

Interactive Comment by Anonymous

- 1) This is an interesting and well-written manuscript that provides further evidence for environmental changes related to postulated cooling at the Smithian-Spathian transition after the Early Triassic hothouse. This work is a valuable contribution applying various geochemical proxies to argue for changes in the weathering rate as well as the oceanic circulation. These environmental changes are further discussed in the light of concomitant changes in the faunal and floral associations.

Response: We thank the reviewer for these comments.

There are some critical points that should be addressed before this ms can be accepted for publication:

- 2) 15362, line 10 to 11: $\delta^{13}\text{C}_{\text{carb}}$ (+4 permil) and $\delta^{34}\text{S}_{\text{CAS}}$ (-14 permil)..... Please explain what is meant by +4 permil or -14 permil – maximum values; shift in isotope ratios or amplitude of an excursion...?

Response: This refers to the concurrent ranges of variation shown by $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ at Shitouzhai during the SSB event.

Action: We have reworded this sentence to more clearly express our intended meaning.

- 3) 15362, line 23 to 24: no new data for a stewise recovery are presented in this contribution .. why then mentioning this in the abstract?

Response: Agreed.

Action: We have deleted this sentence in the abstract.

- 4) 15365, line 2-3: the authors argue that the carbon isotope signals are not significantly affected by diagenetic alteration. However, the line of argumentation in Appendix B is not convincing and unclear. A special focus is on the correlations between the isotope ratios and Mn and/or Sr

contents. If the authors want to use manganese contents as an indicator for carbonate diagenesis, only Mn^{2+} substituting Ca^{2+} in the calcite lattice should be considered (same for Sr). However, no information is given on the methodology of dissolving the rocks and whether the trace element contents refer to whole rock or represent the carbonate-bound fraction. If the given Mn and Sr contents refer to whole rock Mn, no interpretation with respect to a potential diagenetic alteration of the carbonates is possible, since the trace element concentration will not exclusively correspond to Mn and Sr in the calcite lattice.

Response: The reviewer raises a good point. The Mn/Sr ratios cited in the text are for whole-rock samples. However, the study samples are mostly carbonate, containing an average of just $1.10 \pm 0.60\%$ Al (a proxy for clay-mineral content). We tested to see whether accounting for Mn and Sr in the clay-mineral fraction would have any effect on Mn/Sr ratios as follows: (1) we estimated the detrital fraction of Mn and Sr in each sample based on sample %Al and Al, Mn, and Sr concentrations of 8.04%, 600 ppm, and 350 ppm, respectively, for average upper continental crust (McLennan, 2001); (2) we subtracted these values from whole-rock Mn and Sr concentrations to arrive at estimated carbonate Mn and Sr concentrations; and (3) we calculated carbonate Mn/Sr ratios based on these estimates. The carbonate Mn/Sr ratios are nearly identical to the whole-rock Mn/Sr ratios: the distribution of the former (as given by 16th-50th-84th percentile values) is 0.10-0.35-2.76 and that of the latter is 0.16-0.39-2.70. The two distributions of Mn/Sr ratios are very similar because detrital Mn comprises just $8.1 \pm 4.4\%$ of whole-rock Mn, and detrital Sr comprises just $4.0 \pm 2.2\%$ of whole-rock Sr. We could introduce these calculations into the manuscript, but it would add unnecessary complexity.

Action: We have added a statement to Appendix B that calculated carbonate Mn/Sr ratios are nearly the same as whole-rock Mn/Sr ratios.

- 5) 15365, line 22-23: limited fossil occurrences allow recognition of three conodont zones. The authors illustrate these conodont zones by differently coloured bars in Figure 1. However these zones are defined only by 4 determinations of conodonts (blue dots in Figure 1), which is absolutely inadequate to define the illustrated conodont zones. I recommend to delete the coloured bars in Figure 1 and instead correlate the sections exclusively based on carbon isotope patterns, the latter being convincing.

Response: The conodont zonation for the West Pingdingshan reference section in Figure 1 is well established (Zhao et al., 2007). The conodont zonation that is shown for Shitouzhai is not based on the limited ($n = 4$) conodont identifications of the present study. Rather, it is a “model” zonation scheme based on the detailed C-isotope correlations shown in Figure 2.

Action: We have added the citation to Zhao et al. (2007) and have clarified these points in the caption of Figure 1.

- 6) 15366, line 10: Triassic conodont samples of 3 to 4 kgs are not really large.

Response: This study is primarily a geochemical study, and the Shitouzhai section was sampled for that purpose, not for conodont extraction. The collected material was more than adequate for the geochemical analyses that were undertaken.

Action: None requested by reviewer.

- 7) 15366, line 21: the authors have to state whether the given stddevs are 1 or 2 sigma. In addition, they have to provide information how the analyses were calibrated to the V-PDB scale. Measuring a laboratory standard is not sufficient.

Response: The reported standard deviations are 1σ . V-PDB is short for Vienna Pee Dee Belemnite with $\delta^{13}\text{C}_{\text{carb}}$ value given as 0‰. The $\delta^{13}\text{C}_{\text{carb}}$ values of our samples are reported relative to this standard, not the calibration. GBW-04416 is our national standard reference material and used as our laboratory standard.

Action: We have added a note regarding this to the Methodology section and have changed “laboratory standards” to “national reference standard”.

- 8) 15367 line 22: please give details on how the analytical uncertainty was determined.

Response: Multiple measurements of the international standards BHVO-2 and BCR-2 were employed to calculate analytical precision. Analytical precision of the measured samples is mostly better than 2%, according to the relative standard deviation (RSD).

Action: We are changing the method used to report analytical uncertainty, basing it on RSD (which is generally to be preferred) rather than on absolute concentrations. We have modified this part of the Methods section accordingly.

- 9) 15368 line 18: the minimum N4 and the correlation of N4 in various sections (Figure 2) is rather a guess and not really convincing. I recommend to omit the N4 correlation from Figure 2.

Response: There is a clear minimum in carbonate C-isotope curves during the mid-Spathian (e.g., Payne et al., 2004; Tong et al., 2007). Song et al. (2013) labeled this minimum N4. For all C-isotope excursions of the Early Triassic, some appear as sharp peaks in some sections, and as broad excursions in others. Although the broad excursions may not permit as exact a correlation as the sharp peaks, all are useful for global correlation of C-isotope curves. The mid-Spathian minima shown in Figure 2 are clearly N4, even where they appear as a broad excursion (as in the Majiashan section).

Action: No change.

- 10) 15369, line 2: How can the $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ values have a significant negative correlation in case a positive (?) $r^2 = +0.14$ is calculated. This statement has to be revised and the significance of all correlations has to be underlined by further statistic tests

Response: The reviewer's comment reflects a lack of understanding of basic statistics. One must recognize the difference between (1) r^2 , which is the "coefficient of determination" and represents the covariance of two variables; this statistic ranges from 0 to 1.0; and (2) r , which is the "correlation coefficient" and represents the linear relationship of two variables; this statistic ranges from -1.0 to $+1.0$. The two statistics are related to each other in that r^2 is the square of r ; the square of any negative number is going to be a positive number.

Action: We converted the reported r^2 value to an r value so that other readers do not make the same misinterpretation.

11) 15369 Chapter Sediment fluxes: it is completely unclear how the carbonate and clay mass accumulations were calculated. How were carbonate and clay percentages measured? No information is provided.

Response: The methodology of calculating sediment fluxes is described concisely in the caption of Figure 3. More detailed algorithms were presented in Algeo and Twitchett (2010), which is cited in the same caption. There is no need to repeat this material from that earlier publication, to which the reader can refer if interested.

Action: None.

12) 15371 line 20: clay mineral production – please rephrase

Response: There is nothing wrong with this phrase. “Clay mineral production” refers to a combination of processes that generate clay minerals through weathering, including chemical breakdown of feldspars and other minerals, and recycling of clay minerals from older shales and mudstones.

Action: None.

13) 15372 line 4: no Th-normalized element ratios are provided in the appendix...

Response: This is an oversight on our part.

Action: We have added Th-normalized concentrations for the cited elements to Table C2.

14) Appendix 2: D18Ocarb and d13Ccarb values show an $r^2 = 0.0001$ which means that the two variables are not correlated. The authors state a “weak covariation”? Please rephrase throughout Appendix 2.

Response: We intended the phrases “weak covariation” and “little covariation” to mean “no significant covariation”, but we agree with the reviewer’s comment.

Action: We have reworded all such statements to make clear that there is no significant covariation.

15) Tables C1 and C2 of the supplement correspond to Figs A1 and A2 of the Appendix. Why this?

Response: We apologize for any confusion in the labeling of tables and figures in the Appendix.

Action: All tables and figures are correctly labeled in the revised manuscript.

16) Fig. B1a: why presenting a plot of $\delta^{18}\text{O}$ vs. Mn/Sr. Oxygen isotopes are not discussed in this paper

Response: The relationship between $\delta^{18}\text{O}$ vs. Mn/Sr is discussed in Appendix B, as are all geochemical relationships that were used to evaluate the diagenesis of the study section. The detailed discussion of diagenesis was put in an appendix rather than in the main text because it is not essential to the development of the main theme of the paper.

Action: None.

Interactive Comment by S. Takahashi

1) This manuscript reports stable isotope and elemental records across the Smithian-Spathian boundary from shallow carbonate platform section of South China. Main arguments are (1) sedimentary flux decreased during Smithian-Spathian transition, (2) redox environment was oxic to suboxic and not anoxic, and isotope ratios of carbon and sulfur of carbonate vary in inverse relationship. Their data and discussions are worth. But, I would like the authors to improve their discussions.

Response: We would characterize our main arguments somewhat differently than here expressed, but thanks for the reviewer's assessment of our contribution as "worth(y)".

Action: None requested.

- 2) First, authors suggest sedimentary flux variations across Smithian-Spathian focusing on clay and carbonates. Probably they calculated the sedimentation rates using thickness of lithologic column, elemental ratios such as Th/Th*, and absolute age referred from previous reported radiometric ages. But as their calculation process is not shown in the manuscript, readers can not evaluate their calculation results. I ask authors to explain their methods of sedimentary fluxes estimations including calculation formula, assumed ground with some literatures. Further, authors should mention that most of the absolute age numbers have some error ranges. So, they should discuss uncertainness of absolute numbers of their calculated fluxes and/or their estimations are maximum or minimum estimate. Similar points are found in their conodont occurrence ranges in Figure 1. They can not place *Nv. pindingshanensis* zone at the base of Bed 14 of the study section because of lack of fossil occurrences. I recommend authors to show such fossil barren horizon as spaces (no color in Figure for example) or “transitional zone” in the Figure.

Response: The reviewer discusses two issues here. The first relates to the methodology of calculation of sedimentation rates and sediment fluxes, and the second to the presentation of conodont ranges in Figure 1. Both points were raised in review #1 above (points 11 and 5, respectively) and were addressed in response to that review.

Action: See points 11 and 5 of review #1.

- 3) Second, the authors discussed redox condition of the Shitouzhai section using multi elemental proxies. (1) In the first sentence of this discussion part, they argue that redoxsensitive elements of Mo, U, and V are low. But we can not find their data in any tables, despite authors referred “appendix Tables” in sentence (Line 302). So their criteria of “low in all samples “ are uncertain. (2) Authors should indicate their definition of low value. When doing so, enrichment factor (e.g. Tribouillard et al., 2006) would provide useful tool for comparison with each redox conditions. (3) Also, author’s criteria of Mn enrichments is not clear. Relatively high Mn/Th in 20-37 m horizon are interpreted as evidence of sub-oxic conditions. But it is uncertain why interpretation as oxic condition can be ruled out. In this paragraph, they introduce Mn’s pass way, “reducing deep

water mass provide soluble Mn to neighbouring oxic water mass ” and “Mn deposition occur in oxic-suboxic depositional condition”. Using these facts and combination with other redox proxies, more organized explanations on redox environment are required.

Response: The reviewer discusses multiple issues, which we have numbered for greater clarity. (1-2) We agree with the reviewer’s comments. (3) Typical detrital Mn/Th ratios are ~55 (i.e., 600 ppm Mn/11 ppm Th for upper continental crust; McLennan, 2001). Two intervals in the Shitouzhai section have much higher Mn/Th ratios (~1000-3000; Figure 4), which indicates strong authigenic enrichment of Mn. Strong authigenic Mn enrichment is a hallmark of carbonates deposited under suboxic conditions; we have cited multiple studies in Section 5.2 to support these interpretations.

Action: (1) This is an oversight on our part—we have added the missing data to Table C2. (2) We have clarified the comment of “low (concentrations of Mo, U and V) in all samples” by adding a statement that this means that there is little or no authigenic enrichment above the estimated detrital background concentrations of these elements. (3) None.

- 4) Third, authors discussed chemical weathering intensity using CIA (chemical index of alternation). As previous researchers mentioned (examples are following), this elemental ratio can also vary reflecting changes in provenances of sediment. Authors might want to discuss on this possibility. Perhaps, effect of provenance variation could be discussed by Eu-anomaly and REE features.

Borges, J., Huh, Y., 2007. Petrography and chemistry of the bed sediments of the Red River in China and Vietnam: Provenance and chemical weathering. *Sediment. Geol.* 194, 155–168. doi:10.1016/j.sedgeo.2006.05.029

Price, J.R., Velbel, M. a, 2003. Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks. *Chem. Geol.* 202, 397–416. doi:10.1016/j.chemgeo.2002.11.001

Response: CIA shows strong covariation with most detrital proxies, including Al ($r = +0.87$), ΣREE ($r = +0.81$), Th/Th* ($r = +0.81$), and LSR ($r = +0.93$), which is consistent with our

argument that variation in CIA is related to changes in weathering intensity. CIA shows an insignificant correlation to Eu/Eu* ($r = -0.21$) and other REE ratios, which argues against a change in sediment provenance as an explanation for CIA variation at Shitouzhai.

Action: We have added a mention of sediment provenance changes as a possible control on CIA, but have also added the statistical arguments above in favor of our interpretation.

- 5) Fourth, they pointed significance of Smithian-Spathian Boundary as the turning point of oceanic structure from "hyper green house (they assume stratified ocean) to "over turning circulated ocean". But negative co-variation of $\delta^{13}\text{C}$ and $\delta^{34}\text{S}$ could already be recognized in late Smithian warm period. In fact, during negative trough of $\delta^{13}\text{C}$ in Bed 8-13, $\delta^{34}\text{S}$ increase, although resolution of $\delta^{34}\text{S}$ is not so high as authors mentioned. I doubt their argument of coincidence of transition of sulfur isotope profile and cooling trend. They need some explanations on this trend.

Response: We acknowledge that there is a degree of negative covariation between $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ at Shitouzhai during the late Smithian warm interval (Figure 4). However, the range and rate of variation in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ during this interval are more limited than for the SSB proper. More data will be needed to fully assess $\delta^{13}\text{C}_{\text{carb}}-\delta^{34}\text{S}_{\text{CAS}}$ relationships during the Smithian. At the SSB, however, there is a large and abrupt positive shift in $\delta^{13}\text{C}_{\text{carb}}$ and negative shift in $\delta^{34}\text{S}_{\text{CAS}}$, leaving no doubt at all about the pattern of negative covariation in this interval.

Action: We have revised the discussion in this paragraph extensively to make note of the points raised by the reviewer, and to offer some alternative explanations.

- 6) Finally, I can not find this paper's contribution from the final section of discussion (5.3) on temperature, vegetation and Siberian trap volcanic activity. Authors should indicate the significance of sedimentary flux and features of oceanic condition in Smithian-Spathian interval, reviewing previous issues.

Response: Thanks for pointing this out.

Action: We have integrated more fully the results and interpretations from Shitouzhai into the final section of the paper (Section 5.4. Causes and consequences of the SSB event).

- 7) Minor issues: Line 33: This paper can not discriminate the cause of Smithian -Spathian warm and following cooling condition.

Response: The sentence in question reads: “The ultimate cause of the SSB event is uncertain but may have been related to reduced intrusive magmatic activity in the Siberian Traps Large Igneous Province.” Yes, the present study does not determine the cause of the SSB event, as noted here. We offer a bit of speculation at the end of the study, which is phrased accordingly.

Action: None.

- 8) Line 53: What is extreme environmental condition? temperature in concrete ?

Response: Thanks for this request.

Action: We have added specific temperature values to clarify what is meant by “extreme conditions”.

- 9) Line 98: It is better to make an explanation of carbon isotope notations N3 in first.

Response: We had offered a brief explanation of this notation in the caption of Figure 2, as well as a citation to the source (Song et al., 2013) in both the text and the Figure 2 caption.

Action: We have clarified the meaning of this notation in the Figure 2 caption.

- 10) Line 100, 101,109; What are criteria of “globally” “world-wide”? In fact, several sections support carbonate carbon isotope variations during Early Triassic.

Response: “Globally” is short-hand for “in coeval sections on multiple continents”. We believe that this convention is generally understood.

Action: None.

11) Line 128: absolute age must have error ranges. "_252 Ma" means maximum assumption?

Response: The uncertainties for all reported radiometric ages were given in the original studies, which are cited in our paper. It is not essential to report age uncertainties here—the reader can check the original sources if interested in this information.

Action: None.

12) Line 189 and figure explanation of Fig.3: It is not enough for explanation of sedimentation flux calculations.

Response: The reviewer has already raised this issue in point #2 above.

Action: See response to point #2.

13) Line 202: Still needing explanation on N3, P3, and N4 by Song et al.

Response: The reviewer has already raised this issue in point #9 above.

Action: See response to point #9.

14) Line 324: suboxic trend is discussed by covariance of another redox indicator together.

Response: The intended meaning of the reviewer's comment is unclear.

Action: We are unable to respond.

15) In Figure 5-B, ammonite or benthic foraminifera (?) is drawn on the deep-seafloor. I think there are few evidence of that "bio-diversity loss" of calcareous animals occur pelagic deep water

region. This figure leads to misunderstanding. Biodiversity loss would be occurred on shallow platform at least.

Response: Figure 5 is schematic. We encourage the reviewer and readers not to read too much into placement of the ammonoid shell.

Action: None.

16) In Table S1, Mn/T should be "Mn/Th"

Response: None.

Action: Corrected.

Amelioration of marine environments at the Smithian-Spathian boundary, Early Triassic

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Abstract.

The protracted recovery of marine ecosystems following the Permian–Triassic mass extinction may have been caused, in part, by episodic environmental and climatic crises during the Early Triassic, among which the Smithian–Spathian boundary (SSB) event is conspicuous. Here, we investigate the SSB event in the Shitouzhai section, Guizhou Province, South China, using a combination of carbonate carbon ($\delta^{13}\text{C}_{\text{carb}}$) and carbonate-associated sulfate sulfur isotopes ($\delta^{34}\text{S}_{\text{CAS}}$), rare earth elements, and elemental paleoredox and paleoproductivity proxies. The SSB at Shitouzhai is characterized by a +4‰ shift in $\delta^{13}\text{C}_{\text{carb}}$ and a –10 to –15‰ shift in $\delta^{34}\text{S}_{\text{CAS}}$, recording negative covariation that diverges from the positive $\delta^{13}\text{C}_{\text{carb}}$ – $\delta^{34}\text{S}_{\text{CAS}}$ covariation that characterizes most of the Early Triassic. This pattern is inferred to reflect an increase in organic carbon burial (e.g., due to elevated marine productivity) concurrently with oxidation of isotopically light H_2S , as the result of enhanced vertical advection of nutrient- and sulfide-rich deepwaters to the ocean-surface layer. Enhanced upwelling was likely a response to climatic cooling and re-invigoration of global-ocean overturning circulation at the SSB. Coeval decreases in

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chemical weathering intensity and detrital sediment flux at Shitouzhai are also consistent with climatic cooling. A decline in marine biodiversity was probably associated with the late Smithian thermal maximum (LSTM) rather than with the SSB *per se*. The SSB thus marked the termination of the extreme hothouse conditions of the Griesbachian-Smithian substages of the Early Triassic and is significant as a record of accompanying climatic, environmental, and biotic changes. The ultimate cause of the SSB event is uncertain but may have been related to a reduction in intrusive magmatic activity in the Siberian Traps Large Igneous Province.

Life on Earth underwent a protracted recovery following the Permian–Triassic mass extinction. The slowness of the recovery process may have been caused, in part, by episodic environmental and climatic crises during the Early Triassic, among which the Smithian–Spathian boundary (SSB) event is conspicuous. Here, we investigate the SSB event in the Shitouzhai section, South China, using a combination of carbonate carbon ($\delta^{13}\text{C}_{\text{carb}}$) and carbonate-associated sulfate sulfur isotopes ($\delta^{34}\text{S}_{\text{CAS}}$), rare earth elements, and elemental palaeoredox and palaeoproductivity proxies. Unlike the positive $\delta^{13}\text{C}_{\text{carb}}\text{--}\delta^{34}\text{S}_{\text{CAS}}$ covariation that characterizes most of the Early Triassic, the SSB at Shitouzhai exhibits negative covariation between $\delta^{13}\text{C}_{\text{carb}}$ (+4‰) and $\delta^{34}\text{S}_{\text{CAS}}$ (–14‰). This relationship may reflect an increase in organic carbon burial (e.g., due to elevated marine productivity) concurrently with oxidation of isotopically light H_2S , a pattern that we attribute to enhanced vertical advection of nutrient- and sulfide-rich deepwaters to the ocean surface layer. Enhanced upwelling was a likely response to the well-documented climatic cooling event at the SSB that terminated the extreme hothouse conditions of the Griesbachian–Smithian, a cooling that we infer to have transiently invigorated the global ocean overturning circulation. Evidence at Shitouzhai for concurrent decreases in chemical weathering intensity and detrital sediment influx are also consistent with climatic cooling. A penecontemporaneous decline in marine biodiversity was probably associated with the late Smithian thermal maximum rather than the SSB event itself, and the affected marine faunas did not recover immediately in response to climatic and environmental amelioration at the SSB but, rather, underwent a stepwise recovery during the early to middle Spathian. The ultimate cause of the SSB event is uncertain but may

63 ~~have been related to reduced intrusive magmatic activity in the Siberian Traps Large-~~
64 ~~Igneous Province.~~

65
66 *Keywords:* carbon isotopes; sulfur isotopes; trace elements; rare earth elements;
67 palaeoceanography; palaeoclimatology; chemical index of alteration

69 **1 Introduction**

70
71 The recovery of marine invertebrate faunas and ecosystems after the ~252-Ma
72 end-Permian mass extinction appears to have been the most protracted following any
73 Phanerozoic biocrisis (Erwin, 2001; Bottjer et al., 2008). As with the mass extinction
74 event, many aspects of the Early Triassic recovery remain uncertain, including its timing,
75 pattern, and causes. Species origination rates and biodiversity did not return to
76 pre-extinction levels until the early Middle Triassic, after a protracted process of niche
77 building and increasing ecosystem complexity (Chen and Benton, 2012). The extremely
78 slow recovery process is believed to have resulted, in part, from the effects of sustained
79 or repeated environmental stresses during the Early Triassic (Algeo et al., 2011; Retallack
80 et al., 2011). In particular, the pace of the biotic recovery may have been related to
81 episodic large-scale injection of volcanic CO₂ and thermogenic CH₄ into the atmosphere,
82 probably from the Siberian Traps Large Igneous Province, and a resulting intensification
83 of ocean anoxia (Retallack and Jahren, 2008; Black et al., 2012).

84 The extreme environmental conditions of the first ~1.5 Myr of the Early Triassic
85 came to an end at the ~250-Ma Smithian–Spathian boundary (SSB), which subdivides the
86 Olenekian Stage of the Lower Triassic, and which is defined by the first appearance of
87 the conodont *Novispathodus pingdingshanensis* at Chaohu, Anhui Province, eastern
88 China (Zhao et al., 2007). The SSB witnessed major changes among marine biotas,
89 including a severe loss of biodiversity among conodonts and ammonoids (Orchard, 2007;
90 Stanley, 2009; Brayard et al., 2009), size reduction (Lilliput effect) among surviving
91 conodont taxa (Chen et al., 2013), and a contraction of the palaeolatitudinal range of
92 surviving ammonoid taxa (Galfetti et al., 2007; Brayard et al., 2009). The SSB also
93 marked a major change in global climate, with strong tropical sea-surface cooling (Sun et

al., 2012; Romano et al., 2013) and a steepening of the latitudinal temperature gradient (Galfetti et al., 2007). To date, however, the SSB event has received detailed study only in several sections in South China (Galfetti et al., 2007; Liang et al., 2011) and the Salt Range of Pakistan (Hermann et al., 2011). Here, we report the SSB event from a new Lower Triassic section in southern Guizhou Province, South China. We correlate this section with existing SSB sections using a combination of conodont biostratigraphic and carbon isotopic constraints, and we examine changes in marine environmental conditions using a combination of elemental and isotopic proxies, with the goal of better understanding the role of the SSB in the recovery of Early Triassic marine ecosystems

2 Smithian-Spathian boundary at the study section

The study section (GPS: N25°45'9.6", E106°6'29.7") is located at Shitouzhai village, about 3 km east of Ziyun county town in southern Guizhou Province, South China (Fig. A1). The geologic and palaeontologic background of the Shitouzhai section is described in Appendix A. Its conodont biostratigraphy has been only partly worked out to date due to sporadic fossil occurrence. Ding and Huang (1990) identified a few conodont zones that served to demonstrate an Early to Middle Triassic age for the outcrop. In this study, we have detected three key Early Triassic zonal species in the middle to upper Luolou Formation: *Novispathodus waageni waageni*, which ranges from the late Smithian to early Spathian, and *Nv. pingdingshanensis* and *Nv. homeri*, which are early Spathian in age (Zhao et al., 2007) (Fig. 1). The first occurrence of *Nv. pingdingshanensis* is considered to be a marker of the SSB globally (Zhao et al., 2007) (Fig. 2), so its appearance in Bed 14 of the study section provides a firm constraint on the stratigraphic position of the SSB at Shitouzhai. Although the evolutionary progression of *Nv. waageni waageni* to *Nv. pingdingshanensis* was demonstrated at the better-studied West Pingdingshan section near Chaohu in Anhui Province (Zhao et al., 2007), this pattern cannot be established for the present study section owing to the scarcity of conodont fossils (Fig. 1).

Carbon-isotope chemostratigraphy allows exact placement of the SSB at Shitouzhai as well as detailed correlation of the study section to biostratigraphically

better-studied sections elsewhere. The $\delta^{13}\text{C}_{\text{carb}}$ profile for Shitouzhai shows a pattern of excursions similar to those of other SSB sections in South China and globally (Fig. 2; [see Song et al., 2013, for a review](#)), indicating that carbonate carbon isotopes were not significantly affected by diagenesis (Appendix B). The mid to late Smithian is characterized by a major negative excursion (N3 of Song et al., 2013), with a minimum $\delta^{13}\text{C}$ of -3.2‰ at Shitouzhai (compared to ca. -1 to -4‰ globally). The SSB is located in the middle of a rapid positive shift in $\delta^{13}\text{C}$ having a magnitude ranging from +3 to +7‰ globally. At Shitouzhai, this shift amounts to +3.5‰ and the midpoint of the shift is located in the upper part of Bed 13, about 50 cm below the base of Bed 14, thus narrowly constraining the position of the SSB (Fig. 2). There was limited $\delta^{13}\text{C}_{\text{carb}}$ variation during the early Spathian, with the Shitouzhai study section showing a weak positive drift, whereas most other sections show a weak negative trend within this interval. All sections exhibit a large negative $\delta^{13}\text{C}_{\text{carb}}$ shift in the mid to late Spathian, with minimum values ranging from ca. -1 to -4‰ (Fig. 2). These $\delta^{13}\text{C}_{\text{carb}}$ trends have been well-documented in Lower Triassic sections from around the world (Payne et al., 2004; Tong et al., 2007; Horacek et al., 2007; Song et al., 2013; Grasby et al., 2013).

We have correlated the $\delta^{13}\text{C}_{\text{carb}}$ profile for Shitouzhai with that for the biostratigraphically well-constrained West Pingdingshan section (Tong et al., 2007) (Fig. 1), in which four conodont zones were recognized within the Olenekian Stage. They are the *Nv. w. eowaageni* sub-Zone, *Nv. w. waageni* sub-Zone, *Nv. pingdingshanensis* Zone, and *Tr. homeri* Zone (Zhao et al., 2007). The *Nv. pingdingshanensis* Zone is demarcated by the first occurrences of *Nv. pingdingshanensis* and *Tr. homeri* at its base and top, respectively. At Shitouzhai, limited fossil occurrences allow recognition of three of these conodont zones: the *Nv. w. waageni* sub-Zone, *Nv. pingdingshanensis* Zone and *Tr. homeri* Zone (Fig. 1). The base of the *Nv. pingdingshanensis* Zone (= SSB) also coincides with a sharp positive $\delta^{13}\text{C}_{\text{carb}}$ excursion that can be correlated globally (Fig. 2).

An age-depth model was developed in order to calculate sediment fluxes at Shitouzhai (Fig. 3). Age constraints for rate calculations were provided by chemical abrasion–thermal ionization mass spectrometry (CA-TIMS) studies of U-Pb in zircons (Ovtcharova et al., 2006), from which the ages of the Smithian-Spathian and Induan-Olenekian boundaries were estimated at ~250.55 Ma and ~251.25 Ma,

respectively. The Olenekian-Anisian boundary age (~247.3 Ma) was determined from U-Pb ages (Lehrmann et al., 2006) combined with conodont biostratigraphic analysis (Orchard, 2007). These dates yield durations for the Smithian and Spathian substages of ~0.7 Myr and ~3.25 Myr, respectively. Ages for the remaining samples were linearly interpolated between these dated horizons (Fig. 3a) and used to calculate sediment fluxes (Fig. 3b).

3 Methods

3.1 Sampling

Large fresh samples, weighing about 3-4 kg each, were collected in outcrop at the Shitouzhai section. Weathered surfaces and diagenetic veins were trimmed off, and the remaining sample was crushed into small pieces and powdered with a rock mill to <200 mesh for geochemical analysis.

3.2 Carbonate carbon isotope analysis

About 80-120 mg of powder was placed in a 10 mL Na-glass vial, sealed with a butyl rubber septum, and reacted with 100% phosphoric acid at 72 °C after flushing with helium. The evolved CO₂ gas was analyzed for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ using a MAT 253 mass-spectrometer in the State Key Laboratory of Geological Processes and Mineral Resources at the China University of Geosciences-Wuhan. All isotopic data are reported as per mille variation (‰) relative to Vienna Pee Dee belemnite (V-PDB) standard. The analytical precision is better than $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$ based on duplicate analyses of the laboratory standards GBW-04416 ($\delta^{13}\text{C} = 1.61\text{‰}$).

3.3 CAS extraction and sulfur isotope analysis

Carbonate-associated sulfate (CAS) concentrations and isotopes ($\delta^{34}\text{S}_{\text{CAS}}$) were determined for samples containing >30 wt% CaCO₃. These samples were powdered,

leached of soluble sulfates in a 10% NaCl solution, rinsed three times in deionized water, and dissolved in 3N HCl. The acidified samples were filtered, and an excess of 1M BaCl₂ was added to the filtrate to precipitate BaSO₄. The BaSO₄ precipitate was rinsed, filtered, dried and then combined with an excess of V₂O₅ and analyzed for its S-isotope composition in the State Key Laboratory of Biogeology and Environmental Geology at the China University of Geosciences-Wuhan. Sulfur isotope compositions are expressed in standard δ -notation as per mille (‰) variation with respect to V-CDT, with an analytical error of ~0.1‰ calculated from replicate analyses of samples and the laboratory standards NBS 127 (21.1‰), IAEA SO-5 (0.49‰) and IAEA SO-6 (-34.05‰). CAS concentrations were calculated from the mass of recovered BaSO₄.

3.4 Elemental analysis

The measurement of major and trace element concentrations was carried out in the State Key Laboratory of Geological Processes and Mineral Resources at the China University of Geosciences-Wuhan following the procedure of national standards (GB/T 14506–2010) and Liu et al. (2008). A Hitachi atomic absorption spectrophotometer (180–70) and an ultraviolet-visible spectrophotometer (UV-754) were utilized in major element analysis. An Agilent 7500a ICP-MS was used to analyze trace element concentrations with an average analytical uncertainty of better than 2% (RSD), of ~~±5 ppm~~, and results were calibrated using the laboratory standards AGV-2, BHVO-2, and BCR-2. Rare earth element (REE) concentrations were normalized (N) to the average upper crustal composition of McLennan (2001). In order to calculate enrichment ratios, lanthanum (La), samarium (Sm), and ytterbium (Yb) were used as proxies for the light (LREE), middle (MREE) and heavy rare earth elements (HREE), respectively. The europium anomaly (Eu/Eu*) was calculated as $2Eu_N / (Sm_N + Gd_N)$ and the cerium anomaly (Ce/Ce*) as $3Ce_N / (2La_N + Nd_N)$. The chemical index of alteration (CIA) was calculated as $Al_2O_3 / (Al_2O_3 + K_2O + Na_2O)$. This is a modified form of the original CIA equation (Kidder and Eddy-Dilek, 1994) that eliminates CaO from the denominator, which is superior for use in carbonate-rich sedimentary successions. The Th/Th* ratio, where Th* represents the average thorium concentration of the upper crust (10.7 ppm; Bau, 1996),

can be used to estimate the fraction of clay minerals in carbonate units.

4 Results

4.1 Carbonate carbon isotopic excursions

$\delta^{13}\text{C}_{\text{carb}}$ values range from -3.2‰ to 1.8‰ through the SSB interval in the study section, with a mean value of about 0.01‰ (Fig. 4; Appendix C). A sharp positive shift in $\delta^{13}\text{C}_{\text{carb}}$, from -3.1‰ to 1.0‰, occurs across the SSB. The large excursions in the $\delta^{13}\text{C}_{\text{carb}}$ profile for the whole Shitouzhai section mirror excursions seen in Smithian-Spathian sections globally, providing a strong basis for interregional correlations (Fig. 2). These excursions allow recognition of four carbon-isotope intervals, with Interval I characterized by decreasing $\delta^{13}\text{C}$ to a minimum at N3 (late Smithian), Interval II by increasing $\delta^{13}\text{C}$ to a maximum at P3 (the SSB), Interval III by decreasing $\delta^{13}\text{C}$ to a minimum at N4 (mid-Spathian), and Interval IV by increasing $\delta^{13}\text{C}$ to a maximum at P4 (earliest Anisian) (Fig. 2; cf. Song et al., 2013). At Shitouzhai, Interval I encompasses Beds 6-7, Interval II Beds 8-13, Interval III Beds 14-15, and Interval IV Beds 16-17.

4.2 CAS-sulfur isotopes

$\delta^{34}\text{S}_{\text{CAS}}$ values range from 23.6‰ to 37.9‰ with a mean value of 29.7‰. The $\delta^{34}\text{S}_{\text{CAS}}$ profile exhibits a slight negative trend up section, although interrupted by several negative and positive excursions (Fig. 4; Appendix C). The $\delta^{34}\text{S}_{\text{CAS}}$ profile exhibits significant negative covariation with the $\delta^{13}\text{C}_{\text{carb}}$ profile ($r^2 = 0.14$). This covariation is particularly pronounced around the SSB, where a 3‰ positive shift in the $\delta^{13}\text{C}_{\text{carb}}$ profile is mirrored by a 14‰ negative shift in the $\delta^{34}\text{S}_{\text{CAS}}$ profile (Fig. 4).

4.3 Trace element concentrations

ΣREE values range from 17 ppm to 46 ppm, with higher mean values below the SSB (43 ppm) than above it (23 ppm) (Fig. 4; Appendix C). Th/Th* ratios exhibit a similar pattern

to Σ REE, with higher mean values below the SSB (0.27) than above it (0.13). Y/Ho ratios range from 30.7 to 37.2 with a mean value of ~ 34 . Eu/Eu* ratios range from 0.95 to 1.20 and are mainly close to 0.9–1.0 throughout the section. Sm_N/Yb_N ratios fluctuate between 0.98 and 1.42, with relatively higher and stable values below the SSB and more variable values above the SSB (Fig. 4).

Th/U ratios range from 0.34 to 1.56, with values mostly >1.0 below the SSB and mostly <1.0 above it (Fig. 4; Appendix C). Ce/Ce* ratios range from 0.73 to 0.88, with higher values below the SSB than above it. The chemical index of alteration (CIA) values range from 0.69 to 0.78 but are consistently higher below the SSB (>0.75) than above it (<0.73). Mn/Th ratios are uniformly low (<300) below the SSB but more variable and generally higher (to ~ 1900) above the SSB (Fig. 4). Sr concentrations range from 508 ppm to 2160 ppm, and Mn concentrations range from 230 ppm to 3776 ppm (Appendix C). Mn/Sr values are uniformly <1 below the SSB and range from 0.2 to 3.8 with a mean of ~ 2.1 above the SSB (Fig. B1). All of these elemental proxies exhibit a significant excursion at or close to the SSB (Fig. 4).

4.4 Sediment fluxes

Bulk accumulation rates (BAR) are higher in the Smithian ($\sim 11 \text{ g cm}^{-2} \text{ kyr}^{-1}$) than in the Spathian ($\sim 5 \text{ g cm}^{-2} \text{ kyr}^{-1}$) (Fig. 3b). Carbonate mass accumulation rates (MAR_{carb}) fluctuated in the range of 7–9 $\text{g cm}^{-2} \text{ kyr}^{-1}$ below the SSB and declined to 4–5 $\text{g cm}^{-2} \text{ kyr}^{-1}$ above the SSB. Clay mass accumulation rates (MAR_{clay}) fluctuated in the range of 2–4 $\text{g cm}^{-2} \text{ kyr}^{-1}$ below the SSB and declined to $<1 \text{ g cm}^{-2} \text{ kyr}^{-1}$ above the SSB. At a fine scale below the SSB, MAR_{carb} and MAR_{clay} varied inversely because carbonates and clays are the two main components of the study section and, hence, produced dilutional effects of one component by the other.

5 Discussion

5.1 Weathering rate changes

Studies of both modern and ancient carbonates show that a primary seawater signature is

characterized by low total REE concentrations (Σ REE) and relative HREE enrichment (Webb et al., 2009). However, carbonate sediments containing even a minor amount of clay minerals tend to acquire a terrigenous REE signal characterized by high Σ REE and strong LREE or MREE enrichment (Sholkovitz and Shen, 1995; Bright et al., 2009). At Shitouzhai, Σ REE exhibits strong positive covariation with Th ($r^2 = 0.95$; Fig. B1-f), indicating that REEs came from the detrital clay fraction, not the hydrogenous (seawater) fraction (Zhao et al., 2013). Moreover, the clay fraction (as estimated from Th/Th*) is substantial, ranging from ~10% to 30% of the total sample, which reflects the argillaceous/muddy character of carbonates in the study section.

All samples at Shitouzhai yield Y/Ho ratios of ~30–35 (Appendix C), which are closer to terrestrial values (~25–30) than to seawater values (44–74; Bau, 1996; Webb et al., 2009). Σ REE also exhibits modest negative covariation with Y/Ho ($r^2 = 0.42$; Fig. B1-g). Thus, a large component of the REEs in the study section is terrestrially derived, probably through release from clay minerals during diagenesis. Nearly all Eu/Eu* ratios are in the range of 0.9–1.0 (Appendix C), which are typical of crustal rocks and are consistent with uptake of REEs from clay minerals (McLennan, 2001). MREE enrichment is rather strong (most samples yield $\text{Sm}_N/\text{Yb}_N > 1.0$; Fig. 4), suggesting the presence of phosphate in the sediment, or the influence of pore waters previously in contact with phosphate (Kidder and Eddy-Dilek, 1994; Bright et al., 2009).

All of the detrital proxies from the study section provide evidence of a major decrease in weathering intensity at the SSB. The age-depth model for the study section (Fig. 3a) shows that the SSB is characterized by a large decline in linear sedimentation rates (LSR) from 43 m Myr⁻¹ to 21 m Myr⁻¹ and a proportional decrease in bulk accumulation rates (BAR) from 10.7 g cm⁻² kyr⁻¹ to 5.3 g cm⁻² kyr⁻¹ (Fig. 3b). The mass accumulation rates (MAR) of both clays and carbonate also declined across the SSB, although the decline was larger for clays (~80–90%) than for carbonate (~30–40%; Fig. 3b). These proportional differences reflect the greater concentration of clays in Smithian beds relative to Spathian beds. The sharp decline in Σ REE concentrations near the SSB (Fig. 4) is also evidence of a decrease in clay-mineral content upsection. The CIA has been widely used as a proxy for chemical weathering intensity in sediment source regions (Nesbitt and Young, 1982; Goldberg and Humayun, 2010). The abrupt decline in CIA

values at the SSB, from ~0.76–0.78 to ~0.70–0.72 (Fig. 4), implies a major decrease in chemical weathering intensity. This interpretation is supported by strong correlations of CIA with many detrital proxies, including Al ($r = +0.87$), ΣREE ($r = +0.81$), Th/Th* ($r = +0.81$), and LSR ($r = +0.93$). Although changes in CIA potentially can be due to changes in sediment provenance (e.g., Price and Velbel, 2003), the weak correlation of CIA to Eu/Eu* ($r = -0.21$) argues against this interpretation.

All detrital proxies for the Shitouzhai section are thus consistent in documenting a major decrease in both chemical and physical weathering intensity at the SSB (Fig. 5). These changes are reflected in lower CIA values, greatly reduced clay-mineral production, and more limited transport of siliciclastics to shallow-marine systems. Lower bulk sediment fluxes merely reflect a return to more typical long-term values, however, as the Griesbachian-Smithian interval of the Early Triassic was characterized by exceptionally high sediment fluxes and chemical weathering rates (Algeo and Twitchett, 2010). These weathering-related changes at the SSB are likely to have been due to a sharp, ~5 °C temperature decrease in the tropics (Sun et al., 2012; Romano et al., 2013). Even the decline in carbonate flux may have been a consequence of reduced riverine inputs of Ca^{2+} and CO_3^{2-} ions to marine systems, although other factors such as climatic cooling or changes in oceanic thermohaline circulation may have influenced marine carbonate production.

5.2 Oceanic redox variation

The concentrations of redox-sensitive trace elements (e.g., Mo, U, and V) are low (i.e., close to detrital background values) in all samples from the study section, although there is a slight increase around the SSB, especially on a Th-normalized basis (Appendix C). However, there is an even larger increase in Mn/Th at this level (Fig. 4). Under reducing conditions, Mn^{2+} is highly soluble and does not accumulate in substantial amounts in marine sediments. However, suboxic to oxic conditions commonly result in Mn enrichment through accumulation of Mn(II) in carbonates or Mn(III) in oxyhydroxides (Okita et al., 1988). Strong Mn enrichment is thus common on the margins of reducing deep watermasses (Landing and Bruland, 1987). Mn enrichment in carbonates is accepted

as a good indicator of suboxic conditions (Rue et al., 1997; Pakhomova et al., 2007). At Shitouzhai, the Mn/Th profile suggests dominantly anoxic conditions below the SSB (0–18 m) and suboxic conditions above it (20–37 m), although with a brief interlude of more reducing conditions during the early Spathian (28–32 m; Fig. 4).

Cerium (Ce) is the only REE that is affected by oxidation-reduction processes in the Earth-surface environment. Under reducing conditions, Ce^{3+} has the same valence as other REEs and, therefore, is not fractionated relative to them, yielding Ce/Ce* ratios of ~1.0 (German and Elderfield, 1990). Under oxidizing conditions, Ce^{4+} is preferentially removed from solution, yielding local sedimentary deposits with Ce/Ce* > 1.0, whereas the Ce/Ce* ratio of seawater and of any hydrogenous deposits incorporating REEs from seawater is < 1.0 (e.g., 0.3–0.4 in the modern ocean). Thus, Ce is potentially a good proxy for marine palaeoredox conditions, provided that a hydrogenous signal can be measured (Wright et al., 1987). Terrigenous influence (e.g., addition of REEs from clay minerals) will generally cause Ce/Ce* ratios to converge on 1.0, which is by definition the value for average upper crustal rocks. In the study section, Ce/Ce* ratios vary from 0.79 to 0.88 (Fig. 4). These moderately high values are nominally indicative suboxic conditions. However, the Ce/Ce* ratio was probably heavily influenced by REEs from the clay fraction of the sediment, making the Ce/Ce* ratio of any hydrogenous contribution uncertain.

Th/U ratios are useful for palaeoredox analysis owing to the redox-dependent behavior of U. Under oxidizing conditions, U(VI) tends to form stable carbonate complexes in seawater (Langmuir, 1978; Algeo and Maynard, 2004). Under reducing conditions, U(IV) is readily removed to the sediment. Th, however, is not subject to the influence of redox condition, resulting in higher Th/U ratios under reducing conditions as aqueous U is lost (Wignall and Myers, 1988). In the study section, a distinct decrease in the Th/U ratio at the SSB indicates a shift toward more oxygenated conditions, which was sustained into the early Spathian (Fig. 4). These results are consistent with dominantly oxic to suboxic conditions in the study area following the SSB (Fig. 5).

5.3 Significance of C-S isotopic variation at the SSB

Seawater sulfate $\delta^{34}\text{S}$ rose sharply from $\sim +15\text{‰}$ in the Late Permian to $> +30\text{‰}$ in the Middle Triassic (Claypool et al., 1980; Kampschulte and Strauss, 2004), although the pattern of increase during the Early Triassic has only recently begun to be worked out (Song et al., 2014). The present study provides the most comprehensive analysis of $\delta^{34}\text{S}_{\text{CAS}}$ variation at the SSB of any study to date. The Shitouzhai section exhibits a distinct, $\sim 10\text{--}15\text{‰}$ negative shift in $\delta^{34}\text{S}_{\text{CAS}}$ that is paired with a $\sim 4\text{‰}$ positive shift in $\delta^{13}\text{C}_{\text{carb}}$ (Fig. 4). Both shifts are limited to a narrow interval around the SSB, probably representing no more than $\sim 75\text{--}150$ kyr based on average sedimentation rates for the study section (Fig. 3a). These two features (i.e., negative covariation and a short event interval) impose significant constraints on the underlying causes of the isotopic shifts. Most of the Early Triassic is characterized by positive $\delta^{13}\text{C}_{\text{carb}}\text{--}\delta^{34}\text{S}_{\text{CAS}}$ covariation, a pattern that is consistent with control by sediment burial fluxes, i.e., co-burial of organic carbon and pyrite, linked to variations in marine productivity and/or redox conditions (Luo et al., 2010; Song et al., 2014). In contrast, negative $\delta^{13}\text{C}_{\text{carb}}\text{--}\delta^{34}\text{S}_{\text{CAS}}$ covariation during a short-term event at the SSB is indicative of oceanographic controls. Specifically, we hypothesize that cooling-driven re-invigoration of oceanic overturning circulation led to stronger upwelling, mixing nutrient- and sulfide-rich deep waters upward into the ocean-surface layer, and causing both enhanced marine productivity (hence higher $\delta^{13}\text{C}_{\text{DIC}}$) and oxidation of advected H_2S (hence lower $\delta^{34}\text{S}_{\text{sulfate}}$) (Fig. 6). Such an oceanographic process was inherently transient, lasting only until the nutrients and sulfide that had accumulated in the deep ocean during the Griesbachian-Smithian interval of intense oceanic stratification (Song et al., 2013) became depleted. The same process was inferred for the latest Spathian by Song et al. (2014), an interval also characterized by short-term negative $\delta^{13}\text{C}_{\text{carb}}\text{--}\delta^{34}\text{S}_{\text{CAS}}$ covariation (Song et al., 2014, their figure 6) and linked to global climatic cooling (Sun et al., 2012). These considerations underscore the fundamental significance of the SSB, which represents the termination of the Early Triassic hyper-greenhouse climate and re-invigoration of global-ocean overturning circulation (Fig. 6).

Compilative studies for the Phanerozoic have demonstrated that seawater sulfate $\delta^{34}\text{S}$ increased sharply during the Early Triassic, from $\sim +15\text{‰}$ in the Late Permian to $> +30\text{‰}$ by the Middle Triassic (Claypool et al., 1980; Kampschulte and Strauss, 2004). Studies of

the narrow PTB interval have shown even greater variation, with $\delta^{34}\text{S}$ ranging from at least 0‰ to +30‰ (see Claypool et al., 1980, for a review). Owing to its high-frequency character, this $\delta^{34}\text{S}$ variation is not correlatable between sections. Recently, $\delta^{34}\text{S}_{\text{CAS}}$ -variation through the entire Early Triassic was analyzed in a high-resolution composite section from the Nanpanjiang Basin of South China (Song et al., 2014). In that study, $\delta^{34}\text{S}_{\text{CAS}}$ exhibited strong positive covariation with $\delta^{13}\text{C}_{\text{carb}}$ from the latest Permian through the mid-Smithian, followed by a shift to strong negative covariation at the SSB and into the earliest Spathian. In general, positive $\delta^{13}\text{C}_{\text{carb}}$ - $\delta^{34}\text{S}_{\text{CAS}}$ covariation has been attributed to co-burial of reduced carbon and sulfur species (i.e., organic carbon and pyrite) linked to variations in marine productivity and/or redox conditions (e.g., Luo et al., 2010; Song et al., 2014). On the other hand, Song et al. (2014) inferred oceanographic controls on the pattern of negative $\delta^{13}\text{C}_{\text{carb}}$ - $\delta^{34}\text{S}_{\text{CAS}}$ covariation at the SSB—specifically, a short-term mixing of nutrient- and sulfide-rich deep waters into the ocean surface layer, triggering a transient increase in marine productivity (hence higher $^{13}\text{C}_{\text{carb}}$) concurrently with a decrease in seawater sulfate $\delta^{34}\text{S}$ through oxidation of vertically advected H_2S . They inferred that this transient mixing event was triggered by abrupt climatic cooling at the SSB (Fig. 5; cf. Sun et al., 2012; Romano et al., 2013).

The present study provides the most comprehensive analysis of $\delta^{34}\text{S}_{\text{CAS}}$ variation at the SSB of any study to date. The Shitouzhai section exhibits a distinct, ~14‰ negative shift in $\delta^{34}\text{S}_{\text{CAS}}$ across the SSB that is paired with a positive shift in $\delta^{13}\text{C}_{\text{carb}}$ (Fig. 4). This pattern was previously reported for a more broadly defined interval around the SSB (Song et al., 2014), although their dataset offered only limited resolution at the SSB *sensu stricto*. Our results show that this relationship is limited to a narrow interval bracketing the SSB, probably representing no more than ~75–150 kyr based on average sedimentation rates for the study section (Fig. 3a). The brevity of this interval of negative $\delta^{13}\text{C}_{\text{carb}}$ - $\delta^{34}\text{S}_{\text{CAS}}$ covariation is consistent with the hypothesis of oceanographic controls, i.e., a mixing of nutrient- and sulfide-rich deep waters into the ocean surface layer (Fig. 5). Such a process would have been inherently transient, lasting only as long as it took to disperse the nutrients and sulfide that had accumulated in the deep ocean during the preceding ~1.5 Myr-long interval of intense stratification of the oceanic water column (Song et al., 2013). These relationships thus point to the fundamental significance of the

~~SSB, which represents the termination of the Early Triassic hyper-greenhouse climate and re-invigoration of global ocean overturning circulation (Fig. 5).~~

5.4 Causes and consequences of the SSB event

Oceanographic changes at the SSB had a major effect on contemporaneous marine biotas. Several invertebrate clades, including ammonoids, conodonts, and foraminifera, appear to have suffered severe losses of biodiversity at this time (Orchard, 2007; Stanley, 2009; Song et al., 2011). Ammonoids diversified greatly during the Griesbachian to Smithian but underwent a major evolutionary turnover at the SSB, followed by a stepwise increase in biodiversity in the early to middle Spathian (Brayard et al., 2009). Conodonts show a similar pattern, with a rapid radiation in the early-middle Smithian terminated by a severe extinction at the SSB, followed by a second radiation in the early to middle Spathian (Orchard, 2007). Changes in biodiversity were mirrored by changes in body size. Chen et al. (2013) documented a brief but significant size reduction among conodonts, coinciding with extremely high seawater temperature just prior to the SSB (Sun et al., 2012) based on bulk sample analysis from an outcrop section in Guizhou Province, southwestern China. Conodonts remained diminutive during the SSB transition and the earliest Spathian and then underwent a stepwise size increase during the early to middle Spathian (Chen et al., 2013).

Although literature surveys show that marine clades such as conodonts, ammonoids, and foraminifera experienced a sharp decline in diversity at the SSB (Orchard, 2007; Stanley, 2009; Song et al., 2011), this pattern may be biased by data binning effects. In fact, examination of the stratigraphic distribution of these marine clades in actual geological sections suggests that diversity losses occurred slightly prior to the SSB (Zhao et al., 2007; Song et al., 2011; Zakharov and Popov, 2014) and were probably associated with the late Smithian thermal maximum (Sun et al., 2012; Romano et al., 2013; Fig. 5), rather than the Smithian-Spathian boundary itself. The affected marine clades also did not recover immediately when climatic and environmental conditions ameliorated abruptly at the SSB but, rather, underwent a stepwise recovery during the early to middle Spathian (Orchard, 2007; Stanley, 2009; Brayard et al., 2009).

466 The SSB was characterized by a major change in terrestrial flora.
467 Lycopsid-dominated assemblages were replaced by conifer-dominated or mixed
468 lycopsid-conifer vegetation, as indicated by palynological data from Pakistan (Hermann
469 et al., 2011), Norway (Galfetti et al., 2007; Hochuli and Vigran, 2010), and central
470 Europe (Kurscher and Herengreen, 2010). A similar floral change was reported from the
471 Spathian–Anisian boundary in Hungary (Looy et al., 1999), suggesting some variation in
472 the timing of terrestrial floral recovery in different regions of the world. Macrofloral
473 fossil evidence indicates a more volatile record of vegetation change, with multiple
474 short-term expansions of lycopsids from tropical regions temporarily displacing conifers
475 during the Olenekian (Retallack et al., 2011; Hochuli et al., 2010; Looy et al., 2001).
476 These inferences are supported by biomarker and biogeochemical studies. Saito et al.
477 (2013) reported that sediments of Griesbachian to Smithian age yield carbon/nitrogen
478 (C/N) ratios <10 and contain abundant retene, simonellite, and dehydroabietan, which are
479 interpreted to have been sourced from lycopsids and/or bryophytes. After the SSB,
480 sediments yield C/N ratios >10 and exhibit a large increase in pimarane abundance,
481 suggesting dominance of terrestrial floras by conifers. As a result, a highly diverse
482 coniferous flora became widely re-established around the SSB, replacing the lycopsid-
483 and fern-dominated disaster-type vegetation that had dominated the Griesbachian to
484 Smithian interval (Saito et al., 2013; Fig. 6).

485 The SSB was also characterized by major environmental changes. Strong climatic
486 cooling has been inferred from both faunal (Galfetti et al., 2007) and oxygen-isotope
487 evidence (Sun et al., 2012; Romano et al., 2013). Changes in oceanic circulation appear
488 to have occurred at the same time. Saito et al. (2013) interpreted an increase in extended
489 tricyclic terpane ratios (ETR) around the SSB as due to a shift from limited to vigorous
490 overturning circulation (Fig. 6). These climatic and oceanographic changes were
491 probably linked: an increase in the intensity of global meridional circulation would have
492 been a natural consequence of climatic cooling (e.g., Rind, 1998), leading to more
493 vigorous deepwater formation in high-latitude regions (Kiehl and Shields, 2005).

494 The environmental and climatic changes documented at Shitouzhai reinforce
495 observations made in other SSB sections globally and, thus, serve to demonstrate that
496 these changes were widespread and characteristic of the SSB. We propose that all of the

changes in our model (Fig. 6) were due to a cooling event that commenced following the LSTM and that continued strongly across the SSB. In particular, we infer that cooling led to re-invigoration of global-ocean overturning circulation. It should be noted that we are not envisioning complete ocean stagnation during the preceding Griesbachian-Smithian interval, which is unlikely based on physical oceanographic principles (e.g., Kiehl and Shields, 2005), but, rather, a strong slowing of overturning circulation that led to a buildup of nutrients in the deep ocean (Fig. 6). Reinvigoration of global-ocean circulation at the SSB flushed this buildup of nutrients back into the ocean-surface layer, triggering a transient increase in marine productivity and expansion of thermoclinal anoxia that lasted until this deepwater nutrient source was depleted. The brevity of the SSB anoxic event at Shitouzhai, which lasted ~75–150 kyr, is consistent with such a mechanism. This mechanism also accounts for the abrupt, large positive shift in $\delta^{13}\text{C}_{\text{carb}}$ at the SSB, which was due to a productivity-related increase in organic carbon burial rates (Fig. 6).

~~On land, the SSB was characterized by a major change in terrestrial floral assemblages, as shown by palynological and macrofloral analyses of terrestrial facies as well as by elemental and biomarker data from marine sediments. A transition from lycopsid-dominated to conifer-dominated or mixed vegetation across the SSB has been documented from sites in Pakistan (Hermann et al., 2011), Norway (Galfetti et al., 2007; Hochuli and Vigran, 2010), and central Europe (Kurscher and Herengreen, 2010). Recently, Saito et al. (2013) reported that Griesbachian-Smithian sediments contain abundant retene, simonellite, and dehydroabietan and exhibit carbon/nitrogen (C/N) ratios <10, reflecting lycopsid and/or bryophyte sources, whereas Spathian sediments contain abundant pimarane and exhibit C/N ratios >10, suggesting dominance of terrestrial floras by conifers. Collectively, these studies indicate that a highly diverse coniferous flora became widely re-established around the SSB, replacing the lycopsid and fern-dominated disaster-type vegetation that prevailed during the Griesbachian to Smithian (Fig. 5). However, some differences in the timing and pattern of this floral transition have been reported, e.g., Looy et al. (1999) showed that the transition from lycopsid-dominated to conifer-dominated vegetation occurred at the Spathian-Anisian boundary in Hungary, and several studies (Retallack et al., 2011; Hochuli et al., 2010; Looy et al., 2001) have inferred multiple short-term expansions of lycopsids from tropical~~

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regions temporarily displacing conifers during the Olenekian (Retallack et al., 2011; Hochuli et al., 2010; Looy et al., 2001).

The SSB was also characterized by significant environment changes. Major climate cooling at that time has been proposed on the basis of faunal (Galfetti et al., 2007) and oxygen isotope evidence (Sun et al., 2012; Romano et al., 2013). Changes in oceanic circulation also probably occurred at the same time. Saito et al. (2013) interpreted an increase in extended triacyclic terpane ratios (ETR) around the SSB as the product of a shift from limited to vigorous overturning circulation (Fig. 5). An increase in the intensity of global meridional circulation at the SSB would have been a natural consequence of climatic cooling (Sun et al., 2012; Romano et al., 2013), leading to more vigorous deepwater formation in high latitude regions (cf. Kiehl and Shield, 2005). Although fluctuations in marine carbonate $\delta^{13}\text{C}$ records are open to multiple interpretations, the environmental changes discussed above constrain the range of viable mechanisms for the rapid positive shift at the SSB (P3 of Song et al., 2013). This shift is most readily explained as a response to a major increase in marine productivity and organic carbon burial (Fig. 5), possibly triggered by cooling-induced reinvigoration of oceanic thermohaline circulation and a consequent upwelling of nutrients that had been sequestered in the deep ocean during the ~1.5 million year interval of relative oceanic stagnation in the Griesbachian to Smithian interval (Song et al., 2013). The brevity of the SSB event in the Shitouzhai section, which lasted ~75–150 kyr, is consistent with this mechanism. Thus, we propose that improved global ocean overturning circulation was likely associated with global cooling at the SSB (Fig. 5).

The ultimate cause of the SSB event is uncertain. Given that the onset of the Permian-Triassic boundary crisis has been firmly linked to initiation of the main eruptive phase of the Siberian Traps Large Igneous Province (STLIP) (Renne et al., 1995; Kamo et al., 2003) and that the Early Triassic was an interval of repeated environmental disturbances (Algeo et al., 2011; Retallack et al., 2011) and elevated global temperatures (Sun et al., 2012; Romano et al., 2013) linked to volcanogenic greenhouse gas emissions (Retallack and Jahren, 2008; Black et al., 2012), the obvious explanation for the SSB is a reduction in the intensity of magmatic activity in the STLIP source region (Fig. 5). The available radiometric age data for the Siberian Traps, although sparse, are consistent with

this possibility. U–Pb dating of perovskites in the early Arydzhangsky flow and zircons from the late Delkansky silicic tuff of extrusive suites in the Maymecha-Kotuy region suggests that the STLIP flood basalt eruptions commenced at 251.7 ± 0.4 Ma and ended at 251.1 ± 0.3 Ma, i.e., an interval of ~600 kyr (Renne et al., 1995; Kamo et al., 2003). However, an Ar–Ar date of 250.3 ± 1.1 Ma was obtained for the final stage of extrusive volcanism at Noril'sk, the core area of the STLIP (Reichow et al., 2009; see also review of evidence for a late eruptive stage by Ovtcharova et al., 2006). The more critical issue, in any case, is the duration not of flood basalt eruptions but of intrusive magmatism in the West Siberian Coal Basin, which was probably the main source of volcanogenic greenhouse gases (Retallack and Jahren, 2008; Black et al., 2012). Reichow et al. (2009) reported ages for STLIP-related intrusives spanning several million years, which is consistent with the hypotheses that large-scale intrusive activity continued at least until the SSB, and that cessation of most such activity at the SSB was responsible for contemporaneous climatic cooling (Sun et al., 2012; Romano et al., 2013). Further work on the chronology of the STLIP will be needed to conclusively evaluate controls on the SSB event.

6 Conclusions

The SSB event (late Early Triassic) has been multidisciplinarily studied in the Shitouzhai section, South China, using a combination of carbonate carbon ($\delta^{13}\text{C}_{\text{carb}}$) and carbonate-associated sulfate sulfur isotopes ($\delta^{34}\text{S}_{\text{CAS}}$), rare earth elements, and elemental palaeoredox and palaeoproductivity proxies. Like these recorded in other SSB sections, a large (+4‰) positive $\delta^{13}\text{C}_{\text{carb}}$ shift across the SSB is observed in Shitouzhai, indicating enhanced marine productivity and organic carbon burial. Various elemental and isotopic proxies suggest that a major decrease in chemical weathering intensity and detrital sediment input, a shift toward a better-ventilated oceanic thermocline, and a diminished burial flux of reduced sulfur also coincided with a large cooling of sea-surface temperature within the Early Triassic hothouse regime. The extremely high sea-surface temperature just prior to the S-S transition may have triggered a biocrisis near the SSB. Biota, however, did not recover immediately when climatic and environmental

ameliorations occurred at the SSB, instead, underwent a stepwise recovery during the early-middle Spathian times. The cause of the SSB event is uncertain but may have been related to reduced intrusive magmatic activity in the Siberian Traps Large Igneous Province.

Author contributions:

Z.Q.C., L.S.Z. and L.Z. conceived the study. Z.Q.C., T.J.A. and L.Z. interpreted the data and wrote the manuscript. L.S.Z., J.C., R.W., J.H., Y.L. and H.Q. analyzed the data. L.Z., J.C., R.W., L.C., X.F., Z.L., X.W., and Y.H. participated in the field trip.

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Figure captions

Fig. 1. Biostratigraphic and C-isotopic correlation of the Shitouzhai section near Ziyun, southern Guizhou Province, with the West Pingdingshan section in Chaohu, Anhui Province, South China. Fm. = Formation, Ht. = Height.

Fig. 2. Biostratigraphic and C-isotopic correlations of the Shitouzhai section with other Smithian–Spathian sections. Note that Intervals I–IV of $\delta^{13}\text{C}_{\text{carb}}$ profiles are recognizable globally. The standard notation (P2, P3, N3 and N4) for Early Triassic C-isotope excursions is after Song et al. (2013). Data for the Guandao, West Pingdingshan, and Majiashan sections are from Tong et al. (2007) and for the L'Uomo section from Horacek et al. (2007). The different colour columns represent corresponding conodont zones from old to young in an ascending order. Question marks represent problematic conodont biozones that still need further studies in both the Shitouzhai and Guandao sections. An. = Anisian, Ind. = Induan, Dien. = Dienerian.

Fig. 3. (a) Age-depth model and **(b)** sediment accumulation rates around the SSB in the Shitouzhai section. BAR, MAR_{clay} , and MAR_{carb} stand for bulk accumulation rate, clay mass accumulation rate, and carbonate mass accumulation rate, respectively, where $\text{MAR}_{\text{clay}} + \text{MAR}_{\text{carb}} = \text{BAR}$. BAR was calculated as $\text{LSR} \times \text{BSD}/10$, where LSR is linear sedimentation rate in units of m Myr^{-1} , BSD is bulk sediment density for which a value of 2.5 g cm^{-3} was assumed, and 10 is a unit-conversion coefficient. The algorithmic method follows Algeo and Twitchett (2010). SSB = Smithian–Spathian boundary.

Fig. 4. Chemostratigraphic profiles and environmental changes during the Smithian–Spathian transition. The $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{34}\text{S}_{\text{CAS}}$ profiles and trace element ratios at Shitouzhai show coupling with vertical gradients in marine carbonate $\delta^{13}\text{C}$ ($\Delta\delta^{13}\text{C}_{\text{DIC}}$), global sea-level elevation, and terrestrial vegetation changes during the Olenekian. $\Delta\delta^{13}\text{C}_{\text{DIC}}$ is from Song et al. (2013), sea-level variation from Yin and Tong (1996), and terrestrial vegetation from Saito et al. (2013). REE = rare earth elements,

CIA = chemical index of alteration, SL = sea level, Terr. veg. = Terrestrial vegetation,
Temp. = Temperature.

Fig. 5. Crossplots of (a) Σ REE versus Th, and (b) Σ REE versus Y/Ho. Strong positive covariation demonstrates derivation of REEs primarily from the terrigenous siliciclastic (clay-mineral) fraction of the sediment.

Fig. 6. Evolution of terrestrial and marine environments during the late Early Triassic: (a) early Smithian, (b) late Smithian thermal maximum, (c) Smithian-Spathian boundary, and (d) early Spathian. This model integrates changes in subaerial weathering rates and oceanic productivity and redox conditions documented in this study with data regarding paleoclimate variation, terrestrial floral assemblages, and marine biodiversity patterns from other sources (cited in text). We infer that the modeled environmental changes were ultimately due to variation in eruption rate of the Siberian Traps, although this has not been proven to date. See text for further discussion.

Appendix A

Geologic and palaeontologic background

The study section is located at Shitouzhai village (GPS: N25°45'9.6", E106°6'29.7"), about 3 km east of Ziyun County town in southern Guizhou Province, South China (Fig. A1). During the Early to Middle Triassic, the Ziyun area was located on the southern margin of the Yangtze Platform, to the north of the Nanpanjiang Basin (Enos et al., 2006). The palaeogeographic configuration of the Ziyun area changed from a platform-margin reef system in the latest Permian to a platform-ramp environment in the Early Triassic (Feng et al., 1997). In this area of the Nanpanjiang Basin in southern Guizhou Province, the Upper Permian successions usually comprise bioclastic rocks, which are collectively assigned to the Wujiaping Formation. However, unlike the same formation exposed elsewhere in South China, which is confined to the Wuchiapingian Stage of the Late Permian, the Wujiaping Formation in the Nanpanjiang Basin yields biotas of Wuchiapingian and Changhsingian age. This means that, in the study area, the Changxing Formation of Changhsingian age cannot be separated on the basis of lithology from the Wujiaping Formation. In most areas of the Nanpanjiang Basin, the contact of Upper Permian limestones with the overlying Lower Triassic Luolou Formation is conformable, although karstic phenomena may occur locally due to the end-Permian regional regression that affected the entire South China block (Yin et al., 2014).

At Shitouzhai, Upper Permian to Middle Triassic strata are assigned to the Wujiaping, Luolou, and Xinyuan formations, in ascending order (Ding and Huang, 1990). The upper Wujiaping Formation consists largely of massive sponge reef limestone and yields the fusulinid *Paleofusulina sinse* and the conodont *Clarkina changxingensis*, both of which point to a late Changhsingian age (Ding and Huang, 1990; Shen and Xu, 2005; Wu et al., 2010). The Luolou Formation is composed of thin-bedded calcareous mudstone, muddy limestone, and vermicular limestone with interbeds of breccia, from which conodont zones of definite Early Triassic age have been established (Ding and Huang, 1990). The lower Xinyuan Formation is also well exposed and consists of thin-bedded calcareous mudstone, yielding small bivalves of Middle Triassic age (Ding and Huang, 1990).

Fig. A1. (a) Geographic map of southern Guizhou Province, South China showing location of the Shitouzhai section in Ziyun County (modified from the Geographic Map of China, <http://map.baidu.com>). The red rectangle in the inset map of China shows the location of the study area. Early Triassic palaeogeography of **(b)** the South China block and **(c)** the study area (modified from Feng et al., 1997). Note that the locations of the West Pingdingshan (WPDS) and Majiashan (MJS) sections are shown in (b) and that of the Guandao section in (c). GBG = Great Bank of Guizhou.

Appendix B

Assessment of diagenesis

We evaluated potential diagenetic alteration of the carbonate beds in the Shitouzhai based on Mn and Sr concentrations and ratios. Diagenesis of marine carbonates generally results in an increase in Mn and a loss of Sr (Huang et al., 2003; Hu et al., 2010). In general, Mn/Sr ratios <3 are indicative of minimal diagenetic alteration, suggesting that elemental and isotopic signals are representative of the original chemistry of the sediment (Brand, 2004; Dehler et al., 2005; Le Guerroué et al., 2006). Primary $\delta^{13}\text{C}$ values can be retained through diagenesis to Mn/Sr ratios as high as 10 (Shen, 2002; Le Guerroué et al., 2006). The relatively low Mn/Sr ratios of the study section (1.2 ± 1.2 ; Appendix C) are evidence of relatively limited diagenetic alteration.

Conservation of the original $\delta^{13}\text{C}_{\text{carb}}$ of the samples is also evidenced by relative ^{18}O enrichment (i.e., $\delta^{18}\text{O}$ heavier than -5‰ ; Appendix C), which is close to primary marine O-isotope values (ca. $0 \pm 5\text{‰}$; Algeo et al., 1992; Zhao and Zheng, 2011). Only limited diagenetic alteration is also indicated by little or no covariation between Mn/Sr and $\delta^{18}\text{O}_{\text{carb}}$ for both Smithian ($r^2 = 0.05$) and Spathian samples ($r^2 = 0.005$; Fig. B1-a), as well as between Mn/Sr and $\delta^{13}\text{C}_{\text{carb}}$ for both Smithian ($r^2 = 0.32$) and Spathian samples ($r^2 = 0.0008$; Fig. B1-b). Mn/Sr exhibits stronger covariation with both $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ for the full sample set, although this variation mainly reflects secular differences in O- and C-isotopic compositions between Smithian and Spathian samples rather than diagenetic effects. Weak covariation between $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ is seen in Smithian (r^2

= 0.001) and Spathian ($r^2 = 0.09$) samples (Fig. B1-c), which may be a primary signal, e.g., related to variations in watermass chemistry (cf. Wenzel and Joachimski, 1996). Little covariation between Mn/Sr and $\delta^{34}\text{S}_{\text{CAS}}$ exists for the Smithian ($r^2 = 0.02$) and Spathian ($r^2 = 0.06$) samples (Fig. B1-d). This means that CAS from the study section was subject to minimal diagenetic influences. Moreover, covariation between $\delta^{34}\text{S}_{\text{CAS}}$ and CAS concentration is also weak ($r^2 = 0.06$ and 0.40 for Smithian and Spathian samples, respectively; Fig. B1-e), suggesting that little pyrite oxidation occurred during the CAS extraction procedure. If significant amounts of pyrite sulfur had been admixed through oxidation, $\delta^{34}\text{S}_{\text{CAS}}$ values would have been lowered considerably relative to the actual CAS isotopic composition (cf. Marengo et al., 2008). In fact, the $\delta^{34}\text{S}_{\text{CAS}}$ values reported here are similar to those attained from other Early Triassic studies (Song et al., 2014). We therefore infer that both the carbon and sulfur isotope profiles for the Shitouzhai section have largely preserved original marine compositions.

Fig. B1. Elemental and stable isotope crossplots. **(a)** $\delta^{18}\text{O}_{\text{carb}}$ versus Mn/Sr ratio. **(b)** $\delta^{13}\text{C}_{\text{carb}}$ versus Mn/Sr ratio. **(c)** $\delta^{18}\text{O}_{\text{carb}}$ versus $\delta^{13}\text{C}_{\text{carb}}$. **(d)** $\delta^{34}\text{S}_{\text{CAS}}$ versus Mn/Sr ratio. **(e)** CAS concentrations versus $\delta^{34}\text{S}_{\text{CAS}}$. **(f)** $\sum\text{REE}$ versus Th. **(g)** $\sum\text{REE}$ versus Y/Ho. CAS (carbonate-associated sulfate) concentration is given as ppm SO_4^{2-} .

Appendix C

Data tables

Table C1. Isotopic and trace element data from the Shitouzhai section

Table C2. Major and trace element concentrations and ratios from the Shitouzhai section