, V(III) can form resulting in the subsequent precipitation of V₂O_{3(s)} or V(OH)_{3(s)} and accumulation in sediments (Sadiq, 1988; Wehrli and Stumm, 1989).

Cr is associated with organic matter and is subsequently released during organic matter oxidation (e.g., Brumsack and Gieskes, 1983; Shaw et al., 1990; Beck et al., 2008; O'Connor et al., 2015). Primarily present in oxic waters as Cr(VI)O₄²⁻, authigenic precipitation of Cr occurs under reducing conditions (e.g., Shaw et al., 1990; Zwolsman et

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