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

Devon B. Cole [*], Shuang Zhang, Noah J. Planavsky

Department of Geology & Geophysics, Yale University, New Haven, CT 06511, USA

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.
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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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* Corresponding author.
E-mail address: Devon.Cole@yale.edu (D.B. Cole).

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,

1889; Condie, 1993), or compiling average composition from siliciclastic sedimentary rocks or glacial deposits which sample the crust (e.g., Goldschmidt, 1937; Taylor and McLennan, 1985). The strengths and weaknesses of each of these studies and the level of consistency between them is discussed at length by Rudnick and Gao (2014), who, present their own best estimate of average crustal composition which we refer to throughout this study. It should be noted however, that non-negligible variation remains in the compilation of these estimates, particularly for trace metals.

While likely broadly representative of global means, especially considering the overall consistency of these numerous studies, none of the work outlined above provides constraints on regional-scale variability—a critical missing link in understanding redox-sensitive trace metal enrichments in sediments. This is especially relevant to studies working on a basinal or local scale, or in the case of small but non-negligible authigenic enrichments. The latter is particularly pertinent in both the Precambrian and in restricted basins, where the marine reservoir of metals such as Cr, U, and V is already depleted due to widespread anoxic waters (Algeo, 2004; Algeo and Rowe, 2012; Partin et al., 2013; Reinhard et al., 2013). Further, at very low oxygen levels (i.e., much of the Precambrian), there is an effect on the detrital flux of the redox-sensitive metals as a result of the availability of oxidants. For Fe, in particular, oxygen levels of at least 0.01% but possibly as high as 1% present atmospheric levels (Crowe et al., 2013) are needed to limit runoff of Fe(II). Below these levels, it is possible the detrital flux could appear 'depleted'.

Traditionally, researchers have relied on accepted crustal average values to elucidate redox-induced enrichments, and occasionally to demonstrate depletions (e.g., Reinhard et al., 2014; Zhang et al., 2016). In the place of empirical constraints on detrital flux to a basin, which are often limited to recent deep sea cores, or even the relationship of a basin with the open ocean (frequently the case in deep time), crustal averages are used as cutoffs for authigenic enrichment with no consideration for potential variability both laterally (between basins) or through time (within a single basin experiencing changes in detrital input source, rate of erosion, or rate of deposition). Unfortunately, this can result in the failure to clearly distinguish a redox driven signal, especially in the case of depletions or small enrichments. Some researchers (e.g., Algeo and Maynard, 2004) have used trace metal concentrations in grey shales within the same or adjacent sedimentary units as a baseline for detrital input (assuming oxic deposition of these sediments), however this still fails to account for variation of the detrital input through time, and lithology (e.g., low organic content) is not a practically robust redox indicator (e.g., Myrow, 1990). Further, such an approach is not always possible in many settings. Others such as Perkins et al. (2008) have used redox-sensitive/detrital tracer ratios to identify a slope associated with detrital contribution and identify points above this lower limit to be authigenically enriched. Unfortunately this approach requires a shift in the depositional redox environment within the measured section, and if that shift does not reflect a change from a system where authigenic metal enrichment is not possible, then this slope will represent a mixing line between authigenic and detrital components, rather than a solely detrital contribution. More recently, variability has been demonstrated for Cr/Ti in modern oxic marine sediments (Gueguen et al., 2016). However, there is potential for processes resulting in the loss or gain of metals in oxic sediment, adding complexity to the problem, and suggesting that a clearer picture of the detrital contribution may come from investigating continental source material.

To investigate the potential variability of detrital input to the ocean we have examined the source of this material – modern soils – from the United States Geologic Survey (USGS) North American Soil Geochemical Landscapes Project covering the continental United States. The results of the sampling campaign are available from the USGS archives and were released in USGS open file report 2014–1082 (Smith et al., 2014). We suggest that topsoils provide a reasonable analogue for marine detrital contribution as these sediments will be eroded and directly transferred to the marine system. These findings indicate that a more holistic approach, beyond the use of a mean crustal cutoff value to quantify the detrital contribution, is required to make a significant and unique paleoenvironmental interpretation of depositional redox conditions. This database has allowed a new estimate of surficial variability in trace metal composition of sediments just prior to their transport to the ocean, allowing a first approximation of confidence intervals ('error bars') associated with enrichment-based redox interpretations.

2. METHODS

In order to provide new estimates of the detrital contribution of redox-sensitive metals to marine sediments, and emphasize both the complexity and variability of these systems we have investigated a suite of redox-sensitive metal/detrital tracer ratios from across the continental United States. Our analysis builds from a soil database (see Smith et al., 2014), which includes elemental concentrations of 45 major and trace elements from more than 4850 localities. All of the samples in this database were collected between 2007 and 2010 based on the sampling procedure outlined in Smith et al. (2014). All samples were sieved to <2 mm grain size, specifically targeting the fine fraction and to avoid the anomalous analysis of individual large grains. All elemental analyses were made on inductively-coupled plasma atomic emission spectrometry (ICP-AES) or inductively-coupled plasma mass spectrometry (ICP-MS) following a multi-acid total digestion. For further details on collection and analyses, see Smith et al. (2014).

Using this database, we have compiled ratios of widely used redox-sensitive proxies to their most commonly employed detrital tracers. That is, we have examined the ratios of often studied elements with non-conservative behavior during redox-dependent surface processes relative to tracers that are considered conservative (i.e., they will remain in particulate form). These ratios, rather than just concentrations, are employed in order to ideally circumvent dilution effects, changes in sedimentation rate, and changes

in flux related to continental weathering. The following ratios were compiled, and the data was then interpolated over maps of the continental US; V/Al, V/Ti, V/Sc, U/Al, U/Th, Cr/Ti, Cr/Al, Fe/Al, and the detrital tracer Al/Ti. We have then examined the distribution of values for each elemental ratio in comparison to widely accepted continental crustal average estimates of Rudnick and Gao (2014).

In addition, we have examined large-scale variation that can present on catchment-size scales. To quantify the lateral persistence of deviation from crustal means in the database, a 1000 iteration Monte Carlo resampling procedure was executed for Cr/Ti, V/Al, and Fe/Al. More specifically: An area was randomly selected from a database of the world's 405 largest modern drainage basins from the Global Runoff Data Center (GRDC, 2016) and a height-width ratio (ranging from 0.5 to 2) was randomly assigned to a rectangle of that area. This rectangle was then overlain on the geographic dataset for each elemental ratio and the mean and standard deviation of the data points within that area were calculated. This process was then repeated 1000 times for each elemental ratio. Herein, the means generated from this resampling procedure are referred to as the catchment resampled means.

Finally, to investigate variability with soil depth for cases where the primary physical erosion is the result of catastrophic erosion events (i.e., mass wasting, e.g., Osterkamp and Friedman (2000)), we have examined the difference and variability between the topsoil (0–5 cm depth), A horizon (composite of soil A horizon), and C horizon (soil C horizon – partially weathered parent material) or a sample from 80 to 100 cm depth if the C horizon is deeper than 1 m (Smith et al., 2014). Ratios of Cr/Ti and V/Al from each of these three horizons were examined to investigate shifts in mean values and variability, both laterally and vertically. This vertical variation through the soil profile also provides information about preferential loss during weathering, and the variable nature of these processes, in addition to evidence for inherited variability from the regolith.

3. RESULTS

For all elemental ratios considered, we find significant variance away from crustal average values of Rudnick and Gao (2014) in topsoils across the continental US. Cr, V, and Fe show very large distributions, while U remains closer to the crustal average. These observations of significant heterogeneity are consistent regardless of the detrital tracer chosen, though the relationship between soil means and crustal means can vary depending on the detrital tracer (e.g., V/Ti and V/Al). Further, we find that variations from the crustal averages are consistently maintained on large, laterally continuous scales, demonstrated by the catchment resampled means of topsoil ratios for Cr/Ti, V/Al, and Fe/Al. Means and standard deviations of the U.S. soil data and crustal averages for each elemental ratio considered are summarized in Table 1.

3.1. Chromium

The mean topsoil value for Cr/Ti is 0.015 ± 0.094 (2SD), which is substantially lower than the continental crustal average of 0.02 (Rudnick and Gao, 2014), while the mean topsoil value for Cr/Al is 9.015 ± 46.101 (2SD) compared to the crustal average of 11.288 (Rudnick and Gao, 2014). Rudnick and Gao (2014) report 1 sigma errors, however these are based on variation between other published crustal estimates, and are rarely considered in redox-focused geochemical studies, thus, herein we refer only to the crustal average. Chromium shows the largest disparity between the topsoil mean and the continental crustal averages of all elemental ratios considered in this study. The Cr/Ti data is also highly variable and this variability is maintained in the catchment resampled data, where the catchment resampled mean is 0.015 ± 0.015 (2SD) (Fig. 1). Further, when the standard deviations for each of the 1000 resampled areas are compiled, the mean of these standard deviations is 0.016, demonstrating sustained variation on all sampling scales. The similarity of the resampled mean to that of the raw data demonstrates that our resampling procedure accurately reflects the true distribution of the data. In addition, we have examined the soil data from the A and C horizons, in addition to the topsoil (Fig. 2). The A horizon mean is 0.013 ± 0.014, while the C horizon mean is 0.015 ± 0.128. With consideration of the large standard deviations for all three soil horizons, these means show no significant difference related to soil depth, using a T-test (p-value = 0.94 for C horizon compared to topsoil, and p-value = 0.88 for C horizon compared to A horizon).

3.2. Vanadium

Three ratios were examined for V (V/Al, V/Ti, V/Sc), along with catchment resampling for V/Al, and the percentage change between the C horizon and the topsoil ratios of V/Al (Figs. 3, 4). The mean topsoil value for V/Al is 13.279 $\pm$ 12.758 (2SD) compared to the crustal average of 11.9 (Rudnick and Gao, 2014). The mean topsoil value for V/Ti is 229.283 ± 246.471 (2SD) compared to the crustal average of 252.8 (Rudnick and Gao, 2014). Finally, the mean topsoil value for V/Sc is 9.135 ± 5.598 (2SD) compared to the crustal average of 6.9 (Rudnick and Gao, 2014). The large-scale lateral variability of V was tested with catchment resampling for V/Al, where the catchment resampled mean is 13.127 ± 6.182 (2SD), while the mean 2SD of the resampled areas is 9.155 (Fig. 3). Significantly, this mean is similar to the topsoil mean, indicating that the resampling procedure accurately reflects the distribution of the original data. We also examined variation within the soil profile for V/Al, and find that the mean for the C horizon is 13.470 $\pm$ 13.582 (2SD). Using a t-test, we find that the C horizon and topsoil do not show a statistically significant difference (p-value = 0.23). The percentage change of V/Al between the C horizon and topsoil is also highly variable with an average shift of $-3.47\% \pm 70.36$ (2SD) (Fig. 4).

Table 1
Soil and crustal means.

Elemental ratio	Topsoil mean[a]	2 Std Dev (±)	A horizon mean[a]	2 Std Dev (±)	C horizon mean[a]	2 Std Dev (±)	Upper continental crust[b]	Units
V/Ti	229.28	246.47					252.80	ppm/wt%
V/Al	13.28	12.76	13.34	12.92	13.47	13.58	11.90	ppm/wt%
V/Sc	9.13	5.60					6.90	ppm/ppm
Cr/Ti	0.015	0.094	0.013	0.014	0.015	0.128	0.02	ppm/ppm
Cr/Al	9.015	23.050					11.29	ppm/wt%
U/Al	0.578	1.134					0.33	ppm/wt%
U/Th	0.285	0.369					0.26	ppm/ppm
Fe/Al	0.476	1.223			0.475	0.427	0.48	wt%/wt%
Al/Ti	19.03	17.64					21.24	wt%/wt%

[a] Smith et al. (2014).
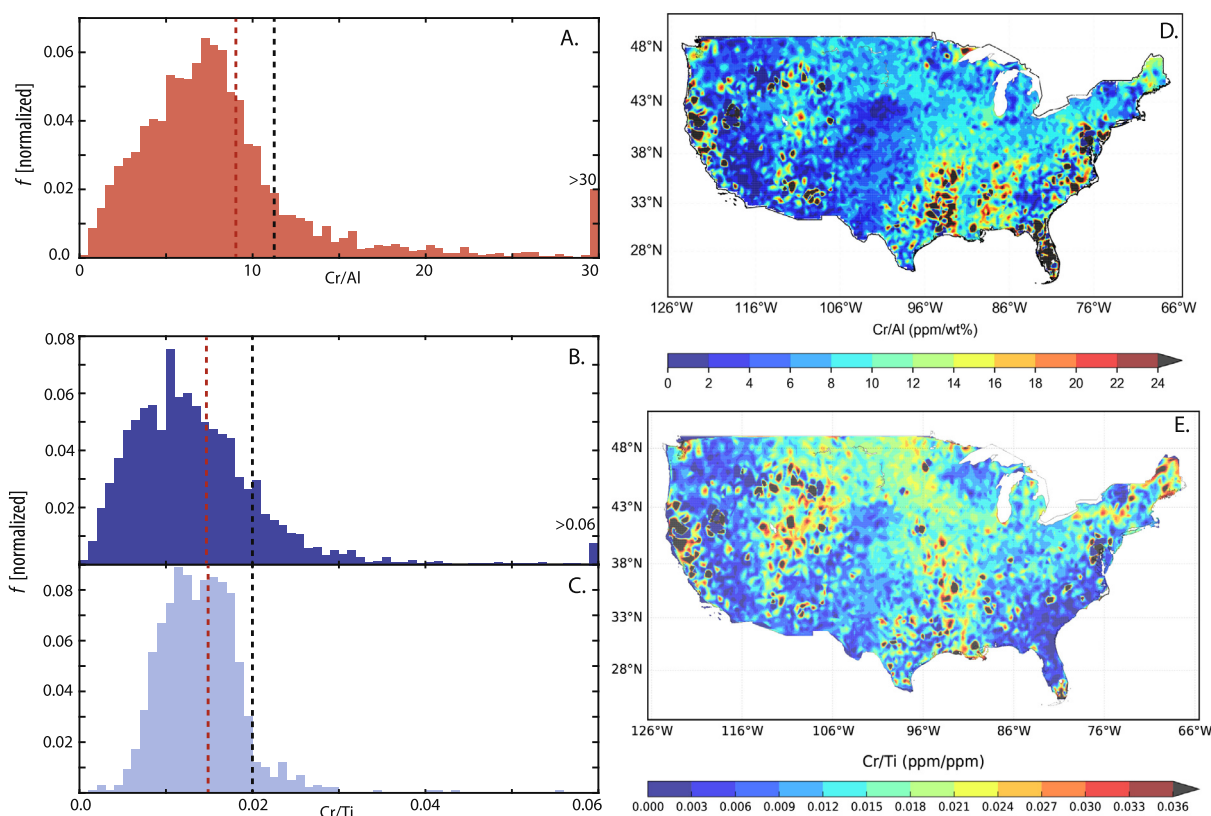[b] Rudnick and Gao (2014).

Fig. 1. Distribution of Cr/Al and Cr/Ti in topsoils from the continental US. (A) Distribution of Cr/Al raw data. (B) Distribution of Cr/Ti raw data and (C) the catchment resampled distribution. Red dashed lines denote the mean of the raw or resampled distribution respectively, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (D and E) Raw data interpolated across the continental US for Cr/Al and Cr/Ti respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Uranium

Uranium was compared to the two detrital tracers Al and Th. The topsoil mean for U/Al is 0.578 ± 1.134 (2SD) in comparison to the crustal mean of 0.33 (Rudnick and Gao, 2014), while the topsoil mean of U/Th is 0.285 ± 0.369 (2SD) compared to the crustal mean of 0.26 (Rudnick and Gao, 2014) (Fig. 5). The catchment resampled mean for U/Th is 0.282 ± 0.102 (2SD), while the mean 2SD of the resampled areas is 0.179.

3.4. Iron

Iron was investigated in comparison to Al. The topsoil mean of Fe/Al is 0.476 ± 1.223 (2SD) in comparison to the crustal average of 0.48 (Rudnick and Gao, 2014). The
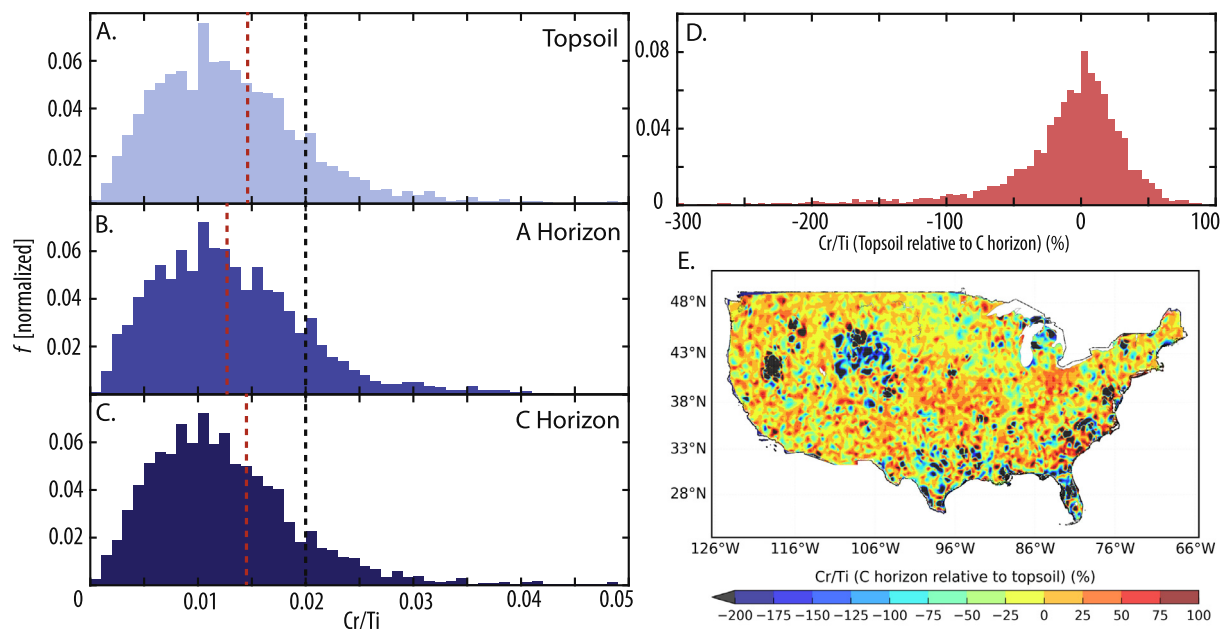
Fig. 2. Distribution of Cr/Ti in topsoil (A), A horizon (B), and C horizon (C). Red dashed lines denote the mean of the raw data, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (D) Distribution of the percentage change between C horizon Cr/Ti and topsoil. (E) Interpolated map of the data in (D). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

catchment resampled mean is 0.472 ± 0.302 (2SD), while the mean 2SD of the resampled areas is 0.406 (Fig. 6). The mean of the C horizon is 0.475 ± 0.427 (2SD), consistent with, on average, quantitative iron retention during weathering. Using a T-test we find that the C horizon and topsoil do not show a statistically significant difference (p-value = 0.90).

3.5. Aluminum and Titanium

Finally, we examined Al/Ti ratios, which are utilized as a detrital or provenance tracer. The topsoil mean of Al/Ti is 19.026 ± 17.640 (2SD) in comparison to the crustal mean of 21.24 (Rudnick and Gao, 2014) (Fig. 7). We have also considered the relationship between Cr/Ti and Al/Ti. Because Cr contribution is primarily derived from mafic igneous rocks, an inverse relationship might be expected between Cr/Ti and Al/Ti, given that these ratios are lower and higher, respectively, in felsic versus mafic igneous rocks. If this is the case, the use of Ti as a normalizing detrital tracer should also help to normalize for the influence of mafic vs. felsic contributions of Cr. However we find no correlation between these two ratios (r-squared = 0.002) (Fig. 8).

We have also examined the relationship between Al contents and each of the four primary ratios (Cr/Ti, V/Al, U/Th, Fe/Al), and compared this data to the global average values for suspended sediment in rivers from Viers et al. (2009). We find that our distributions show no relationship with Al contents, and reflect the published riverine values and their ranges, despite some slight offsets, which are discussed below (Fig. 9).

4. DISCUSSION

Accepting the significant heterogeneity of trace metal concentrations and ratios in surface sediments observed in this study, we consider the use of crustal cutoff values for distinguishing authigenic enrichments an inaccurate oversimplification. The pitfalls of normalization of trace elements have been discussed previously (Van der Weijden, 2002), however we seek to emphasize an awareness of the surface heterogeneity that can plague normalization schemes, based on empirical data from surface sediments. The potential for deviations from crustal means on catchment-size scales is very high, especially for V and Cr, as discussed below. This type of variation can present on both lateral, basin-wide scales, as well as vertically, in the rock record (Walther, 1894), leading to flawed paleoredox reconstructions. Though this study does not build from a global dataset, the continental US is composed of a wide variety of bedrock compositions, climates, and drainage basins that collectively can at least provide an approximation of the magnitude of variability that may be expected from a larger, global dataset. It is likely that pollution has affected some samples of this study, however it is unlikely that these samples drive the broad spatial variability observed in the elemental ratios examined. Minimally, recognition of the capacity for background variability is especially critical in the analyses of individual stratigraphic sections, or even multiple sections within a single basin. The magnitude of the variation observed in plausible detrital contributions of Cr and V indicates that the resolvability of truly redox-driven signals is, in many cases, too poor to draw any conclusions without further analytical work.
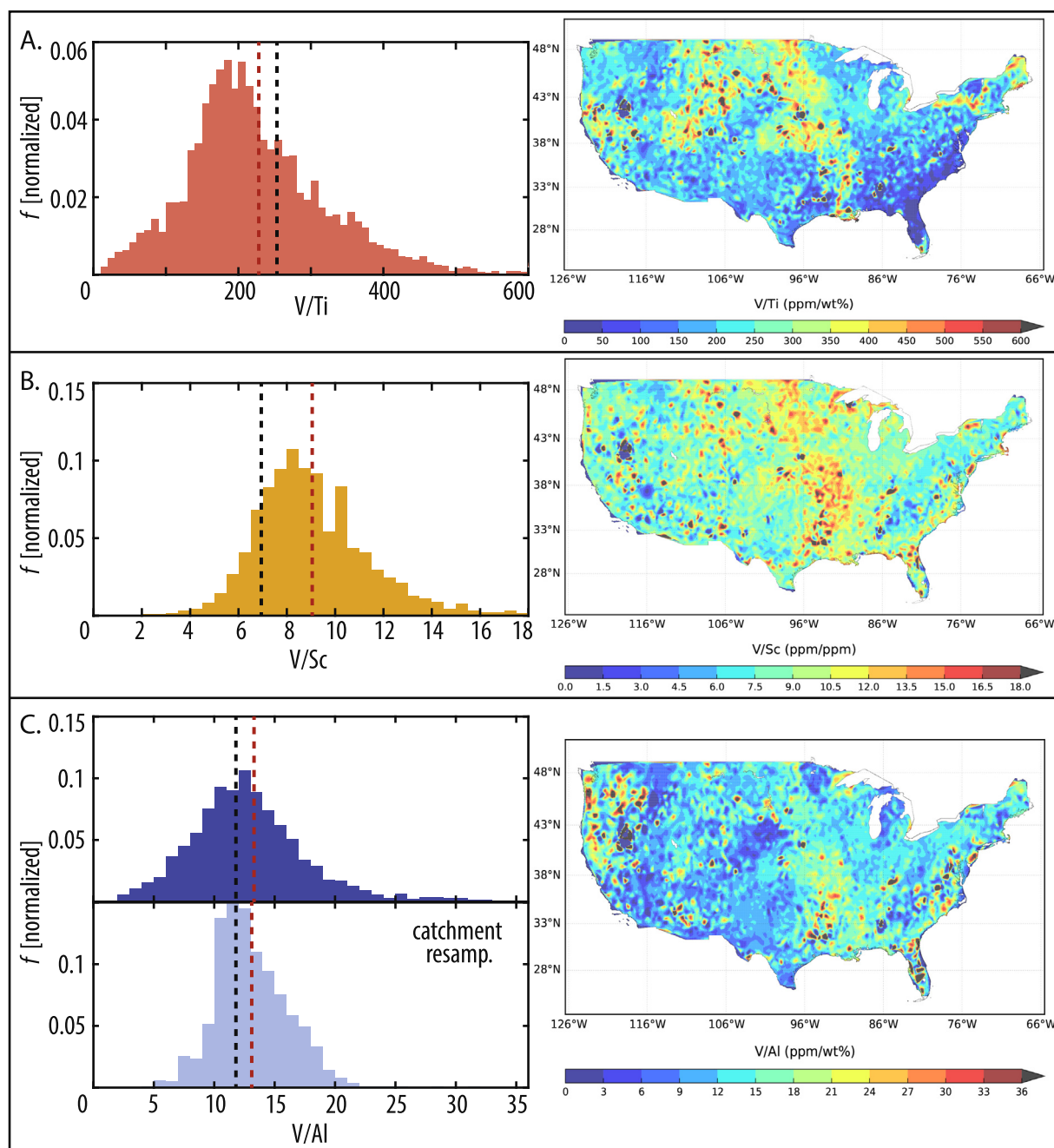
Fig. 3. Topsoil distributions (left) and interpolated maps (right) of V/Ti (A), V/Sc (B), and V/Al (C) which shows the raw data (dark blue) and catchment resampled distribution (light blue). Red dashed lines denote the mean of the raw data, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.1. Chromium

Chromium variability was assessed in comparison to Ti and Al – the most commonly used detrital tracers for Cr (e.g., Crowe et al., 2013; Konhauser et al., 2011; Reinhard et al., 2013, 2014; Cole et al., 2016b; Gueguen et al., 2016). Traditionally, the continental crust average Cr/Ti value of 0.02 (Rudnick and Gao, 2014) is used as a cutoff value to characterize the detrital contribution to mar-

ine sediments, and values above 0.02 are considered evidence of authigenic enrichment resulting from reduction under an anoxic water column. However, significant heterogeneity observed in both Cr/Ti and Cr/Al of topsoils across the US (Fig. 1) indicates a confidence interval rather than a single crustal average cutoff value is a more useful means of gauging Cr enrichments in marine sediments. Importantly, this interval is so large that its practical applications will be notably limited, requiring either the analyses of large and
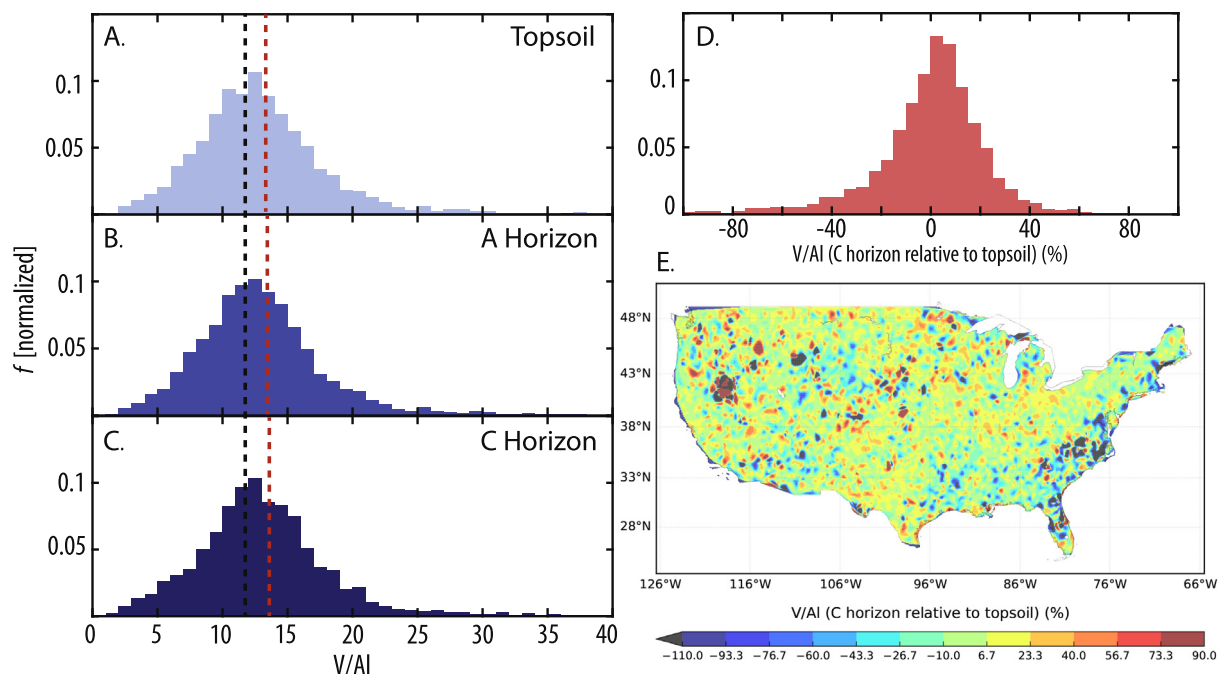
Fig. 4. Distribution of V/Al in topsoil (A), A horizon (B), and C horizon (C). Red dashed lines denote the mean of the raw data, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (D) Distribution of the percentage change between C horizon V/Al and topsoil. (E) Interpolated map of the data in (D). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
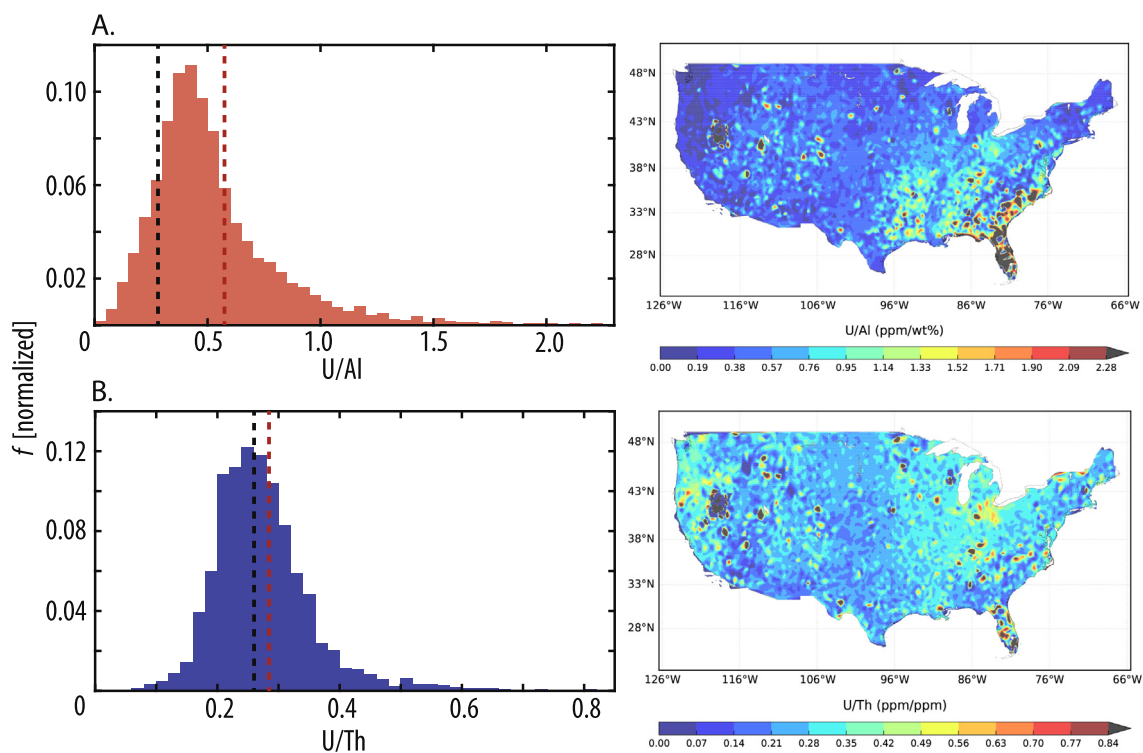

Fig. 5. Topsoil distributions (left) and interpolated maps (right) of U/Al (A) and U/Th (B). Red dashed lines denote the mean of the raw data, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
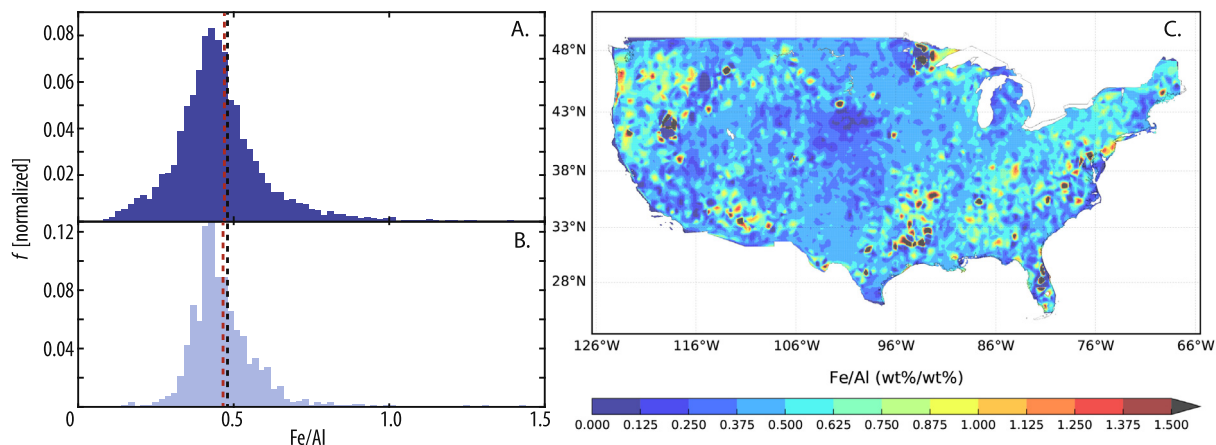
Fig. 6. Distribution of Fe/Al in topsoils from the continental US. (A) Distribution of raw data and (B) the catchment resampled distribution. Red dashed lines denote the mean of the raw or resampled distribution respectively, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (C) Raw data interpolated across the continental US. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
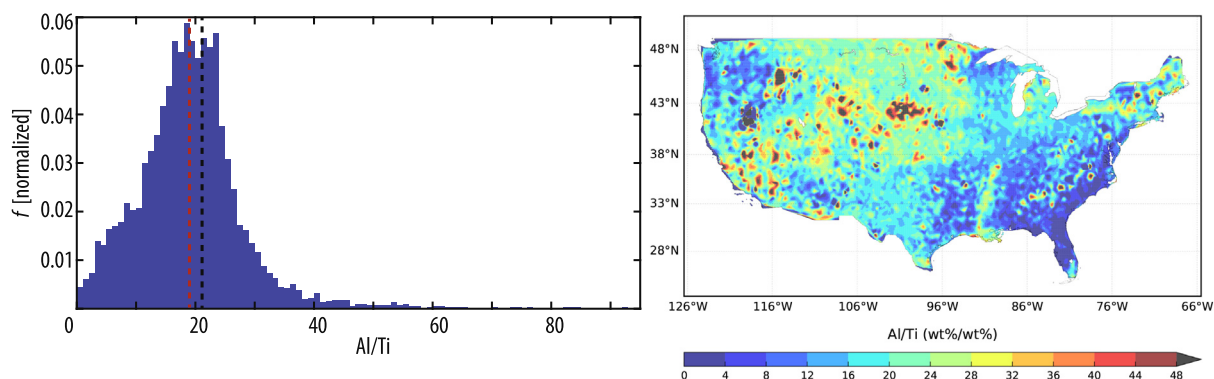

Fig. 7. Distribution of Al/Ti in topsoils from the continental US (left) and interpolated data (right). Red dashed lines denote the mean of the raw or resampled distribution respectively, while the black dashed line denotes the crustal mean value of Rudnick and Gao (2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
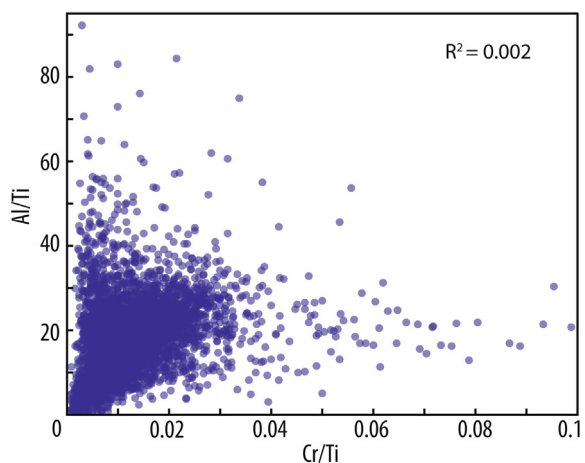

Fig. 8. Al/Ti compared to Cr/Ti from topsoils across the continental US.

statistically substantial data sets, or else use of alternative geochemical techniques such as isotopic analyses (see Section 5.1).

Critically, we find not only major variability away from this crustal average value in individual samples, but also persistent and widespread areas where topsoil Cr/Ti values fall well below the canonical crustal average. This is most apparent in the catchment resampled distributions, which show that sub-crustal means and substantial variation persist on catchment-size scales (Fig. 1C). Most crucially, it is this potential to sustain deviations away from the mean crustal value over a large and continuous areal extent that will most significantly impact the resolvability of the background detrital contribution in the sedimentary record. Additionally, considering the observed distributions, it is likely that a detrital flux well below the crustal average used in many Cr isotope studies could be sustained, leading to the concealment of significant authigenic enrichments critical to the interpretation of isotopic analyses (e.g., Cole et al., 2016b; Gueguen et al., 2016).
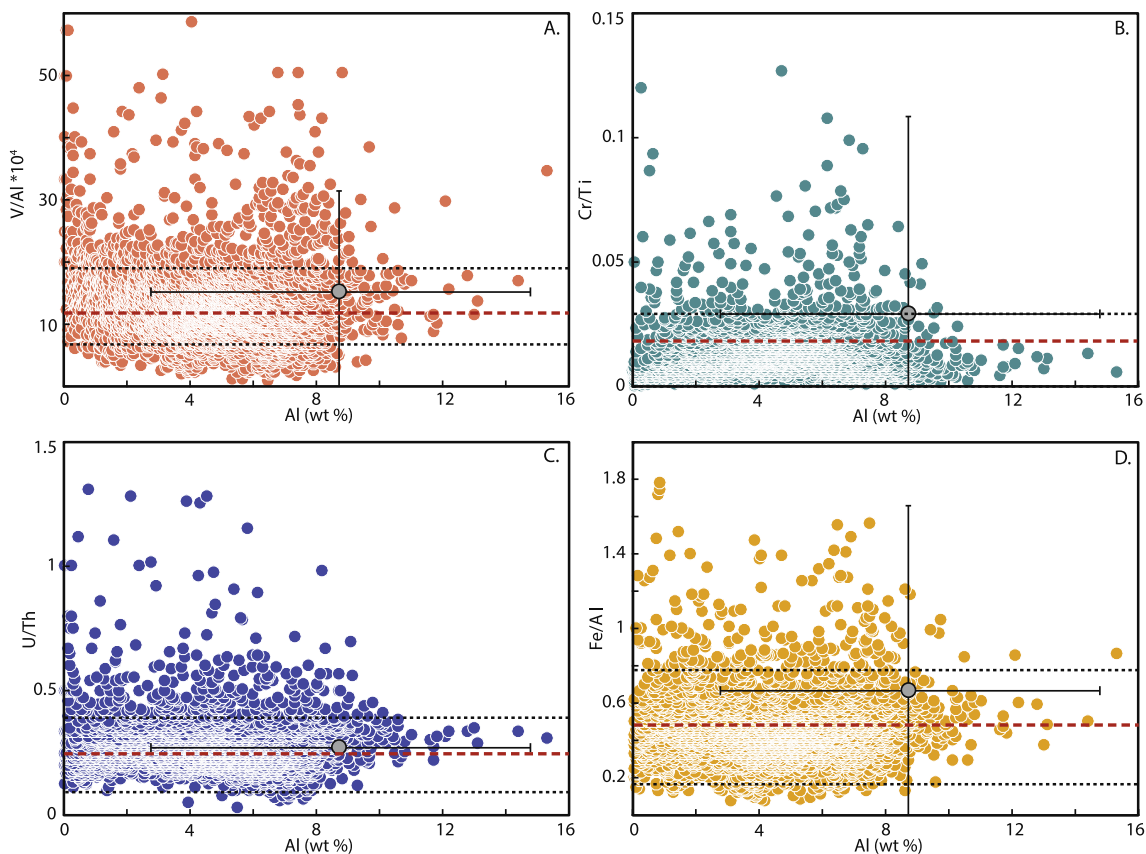
Fig. 9. (A) V/Al, (B) Cr/Ti, (C) U/Th, (D) Fe/Al all compared to Al content. Grey circles and error bars represent average global river suspended sediment element concentrations and 2SD from Viers et al. (2009). Black dashed lines show the upper and lower limit of our recommended confidence intervals while red dashed lines show the crustal means of Rudnick and Gao (2014). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Further, within the soil profile, the mean Cr/Ti value of the topsoil, the A horizon, and the C horizon all fall below the crustal average (Fig. 2). Most notably, we find that overall variability is essentially maintained vertically through the soil profiles on a large scale, indicating that varying degrees and rates of erosion – whether a result of mass wasting or continuous removal – will have little effect on the variation potential of the detrital flux to the ocean. Further, considering the significant range of percentage change in Cr/Ti between the C horizon and topsoil, it is likely a large variety of surface processes enable the mobilization of Cr, making the detrital flux from a particular regolith difficult to classify based only on rock type. These findings suggest that resolving true authigenic enrichments based solely on concentrations will be very difficult, and generally limited to scenarios with either a detailed understanding of source material and sedimentation rate, or else exceptionally high enrichments that are confined to the Phanerozoic.

This lack of resolvability is particularly troublesome when redox interpretations based on small to moderate enrichments are applied on local or basinal scales, or through individual stratigraphic sections. At this scale, variation in the detrital flux has the potential to exert a major control on the Cr/Ti signal, greatly skewing

redox interpretations if this flux is dissimilar from the crustal mean. This includes scenarios with a Cr rich detrital flux that could appear to have an authigenic enrichment or, in contrast, the concealment of significant enrichments when coupled with a Cr-poor detrital flux. Both cases are particularly relevant in Precambrian studies: there is potential for the former in the Archean while weathering an ultramafic crust and the likelihood of the latter case through the Mesoproterozoic where the marine reservoir of Cr has been drawn down by widespread anoxia, making only muted authigenic enrichments possible relative to the Phanerozoic (e.g., Reinhard et al., 2013). Further there is significant variation in the mapped distributions between Cr/Al and Cr/Ti (Fig. 1), suggesting that the choice of detrital tracer could also have an outsized impact on the interpretation of redox-driven enrichments.

While the findings of this study elucidate the presence of a large error bar on the detrital contribution of Cr to shale, challenging the framework of several studies (e.g., Reinhard et al., 2013; Li et al., 2015a), we suggest that as the geographic and temporal scale of a study increases, redox trends tend to become more robust. While some error in interpretation is likely for individual samples, when interpreted in concert with multiple formations globally or as

broad-scale trends through time, such interpretations are likely to remain robust.

Finally, as an emerging isotope system (e.g., Frei et al., 2009, 2013; Wille et al., 2013; Planavsky et al., 2014; Cole et al., 2016b; Wang et al., 2016c), it is vital that researchers recognize the issues of resolvability of the authigenic Cr component, which is the target of these investigations. In some cases, large datasets and a statistical approach can remedy the ambiguity of small authigenic signals (e.g., Cole et al., 2016b). In other cases, as our understanding of the system develops, Cr isotopes have the potential to provide much higher resolution insights regarding redox of past depositional environments (see Section 5.2).

4.2. Vanadium

Vanadium was compared to three different commonly used detrital tracers (Al, Ti, Sc) in order to demonstrate not only variability in V, but also the impact of the chosen detrital tracer and the heterogeneity within these systems that are generally considered stable, constant and frequently interchangeable. Notably, all three V ratios not only show large standard deviations, but also the means of the soil data show no consistent offset direction from crustal averages – the V/Ti soil mean falls below the crustal mean, while both the V/Sc and V/Al soil means fall above the crustal means (Fig. 3). The significance of these incongruous relationships between soil and crustal means is two-fold; first, the lack of consistency between tracers reflects further under-recognized source rock variability related to bedrock type and crustal heterogeneity, and secondly, this further emphasizes that on the scale of small enrichments, the choice of a particular detrital tracer compared solely to the crustal mean could significantly impact the interpretation of the redox signal.

We find, based on catchment resampling of V/Al, that variability in V flux is maintained over large drainage-basin areas, demonstrating the potential for sustained detrital inputs substantially different from the crustal average in the V system (Fig. 3). This widespread lateral variability that exists in the present will result in similar variability through time within the sediment column in the depositional basin (Walther, 1894; Middleton, 1973). While the expression of variability in background detrital V/Al will be the result of a number of factors including weathering and sedimentation rates, we suggest without a local understanding of both the processes at work and V/Al ratio of the source material, a single V/Al cutoff for detrital input cannot be implemented without a confidence interval that accounts for this heterogeneity.

We also find, based on the percentage change in V/Al between the C horizon and the topsoil samples from individual sites, that there is potential for both increases and decreases in the ratio as a result of local processes (Fig. 4). While preferential loss of V from the soil will primarily be the result of chemical weathering – resulting in dissolution and removal of that V from the detrital flux entirely – the potential for variation vertically through the soil profile can influence the nature of the detrital flux, especially if the primary physical weathering in a region is the result of high energy catastrophic erosion (i.e storms) as opposed to the low energy more sustained removal of only the topsoil (e.g., Wolman and Miller, 1960; Osterkamp and Friedman, 2000).

Further, the percentage change in V/Al from C horizon to topsoil provides a measure of the lateral variation in the potential preferential mobilization of V. We find both relative losses and gains in V between the C horizon and the topsoil, indicative of the susceptibility of V to mobilization through a variety of pathways including a ligand-bound fraction and oxidation and dissolution (Wehrli and Stumm, 1989; Emerson and Huested, 1991; Shiller and Mao, 2000). Such added complexities in the surface cycling of V only make unraveling the detrital and authigenic contributions to marine sediment more difficult. This highlights the possibility of varying detrital contribution from a specific area based not just on bedrock composition, but relative activity of surface processes including chemical weathering, oxidation and reduction within the soil profile, and mobilization via organic and oxide sorption. Without additional data that can provide more highly resolved information on the redox setting, it is very difficult to make interpretations based on either depletions or enrichments in V relative to a crustal average.

4.3. Uranium

Uranium was compared to Al and Th, the most commonly used U detrital tracers (e.g., Adams and Weaver, 1958; Wignall and Myers, 1988; Calvert and Pedersen, 1993; Morford et al., 2001; Anbar et al., 2007; Partin et al., 2013; Andersen et al., 2014). Similar to other proxies considered, variation from crustal means does persist, however the standard deviations, especially for U/Th, remain much smaller than those for V or Cr. This suggests that the U detrital flux is much more consistent, and less likely to result in major stratigraphic deviations in the depositional system than V or Cr. Notably, the topsoil mean for U/Th is very similar to the crustal average, however the U/Al mean displays considerably more offset (Fig. 5). This is likely at least in part, the result of similarities in atomic size and elemental behavior of U and Th, and provides a compelling case for choosing a detrital tracer that is most chemically similar to the element of interest.

The smaller scale variability in the U/Th system may make the use of a confidence interval a practical alternative in some cases for distinguishing significant authigenic enrichment (see Section 5.1). Despite these more muted effects compared to other redox-sensitive systems, it still remains important to recognize the potential for small variations. This is particularly the case when considering small-scale changes in U enrichments in the rock record, especially in individual stratigraphic sections. Additionally, in isotopic studies, the isotopic value of the U detrital flux is constant (e.g., De Corte, 2016), however it is likely important to consider the potential for variation in the magnitude of this term in the overall U isotope mass balance. In such studies, the use of a confidence interval rather than a crustal cutoff remains the most conservative and accurate approach, and it is likely conclusions regarding paleoredox

conditions will remain ambiguous without the use of additional techniques.

4.4. Iron

Iron, and in particular iron speciation, has been the focus of decades of work seeking to improve our understanding of depositional paleoredox conditions. The use of iron as local redox proxy, although more complicated, is also based on Fe scavenging under anoxic conditions (e.g., Poulton and Raiswell, 2002). Iron is, of course, more soluble under anoxic conditions. However, Fe is typically enriched in anoxic sediments because of a benthic shuttle of iron from reducing marine sediments (anoxic sediments underlying an oxic water column) and a strong Fe trap in anoxic settings (foremost in euxinic settings) (Raiswell and Canfield, 1998; Lyons and Severmann, 2006; Severmann et al., 2008). Yet, similar to other redox-sensitive metals discussed, studies utilizing Fe enrichments require an understanding of the portion of reactive iron species relative to the total iron content of the sediment (e.g., Berner, 1970; Raiswell and Canfield, 1998; Poulton and Canfield, 2005). Significantly, there is the potential to convert more highly reactive species to the unreactive silicate bound fraction via metamorphism, thus disguising redox driven enrichments. It has been suggested (Raiswell et al., 2011) that Fe/Al ratios could help resolve evidence of this type of alteration, by exposing enrichments relative to crustal averages (i.e., beyond the silicate fraction).

Here, Fe/Al was examined in the topsoil dataset, as this ratio has been employed by researchers, often in conjunction with C and S systematics relating to pyrite formation, to constrain the detrital Fe contribution and further elucidate redox settings (e.g., Lyons et al., 2003; Cruse and Lyons, 2004; Lyons and Severmann, 2006; Partin et al., 2013) (Fig. 6). Enriched Fe/Al ratios are relied upon as an indicator of reducing environments, however we find significant heterogeneity in the crustal ratio of these elements, suggesting – similar to the other redox tracers discussed herein – that, minimally, a confidence interval must be used in assessing sedimentary Fe/Al values, rather than a single average cutoff. As with other proxies discussed, the potential for detrital variability is too great to draw realistic conclusions about redox based on Fe/Al alone, especially on a local scale. Using catchment resampling, we again demonstrate the potential of capturing detrital signals that deviate from crustal averages over large areas, resulting in sustained and non-negligible variation from crustal mean values in the detrital flux to the adjacent depositional basin.

4.5. Aluminum and titanium

In addition to a suite of redox-sensitive elements, we have also examined heterogeneity in Al/Ti ratios, which are a provenance tracer and a ratio generally considered to not be susceptible to alteration during surface processes. This ratio (Al/Ti) has been used to distinguish mafic and felsic source rocks (e.g., Hayashi et al., 1997; Huang et al., 2013). The variability of Al/Ti observed in this study suggests that the detrital tracers themselves, which are

relied upon for remaining relatively constant through the time interval of many sedimentary redox studies (at least on the scale of individual stratigraphic units), have the potential to vary greatly themselves (Huang et al., 2013) (Fig. 7). Given that Al/Ti ratios are likely to reflect the felsic to mafic composition of the parent rock and that the composition of the parent can greatly impact the supply of redox-sensitive trace metals (e.g., Cr is concentrated in mafic rocks), it might be possible for provenance tracers to 'correct' detrital redox-sensitive trace element variability. However, we find no relationship between Cr/Ti and Al/Ti (Fig. 8, r-squared value = 0.002). This not only suggests that the choice of a particular detrital tracer can impact the result of a study, but also suggests that redox-sensitive trace element variability cannot be easily accounted for with a provenance tracer.

Considering the lack of a strong relationship between Cr/Ti and Al/Ti, and given the lack of clear redox-sensitive metal depletion in the topsoil, we suggest that surficial variability is primarily driven by inherited variation, rather than the result of variable surface weathering within the soil. The majority of the Earth's weatherable surface area (i.e., exposed continental area) is comprised of sedimentary rocks (Bluth and Kump, 1991), driving this inherited variability and adding complexity beyond what is observed in igneous rocks. While, for example, Cr is primarily sourced from mafic rocks and it may appear possible correct for this with a detrital tracer such as Ti, we find instead that the variation within the weatherable sources is too great for this to be an effective method of quantifying the detrital contribution.

4.6. Aluminum content

Lastly, we have compared each of our redox sensitive metal ratios for which we have suggested new confidence intervals (Cr/Ti, V/Al, U/Th, Fe/Al) to aluminum content, and then examined this data in relation to average global river suspended sediment values from Viers et al. (2009) (Fig. 9). We find that for all ratios, increasing Al content results in sustained variability within that ratio, and that this variability remains too high to further constrain detrital flux ratios based on Al content. While our database only investigates the fine sediment fraction (<2 mm), it is this fraction that is likely to be the most consistent (e.g. larger grain sizes tend to be even more variable; e.g., Bouchez et al., 2011). Further, the global averages fall within our suggested confidence intervals for all four ratios (Fig. 9), providing a second line of evidence for our dataset being generally representative of the detrital material being transported to the marine system. However, it is apparent that the river averages tend toward higher ratios and Al concentrations than the majority of our soil data. This is likely a result of sorption effects of dissolved elements present in the riverine system, as well as the exclusion of material being transported in the bed load. As such, we suggest our examination of soil data as opposed to an extensive survey of riverine data provides a simpler window into establishing a baseline range for detrital fluxes that is

not complicated by additional factors involved in riverine transport.

5. FUTURE DIRECTIONS

5.1. Recommendations

We suggest use of confidence intervals for Cr/Ti, V/Al, U/Th, and Fe/Al based on the catchment resampled mean values and two times the standard deviation of these means, which are summarized in Table 2. For U and V, the least variable ratios (U/Th and V/Al) were chosen and are recommended for future studies. In some cases, these confidence intervals (especially for U/Th) may provide a narrow enough constraint to elucidate significant enrichments in some (likely Phanerozoic) studies, where very large enrichments are likely to develop. In other cases, especially for Cr and V, the observed variation in soils is so extensive that the confidence intervals define a very broad range that will generally fail to distinguish authigenic enrichments, except for in the most extreme cases of enrichments (e.g., Bakken Shale, Karma and Parslow, 1989). In these cases, further analyses such as isotopic work will be required to definitively classify the paleoredox conditions.

As shown in this study, the use of single crustal averages to distinguish authigenic enrichments of most redox-sensitive metals does not account for the considerable crustal heterogeneity in these systems. This leads to an oversimplification of these redox proxies, most of which frequently lack the resolvability to independently distinguish redox driven enrichments without additional analyses. These issues are most problematic in analyses based on individual stratigraphic sections or basins (e.g., Li et al., 2015b; Zhang et al., 2016). As data sets increase in size and global distribution, there is potential to highlight redox-driven enrichments using a statistical approach. For example, to deal with detrital Cr/Ti element variability, Cole et al. (2016a, b) compared large datasets from several formations from different time intervals with similar Cr/Ti ranges. The basic idea behind this approach was that although a single formation may have an anomalous Cr/Ti ratio, large datasets from many units capture the full variability of different crustal inputs, that is, samples with high and low detrital Cr/Ti ratios.

While this study is based on a dataset restricted to the continental United States, we suggest that this assessment of detrital variability represents a major step forward in understanding the potential for lateral, large-scale variation. The U.S. also encompasses a wide variety of exposed lithologies, weathering regimes, and climates, acting as a reasonable microcosm of the global weatherable shell. As larger databases emerge, this could be assessed with a similar study using a more expansive global dataset, however considering the catchment scale variability observed here, we suggest that our recommended confidence intervals provide at least a first approximation of expected variation, and would certainly be a step forward from the use of a single cutoff value.

5.2. Applications of isotope systems

Iron can provide a success story for the future of redox-sensitive transition metals, as a more thoroughly explored system than other transition metals discussed here. The use of both Fe speciation and the Fe isotope system have proven very powerful tools to improve the resolvability of the system beyond the more ambiguous enrichments (e.g., Poulton and Canfield, 2005; Severmann et al., 2008; Sperling et al., 2015). Using a similar framework of coupled techniques from other systems (Cr, U, V), it is conceivable that the resolution of redox studies can be greatly enhanced. To add such resolvability to trace metal redox proxies, we highlight the utility of emerging isotopic systems such as Cr and V to distinguish authigenic enrichments, providing higher resolution constraints on local marine redox. Further, isotopic approaches can prove particularly useful in identifying potential shifts in the efficiency of chemical weathering (i.e. supply of oxidants), but if taken a step further, this can also provide information about the subsequent impact on the magnitude of the detrital flux. While our understanding of these systems is still developing, the established basic framework can already function as a valuable new tool to distinguish moderately reducing systems, and provide improved resolvability in redox studies.

The Cr isotope system has the potential to provide new insights about weakly reducing environments or those with vacillating redox conditions, as Cr is easily and rapidly removed through a variety of reduction pathways, including nitrate reduction, and sequestered in the sediment (Pettine et al., 1994; Rue et al., 1997; Graham and Bouwer, 2010). The detrital Cr fraction appears in most cases to retain the unfractionated bulk silicate earth value of δ^{53}Cr $= -0.124 \pm 0.101‰$ (Schoenberg et al., 2008; Gueguen et al., 2016; Wang et al., 2016b), however, in the case of a well-oxidized earth atmosphere, authigenic Cr will have undergone oxidation during terrestrial weathering, and subsequent reduction in the marine system, imparting a fractionated signal (Kotaś and Stasicka, 2000; Ellis et al., 2002; Schauble et al., 2004; Reinhard et al., 2014),

Table 2
Recommended confidence intervals.

Elemental ratio	Catchment resampled mean	2 Std Dev ($\pm$)	Confidence interval	Upper continental crust[a]
V/Al	13.13	6.18	6.95–19.31	11.90
Cr/Ti	0.015	0.015	0–0.030	0.02
U/Th	0.282	0.102	0.180–0.384	0.26
Fe/Al	0.472	0.302	0.170–0.773	0.48

[a] Rudnick and Gao (2014).

resulting in a recognizable authigenic fraction. For example, in a hypothetical sample with a Cr/Ti ratio of 0.025, let us consider two cases; (1) 100% of the Cr is detrital or (2) 50% of the Cr is detrital, while the other 50% is derived from seawater. If we assume a seawater δ^{53}Cr value of 1.0‰, the sample from the first scenario would retain an unfractionated crustal value, while the second would likely have a distinctly fractionated value of $\sim$0.5‰, representing the relative isotopic mass balance of the two components. Significantly, both of these scenarios are likely based on our predicted range of detrital Cr/Ti ratios. Acknowledging the very limited extent of Cr isotope variability in oxic sediments, despite variation in Cr/Ti (Gueguen et al., 2016), a coupled isotope – enrichment approach is likely to yield highly resolved information regarding redox conditions of individual depositional environments that more poorly constrained enrichments alone are unable to provide (Cole et al., 2016a).

Vanadium, similar to Cr, also has the potential to elucidate suboxic conditions (*sensu* Scott et al., 2008), filling in the gradient of potential redox environments. It has been suggested that V can be sourced from suboxic sediment (Hastings et al., 1996; Morford and Emerson, 1999; Sahoo et al., 2012; Thomson et al., 2015), released along with Mn^{2+} (Morford et al., 2005) – thus a decrease in V could potentially signal a shift to a more oxidized system. Additionally, V can be reduced twice – first from its oxidized state V(V) to V(IV) under mildly reducing conditions and then removed from the sediment via formation of ligands or adsorption (van der Sloot et al., 1985; Emerson and Huested, 1991; Morford and Emerson, 1999), and secondly to V(III) in the presence of H_2S which can be removed as oxides (V_2O_3), hydroxide $V(OH)_3$ or incorporated into geoporphyrins (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). This two-step reduction of V lends this system to tracking varying states of anoxia in the marine system resulting from different solubilities of V phases. Unfortunately, because of the large potential range of detrital V contribution, it is unlikely that such shifts can be recognized based on changes in concentration alone. However, with the emergence of the V isotope system, though still in incipient stages, there is potential that isotopic fractionations paired with elemental concentrations can enhance our understanding of these intermediate redox environments (Prytulak et al., 2013). Further it is also conceivable that with a large enough dataset, a statistical analysis of V concentration changes through large time intervals, and the relationship of these V concentrations with other redox-sensitive trace metals, that some broad-scale shifts in suboxic area of the ocean can be recognized.

In sum, despite the current limitations of these nascent systems, major insights can still be gained from simplistic applications of the Cr and V isotope systems. The coupled approach described above has the capacity to provide high-resolution redox interpretations regardless of fluctuations in detrital input or more moderately reducing conditions and in spite of a poor understanding of the V and Cr global isotope mass balances.

Uranium isotopes, though also still in the early stages, have been explored more widely than the Cr and V systems (e.g., Weyer et al., 2008; Asael et al., 2013; Kendall et al., 2013, 2015; Andersen et al., 2014, 2016; Tissot and Dauphas, 2015). Uranium is primarily reduced within the sediment column (Algeo and Maynard, 2004; McManus et al., 2005), and reduction under anoxic conditions imparts large fractionations from seawater values. Thus, the areal extent of this sink can impact the U isotopic value of seawater compared to the riverine input, the latter of which is considered constant (De Corte, 2016). Using a quantitative mass balance framework, these relationships can be used to reconstruct the areal extent of reducing marine environments (e.g., Kendall et al., 2015; Tissot and Dauphas, 2015). However, detrital corrections must be made in order to elucidate the isotopic value of the authigenic component (e.g., Asael et al., 2013; Lu, 2016), yet the potential for variation of this term is rarely considered. Use of the confidence intervals suggested in this study can thus provide a means of assessing the potential variation in this term, the subsequent 'error bars' on estimations of reducing ocean area.

6. CONCLUSIONS

In examining some of the most commonly used redox-sensitive transition metals and a variety of detrital tracers in the soils of the continental US, we find pervasive and laterally extensive heterogeneity in all systems that suggests the detrital contribution of these elements in the rock record must be assessed with extreme caution. The prevalence of detrital material with trace metal/detrital tracer ratios significantly different from those of the average crust suggests that using crustal averages to estimate detrital metal fluxes is a serious oversimplification. Recognition of surficial variability is necessary in sedimentary redox studies, and must be considered especially carefully in local and basinal contexts. We suggest new confidence intervals, based on catchment resampled means for Cr/Ti, V/Al, U/Th, and Fe/Al to quantify the potential for detrital contribution in these systems, which can help to elucidate enrichments clearly driven by redox conditions even in the face of major surficial variability. In cases where enrichments remain ambiguous, the application of emerging isotope systems can provide a means to improve the resolvability of trace element enrichment redox proxies, and the coupled use of these tools will be a major step forward in our ability to understand a spectrum of redox environments.

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Associate Editor: Jerome Gaillardet