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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 H₂S content, hydrothermal input, seawater restriction, trace element inventory

1 **1. Introduction**

Redox-sensitive trace elements (TEs: Mo, U, V, Zn) in sediments can be used to 2 infer oxygen concentration in the overlying water column or atmosphere, and have been 3 widely used as proxies for redox conditions in ancient oceans (Jones and Manning, 4 1994; Algeo and Maynard, 2004; Tribovillard et al., 2006; Scott et al., 2017; Algeo and 5 Liu, 2020). TEs are commonly reduced from high to low valence state under low-6 oxygen conditions, and may be complexed with organic acids, adsorbed by authigenic 7 8 sulfides, or precipitated in the form of insoluble oxyhydroxides (Tribovillard et al. 2006; Algeo and Liu, 2020). The geochemical cycle of TEs in the paleo-ocean system is 9 complex and influenced by various factors including terrigenous supply, oceanic metal 10 inventory, seawater restriction, redox condition, and volcanic/hydrothermal input (You 11 12 et al., 1996; Algeo and Tribovillard, 2009; Gill et al., 2011; Cheng et al., 2016; Zou et al., 2018; Paschall et al., 2019). Ferruginous water masses (anoxic condition without 13 free H₂S) are comparatively common in early Cambrian or older geological time 14 intervals (Canfield, 1998; Algeo and Li, 2020), while euxinic environments have 15 16 appeared several times in geological history and modern ocean systems (Feng et al., 2014; Li et al., 2019). Anoxic oceans in different periods of geological history may 17 exhibit unique trace element enrichment and migration patterns. 18

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

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

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

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

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

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

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

Concentrations of major oxides (SiO₂, Al₂O₃, Fe₂O₃, P₂O₅, and MnO) were 92 determined by X-ray fluorescence (XRF) on molten glass beads at Central South 93 University. For major oxides with concentrations greater than 0.3%, the accuracy was 94 95 better than 2%. Trace elements (Mo, U, V, and Zn) were determined by ICP-MS at Societe Generale de Surveillance S.A. (SGS). A 50 mg sample powder was dissolved 96 in a high-pressure Teflon bomb with 1 ml HF and 2 ml HNO₃ at 190 °C for 48 h. After 97 removing HF by heating, the residue was dissolved in 2 ml H₂O and 2 ml HNO₃ at 98 145 °C for 12 h. Analytical precision was better than 10 % relative standard deviation. 99 For measurements of TOC and TS content, 100 mg samples were first treated with 100 excess hydrochloric acid solution (volume ratio 1:7), and then washed with distilled 101 water to remove the HCl. TOC content was determined using a high-frequency infrared 102 103 carbon and sulfur analyzer (LECO CS-744) at Central South University. For TS measurements, separate 100 mg samples, not treated with HCl, were dried more than 2 104 h at 105 °C. Then, TS content was measured on a carbon and sulfur analyzer. The 105 analytical precision was better than 0.2 %. 106

For sulfide mineral identification, the selected samples were firstly cut into 1 cm³ 107 cubes with a cutting machine. Then the surface to be observed was ground, polished, 108 and sprayed with a carbon coating. Finally, a FEI Quanta 200 Scanning Electron 109 Microscope (SEM) with Energy Dispersive Spectrometer (EDS) at China University of 110 111 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. Enrichment factors (EF) were calculated based on the ratio between trace element 113 concentration and aluminum (Al) within the sample, compared to the same ratio in 114 Upper Continental Crust (UCC) (Tribovillard et al., 2006; Algeo and Tribovillard, 115

116 2009). The equation is as follows:

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

where UUC data for normalization were taken from McLennan (2001), and $X_{EF} > 1.0$ 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*

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

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

138

139 *4.2. TOC and TS contents*

The TOC and TS contents of the Niutitang shale from the Xa1 and Xb1 wells are shown in Figures 5 and 6 and the Supplementary Data. From the Xa1 well, LM shale TOC contents range from 8.1–31.5 % (avg. 14.0 %) and TS contents range from 0.4– 2.6 % (avg. 0.9 %), while in the UM shale TOC contents range from 2.6–8.1 % (avg. 5.1 %) and TS contents range from 1.5–3.8 % (avg. 2.3 %). From the Xb1 well, LM 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*

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

165

166 **5. Discussion**

167 *5.1. Redox conditions during the early Cambrian*

Analysis of redox state is an important paleoenvironmental method, which mainly includes iron speciation (Raiswell et al., 1988; Poulton and Canfield, 2005), redoxsensitive trace element geochemistry (Scott and Lyons, 2012), and assessment of Mo– U enrichment factor (Mo_{EF} and U_{EF}) data (Tribovillard et al., 2006, 2012; Algeo and Tribovillard, 2009). Scott and Lyons (2012) systematically evaluated Mo geochemistry in modern anoxic basin systems and suggested that Mo content < 25 ppm indicates an 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 Mo_{EF} -U_{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

The Mo_{EF}-U_{EF} correlation of the LM shale in the Xa1 and Xb1 wells can be seen 181 in Figure 7. Almost all samples in the Xa1 well are characterized by high Mo content 182 (>100 ppm), U content (30–207 ppm), Mo_{EF} (90–678) and U_{EF} (30–207). The Mo_{EF}/U_{EF} 183 ratio is between 1 and 3 times that of modern seawater (Figure 7A). These 184 characteristics suggest a euxinic environment persisted during the depositional period 185 of the LM shale in the Xa1 well. The Yuanjia section is close to the Xa1 well (Cheng et 186 al., 2020), and its iron speciation data are Fe_{HR}/Fe_T =0.88-1 (avg. 0.98) and 187 Fe_{Py}/Fe_{HR}=0.58–0.97 (avg. 0.89). The trace elements data in the Xa1 well are consistent 188 with the iron speciation data in the Yuanjia section, both indicating extremely euxinic 189 190 conditions in the basin facies from 521–518 Ma (Figure 8). The Mo_{EF}/U_{EF} ratio of the LM shale in the Xb1 well is between 0.1 and 0.3 times that of modern seawater (Figure 191 7B). Due to the TOC, Mo, U, and V contents, and Mo_{EF}-U_{EF} variation, the LM shale of 192 193 the Niutitang Formation in the Xb1 well can be divided into the LM-1 and LM-2 submembers (Figure 6). The LM-1 submember shale in the Xb1 well exhibit high Mo 194 content (>100 ppm), Mo_{EF} (65–142), and U_{EF} (21–100), which suggest a euxinic 195 environment. The Longbizui section is adjacent to the Xb1 well (Figure 1), and its iron 196 speciation data also show Fe_{HR}/Fe_T =0.79-1.13 (avg. 0.98) and Fe_{Py}/Fe_{HR}=0.13-0.86 197 198 (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 (2-41 ppm), U (3-11 ppm), Mo_{EF} (2-37), and U_{EF} (2-8) contents, which are consistent 200 with the iron speciation data (Fe_{HR}/Fe_T =0.21-1.4 (avg. 0.82) and Fe_{Py}/Fe_{HR}=0.01-0.69201 202 (avg. 0.33) in the Longbizui section (Figure 7B). Both of these lines of evidence above suggest a ferruginous with intermittent euxinic condition existed in the slope facies 203

204 from 521–518 Ma.

205

206 5.1.2. Redox condition of the UM shale

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

216

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

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

there was no free sulfur in the water column, and euxinic environments were not obvious during this time interval. The water column exhibited ferruginous conditions in the basin setting (i.e., Yuanjia section and Xa1 well). Subsequently, marine environments were dominated by oxic conditions in South China, which were 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 with a high valence (VI, MoO_4^{2-}) in oxic conditions (Taylor and McLennan, 1995). In 241 an anoxic water column, Mo is reduced to MoO_2^+ or $MoO_xS_{4-x}^{2-}$, and the latter may be 242 formed as organic thiomolybdate, or further reduced to MoS4²⁻ (Brumsack, 1989; 243 Adelson et al., 2001; Algeo and Rowe, 2012). Mo has a long residence time in water 244 (approximately 731 kyr). This unique feature of Mo is commonly used to assess the 245 restriction of modern and ancient seawater (Tribovillard et al., 2012; Zhao et al., 2016). 246 The relationship between Mo and TOC can reveal the degree of anoxic water restriction 247 (Figure 9). 248

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

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

271

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

273 5.3.1. Vanadium

During the early Cambrian Stage 3, a global transgression event contributed to the 274 expansion of euxinic seawater, resulting in abnormally high trace element contents 275 (Guo et al., 2016). For the Xa1 well, the V_{EF} is high in the LM shale (7.0–145.2), and 276 277 moderate in the UM shale (1.5–4.6) (Figure 10A, Table 1). Similarly, the Xb1 well also exhibits relatively high V_{EF} in the LM-1 submember shale (5.2–18.3), moderate V_{EF} in 278 the LM-2 submember shale (1.6–4.0), and low V_{EF} in the UM shale (1.1–2.5) (Figure 279 10C). The redox proxies suggest the water column of the LM and UM shales in the Xa1 280 well was persistently euxinic and with ferruginous conditions, while those of the LM-281 1, LM-2, and UM shales in the Xb1 well were intermittent euxinic, ferruginous, and 282 suboxic, respectively (Figures 7 and 8). Vanadium is present as different valance states 283 in oxic to anoxic conditions (Sadiq, 1988). Under oxic conditions, V exists as soluble 284 HVO_4^{2-} and $H_2VO_4^{-}$ (V) in seawater, but is reduced to $VO(OH)_3^{-}$ (IV) or insoluble 285 hydroxide (IV) and complexed by dissolved organic matter in seawater (Wehrli and 286 Stumm, 1989; Scholz et al., 2011). Due to the large specific surface area of smectite, 287 V-rich OM is then adsorbed or intercalated onto this clay mineral. When the reducibility 288 of the water column is enhanced and free H₂S exists, V is further reduced to V₂O₃ or 289 V(OH)₃ (III) (Breit and Wanty, 1991; Wanty and Goldhaber, 1992). Microscopic 290

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

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

321 5.3.2. Zinc

In the Xa1 well, Zn_{EF} is high in the LM shale (1.4–210.0), but low in the UM shale 322 (0.3–1.2, Figure 10B). Similarly, the Xb1 well exhibits relatively high Zn_{EF} values in 323 the LM-1 submember shale (1.8–13.4), moderate values in the LM-2 submember shale 324 (1.4–3.7), and low values in the UM shale (1.4–1.9, Figure 10D). Zinc is present as 325 Zn²⁺ under oxic/suboxic conditions, while it precipitates rapidly in the form of ZnS 326 327 under anoxic conditions (Brumsack, 1989; Morse and Luther Iii, 1999). Sulfate reducing bacteria can release Zn from organometallic complexes that can be absorbed 328 by adjacent authigenic sulfides (Fleurance et al., 2013; Slack et al., 2015). The Zn 329 content also exhibits coupled patterns with Mo, U, MoEF/UEF ratio, and TOC content in 330 the Xa1 and Xb1 wells (Figures 5, 6, 9), which may be attributed to the redox condition 331 and dissolved organic matter. There are two different authigenic enrichment 332 mechanisms of Zn in modern and ancient oceans, termed primary and secondary 333 authigenic enrichment (Scott et al., 2017; Wang et al., 2020b). Primary enrichment is 334 335 related to H₂S in pore waters, and results in relatively low Zn content. Secondary enrichment requires excess H₂S content, affects the activity phototrophic sulfide-336 oxidizing bacteria, and results in "hyper-enrichment" of Zn (Overmann et al., 1996; 337 Findlay et al., 2014). The Zn content of the LM-1 submember shale in the Xb1 well and 338 the LM shale in the Xa1 well is abnormally high, which may be related to the free H₂S 339 in the paleo-ocean (Scott et al., 2017). Interestingly, the Zn content of the UM shale in 340 the Xa1 well was in a deficit state ($Zn_{EF} < 1$), while that in the Xb1 well was slightly 341 enriched (Zn_{EF}>1, Table 1). The Zn content shows coupled patterns with V content in 342 the Niutitang shale (Figures 5, 6). Collectively this information indicates that the Zn 343 inventory in the ocean was similar to the V inventory, both of which were in a 344 downward trend. The drawdown of trace elements in seawater may provide an early-345 stage preparation of the marine environment for the subsequent Chengjiang Biota (Han 346 347 et al., 2018).

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

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

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

environment during this time interval, including enrichment of the toxic element 378 mercury (Zhu et al., 2021), formation of chert and siliceous shale (Liu et al., 2015; Xie 379 380 et al., 2021), and causing organismal extinctions (Wang et al., 2020b). Hyalophane minerals are present at different depths in the Xa1 and Xb1 wells. The formation 381 mechanism of hyalophane can be divided into two types: metasomatism of authigenic 382 barite, and crystallization of Ba-Al-Si colloid (McSwiggen et al., 1994; Raith et al., 383 2014). Barite minerals are rare and do not exhibit obvious metasomatic residual 384 385 structure in our study areas (Figure 3). The formation of Ba-Al-Si colloids is generally related to hydrothermal action (Jacobsen et al., 1990; Moro et al., 2001), which can 386 release large amounts of Ba and SiO₂ into seawater and precipitate to form siliceous 387 colloids in the reducing environment. The anoxic environment in the study area also 388 favors the formation of Ba-Al-Si colloids. The hyalophane mineral can therefore be an 389 important indicator of hydrothermal activity (Figure 5). Furthermore, Zn is an 390 important biological nutrient. The TM/C ratio (Zn=0.036 mmol/mol) of phytoplankton 391 can be used to calculate the biological contribution to Zn content in sediment (Little et 392 393 al., 2015). The TOC content of the LM shale is < 20% and the calculated biological contribution to Zn content is only 40 ppm. As the Zn content of the LM shale generally 394 exceeds 500 ppm and can extend up to 5672 ppm, it shows that the contribution from 395 organisms is negligible. Furthermore, the Zn content of the UM shale in the Xa1 well 396 was in a deficit state ($Zn_{EF} < 1$), while that in the Xb1 well was slightly enriched 397 $(Zn_{EF}>1)$. Due to the redox condition (Table 1), an oxic condition in the Xb1 well is 398 399 more conducive to the blooming of phytoplankton, and the biological contribution to Zn content should be relatively higher. Fan et al. (2020) also analyzed Zn isotopes in 400 401 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 0.5–1.2%, with this concentration reaching the industrial mining grade (Zhou et al., 403 2020). Hydrothermal fluids may have carried abundant trace element (V, Zn, and Ba) 404 into the ocean during the depositional period of the LM shale, forming shales with 405 anomalously high trace elements content in the euxinic environment (Figure 8). 406

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

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

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

During the depositional period of the LM shale, the paleo-ocean presented a 419 "euxinic wedge" model (Figure 13B), with the surface, middle, and deep ocean layers 420 characterized by oxic, euxinic, and ferruginous conditions, respectively (Li et al., 2015; 421 422 2020). Free H₂S content was abundant in the seawater, and photic zone euxinia may have occurred in the slope-basin facies zone (Wang et al., 2020b). The shallow-water 423 areas mainly experienced suboxic conditions, while the deep-water areas were 424 persistently euxinic with intermittent ferruginous conditions (Figure 8). The ocean was 425 also affected by multiple phases of hydrothermal activity during this period (Chen et 426 al., 2009; Gao et al., 2018; Xie et al., 2021; Zhu et al., 2021). There existed a relatively 427 high availability of fluvial Fe-Mn oxides and their subsequent reduction below the 428 chemocline in the shallow-water areas (Cheng et al., 2016). The Mo/TOC ratio in the 429 430 study area is close to present-day value of the Black Sea, indicating a strongly to moderately restricted condition. The V enrichment started at the suboxic-euxinic 431 threshold, while Zn enrichment requires a more euxinic environment. Although the 432 trace elements of seawater were in a dwindling state, episodic hydrothermal activities 433 may have carried abundant trace elements (V, Zn, and Ba) into the ocean. V element is 434 usually complexed by dissolved organic matter in seawater during the depositional 435

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

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

466 6. Conclusions

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

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8 **Figures and Tables**

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

715

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

et al., 2016); 4-Xy1 well, Guizhou Province (Li et al., 2018); 5-Yangjiaping section,

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:

small shelly fossil assemblages, LCP: Liuchapo Formation, DY: Dengying Formation,

725 CLP: Canglangpu Formation, MXS: Mingxinsi Formation, LM: lower member of the

Niutitang/Yu'anshan Formation, UM: upper member of the Niutitang/Yu'anshan

727 Formation.

728

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,

hyalophane and pyrite (depth 849.8m, Xa1 well); (C) Celsian, monazite and pyrite

(depth 849.8m, Xa1 well); (D) Celsian, barite and pyrite (depth 856.4m, Xa1 well);

- (E) Barite and pyrite (depth 2002.0m, Xb1 well); (F) Celsian (depth 2012.0m, Xb1
- well); (G) Hyalophane and rutile (depth 2015.0m, Xb1 well); (H) Sphalerite and

pyrite (depth 2018.0m, Xb1 well); (I) Sphalerite, calcium carbonate and pyrite (depth

736 2020.0m, Xb1 well).

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, $Mo_{\text{EF}}/U_{\text{EF}}$, 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.
774	
775	
776	Table 1 Redox condition, TOC content, Mo/TOC ratio, V_{EF} and Z_{NEF} of Niutitang
777	shale in Xa1 well and Xb1 well.
778	
779	













Figure 4







794 Figure 6























