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The distribution of dissolved and particulate Mo and V along the U.S. GEOTRACES East Pacific Zonal Transect (GP16): The roles of oxides and biogenic particles in their distributions in the oxygen deficient zone and the hydrothermal plume

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ABSTRACT

Molybdenum and vanadium are under-studied elements in the ocean due to their largely conservative natures. Thus, no detailed ocean sections of these elements exist although previous reports do suggest possible anomalies in their distributions due to biological, redox, or sorptive processes. Here we present the first detailed ocean sections of dissolved and particulate Mo and V, obtained as part of the 2013 US GEOTRACES East Pacific Zonal Transect (GP16) from Peru to Tahiti. Similar to previous work, the distribution of dissolved Mo was largely conservative, while dissolved V showed a ~5% depletion in the upper waters. For dissolved Mo, a small number of samples showed significantly depleted concentrations which, in most cases, gradually increased with time after samples were acidified. This implies the original sample had experienced a partial change in speciation of dissolved Mo from the predominant molybdate to another, as yet, unknown form. In the oxygen deficient zone (ODZ) off the Peru margin, depleted dissolved Mo and V in a few samples corresponded with the nitrite maximum, suggesting the possible involvement of both elements in the nitrogen cycle. Particulate Mo and V enrichments in the ODZ are likely indicative of scavenging by Fe oxyhydroxides and/or biogenic particles. In near surface waters close to the Peru margin, dissolved Mo and V concentrations slightly decreased with increasing total chlorophyll a, suggesting the removal of both elements by biological uptake and/or adsorption onto biogenic particles. In contrast to previous reports that removal to reducing coastal/estuarine sediments resulted in surface water depletion of dissolved V, there is no evidence from the EPZT section that this process plays a strong role in the development of the ~5% dissolved V depletion in the surface ocean. Additionally, dissolved V and Mo depletions were seen in some hydrothermal plume waters above the ridge crest, likely due to adsorption onto Fe/Mn oxides and suggesting that these plume waters are a net sink for these two elements. Associations of ridge crest particulate Mo and V with the particulate Mn and Fe carrier phases suggests V was largely scavenged by Fe oxyhydroxides while Mo was likely scavenged by both Fe oxyhydroxides and Mn oxides. Away from the ridge crest, depletions of dissolved V and Mo are seen along the boundaries of the far field hydrothermal plume, though the reasons for this remain obscure. Future studies of these elements could benefit from determination of speciation as well as increased focus on margin areas.

1. Introduction

Molybdenum and vanadium both occur as oxyanions in oxic waters and have somewhat similar geochemical behaviors in the ocean. For instance, both elements are redox-sensitive, with decreased solubility in oxygen-depleted water. Also, Mo and V are micro-nutrients, although their biochemical functions and uptake differ. Conventionally, Mo is thought to be conservative in seawater (Bruland, 1983; Collier, 1985) and V nearly so, with only a ~10% depletion in the shallow ocean relative to deep waters (Collier, 1984; Middelburg et al., 1988; Sherrell and Boyle, 1988). Thus, the distributions of these elements have tended not to be studied in detail in the open ocean and the possibility remains that interesting aspects of their oceanic geochemistries have been overlooked.

The distribution of dissolved Mo is generally thought to be

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essentially conservative in the open ocean (Morris, 1975; Bruland, 1983; Collier, 1985). Likewise, the uniform distribution of Mo stable isotope ratios in the ocean (Nakagawa et al., 2012) also suggests the relative unreactivity of oceanic Mo. However, a number of studies have reported non-conservative behavior of dissolved Mo in coastal and estuarine waters (e.g., Dalai et al., 2005; Dellwig et al., 2007; Joung and Shiller, 2016; Wang et al., 2016). The reasons for this non-conservative behavior are varied and likely relate to biological processes, organic complexation, redox processes, scavenging, and sedimentary interactions. For example, scavenging of Mo by ferromanganese oxides appears to be a mechanism of importance for removal of Mo from the water column (Goldberg et al., 2009; Kashiwabara et al., 2011) and the diagenesis of these oxides plays a role in the enrichment of Mo in reducing sediments (Scholz et al., 2011). Also, the formation of Mo-enriched organic aggregates has been observed to deplete coastal water dissolved Mo (e.g., Dellwig et al., 2007; Kowalski et al., 2013). Mo plays an important biological role in the nitrogen cycle as a co-factor in nitrogenase, nitrate reductase, and nitrite oxidoreductase (Stiefel, 1996; Moreno-Vivián et al., 1999; Maia et al., 2017) as well as in DMSO reductase (Schindelin et al., 1996). Based on thermodynamics, Mo is present in the + VI oxidation state in seawater, predominantly as the highly soluble MoO_4^{2-} species (Baes and Mesmer, 1976; Manheim, 1978). However, small amounts of the more particle-reactive Mo(V), which should be thermodynamically stable in reducing waters (Bertine, 1972; Brookins, 1988), have been reported in low-oxygen estuarine waters (Wang et al., 2009). Furthermore, when there is sufficient sulfide present (~ 11 μM $H_2S_{(aq)}$), molybdate can be sulfidized to more readily scavenged thiomolybdates without reduction of the Mo (Erickson and Helz, 2000; Dahl et al., 2010; Vorlicek et al., 2015). Helz et al. (2011) proposed that the Mo scavenging in sulfidic water is controlled not only by H_2S concentration but also by pH and the availability of reactive Fe(II). This may account for the high levels of Mo found in sediments and pore waters of anoxic depositional environments (e.g., Emerson and Huested, 1991).

As outlined above, the utilization of Mo as an enzymatic co-factor, the interaction of Mo with organic matter, the change of Mo speciation in redox gradients and association with Fe/Mn cycling along with the diagenesis of Mo in sediments/pore waters supports the prior observations of non-conservative Mo behavior in various marginal environments. In the open ocean, however, the limited observations of the Mo distribution are more equivocal. Both slight depletion and enrichment of Mo concentration were reported in the eastern tropical Pacific Ocean by Tuit (2003). However, no significant depletion of Mo was observed either in the extreme oxygen minimum zone (OMZ) of the Arabian Sea (Goswami et al., 2012) or in the eastern tropical North Pacific OMZ (Nameroff et al., 2002). In oceanic hydrothermal systems, Elderfield and Schultz (1996) suggested there was no direct hydrothermal source/sink of Mo, but that scavenging removal in hydrothermal plumes did remove Mo from seawater, albeit at a rate of only ~1% of the fluvial input. However, Mo depletion was observed in vent fluids from the Southern Juan de Fuca Ridge (Trefry et al., 1994). Thus, hydrothermal effects on the oceanic Mo distribution may be variable.

Dissolved V concentrations are generally found to be ~35 nmol/kg in the deep ocean with a slight reduction in concentration in the upper water column (e.g., Collier, 1984; Middelburg et al., 1988; Sherrell and Boyle, 1988). There is one report suggesting deep Pacific concentrations might be 10–15 nmol/kg higher than this (Jeandel et al., 1987), though their intercalibration effort showed somewhat variable results and Middelburg et al. (1988) showed only a few nmol/kg inter-basin increase. Thermodynamically, the predominant species of V in oxic seawater should be $H_2VO_4^-$ (Baes and Mesmer, 1976; Wang and Sanudo-Wilhelmy, 2008), which has similar chemical characteristics as phosphate. Thus, the slight V depletion in surface waters has been attributed to biological uptake of V(V) (Collier, 1984).

V is used as a nutrient by some species (Taylor and van Staden, 1994) and is found in some enzymes (Antipov et al., 1998; Rehder, 2000; Butler and Carter-Franklin, 2004). More specifically, V is found in V-nitrogenases and V-haloperoxidases (Crans et al., 2004). Observation of V-nitrogenase in the ocean may not be likely, since its expression seems to require Mo-limitation (Rehder, 2000). V-haloperoxidases are commonly found in marine macroalgae (Crans et al., 2004). Additionally, previous studies have hypothesized that the intracellular V enrichment in Trichodesmium colonies is related to the V-haloperoxidases (Tovar-Sanchez and Sañudo-Wilhelmy, 2011; Nuester et al., 2012). High concentrations of V(III) are also found in certain tunicates (Michibata et al., 2003). While the effect of these types of biological V uptake may be limited, Klein et al. (2013) has speculated on an unknown mechanism of biological V uptake from surface waters based on correlations between intracellular V, biogenic Si, and total chlorophyll *a* and Osterholz et al. (2014) presented evidence that diatoms are a major factor in oceanic V depletion.

In contrast to the biological uptake hypothesis for surface ocean dissolved V depletion, Shiller and Mao (1999) found no evidence of biological V removal in productive waters of the Louisiana Shelf and suggested that V depletion in those shelf waters resulted from V reduction and removal to the sediments. While the details of this mechanism were not specified, it likely involves adsorption of V onto ferromanganese oxide particles, possibly with water column reduction of V(V) to the more readily scavenged V(IV) (Wehrli and Stumm, 1989), and removal to and incorporation into reducing sediments (e.g., Scholz et al., 2011). Thus, an alternative or additional mechanism for surface ocean V depletion might involve V redox chemistry along the continental margins. Other studies have also found dissolved V is lower in concentration in suboxic/anoxic water columns than in oxic waters (Emerson and Huested, 1991; Shiller and Mao, 1999; Wang and Sanudo-Wilhelmy, 2008). Similarly, it has been shown that V is enriched in the solid phase of anoxic and organic-rich sediments (Lewan and Maynard, 1982; Holland, 1984; Breit and Wanty, 1991). Under extremely reducing conditions, V(IV) could be further reduced to V(III) by humic acid or sulfides, and be present as V_2O_3 or $V(OH)_3$ (Goodman and Cheshire, 1975; Breit and Wanty, 1991).

Jeandel et al. (1987) suggested that hydrothermal processes are a minor factor in the cycling of vanadium. However, V has been characterized as an enriched element in hydrothermal vent fluids relative to seawater (German and Von Damm, 2006). Nonetheless, several studies have demonstrated that V is scavenged from seawater and adsorbed onto iron oxyhydroxides within rising hydrothermal plume waters, which is supported by evidence of particulate V enrichments in hydrothermal particles (Trefry and Metz, 1989; Feely et al., 1994; Edmonds and German, 2004). Thus, Elderfield and Schultz (1996) concluded that there is no significant direct hydrothermal input of V to the ocean and that the scavenging removal flux of V from the hydrothermal plumes is roughly equal to the river input flux of V.

Clearly the past work on Mo and V has demonstrated the basics of their oceanic distributions, but uncertainties remain in some of the details. Understanding these details may aid both in understanding modern ocean processes as well as in the interpretation of paleo-environmental data on the ocean's Mo (e.g., Anbar, 2004; Tribovillard et al., 2006; Scott et al., 2008) and V composition (e.g., Hastings et al., 1996; Tribovillard et al., 2006). In this study, we present the first detailed oceanic sections of dissolved Mo and V, obtained along the US GEOTRACES East Pacific Zonal Transect (EPZT). This transect (Fig. 1a) crossed a variety of contrasting oceanic regimes including an extreme OMZ, hydrothermal plumes, and the pelagic realm, thus providing an opportunity to more thoroughly examine the distributions of these two elements.

2. Methods

2.1. Seawater sampling

The U.S. GEOTRACES EPZT was conducted during 25 October–20 December 2013 aboard R/V Thomas G. Thompson from Manta,