# Volcanic disturbance during the recovery of biota in the aftermath of Permian-Triassic boundary mass extinction

Shen Lijian<sup>1</sup>, Zhao Yanjun<sup>2</sup>, Zhu Zhengjie<sup>3</sup>, Liu Chenglin<sup>4</sup>, Zhao Jian-xin<sup>5</sup>, Feng Yue-xing<sup>5</sup>, Zhou Wei<sup>6</sup>, Baublys Kim<sup>5</sup>, and Golding Suzanne<sup>5</sup>

<sup>1</sup>Chinese Academy of Geological Sciences
<sup>2</sup>MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, 100037, China
<sup>3</sup>Baise University
<sup>4</sup>MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences
<sup>5</sup>University of Queensland
<sup>6</sup>Radiogenic Isotope Facility, School of Earth and Environmental Sciences, The University of Queensland

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#### Abstract

Evaporites and carbonates intercalated with volcanic beds are distributed in the Jialingjiang and Leikoupo Formations straddling the boundary of the Lower and Middle Triassic in the Sichuan Basin. High-resolution curves of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios and  $\delta^{34}$ S<sub>sulphate</sub> of marine sediments show the study section has relatively stable isotopic compositions of S and Sr except for the volcanic bed. The abrupt positive shift of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios and negative shift of  $\delta^{34}$ S<sub>sulphate</sub> occurred in the volcanic layer. The Sr isotopic curve defines a rough age range of 244 to 248 Ma. The volcanic bed is characterized by high anhydrite Th/U ratios, indicating a strong anoxic environment. The volcanic eruptions released a huge amount of CO<sub>2</sub> and SO<sub>2</sub>, which could lower temperature first by sulphate aerosols and induce subsequent climate warming by greenhouse gases. This cooling-warming cycle has triggered the overturn of the deep anoxia seawater. The synergistic effects of degassing of gases (CO<sub>2</sub> and SO<sub>2</sub>) and overturn of the deep anoxia seawater have caused the negative shifts of  $\delta^{34}$ S<sub>sulphate</sub>, and anoxic event during the volcanic eruption. Meanwhile, volcanic eruptions and associated acid rain could have enhanced the continental weathering, resulting in an increasing flux of radiogenic  ${}^{87}$ Sr. Furthermore, volcanic eruptions and related environmental changes could have imposed severe stress on the full recovery of the ecosystem since the End-Permian mass extinction, which is corroborated by fossil records.

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4 5	Lijian Shen <sup>1,2,3</sup> , Yanjun Zhao <sup>1</sup> , Zhengjie Zhu <sup>4,5</sup> , Chenglin Liu <sup>1</sup> , Jian-xin Zhao <sup>2</sup> , Yuexing Feng <sup>2</sup> , Wei Zhou <sup>2,3</sup> , Kim A. Baublys <sup>3</sup> , Suzanne D. Golding <sup>3</sup>
6 7	1 MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, 100037, China
8 9	2 Radiogenic Isotope Facility, School of Earth and Environmental Sciences, University of Queensland 4072, Australia
10 11	3 Stable Isotope Geochemistry Laboratory, School of Earth and Environmental Sciences, University of Queensland 4072, Australia
12	4 Agriculture and Food Engineering College, Baise University, Baise, 533000, China
13 14	5 Chongqing Key Laboratory of Exogenic Mineralizaton and Mine Environment, Chongqing Institute of Geology and Mineral Resources, Chongqing 400042, China
15	Corresponding author: Lijian Shen (shenlijian1019@126.com)
16	Key Points:
17 18	• This study reports high-resolution curves of Sr, S and Th/U ratios of the Early to Middle Triassic marine sediments from the Sichuan Basin
19 20	• The geochemical results suggest volcanic eruption imposed severe environmental stress in the aftermath of the End-Permian mass extinction

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#### 22 Abstract

Evaporites and carbonates intercalated with volcanic beds are distributed in the Jialingjiang 23 and Leikoupo Formations straddling the boundary of the Lower and Middle Triassic in the 24 Sichuan Basin. High-resolution curves of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios and  $\delta^{34}$ S<sub>sulphate</sub> of marine sediments 25 show the study section has relatively stable isotopic compositions of S and Sr except for the 26 volcanic bed. The abrupt positive shift of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios and negative shift of  $\delta^{34}$ S<sub>sulphate</sub> occurred 27 in the volcanic layer. The Sr isotopic curve defines a rough age range of 244 to 248 Ma. The 28 volcanic bed is characterized by high anhydrite Th/U ratios, indicating a strong anoxic 29 30 environment. The volcanic eruptions released a huge amount of CO<sub>2</sub> and SO<sub>2</sub>, which could lower temperature first by sulphate aerosols and induce subsequent climate warming by greenhouse 31 32 gases. This cooling-warming cycle has triggered the overturn of the deep anoxia seawater. The synergistic effects of degassing of gases (CO<sub>2</sub> and SO<sub>2</sub>) and overturn of the deep anoxia seawater 33 have caused the negative shifts of  $\delta^{34}S_{sulphate}$ , and anoxic event during the volcanic eruption. 34 Meanwhile, volcanic eruptions and associated acid rain could have enhanced the continental 35 weathering, resulting in an increasing flux of radiogenic <sup>87</sup>Sr. Furthermore, volcanic eruptions 36 and related environmental changes could have imposed severe stress on the full recovery of the 37 ecosystem since the End-Permian mass extinction, which is corroborated by fossil records. 38

## 39 **1 Introduction**

The End-Permian mass extinction (EPME) occurred at some 252.3 million years ago (Shen 40 et al., 2011), during which 80-96% of marine animal species and 70% of terrestrial vertebrate 41 species went extinct (Chen & Benton, 2012). The EPME was the largest biotic catastrophe 42 among the last 549 million years, and biotic diversity did not recover to pre-extinction levels 43 until the Middle Triassic (Payne et al., 2004; Shen et al., 2011). After the EPME, high-44 45 temperature environment prevailed during the early Triassic, which suppressed the ecosystem recovery (Sun et al., 2012). The ecosystems were rebuilt stepwisely through Early to Middle 46 Triassic (Chen & Benton, 2012) during which temperature dropped significantly (Sun et al., 47 2012). The establishment of the top-level predator-dominated trophic structure in the Luoping 48 49 ecosystem in China suggested complete biotic recovery and restoration of marine ecosystems during middle-late Anisian (Hu et al., 2011). 50

51 The volcanic ash bed, which subsequently transformed into a clay-type, illite-enriched 52 sedimentary rocks (namely the "green bean" rock, Tan et al., 2014), are widely distributed in 53 South China during the middle to late Triassic period. This layer is defined as the boundary of 54 the Middle and Late Triassic (Zhu, 1990). Major mass extinctions are closely associated with 55 flood volcanism, for instance, Permian-Triassic and late Devonian mass extinctions (Renne & 56 Basu, 1991; Courtillot et al., 1996; Olsen, 1999). During the period of full recovery of the 57 ecosystem until middle-late Anisian, what effects could the volcano activities related to the 58 "green bean" rocks have imposed on the environments are still unclear.

59 Marine sediments are well-developed during Early to Middle Triassic in the Sichuan basin, 60 South China (Chen & Chu, 1988), consisting mainly of rhythmically alternating carbonates and 61 anhydrites with multiple cycles (Li et al., 2014). The "green bean" rock is intercalated within this 62 section. Those sequences offer an opportunity to investigate the marine environmental changes 63 caused by volcanic activities.

64 Sulfur is cycled through a variety of environmental and biological reservoirs (Sim et al., 2015), and Sr can serve as a tool for marine sediment correlation (McArthur et al., 2012). In this 65 paper, we present a crucial study on the Early-Middle Triassic boundary using S and Sr isotopic 66 systematics and redox index of high-resolution record of evaporitic sequence in the Sichuan 67 68 Basin, South China. Published carbonate-associated sulphate (CAS) records often show a large scatter of values and some studies have shown that diagenesis can significantly alter the original 69 70 signal (Present et al., 2015). Certain analytical methods may lead to erroneous results due to the incomplete elimination of non-CAS sulphur-bearing components (Wotte et al., 2012). Claypool 71 72 et al. (1980) proposed that evaporite  $\delta$ 34S is generally accepted as recording true seawatersulphate isotopic values. Thus it is desirable to confirm seawater sulphur isotopes with the 73 analysis of sulphate evaporites. In this study, Sr and S isotopes were analysed by using 74 carbonates/anhydrites and pure anhydrites respectively, to obtain the true seawater Sr and S 75 76 isotopes. C isotope geochemistry is referenced to interpret the evolution of paleoclimate and 77 marine environments during the transition of the Early to Middle Triassic period as well.

#### 78 2 Geologic Background

The South China block (Fig. 1A) contains the Sichuan basin in the northwest (Fig. 1B), which was located near the equator in the eastern Paleotethys Ocean during early Triassic (Fig. 1C). Marine sedimentation dominated in the Sichuan Basin from the Upper Sinian to the Middle Triassic. During the earliest Permian, platform carbonates were deposited due to marine transgression with a typical thickness of 300-500 m. The Upper Permian consists of platform

carbonates with alternating marine and terrestrial coal measure (Cai et al., 2003). The Lower and 84 Middle Triassic were subdivided into three formations (Fig. 1D), Feixianguan ( $T_1f$ ), Jialingjiang 85  $(T_1)$ , and Leiloupo  $(T_2)$ , from the base upward, and are predominantly composed of platform 86 carbonates and evaporites. Basin-wide anhydrite beds occur in Jialingjiang and Leikoupo 87 Formations, whereas Feixianguan Formation contains little anhydrite (Cai et al., 2003). The 88 Sichuan Basin was uplifted during the middle to late Triassic as a result of Indo-China 89 movement. The Upper Triassic sediments are composed of freshwater lacustrine-alluvial clastics 90 91 with local coal beds.



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Figure 1. Schematic maps of the study area. A, Principal continental terranes that form present-day Southeast Asia
(Modified from Carter et al., 2001). B, Map showing the study site signified by the star (modified from Song et al.,
2015). C, Paleogeographic atlas illustrating the position of South China during Early Triassic (modified from
Scotese et al., 1997). D, Evaporite section in the Sichuan Basin.

## 97 **3 Materials and Methods**

98 Seventy-six samples were collected from different gypsum/carbonate layers at 99 approximately 1-3 m intervals, evenly covering a section of 200 m thick from drill core ZK3. 100 The entire section consists mainly of carbonates (Fig. 2A, C), anhydrites (Fig. 2C, D). 101 Carbonates are mainly composed of calcite and dolomite (Fig. 2B). Carbonates generally have black tonalities, and display massive and layered characteristic, whereas anhydrite layers are 102 103 white, and have fibrous texture (Fig. 2C). Nodular and massive anhydrites are found within some carbonate layers (Fig. 2D). Some anhydrite layers contain minor amounts of halite. The "green 104 bean" rock layer was developed in the upper part of our study section. This layer could be 105 identified by its distinct features, such as greenish colour (Fig. 2E), quartz-nuclei with 106 approximately 1 to 3 mm in diameter. Thin-layered or lensed carbonates and/or anhydrites were 107 intercalated in the "green bean" rock. 108





**Figure 2**. Characteristics of marine sediments and "green bean" rock during the latest Early Triassic to the

111 immediate Middle Triassic in Sichuan Basin. A, carbonates in drill core; B,dolomite in field outcrop; C, alternating

anhydrite and carbonate layers in drill core; D, massive anhydrites; E, the "green bean" rock straddles the Early-

113 Middle Triassic.

Based on the relative contents between carbonate and anhydrite, two chemical processes 114 were adopted to acquire the marine chemical signature, i.e., Milli-Q water and dilute acetic acid 115 dissolution. Samples with the predominant mineral of anhydrite (anhydrite samples) were 116 dissolved Milli-Q water at room temperature. Whereas samples with the predominant mineral of 117 118 carbonates (carbonate samples) were crushed to sand-size particles, and approximately 100 mg 119 of each was digested by dilute acetic acid (1 N) at room temperature. The purpose of the above chemical processes is to eliminate the disturbance of detrital components. We suggest that the Sr 120 isotope composition of carbonates and anhydrite could represent the marine Sr signature in the 121 light of high Sr contents in carbonates and anhydrite. All sample solutions were split into 122 aliquots by weight for analysis. One small aliquot was diluted and preserved for trace elements 123 analyses, and the other larger aliquot was acidified with 1 N HCl for column chemistry and 124 strontium isotopic measurement. Strontium was separated and purified using a Sr-spec resin. The 125 detailed information about Sr separation is depicted in Babechuk and Kamber (2011). The Sr 126 isotopic ratios were measured on a Nu Plasma multi-collector inductively coupled plasma mass 127 spectrometer (MC-ICP-MS) in the Radiogenic Isotope Facility, University of Queensland. The 128 Sr isotopic ratios were corrected for mass discrimination using <sup>86</sup>Sr/<sup>88</sup>Sr=0.1194. Replicate 129 analyses of separate loads of SRM987 yielded a mean  ${}^{87}$ Sr/ ${}^{86}$ Sr=0.710237±0.000027 (2 $\sigma$ ). 130

The S isotopic ratios of anhydrites were measured on a stable isotope ratio mass 131 132 spectrometer coupled in continuous flow mode with an elemental analyser in Stable Isotope Geochemistry Laboratory, University of Queensland. About 15 mg of each sample consisting of 133 nearly pure anhydrite, was encapsulated within tin foil cup and then combusted at 1020 °C using 134 column packing mentioned in Baublys et al., (2004). All samples and standards (international 135 and in-lab) were analysed in duplicate and each set of duplicates were separated by a blank to 136 137 avoid memory effects. All sulfur isotope compositions are expressed in standard delta notation as per mil (‰) deviation from Vienna Canyon Diablo Troilite (V-CDT) with analytical errors of 138 less than 0.2‰. 139

The trace element concentrations were determined by a Thermo X-series II ICP-MS. The detailed procedure for ICP-MS trace element analysis is given in Niu and Batiza (1997), except that the weighing data were designated roughly. It is practically impossible to analyse the 143 contents of trace elements accurately based on the above chemical processes. Because the 144 dissolved part of the samples could not be weighed or measured directly. However, the relative 145 concentrations of trace elements are attainable and cogent.

### 146 **4 Results**

The distribution of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios,  $\delta^{34}$ S<sub>sulphate</sub> values and Th/U ratios are shown in Table 1, Figure 3 and 4. In ascending stratigraphic order, the  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios decrease from approximately 0.70820 to 0.70816, and then climbed to 0.70824 with a small spike. The data decreased again from 0.70824 to approximately 0.70820 and stabilized before the "green bean" rock layer. The "green bean" rocks were characterized by a sharp increase of  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios from approximately 0.70820 to a maximum ratio of 0.70831. The  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios then dropped drastically to about 0.70822 which are similar to those below the "green bean" layer (Fig. 3).

Before the "green bean" rocks,  $\delta^{34}S_{sulphate}$  values are relatively stable, with modest fluctuations, from about 30.2‰ to 32.8‰. The "green bean" rock is characterized by a steep decline, from 31‰ on average to 28.6‰. The  $\delta^{34}S_{sulphate}$  data then rise to approximately 32‰ again. The  $\delta^{34}S_{sulphate}$  values are absent from 2563.95 m to 2599.49 m depth due to the lack of sulphate minerals in this section. We assume that the curve in this period is a stable and relatively smooth interpolation from the segments immediately preceding (Fig. 4).

The study section yielded Th/U mass ratios ranging from 0.0008 to 6.4097 (Fig. 4). The Th/U ratios are extremely low (0.0008 to 0.7525) below the volcanic bed in the study section, except two outliers with values of 1.2069 and 3.3335, respectively. In the "green bean" rocks, the Th/U ratio shifts abruptly to very high values (2.7766 to 6.4097). The interval overlying the "green bean" rocks is marked by a trend toward low values analogous to sections below the "green bean" rock.

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Table 1. <sup>87</sup>Sr/<sup>86</sup>Sr ratios, S isotope ratios and Th/U ratios of evaporite sequence straddling early to middle Triassic in
 South China

Sample ID	Depth (m)	Sample type	<sup>87</sup> Sr/ <sup>86</sup> Sr	$\delta^{34}S_{CDT}$ (‰)	Th/U
ZK3-01	2547.98	anhydrite	0.708216	28.6	0.6088
ZK3-02	2528.69	anhydrite	0.708255	30.1	0.0761
ZK3-03	2531.70	anhydrite	0.708219	31.2	0.0517

ZK3-04	2537.55	anhydrite	0.708213	32.2	0.0500
ZK3-05	2534.30	anhydrite	0.708223	32.3	0.0516
ZK3-06	2543.08	anhydrite	0.708224	30.5	0.0843
ZK3-07	2539.53	anhydrite	0.708246	31.3	0.0361
ZK3-08	2544.54	anhydrite	0.708213	29.5	0.2068
ZK3-09	2546.56	anhydrite	0.708213	29.9	0.1154
ZK3-10	2547.87	anhydrite	0.708215	31.6	0.2497
ZK3-11	2549.74	anhydrite	0.708204	29.4	3.3873
ZK3-12	2550.07	carbonate	0.708270	-	2.7766
ZK3-13	2550.44	carbonate	0.708223	-	6.4097
ZK3-14	2550.84	anhydrite	0.708289	31.0	3.0441
ZK3-15	2551.10	carbonate	0.708224	-	3.9841
ZK3-16	2551.42	anhydrite	0.708293	30.8	5.7092
ZK3-17	2551.60	anhydrite	0.708284	30.2	0.7525
ZK3-18	2551.80	anhydrite	0.708277	29.9	0.4183
ZK3-19	2551.93	anhydrite	0.708307	29.1	0.1978
ZK3-20	2552.15	anhydrite	0.708210	30.5	0.0312
ZK3-21	2552.46	anhydrite	0.708189	29.0	0.3716
ZK3-22	2552.79	anhydrite	0.708206	30.3	0.6554
ZK3-23	2554.00	anhydrite	0.708224	28.6	0.5951
ZK3-24	2554.20	anhydrite	0.708225	30.7	0.5244
ZK3-25	2561.18	anhydrite	0.708200	30.8	0.1033
ZK3-26	2555.70	anhydrite	0.708204	30.2	0.2280
ZK3-27	2568.30	carbonate	0.708176	-	0.3490
ZK3-28	2563.95	anhydrite	0.708224	29.0	0.0089
ZK3-29	2562.57	carbonate	0.708198	-	0.0027
ZK3-30	2571.62	carbonate	0.708190	-	0.2373
ZK3-31	2574.34	carbonate	0.708195	-	0.0013
ZK3-32	2576.60	carbonate	0.708181	-	0.0011

ZK3-33	2579.52	carbonate	0.708190	-	0.0017
ZK3-34	2587.51	carbonate	0.708178	-	0.2026
ZK3-35	2581.90	carbonate	0.708190	-	0.0700
ZK3-36	2595.25	carbonate	0.708239	-	0.0008
ZK3-37	2590.50	carbonate	0.708184	-	0.0036
ZK3-38	2599.49	anhydrite	0.708183	30.2	0.0359
ZK3-39	2597.21	anhydrite	0.708222	33.2	0.5146
ZK3-40	2602.66	anhydrite	0.708157	31.4	0.0180
ZK3-41	2603.76	anhydrite	0.708170	31.8	0.0046
ZK3-42	2609.50	carbonate	0.708229	-	3.3335
ZK3-43	2611.07	anhydrite	0.708167	31.6	0.1096
ZK3-44	2615.88	anhydrite	0.708182	31.0	0.1423
ZK3-45	2613.49	anhydrite	0.708171	31.8	0.0691
ZK3-46	2618.39	anhydrite	0.708167	31.7	0.0106
ZK3-47	2620.12	anhydrite	0.708173	31.6	0.0283
ZK3-48	2623.82	anhydrite	0.708164	32.3	0.6145
ZK3-49	2627.80	anhydrite	0.708163	31.7	0.0166
ZK3-50	2631.41	anhydrite	0.708186	31.9	0.0049
ZK3-51	2635.48	anhydrite	0.708166	32.1	0.3003
ZK3-52	2638.40	anhydrite	0.708172	30.3	0.0317
ZK3-53	2641.06	anhydrite	0.708165	30.5	0.0237
ZK3-54	2645.20	carbonate	0.708171	-	0.0110
ZK3-55	2647.93	anhydrite	0.708170	32.1	0.1828
ZK3-56	2650.25	anhydrite	0.708160	30.8	0.0552
ZK3-57	2656.19	anhydrite	0.708163	31.5	1.2069
ZK3-58	2652.05	anhydrite	0.708189	32.5	0.0110
ZK3-59	2657.58	anhydrite	0.708169	32.2	0.0153
ZK3-60	2560.62	anhydrite	0.708173	32.0	0.0068
ZK3-61	2673.94	anhydrite	0.708165	30.6	0.0037
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ZK3-62	2675.99	anhydrite	0.708189	32.8	0.0316
ZK3-63	2664.39	anhydrite	0.708181	31.9	0.1814
ZK3-64	2665.42	anhydrite	0.708175	32.5	0.0365
ZK3-65	2664.75	anhydrite	0.708171	32.1	0.1244
ZK3-66	2670.68	anhydrite	0.708174	31.6	0.0343
ZK3-67	2679.00	anhydrite	0.708178	30.3	0.0286
ZK3-68	2680.70	anhydrite	0.708175	32.1	0.0195
ZK3-69	2683.58	anhydrite	0.708176	32.2	0.0341
ZK3-70	2687.78	anhydrite	0.708175	32.4	0.0502
ZK3-71	2689.21	anhydrite	0.708211	32.3	0.0041
ZK3-72	2691.98	carbonate	0.708179	-	0.4431
ZK3-73	2699.80	anhydrite	0.708166	30.6	0.0021
ZK3-74	2703.00	anhydrite	0.708193	30.2	0.1796
ZK3-75	2705.53	anhydrite	0.708203	32.1	0.1912
ZK3-76	2607.65	anhydrite	0.708167	32.6	0.1019

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#### 170 **5 Discussions**

## 171 **5.1 Sr isotopes**

The Sr isotopic composition of seawater is homogeneous due to its long-time residence time 172 ( $\approx 10^6$  yr) compared to the mixing time ( $\approx 10^3$  yr; McArthur et al., 2012). The fact that the 173 <sup>87</sup>Sr/<sup>86</sup>Sr ratio of seawater has varied over time gives the ability to date and correlate marine 174 sediments (McArthur et al., 2012). Although the delineation of seawater <sup>87</sup>Sr/<sup>86</sup>Sr variation 175 through time has been refined recently, a high-resolution data is still needed for dating and 176 177 correlation (McArthur et al., 2001), especially for comparatively short stratigraphic sections (Veizer et al., 1997). Because the variations and oscillations of Sr isotope composition of a 178 certain section could be assigned to any analogical stratotype, improved resolution of a certain 179 section leading to high order oscillations superimposed on the lower order trends on a global 180 scale. Thus an unusual large peak or specific lithologies are required for definitive correlation. 181

And it is more beneficial to correlate different sequences on intrabasinal and regional scales
(Veizer, et al., 1997).

The Sr isotopic reference curve used for correlation in this study is composed of <sup>87</sup>Sr/<sup>86</sup>Sr ratios of well-preserved and well dated conodont samples from South China spanning from the Late Permian to the early Late Triassic (Song et al., 2015). It is suggested that <sup>87</sup>Sr/<sup>86</sup>Sr ratios had undergone the steepest and greatest change during the Late Permian to Early Triassic (McArthur et al., 2001), increased 0.00125 in 3.8 Myr until mid-Spathian (Song et al., 2015), thus favourable for stratigraphic correlation.

In South China, the <sup>87</sup>Sr/<sup>86</sup>Sr profile has a generally decreasing trend during the transition 190 period between the Early and Middle Triassic (Fig. 3, Song et al., 2015). The maximum <sup>87</sup>Sr/<sup>86</sup>Sr 191 ratio of South China seawater occurred at approximately 245.3 Ma, corresponding to the 192 maximum <sup>87</sup>Sr/<sup>86</sup>Sr ratios at the "green bean" rock in this section (Fig. 3). Besides, The U/Pb 193 zircon age of "green bean" rocks in Tongliang County (which is located adjacent to our sampling 194 site, Fig. 1), is of 245.86±0.98 Ma (Sun et al., 2017). There is only one layer of "green bean" 195 rock in the eastern Sichuan Basin, Chongqing (Zhu & Wang, 1986). Thus, the zircon U-Pb age 196 of "green bean" rocks from Sun et al. (2017), in combination with variation of seawater <sup>87</sup>Sr/<sup>86</sup>Sr 197 ratios in South China (Song et al., 2015) suggest that the formation age of "green bean" rocks 198 from this study is approximately 245 Ma. This result also suggests that the obvious bump of 199 <sup>87</sup>Sr/<sup>86</sup>Sr curve of seawater at approximately 245 Ma was very likely caused by volcanic 200 activities. 201

The trend of <sup>87</sup>Sr/<sup>86</sup>Sr ratios in our section mimics the shape of the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of South China seawater curve, albeit with slightly reduced values (Fig. 3). The minimum and maximum ages of our sequence are constrained to range approximately from 244-245 Ma to 247-248 Ma, with <sup>87</sup>Sr/<sup>86</sup>Sr ratio of 0.70822, corresponding to an age range of 244-245 Ma, and <sup>87</sup>Sr/<sup>86</sup>Sr ratio 0.70820, corresponding to an age range of 247-248 Ma.



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Figure 3. Correlation between Sr isotope compositions of marine sediments in the Sichuan Basin and those of South
 China seawater (Song et al., 2015).

The Sr isotopic variation of seawater through time is useful for investigating geologic 210 processes such as tectonic uplifts, continental weathering, climate changes, and hydrothermal 211 circulation (McArthur et al., 2001), because there are two major sources for the seawater Sr 212 isotopes: the riverine input caused by continental weathering (high ratios) and volcanic sources 213 (low ratios) (Allègre et al., 2010). The <sup>87</sup>Sr/<sup>86</sup>Sr ratios increased continuously from Late Permian 214 to mid-Spathian (Fig. 3), which was likely the result of enhanced continental weathering. One of 215 the major factors controlling continental weathering is orogenic uplifting. The major orogenies 216 around the Sichuan basin consist the accretion of Sibumasu to Indochina-South China (Carter et 217 218 al., 2001), and the collision of North and South China blocks (Meng & Zhang, 1999), which bound our study area to the Southwest and Northeast, respectively (Fig. 1A). A zircon U-Pb 219 study of the metamorphic basement of Vietnam indicates that a short-lived episode of ductile 220 deformation and high-temperature metamorphism was caused by the accretion of Sibumasu to 221

Indochina-South China between  $258\pm 6$  Ma and  $243\pm 5$  Ma (Carter et al., 2001). However, there 222 is no temporal correlation between the accretion and seawater Sr isotopic changes. The collision 223 ages of North and South China blocks are of middle Paleozoic and Late Triassic (Meng & 224 Zhang, 1999), which could not account for the elevated  ${}^{87}$ Sr/ ${}^{86}$ Sr ratios at the "green bean" rocks. 225 Moreover, the orogeny was only responsible for large scale seawater Sr isotopic changes, not for 226 local changes of Sr isotopic composition of seawater (Richter et al., 1992). Thus, we suggest that 227 the variations of seawater Sr isotopic compositions during the Early to Middle Triassic were not 228 related to orogenic erosions. Alternatively, elevated <sup>87</sup>Sr/<sup>86</sup>Sr ratios could have been controlled 229 by enhanced weathering by environmental changes. For instance, a combination of climatic 230 warming, vegetation loss (vegetation provides essential erosion resistance) and intensified 231 hydrological cycle, induced enhanced continental weathering, and increased radiogenic <sup>87</sup>Sr flux 232 to the ocean (Song et al., 2015). The Early Triassic has been viewed as an unsuccessful recovery 233 interval after the EPME (Hallam, 1991), and the massive collapse of terrestrial ecosystem could 234 have accounted for the continuous increasing of seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratios during most of the 235 Early Triassic. 236

<sup>87</sup>Sr/<sup>86</sup>Sr ratios began to decline following the recovery of vegetation in the middle-late 237 Spathian (Looy et al., 1999). The biotic recovery from Middle Triassic rendered plants to 238 increase on land, which would have reduced continental weathering and its accompanying influx 239 of <sup>87</sup>Sr into seawater. During the Middle Triassic, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios declined to a stable value 240 241 (Song et al., 2015), which resembles that of our study section, except for those from volcanic bed (Fig. 3). In the "green bean" rock layer, the <sup>87</sup>Sr/<sup>86</sup>Sr ratio culminates in the highest value of 242 0.708307 and then returns to values slightly higher than the previous values before volcanic bed 243 (Fig. 3). Thus, the maximum <sup>87</sup>Sr/<sup>86</sup>Sr ratio at the "green bean" rock indicates strong terrestrial 244 245 weathering.

By contrast, magmatism has been considered responsible for initiating the marked decrease in seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratios (Lo et al., 2002). Therefore, the "green bean" rock and its related volcanic activities could have reduced the seawater <sup>87</sup>Sr/<sup>86</sup>Sr ratios, which is not the case in this study. This indicates the continental weathering outbalanced the volcanic activities on Sr isotopic composition. The radiogenic strontium (<sup>87</sup>Sr) entering the ocean caused by continental weathering have been buffered by <sup>87</sup>Sr-depleted components due to volcanic eruptions, indicating the effect of continental weathering was stronger than estimated.

### 253 **5.2 S isotopes**

There are several factors controlling the variation of seawater  $\delta^{34}$ S values, namely the 254 precipitation and weathering of evaporites, the output of sulphate via bacterial sulfate reduction 255 (BSR) as sedimentary pyrite and the input of as sulphate derived from the oxidation of sulphides 256 and, the input and output of mantle sulphur along the mid-ocean ridges (Kampschulte & Strauss, 257 2004). The isotope fractionation between evaporitic and seawater sulphate is negligible (Kramm 258 & Wedepohl, 1991). The  $\delta^{34}$ S of dissolved component in river is typically thought to be between 259 5 to 15% reflecting weathered minerals (Tostevin et al., 2014, and references therein). Magmatic 260 sulphur derived either from mid-ocean ridges or volcanism on land was thought to be 261 quantitatively minor as compared to continental runoff during the Phanerozoic (Gill et al., 2007, 262 and references therein). The continuous BSR under sulphate-limited conditions result in the 263 enrichment in <sup>34</sup>S of the remaining dissolved sulphate (Strauss, 1999). Taken together, the factors 264 controlling the variations of S isotopes of seawater include biologic activities, continental 265 weathering and oxidation of sulphides from euxinic facies. 266

The relatively positive  $\delta^{34}S_{subpate}$  values (28.6% to 33.2%) of marine sulphates in this study 267 are consistent with previous research (Chen & Chu, 1988). They demonstrated the remarkably 268 heavy  $\delta^{34}S_{sulphate}$  values in the upper Jialingjiang Formation and the lower Leikoupo Formation is 269 a worldwide phenomenon (Chen & Chu, 1988). Claypool et al. (1980) attributed the high  $\delta^{34}S$ 270 values to extensive BSR in localized stagnant basins. The elevated  $\delta^{34}$ S value indicates the Late-271 Early Triassic ocean was strongly stratified and the deep-water may have been predominantly 272 anoxic. Isotopically light <sup>32</sup>S had been sequestered into deep water, resulting in more <sup>34</sup>S-273 enriched shallow seawater. The  $\delta^{34}S_{sulphate}$  is high compared with that of western Tethys, 274 indicating a more euxinic influence in the eastern Tethys (Gorjan et al., 2007). On the contrary, 275 the more anoxic condition in the "green bean" rock layer (evidenced by Th/U ratios, discussed 276 below) coincides with a negative shift of  $\delta^{34}S$  value, which is contradictory to the BSR 277 mechanism. Therefore, the negative  $\delta^{34}S$  value shift at the volcanic bed should have been 278 controlled by other factors. 279

Compared to BSR, enhanced continental weathering, and/or volcanically derived sulphur, and/or oxidation of  $H_2S$  due to the overturn of an anoxic ocean could have been responsible for the negative shift (Kaiho et al., 2001). Sr isotope evidence suggests increased continental weathering during the volcanic eruption(s), engendering more <sup>34</sup>S-depleted material into the ocean. By the addition of volcanogenic isotopically light sulfur, enhanced volcanic emissions would have contributed to negative shifts in seawater  $\delta^{34}$ S values but with a less or negligible contribution (Adams et al., 2010). In contrast to the estimated supply of volcanogenic sulphur, the reoxidation of H<sub>2</sub>S from deeper anoxic portions of the water column would be more than enough to affect a larger shift (Newton et al., 2004).



Figure 4. Variations of S, C (Huang et al., 2016) and Th/U ratios of marine anhydrites and carbonates in the
Sichaun Basin.

## **5.3 Implication for environmental changes and disturbance during biotic recovery**

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According to the variations of S and Sr isotopes, Th/U ratios in this section, 2543.08 to 2563.95 m interval was proposed as the volcano-affected stage (Fig. 4, light grey shadow 2563.95 interval; the dark grey shadow interval indicates the "green bean" rock layer).

As discussed above, continental weathering could have input depleted <sup>34</sup>S and relatively high <sup>87</sup>Sr/<sup>86</sup>Sr ratio materials into seawater. Thus, there would have been a negative correlation between  $\delta^{34}$ S values and <sup>87</sup>Sr/<sup>86</sup>Sr ratios if they were controlled predominantly by the weathering process. Fig. 4 shows that  $\delta^{34}$ S values and <sup>87</sup>Sr/<sup>86</sup>Sr ratios have a visually negative relationship at the "green bean" rock layer. However, plotting  $\delta^{34}$ S versus <sup>87</sup>Sr/<sup>86</sup>Sr reveals that there is no negative relationship between  $\delta^{34}$ S values and <sup>87</sup>Sr/<sup>86</sup>Sr ratios but a slightly positive trend (Fig. 5). This demonstrates that the weathering process was not the underlying or predominant factor controlling the variations of S isotopes.



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Figure 5.  $\delta^{34}$ S values VS. <sup>87</sup>Sr/<sup>86</sup>Sr ratios in this study. Blue dots: samples within volcano-affected stage; Orange squares: remainder of the samples.

Th/U ratios can be used to evaluate oceanic redox conditions (Elrick et al., 2017). Th has 307 only one oxidation state (+4), therefore, its concentration in seawater is not affected by water 308 309 mass redox changes, whereas U is sensitive to redox conditions. In oxidating marine waters, uranium is present mainly as U (+6) in the large uranyl ion  $(UO_2^{2+})$ , which forms a part of 310 soluble carbonate and phosphate complexes (Weyer et al., 2008). In reducing environments, 311 reduction to U (+4) leads to the formation of relatively insoluble hydroxide and phosphate 312 313 complexes and organo-metallic ligands (Klinkhammer & Palmer, 1991). The Th/U ratios of those samples in this study are all derived from relatively dissolved components, i.e., anhydrites 314 and carbonates, instead of insoluble materials. Consequently, an increase in the Th/U ratios of 315 marine carbonates and anhydrites represents enhanced U removal in reducing conditions. 316

Th/U ratios of samples within the volcano-affected interval are strikingly high compared with those of samples within the remainder of this section. It is suggested that an anoxic environment was prevailed in the volcano-affected section compared with others. Our data argue for intense anoxia at the volcanic bed and relatively oxygenated condition preceding and following sections of the "green bean" rock layer.

The coupling or/and decoupling of marine carbonates  $\delta^{13}C$  and sulphate  $\delta^{34}S$  shed light on 322 contemporaneous oceanic and terrestrial processes (Gill et al., 2007). A  $\delta^{13}C_{carb}$  excursion was 323 documented previously in this section by Huang et al. (2016).  $\delta^{13}C_{carb}$  values of approximately 324 0‰ at the lower part of this section decreased abruptly at values around -4‰ at the "green bean" 325 rock (Fig. 4). The data then rapidly increased to approximately 0‰ again over the "green bean" 326 rock. This recorded a negative carbon isotope excursion of about -4‰ through the "green bean" 327 rock interval. The negative  $\delta^{13}C$  shift in the volcanic bed was not caused by the changes of 328 organic burial or weathering, because both processes are too slow for this extremely rapid event. 329 Brand et al. (2012) proposed that the rapid negative excursion was caused by volcanic discharge 330 of CO<sub>2</sub>. Whereas, Payne and Kump (2007) suggested that the introduction of volcanic CO<sub>2</sub> 331 produces small negative carbon isotope excursions. Carbon and sulphur isotope vary 332 sympathetically during this section, reaching their minimum values at the same level, i.e., the 333 "green bean" rock (Fig. 4). Song et al. (2014) proposed that warming events were associated 334 with negative C- and S-isotope shifts and cooling events with positive isotope shifts based on 335 analyses on C and S isotopes of the Early Triassic marine sediments. Seawater temperature may 336 have played an important role on the Early Triassic carbon and sulfur cycles (Song et al., 2014, 337 the mechanism is still not well demonstrated). 338

339 The sulphate aerosols formed by oxidation of SO<sub>2</sub> degassing via volcanisms could lower temperature. Then it will be removed from the atmosphere in a short time (1 to 2 years) (Grard et 340 al., 2005). But the degassing of CO<sub>2</sub> could put large amounts of isotopically light carbon into the 341 atmosphere (Eldholm & Thomas, 1993), leading to a globally warm climate (Grard et al., 2005). 342 343 Meanwhile, the decrease of temperature could induce oceanic overturn and rapid return of  $HCO_3^{-1}$ , H<sub>2</sub>S and CO<sub>2</sub>-charged waters to the surface (Knoll et al., 1996). CO<sub>2</sub> released from the deep 344 ocean combined with that degassing from volcanic eruptions would facilitate a greenhouse 345 climate. A warm climate may have triggered chemocline upward excursions that introduced <sup>34</sup>S-346 depleted sulphide and <sup>13</sup>C-depleted dissolved inorganic carbon into the surface water (Kump et 347 al., 2005). Oxidation of H<sub>2</sub>S would have generated isotopically light sulphate (Riccardi et al., 348 2006), leading to a decline of seawater  $\delta^{34}$ S values. Moreover, volcanic eruptions ejected 349 isotopically light sulphur into seawater although with limited or negligible effect. These two 350

processes could have induced the lowering of seawater  $\delta^{34}$ S values synergistically (Knoll et al., 1996).

In summary, the negative shifts of carbon and sulfur isotopes at the "green bean" rock interval was very likely caused by the volcano-induced cooling-warming climate cycle. Such a climate cycle could have resulted in an environmental crisis capable of causing mass extinction (Renne et al., 1995).

In the Sichuan Basin, several species of ammonoid and lamellibranchia were present within 357 sequence below the "green bean" rock layer. Ammonoids (including Dinarites sp., D. 358 yunnanensis, Leiophyllites aff. Pitamaha, Hanielites sp., Pseudoceltites sp., Dorieranites sp., 359 Xenoceltites cf. compressus, and Ussuria sp.) and lamellibranchia (including Eumorphotis 360 inaequicostata, Entolium discites mierotis, Pteria cf. murchisoni, Myophoria laevigata, and 361 Anodontophora fassaensis) were present below 15-20 m of the "green bean" rock layer. Only 362 lamellibranchia species were found within sequence above approximately 20 m of the "green 363 bean" rock layer, including Myophoria goldfussia, Eumorphotis (Asoella) illyrica, Eu, subillyrica 364 (Fig. 6, Zhu & Wang, 1986). The number of species of lamellibranchia decreased from 8 to 3, 365 and ammonoids were extinct after the deposition of the "green bean" layer. There were not any 366 species existing in the "green bean" rock layer and its adjacent sequences (Fig. 6). 367



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Figure 5.  $\delta^{34}$ S values VS. <sup>87</sup>Sr/<sup>86</sup>Sr ratios in this study. Blue dots: samples within volcano-affected stage; Orange squares: remainder of the samples.

Obviously, the volcanic activity which formed the "green bean" rocks has imposed severe 371 environmental stress on the marine community in the Sichuan Basin. Some species were killed 372 during the volcano eruption. This scenario is similar to that of Permian-Triassic boundary 373 volcanism which may have played an important role in causing the end Permian mass extinction 374 375 (Gao et al., 2013). The eruptions of volcanos could have released sufficiently large quantities of CO<sub>2</sub>, SO<sub>2</sub>, fluorine and chlorine to wreak destruction on atmospheric and biospheric systems 376 (Kamo et al., 2003). Severe atmospheric contamination with H<sub>2</sub>SO<sub>4</sub> aerosols produced by 377 gaseous emissions of volcano activities could have resulted in acidic precipitation, causing 378 379 destabilization of the terrestrial biosphere (Maruoka et al., 2003). When tephra comes in contact with surface waters, acid and metal salts adsorbed onto the tephra surfaces dissolve quickly, 380 381 releasing acids and metals to the environment (Frogner et al., 2001). Volcano eruptions cause acidification and contamination of soils and surface water, which has a series of impact on 382 vegetation and animals (Kockum et al., 2006). Additional detrimental effect on vegetation may 383

have derived from large-scale degassing of hydrothermal organohalogens, contributing to stratospheric ozone depletion and increased flux of harmful UV radiation (Visscher et al., 2004).

#### 386 6 Conclusions

(1) The section composed of alternating marine carbonates and evaporites (mainly anhydrites)
with intercalated volcanic bed straddling the boundary of the Lower and Middle Triassic in
the Sichuan Basin suggests an age range of approximately 244 to 248 Ma, with volcanic bed
of 245.3 Ma.

(2) During the volcanic eruption, enhanced continental weathering and influx of radiogenic <sup>87</sup>Sr
 into seawater increases the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of seawater. Degassing of CO<sub>2</sub> and SO<sub>2</sub> and
 overturn of deep anoxia ocean water induced the negative S and C excursions and anoxic
 environment in the shallow water.

(3) Volcanic eruption could have caused severe environmental stress on the full recovery of
 ecosystem and killed some marine species.

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