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# **Trace element enrichment mechanisms in black shales during the early Cambrian (ca. 521–514 Ma), South China**

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## **ABSTRACT**

It is widely accepted that significant perturbations in ocean redox states are closely related to biological evolution during the early Cambrian. However, the host and geochemical cycle of redox-sensitive elements (V and Zn) of the Niutitang Formation shale in South China have not been well-constrained. This study reports lithofacies, mineralogy and geochemical data of high-resolution samples from slope and basin settings (Xa1 and Xb1 wells, Hunan Province), to evaluate the significance of redox condition and hydrothermal contribution to trace element accumulation during the early Cambrian. Our results reveal the Zn-rich host is primarily sphalerite, while the V-rich host includes organic matter, illite, and anatase minerals in the Niutitang shale. Illite and anatase minerals have significant V concentration (14.8% and 18.3%), whereas organic matter contains relatively lower V concentration (1.4%). Trace elements can be scavenged by dissolved organic matter in seawater, and then taken up by clay minerals or form sulfide during deposition/diagenesis of organic-rich shales. Although seawater restriction of the lower member (LM) shale was stronger than in the upper member (UM) shale, euxinic conditions were more conducive to V and Zn enrichment than ferruginous conditions. Specifically, dwindling concentrations of V and Zn in seawater existed in South China during deposition of the early LM shale. However, the ocean experienced episodic hydrothermal activity, which may have supplied abundant trace elements to supplement seawater content. Overall, we propose that the V and Zn geochemical cycles in the early Cambrian paleo-ocean were controlled by redox condition, organic matter, and the trace element inventory of seawater.

*Keywords:* Niutitang shale, free H<sub>2</sub>S content, hydrothermal input, seawater restriction, trace element inventory

## 1 **1. Introduction**

2 Redox-sensitive trace elements (TEs: Mo, U, V, Zn) in sediments can be used to  
3 infer oxygen concentration in the overlying water column or atmosphere, and have been  
4 widely used as proxies for redox conditions in ancient oceans (Jones and Manning,  
5 1994; Algeo and Maynard, 2004; Tribovillard et al., 2006; Scott et al., 2017; Algeo and  
6 Liu, 2020). TEs are commonly reduced from high to low valence state under low-  
7 oxygen conditions, and may be complexed with organic acids, adsorbed by authigenic  
8 sulfides, or precipitated in the form of insoluble oxyhydroxides (Tribovillard et al. 2006;  
9 Algeo and Liu, 2020). The geochemical cycle of TEs in the paleo-ocean system is  
10 complex and influenced by various factors including terrigenous supply, oceanic metal  
11 inventory, seawater restriction, redox condition, and volcanic/hydrothermal input (You  
12 et al., 1996; Algeo and Tribovillard, 2009; Gill et al., 2011; Cheng et al., 2016; Zou et  
13 al., 2018; Paschall et al., 2019). Ferruginous water masses (anoxic condition without  
14 free H<sub>2</sub>S) are comparatively common in early Cambrian or older geological time  
15 intervals (Canfield, 1998; Algeo and Li, 2020), while euxinic environments have  
16 appeared several times in geological history and modern ocean systems (Feng et al.,  
17 2014; Li et al., 2019). Anoxic oceans in different periods of geological history may  
18 exhibit unique trace element enrichment and migration patterns.

19 The early Cambrian is one of the most critical periods of biological radiation in  
20 Earth history. During the Cambrian Stage 3, from ~521–514 Ma, a marine transgression  
21 event resulted in the widespread deposition of black shale across South China. This  
22 black shale is exceptionally rich in organic carbon and contains unusual concentrations  
23 of V and Zn (Guo et al., 2016; Fan et al., 2020). Previous research has shown that a  
24 “euxinic wedge” developed in the early Cambrian paleo-ocean (Li et al., 2010, 2015,  
25 2020; Feng et al., 2014) in which the surface, middle, and deep layers of the ocean were  
26 characterized by oxic, euxinic, and ferruginous conditions, respectively (Jin et al.,  
27 2016). Han et al (2018) analyzed the geochemical cycle of the element vanadium (V)  
28 in the Longbizui and Duoding sections and suggested that the drawdown of trace  
29 elements in seawater may have affected V enrichment in the black shale. However, the

30 host and enrichment pattern of vanadium in ferruginous and euxinic environments has  
31 not been evaluated during the early Cambrian. In addition, the seawater was also  
32 strongly affected by multiple episodes of volcanic and hydrothermal activity during the  
33 early Cambrian (Chen et al., 2009; Liu et al., 2015; Gao et al., 2018; Wang et al., 2020a;  
34 Tan et al., 2021; Xie et al., 2021). Submarine hydrothermal processes in the early  
35 Cambrian have been suggested to explain bedded polymetallic Ni–Mo–PGE  
36 mineralization (Coveney and Chen, 1991; Li and Gao, 2000; Jiang et al., 2006), extreme  
37 element accumulation in sedimentary rocks (Guo et al., 2016; Han et al., 2017), and  
38 biological evolution (Wang et al., 2020b). Hydrothermal activity with hot, volatile-rich  
39 components may have changed the chemical conditions of the seawater and affected  
40 trace element enrichment and migration. However, the influence of hydrothermal  
41 activity, redox condition, and seawater restriction on the geochemical cycle of trace  
42 elements is still poorly understood.

43 The lower Cambrian black shales in South China offer favorable conditions for  
44 analyzing the geochemical cycle of trace elements in an anoxic stratified paleo-ocean.  
45 The bulk-rock geochemical data are conducive to reconstructing unique environmental  
46 constraints during the early Cambrian. Here, the main purpose of this study is to analyze  
47 the host of V and Zn elements using micro-analytical techniques at a micro- and nano-  
48 scale from two wells in South China, then provide new insights into significance of  
49 redox condition, seawater, and hydrothermal contribution to trace elements  
50 accumulation in organic-rich shales.

51

## 52 **2. Geological setting**

53 During the Ediacaran–Cambrian transition period, the South China Craton was  
54 composed of the Yangtze and Cathaysia blocks. From modern northwest to southeast,  
55 the depositional environments in the Nanhua Basin ranged from shallow- to deep-water  
56 areas comprising mainly carbonate platform, shelf, slope and basin settings (Goldberg  
57 et al., 2007; Li et al., 2008; Okada et al., 2014). Lithologies in the shallow-water areas  
58 were dominated by gray dolomite and limestone, while the deep-water areas were

59 dominated by gray-black shale and chert (Figure 1A). During the early Cambrian Stage  
60 3, a global transgression event submerged the previously deposited carbonate platform,  
61 resulting in the development of organic-rich shale facies across South China (Figure  
62 1B). These organic-rich shales comprise the laterally equivalent Niutitang, Yu'anshan,  
63 and Xiaoyanxi formations (Figures 1, 2). Deposition of the shale facies was  
64 accompanied by hydrothermal activity (Liu et al., 2015), which may have caused the  
65 intermittent development of a Ni-Mo metal layer in South China. The Ni-Mo metal  
66 layer has been used as an important marker for stratigraphic correlation (Xu et al., 2011;  
67 Han et al., 2020). With the gradual decline of sea level after 518 Ma, the lithology of  
68 the upper Niutitang, Yu'anshan, and Xiaoyanxi formations was dominated by grey  
69 siltstone and shale (Figure 2).

70 The shale interval selected in this paper developed after the early Cambrian  
71 transgression event (521–514 Ma) and is located above the Ni-Mo layer. According to  
72 high-resolution petrology, biostratigraphy, isotope dating, and inorganic geochemistry  
73 of nine sections across South China, our previous studies have determined the  
74 development period of the lower member (LM) of the Niutitang, Yu'anshan, and  
75 Xiaoyanxi formations was from 521–518 Ma, and the upper member of (UM) was from  
76 518–514 Ma (Figure 2, Jiang et al., 2012; Yang et al., 2018; Wang et al., 2020a). The  
77 Xa1 and Xb1 wells in our study area, and another seven sections distributed across the  
78 inner shelf to basin depositional facies, have been selected to analyze the geochemical  
79 cycling of V and Zn elements in the paleo-ocean (Figure 1C). These comprise the  
80 Meishucun (Jenkins et al., 2002; Yang et al., 2003; Wen et al., 2015) and Xiaotan  
81 sections in Yunnan Province (Och et al., 2013), the Xy1 well (Li et al., 2018) and the  
82 Jinsha section in Guizhou Province (Jin et al., 2016), and the Yangjiaping (Cheng et al.,  
83 2016), Longbizui (Wang et al., 2012) and Yuanjia sections in Hunan Province (Cheng  
84 et al., 2020).

85

### 86 3. Materials and methods

87 The Xa1 well in Anhua County (111°26'12"E, 28°17'58"N) and the Xb1 well in

88 Jishou County (109°49'15"E, 28°23'03"N), South China, were located in different  
89 depositional facies during the early Cambrian. We have selected 50 samples from the  
90 two wells for geochemical analyses. All samples were crushed into powder for analyses  
91 of total organic carbon (TOC), total sulfur (TS), major elements, and trace elements.

92 Concentrations of major oxides (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, and MnO) were  
93 determined by X-ray fluorescence (XRF) on molten glass beads at Central South  
94 University. For major oxides with concentrations greater than 0.3%, the accuracy was  
95 better than 2%. Trace elements (Mo, U, V, and Zn) were determined by ICP-MS at  
96 Societe Generale de Surveillance S.A. (SGS). A 50 mg sample powder was dissolved  
97 in a high-pressure Teflon bomb with 1 ml HF and 2 ml HNO<sub>3</sub> at 190 °C for 48 h. After  
98 removing HF by heating, the residue was dissolved in 2 ml H<sub>2</sub>O and 2 ml HNO<sub>3</sub> at  
99 145 °C for 12 h. Analytical precision was better than 10 % relative standard deviation.

100 For measurements of TOC and TS content, 100 mg samples were first treated with  
101 excess hydrochloric acid solution (volume ratio 1:7), and then washed with distilled  
102 water to remove the HCl. TOC content was determined using a high-frequency infrared  
103 carbon and sulfur analyzer (LECO CS-744) at Central South University. For TS  
104 measurements, separate 100 mg samples, not treated with HCl, were dried more than 2  
105 h at 105 °C. Then, TS content was measured on a carbon and sulfur analyzer. The  
106 analytical precision was better than 0.2 %.

107 For sulfide mineral identification, the selected samples were firstly cut into 1 cm<sup>3</sup>  
108 cubes with a cutting machine. Then the surface to be observed was ground, polished,  
109 and sprayed with a carbon coating. Finally, a FEI Quanta 200 Scanning Electron  
110 Microscope (SEM) with Energy Dispersive Spectrometer (EDS) at China University of  
111 Geosciences, Wuhan was used to identify the minerals in shale and perform elemental  
112 mapping. The element content of every metallic mineral was tested to determine its host.

113 Enrichment factors (EF) were calculated based on the ratio between trace element  
114 concentration and aluminum (Al) within the sample, compared to the same ratio in  
115 Upper Continental Crust (UCC) (Tribovillard et al., 2006; Algeo and Tribovillard,  
116 2009). The equation is as follows:

117  $X_{EF} = [(X/Al)_{\text{sample}}] / (X / Al)_{\text{ucc}}$

118 where UUC data for normalization were taken from [McLennan \(2001\)](#), and  $X_{EF} > 1.0$   
119 and  $X_{EF} < 1.0$  indicate enrichment and depletion of X element, respectively.

120

## 121 **4. Results**

### 122 *4.1. Metallic minerals in black shale*

123 In order to analyze the types of metallic minerals present in the lower Cambrian  
124 black shale, minerals from samples in the Xa1 and Xb1 wells have been preliminarily  
125 identified. The main sulfur-bearing mineral is pyrite that forms clumps and bands  
126 ([Figure 3](#)). The Ba-bearing minerals in the study area are mainly celsian and hyalophane  
127 ([Figures 3B, C, D](#)). There are also some sulfur-bearing minerals, such as barite ([Figures](#)  
128 [3D, E](#)). The barite minerals are rare and do not exhibit obvious metasomatic residual  
129 structure. The element Zn exists mainly in the form of sphalerite, and can be seen in  
130 low concentration in several samples ([Figure 3H](#)).

131 In addition, we found that the element V is mainly enriched in organic matter  
132 ([Figure 4A](#)), illite ([Figure 4B](#)) and the mineral anatase ([Figures 4C, 4E, 4F](#)) from black  
133 shales the study area. The element V can also be scavenged by dissolved organic matter  
134 in seawater, and then taken up by clay minerals during transport or deposition ([Lu et](#)  
135 [al., 2021](#)). Furthermore, V can replace the element Ti in anatase with isomorphism. The  
136 V content in the anatase mineral is relatively higher (18.3%), while that in organic  
137 matter is relatively lower (1.4%, [Figure 4D](#)).

138

### 139 *4.2. TOC and TS contents*

140 The TOC and TS contents of the Niutitang shale from the Xa1 and Xb1 wells are  
141 shown in [Figures 5 and 6](#) and the Supplementary Data. From the Xa1 well, LM shale  
142 TOC contents range from 8.1–31.5 % (avg. 14.0 %) and TS contents range from 0.4–  
143 2.6 % (avg. 0.9 %), while in the UM shale TOC contents range from 2.6–8.1 % (avg.  
144 5.1 %) and TS contents range from 1.5–3.8 % (avg. 2.3 %). From the Xb1 well, LM  
145 shale TOC contents range from 1.4–12.4 % (avg. 5.5 %) and TS content range from



146 1.2– 5.3 % (avg. 2.6 %), whereas in the UM shale TOC contents range from 0.8–2.1 %  
147 (avg. 1.6 %) and TS contents range from 1.3–1.7 % (avg. 1.4 %).

148

#### 149 *4.3. Trace elements*

150 Trace element concentrations and  $M_{\text{OEF}}/U_{\text{EF}}$  values can be seen in [Figures 5 and 6](#).  
151 The Niutitang shale exhibits variable Mo, U, V, Zn concentrations in the Xa1 and Xb1  
152 wells. In the LM shale from the Xa1 well, concentrations range from 29–506 ppm for  
153 Mo, 30–209 ppm for U, 308–4075 ppm for V, and 21–3145 ppm for Zn. Enrichment  
154 factors of these trace elements are 90–678 for  $M_{\text{OEF}}$ , 28–586 for  $U_{\text{EF}}$ , 7–145 for  $V_{\text{EF}}$ ,  
155 and 1–231 for  $Zn_{\text{EF}}$ . The  $M_{\text{OEF}}/U_{\text{EF}}$  ratio in the LM shale is 0.4–6.7 (avg. 2.3). In contrast,  
156 the UM shale in the Xa1 well exhibits relatively lower Mo (24–76 ppm), U (8–46 ppm),  
157 V (103–348 ppm), and Zn (16–64) concentrations. The  $M_{\text{OEF}}/U_{\text{EF}}$  ratio in the UM shale  
158 is 3.1–6.0 (avg. 5.3) and is higher than in the LM shale. Similar features of the trace  
159 element concentrations and  $M_{\text{OEF}}/U_{\text{EF}}$  ratios are exhibited in the Xb1 well. From the  
160 Xb1 well, Mo content is > 100 ppm at the bottom of the LM shale, and < 25 ppm in the  
161 UM shale. Additionally, the  $V_{\text{EF}}$  and  $Zn_{\text{EF}}$  is 1.6–18.3 (avg. 6.0) and 1.4–13.4 (avg. 3.5)  
162 in the LM shale, and 1.2–2.5 (avg. 1.5) and 1.4–2.0 (avg. 1.7) in the UM shale,  
163 respectively. Like the Xa1 well, in the Xb1 well the  $M_{\text{OEF}}/U_{\text{EF}}$  ratio is lowest in the LM  
164 shale (1.0–9.3, avg. 4.1), and higher in the UM shale (3.0–6.5, avg. 4.8).

165

## 166 **5. Discussion**

### 167 *5.1. Redox conditions during the early Cambrian*

168 Analysis of redox state is an important paleoenvironmental method, which mainly  
169 includes iron speciation ([Raiswell et al., 1988](#); [Poulton and Canfield, 2005](#)), redox-  
170 sensitive trace element geochemistry ([Scott and Lyons, 2012](#)), and assessment of Mo–  
171 U enrichment factor ( $M_{\text{OEF}}$  and  $U_{\text{EF}}$ ) data ([Tribovillard et al., 2006, 2012](#); [Algeo and](#)  
172 [Tribovillard, 2009](#)). [Scott and Lyons \(2012\)](#) systematically evaluated Mo geochemistry  
173 in modern anoxic basin systems and suggested that Mo content < 25 ppm indicates an  
174 oxic condition; 25–100 ppm indicates intermittent or seasonal euxinic conditions; while

175 Mo content >100 ppm indicates a persistent euxinic condition. The enrichment factors  
176 of Mo and U are generally lower than 10 in suboxic conditions, and higher in anoxic  
177 conditions. Here, the  $M_{\text{OEF}}-U_{\text{EF}}$  correlation was mainly used to constrain the redox  
178 condition for the LM and UM shales of the Niutitang Formation in the study area  
179 (Figure 7).

#### 180 5.1.1. Redox condition of the LM shale

181 The  $M_{\text{OEF}}-U_{\text{EF}}$  correlation of the LM shale in the Xa1 and Xb1 wells can be seen  
182 in Figure 7. Almost all samples in the Xa1 well are characterized by high Mo content  
183 (>100 ppm), U content (30–207 ppm),  $M_{\text{OEF}}$  (90–678) and  $U_{\text{EF}}$  (30–207). The  $M_{\text{OEF}}/U_{\text{EF}}$   
184 ratio is between 1 and 3 times that of modern seawater (Figure 7A). These  
185 characteristics suggest a euxinic environment persisted during the depositional period  
186 of the LM shale in the Xa1 well. The Yuanjia section is close to the Xa1 well (Cheng et  
187 al., 2020), and its iron speciation data are  $Fe_{\text{HR}}/Fe_{\text{T}}=0.88-1$  (avg. 0.98) and  
188  $Fe_{\text{Py}}/Fe_{\text{HR}}=0.58-0.97$  (avg. 0.89). The trace elements data in the Xa1 well are consistent  
189 with the iron speciation data in the Yuanjia section, both indicating extremely euxinic  
190 conditions in the basin facies from 521–518 Ma (Figure 8). The  $M_{\text{OEF}}/U_{\text{EF}}$  ratio of the  
191 LM shale in the Xb1 well is between 0.1 and 0.3 times that of modern seawater (Figure  
192 7B). Due to the TOC, Mo, U, and V contents, and  $M_{\text{OEF}}-U_{\text{EF}}$  variation, the LM shale of  
193 the Niutitang Formation in the Xb1 well can be divided into the LM-1 and LM-2  
194 submembers (Figure 6). The LM-1 submember shale in the Xb1 well exhibit high Mo  
195 content (>100 ppm),  $M_{\text{OEF}}$  (65–142), and  $U_{\text{EF}}$  (21–100), which suggest a euxinic  
196 environment. The Longbizui section is adjacent to the Xb1 well (Figure 1), and its iron  
197 speciation data also show  $Fe_{\text{HR}}/Fe_{\text{T}}=0.79-1.13$  (avg. 0.98) and  $Fe_{\text{Py}}/Fe_{\text{HR}}=0.13-0.86$   
198 (avg. 0.51), indicating a ferruginous to euxinic condition (Wang et al., 2012). In  
199 addition, the LM-2 submember shale in the Xb1 well are characterized by moderate Mo  
200 (2–41 ppm), U (3–11 ppm),  $M_{\text{OEF}}$  (2–37), and  $U_{\text{EF}}$  (2–8) contents, which are consistent  
201 with the iron speciation data ( $Fe_{\text{HR}}/Fe_{\text{T}}=0.21-1.4$  (avg. 0.82) and  $Fe_{\text{Py}}/Fe_{\text{HR}}=0.01-0.69$   
202 (avg. 0.33) in the Longbizui section (Figure 7B). Both of these lines of evidence above  
203 suggest a ferruginous with intermittent euxinic condition existed in the slope facies

204 from 521–518 Ma.

205

### 206 5.1.2. Redox condition of the UM shale

207 In the Xa1 well, the UM shale is characterized by Mo content between 24 and 76  
208 ppm and is consistently higher than 25 ppm. The  $M_{\text{OEF}}$  and  $U_{\text{EF}}$  are also relatively high  
209 and can reach up to 86 and 28, respectively, indicating a ferruginous condition (Figure  
210 7A). The  $M_{\text{OEF}}/U_{\text{EF}}$  ratio is between 1 and 3 times that of modern seawater. Due to the  
211 gradual decline of sea level, the redox proxies shows that the water column in the basin  
212 facies changed from a euxinic to ferruginous condition from 518–514 Ma. In addition,  
213 the Mo content of the UM shale in the Xb1 well is generally lower than 25 ppm. The  
214 Xb1 well also exhibits relatively low  $M_{\text{OEF}}$  (7–16) and  $U_{\text{EF}}$  (2–4), suggesting a suboxic  
215 environment persisted during the depositional period of the UM shale.

216

### 217 5.1.3. Evolution of redox conditions in the Nanhua Basin from 521–514 Ma

218 The redox conditions of the other seven sections considered here have been  
219 systematically analyzed with iron speciation and redox-sensitive trace element data  
220 (Jenkins et al., 2002; Yang et al., 2003; Och et al., 2013; Wen et al., 2015; Jin et al.,  
221 2016; Li et al., 2018; Cheng et al., 2020). As shown in the redox proxy comparison  
222 from the inner shelf to basin setting in Figure 8, the depositional environment was  
223 characterized by euxinic conditions during the LM shale deposition period. In addition,  
224 an oxic environment first appeared in the inner shelf facies (i.e., Meishucun and Xiaotan  
225 sections) during the late LM shale depositional period, pre-dating the “Cambrian  
226 explosion” (Jin et al., 2016; Xiang et al., 2017). It is plausible that it took time for life  
227 to adapt to the newly increased oxygenation levels with a delay until lifeforms reached  
228 a critical threshold before undergoing an explosive evolutionary radiation. Depositional  
229 environments of the outer shelf facies were characterized by intermittent euxinic  
230 conditions, while basin facies were characterized by persistent euxinic conditions.  
231 During the UM shale deposition period, oxic conditions gradually spread from inner  
232 shelf to outer shelf facies (i.e., Jinsha section and Xy1 well, Figure 8). Additionally,

233 there was no free sulfur in the water column, and euxinic environments were not  
234 obvious during this time interval. The water column exhibited ferruginous conditions  
235 in the basin setting (i.e., Yuanjia section and Xa1 well). Subsequently, marine  
236 environments were dominated by oxic conditions in South China, which were  
237 conducive to biological reproduction during the deposition of the late UM shale.

238

## 239 5.2. Seawater restriction

240 Mo generally has an average concentration of 1.5 ppm and presents as stable state  
241 with a high valence (VI,  $\text{MoO}_4^{2-}$ ) in oxic conditions (Taylor and McLennan, 1995). In  
242 an anoxic water column, Mo is reduced to  $\text{MoO}_2^+$  or  $\text{MoO}_x\text{S}_{4-x}^{2-}$ , and the latter may be  
243 formed as organic thiomolybdate, or further reduced to  $\text{MoS}_4^{2-}$  (Brumsack, 1989;  
244 Adelson et al., 2001; Algeo and Rowe, 2012). Mo has a long residence time in water  
245 (approximately 731 kyr). This unique feature of Mo is commonly used to assess the  
246 restriction of modern and ancient seawater (Tribovillard et al., 2012; Zhao et al., 2016).  
247 The relationship between Mo and TOC can reveal the degree of anoxic water restriction  
248 (Figure 9).

249 During the depositional period of the LM shale, the Mo/TOC ratio of the Xb1 well  
250 (1–24, avg. 11.5) is higher than the present-day value of the Framvaren Basin (Mo/TOC  
251 = 9), indicating a moderately restricted water environment (Figure 9B). However, there  
252 is no obvious correlation between the Mo content and TOC content in the LM shale of  
253 the Xa1 well. The Mo-TOC covariant relationships of the Xa1 well cannot be used to  
254 assess watermass restriction. The Yuanjia section is close to the Xa1 well, and its  
255 Mo/TOC ratio is close to Black Sea Basin (Mo/TOC=4.5), indicating a moderately to  
256 strongly restricted water environment (Chen et al., 2022). However, Cheng et al. (2020)  
257 found that the authigenic Mo and U content in the black shale of the Yuanjia section  
258 were not depleted, and the normal-marine-like Mo/U ratios ( $1 \times \text{SW}$ ) are also similar  
259 to the Xa1 well (Figure 7A). It is noteworthy that the  $\text{Mo}_{\text{EF}}\text{-U}_{\text{EF}}$  correlation of the  
260 modern Cariaco Basin or Saanich Inlet Basin are not significant. The paleo-ocean in  
261 South China also suffered from multiple phases of hydrothermal activity (see Section

262 5.4), which may have provided abundant trace elements during the early Cambrian  
263 (Han et al., 2017). The  $M_{\text{OEF}}-U_{\text{EF}}$  correlation of basin facies shows these may have been  
264 affected by hydrothermal activity, and the seawater should be moderately to strongly  
265 restricted during the depositional period of LM shale. Figure 9A shows a modest  
266 correlation that is interpretable in terms of watermass restriction degree of the UM shale.  
267 The Mo/TOC ratio of the Xa1 shale was 5–9 (avg. 8), and indicated a moderate seawater  
268 restriction, closer to the Framvaren Fjord Basin conditions during the depositional  
269 period of the UM shale. The depositional environment was also weakly restricted in the  
270 Xb1 well (Figure 9A).

271

### 272 5.3. Geochemical cycling of trace elements in the paleo-ocean from 521–514 Ma

#### 273 5.3.1. Vanadium

274 During the early Cambrian Stage 3, a global transgression event contributed to the  
275 expansion of euxinic seawater, resulting in abnormally high trace element contents  
276 (Guo et al., 2016). For the Xa1 well, the  $V_{\text{EF}}$  is high in the LM shale (7.0–145.2), and  
277 moderate in the UM shale (1.5–4.6) (Figure 10A, Table 1). Similarly, the Xb1 well also  
278 exhibits relatively high  $V_{\text{EF}}$  in the LM-1 submember shale (5.2–18.3), moderate  $V_{\text{EF}}$  in  
279 the LM-2 submember shale (1.6–4.0), and low  $V_{\text{EF}}$  in the UM shale (1.1–2.5) (Figure  
280 10C). The redox proxies suggest the water column of the LM and UM shales in the Xa1  
281 well was persistently euxinic and with ferruginous conditions, while those of the LM-  
282 1, LM-2, and UM shales in the Xb1 well were intermittent euxinic, ferruginous, and  
283 suboxic, respectively (Figures 7 and 8). Vanadium is present as different valance states  
284 in oxic to anoxic conditions (Sadiq, 1988). Under oxic conditions, V exists as soluble  
285  $\text{HVO}_4^{2-}$  and  $\text{H}_2\text{VO}_4^-$  (V) in seawater, but is reduced to  $\text{VO}(\text{OH})_3^-$  (IV) or insoluble  
286 hydroxide (IV) and complexed by dissolved organic matter in seawater (Wehrli and  
287 Stumm, 1989; Scholz et al., 2011). Due to the large specific surface area of smectite,  
288 V-rich OM is then adsorbed or intercalated onto this clay mineral. When the reducibility  
289 of the water column is enhanced and free  $\text{H}_2\text{S}$  exists, V is further reduced to  $\text{V}_2\text{O}_3$  or  
290  $\text{V}(\text{OH})_3$  (III) (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). Microscopic

291 observations suggest that vanadium is hosted in the Cambrian shale by organic matter,  
292 clay minerals, and the anatase, respectively (Figure 4). The complexation of organic  
293 matter and absorption of minerals played a critical role in the enrichment and  
294 redistribution of V in the black shale during the early Cambrian.

295 The V contents of the Niutitang shale in the Duoding and Longbiuzi sections also  
296 exhibit relatively high values at the bottom of the Niutitang shale, but low values in its  
297 upper part. Han et al (2018) suggested that dwindling concentrations of V and Zn in  
298 seawater existed in South China during the early Cambrian. This phenomenon should  
299 be the primary driver for this drawdown in the black shale, while redox condition and  
300 dissolved organic matter of seawater have little influence on it. However, the V content  
301 exhibits coupled patterns with Mo, U, and the  $M_{\text{OEF}}/U_{\text{EF}}$  ratio in our study area (Figures  
302 5, 6, 10), which suggest that euxinic conditions are more conducive to the enrichment  
303 of V than ferruginous and suboxic conditions. Furthermore, the distribution of the TOC  
304 and V contents in the Xa1 and Xb1 wells also indicate that the uptake capacity of  
305 dissolved organic matter in seawater for V through reduction and adsorption can  
306 improve the removal capacity of V scavenging in the seawater (Table 1). Then, V ions  
307 can replace Al ions in illite and Ti ions in anatase by isomorphism (Figure 4, Lu et al.,  
308 2021). Adsorption of clay minerals and mineral isomorphism also play important roles  
309 in the removal of V from seawater. This raises the question to why the geochemical  
310 behavior of V element in the Longbizui and Duoding sections and our study area seem  
311 contradictory? The iron speciation data suggest that the water columns in the Longbizui  
312 and Duoding sections were mainly suboxic to ferruginous environments (Wang et al.,  
313 2012; Jin et al., 2016). The difference of V enrichment in ferruginous and euxinic  
314 environments has been well-characterized in our study area. The depositional period of  
315 the LM shale in the Longbizui and Duoding sections was mainly from 521–518 Ma  
316 (Figure 2) at which time the drawdown of the element V in seawater occurred across  
317 South China (see above). In conclusion, the V inventory in the ocean, redox condition,  
318 organic matter, and clay minerals may jointly affect the enrichment of V in the black  
319 shale during the early Cambrian.

320

### 321 5.3.2. Zinc

322 In the Xa1 well,  $Z_{NEF}$  is high in the LM shale (1.4–210.0), but low in the UM shale  
323 (0.3–1.2, [Figure 10B](#)). Similarly, the Xb1 well exhibits relatively high  $Z_{NEF}$  values in  
324 the LM-1 submember shale (1.8–13.4), moderate values in the LM-2 submember shale  
325 (1.4–3.7), and low values in the UM shale (1.4–1.9, [Figure 10D](#)). Zinc is present as  
326  $Zn^{2+}$  under oxic/suboxic conditions, while it precipitates rapidly in the form of ZnS  
327 under anoxic conditions ([Brumsack, 1989](#); [Morse and Luther III, 1999](#)). Sulfate  
328 reducing bacteria can release Zn from organometallic complexes that can be absorbed  
329 by adjacent authigenic sulfides ([Fleurance et al., 2013](#); [Slack et al., 2015](#)). The Zn  
330 content also exhibits coupled patterns with Mo, U,  $Mo_{EF}/U_{EF}$  ratio, and TOC content in  
331 the Xa1 and Xb1 wells ([Figures 5, 6, 9](#)), which may be attributed to the redox condition  
332 and dissolved organic matter. There are two different authigenic enrichment  
333 mechanisms of Zn in modern and ancient oceans, termed primary and secondary  
334 authigenic enrichment ([Scott et al., 2017](#); [Wang et al., 2020b](#)). Primary enrichment is  
335 related to  $H_2S$  in pore waters, and results in relatively low Zn content. Secondary  
336 enrichment requires excess  $H_2S$  content, affects the activity phototrophic sulfide-  
337 oxidizing bacteria, and results in “hyper-enrichment” of Zn ([Overmann et al., 1996](#);  
338 [Findlay et al., 2014](#)). The Zn content of the LM-1 submember shale in the Xb1 well and  
339 the LM shale in the Xa1 well is abnormally high, which may be related to the free  $H_2S$   
340 in the paleo-ocean ([Scott et al., 2017](#)). Interestingly, the Zn content of the UM shale in  
341 the Xa1 well was in a deficit state ( $Z_{NEF}<1$ ), while that in the Xb1 well was slightly  
342 enriched ( $Z_{NEF}>1$ , [Table 1](#)). The Zn content shows coupled patterns with V content in  
343 the Niutitang shale ([Figures 5, 6](#)). Collectively this information indicates that the Zn  
344 inventory in the ocean was similar to the V inventory, both of which were in a  
345 downward trend. The drawdown of trace elements in seawater may provide an early-  
346 stage preparation of the marine environment for the subsequent Chengjiang Biota ([Han  
347 et al., 2018](#)).

348

349 *5.4. Indicative significance of V and Zn anomalies during the early Cambrian*

350 To address the question when did the V and Zn content of seawater decline in  
351 South China during the early Cambrian, we have collected trace element data from  
352 another seven sections in South China (Figure 11). The V and Zn content of the UM  
353 shale remains almost unchanged (Figures 11A, 11C), while those of the LM shale show  
354 large differences from the inner shelf to the basin facies (Figures 11B, 11D). Euxinic  
355 conditions are more favorable for the enrichment of trace elements (Figure 8). The LM  
356 shale with anomalously high V content firstly appeared in the outer shelf facies (Xy1  
357 well and Jinsha section), while the samples with anomalously high Zn content appeared  
358 in the slope facies (Xb1 well). In terms of its sensitivity to redox changes, V is more  
359 redox-sensitive than Zn and removed earlier from seawater to sediments (Algeo and  
360 Maynard, 2004, 2008). Although the V content of the LM shale is abnormally high,  
361 there are also 20 samples with low V content in the LM shale (Figures 5, 6). The Zn  
362 contents of these samples are relatively low, and the Mo/TOC values are less than 10  
363 (avg. 6), which is close to the values from the modern Black Sea (Algeo and Lyons,  
364 2006; Algeo and Rowe, 2012). There is no difference in TOC content, redox condition,  
365 and seawater restriction between the samples with low V and anomalously high V  
366 content (Figures 5, 6, 10). The complexation of organic matter and absorption of clay  
367 minerals may remove the trace elements from seawater to sediment rapidly during the  
368 euxinic condition (Lu et al., 2021). We suggest that the samples with low trace element  
369 contents may be affected by dwindling seawater trace element inventory (Han et al.,  
370 2018). Considering how the shale samples with high content of V and Zn formed during  
371 this critical period, we suggest that the high trace element contents in the ocean would  
372 have had to be supplemented from other sources.

373 Hydrothermal activity in South China at 521 Ma is evidenced by intermittently  
374 distributed Ni-Mo ore layers developed at the bottom of the LM shale (Xu et al., 2011;  
375 Fan et al., 2020). The ocean was affected by multiple phases of hydrothermal activity  
376 during the depositional period of the LM shale (Chen et al., 2009; Fan et al., 2013; Liu  
377 et al., 2015; Gao et al., 2018). Hydrothermal activity strongly affected the marine



378 environment during this time interval, including enrichment of the toxic element  
379 mercury (Zhu et al., 2021), formation of chert and siliceous shale (Liu et al., 2015; Xie  
380 et al., 2021), and causing organismal extinctions (Wang et al., 2020b). Hyalophane  
381 minerals are present at different depths in the Xa1 and Xb1 wells. The formation  
382 mechanism of hyalophane can be divided into two types: metasomatism of authigenic  
383 barite, and crystallization of Ba-Al-Si colloid (McSwiggen et al., 1994; Raith et al.,  
384 2014). Barite minerals are rare and do not exhibit obvious metasomatic residual  
385 structure in our study areas (Figure 3). The formation of Ba-Al-Si colloids is generally  
386 related to hydrothermal action (Jacobsen et al., 1990; Moro et al., 2001), which can  
387 release large amounts of Ba and SiO<sub>2</sub> into seawater and precipitate to form siliceous  
388 colloids in the reducing environment. The anoxic environment in the study area also  
389 favors the formation of Ba-Al-Si colloids. The hyalophane mineral can therefore be an  
390 important indicator of hydrothermal activity (Figure 5). Furthermore, Zn is an  
391 important biological nutrient. The TM/C ratio (Zn=0.036 mmol/mol) of phytoplankton  
392 can be used to calculate the biological contribution to Zn content in sediment (Little et  
393 al., 2015). The TOC content of the LM shale is < 20% and the calculated biological  
394 contribution to Zn content is only 40 ppm. As the Zn content of the LM shale generally  
395 exceeds 500 ppm and can extend up to 5672 ppm, it shows that the contribution from  
396 organisms is negligible. Furthermore, the Zn content of the UM shale in the Xa1 well  
397 was in a deficit state ( $Zn_{NEF} < 1$ ), while that in the Xb1 well was slightly enriched  
398 ( $Zn_{NEF} > 1$ ). Due to the redox condition (Table 1), an oxic condition in the Xb1 well is  
399 more conducive to the blooming of phytoplankton, and the biological contribution to  
400 Zn content should be relatively higher. Fan et al. (2020) also analyzed Zn isotopes in  
401 the Ni-Mo layer, and suggested that hydrothermal activity provided another Zn source.  
402 The Ni-Mo layer developed at 521 Ma is also rich in V where its content varies between  
403 0.5–1.2%, with this concentration reaching the industrial mining grade (Zhou et al.,  
404 2020). Hydrothermal fluids may have carried abundant trace element (V, Zn, and Ba)  
405 into the ocean during the depositional period of the LM shale, forming shales with  
406 anomalously high trace elements content in the euxinic environment (Figure 8).

407 Furthermore, the samples with high Zn content are also characterized by high V content  
408 (Figures 5, 6). There seems to be little correlation between V content and Zn content in  
409 the LM shale (Figure 12A). Here, we have selected the samples with high Zn and V  
410 contents, and found that the correlation between Zn and V content is strong in the LM  
411 shale ( $n = 22$ ,  $p < 0.01$ ,  $r = 0.79$ , Figure 12B). The above suggests that the trace element  
412 contents of seawater were intermittently supplied by hydrothermal activity, which  
413 strongly affected the enrichment of V and Zn elements.

414

#### 415 *5.5. Depositional environment and biological evolution from 521–514 Ma*

416 The marine environment was significantly different during the depositional  
417 periods of the UM and LM shales, affected by redox condition, seawater restriction,  
418 hydrothermal activity, and the trace element inventory of seawater (Figure 13).

419 During the depositional period of the LM shale, the paleo-ocean presented a  
420 “euxinic wedge” model (Figure 13B), with the surface, middle, and deep ocean layers  
421 characterized by oxic, euxinic, and ferruginous conditions, respectively (Li et al., 2015;  
422 2020). Free H<sub>2</sub>S content was abundant in the seawater, and photic zone euxinia may  
423 have occurred in the slope-basin facies zone (Wang et al., 2020b). The shallow-water  
424 areas mainly experienced suboxic conditions, while the deep-water areas were  
425 persistently euxinic with intermittent ferruginous conditions (Figure 8). The ocean was  
426 also affected by multiple phases of hydrothermal activity during this period (Chen et  
427 al., 2009; Gao et al., 2018; Xie et al., 2021; Zhu et al., 2021). There existed a relatively  
428 high availability of fluvial Fe–Mn oxides and their subsequent reduction below the  
429 chemocline in the shallow-water areas (Cheng et al., 2016). The Mo/TOC ratio in the  
430 study area is close to present-day value of the Black Sea, indicating a strongly to  
431 moderately restricted condition. The V enrichment started at the suboxic-euxinic  
432 threshold, while Zn enrichment requires a more euxinic environment. Although the  
433 trace elements of seawater were in a dwindling state, episodic hydrothermal activities  
434 may have carried abundant trace elements (V, Zn, and Ba) into the ocean. V element is  
435 usually complexed by dissolved organic matter in seawater during the depositional

436 period. Due to the large specific surface area of smectite, the clay mineral then adsorbed  
437 or intercalated this V-rich OM (Lu et al., 2021). During pyrolysis of source rocks, the  
438 element V can be released from the organic matter and incorporated into the lattice of  
439 illite (conversion of smectite to illite mineral) and the mineral anatase, allowing V ions  
440 to replace Al ions in illite and Ti ions in anatase through isomorphism (Figure 4). Thus,  
441 the uptake of organic matter, and mineral isomorphism played critical roles in the  
442 enrichment and redistribution of V in the black shale during diagenesis. The element  
443 Zn is also associated with the adsorption of dissolved organic matter, and present as  
444 sphalerite in anoxic environments (Figure 3). The euxinic condition, organic matter,  
445 clay minerals, and sufficient trace element inventory were conducive to V and Zn  
446 enrichment. Oxidic environments firstly appeared in the shallow-water areas during the  
447 late LM shale depositional period (Figure 8). Furthermore, the TOC content in the LM  
448 shale is higher than that in the UM shale. Previous studies suggest that the introduction  
449 of nutrient elements into the ocean via continental weathering and hydrothermal activity  
450 would lead to the blooming of phytoplankton (Gao et al., 2016; 2021; Xie et al., 2021).  
451 This should be considered as one of the main factors for organic matter enrichment in  
452 the Niutitang black shale.

453 During the depositional period of the UM shale, the surface layer in the ocean was  
454 in an oxidic condition, and the middle and deep layers were in a ferruginous condition  
455 (Figure 13A). Oxidic seawater gradually spread from the inner shelf to deeper basin  
456 settings (Figure 8). The Mo/TOC ratios of the UM shale suggest the marine  
457 environment was weakly restricted. Due to the cessation of hydrothermal activity and  
458 uptake of organic matter and clay minerals, the seawater trace element abundance was  
459 relatively low during the 518–514Ma interval. The TOC content of the UM shale was  
460 also lower than that of the LM shale. The enrichment of V and Zn in the UM shale was  
461 controlled by suboxic/ferruginous conditions, weakly restricted seawater, and  
462 dwindling trace element inventory of seawater. Expansion of oxidic conditions and the  
463 introduction of nutrient elements may have provided an early-stage preparation of the  
464 marine environments for the subsequent Chengjiang/Qingjiang Biota.

465

## 466 **6. Conclusions**

467       Based on the analysis of lithofacies, mineralogy, and inorganic geochemistry of  
468 two wells in our study area and another seven sections from the inner shelf to basin  
469 facies in South China, we have elucidated the effects of redox condition, trace element  
470 contents of seawater and hydrothermal activity on the enrichment mechanisms for V  
471 and Zn during the early Cambrian. The V-rich hosts are mainly organic matter, illite,  
472 and anatase minerals, while the Zn-rich minerals are primarily sphalerite. Complexation  
473 of dissolved organic matter and adsorption of minerals should be the main ways to  
474 remove trace elements from seawater to sediments. In addition, the euxinic environment  
475 is more conducive to V and Zn accumulation than ferruginous condition during the  
476 early Cambrian. Although the dwindling V and Zn concentration of seawater existed in  
477 South China, episodic hydrothermal activity carried other source into the ocean,  
478 resulting in the shale formation with relatively high trace element contents.  
479 Consequently, organic matter, clay minerals, redox state of the water column, and trace  
480 elements of seawater, jointly affected the enrichment and migration of V and Zn in the  
481 Niutitang shale.

482

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## 491 **References**

- 492 Adelson, J., Helz, G., Miller, C., 2001. Reconstructing the rise of recent coastal anoxia; molybdenum in  
493 Chesapeake Bay sediments. *Geochimica et Cosmochimica Acta* 65, 237–252.  
494 Algeo, T.J., Li, C., 2020. Redox classification and calibration of redox thresholds in sedimentary systems.  
495 *Geochimica et Cosmochimica Acta* 287, 8–26.

496 Algeo, T.J., Liu, J., 2020. A re-assessment of elemental proxies for paleoredox analysis. *Chemical*  
497 *Geology* 540, 119549.

498 Algeo, T.J., Lyons, T.W., 2006. Mo–total organic carbon covariation in modern anoxic marine  
499 environments: Implications for analysis of paleoredox and paleohydrographic conditions.  
500 *Paleoceanography* 21, 1016.

501 Algeo, T.J., Maynard, J.B., 2004. Trace-element behavior and redox facies in core shales of Upper  
502 Pennsylvanian Kansas-type cyclothems. *Chemical Geology* 206, 289–318.

503 Algeo, T.J., Maynard, J.B., 2008. Trace-metal covariation as a guide to water-mass conditions in ancient  
504 anoxic marine environments. *Geosphere*, 4, 872–887.

505 Algeo, T.J., Rowe, H., 2012. Paleoceanographic applications of trace-metal concentration data. *Chemical*  
506 *Geology* 324–325, 6–18.

507 Algeo, T.J., Tribovillard, N., 2009. Environmental analysis of paleoceanographic systems based on  
508 molybdenum–uranium covariation. *Chemical Geology* 268, 211–225.

509 Breit, G.N., Wanty, R.B., 1991. Vanadium accumulation in carbonaceous rocks: A review of geochemical  
510 controls during deposition and diagenesis. *Chemical Geology* 91, 83–97.

511 Brumsack, H.J., 1989. Geochemistry of recent TOC-rich sediments from the Gulf of California and the  
512 Black Sea. *Geologische Rundschau* 78, 851–882.

513 Canfield, D., 1998. A new model for Proterozoic ocean chemistry. *Nature* 396, 450–453.

514 Chen, D., Wang, J., Qing, H., Yan, D., Renwei, L.I., 2009. Hydrothermal venting activities in the Early  
515 Cambrian, South China: Petrological, geochronological and stable isotopic constraints.  
516 *Chemical Geology* 258, 168–181.

517 Chen, Z., Wang, G., Jin C., 2022. Marine redox variation and hydrographic restriction in the early  
518 Cambrian Nanhua Basin, South China. *Palaeogeography, Palaeoclimatology, Palaeoecology*  
519 607, 111263.

520 Cheng, M., Li, C., Jin, C., Wang, H., Algeo, T.J., Lyons, T.W., Zhang, F., Anbar, A., 2020. Evidence for  
521 high organic carbon export to the early Cambrian seafloor. *Geochimica et Cosmochimica Acta*  
522 287, 125–140.

523 Cheng, M., Li, C., Zhou, L., Algeo, T.J., Zhang, F., Romaniello, S., Jin, C., Lei, L., Feng, L., Jiang, S.,  
524 2016. Marine Mo biogeochemistry in the context of dynamically euxinic mid-depth waters: A  
525 case study of the lower Cambrian Niutitang shales, South China. *Geochimica et Cosmochimica*  
526 *Acta* 183, 79–93.

527 Coveney, R., Chen, N., 1991. Ni-Mo-PGE-Au-rich ores in Chinese black shales and speculations on  
528 possible analogues in the United States. *Mineralium Deposita* 26, 83–88.

529 Fan, H., Wen, H., Zhu, X., Hu, R., Tian, S., 2013. Hydrothermal activity during Ediacaran–Cambrian  
530 transition: Silicon isotopic evidence. *Precambrian Research* 224, 23–35.

531 Fan, H., Zhang, H., Xiao, C., Pašava, J., Han, T., Zhou, T., Wen, H., 2020. Large Zn isotope variations  
532 in the NiMo polymetallic sulfide layer in the lower Cambrian, South China. *Gondwana*  
533 *Research* 85, 224–236.

534 Feng, L., Li, C., Huang, J., Chang, H., Chu, X., 2014. A sulfate control on marine mid-depth euxinia on  
535 the early Cambrian (ca. 529–521 Ma) Yangtze platform, South China. *Precambrian Research*  
536 246, 123–133.

537 Findlay, A.J., Gartman, A., MacDonald, D.J., Hanson, T.E., Shaw, T.J., Luther III, G.W., 2014.  
538 Distribution and size fractionation of elemental sulfur in aqueous environments: The  
539 Chesapeake Bay and Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta* 142, 334–348.

- 540 Fleurance, S., Cuney, M., Malartre, F., Reyx, J., 2013. Origin of the extreme polymetallic enrichment  
541 (Cd, Cr, Mo, Ni, U, V, Zn) of the Late Cretaceous–Early Tertiary Belqa Group, central Jordan.  
542 *Palaeogeography, Palaeoclimatology, Palaeoecology* 369, 201–219.
- 543 Gao, P., Liu, G., Jia, C., Young A., Wang, Z., Wang, T., Zhang, P., Wang, D., 2016. Redox variations and  
544 organic matter accumulation on the Yangtze carbonate platform during Late Ediacaran–Early  
545 Cambrian: Constraints from petrology and geochemistry. *Palaeogeography, Palaeoclimatology,*  
546 *Palaeoecology*, 450, 91–110.
- 547 Gao P., He Z., Lash G., Zhou, Q., Xiao, X., 2021. Controls on silica enrichment of lower Cambrian  
548 organic-rich shale deposits. *Marine and petroleum Geology*, 130, 105126.
- 549 Gao, P., He, Z., Li, S., Lash, G.G., Li, B., Huang, B., Yan, D., 2018. Volcanic and hydrothermal activities  
550 recorded in phosphate nodules from the Lower Cambrian Niutitang Formation black shales in  
551 South China. *Palaeogeography, Palaeoclimatology, Palaeoecology* 505, 381–397.
- 552 Gill, B.C., Lyons, T.W., Young, S.A., Kump, L.R., Knoll, A.H., Saltzman, M.R., 2011. Geochemical  
553 evidence for widespread euxinia in the Later Cambrian ocean. *Nature* 469, 80–83.
- 554 Goldberg, T., Strauss, H., Guo, Q., Liu, C., 2007. Reconstructing marine redox conditions for the Early  
555 Cambrian Yangtze Platform: Evidence from biogenic sulphur and organic carbon isotopes.  
556 *Palaeogeography, Palaeoclimatology, Palaeoecology* 254, 175–193.
- 557 Guo, Q., Deng, Y., Hippler, D., Franz, G., Zhang, J., 2016. REE and trace element patterns from organic-  
558 rich rocks of the Ediacaran–Cambrian transitional interval. *Gondwana Research* 36, 94–106.
- 559 Han, T., Fan, H., Wen, H., 2018. Dwindling vanadium in seawater during the early Cambrian, South  
560 China. *Chemical Geology* 492, 20–29.
- 561 Han, T., Fan, H., Wen, H., Mo, B., Murowchick, J.B., Lu, Z., Algeo, T.J., 2020. Petrography and sulfur  
562 isotopic compositions of SEDEX ores in the early Cambrian Nanhua Basin, South China.  
563 *Precambrian Research* 345, 105757.
- 564 Han, T., Fan, H., Zhu, X., Wen, H., Zhao, C., Xiao, F., 2017. Submarine hydrothermal contribution for  
565 the extreme element accumulation during the early Cambrian, South China. *Ore Geology*  
566 *Reviews* 86, 297–308.
- 567 Jakobsen, U. H. 1990. A hydrated barium silicate in unmetamorphosed sedimentary rocks of central  
568 North Greenland. *Mineralogical Magazine*, 374 81-89.
- 569 Jenkins, R., Cooper, J.A.a., Compston, W., 2002. Age and biostratigraphy of Early Cambrian tuffs from  
570 SE Australia and southern China. *Journal of the Geological Society* 159, 645–658.
- 571 Jiang, G., Wang, X., Shi, X., Xiao, S., Zhang, S., Dong, J., 2012. The origin of decoupled carbonate and  
572 organic carbon isotope signatures in the early Cambrian (ca. 542–520 Ma) Yangtze platform.  
573 *Earth and Planetary Science Letters* 317, 96–110.
- 574 Jiang, S.-Y., Chen, Y.-Q., Ling, H.-F., Yang, J.-H., Feng, H.-Z., Ni, P., 2006. Trace-and rare-earth element  
575 geochemistry and Pb–Pb dating of black shales and intercalated Ni–Mo–PGE–Au sulfide ores  
576 in Lower Cambrian strata, Yangtze Platform, South China. *Mineralium Deposita* 41, 453–467.
- 577 Jin, C., Li, C., Algeo, T.J., Planavsky, N.J., Cui, H., Yang, X., Zhao, Y., Zhang, X., Xie, S., 2016. A highly  
578 redox-heterogeneous ocean in South China during the early Cambrian (~529–514 Ma):  
579 Implications for biota-environment co-evolution. *Earth and Planetary Science Letters* 441, 38–  
580 51.
- 581 Jones, B., Manning, D.A., 1994. Comparison of geochemical indices used for the interpretation of  
582 palaeoredox conditions in ancient mudstones. *Chemical geology* 111, 111–129.
- 583 Li, C., Love, G.D., Lyons, T.W., Fike, D.A., Sessions, A.L., Chu, X., 2010. A stratified redox model for

584 the Ediacaran ocean. *Science* 328, 80–83.

585 Li, C., Cheng, M., Algeo, T.J., Xie, S., 2015. A theoretical prediction of chemical zonation in early oceans  
586 (> 520 Ma). *Science China Earth Sciences*, 58, 1901–1909.

587 Li, C., Shi, W., Cheng, M., Jin, C.,  
588 Algeo, T.J., 2020. The redox structure of Ediacaran and early Cambrian oceans and its controls.  
*Science Bulletin*, 65, 2141–2149.

589 Li, J., Tang, S., Zhang, S., Xi, Z., Yang, N., Yang, G., Li, L., Li, Y., 2018. Paleo-environmental conditions  
590 of the Early Cambrian Niutitang Formation in the Fenggang area, the southwestern margin of  
591 the Yangtze Platform, southern China: Evidence from major elements, trace elements and other  
592 proxies. *Journal of Asian Earth Sciences* 159, 81–97.

593 Li, N., Li, C., Fan, J., Algeo, T.J., Yan, D., Zhu, G., Wu, S., Tang, S., Cheng, M., Jin, C., 2019. Sulfate-  
594 controlled marine euxinia in the semi-restricted inner Yangtze Sea (South China) during the  
595 Ordovician-Silurian transition. *Palaeogeography, Palaeoclimatology, Palaeoecology* 534,  
596 109281.

597 Li, S., Gao, Z., 2000. Source tracing of noble metal elements in Lower Cambrian black rock series of  
598 Guizhou-Hunan Provinces, China. *Science in China Series D: Earth Sciences* 43, 625–632.

599 Li, Z.X., Bogdanova, S.V., Collins, A.S., Davidson, A., De Waele, B., Ernst, R.E., Fitzsimons, I.C.W.,  
600 Fuck, R.A., Gladkochub, D.P., Jacobs, J., Karlstrom, K.E., Lu, S., Natapov, L.M., Pease, V.,  
601 Pisarevsky, S.A., Thrane, K., Vernikovsky, V., 2008. Assembly, configuration, and break-up  
602 history of Rodinia: A synthesis. *Precambrian Research* 160, 179–210.

603 Little, S.H., Vance, D., Lyons, T.W., McManus, J., 2015. Controls on trace metal authigenic enrichment  
604 in reducing sediments: insights from modern oxygen-deficient settings. *American Journal of*  
605 *Science* 315, 77–119.

606 Liu, Z.H., Zhuang, X., Teng, G., Xie, X., Yin, L., Bian, L., Feng, Q., Algeo, T.J., 2015. Organic matter  
607 enrichment and source rock potential of the lower Cambrian Niutitang Formation at Yangtiao,  
608 Guizhou, SW China. *Journal of Petroleum Geology*, 38, 411–432.

609 Lu, Z., Hu, R., Han, T., Wen, H., Mo, B., Algeo, T.J., 2021. Control of V accumulation in organic-rich  
610 shales by clay-organic nanocomposites. *Chemical Geology*, 567, 120100.

611 McLennan, S.M., 2001. Relationships between the trace element composition of sedimentary rocks and  
612 upper continental crust. *Geochemistry, Geophysics, Geosystems* 2.

613 McSwiggen P. L., Morey G. B., Cleland J M., 1994. Occurrence and genetic implications of hyalophane  
614 in manganese-rich iron-formation, Cuyuna Iron Range, Minnesota, USA. *Mineralogical*  
615 *Magazine*, 58, 387–399.

616 Moro, M.C., Cembranos, M.L., Fernandez, A., 2001. Celsian, (Ba, K)-feldspar and cymrite from sedex  
617 barite deposits of Zamora, Spain. *The Canadian Mineralogist* 39, 1039–1051.

618 Morse, J., Luther Iii, G., 1999. Chemical influences on trace metal-sulfide interactions in anoxic  
619 sediments. *Geochimica et Cosmochimica Acta* 63, 3373–3378.

620 Och, L.M., Shields-Zhou, G.A., Poulton, S.W., Manning, C., Thirlwall, M.F., Li, D., Chen, X., Ling, H.,  
621 Osborn, T., Cremonese, L., 2013. Redox changes in Early Cambrian black shales at Xiaotan  
622 section, Yunnan Province, south China. *Precambrian Research* 225, 166–189.

623 Okada, Y., Sawaki, Y., Komiya, T., Hirata, T., Takahata, N., Sano, Y., Han, J., Maruyama, S., 2014. New  
624 chronological constraints for Cryogenian to Cambrian rocks in the Three Gorges, Weng'an and  
625 Chengjiang areas, South China. *Gondwana Research* 25, 1027–1044.

626 Overmann, J., Beatty, J.T., Krause, H.R., Hall, K.J., 1996. The sulfur cycle in the chemocline of a  
627 meromictic salt lake. *Limnology and oceanography* 41, 147–156.

- 628 Paschall, O., Carmichael, S.K., Königshof, P., Waters, J.A., Ta, P.H., Komatsu, T., Dombrowski, A., 2019.  
629 The Devonian-Carboniferous boundary in Vietnam: Sustained ocean anoxia with a volcanic  
630 trigger for the Hangenberg Crisis? *Global and Planetary Change* 175, 64–81.
- 631 Poulton, S.W., Canfield, D.E., 2005. Development of a sequential extraction procedure for iron:  
632 implications for iron partitioning in continentally derived particulates. *Chemical geology* 214,  
633 209–221.
- 634 Raiswell, R., Buckley, F., Berner, R.A., Anderson, T., 1988. Degree of pyritization of iron as a  
635 paleoenvironmental indicator of bottom-water oxygenation. *Journal of Sedimentary Research*  
636 58, 812–819.
- 637 Raith M., Devaraju T., Spiering B., 2014. Paragenesis and chemical characteristics of the celsian  
638 hyalophane–K-feldspar series and associated Ba-Cr micas in barite-bearing strata of the  
639 Mesoarchaeon Ghattihosahalli Belt, Western Dharwar Craton, South India. *Mineralogy and*  
640 *Petrology*, 108, 153–176.
- 641 Sadiq, M., 1988. Thermodynamic solubility relationships of inorganic vanadium in the marine  
642 environment. *Marine Chemistry* 23, 87–96.
- 643 Scholz, F., Hensen, C., Noffke, A., Rohde, A., Liebetrau, V., Wallmann, K., 2011. Early diagenesis of  
644 redox-sensitive trace metals in the Peru upwelling area – response to ENSO-related oxygen  
645 fluctuations in the water column. *Geochimica et Cosmochimica Acta* 75, 7257–7276.
- 646 Scott, C., Lyons, T.W., 2012. Contrasting molybdenum cycling and isotopic properties in euxinic versus  
647 non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. *Chemical Geology*  
648 324, 19–27.
- 649 Scott, C., Slack, J.F., Kelley, K.D., 2017. The hyper-enrichment of V and Zn in black shales of the Late  
650 Devonian–Early Mississippian Bakken Formation (USA). *Chemical Geology* 452, 24–33.
- 651 Slack, J.F., Selby, D., Dumoulin, J.A., 2015. Hydrothermal, biogenic, and seawater components in  
652 metalliferous black shales of the Brooks Range, Alaska: synsedimentary metal enrichment in a  
653 carbonate ramp setting. *Economic Geology* 110, 653–675.
- 654 Tan, J., Wang, Z., Wang, W., Hilton, J., Guo, J., Wang, X., 2021. Depositional environment and  
655 hydrothermal controls on organic matter enrichment in the lower Cambrian Niutitang shale,  
656 southern China. *AAPG Bulletin* 105, 1329–1356.
- 657 Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. *Reviews of*  
658 *geophysics* 33, 241–265.
- 659 Tourtelot, H.A., 1979. Black shale—its deposition and diagenesis. *Clays and clay minerals* 27, 313–321.
- 660 Tribouillard, N., Algeo, T.J., Baudin, F., Riboulleau, A., 2012. Analysis of marine environmental  
661 conditions based on molybdenum–uranium covariation—Applications to Mesozoic  
662 paleoceanography. *Chemical Geology* 324, 46–58.
- 663 Tribouillard, N., Algeo, T.J., Lyons, T., Riboulleau, A., 2006. Trace metals as paleoredox and  
664 paleoproductivity proxies: An update. *Chemical Geology* 232, 12–32.
- 665 Wang, J., Chen, D., Yan, D., Wei, H., Xiang, L., 2012. Evolution from an anoxic to oxic deep ocean  
666 during the Ediacaran–Cambrian transition and implications for bioradiation. *Chemical Geology*  
667 306–307, 129–138.
- 668 Wang, Z., Tan, J., Boyle, R., Hilton, J., Ma, Z., Wang, W., Lyu, Q., Kang, X., Luo, W., 2020a. Evaluating  
669 episodic hydrothermal activity in South China during the early Cambrian: Implications for  
670 biotic evolution. *Marine and Petroleum Geology* 117, 104355.
- 671 Wang, Z., Tan, J., Boyle, R., Wang, W., Kang, X., Dick, J., Lyu, Q., 2020b. Mercury anomalies within



672 the lower Cambrian (stage 2–3) in South China: Links between volcanic events and  
673 paleoecology. *Palaeogeography, Palaeoclimatology, Palaeoecology* 558, 109956.

674 Wanty, R.B., Goldhaber, M.B., 1992. Thermodynamics and kinetics of reactions involving vanadium in  
675 natural systems: Accumulation of vanadium in sedimentary rocks. *Geochimica et*  
676 *Cosmochimica Acta* 56, 1471–1483.

677 Wehrli, B., Stumm, W., 1989. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation.  
678 *Geochimica et Cosmochimica Acta* 53, 69–77.

679 Wen, H., Fan, H., Zhang, Y., Cloquet, C., Carignan, J., 2015. Reconstruction of early Cambrian ocean  
680 chemistry from Mo isotopes. *Geochimica et Cosmochimica Acta* 164, 1–16.

681 Xiang, L., Schoepfer, S.D., Shen, S.-z., Cao, C.-q., Zhang, H., 2017. Evolution of oceanic molybdenum  
682 and uranium reservoir size around the Ediacaran–Cambrian transition: evidence from western  
683 Zhejiang, South China. *Earth and Planetary Science Letters* 464, 84–94.

684 Xie, X., Zhu, G., Wang, Y., 2021. The influence of syngenetic hydrothermal silica fluid on organic matter  
685 preservation in lower Cambrian Niutitang Formation, South China. *Marine and Petroleum*  
686 *Geology* 129, 105098.

687 Xu, L., Lehmann, B., Mao, J., Qu, W., Du, A., 2011. Re-Os age of polymetallic Ni-Mo-PGE-Au  
688 mineralization in Early Cambrian black shales of South China—a reassessment. *Economic*  
689 *Geology* 106, 511–522.

690 Yang, A., Zhu, M., Zhang, J., Li, G., 2003. Early Cambrian eodiscoid trilobites of the Yangtze Platform  
691 and their stratigraphic implications. *Progress in Natural Science* 13, 861–866.

692 Yang, C., Li, X.-H., Zhu, M., Condon, D.J., Chen, J., 2018. Geochronological constraint on the Cambrian  
693 Chengjiang biota, South China. *Journal of the Geological Society* 175, 659–666.

694 You, C.-F., Castillo, P., Gieskes, J., Chan, L., Spivack, A., 1996. Trace element behavior in hydrothermal  
695 experiments: Implications for fluid processes at shallow depths in subduction zones. *Earth and*  
696 *Planetary Science Letters* 140, 41–52.

697 Zhao, J., Jin, Z., Jin, Z., Geng, Y., Wen, X., Yan, C., 2016. Applying sedimentary geochemical proxies  
698 for paleoenvironment interpretation of organic-rich shale deposition in the Sichuan Basin, China.  
699 *International Journal of Coal Geology* 163, 52–71.

700 Zhou, Y., Ling, L., Wen, C., Mi, W., Zhu, L., Zhu, K., Yang, W., Pang, Y., 2020. Study on the occurrence  
701 state of Ni-Mo-V from the polymetallic layers in Niutitang Formation, Weng'an County,  
702 Guizhou. *Mineralogy and Petrology* 40, 67–81(In Chinese with English Abstract).

703 Zhu, G., Zhao, K., Li, T., Zhang, Z., Tang, S., Wang, P., 2021. Anomalously high enrichment of mercury  
704 in early Cambrian black shales in South China. *Journal of Asian Earth Sciences* 216, 104794.

705 Zou, C., Qiu, Z., Poulton, S.W., Dong, D., Wang, H., Chen, D., Lu, B., Shi, Z., Tao, H., 2018. Ocean  
706 euxinia and climate change “double whammy” drove the Late Ordovician mass extinction.  
707 *Geology* 46, 535–538.

708 **Figures and Tables**

709

710 **Figure 1.** Paleogeographic maps of the Yangtze Block during the late Ediacaran and  
711 early Cambrian. (A) Latest Ediacaran to earliest Cambrian Fortunian Stage (539 Ma,  
712 modified after Jiang et al. (2012). (B) Early Cambrian Stage 3 (521 Ma). (C) Depth and  
713 relative position of the nine studied early Cambrian Stage 3 period sections in South  
714 China.

715

716 **Figure 2** Stratigraphic correlation with biostratigraphic dating of lower Cambrian  
717 (Ca. 539–514 Ma) sections across South China. Data sources: 1-Meishucun section,  
718 Yunnan Province (Jenkins et al., 2002; Yang et al., 2003; Wen et al., 2015); 2-Xiaotan  
719 section, Yunnan Province (Och et al., 2013); 3-Jinsha section, Guizhou Province (Jin  
720 et al., 2016); 4-Xy1 well, Guizhou Province (Li et al., 2018); 5-Yangjiaping section,  
721 Hunan Province (Cheng et al., 2016); 6-Xb1 well, Hunan Province (this study); 7-  
722 Longbizui section, Hunan Province (Wang et al., 2012); 8-Yuanjia section, Hunan  
723 Province (Cheng et al., 2020); and 9-Xa1 well, Hunan Province (this study). SSF:  
724 small shelly fossil assemblages, LCP: Liuchapo Formation, DY: Dengying Formation,  
725 CLP: Canglangpu Formation, MXS: Mingxinsi Formation, LM: lower member of the  
726 Niutitang/Yu'anshan Formation, UM: upper member of the Niutitang/Yu'anshan  
727 Formation.

728

729 **Figure 3** Petrographic observations of studied samples in the Xa1 and Xb1 wells by  
730 scanning electron microscopy. (A) Pyrite (depth 843.3m, Xa1 well); (B) Celsian,  
731 hyalophane and pyrite (depth 849.8m, Xa1 well); (C) Celsian, monazite and pyrite  
732 (depth 849.8m, Xa1 well); (D) Celsian, barite and pyrite (depth 856.4m, Xa1 well);  
733 (E) Barite and pyrite (depth 2002.0m, Xb1 well); (F) Celsian (depth 2012.0m, Xb1  
734 well); (G) Hyalophane and rutile (depth 2015.0m, Xb1 well); (H) Sphalerite and  
735 pyrite (depth 2018.0m, Xb1 well); (I) Sphalerite, calcium carbonate and pyrite (depth  
736 2020.0m, Xb1 well).

737

738 **Figure 4.** Petrographic observations of V-rich shale samples in the Xa1 and Xb1 wells  
739 by scanning electron microscopy. (A) Anatase, organic matter and celsian (depth  
740 849.8m, Xa1 well); (B) Anatase, celsian and hyalophane (depth 2010.5m, Xb1 well);  
741 (C) Anatase and calcium phosphate (depth 2013.2m, Xb1 well); (D) V concentration  
742 in organic matter, anatase, and illite minerals of A and B; (E) Anatase and Hyalophane  
743 (depth 855.2m, Xa1 well); (F) Anatase, pyrite and monazite (depth 2017.0m, Xb1  
744 well).

745

746 **Figure 5** Distribution of Mo, U, V, Zn, TOC content,  $Mo_{EF}/U_{EF}$ , and Mo/TOC ratios  
747 of the Niutitang Formation at the Xa1 well, Hunan Province.

748

749 **Figure 6** Distribution of Mo, U, V, Zn, TOC content,  $Mo_{EF}/U_{EF}$ , and Mo/TOC ratios  
750 of the Niutitang Formation at the Xb1 well, Hunan Province.

751

752 **Figure 7** The Mo enrichment factor ( $Mo_{EF}$ ) versus U enrichment factor ( $U_{EF}$ ) plot in  
753 the Xa1 (A) and Xb1 wells (B).

754

755 **Figure 8** Spatio-temporal variations of redox conditions from the inner shelf to basin  
756 facies.

757

758 **Figure 9** Mo concentrations versus total organic carbon (TOC) contents in the UM  
759 shale (A) and LM shale (B). Dashed lines represent four modern anoxic basin systems  
760 in the Saanich Inlet, Cariaco Basin, Framvaren Fjord, and Black Sea (Algeo and Lyons,  
761 2006), showing different seawater restriction environments.

762

763 **Figure 10**  $Mo_{EF}/U_{EF}$  versus  $V_{EF}$  (A) and  $Zn_{EF}$  (B) in the Xa1 well,  $Mo_{EF}/U_{EF}$  versus  
764  $V_{EF}$  (C) and  $Zn_{EF}$  (D) in the Xb1 well.

765

766 **Figure 11** TOC content versus V content (A) and Zn content (C) in the UM shale,

767 TOC content versus V content (B) and Zn content (D) in the LM shale.

768

769 **Figure 12** Zn content versus V content in LM shale (A); Zn content versus V content  
770 in LM shale with abnormally high Zn content.

771

772 **Figure 13** Depositional models and inferred geochemical cycle of V and Zn in the early  
773 Cambrian paleo-ocean in South China.

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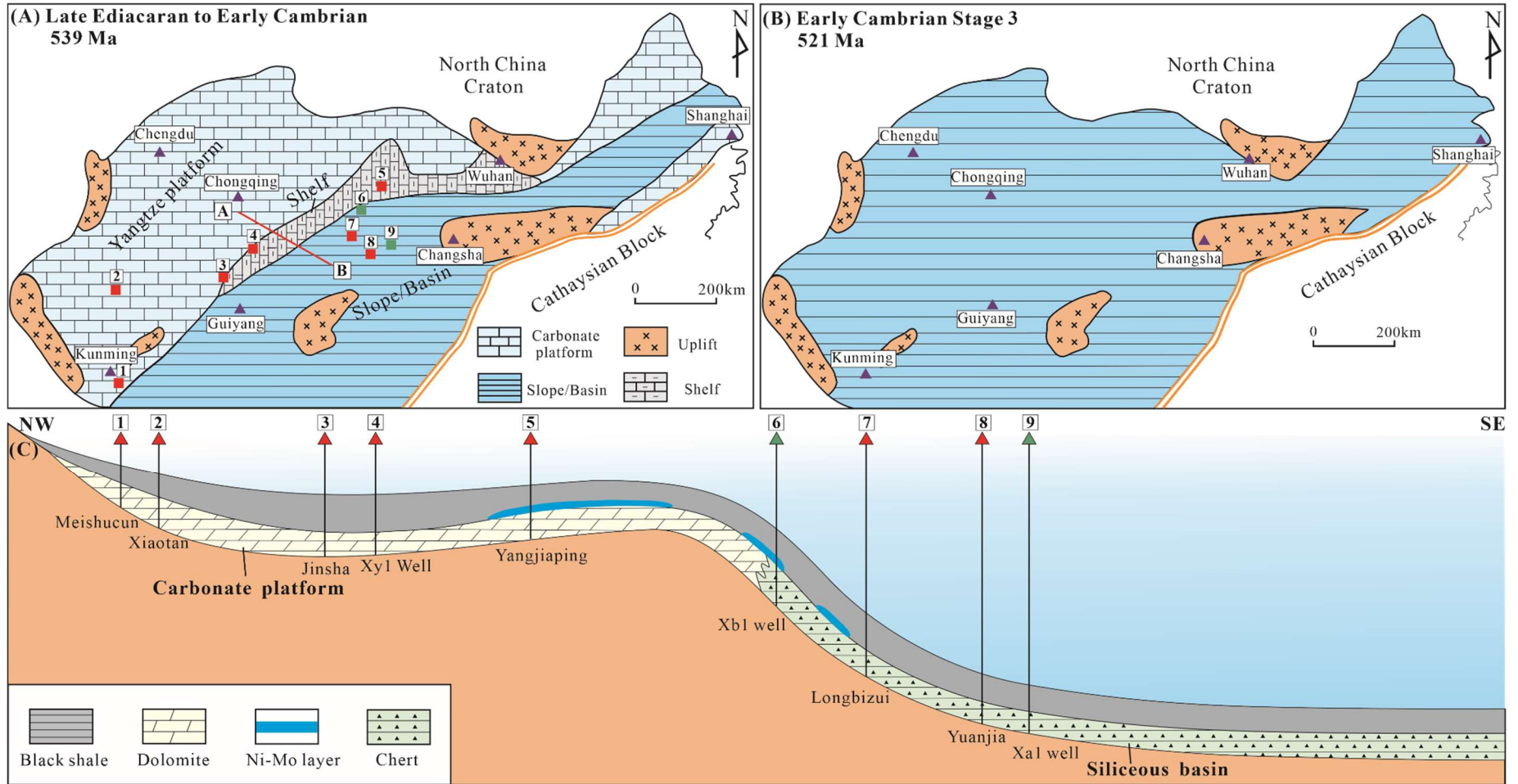
776 **Table 1** Redox condition, TOC content, Mo/TOC ratio,  $V_{EF}$  and  $Zn_{EF}$  of Niutitang  
777 shale in Xa1 well and Xb1 well.

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779

780 **Figure 1**

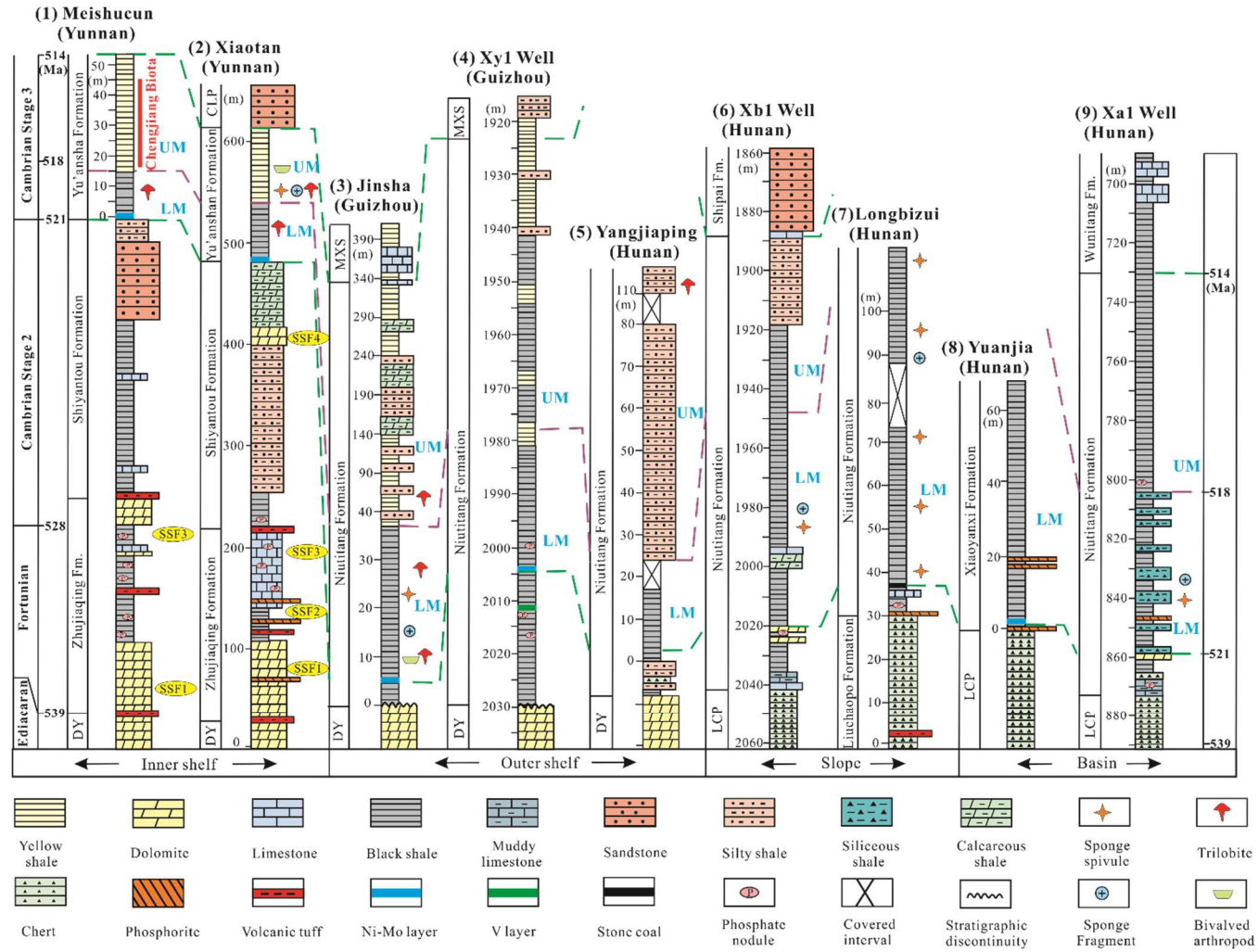
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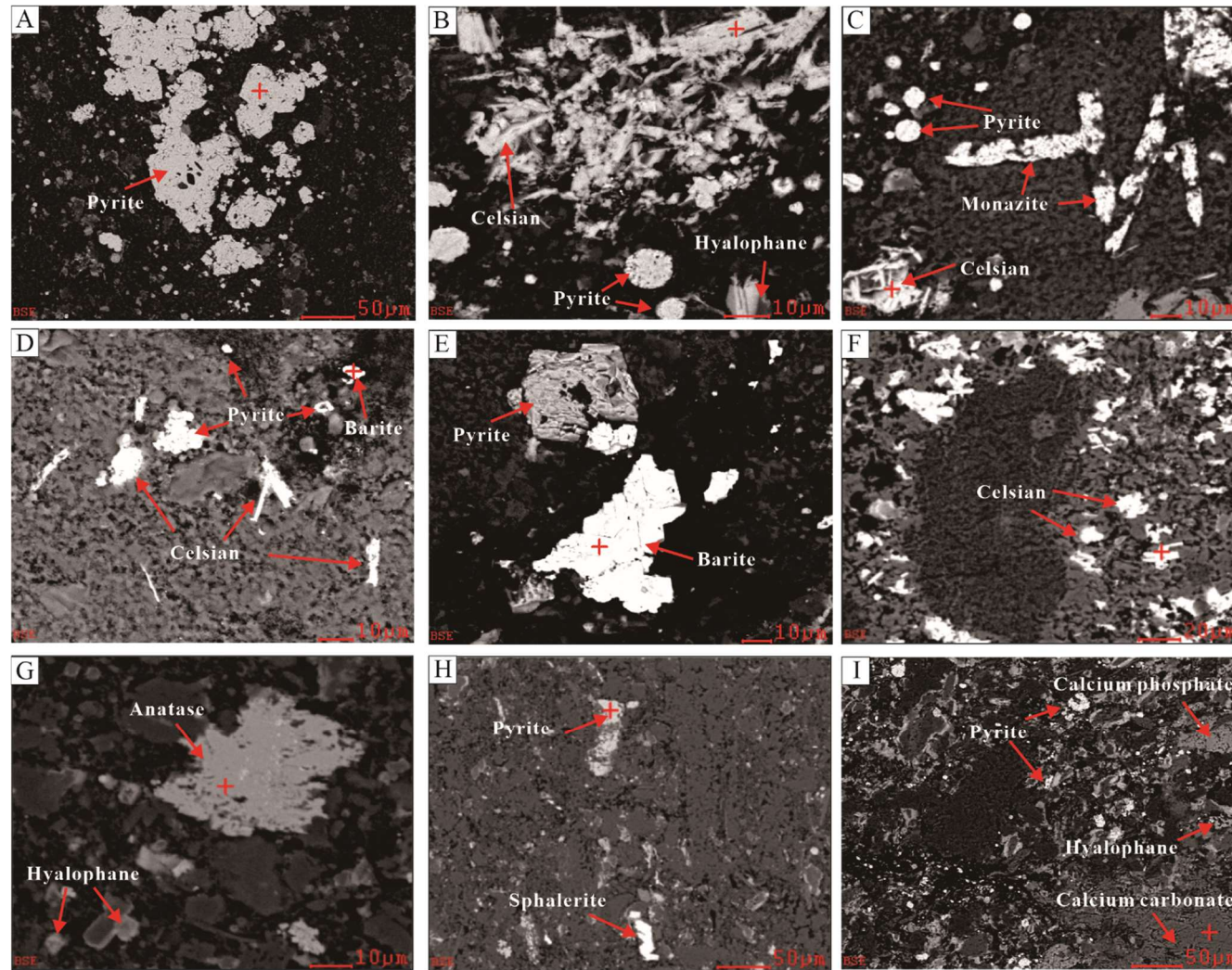
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784 **Figure 2**

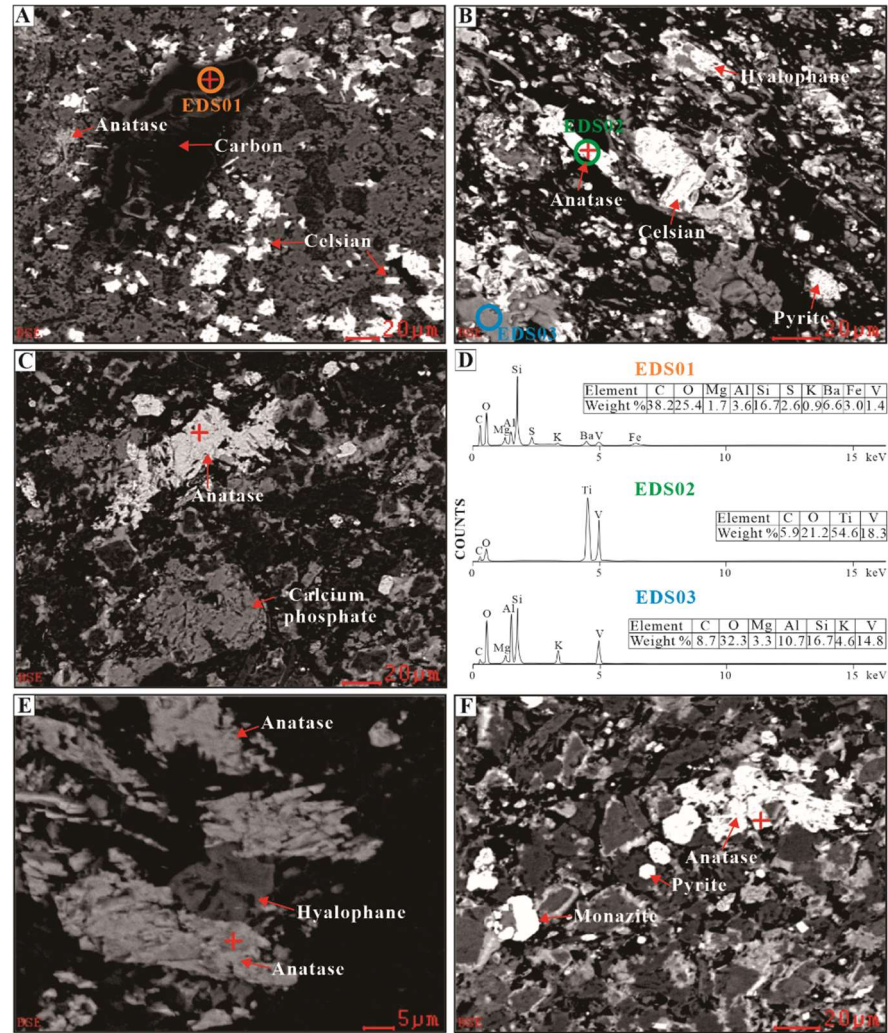


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786 **Figure 3**



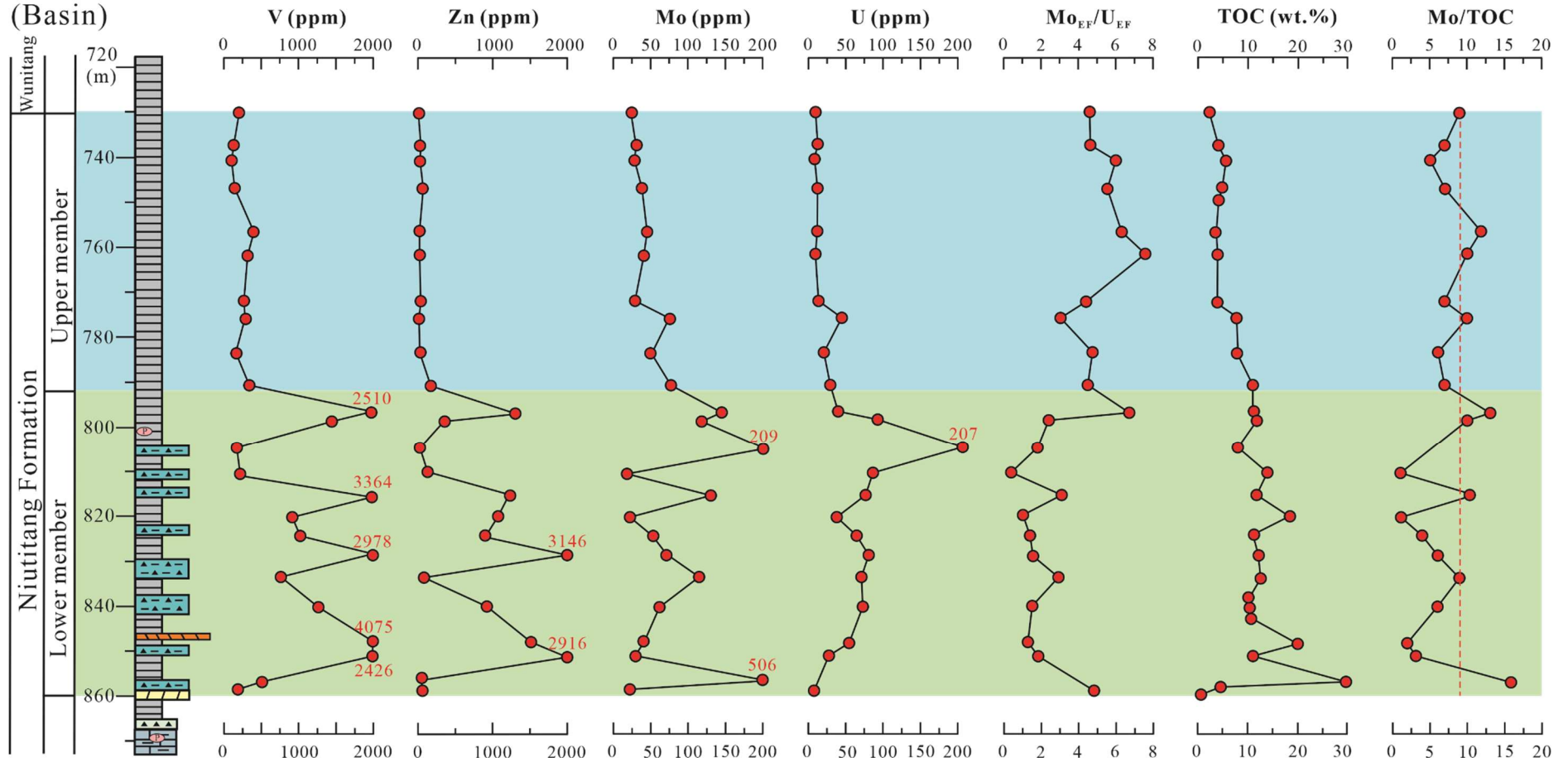
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**Figure 5**  
Xa1 well  
(Basin)



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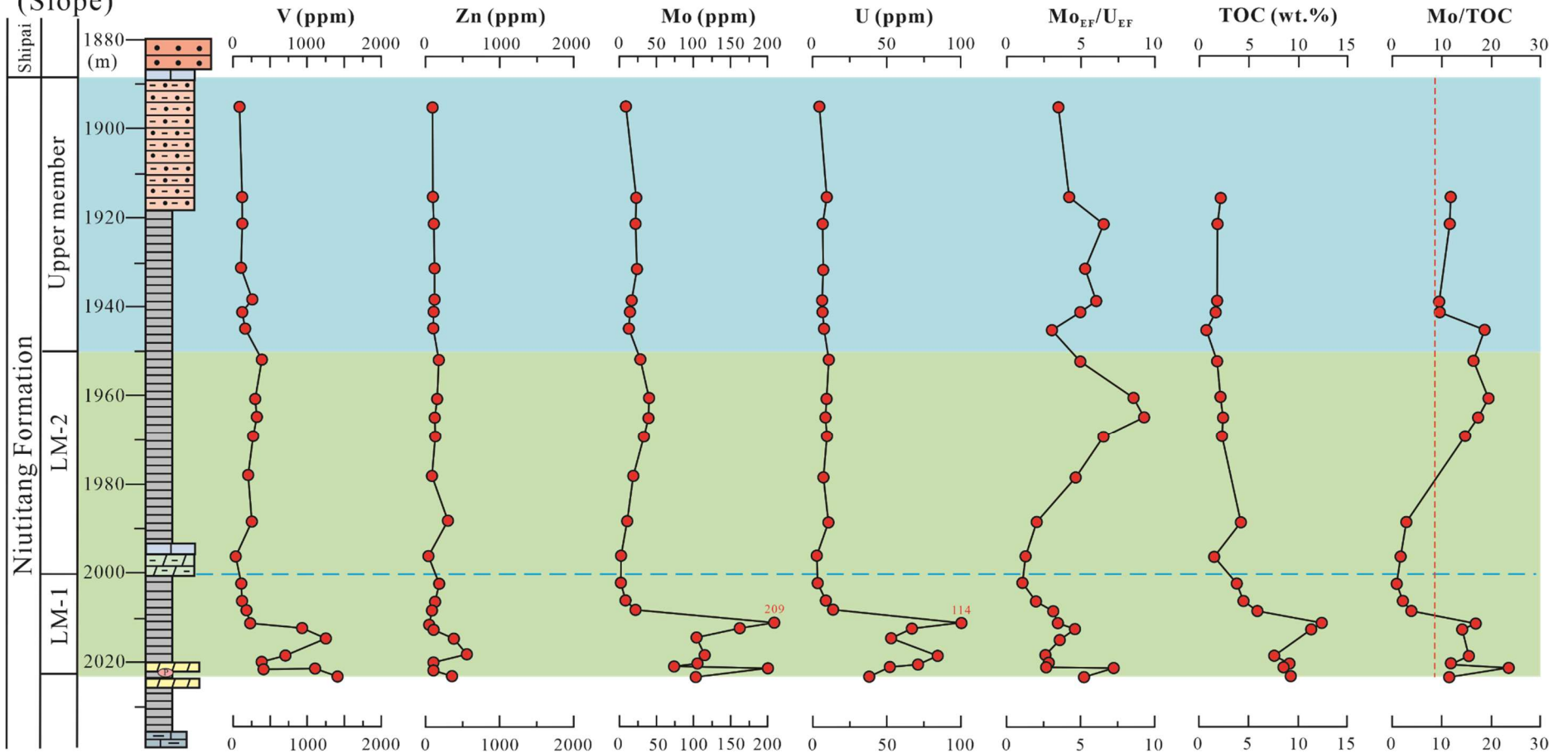
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**Figure 6**

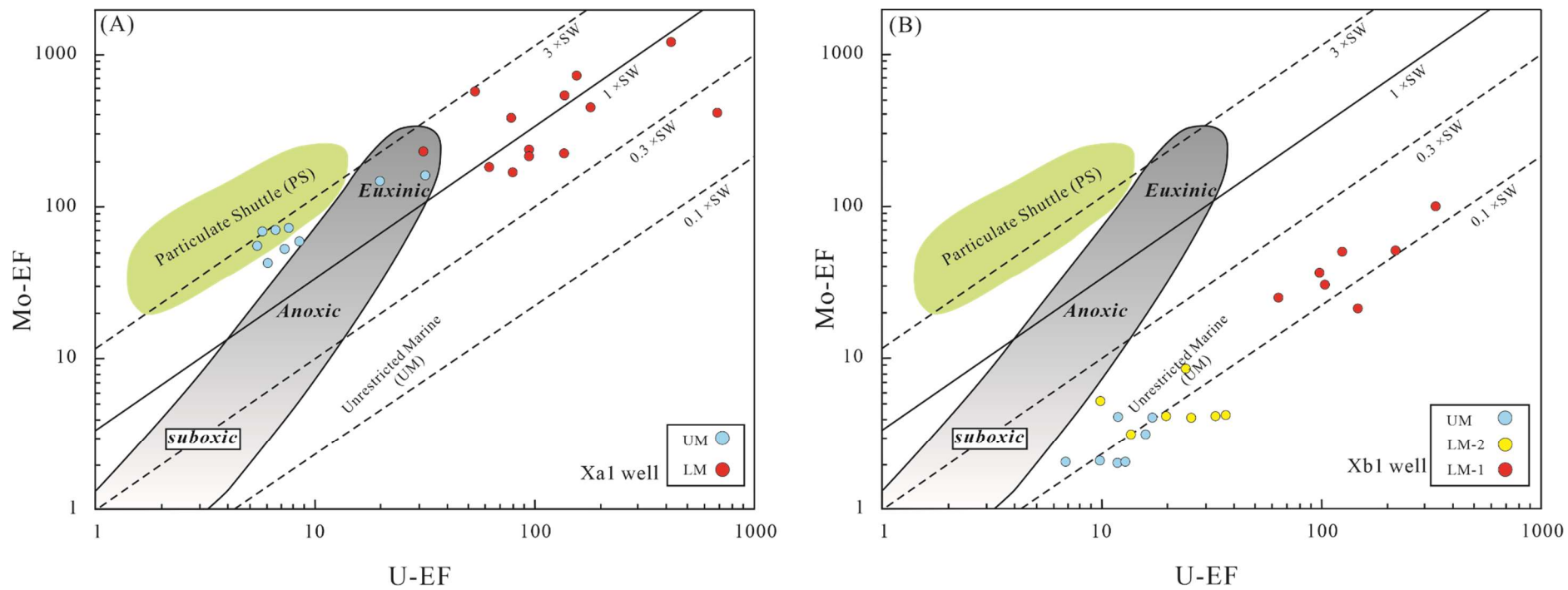
Xb1 well  
(Slope)



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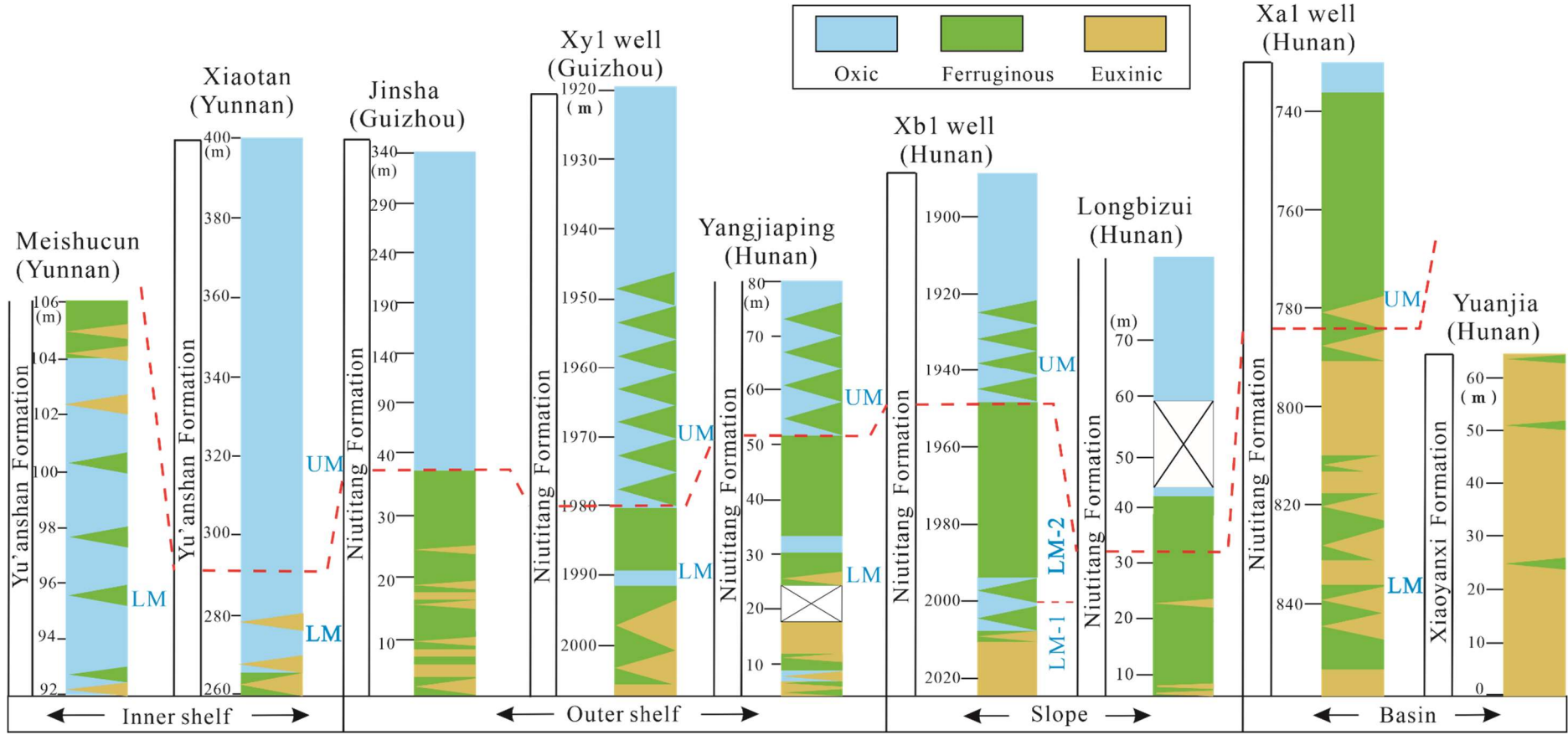
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797 **Figure 7**  
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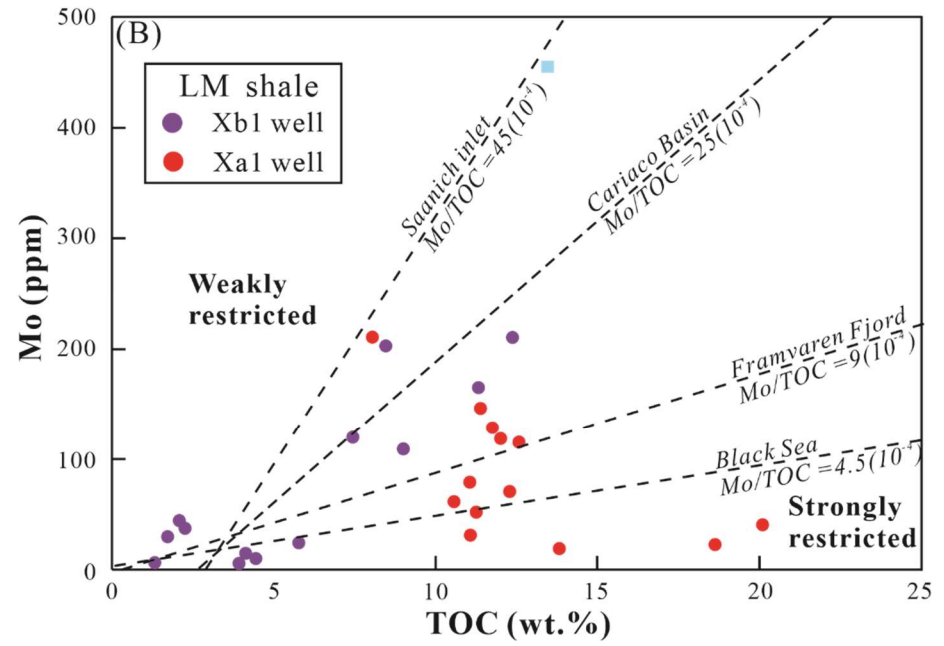
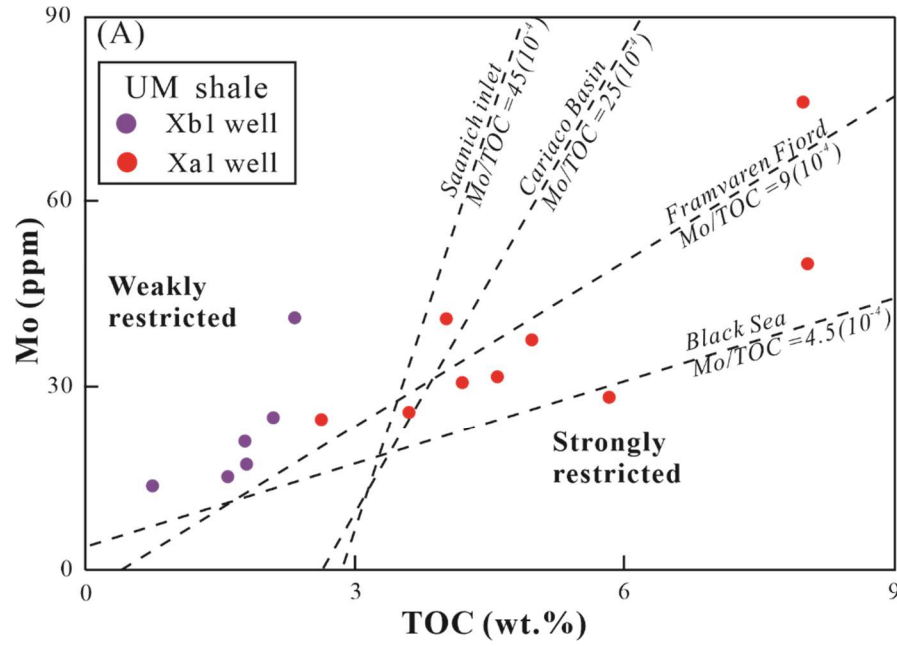
807 **Figure 8**  
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813 **Figure 9**

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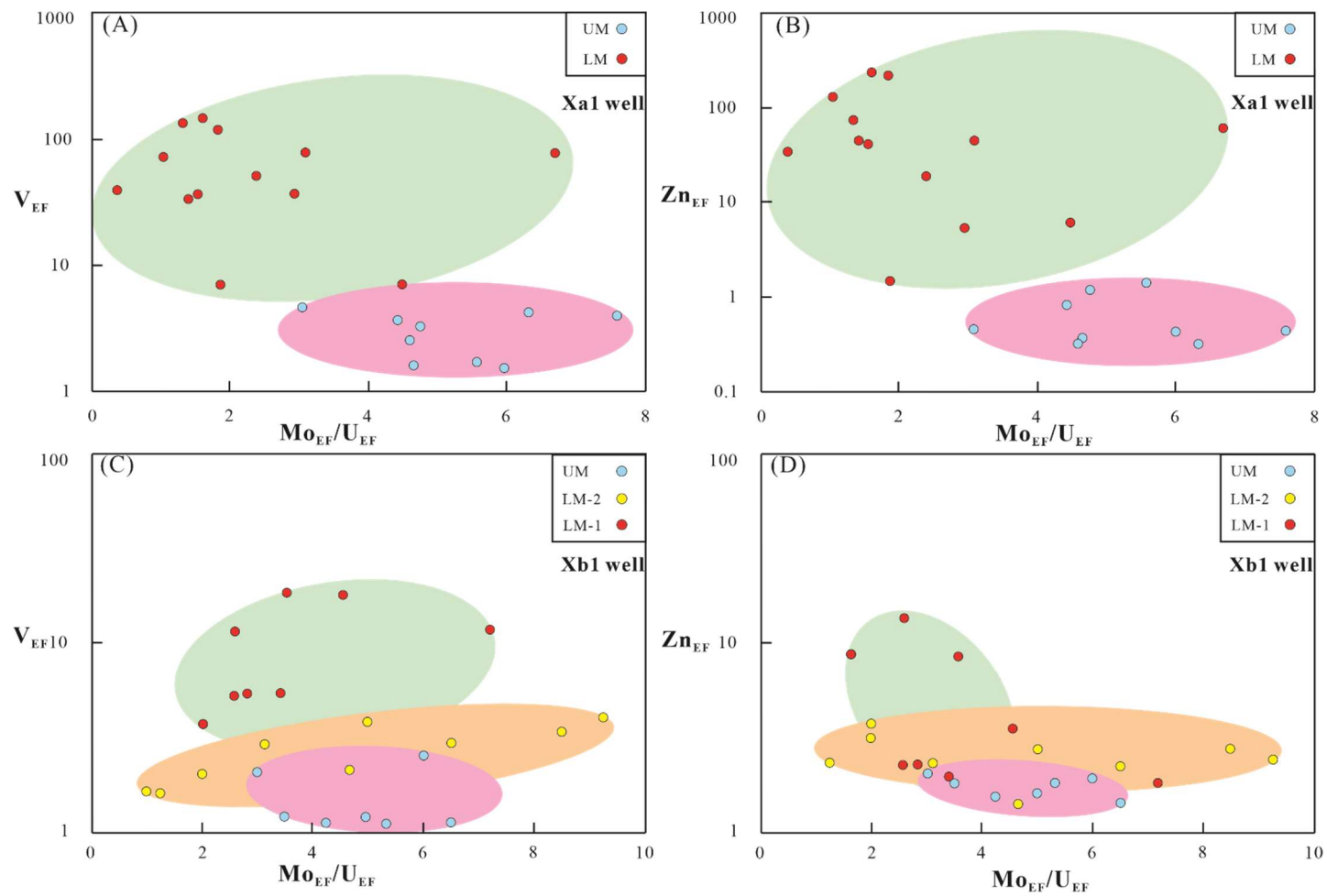
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824 **Figure 10**

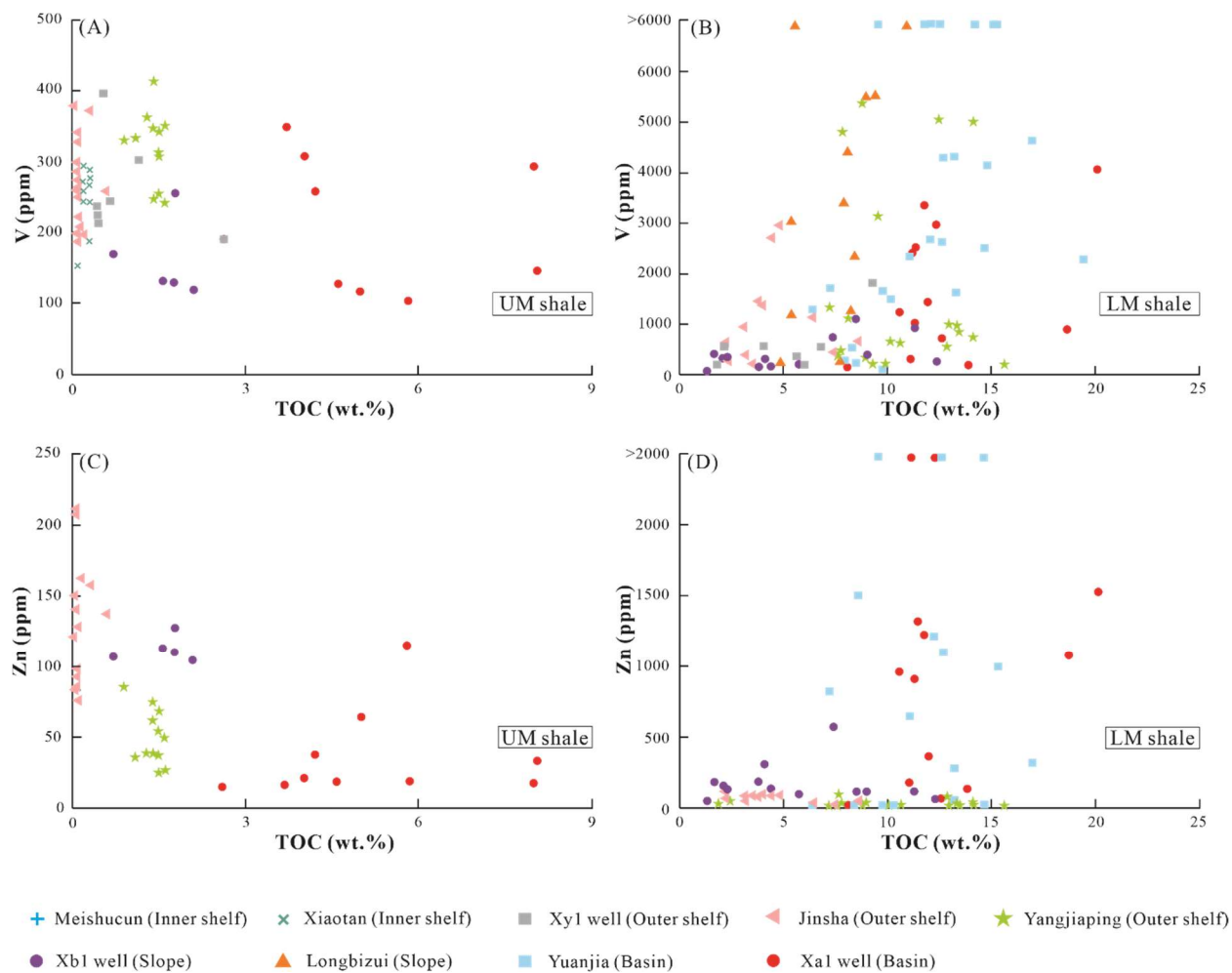


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827 **Figure 11**

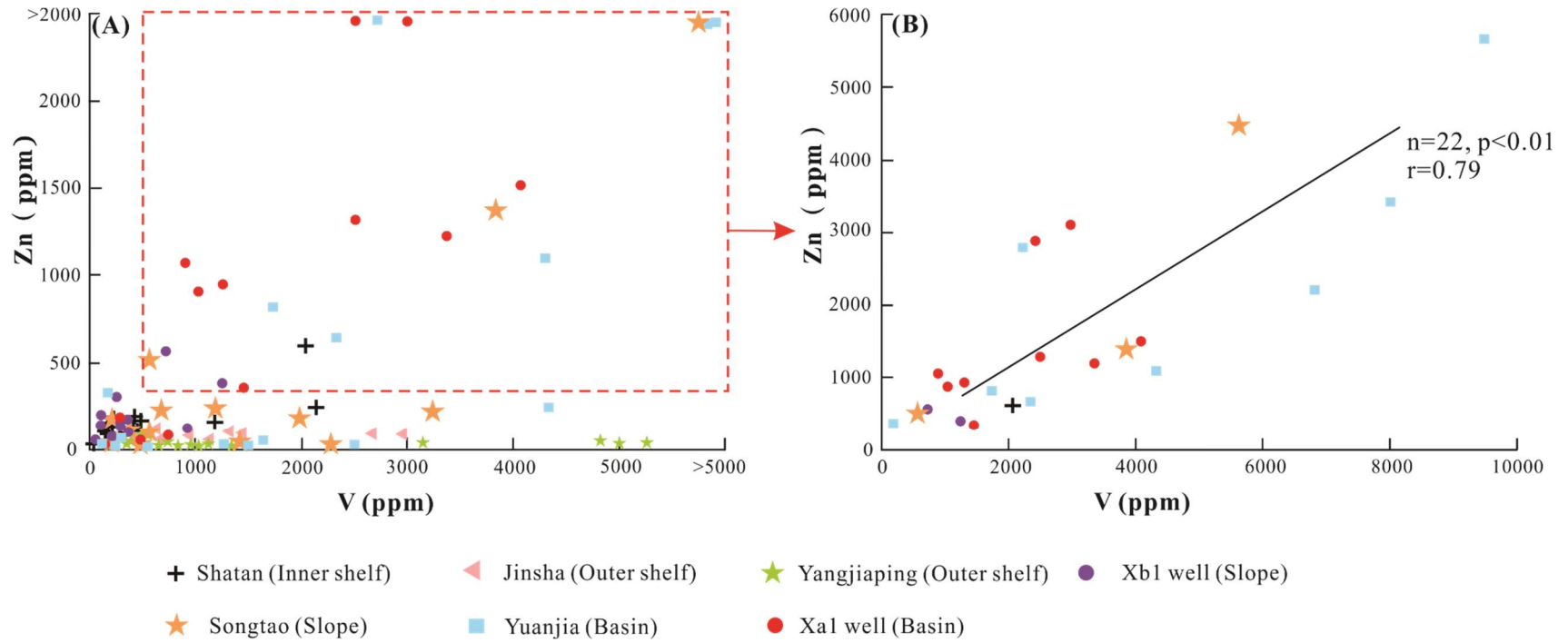
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830 **Figure 12**

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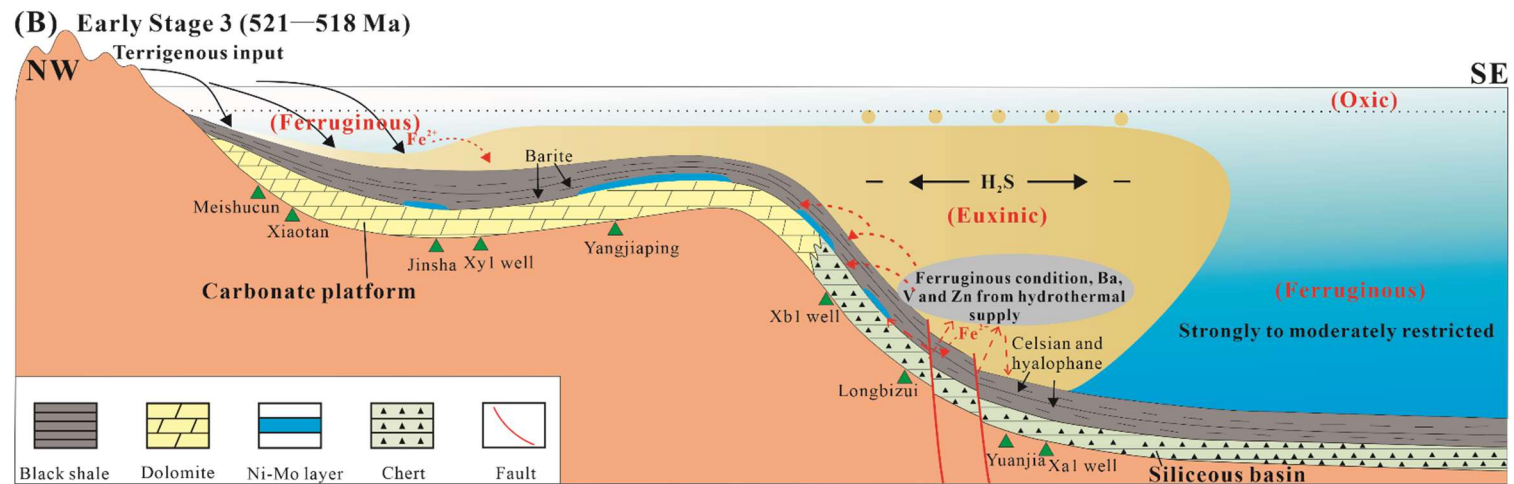
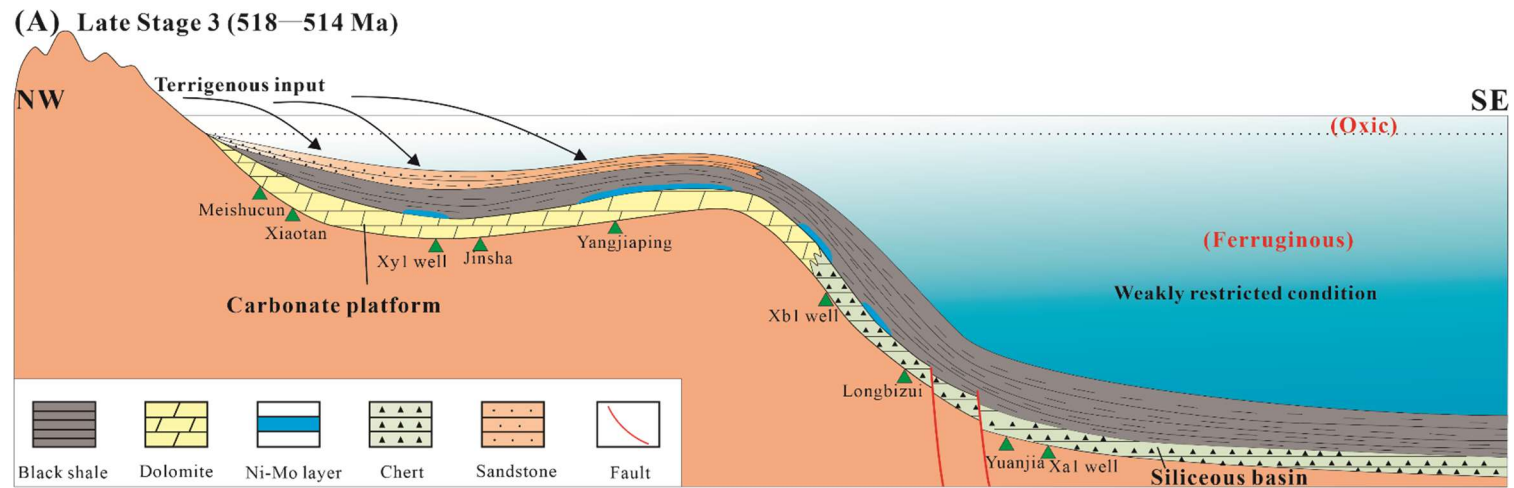
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840 **Figure 13**



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