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A new estimate of detrital redox-sensitive metal concentrations and variability in fluxes to marine sediments

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Abstract

The enrichment and depletion of redox sensitive trace metals in marine sediments have been used extensively as paleoredox proxies. The trace metals in shale are comprised of both detrital (transported or particulate) and authigenic (precipitated, redox-driven) constituents, potentially complicating the use of this suite of proxies. Untangling the influence of these components is vital for the interpretation of enrichments, depletions, and isotopic signals of iron (Fe), chromium (Cr), uranium (U), and vanadium (V) observed in the rock record. Traditionally, a single crustal average is used as a cutoff for detrital input, and concentrations above or below this value are interpreted as redox derived authigenic enrichment or depletion, while authigenic isotopic signals are frequently corrected for an assumed detrital contribution. Building from an extensive study of soils across the continental United States – which upon transport will become marine sediments – and their elemental concentrations, we find large deviations from accepted crustal averages in redox-sensitive metals (Fe, Cr, U, V) compared to typical detrital tracers (Al, Ti, Sc, Th) and provide new estimates for detrital contributions to the ocean. The variability in these elemental ratios is present over large areas, comparable to the catchment-size of major rivers around the globe. This heterogeneity in detrital flux highlights the need for a reevaluation of how the detrital contribution is assessed in trace metal studies, and the use of confidence intervals rather than single average values, especially in local studies or in the case of small authigenic enrichments.

Keywords: Redox; Redox-sensitive metals; Geochemistry

1. INTRODUCTION

1.1. Redox proxies

Enrichments of transition metals in marine sediments, such as Cr, V, U, Mo, and Fe, are some of the most widely used redox proxies in modern and ancient sedimentary systems (e.g., Tribovillard et al., 2006). The basic idea behind using these trace elements as redox proxies is straightforward—their solubility is strongly controlled by local redox conditions. With Cr, V, U, and Mo (herein referred to redox sensitive trace metals), increased solubility in oxic conditions results in large metal enrichments under oxygen-poor conditions. Iron, though the system is slightly more complex, is also typically enriched in anoxic sediments as the result of a benthic shuttle from reducing sediments underlying oxic waters and an efficient Fe trap in anoxic settings (e.g., Lyons and Severmann, 2006). Mobilization of redox sensitive trace metals occurs during oxidative chemical weathering at Earth's surface, and subsequent riverine transport to the ocean. Upon entering reducing conditions in the marine system, in either the water column or the sediment pile, these metals can be reduced and or converted to more insoluble particle reactive phases (e.g., Algeo and Maynard, 2004), resulting in precipitation and sequestration within the sediment. Because solubility is linked to redox state, metal enrichments in sediments have the potential to act as a very powerful tracer of past redox conditions.

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Redox sensitive trace metals enrichments have also been used extensively to explore global marine redox conditions (e.g., Algeo, 2004; Partin et al., 2013; Reinhard et al., 2013; Scott et al., 2008). The dissolved marine reservoir size of redox sensitive trace metals is directly linked to the global marine redox landscape (e.g., Emerson and Huested, 1991; Hastings et al., 1996; Algeo, 2004). Assuming a constant input term, in a well oxygenated ocean the size of the dissolved marine redox sensitive metal reservoir is larger than in an anoxic ocean due to inhibited marine burial under oxic conditions. This results in large metal enrichments in the few anoxic regions of a well-oxygenated ocean and small enrichments in anoxic settings in a largely anoxic ocean (see Scott et al., 2008; Reinhard et al., 2013). One of the major appeals of this approach is that these enrichments can be directly translated into a quantitative mass balance models (e.g., Partin et al., 2013; Reinhard et al., 2013).

More recently, this approach has been taken a step further with the use of redox sensitive metal isotope systems (e.g., δ^{53}Cr, δ^{98}Mo, δ^{238}U). Beyond enrichments, isotopic data can provide much more detailed information about the surface cycling of these elements and potentially the nature of the reductive sinks (i.e., euxinic, ferruginous, suboxic). These systems are also appealing as they can be translated into quantitative isotope mass balances, which have led to substantial insights into the evolution of global redox conditions (e.g., Arnold et al., 2004; Weyer et al., 2008; Dahl et al., 2010; Kendall et al., 2011; Tissot and Dauphas, 2015; Wang et al., 2016a,c). It should be recognized however, that a detrital correction has to be applied for many potential seawater archives, thus first requiring recognition of the potential for variation within this term.

Chromium, vanadium, and uranium are emerging isotope proxies of particular interest as they have the potential to transform our understanding of variable redox systems. Acknowledgment of the heterogeneity in the detrital input of these metals is critical in for the quantification of authigenic isotope signals, and for the recognition of small but significant redox-driven authigenic enrichments of Cr, V, and U. Further, Cr and V can potentially provide a unique signal for weakly reducing (suboxic) or oscillating redox conditions, as these two elements are the most easily reduced of the redox-sensitive suite of trace metals (Calvert and Pedersen, 1993; Algeo and Maynard, 2004; Li et al., 2015b). Chromium can be reduced via nitrate reduction, making it the most easily reduced of the traditional suite of trace metals (Rue et al., 1997; Gueguen et al., 2016). Vanadium also has unique redox behavior as it can be reduced twice, and can be sourced from suboxic sediments (Calvert and Pedersen, 1993; Hastings et al., 1996). In the case of Cr, small enrichments indistinguishable from the detrital component might be expected, however these could likely be revealed with isotopic analyses, which would distinguish an unfractionated detrital flux from a fractionated authigenic component (assuming deposition under an oxidizing earth atmosphere). The V isotope system is also likely to provide a unique signature of suboxic conditions, making both of these systems critically important to improving the resolution of our understanding of the oxygenation of the Earth's oceans.

1.2. Detrital contribution

Although there have been, without question, large steps forward in our understanding of marine redox evolution from trace metal geochemistry, uncertainties about the magnitude of background particulate flux – or detrital signal – unrelated to the redox conditions at the time of deposition have been problematic and may have led, in some cases, to spurious conclusions from redox sensitive trace metal studies. The detrital particulate component of a specific metal will eventually be delivered to the sediment regardless of the redox state of the depositional environment. Therefore, a baseline detrital value must be established for paleoredox proxies of interest, in order to resolve enrichments beyond this background value (e.g., Tribovillard et al., 2006). It is assessment of this authigenic component – the target of both enrichment and isotopic studies – that is critical to making paleoenvironmental interpretations.

All redox-sensitive trace elements are delivered to the ocean in both dissolved form and as detrital particulate material. For some metals, such as molybdenum (Mo), there is a very small detrital component, in most cases making redox interpretations robust with respect to, and regardless of, changing background detrital input (Crusius et al., 1996). Molybdenum however, is likely reduced via the thiomolybdate pathway whereby Mo becomes particle-reactive, and increasingly so with each successive sulfidation reaction (i.e., dithio-, trithio-, tetrathiomolybdate), though each successive step is roughly one order of magnitude slower (Helz et al., 1996; Erickson and Helz, 2000). Thus, enrichments are strongly tied to sulfide levels and the presence of persistent euxinia (Erickson and Helz, 2000; Scott and Lyons, 2012). Other redox-sensitive metals, such as Cr and V, have the potential to be much more easily reduced, and thus function as more sensitive indicators of reducing environments (Rue et al., 1997; Algeo and Maynard, 2004). Similarly, U also responds to all reducing conditions, though reduction occurs primarily in the sediment column (Algeo and Maynard, 2004). Unfortunately, Cr and V, in particular, have a very large detrital component, adding significant complexity to the disentanglement of environmental signals (authigenic enrichments) and provenance (background detrital input) (e.g., Perkins et al., 2008). Indeed, the majority of transition metals used in redox studies (i.e., Fe, Cr, V, U) have a substantial detrital component (e.g., Algeo, 2004; Sahoo et al., 2012; Reinhard et al., 2013), requiring careful assessment in order to interpret enrichments truly driven by redox conditions.

Understanding the average composition of the crust has been the focus of numerous studies since as early as the late 19th century, eventually expanding to estimates of average crustal trace element values (e.g., Clarke, 1889; Goldschmidt, 1937; Turekian and Wedepohl, 1961; Shaw et al., 1967; Eade and Fahrig, 1971; Taylor and McLennan, 1985; Condie, 1993; Wedepohl, 1995; Gao et al., 1998; Kamber et al., 2005; Rudnick and Gao, 2014). Broadly, there are two basic approaches used to make these estimates – either calculating weighted average values for rocks exposed on Earth's surface (e.g., Clarke,