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1 Trace metal elements as paleoenvironmental proxies: Why
2 should we account for sedimentation rate variations?

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13 **ABSTRACT**

14 Trace metal elements (TMEs) are commonly used to reconstruct the
15 environmental conditions present during the deposition of organic-rich sediments. For
16 example, TME concentrations controlled by changes in primary productivity and redox
17 conditions are widely used in paleoenvironmental studies. Recently, these proxies have
18 undergone a resurgence of interest and are commonly used in large-scale (10–1000 km)
19 studies. However, applying these geochemical proxies at basin scale while ignoring
20 variations in sedimentation rates (SR) may lead to misinterpretation of
21 paleoenvironmental conditions. Here, we show how SR can affect the geochemical
22 records and may lead to incorrect interpretations of TME evolution. Accounting for SR,

we computed the authigenic fraction accumulation rates of key TMEs in the Upper Montney and Doig Phosphate formations (Triassic, western Canada), and we correct the concentration of these elements in the Vaca-Muerta Formation (Jurassic–Cretaceous, Argentina). Our SR-corrected TME proxies require a different interpretation of paleoenvironmental conditions (e.g., primary productivity, basin restriction) compared to conventional TME results and highlight that elementary enrichments commonly interpreted as indicative of anoxic depositional environments may reflect low SR and the formation of condensed intervals. This work also introduces a new workflow to account for SR in paleoenvironmental studies at basin scale and over long time periods.

INTRODUCTION

The recent development of shale plays requires an understanding of the distribution of organic matter (OM) at both high resolution and basin scale. The OM content in marine sedimentary records is mainly driven by three processes: organic (primary) productivity, preservation of the OM (controlled by redox conditions and the burial efficiency), and its dilution by nonorganic particles (Bohacs et al., 2005). In practice, dilution rates of OM can be approached by using sedimentological and stratigraphic techniques, whereas reconstruction of primary productivity and redox dynamics is facilitated by geochemical proxies such as trace metal element (TME) concentrations (Tribovillard et al., 2006). For instance, variations in U/Th ratios are interpreted to reflect changes in oxygen concentration (Jones and Manning, 1994), whereas variations in Ba/Al ratios are thought to reflect the variation in primary productivity (McManus et al., 1998).

To study the authigenic (or paleoenvironment-related) fraction of an element, TME proxy analysis commonly includes: a normalization with immobile elements (Calvert and Pedersen, 1993), and the computation of an enrichment factor using a reference standard (Brumsack, 2006). Limitations of normalizations were presented by Van Der Weijden (2002) and include the effects of low-denominator concentration (e.g., Al in carbonaceous rocks) and the spurious correlations that can result from normalization to the same elements. Furthermore, many proxies have been defined in case studies with limited vertical/stratigraphic scale (centimeter to decimeter), relatively homogeneous sedimentary facies, and stable sedimentation rates (SRs; within the same order of magnitude; e.g., Warning and Brumsack, 2000; Borchers et al., 2005, etc.). However, it is widely accepted that SR can vary by several orders of magnitude within a sedimentary basin, depending on the distance between the source and the depositional environment.

Here, we used two organic-rich intervals with chronostratigraphic frameworks to investigate the impact of SR variability on TME proxy interpretations. In western Canada, the transition between the Lower Triassic Upper Montney Formation and the Middle Triassic Doig Phosphate Zone is marked by a sudden drop in the SR—from 100 to 29 m/m.y.—accompanied by a twofold increase in the OM content. Based on TME concentrations, this OM increase was initially interpreted to reflect a rise in primary productivity (Crombez et al., 2017a). However, subsequent, regional process-based models of OM-rich sediment deposition suggested constant primary productivity across the Upper Montney–Doig Phosphate boundary (Crombez et

al., 2017b). As a consequence, a first-order control of SR on OM abundance was favored (Crombez et al., 2017b). This lack of consideration for the impact of SR is also present in studies on the Vaca-Muerta Formation in Latin America, where several OM-rich intervals associated with variable TME concentrations are present (e.g., Kietzmann et al., 2014; Dominguez et al., 2016; Hernández Bilbao, 2016).

While numerous studies have addressed the dependency between the OM content in shales and SR (e.g., Stein, 1990; Tyson, 2001; Burdige, 2007; Passey et al., 2010), the impact of temporal variability of SR on paleoenvironmental proxies has been overlooked (e.g., Lyons and Severmann, 2006; Little et al., 2015). In this contribution, we voluntarily used different TMEs from different case studies to show how TME concentrations are affected by SR and suggest two workflows to evaluate paleoenvironmental changes. Furthermore, we discuss the implication of the lack of SR integration in previous works and the limitations of the proposed workflows.

DATA AND METHODS

The stratigraphic frameworks presented are based on Crombez et al. (2019) and Euzen et al. (2018) for the Upper Montney and Doig Phosphate formations, and on Sattler et al. (2016) for the Vaca-Muerta Formation. SR values were computed using an estimated interval thickness and duration ($SSSS = \frac{\text{Thickness}}{\text{Duration}}$). Geochemical analyses were conducted on samples from (1) a core transecting the Upper Montney and Doig Phosphate formations (well 0/16–17–83–25W6; 67 samples) in British Columbia, and (2) on cuttings from the Vaca-Muerta Formation (well Jaguel del Rosauros X-1, 53 samples; and well Medano de la Mora X-1, 77 samples; where the distance between both wells is ~20 km) in

the Neuquén Basin. Element analyses on the Upper Montney and Doig Phosphate formations were conducted by ACT Labs following their 4A-4B protocol. Element analyses on the Vaca-Muerta Formation were conducted using a handheld energy-dispersive X-ray fluorescence analyzer and processed following the Rowe et al. (2012) method.

AUTHIGENIC FRACTION ACCUMULATION RATE

To illustrate the impact of SR on TME content across the Upper Montney and Doig Phosphate formations (offshore to lower shoreface conditions; for sedimentologic description, see Crombez et al., 2017a), we computed the authigenic fraction accumulation rate (AFAR) of Mo and Ni using a high-resolution stratigraphic framework, and we compared their evolution with conventional TME proxies. The computation of the AFAR for an element E (in $\mu\text{g}/\text{cm}^2/\text{yr}$) requires the estimation of the SR (assuming a constant sedimentation rate in an interval), bulk rock density (ρ , defined here as the Bouguer density), and the authigenic element concentration E_{Aut} of a sample:

$$\text{AFAR}_E = E_{\text{Aut}} \text{ SR } \rho . \quad (1)$$

Here, E_{Aut} was determined using a detrital element D by estimating a detrital $(E/D)_{\text{Source}}$ value (minimum acceptable value in the data set) from an E versus D cross-plot (assuming a constant chemical nature in the sediment sources) and subtracting the detrital fraction from the total E concentration of each sample:

$$E_{\text{Aut}} = E - DD_{\text{Source}} \frac{E}{D} . \quad (2)$$

The SR drop across the Upper Montney–Doig Phosphate boundary is accompanied by an increase in Mo/Al and Ni/Al ratios (Fig. 1A). In contrast, accounting for SR variations resulted in no increase of the Mo and Ni AFAR. Here, the drop in

sediment supply across the boundary decreased the dilution of the authigenic fraction, which resulted in elevated Mo/Al and Ni/Al ratios. It is therefore unlikely that these increases were related to changes in paleoenvironmental condition.

A closer look at the AFAR showed significant variations in the proxies in the Upper Montney Formation. In Figure 1A, the SR of the Upper Montney Formation is considered constant; thus, the observed AFAR variations could be related to high-frequency changes in SR and not to paleoenvironmental changes. To test this hypothesis, we used a high-resolution stratigraphic framework (Euzen et al., 2018) highlighting high-frequency SR variations (Fig. 1B). SR values vary from 50 to 75 m/m.y. in parasequences UM1–UM5 and increase to 190–215 m/m.y. in UM6–UM7. The absolute values of the AFAR are low in UM1–UM5 and high in the UM6–UM7 when compared to the AFAR computed using the average Upper Montney Formation SR (Fig. 1A). However, the high-frequency variations of the AFAR in UM1–UM5 and UM6–UM7 are not significantly different (Fig. 1A versus Fig. 1B). The only significant difference occurs across the UM5-UM6 boundary, where the average value of the AFAR increases. We interpret these variations to be related to the amplitude of the change in SR. Across the UM5-UM6 boundary, the SR increases from 60 to 190 m/m.y., which causes the significant increase of the AFAR. Within UM1–UM5 and UM6–UM7, the units' average SR does not present sufficient amplitude variation to affect the AFAR or the conventional TME proxies in a way that could bias the interpretation. Based on these observations, we propose that variations in SR of at least one order of magnitude are necessary to affect the interpretation of conventional TME proxies.

CORRECTED ELEMENTARY CONCENTRATION

137 Computation of an element corrected elementary concentration (CEC, in ppm)

138 requires reference sedimentation rates (SR_{Ref}):

$$139 \quad CEC = \frac{E_{Aut}}{E_{Ref}} \frac{SSS_{Ref}}{SSS} + \frac{D}{D_{Source}} \quad (3)$$

140 In the computation, SR_{Ref} relates to the SR in other parts of the basin or to the SR
141 in other case studies The CEC shows what the elementary concentration should be if the
142 SR were equal to SR_{Ref} . This computation assumes $D \gg E$, which implies that variations
143 of E will only marginally affect D (e.g., D in % and E in ppm).

144 As in the Upper Montney and Doig Phosphate formations, the Vaca-Muerta
145 Formation shows varying SR. In the two investigated wells, located in the same
146 paleogeographic setting, the SR values vary from 24 m/m.y. (in unit 1) to 90 m/m.y. (in
147 unit 2) along well JDRx1 and from 16 m/m.y. (in unit 1) to 100 m/m.y. (in unit 2) along
148 well MDMEx1. Using JDRx1 unit 2 SR as SR_{Ref} , Figure 2 displays V-Ti and Cu-Ti cross-
149 plots of two well intervals that intersect the basal units of the Vaca-Muerta Formation.
150 The uncorrected data plotted on Figure 2 suggest stronger authigenic enrichments in V
151 and Cu, which are respectively related to redox conditions and primary productivity, in
152 unit 1, with V up to 300 ppm and Cu up to 40 ppm. However, accounting for SR
153 differences between these units by computing the CEC highlights a weaker authigenic
154 enrichment signature in unit 1. Comparable to the Upper Montney and Doig Phosphate
155 formations, the conventional TME proxies are affected by SR in the Vaca-Muerta
156 Formation. Not accounting for SR, the TME records suggest an increase in bottom-water
157 oxygen levels associated with relatively constant primary productivity from unit 1 to unit
158 2 (Calvert and Pedersen, 1993; Tribovillard et al., 2006). Accounting for SR by
159 calculating the CEC shows the opposite, i.e., decreasing bottom-water oxygen levels and

160 increasing primary productivity, in unit 2. In part of the Vaca-Muerta Formation, the
161 higher TME authigenic concentration is an artifact of a lower SR, which leads to the
162 concentration of the authigenic elements.

163 **IMPLICATION FOR PREVIOUS AND FUTURE STUDIES**

164 The influence of SR on TME content is summarized in Figure 3. In this
165 conceptual model, paleoenvironmental variations are assumed to control the TME
166 accumulation rates. It suggests that these variations and the SR will represent the two end
167 members on the control of the authigenic fractions. SR differences exceeding one order
168 of magnitude lead to a significant concentration (i.e., low SR) or dilution (i.e., high SR)
169 of the authigenic fraction of TMEs. In the latter case, normalizing to a detrital element
170 will only increase the effect of the SR. As the relative proportion of the detrital element
171 will increase in tandem with the increasing sediment supply, the ratio will decrease and
172 therefore show variations not caused by paleoenvironmental changes. This phenomenon
173 is illustrated by the vertical evolution of the ratios in Figure 3B, where: (1) the absolute
174 values of the ratios are different yet related to the same paleoenvironmental conditions,
175 and (2) the vertical evolution of the ratios are not representative of paleoenvironmental
176 changes, but instead they result from progradation of the sedimentary system and a
177 progressive increase in SR.

178 These observations have important implications for the use of TMEs as
179 paleoenvironmental proxies. The elemental ratios that characterize boundaries between
180 oxic, dysoxic, and anoxic conditions (e.g., Hatch and Leventhal, 1992; Jones and
181 Manning, 1994) vary depending on SR. In contrast, proxies that are based on ratios of
182 two authigenic components, for example, total organic carbon and Mo (a measure of

basin restriction; Algeo and Lyons, 2006) or Mo and U (a measure of anoxia; Algeo and Tribovillard, 2009), should proportionately be affected by changes in SR, making them more robust indicators of paleoenvironmental change as long as their concentrations exceed those in the detrital fraction (i.e., by at least one order of magnitude).

When reconstructing large-scale paleoenvironmental conditions, it is important to consider that the SR values were probably not the same. In studies where absolute durations are not known, but where stratigraphic correlation suggests that sections represent the same time interval, the authigenic fraction should be normalized to the sedimentary thickness to approximately account for different dilutions.

It is important to acknowledge the limitations of calculated AFAR and CEC values when studying paleoenvironmental conditions. The main limitations on the interpretation of a TME proxy will also apply, as the studied element might be affected by post- and syndepositional processes independent of the paleoenvironmental conditions. In addition, a well-constrained SR quantification is required. Therefore, it is important to acknowledge the uncertainties related to the compaction of the sediments. In the computation of the AFAR, we recommend using a density representative of the investigated interval compaction state (e.g., higher density for compacted strata and lower density for uncompacted/recent sediments). For the computation of the CEC, if the studied intervals are at the same compaction state, we recommend using the apparent SR (i.e., computed using the compacted thickness); however, if the objective of the study is to compare different sedimentary systems from different basins, we recommend computing the uncompacted thickness of sedimentary strata (Fowler and Yang, 1998; Bahr et al., 2001) to obtain comparable SR values. In addition, Enos (1991) presented a

wide range in SR variations across different sedimentary environments, and Droxler and Schlager (1985) demonstrated high-frequency SR variations within one single environment. Unfortunately, in ancient sediments, millimeter-scale SR values are not accessible, and therefore best practice interpretation of the AFAR and the CEC should focus on variation of the trends between units where SR values can be assumed to be constant.

Last, the AFAR in UM7 (Fig. 1B) presents a “Christmas tree” pattern. High AFAR values are often present above parasequence set boundaries. These intervals are interpreted as flooding surfaces followed by regression (Euzen et al., 2018) and are likely associated with low SR, followed by increasing SR. The “Christmas tree” pattern is thus likely linked to the progressive increase in SR during deposition of the parasequence, and the peaks in AFAR are interpreted to relate to condensed intervals and concentration of TMEs with associated OM.

CONCLUSION

To avoid misinterpretation of the geochemical record, we suggest calculating the authigenic fraction accumulation rate or the corrected elementary concentration of TMEs, instead of using simple corrections such as elemental normalizations, enrichment factors, or authigenic enrichments. These new proxies account for variations in SR and focus on the temporal fluxes of authigenic elements rather than on their total concentration within a sedimentary unit. With the increasing need to understand the high-resolution distribution of OM, accounting for SR variations will improve the quantification of temporal and spatial variations of anoxia and primary productivity. This will result in an

improved understanding of the controlling factors for OM accumulation and lead to better predictions of the three-dimensional distribution of OM-rich intervals.

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FIGURE CAPTIONS

Figure 1. Gamma ray (GR), sedimentation rate (SR), trace metal element (TME) ratios, and authigenic fraction accumulation rates (AFAR) of Mo and Ni in the Upper Montney and Doig Phosphate formations, western Canada. AFAR values are presented with confidence interval accounting for $\pm 20\%$ incertitude in SR. (A) Variation of TME proxies and Mo and Ni AFAR across the Upper Montney–Doig Phosphate boundary. (B) Variations of proxies within the Upper Montney Formation, considering high-resolution SR changes across seven parasequences. In B, duration of each parasequence is estimated to be 0.2 m.y. (Euzen et al., 2018). White dash lines represent moving average on five samples.

Figure 2. Scatter plots of V versus Ti (A) and Cu versus Ti (B) in units 1 and 2 of the Vaca-Muerta Formation (Argentina) from two wells. Uncorrected data are shown in shades of gray, and corrected elementary concentrations are shown in shades of blue. Here, source trends are identical between wells to reflect same nature of detrital material.

Figure 3. Influence of different sedimentation rates on concentration of authigenic elements. (A) Conceptual basin where sediment supply at each margin is different. (B)

385 Variations in dilution of authigenic elements in two locations, each related to different
386 sediment supplies. OM—organic matter; SR—sedimentation rate.