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DOI: 10.1016/j.jseaes.2022.105533

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Document Version Peer reviewed version

Citation for published version (Harvard):

Fu, W, Turner, P, Clements, T, Spencer, ART, Yu, J, Yang, Y, Guo, B, Ning, Z, Zhuo, Z, Riley, M & Hilton, J 2023, 'Taphonomic and diagenetic implications of reduction spot formation in Cretaceous red beds from the Jiaolai Basin, Eastern China', *Journal of Asian Earth Sciences*, vol. 243, 105533. https://doi.org/10.1016/j.jseaes.2022.105533

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1	Taphonomic and diagenetic implications of reduction spot
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4	
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23 Abstract

Green-grey coloured reduction spots are common in continental red beds through 24 25 geological history and occur in a range of different lithologies and depositional environments, but their timing and mode of formation remain controversial. We 26 27 investigate the Late Cretaceous to earliest Paleogene Jiaozhou Formation using borehole data from the Jiaolai Basin in Shandong province of northern China, and 28 consider the distribution, morphology, and geochemistry of reduction spots in these 29 continental red beds to evaluate how the reduction spots formed. Here, we report a 30 31 novel application of three-dimensional X-ray Computed Tomography (XCT) to analyse reduction spot morphology, composition and density. Our data show that 32 33 individual reduction spots are spheroidal, tubular or irregular shaped, and often 34 contain small, grey, dark brown or black organic cores, referred to as loci. Typically, reduction spots have a similar chemical composition to the host red beds, but with 35 elevated levels of vanadium (Va), lower levels of iron (Fe), and lower density. 36 37 Isolated, small refractory fossils (e.g., charcoal) in the sediment alongside reduction spots but not within them indicates that microbial decay of organic labile (reactive) 38 tissues in early diagenesis is an important control in reduction spot formation. We 39 propose a new taphonomic model of reduction spot formation: post burial, during the 40 primary sedimentary cycle in the groundwater zone, vanadium is released by 41 intrastratal oxidation of titanomagnetite. Decay of organic matter creates localised 42 reducing conditions resulting in the reduction of Fe^{3+} and the eventual depletion or 43 removal of the resulting Fe^{2+} (altering the colour of the reduction spot). 44

45	Simultaneously, the reduction of V^{4+} and the consequent lowering of the concentration
46	of V as V^{2+} minerals occur in the reduction spot, explaining their lower density than
47	the host sediment.
48	
49	Keywords: continental red beds; diagenesis, vanadium, redox, taphonomy, 3D X-ray
50	Computed Tomography analysis
51	
52	1. Introduction
53	Green-grey coloured reduction spots are common throughout geological history
54	and have been observed stratigraphically from the Mesoproterozoic through the
55	Phanerozoic (see Turner 1980; Hofman, 1991; Spinks et al., 2010; Table 1). Although
56	they occur in various lithologies and depositional environments, their mode of
57	formation remains controversial (Turner, 1980; Hofmann, 1991; Parnell, 1985, 1988;

58 Parnell et al., 1987, 2016, 2018; Spinks, 2010, 2014). Hofmann (1991) summarised

59 reduction 'spheroid' (referred to here as reduction spot) mineralogy and geochemistry

60 across a range of stratigraphic contexts, and concluded that, despite the variation in

age and lithology, reduction spots are similar in terms of their morphology,

62 mineralogy, and geochemistry, potentially indicating a shared mode of formation.

63 Typically, reduction spots cross-cut depositional laminations and bedding which, in

64 combination with their shape and colour variations, suggest that they formed during

65 diagenesis (Turner, 1980). However, the timing of formation is debated: the

66 spheroidal nature of reduction spots has been used to suggest that they formed after

67	sedimentary compaction, whilst vertically shortened examples may indicate growth
68	prior to compaction (Spinks et al., 2010). Another feature of reduction spots is that
69	many of them have a dark grey-black locus (or core), which has been inferred to be
70	organic matter (OM) (Hofmann, 1990; Yang et al., 2019). Reduction spots tend to
71	mimic the shape of the loci, suggesting a direct relationship between the development
72	of a spot and its locus.

What triggers the formation of green-grey coloured reduction spots is 73 contentious. Previously, it has been suggested that organic matter acts as a fuel source 74 75 for microbial activity, and the decay of organic matter may have triggered localised reducing conditions around these loci points (e.g., Durrance et al. 1978; Turner 1980). 76 However, Hofmann (1993) demonstrated that some reduction spot loci contained the 77 78 mica roscoelite, which weathers to a dark brown colour (similar to that of organic 79 matter), suggesting the possibility that some loci may not be organic rich. However, the absence of organics does not indicate that organics were never present; Hofmann 80 (1990, 1993) concluded that microbial action was the most likely mode of reduction 81 spot formation (see also Spinks et al., 2010) and that the absence of organic matter in 82 some reduction spot loci could indicate simply that it had been fully consumed by 83 microbial activity (Hofmann 1993). 84

The cause of the colour bleaching of reduction spots is primarily due to the absence of pigmentary iron oxide which gives the surrounding host sediment its red colour. Reduction spots and surrounding sediment contain a wide variety of minerals including roscoelite (V- mica), coffinite (U-silicate), cuprite (Cu-oxide), a variety of

89	nickel (Ni), copper (Cu) and cobalt (Co) arsenides and sulphides, and a wide range of
90	vanadate and uranyl vanadates (Hofmann, 1990; Chong et al., 2019). The origin of
91	these minerals provides clues to the mechanisms of reduction spot formation. Many of
92	these minerals are also present in large scale sedimentary hosted mineral deposits
93	(Rose 1976; Brown et al 2014) for which leaching and transport of metals from host
94	sediment with precipitation under changing redox conditions is a well-established
95	mechanism. However, it is not clear if the formation of reduction spots and larger
96	scale Uranium-vanadium (U-V) mineral deposition are part of a continuous process.
97	Thorson (2004) and Hahn and Thorson (2005) suggested a two-stage process in which
98	leaching occurred prior to a mineralization stage, while Asael et al. (2022) have
99	shown the importance of redox controls at both local and regional scale using Copper
100	(Cu) and lead (Pb) isotopes. These processes include the formation of reducing fluids
101	by the alteration of organic material and the bleaching of formerly red sediments so
102	that they are drab-coloured greens and greys (Barton et al 2018). Sufficiently reducing
103	conditions would cause reduction of U^{6+} to U^{4+} and V^{4+} to V^{2+} ; and in the reduced
104	state these elements are less mobile, and mineralization can occur by combination
105	with other elements. By contrast, the reduction of Fe^{3+} to the more mobile Fe^{2+} would
106	result in the solution and removal of iron and subsequent bleaching of the reduced
107	zone. It has been previously argued that diagenetic alteration of red beds can provide
108	sufficient Cu for stratiform copper mineralization. The solubility of Cu is much
109	increased in the presence of Cl ⁻ rich solutions (Rose, 1976; Rose and Bianchi-
110	Mosquera, 1993) and this could explain the common association of major bleached

111	zones with evaporitic, arid climate deposits. The colour difference from the
112	surrounding red sediment suggests <i>in-situ</i> reduction of ferric iron (Fe^{3+}) to ferrous
113	iron (Fe ^{$2+$}) and the dissolution and removal of pigmentary oxides (Sherlock, 1974).
114	Cu ⁺ in mineral deposits and reduction spots is frequently present as copper sulphide
115	and in large scaled bleached zones the bacterial reduction of sulphate leached from
116	associated evaporites is a likely mechanism of formation. The importance of faults in
117	the migration of reducing fluids in bleached zones has been emphasised previously
118	(Naylor et al. 1989) and described in more detail by Brown (2005).
119	Reduction spots are closely linked to the mechanism of formation of continental
120	red beds and this is linked to palaeoclimate and the accumulation of organic material.
121	In arid climates intrastratal alteration of non-red sediment (Walker et al., 1978) is
122	dominant, but in humid, tropical climates partially reddened clay-rich alluvium is
123	deposited. In the Late Triassic Newark Trough, Van Houten cycles recording
124	lacustrine transgression and regression have colour variations ranging from black
125	(perennial lake) to red (desiccated playa lake). These processional cycles result from
126	the \sim 20kyr astronomical forcing cycle and now form the basis of the Late Triassic
127	time scale (Olsen and Kent, 1996).
128	Within the continental red-beds of the Late Cretaceous-earliest Paleogene
129	Jiaozhou Formation in the Jiaolai Basin, northeast China, gray-green reduction spots
130	(typically with dark grey-black loci) are common making them an excellent case
131	study for investigating the mode of reduction spot formation. Currently, the mode of

132 reduction spot formation in the Jiaozhou Formation remains enigmatic (Yang et al.,

133	2019). In this paper we evaluate the formation mechanism of reduction spots in the
134	Jiaozhou Formation from the JK-1 borehole in Shandong Province and consider how
135	this relates to their formation in other geological contexts. We achieve this by (i)
136	reinterpreting the previoulsy identified depositional sedimentary environments by
137	correlating the sediments of the JK-1 borehole with the nearby LK-1 borehole and
138	interpreting lithological and faunal evidence, (ii) evaluating the physical and
139	geochemical properties of the reduction spots and their host sediments, and (iii)
140	proposing a new model for the formation of the reduction spots incorporating
141	formation and eventual discoloration. We also (iv) propose a revised temporal
142	framework for the lower part of the Jiaozhou Formation based upon a re-evaluation of
143	a recently published cyclostratigraphic analysis (Yang et al., 2021), allowing us to
144	consider the duration of its deposition and rates of change in sedimentary facies.
145	Collectively, our data should help develop our understanding of the formation of
146	reduction spots in continental red beds.

148 **2. Geological background**

The Jiaolai Basin is an Early Cretaceous composite rift basin with an area of approximately 12,000 km² in the Jiaozhou Peninsula of Shandong Province, northeast China (Fig. 1a, b). Formation of the Jiaolai Basin is related to subduction and retracement of the palaeo-Pacific plate into the Eurasian plate and the changing direction of their relative movement during the Mesozoic (Shen et al., 2020). Li and Hou (2018) identified three phases of stress field orientation during the Cretaceous

155	evolution of the Jiaolai Basin, comprising NE-SW extension in the early Early
156	Cretaceous, NNE-SSW extension in the later Early Cretaceous, and then E-W
157	extension in the Late Cretaceous. The basin is bounded by the Jiaobei Terrane to the
158	north, the NE trending Muping-Jimo Fault to the east, the NNE trending Tanlu Fault
159	to the west (Fig. 1b, c), and the Sulu Ultra-High Pressure (UHP) metamorphic zone to
160	the south (Zhang et al., 2003; Li, et al. 2020). The basin fill comprises Lower
161	Cretaceous sediments of the Laiyang Group and igneous lithologies of the Qingshan
162	Group, and the Late Cretaceous to early Paleocene Wangshi Group (Zhang et al.,
163	2003; Tian et al., 2021). The Wangshi Group is dominated by purple to brick red
164	conglomerate-sandstone-siltstone sets intercalated with marlstone from alluvial fan-
165	fluvial-lacustrine facies, and also includes volcanic rocks. From the bottom to the top
166	the Wangshi Group comprises the Linjiazhuang, Xingezhuang, Hongtuya, Shijiatun
167	and Jiaozhou formations (Zhang et al., 2003; Tian et al., 2021). Zhang et al. (2021)
168	inferred that the sediments of the Jiaozhaou Formation were provenanced from rocks
169	in the Sulu UHP metamorphic zone to the south. Here we focus on the Shijiatun and
170	Jiaozhou formations.
171	The Shijiatun Formation, comprising grey andesites in the lower part and black
172	to greyish-brown basalts in the upper part, interbedded with red sandstones, siltstones
173	and claystones, has been regarded by some authors to be the lowermost member of the
174	Hongtuya Formation that occurred only locally in the Jiaozhou-Zhucheng area of the

- 175 Jiaolai Basin (Ji, 2017; Tian et al., 2021). However, Ji (2017) and Li et al. (2020)
- 176 considered it a separate formation restricted to the Jiaozhou-Zhucheng area based on

177	its distinctive features. It comprises approximately 970 m of sedimentary and volcanic
178	rocks that includes three separate eruptive phases intervened by two intervals of
179	clastic deposition.
180	The Jiaozhou Formation is composed of purple, red, and pale green siltstones
181	and claystones with occasional conglomerates and sandstones (Ji, 2017; Tian et al.,
182	2021). Stratigraphically, the Jiaozhou Formation spans the K/Pg boundary, has been
183	identified from gamma ray log (GR) profiles and anomalies in the concentration of the
184	platinum group metal element, Iridium (Ir) (Xu, 2017). Based on this, Yang et al.
185	(2021) used Gamma Ray log data from the JK-1 borehole (referred to in error as the
186	ZK-1 borehole) to establish an astronomical timescale to determine the position of the
187	K/Pg boundary. These studies demonstrate that continuous fluvial and lacustrine
188	deposition occurred through the K/Pg boundary interval (Xu et al., 2019; Yang et al.,
189	2021). The Jiaozhou Formation preserves a rich biota including charophytes,
190	ostracods, and gastropods from shallow lacustrine settings, and sporopollen
191	assemblages derived from terrestrial floras (Du et al., 2020; Li et al. 2020; Tian, et al.
192	2021; Yu et al. 2021). The charophyte flora of the Jiaozhou Formation have been
193	analyzed biostratigraphically by Tian et al. (2021), and include typical Maastrichtian
194	species (Tolypella grambastii, Peckichara praecursoria, Microchara cristata, M.
195	prolixa, Lamprothamnium ellipticum, Nodosochara (Turbochara) specialis, and
196	Lychnothamnus aff. vectensis) and Paleocene species (Lychothamnus lanpingensis), as
197	well as species with ranges that span the boundary (Chara changzhouensis). The
198	gastropod Hydrobia datangensis indicates a Late Cretaceous age, while the ostracod

199	species Porpocypris sphaeroidalis indicates a Paleocene age (Yu et al., 2021).
200	Regarding palaeoenvironmental interpretations, Tan et al. (2019) suggested that
201	the Jiaozhou Formation in LK-1 borehole (614–0 m) consists mainly of floodplain
202	facies purple mudstones, grey-greenish siltstones and sandstones in the lower part
203	(614–452 m), shore-shallow lacustrine, sage-green to purple mudstone in the middle
204	part (452–250 m), and meandering fluvial, upward-thinning sandstones and
205	mudstones with intercalated conglomerates and marlstones in the upper part (250-
206	0 m). Subsequently, Li et al. (2020) divided the Jiaozhou Formation in the LK-1
207	borehole into seven intervals based primarily on lithological associations, in which the
208	interval from 533-499 m is interpreted as shallow lake deposits, the interval from
209	498–426 m are channels and floodplain facies, while the interval of 425–311 m is
210	returned to shallow lake deposits (Li et al., 2020, 2021; Yu et al., 2021). The other
211	parts of the Jiaozhou Formation in the LK-1 borehole lack charophyte flora, which
212	was interpreted to reflect climate cooling (Li et al., 2020, 2021). The K/Pg boundary
213	transition charophyte flora of the Jiaolai Basin are composed of Nodosochara
214	(Turbochara) specialis, which is characteristic of the deeper lacustrine facies, with
215	seven other species, which inhabit mainly shallow lake facies. The Jiaolai Basin is
216	considered to have developed as a high elevation intramontane palaeolake (Tian et al.,
217	2021).

In the recently drilled JK-1 borehole, situated 1 km from the LK-1 borehole, reduction spots only occur in a 74 m thick interval at the bottom of the Jiaozhou Formation, situated between basalts of the Shijiatun Formation and green lacustrine

221	mudstones that span the K/Pg boundary (Yu et al., 2021; Fig. 2). This 74 m interval
222	comprises an alluvial-lacustrine continental red bed sequence (Tan et al., 2019; Li et
223	al., 2020, 2021; Yu et al., 2021; Tian et al., 2021), but detailed sedimentological
224	investigations and palaeoenvironmental interpretations of the JK-1 core, and precise
225	correlation with the nearby LK-1 borehole, are yet to be undertaken. It is also
226	unknown if diagenetic alteration of titanomagnetites from basalts from the Shijiatun
227	Formation during the primary sedimentary cycle played a role in reduction spot
228	formation as a source of vanadium in the Jiaozhou Formation. A more detailed
229	sedimentological analysis involving the identification of transitional facies, like
230	lacustrine shorefaces, can only be undertaken by consideration of surface outcrops
231	and the 3D geometry of the facies (e.g., Deschamps et al. 2020). Such an analysis will
232	be the focus of future research.

3. Materials and Methods

This study is based on analysis of the JK-1 borehole from Jiaozhou City in 235 Shandong Province and its correlation to the LK-1 borehole that is approximately 236 1 km away. The JK-1 borehole (referred to as LX-1 by Yang et al., 2019) is located in 237 the north of Dongxinzhi Village, Jiaozhou City (36°16'39"N; 119°58'06" E) and was 238 239 drilled by the Shandong Institute of Geological Survey. Borehole LK-1 is located to the west of Beixinzhi Village (36°15′57.98″N; 119°57′10.76″E) and was drilled by the 240 Institute of Geology of the Chinese Academy of Geological Sciences and Shandong 241 Institute of Geology in Jiaozhou (Li, Wang et al., 2016, 2020; Tian et al. 2021; Yu et 242

243 al., 2021; Fig. 1).

244	Cores from the boreholes were logged, and lithology, grain size, sedimentary
245	structures (along with a detailed log of the colour variations) were collected. Vertical
246	profiles, coarse grain size, arrangement of facies and associated biota indicate that the
247	sediments were deposited in an alluvial-fan lacustrine environment. The charophyte
248	flora in LK-1 (Li et al., 2020) indicate the presence of shallow freshwater lakes and
249	minor brackish ephemeral lakes associated with gypsum crusts and calcareous soils.
250	Reduction spots occur from 624–550 m in borehole JK-1 in brick red siltstone to
251	fine sandstone. Samples were collected from 628 m, 624.8 m, 621.4 m, 611.1 m,
252	600 m, and 593.2 m depth and numbered $zk01$ to $zk06$ respectively. Of the samples,
253	zk01 to $zk04$ did not contain reduction spots and had the suffix r added to denote their
254	red colour, while $zk05$ contained a few small reduction spots and also had the suffix r
255	added to denote its dominantly red colour. Sample $zk06$ was divided into two and re-
256	labelled $zk06r$ for red sediment and $zk06g$ for the green part. In addition, 16 samples
257	containing frequent reduction spots were photographed from 550.8 m to 599 m in the
258	borehole core to analyze their physical features.
259	Samples with reduction spots were prepared by petrographic thin section before
260	being observed under stereomicroscope and transmission polarizing microscopy in the
261	Geological Lab Center at Liaoning Technical University (LNTU). Samples were
262	powdered to 180 μ m mesh to analyze clay mineral composition using X-ray
263	diffraction, and to analyze major and trace elements using an Axiosm AX AB104L X-
264	ray fluorescence spectrometer and NexION300D Plasma mass spectrometer. To

265	determine loss on ignition values, individual samples were weighed then heated in
266	crucible from 500 $^\circ\!\mathrm{C}$ to 1000 $^\circ\!\mathrm{C}$ for 60 mins and weighed again to determine loss.
267	Using the results from the major elemental analysis, we calculated the Chemical Index
268	of Alteration (CIA; Nesbitt and Young, 1982) and the Weathering Index of Parker
269	(WIP; Parker, 1970) to quantitatively evaluate the weathering state of the investigated
270	rock samples. The CIA is calculated as
271	$Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100$
272	while the WIP is expressed as
273	$(2Na_2O/0.35 + MgO/0.9 + 2K_2O/0.25 + CaO^*/0.7) \times 100$
274	CaO* in the CIA refers to the calculated calcium content in the silicate fraction
275	(McLennan et al., 1993).
276	Sample <i>zk06g</i> was scanned for Micro X-ray Computed Tomography (XCT) using
277	a Zeiss Xradia 510 Versa at the Key Laboratory of the Institute of Geomechanics,
278	Chinese Academy of Geological Sciences, Beijing. This method uses X-rays to collect
279	3D data of the sample's internal structure in which material density differences are
280	reflected in the data by changes in X-ray attenuation. The scan was performed with
281	112 kV voltage, 112 μ A current, and an exposure time of 1.5 s. No optical
282	magnification was employed. The resultant 3D data attained a resolution of 22.01 μm
283	per voxel (3D pixel). An image stack containing 1024 16-bit grayscale image slices,
284	each 1024x1024px in size, was created. These were imported into a non-commercial
285	version of Dragonfly (v2021.1; Object Research Systems (OSR) Inc.;
286	https://www.theobiects.com/dragonfly/) for 3D volume rendering and analysis. In

287	addition, a second 8-bit version of the dataset was generated with stretched
288	brightness/contrast to aid the 3D surface rendering. First the datasets were cleaned by
289	masking and removal of extraneous noise from outside the specimen. Then five
290	regions of interest (ROIs) were selected and segmented by pixel thresholding of the
291	16-bit data, each representing a different material density range and visualised by a
292	separate false colour. The false colours used are from (lower density) dark blue > light
293	blue > yellow > red (higher density). Statistics from ten selected areas within the
294	specimen were obtained, five from the red sediment and five from the reduction spot,
295	using manually placed 1 mm ³ cube-shaped ROIs within the 16-bit data, for which
296	minimum, maximum, mean, and standard deviation of the voxel values were
297	calculated to determine density variations. Video animations of the 3D data were
298	composed from Dragonfly generated images within the open-source software Blender
299	(v3.1; The Blender Foundation; https://www.blender.org/).
300	Finally, samples $zk06r$ and $zk06g$ were broken into parts and the different
301	coloured sediments were analyzed with a FEI Nova Nano SEM450 field emission
302	scanning electron microscope (FE-SEM) at the Analysis and Testing Center of Beijing
303	Research Institute of Uranium Geology. This analysis was to observe surficial features
304	of the samples and to undertake geochemical analysis using the machine's Energy
305	Dispersive Spectrometer (EDS) to identify the chemical composition at specific
306	points.

4. Results and interpretation

4.1. Correlation of the LK-1 and JK1 boreholes and depositional facies

310	Sedimentary logs of JK-1 and LK-1boreholes are shown in Figure 2. Correlation
311	between the boreholes is made from the position of the top of the stratigraphically
312	youngest basalt (614 m in LK-1, 628 m in JK-1) which marks the boundary between
313	the Shijiatun and Jiaozhou formations (Ding, 2016; Ji, 2017; Li et al., 2018; Wang et
314	al., 2019; Han et al., 2020; Li et al., 2020). The depth of the K/Pg boundary has been
315	identified from the Ir anomaly and GR profile at 523.35m in LK-1, and the GR profile
316	at 537 m in JK-1 (Xu et al. 2017; Yang et al. 2021). After the volcanism of the
317	Shijiatun Formation, the sedimentary succession commenced with a high energy
318	alluvial fan facies that changed into lacustrine facies just below the K/Pg boundary.
319	The two episodes of lacustrine facies are typified by mudstones and siltstones in the
320	distal settings and sandstones in more proximal settings (Fig. 2).
321	Variations in the lithological features allow us to characterise the depositional
322	environments further. Based on grain size trends and sandstone/mudstone ratios, there
323	are clearly differences between the two boreholes. The lower part of the Jiaozhou
324	Formation below the K/Pg boundary is similar in both the JK-1 and LK-1 boreholes.
325	Similarly, the lacustrine interval which spans the K/Pg boundary is of similar
326	thickness and shows a similar profile in both boreholes. Above the K/Pg boundary
327	there are marked differences between the boreholes. In JK-1, the almost 50 m thick
328	alluvial section from 517–463 m is very variable in grain size. The equivalent section
329	in LK-1 from 500-448 m is coarser grained and less variable. Above this level the
330	differences become accentuated even further: JK-1 is represented by finer grained

331	sediments as lacustrine systems become dominant from 463–364 m, whereas in LK-1,
332	coarse alluvial sediments dominate the section. Near the top of the profile (364–324 m
333	in JK-1 and 351–310 m in LK-1) there is a return to more widespread lacustrine
334	conditions. The lacustrine sections in JK-1 are in a more distal position within the
335	depositional basin with finer grained sediments (Fig. 2).

337 4.2. Reduction spot morphology

In the JK-1 borehole, pale green reduction spots occur from 624–550m. 338 339 Typically, these reduction spots have a dark grey, brown or black locus (or core) surrounded by a 'bleached' grey-green outer zone which contrasts sharply with the 340 surrounding host red sediment. Figure 3 shows typical reduction spots including 341 342 spheroidal (Fig. 3A, 3B), irregular (Fig. 3C–3F, 3H), and tubular (Fig. 3C, 3G, 3I) forms. The largest reduction spot in Figure 3C is irregular but has a tubular part with 343 an elongated locus. In all cases where a locus is visible, the shape of the reduction 344 345 spot exaggerates the overall shape of its locus, so the reduction spot appears to have developed around its locus. The irregular reduction spot shown in Figure 3C branches 346 347 and has the appearance of a fossil plant axis or a palaeosol root. The other two reduction spots are tubular and have elongated loci; the overall reduction spot shapes 348 exaggerate the shapes of their loci. Figure 3G shows vertical and near-vertical 349 orientated tubular reduction spots that may represent 'rhizohalos' which formed 350 around rhizoliths in palaeosols that developed on floodplains and around lake margins 351 (Trendall et al., 2013). The reduction and removal of iron oxides around rhizoliths is 352

widely reported in palaeosol studies (see Retallack, 2008; Kraus and Hasiotis, 2006).
The spheroidal reduction spots illustrated in Figures 3A, B do not show visible loci
but most likely formed around small fragments of organic material that was
incorporated from plant communities on the floodplain and lake margins. It is possible
that the loci in some reduction spots may not be visible because the plane of the image
does not pass sufficiently close to the center of the spot.

Irregular and tubular forms typically have their long axes orientated parallel to 359 bedding (Fig. 3C, 3I) and have smaller vertical extents suggesting they formed in 360 361 early diagenesis prior to sedimentary compaction. In the JK-1 borehole, reduction spots range from 0.1 mm diameter spheroids (Fig. 3A; Table 2) to irregular bodies up 362 to 65 x 40 mm (Fig. 3C–H; Table 2) in maximum dimension. Unlike larger reduction 363 364 spots, the smallest ones of less than 0.5 x 0.5 mm diameter do not noticeably affect the overall red colour of the rock (Fig. 3C, 3E). In many of the reduction spots, the 365 colour is slightly heterogenous with occasional small flecks of red less than 0.5 mm in 366 diameter (Fig. 3D, 3E). 367

Reduction spots occur in red coloured mudstone, argillaceous siltstone,
siltstone and fine sandstone (Table 2). Measurements taken come from two
dimensional planes for which three-dimensional structure is more accurately
characterised from X-CT results (see below). Maximum dimensions of reduction
spots in mudstones are 22 x 20 mm (Fig. 4A; Table 2), while in argillaceous siltstone,
siltstone and fine sandstone, there are abundant small ones less than 0.3 x 0.3 mm,
while the largest are up to 60 x 40 mm in argillaceous siltstone, 65 x 25 mm in

375	siltstone, and 50 x 40mm in fine sandstone (Fig. 4A; Table 2). Spherical reduction
376	spots vary in size from 0.1–40 mm in diameter, while tubular ones from 6–65 mm and
377	irregular ones from 3–50 mm in their maximum dimensions (Fig. 4B; Table 2); there
378	is no consistent relationship of the reduction spot size to shape. Reduction spots with
379	diameters of less than 10 x 10 mm consistently lack distinguishable loci, while larger
380	reduction spots typically have distinguishable loci and occur in argillaceous siltstone,
381	siltstone and fine sandstones (Fig. 4C; Table 2). There is no clear relationship between
382	reduction spot size and how sharp or gradual their boundary is with the surrounding
383	sediment other than those with largest diameters (>40 mm) have sharp rather than
384	gradual boundaries (Fig. 4D; Table 2). Reduction spots with loci and a sharp boundary
385	usually occur in very fine grained lithologies from mudstone and argillaceous siltstone
386	(Fig. 4D), whereas reduction spots in sandstones more often contain gradual
387	boundaries with the surrounding red sediment.
388	Petrographic images through the margin of a reduction spot in a red, fine-grained
389	sandstone are shown in Figure 5A and 5B. Figure 5A shows a stereoscopic image of
390	the very sharp boundary between the reduction spot and host sediment. In the drab
391	area clear quartz grains are completely free of pigmentary iron oxides. The red host
392	rock shows pigmentary grain coatings and the interstitial matrix is also stained red
393	with fine grained iron oxides. Figure 5B shows a thin section photomicrograph of a
394	reduction spot (left) and red host sediment (right). Red pigmentary oxides are
395	interspersed in the matrix and there are also abundant opaque specularite grains that

396 are probably oxidized titanomagnetite. Note that these opaque grains have a strong

pigmentary grain coating. In contrast the reduction spot lacks abundant opaque
minerals and pigmentary hematite. The sediment is arkosic with abundant feldspar
overgrowths.

400

401 **4.3. Fossil composition**

402 In the JK-1 borehole from the 74m interval with reduction spots, plant fossils are typically from 1–7 mm wide and up to 50 mm long with sinuous rather than straight 403 profiles and occasionally branch; these represent roots from palaeosols. Invertebrate 404 405 fossils are extremely rare in this interval and, where present, are fragmentary, small (typically 1-3 mm) and often unidentifiable. Occasional fossils or fragments of fossil 406 407 occur without reduction spots enveloping them, including shell fragments and the 408 charcoal fragment shown in Figure 3I and 3J. These organic particles appear to have been inert during diagenesis and did not result in reduction spot formation around 409 them. Variations in the nature of the organic matter in the sediment and its relationship 410 to reduction spot formation is further considered below (see discussion). 411

412

413 4.4 Major and trace elements analysis

414 Major and trace element compositions of green reduction spots and the red host 415 sediments are shown in Table 3 and Figure 6. The overall composition of the samples 416 is very similar to that seen for sandstones in comparable tectonic settings (Middleton, 417 1960). There are only minor variations in major elements; the SiO₂ content ($\bar{x} = 52\%$) 418 of siltstone and argillaceous siltstone samples numbered zk04 and zk05 is lower than

419	that of fine sandstone samples zk02, zk03, zk06r and zk06g ($\bar{x} = 64\%$) (Fig. 6A, C).
420	This is consistent with the fact that the finer grained lithologies are more poorly sorted
421	and contain a higher proportion of clay minerals. Al ₂ O ₃ , Na ₂ O, K ₂ O, MnO, TiO ₂ , P ₂ O ₅
422	and FeO contents of all samples show little difference (Fig. 6A, C). Sample zk05r
423	contains much more CaO than any other samples, which suggests the siltstone to have
424	a calcium carbonate cement, possibly of pedogenic origin (Fig. 6C).
425	Chemical Index of Alteration (CIA) values varies from 64.9–69.0 except for
426	sample zk05r which is significantly lower at 37.0 (Table 3), while Weathering Index
427	of Parker (WIP) values vary from 36.5–49.8. Both of CIA and WIP results show the
428	siliclastic sediments in the source area have undergone moderate weathering.
429	The total iron content (Fe ₂ O ₃) of the measured samples varies from 1.94 to
430	6.84% and the mean of red samples is 4.8%, a little higher than the overall average for
431	red sandstones which is 1.7–3.5% according to Van Houten (1973). Typically, the
432	amount of total iron increases with decreasing grain size and the average value of red
433	mudstones is between 3.3–4.7%. The data presented here show a strong negative
434	correlation between total iron and ferrous iron. The reason for this is unclear, but it
435	maybe that grain size exerts a strong influence on iron composition.
436	Loss on ignition (LOI) values are shown in Table 3 and Figure 6A. Values range
437	6.65–14.93% ($\bar{x} = 9.42$) and are relatively high. The lowest LOI values occur in
438	sample zk06r (red sediment, 6.65%) and zk06g (green reduction spot, 6.66%), with
439	other samples from the red sediments having significantly higher values than the
440	reduction spots. LOI has been routinely used as a proxy for organic material in soil

441	science (Jensen et al., 2018). These authors showed that the conventional conversion
442	of soil organic carbon = 0.58 LOI can be misleading, especially when the clay content
443	is high, such that LOI values by themselves cannot be used to infer organic materials
444	(OM) concentrations. The high values we record might be attributed to a higher clay
445	(montmorillonite) content. The fact that the LOI values in zk06r and zk05g are similar
446	would suggest similar organic carbon contents. Hofmann (1993) noted that the locus,
447	reduction spot body sand host rock in a wide range of reduction spots had very low
448	organic content (0.02% or less) but were always mineralised and characterised by the
449	presence of roscoelite.
450	Comparison of trace elements (Fig. 6B, D) shows that each sample has nearly the
451	same trace element composition except for the elements V, Sr, Ba and Zr, although
452	there are small differences in Sr, Ba and Zr. However, the reduction spot sample $zk06g$
453	has a concentration of up to 512 $\mu g/g$ and contains almost five times the vanadium
454	content of the other samples that have an average content of 77.56 μ g/g. The average
455	content of vanadium in the Earth's crust is approximately $135-140\mu g/g$, while it is
456	approximately 130 $\mu g/g$ in shales and 20 $\mu g/g$ in sandstones and carbonate rocks (Li,
457	1976; Mason and Moore, 1982; Tian and Zhang, 2016). Therefore, the vanadium
458	content in the reduction spot sample $zk06g$ is anomalously enriched. Vanadium
459	enrichment in drab zones and reduction spots has been described by multiple authors
460	(Turner, 1980; Hofmann, 1991).
461	

4.5 X-ray diffraction analysis

463	Samples <i>zk03r</i> , <i>zk05r</i> and <i>zk06r</i> (red beds) and <i>zk06g</i> (reduction spot) were
464	analyzed by X-ray diffraction to identify their mineral compositions to consider if
465	there is a difference between the reduction spots and host red bed sediments (Fig. 8).
466	Results indicate similar mineral compositions in the host red sediment and reduction
467	spots, comprising quartz, feldspar, mica, montmorillonite, maghemite and harmotome.
468	The overall mineral composition of the Jiaozhou Formation is comparable to
469	many other continental red beds, especially those composed of first cycle alluvium
470	(Suttner and Dutta, 1986) with quartz, feldspar and mica, the main framework
471	constituents. The iron oxide maghemite (oxidized titanomagnetite) and the barium
472	zeolite mineral harmotome may represent minor detrital components derived from the
473	intercalated basalts; harmotome is normally associated with higher temperatures and
474	is most commonly found in basaltic rocks. The swelling clay montmorillonite forms
475	as a result of intrastratal alteration of feldspars and ferromagnesian silicates (Walker,
476	1976; 1978) and represents cements formed during diagenesis. During burial
477	montmorillonite is transformed into illite (Pytte and Reynolds, 1989). This transition
478	has widely been used as a geothermomenter (Pollastro, 1993) with the onset of
479	transition starting at about 100°C closely coincident with the start of petroleum
480	generation. The XRD results indicate that montmorillonite (smectite) is the dominant
481	clay mineral. On this basis we conclude that the rocks have not been deeply buried or
482	subjected to petroleum generation. Although we are not able to identify the mineral
483	from whole rock XRD data, the data do show a small peak at $9^{\circ} 2\theta$ which would
484	correspond to the 001 reflection of roscoelite (Fig. 8).

4.6 3D X-ray Computed Tomography (XCT)

487	Sample <i>zk06g</i> including a spherical reduction spot with dark locus in red
488	sediment was observed under 3D XCT to analyse three-dimensions density variations
489	in its internal structure. Results from the XCT data surface rendering (Fig. 9A-C),
490	relative density false colour segmentation (Fig. 9D–F) and combination of the surface
491	rendering and false colour segmentation (Fig. 9G-I) all enable the boundary of the
492	reduction spot to be distinguished from the surrounding sediment. The CT rendering
493	(Fig. 9A–C) allows the external surface of the specimen to be visualised, with the
494	reduction spot visible as a darker zone compared to the surround red sediment. This
495	distinction is more visible in the false colored segmentations (Fig. 9D–F), where
496	discrete ranges of different relative density material, from lower to higher density, are
497	shown as: dark blue > light blue > green > yellow > orange > red. The sharp boundary
498	of the reduction spot can be readily identified from the false colour images due to its
499	general relative low-density reflected by its overall blue colour, whereas the
500	surrounding sediment has an overall orange colour (Fig. 9 D-F) depicting relative
501	higher-density composition. The reduction spot also has a lower frequency of relative
502	high-density contents compared to the surrounding sediment, and these are typically
503	of smaller size (Fig. 9D–F). The combined CT rendering and false colour overlays
504	(Fig. 9G–I) show the same as the separate lines of evidence but make it easier to
505	identify the position individual minerals on the surface of the specimen.
506	Analysis of the ten manually placed regions of interest in the sample show the

mean 16-bit grayscale pixel value, which equate to relative density. For the five values 507 from the reduction spot this is 8359.9, whereas the mean of the five values attained 508 509 from the red sediment is approximately 4.1% higher at 8704.8 (Table 4). Small, irregular and high-density features occur throughout the sample in both 510 511 red sediment and reduction spots, but this method does not permit their composition 512 to be identified with certainty. The high-density objects shown in red in the false colour model may represent metallic-rich minerals of detrital origin or organic tissues 513 that have decayed and been mineralized by vanadium or other transition metals. The 514 515 relative mid-density features in orange are smaller and appear much more frequent in the red sediment than within the reduction spot. 516

517

518 **4.7 Energy Dispersive Spectrometry (EDS)**

The positions of Energy Dispersive Spectrometer (EDS) point analyses are shown in Figure 10 and the corresponding results in Table 5. Samples P7, P10 and P11 (Table 5) are from the reduction spot loci whilst P17, P18 and P19 are from green reduction spot bodies. Two of the sample points P3 and P5 show higher proportions of iron (78.7–79.8%) and chromium (17.5–18.1%), possibly indicating the presence of chromite (FeCr₂O₄), most likely of detrital origin. The composition of samples from the reduction spot loci and bodies are broadly

- similar with only minor differences between silica, magnesium, sodium, and calcium
- 527 (Table 4). There are however important differences between potassium (0.85% vs
- 528 1.51%), aluminium (10.63% vs 8.44%), iron (0.85% vs 1.17%) and vanadium (0 vs

529	1.51%) (spots P3 and P5 are excluded from the mean calculation). These data lend
530	further support to the idea of redistribution of elements during reduction spot
531	formation. It suggests to us that whilst vanadium was originally sequestered by
532	organic material in the loci of the reduction spot, as the organic material was
533	metabolized V was released back into the system along with other elements including
534	potassium and iron. During subsequent diagenesis it may well have been incorporated
535	into other inorganic minerals. Although not identified in our XRD data, probably
536	because of limitations on the detection limits, it seems likely that the V may be
537	present in the reduction spots as roscoelite (K (V^{3+} , Al.Mg) ₂ AlSi ₃ O ₁₀ (OH) ₂).
538	
539	5. Discussion
540	5.1. Palaeoenvironment of red beds in the Jiaozhou Formation
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551	iron oxides. Colour variations are noted relating to the degree of pedogenesis on
552	alluvial floodplains. The red colouration is produced by the aging of hydrated iron
553	oxides and the formation of hematite during diagenesis and pedogenesis. The late
554	Cretaceous red beds of the Jiaozhou Formation comprise first cycle detritus supplied
555	by the high-grade metamorphic rocks and Cretaceous igneous lithologies of the Sulu
556	Orogen and the basic igneous lithologies underlying the formation. Furthermore, the
557	influx of terrigenous sediment also introduced allochthonous labile and refractory OM
558	(discussed below). The presence of occasional gypsum crystals indicates periods of
559	periodic evaporation, in which plants colonized the sediment, developing root
560	complexes, and eventually calcareous palaeosols. Continued high sedimentation rates
561	would have led to these palaeosols becoming inundated in turn.
562	The sandstones show dissolution and alteration of feldspars and ferromagnesian
563	silicates with the precipitation of authigenic quartz, clay minerals, feldspars and iron
564	oxides. The presence of finely crystalline hematite on detrital grains is consistent with
565	a diagenetic origin of the red colour (Walker, 1967, 1974, Turner, 1980), however, we
566	cannot rule out the presence of detrital ferric hydroxides. The clear implication is that
567	the sediment was non-red at the time of deposition and has become red during burial
568	and diagenesis.
569	Sr/Ba and Fe/Mn ratios and MnO_2 content can reflect the palaeosalinity of
570	sedimentary environment (Liu, 1980). All the samples from the JK-1 core have Sr/Ba

- 571 < 0.6, Fe/Mn>5, and the average content of MnO₂ is 0.00052 indicating that the
- 572 clastic rocks formed in continental freshwater sedimentary environments (e.g. Turner,

1980). 573

574	The ratios of Cu/Zn, (Cu+Mo)/Zn, and Sr/Cu can indicate redox conditions in
575	sedimentary environments (Hallberg et al., 1976). In the JK-1 borehole, the red beds
576	formed in an oxidizing environment with high temperature because the ratio value of
577	Cu/Zn and (Cu+Mo)/Zn were less <1 and value of Sr/Cu were close to and slightly
578	higher than 10.
579	Quality fraction of oxides and the corresponding ratio of K ₂ O/Na ₂ O plotted
580	against SiO_2/Al_2O_3 (Fig. 7a) shows that samples from the JK-1 borehole formed in an
581	active continental margin setting (Roser and Korsch, 1986). Composition of the trace
582	elements La, Th and SC in sandstone, plotted in a ternary diagram (Fig. 7b), shows
583	that red beds have composition similar to those from active continental margins
584	settings and formed related to volcanism (Mao and Liu, 2011; Tian and Zhang, 2016;
585	Fig. 7b).
586	
587	5.2. Origin and nature of organic matter in the Jiaozhou Formation
588	In the Jiaozhou Formation, organic matter (OM) is abundant and derived from
589	organisms living in the alluvial to lacustrine environments including terrestrial and
590	aquatic plants, wind- and water-borne pollen and spores, invertebrate and vertebrates.
591	In the JK-1 core, the OM comprises fine-grained, amorphous particles that have been
592	reworked and distributed by sedimentary processes, and larger (mm-cm diameter)
593	carbonaceous plant axes and roots from palaeosols, as well as occasional charcoalified
594	plant matter. From the LK-1 borehole Li et al. (2020) and Tian et al. (2021)

595	documented charophyte and gastropod assemblages, with charophytes restricted to
596	aquatic environments while gastropods are vagrant and can live in water and damp
597	terrestrial conditions. In the JK-1 borehole, reduction spots formed over a relatively
598	narrow stratigraphic interval in the basal 74 m of the Jiaozhou Formation spanning an
599	estimated duration of 0.45 Ma (Fig. 2). During this interval, palaeosol development
600	indicates a hiatus in sedimentation for plants to grow, increasing the concentration of
601	OM as rootlets and litter.
602	The survival of plant matter in the Jiazhou Formation is unsurprising but it only
603	occurs within reduction spots. Plant tissues, especially those that provide structural

604 support (i.e. contain cross-linked macro molecules such as lignin) may be

605 taphonomically recalcitrant and geologically stabilized during diagenesis (Briggs,

606 1999). Similarly, as products of wildfire, charcoalified plant tissues (= the coal

607 maceral inertinte) are refractory and do not undergo decay post-mortem during burial

and early diagenesis due to high carbon content (e.g., Scott, 2010). However, non-

609 plant OM in the Jiaozhou Formation is often difficult to identify, most likely due to

610 the taphonomic processes that occurred pre and post burial. Labile organic

611 components (e.g. non-biomineralised, soft tissues such as skin, internal organs, hair,

612 feathers) rapidly undergo post-mortem decay from microbial activity either before or

during burial or early diagenesis (e.g., Brenchley and Harper, 1998; Tyson, 1995). In

614 contrast, refractory organic components comprising organic hard parts containing

615 collagen and inorganic minerals, including calcium phosphate (e.g., vertebrate bones,

teeth, scales), calcite, or aragonite (e.g., mollusc shells) are more recalcitrant,

617	decaying at a slower rate (Brenchley and Harper, 1998, Tyson, 1995). The principal
618	abiotic process of collagen breakdown is hydrolysis, which may occur alongside
619	microbial degradation. Demarchi et al. (2016) identify the major control on collagen
620	preservation in porous minerals to be the surface binding of the component collagen
621	peptides to the mineral skeleton, which stabilizes both the peptides and the water in
622	contact with them. They suggest that collagen under these conditions may remain
623	substantially intact for millennia. Consequently, the release of collagen from
624	refractory organics due to hydrolysis is extremely slow, which suggests that the
625	concentrations of organic material produced abiotically from a refractory organic
626	would be unlikely to build up sufficiently to generate reduction spot loci, which is
627	consistent with the absence of refractory organics in the reduction spots seen in our
628	data. Acidic burial conditions and microbial metabolism will cause mineral
629	dissolution and exacerbate the speed of collagen break down (Collins et al. 1995,
630	2003; Collins and Riley, 2000). The abiotic breakdown of collagen is also temperature
631	dependent, with degradation rates increasing at higher temperatures (Collins et al.
632	1995) and higher temperatures also increase the rate of degradation due to microbial
633	action (Briggs and Kear 1993b). The breakdown of organics by microbial action
634	would alter the geochemistry of the surrounding sediment and would be the potential
635	trigger/driver to the formation of reduction spots. A potential model for the formation
636	of these reduction spots is discussed below.
637	

5.3. Source of vanadium

639	The origin of vanadium is unknown but is likely to have been derived from the
640	underlying basic igneous lithologies either through the weathering and its absorption
641	into groundwater, or as detrital grains in the first alluvial cycle. It is likely to have
642	been ubiquitous in the interstitial water through the sediment but in very low
643	concentrations as suggested by its low concentration in the sedimentary red beds
644	(Tables 3, 4). Vanadium is concentrated and precipitated in reduction spots as outlined
645	below.

647 **5.4. Model for reduction spot formation in the Jiaozhou Formation**

A model showing the formation of the reduction spots is shown in Figure 11. 648 649 After burial, labile OM decays in the sediment under aerobic conditions (Stage 1 in 650 Figure 11). Microbial metabolism of labile tissues would use, and deplete, the available free oxygen from porewater, while increasing levels of waste bi-products 651 including CO₂ (aq), H₂SO₄, as well as liberating organic ligands from the OM, such as 652 fatty acids, (see Briggs and Kear, 1993a, 1993b). The release of these metabolic bi-653 products would alter the geochemical conditions directly around the OM, creating 654 655 localised microenvironments that were oxygen depleted, acidic, and increasingly reducing (e.g. Sagemann et al. 1999; Raiswell and Fisher 2000) (Stage 2 in Figure 656 11). At this stage the microbial communities would begin to use iron oxides as a 657 respirant and the migration of released iron would be set in place. Lentini et al. (2012) 658 have shown that iron-reducing bacterial communities are influenced by the oxide 659 mineralogy and the nature of the carbon substrate. The hydrated oxides ferrihydrite 660

and goethite are more reactive than hematite. Lentini et al. (2012) showed that only 661 ferrihydrite was reduced in the presence of acetate, but when glucose and lactate were 662 663 available goethite and hematite were also reduced. This change coincided with the presence of *Desulfobrivio* spp. and *Enterobacter* spp. indicating the presence of 664 sulphate reduction and fermentation processes. Information on the range of microbial 665 groups and their activity with different carbon sources is described by Su et al. (2020). 666 As OM consisting of labile tissues was the fuel source for the microbial metabolism, 667 these OM would have, therefore, acted as the locus points for these geochemically 668 669 distinct microenvironments that typically would have expanded isotropically by molecular diffusion (Stages 3 and 4 in Figure 11). This explains the typical spherical 670 nature of many of the reduction spots observed surrounding smaller fragments of OM. 671 672 Around larger OM fragments (e.g., plant roots), the reduction spots are larger and often mimic the morphology of the OM – adding further evidence that the OM acted 673 as a fuel source for the generation of microbial-induced microenvironments. In the 674 675 Jiaozhou Formation, fossil plant remains are only found in association with reduction spots. Conversely, we do not observe reduction spots around refractory OM such as 676 charcoalified plant matter (fusinite) or non-labile shell material, further strengthening 677 the hypothesis that the microbial metabolism of labile tissues drove the generation of 678 reducing microenvironments within the sediment. 679

680 Sediment porosity would have been a key factor in limiting the diffusion of decay 681 products away from the OM (see McCoy et al. 2015). In the Jiaozhou Formation we 682 observe that the boundary of the reduction spot is diffuse in the coarser-grained fine sandstones, whereas the boundaries of these redox zones are much sharper in mud and silt dominated sediments. The spherical nature of many reduction spots suggests that there was little or no flow in the groundwater during their formation; asymmetry or diffusion (and eventually obliteration of the microenvironment) might be envisaged along the primary flow direction if present. In our analysis, irregular shaped reduction spots only developed around irregular shaped fossil plant loci, with reduction spot margins developing uniformly around these irregular shapes.

Once the available oxygen in porewater has been consumed, bacterial populations 690 691 within the sediment would be forced to utilise other oxidants during the breakdown of OM (Allison, 1988). In terrigenous sediment with ample supply of Fe, it is highly 692 likely that within the localised anerobic reduction zone, Fe was utilised by the bacteria 693 694 as an electron acceptor. Furthermore, it is possible that as the iron oxides are reduced, the Fe^{2+} is more mobile and may have diffused away from the reduction spot further 695 depleting the microenvironment around the OM. This would explain the lower 696 697 relative density of the reduction spots in relation to the surrounding red beds which would have higher proportions of dense pigmentary iron oxides including hematite 698 (see XCT results). 699

As the pore water becomes more reduced, the vanadium and is fixed in association with the OM and changes valency from V^{4+} to V^{2+} . It should be noted that anerobic bacteria often show anerobic plasticity, and that some species of vanadium reducing bacteria have been identified (Myers *et al.* 2004). This results in a reduction spot with elevated V concentrations compared to the host sediment. The form in which the V is present is not known; we have not identified any of the common V-bearing minerals such as roscoelite.

The microenvironments around the OM would have been sustained until the OM fuel source was exhausted — as can be potentially identified by our LOI values but agreeing with the low OM concentrations in reduction spots reported by Hofmann (1993), or until conditions became unfavorable for bacterial activity to continue. Our observations of smaller reduction spots without OM loci could represent an exhausted fuel source.

713 Finally, as the sediment became buried, compacted, and moved into early diagenesis, the localised sediment surrounding OM became green due to the removal 714 of Fe and the fixation of V and U, while the main sedimentary matrix became red as 715 716 iron oxide precipitated. Where reduction spots have very sharp boundaries (e.g., Fig. 5A-C) it indicates the maximum extent or outer limit of the removal of pigmentary 717 iron oxides. The fate of the iron removed in this way is not clear, but it is plausible 718 that it has been used as a metabolic agent for anerobic bacterial metabolism (Berner, 719 1981; Allison, 1988). It would depend on the chemical conditions of the reducing 720 fluid, not least the presence of Cl⁻ which would increase the solubility of iron. Iron 721 oxide would be reprecipitated as soon as oxidizing conditions return, for example as 722 small Fe-Mn nodules as seen in some Triassic palaeosols (Trendall et al., 2013), or it 723 could become incorporated into other authigenic minerals which might be forming at 724 the same time e.g. as newly formed pigmentary hematite. 725

727 **6. Conclusions**

728	(1) The palaeoenvironement of the latest Cretaceous continental red beds from
729	the basal part of the Jiaozhou Formation in the Jiaolai Basin, North China, is
730	reinterpreted as high energy alluvial fan and fan delta facies that changed into
731	lacustrine facies just below the K/Pg boundary.
732	(2) In the Jiaozhou Formation, reduction spots formed in the first alluvial cycle
733	around fossil plant tissues in palaeosols during early diagenesis. The geochemical data
734	from reduction spots is consistent with the migration of Fe^{2+} from the reduction spot
735	into the surrounding sediment. Subsequent oxidation would likely enhance its red
736	colouration. Vanadium is strongly enriched in the reduction spot loci due to
737	incorporation of VO^{2+} in organic compounds, thereby contributing to the dark colour
738	of the reduction spot loci.
739	(3) In the past there has been disagreement on how continental red beds became
740	red, with different studies suggesting it was either from incorporation of oxidized,
741	reddened alluvial sediments, or through in-situ intrastratal alteration during
742	diagenesis. In the Jiaolai Basin the sharp colour contrast between the grey-green
743	lacustrine and red alluvial sediment shows that there was an important depositional
744	control. Our observations of intrastratal oxidation of silicates and titanomagnetites
745	shows that both processes were operative and provided a complex environment in
746	which the reduction spots formed.
747	(4) X-CT analysis reveals reduction spots have a lower relative density,

748 presumably resulting from the migration of Fe from the reduction spot to the

surrounding sediment where it deposited as thin coatings of pigmentary iron oxides onmineral grain surfaces during diagenesis.

(5) We develop a four-stage taphonomic model for the formation of reduction 751 spots in the Jiaozhou Formation. Microbial metabolism of labile fossil components 752 generated localized geochemical conditions that reduced Fe³⁺ into the more mobile 753 Fe²⁺, which would be depleted or removed via continued metabolism or diffusion, 754 while simultaneously the reduction of V^{4+} to V^{2+} reduced the density of the reduction 755 spots. This process would also change the colour of the spots into the grey-green hue. 756 Meanwhile refractory fossils within the sediment, such as charcoal, could not be 757 utilized by microbial activity, which explains why these fossils do not act as loci for 758 the reduction spots. 759

760

761 Acknowledgments

762	This research was financially supported by the Liaoning Provincial Department
763	of Education Youth Foundation (Grants LJ2017QL027), China Scholarship Council
764	State Scholarship Fund (Grant 201908210471), Shandong Provincial Key Laboratory
765	of Depositional Mineralization and Sedimentary Minerals Opening Foundation
766	(Grants DMSM201405), Shandong Geological Prospecting Project (Grant
767	Lukan2021-1), and National Science Foundation of China (Grant 41472092). TC is
768	funded by a Leverhulme Early Career Fellowship (ECF-2019-097). We thank
769	Engineers Kemin XU and Zhigang ZHANG (Shandong Institute of Geological
770	Survey) for sampling assistance, Junhu WANG (Beijing Research Institute of

771	Uranium Geology) and Shengxin LIU (Key Laboratory of the Institute of
772	Geomechanics, Chinese Academy of Geological Sciences) for sample analysis
773	assistance. This manuscript was improved by editorial recommendations from A. E.
774	Radwan and MeiFu Zhou, and two anonymous reviews.
775	
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1038 Figure captions



1060	sediment most likely representing palaeosol roots. H, Reduction spots in vertically
1061	split core showing intricate and irregular nature that cross-cuts bedding. I, Bedding
1062	plane showing large, tubular reduction spot with elongated black locus, and several
1063	smaller, isolated, spheroidal reduction spots. J, Enlargement from 3I showing sharp
1064	reduction spot margin with adjacent white gypsum crystal and isolated, black,
1065	refractory fossil charcoal fragment that each lack enveloping reduction spots.
1066	
1067	Figure 4. Reduction spots characteristics. A, Distribution of diameters with the
1068	lithology; B , Distribution of diameters with the shape of reduction spots; C ,
1069	Distribution of diameters with the cores contained in reduction spots; D , Distribution
1070	of diameters with the different boundary between reduction spots and red beds;
1071	
1072	Figure 5. Details of the boundary between reduction spots and host sediment. A.
1073	Stereoscope image showing the clear boundary between the reduction spot and
1074	surrounding host red sediment. B. Thin section photomicroscope illustrating the
1075	differences in opaque and pigmentary iron oxide content between host red sediment
1076	and reduction spot. Opaque specularite grains with pigmentary grain coatings are
1077	abundant in the red host sediment. Specualrite grains are less abundant and much
1078	smaller in the reduction spot area. C. Detailed thin section photomicroscope

- 1079 illustrating the sharp boundary (dashed yellow line) of the red sediments with
- abundant pigmentary hematite coating grains and the reduction spot with no
- 1081 pigmentary hematite.

1083 Figure 6. Elemental composition of reduction spot and surrounding sediments. A, Major element content of samples in JK-1 borehole; **B**, Trace element content of 1084 samples in JK-1 borehole; C, Major elements in from sediment and reduction spots in 1085 1086 the JK-1 borehole showing overall similar compositions. D, Trace element 1087 composition from the JK-1 borehole showing elevated Vanadium (V) and Barium (Ba) and depleted Cadmium (Cd) concentrations. E, Trace element composition in the 1088 JK1 borehole compared with reduction spots from Colorado (Hofmann, 1991) that 1089 1090 also show elevated Vanadium (V) but at significantly higher concentrations. 1091 1092 Figure 7. A, K₂O/Na₂O-SiO₂/Al₂O₃ diagram plotting samples from the JK-1 borehole 1093 (empty circles) against lithologies typical of continental island arcs (I), oceanic island arcs (II), active continental margin (III) and passive continental margin (IV). B, La-1094 Th-Sc discrimination diagram plotting samples from the JK-1 borehole (cope circles) 1095 1096 with sediments from passive continental margins (A), sediments related to magmatic arcs (B), ocean island alkaline basalt (C), and shale sediments in post-Archean 1097 Australia (D) (modified from Mao and Liu, 2011; Tian and Zhang, 2016). 1098 1099 1100 Figure 8. Whole rock X-ray diffraction analysis results of samples from red host 1101 rocks compared with a green reduction spot. Harmotome and maghemite are largely absent in the green reduction spot and there is a notable reduction in the amount of 1102 montmorillonite. The results are consistent with those from the XCT. 1103

1105	Figure 9. 3D X-ray Computed Tomography (XCT) analysis of sample <i>zk06g</i> showing
1106	relative density differences in the sample. Three views are shown, each rotated in a
1107	vertical plane ~45 degrees apart in a clockwise direction from left to right (e.g., D to E
1108	to F; white arrows represent the same features across views). Each view has three
1109	corresponding but distinct data visualizations (View 1 = A, D, G; View 2 = B, E, H;
1110	View $3 = C, F, I$). First visualisation A , B , C shows the surface rending of the CT data
1111	after converting and stretching to the 8-bit pixel range (corresponding grayscale scale
1112	given on right). The second D , E , F shows the false colour volume rendering based of
1113	the raw unaltered 16-bit CT data (corresponding colour scale given on right). The
1114	third G, H, I shows a combination of the previous two visualisations, overlaying the
1115	false colour data on the 3D geometry of the sample. In all views the boundary of the
1116	reduction spot and red sediment can be readily distinguished (dotted line) and is most
1117	clearly delimited in false colour images in which the reduction spot has a lower
1118	relative density (blue), contains fewer high relative density (red) features, and the
1119	contains fewer and smaller mid-high relative density orange features. The specimen
1120	does not contain the center of the reduction spot to identify the core but contains a
1121	large, rhomboidal, relative mid-density (yellow orange) crystal (labeled as X, in C, F,
1122	and I). This is particularly apparent in false colour image (F) were it stands out from
1123	the low-density background of the reduction spot. This method does not permit the
1124	density to be quantified in absolute nor the composition of the different density
1125	materials to be identified. Note that the 1cm scale bar (bottom right) is an indication

1126	of scale in the foreground only due to the orthographic projection of 3D data onto a
1127	3D plane.

	1129	Figure 10	. Back scattered	electron (BSE) analy	ses of reduction	on spots and	l black core
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- 1130 from the sample zk06g. A. P17, P18 and P19 located in the green reduction spot. B.
- 1131 P7, P10, P11in the black core area. C, D, E show analyses for the green reduction spot
- 1132 with the presence of vanadium. **D**, **E**, **F** show analyses from the black core area
- 1133 showing the absence of vanadium
- 1134
- 1135 Figure 11. Model for the formation of reduction spots in Cretaceous red beds in the
- 1136 Jiaolai Basin, China. Abbreviations: Eh=+ve = positive activity of electrons; VO =
- 1137 Vanadium oxide.
- 1138



1140 Figure 1



1143 Figure2



1146 Figure 3





- 1155 Figure 5









1165 Figure 8





1169 Figure 9





- Sediment depositied in humid, warm, freshwater depositional environment. Input of terriginous sediment and labile (
) and refractory (
) organic material (OM).
- Water table drops. Plant growth in waterlogged conditions. Some O₂ depletion. Reduction of Fe³⁺ and Mn⁴⁺





- Microbial metabolism uses available O₂ forming mildly reducing conditons in organic rich zone.
- Aging of detrital iron oxides.
- •Oxidation of Ti-magnetite with release of V, Ni into groundwater

Stage 3: Intermediate burial diagenesis (30 - 1000 m)



- Microbial respiration depletes O₂ levels creating anerobic conditions. Microbial repiratory bi-products form highly reducing microenvironments around labile OM.
- Fe²⁺ depleted by bacterial metabolism or migrates away from OM along diffusion gradients. VO combines with organics to form V-porphyrins derived from labile material.
- Intrastratal solution of silicates and precipitation of authigenic quartz, clay minerals, and hematite continues under oxidizing conditions of host sediment

Stage 4: Deeper burial diagenesis (1000 m+)



- Sediment matrix progressively reddened during diagenesis.
- Microenvironments around OM fully depleted of Fe²⁺ creating green reduction spots.
- OM cores enriched in V.
- Bacterial metabolism continues until OM exhausted (or conditions become unfavourable).

1175

1176 Figure 11