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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,

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

32 **INTRODUCTION**

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

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

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

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

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

80 **DATA AND METHODS**

81 The stratigraphic frameworks presented are based on Crombez et al. (2019) and
82 Euzen et al. (2018) for the Upper Montney and Doig Phosphate formations, and on
83 Sattler et al. (2016) for the Vaca-Muerta Formation. SR values were computed using an
84 estimated interval thickness and duration ($SSSS = \frac{\text{Thickness}}{\text{Duration}}$). Geochemical analyses were
85 conducted on samples from (1) a core transecting the Upper Montney and Doig
86 Phosphate formations (well 0/16–17–83–25W6; 67 samples) in
87 British Columbia, and (2) on cuttings from the Vaca-Muerta Formation (well Jaguel del
88 Rosauros X-1, 53 samples; and well Medano de la Mora X-
89 1, 77 samples; where the distance between both wells is ~20 km) in

90 the Neuquén Basin. Element analyses on the Upper Montney and Doig Phosphate
91 formations were conducted by ACT Labs following their 4A-
92 4B protocol. Element analyses on the Vaca-Muerta Formation were conducted using a
93 handheld energy-dispersive X-ray fluorescence analyzer and processed following the
94 Rowe et al. (2012) method.

95 AUTHIGENIC FRACTION ACCUMULATION RATE

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

$$105 \quad \text{AFAR}_{EE} = EE_{\text{Aut}} \text{ SR } \rho . \quad (1)$$

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

$$110 \quad EE_{\text{Aut}} = EE - DD \frac{EE}{DD_{\text{Source}}} . \quad (2)$$

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

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

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

136 **CORRECTED ELEMENTARY CONCENTRATION**

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

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

139
$$CEC = \frac{E_{Aut}}{E} \frac{SSSS}{SSSS_{Ref}} + \frac{D}{D_{Source}} \quad (3)$$

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

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

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

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

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

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

220 **CONCLUSION**

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

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

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366 **FIGURE CAPTIONS**

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

377
378 Figure 2. Scatter plots of V versus Ti (A) and Cu versus Ti (B) in units 1 and 2 of the
379 Vaca-Muerta Formation (Argentina) from two wells. Uncorrected data are shown in
380 shades of gray, and corrected elementary concentrations are shown in shades of blue.
381 Here, source trends are identical between wells to reflect same nature of detrital material.

382

383 Figure 3. Influence of different sedimentation rates on concentration of authigenic
384 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.