Contents lists available at ScienceDirect



Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

# Controls on regional marine redox evolution during Permian-Triassic transition in South China



PALAEO 🚟 3

Li-Dan Lei <sup>a,b,c</sup>, Jun Shen <sup>c</sup>, Chao Li <sup>a,\*</sup>, Thomas J. Algeo <sup>a,b,c</sup>, Zhong-Qiang Chen <sup>a</sup>, Qing-Lai Feng <sup>c</sup>, Meng Cheng <sup>a</sup>, Cheng-Sheng Jin <sup>a</sup>, Jun-Hua Huang <sup>c,\*</sup>

<sup>a</sup> State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, PR China

<sup>b</sup> Department of Geology, University of Cincinnati, Cincinnati, OH 45221-0013, USA

<sup>c</sup> State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, PR China

# A R T I C L E I N F O

Article history: Received 10 October 2016 Received in revised form 5 February 2017 Accepted 7 February 2017 Available online 10 February 2017

Keywords: Euxinia Iron speciation Weathering flux Sulfur isotopes Permian-Triassic boundary Mass extinction

### ABSTRACT

Although oceanic anoxia is regarded as a leading cause of the Permian-Triassic boundary (PTB) mass extinction, its timing, extent, and underlying causes remain unclear. Here, we conducted a high-resolution Fe-S-C-Mo geochemical study of the entire Changhsingian and lowermost Induan succession in a carbonate-ramp setting at Ganxi, western Hubei Province, South China. Six stratigraphic units representing discrete redox intervals were identified based on integrated Fe-S-C-Mo data. Units I-III are of latest Wuchiapingian to early Changhsingian age, with Units I and III characterized by euxinia and Unit II by uncertain redox conditions. Unit IV, of mid-Changhsingian age, records a gradual transition from euxinic to ferruginous conditions. Units V and VI, spanning the latest Permian mass extinction (LPME) to earliest Triassic interval, were deposited under dominantly ferruginous conditions punctuated by both euxinic and oxic episodes. Redox variations at Ganxi were controlled by contemporaneous oceanographic changes in the upper oceanic thermocline region: (i) euxinia in Units I and III may record elevated marine productivity (as suggested by mean organic carbon accumulation rates, or OCAR, of 6.5 and 5.1 mg/cm<sup>2</sup>/kyr, respectively) that was possibly related to upwelling; (ii) the euxinic-to-ferruginous transition from Unit IV to Units V-VI can be attributed to a combination of reduced sulfate availability and rising terrigenous iron inputs (mean Fe of 1.7% and 3.9%, respectively, for Units V–IV and VI compared to 1.0% for Units I-III); and (iii) transient intervals of euxinia in Units V and VI were facilitated by enhanced sulfate fluxes related to episodic volcanism during this interval. An integration of the redox data from Ganxi with previously published data from the Shangsi and Xiakou sections suggests that enhanced weathering fluxes were most likely the key factor controlling the marine redox transition from euxinic to ferruginous conditions during the latest Permian across the South China region.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

Oceanic anoxia has been widely regarded as a major contributor to the ~252-Ma latest Permian mass extinction (LPME) (Wignall and Twitchett, 1996, 2002; Isozaki, 1997; Grice et al., 2005; Algeo et al., 2007, 2008, 2011a; Brennecka et al., 2011; Shen et al., 2011; Payne and Clapham, 2012; Kaiho et al., 2012; Chen et al., 2015; Clarkson et al., 2016). Despite extensive investigation, the extent and duration of oceanic anoxia during the Late Permian and Early Triassic remain uncertain. Isozaki (1997) postulated a 20-Myr-long interval of near-global oceanic anoxia during this interval. More recent studies have concluded that oceanic anoxia/euxinia began later, around the early Changhsingian, although still at least 2 Myr prior to the LPME (Nielsen and Shen, 2004; Cao et al., 2009; Takahashi et al., 2014; Clarkson et al., 2016). Anoxia and/or euxinia may have developed initially at intermediate ocean depths (e.g., within the thermocline region, as for modern oxygen minimum zones, or OMZs) and subsequently expanded to shallower depths just prior to and during the LPME (Feng and Algeo, 2014; Clarkson et al., 2016), although oxic surface waters extended downward below fair-weather wave base (FWWB) in some areas (e.g., Loope et al., 2013; Proemse et al., 2013). A strong intensification of oceanic anoxia/euxinia occurred in conjunction with the LPME catastrophe (Brennecka et al., 2011; Shen et al., 2011; Shen et al., 2016; Lau et al., 2016). Although Isozaki's (1997) model invoked global-ocean anoxia, more recent studies have concluded that anoxia was spatially variable and limited mainly to intermediate water depths in low-latitude regions (Algeo et al., 2011a; Winguth and Winguth, 2012). In order to better understand the extent and duration of oceanic anoxia and its role in the end-Permian crisis, additional detailed studies of marine redox variation and its controlling factors during the Permian-Triassic crisis interval are needed.

<sup>\*</sup> Corresponding authors. Tel.: +862767883606; fax: +862767883456.

E-mail addresses: chaoli@cug.edu.cn (C. Li), jhhuang@cug.edu.cn (J.-H. Huang).

The Ganxi section (30°07.4′N, 109°26.8′E) in western Hubei Province has the potential to provide insights into latest Permian marine redox changes in peri-equatorial ramp settings (Fig. 1), which appear to have been highly sensitive to environmental perturbations (Shen et al., 2013, 2016). In this study, we conducted an integrated, high-resolution Fe-S-C-Mo study of the entire Changhsingian and lower Induan stages at Ganxi, in order to explore long-term oceanic redox variations of intermediate depth waters and their environmental controls. Integrated Fe-S-C-Mo systematics (Fe speciation, pyrite sulfur isotope, total organic carbon, and Mo concentration) are sensitive and efficient paleoredox indicators (Raiswell and Canfield, 1998) that have been widely applied to Precambrian ocean systems (e.g., Li et al., 2010; Poulton et al., 2010; Scott et al., 2011) but less frequently to Permian-Triassic boundary (PTB) successions.

# 2. Paleogeographic and stratigraphic background

The South China Craton was situated north of the paleo-equator in the eastern Paleo-Tethys Ocean during the Permian-Triassic transition (Fig. 1A; Ziegler, 1998). Two land areas (the Kangdian and Cathaysia oldlands) were located on the paleo-southern and northeastern margins of the craton, respectively (Fig. 1B; Feng et al., 1997) [note: the South China Craton at that time was rotated about 80–90° counterclockwise from its modern orientation; all compass directions below refer to paleo-orientations]. The central part of this craton was occupied by the carbonate Yangtze Platform, which was flanked by relatively deep shelf-basins to the west (Western Ramp) and east (Nanpanjiang Basin). During the Late Permian, the Ganxi section was situated on the Western Ramp, facing the Qinling Sea (i.e., the eastern arm of the Paleo-Tethys Ocean) (Fig. 1B). It was located in a deepwater embayment (shared with the Xiakou section) on the western margin of the Yangtze Platform known as the Xiakou-Lichuan Bay (Yin et al., 2014) or the Guangwang Basin (Wei et al., 2015).

In this study, we focused on a ~ 20-m-thick, continuously deposited succession at Ganxi that includes the Upper Permian Dalong and Lower Triassic Daye formations, which exhibit excellent exposure in outcrop (Fig. 2A). The ~15-m-thick Dalong Formation mainly consists of organic carbon-rich marly limestone, consistent with deposition in a deep-slope setting (Mutwakil et al., 2006). However, detailed lithological analysis reveals that water depths varied during deposition of the Dalong



**Fig. 1.** Geological background. (A) Global paleogeography of the Permian-Triassic transition (after Ziegler, 1998). Inset red rectangle shows area of South China map in B. (B) Paleogeographic map of South China during Late Permian (at the time of the *Clarkina meishanensis* Zone) showing location of the Ganxi section, western Hubei Province (modified after Feng et al., 1997). Other correlated sections (Xiakou, Shangsi and GSSP Meishan) are also marked. Abbreviations: Xiakou-Lichuan (XL); Guangyuan-Liangping (GL).



Fig. 2. Field photos of Ganxi section. (A) View of extended Permian-Triassic boundary (PTB) interval (Beds 83–248); Formation (Fm.) close-ups of (B) Wuchiapingian-Changhsingian boundary (WCB) interval (Beds 83–106); (C) upper Dalong Formation (Beds 218–233); and (D) PTB interval including the latest Permian mass extinction horizon (LPME) (Beds 233–239). The PTB is a tentative placement.

Formation (Fig. 3): the base of the section (0–2.2 m) consists of siliceous and calcareous mudstone, which is overlain by marly limestone with some calcareous mudstone interbeds (2.2–10.7 m), suggesting a short marine regression in the late Permian. The upper Dalong and Daye formations at Ganxi (10.7–20 m) show increasing mudstone content upsection. The lithologic transition to dominant mudstone in the earliest Triassic is a common feature of PTB sections in South China, consistent with the general marine transgression recognized widely for the Permian-Triassic transition (Yin et al., 2007). The uppermost 2 m of the Dalong Formation (13–15 m) and lowermost Triassic Daye Formation contain a few volcanic ash beds (Fig. 3).

The Ganxi section has a well-established conodont biostratigraphy consisting of five zones (in ascending order), i.e., the Clarkina orientalis, C. wangi, C. changxingensis, C. yini, and C. meishanensis zones (Mutwakil et al., 2006). The Wuchiapingian-Changhsingian boundary (WCB), which is defined by the first appearance datum of C. wangi, was placed at the base of Bed 104 (at ~1.6 m, Figs. 2B and 3). The C. changxingensis and C. yini zones (at ~6-15.2 m) are overlain by the C. meishanensis zone (at 15.2-15.7 m) (Figs. 2C and 3; Mutwakil et al., 2006). Based on correlations to the Meishan D global stratotype section and point (GSSP) for the PTB, the LPME is located at ~15.3 m, where it is associated with a >5cm-thick volcanic ash layer (Bed 234) that is followed by a second, similar ash layer (Bed 238) ~0.5 m higher in the section (Fig. 2D). These two thick tuff layers are a distinctive feature of PTB sections across South China (e.g., the equivalents at Meishan are Beds 25 and 28) and are referred to as "boundary clays" (Peng et al., 2001; Yin et al., 2007, 2012). Bed 237 is a 45-cm-thick homogeneous silty marlstone that can be correlated with the 18-cm-thick Bed 27 at Meishan (Yin et al., 2007, 2012; Zheng et al., 2013). Because the PTB index taxon Hindeodus parvus has not been recovered at Ganxi, placement of the PTB within Bed 237 is based on overall correlations to the Meishan GSSP.

#### 3. Background: Fe-Mo proxies for watermass redox conditions

Iron speciation has been widely applied as a proxy for local watermass redox conditions in ancient oceans (e.g., Canfield et al., 2008; Li et al., 2010, 2012, 2015; Poulton et al., 2010; Poulton and Canfield, 2011; Jin et al., 2016; Clarkson et al., 2016). Highly reactive iron ( $Fe_{HR}$ ) includes iron in pyrite ( $Fe_{py}$ ), carbonate ( $Fe_{carb}$ ), magnetite  $(Fe_{mag})$  and ferric oxides  $(Fe_{ox})$ . Unreactive Fe  $(Fe_{U})$ , which is dominantly present in clay minerals and other silicates, is calculated as the difference between total iron concentrations (Fe<sub>T</sub>) and Fe<sub>HR</sub>. A large compilation of data from siliciclastic marine sediments showed that Fe<sub>HR</sub>/Fe<sub>T</sub> < 0.38 is indicative of oxic bottomwater conditions and Fe<sub>HR</sub>/  $Fe_T > 0.38$  of anoxic conditions, and for the latter,  $Fe_{pv}/Fe_{HR} > 0.7-0.8$ and <0.7-0.8 correspond to euxinic and ferruginous conditions, respectively (Poulton and Canfield, 2011). Fe speciation proxies are rarely used in carbonate-rich sediments partially due to dilution of Fe<sub>T</sub> to low values, but a recent study inferred that Fe speciation analysis is generally valid for carbonates containing  $Fe_T > 0.5\%$  (Clarkson et al., 2014).

Mo, as a redox-sensitive metal, can be converted from molybdate into particle-reactive thiomolybdate under euxinic conditions. In the latter form, it is readily removed from seawater through incorporation in Fe-Mo-S nano-minerals or organo-metallic ligands in organic matter, resulting in high abundances in the sediment (Helz et al., 1996, 2011). Conversely, Mo in oxic waters is conservative, yielding values close to continental crustal levels (~1–2 ppm) in the sediment. Empirically, Mo concentrations of >100 ppm require persistently euxinic conditions



Fig. 3. Chemostratigraphy of Ganxi section with six interval division. Biostratigraphic data are from Mutwakil et al. (2006). The vertical dashed lines in Fe<sub>T</sub> (0.5%), Mo (25 and 100 ppm), Fe<sub>HR</sub>/Fe<sub>T</sub> (0.38) and Fe<sub>py</sub>/Fe<sub>HR</sub> (0.7) columns indicate those key threshold values. See text for more explanations on interval division and those threshold values. Abbreviations: latest Permian mass extinction horizon (LPME), Permian Triassic boundary (PTB), *Clarkina* (C.), *Orientalis* (Orien.), *Hindeodus* (H.), *Isarcicella* (I.), Formation (Fm.), Conodont zone (Z), Lithology (Litho.).

in an open-marine system, whereas Mo concentrations of <25 ppm and 25–100 ppm indicate non-euxinic waters and intermittently/seasonally euxinic bottomwaters, respectively (Scott and Lyons, 2012). Levels of sedimentary Mo enrichment also track the size of the local (Algeo and Lyons, 2006) or global (Scott et al., 2008) seawater Mo reservoir. A complete review of the Mo abundance proxy can be found in Cheng et al. (2015).

#### 4. Materials and methods

A total of 180 fresh rock samples were collected from the ~20-mthick outcrop at Ganxi, representing the entire Changhsingian through lowermost Induan stages. After removal of visibly weathered surfaces, each sample was cut into small chips and ground to fine powder (~200 mesh). Most samples were analyzed for total inorganic carbon (TIC), total organic carbon (TOC), Fe<sub>T</sub>, Al and Mo abundances as well as pyrite sulfur ( $\delta^{34}S_{py}$ ). Only samples with Fe<sub>T</sub> > 0.5% were selected for iron speciation analysis (note: all concentrations are weight percent unless otherwise noted).

Samples for TOC analysis were first treated with 3-N hydrochloric acid to remove all carbonate, then rinsed to a neutral pH with deionized water and oven-dried. TOC was determined using an Eltra 2000 C-S analyzer. Data quality was monitored via the USGS SDO-1 standard (C: 9.68%) and internal laboratory standards. Reproducibility based on multiple analyses of standards is better than  $\pm 0.2\%$  (1 $\sigma$ ) of reported values. For a subset of Lower Triassic samples, TOC was determined using a Jena multi-EA 4000 carbon-sulfur analyzer after decarbonation. Analytical precision are better than  $\pm$  0.2% (1 $\sigma$ ) according to replicate analyses of Alpha Resources standard AR4007 (C: 7.27%). To eliminate the effects of sedimentation rate on organic matter preservation and to better assess marine primary productivity (cf. Schoepfer et al., 2015), organic carbon accumulation rate (OCAR) was calculated for each conodont zone at Ganxi according to the equation:  $OCAR = TOC \times LSR \times \rho$ , where LSR (linear sedimentation rate) is equal to thickness/duration and  $\rho$  is sediment bulk density, which was assumed to be 2.5 g cm<sup>-3</sup> (cf. Algeo et al., 2011a). Related parameters for calculation of LSR are given in Table 1. Total carbon (TC) content was determined using the Eltra 2000 C-S analyzer and TIC was given by difference between TC and TOC.

Mo abundances were measured by using an Agilent inductively coupled plasma-mass spectrometer (ICP-MS) following a complete digestion. About 50 mg of powdered samples were dissolved and sequentially digested using a standard HF-HNO<sub>3</sub>-HClO<sub>4</sub> protocol, and the final solution was diluted with 2% nitric acid for ICP-MS analysis. The analytical precision is better than  $\pm$  5% (1 $\sigma$ ) of reported values based on replicate analyses of international standards BHVO-2 (3.29 ppm), RGM-1(2.47 ppm), AGV-2(2.14 ppm), and BCR-2 (248 ppm). Mo concentrations are also given in the form of "enrichment factors", where Mo<sub>EF</sub> = [(Mo/Ti)<sub>sample</sub> / (Mo/Ti)<sub>detrital</sub>] and the detrital Mo/Ti ratio

#### Table 1

Parameters used for calculation of linear sedimentary rate (LSR) of Ganxi section by conodont zone.

Conodont zone	Lower boundary age <sup>a</sup> (Ma)	Duration (Myr)	Thickness (m)	LSR (m/Myr)
H. parvus <sup>b</sup>	252.17	0.27	2.86	10.59
C. meishanensis	252.28	0.11	0.425	3.86
C. yini	252.32	0.04	2.08	52.00
C. changxingensis	253.27	0.95	6.574	6.92
C. wangi	254.14	0.87	4.425	5.09
C. orientalis <sup>c</sup>	-	-	-	5.09

<sup>a</sup> Data adopted from Shen et al. (2015).

<sup>b</sup> Because *H. parvus* has not been recovered yet, the full duration (0.27 Myr) of the earliest Induan was assumed, which may result in a calculated LSR lower than its true value.

<sup>c</sup> Because the lower boundary of the *C. orientalis* Zone was not identified at Ganxi, the LSR value of the *C. wangi* Zone was used.

was based on average upper crustal concentrations in McLennan (2001).

Fe<sub>T</sub> was determined by the sulfosalicylic acid spectrophotometric method and Al was tested by fluoride replacement-EDTA titrimetry based on Chinese GB/T 14506.5-2010. Analytical precision for Fe and Al are both better than  $\pm 0.2\%$  (1 $\sigma$ ) based on replicate analyses of the Chinese GSR-2 standard (Fe: 3.43%, Al: 8.56%). For samples with Fe<sub>T</sub> > 3%, Fe<sub>T</sub> concentrations were conducted using an Olympus DP-6000 hand-held X-ray fluorescence spectroscope (HH-XRF) with a Rh tube. The analytical precisions of HH-XRF for Fe<sub>T</sub> were determined based on replicate analyses of two USGS standards (SBC-1, 11.1%; SGR-1b, 3.5%) and three Chinese standards (GSR-1, 1.5%; GSR-2, 3.4%; GSR-5, 5.3%) (n = 6 for each standard), yielding precisions of  $\pm 0.7\%$  (1 $\sigma$ ),  $\pm 0.49\%$  (1 $\sigma$ ),  $\pm 0.15\%$  (1 $\sigma$ ),  $\pm 0.45\%$  (1 $\sigma$ ) and  $\pm 0.18\%$  (1 $\sigma$ ), respectively. These values are better than the  $\pm 2\%$  (1 $\sigma$ ) recommended for Fe<sub>T</sub> analyses by Lenniger et al. (2014).

Four Fe<sub>HR</sub> pools (Fe<sub>py</sub>, Fe<sub>carb</sub>, Fe<sub>ox</sub>, and Fe<sub>mag</sub>) were measured. Fe<sub>py</sub> content was stoichiometrically calculated from the concentration of pyrite sulfur (FeS<sub>2</sub>) that was extracted using the CrCl<sub>2</sub> reduction method and precipitated as Ag<sub>2</sub>S in silver nitrate traps (Canfield et al., 1986). Recovery rates for pyrite extractions, as determined from multiple analyses of a pure pyrite standard (Alfa Aesar), were >92%. The Fe<sub>carb</sub>, Fe<sub>ox</sub>, and Femag fractions were extracted by the sequential procedure described in Poulton and Canfield (2005) and measured by atomic absorption spectroscopy (AAS) with a relative standard deviation (RSD) of <5%(Li et al., 2015). Because there are no internationally certificated standards for sequential extraction of Fe species, two internal laboratory standards (CUG-2, CUG-3) which have been repeatedly tested in the Lyons Biogeochemistry Laboratory at the University of California, Riverside (UCR) were used to monitor the accuracy of sequential extractions. Values obtained from duplicate analyses of CUG-2 are 0.15  $\pm$  0.02% (mean  $\pm$  1 $\sigma$ , n = 6, UCR value = 0.11%) for Fe<sub>carb</sub>, 0.22  $\pm$  0.02% ( n= 6, UCR value = 0.20%) for Fe\_{ox}, and 0.10  $\pm$  0.01% ( n= 6, UCR value = 0.10%) for Fe<sub>mag</sub>. Values obtained from duplicate analyses of CUG-3 are 1.10  $\pm$  0.15% (mean  $\pm$  10, n = 4, UCR value = 1.26%) for Fe\_carb, 0.22  $\pm$  0.03% (n = 4, UCR value = 0.20%) for Fe\_ox, and 0.58  $\pm$ 0.10% (n = 4, UCR value = 0.64\%) for Fe<sub>mag</sub>.

Pyrite sulfur isotopic composition ( $\delta^{34}S_{py}$ ) was measured on a Thermo Fisher Scientific Delta V Plus isotope ratio mass spectrometer coupled with a Flash elemental analyzer by using the Ag<sub>2</sub>S precipitates from the CrCl<sub>2</sub> reduction mentioned above. The  $\delta^{34}$ S values are reported relative to the VCDT standard. Analytical precision is better than  $\pm 0.2\%$  (1 $\sigma$ ) based on replicate analyses of three standards: IAEA S1 (-0.3%), IAEA S2 (+22.65%), and IAEA S3 (-32.5%).

#### 5. Results

The key geochemical data for the Ganxi section are summarized in Table 2 and illustrated in Figs. 3, 4 and 5. TOC contents range from 0.13 to 9.1% (mean 2.0%), with peaks at 0–1.41 m (mean 5.1%) and 3.27–8.28 m (mean 3.6%) but low values in the remainder of the section (mean 0.5%). OCAR exhibits similar peaks at 0–1.41 m (mean 6.5 mg/cm<sup>2</sup>/kyr) and 3.27–8.28 m (mean 5.1 mg/cm<sup>2</sup>/kyr). In addition, the OCAR profile shows a third peak at 13–15.3 m (mean 14.1 mg/cm<sup>2</sup>/kyr) despite mean TOC content of only 1.1% in this interval (Fig. 3). This pattern is consistent with significant dilution of TOC owing to high sedimentation rates within the 13.15–15.23 m interval. TIC contents range from 0.04% to 11.46% (mean 5.6%), with relatively stable high values within the 1.41–13.15 m (mean 7.1%).

Mo abundance also shows a similar pattern to TOC, with peaks at 0– 1.41 m (mean [Mo] 144 ppm; mean Mo<sub>EF</sub> 374) and 3.27–8.28 m (mean [Mo] 155 ppm; mean Mo<sub>EF</sub> 710), but lower values in the remainder of the section (mean [Mo] 6.3 ppm; mean Mo<sub>EF</sub> 14). Fe<sub>T</sub> ranges from 0.2 to 5.1% (mean 1.7%). There is pronounced secular variation in Fe<sub>T</sub>, with low concentrations at 0–8.65 m (0.2–2.5%; mean 1.0%), rising

** *.	<b>C</b> 1	** * 1 .			TOC	0.0410	TIC			0340							F (F	<b>F</b> (F	F (F	<b>F</b> ( <b>F</b>		E (E
Unit	Sample	Height	Fe <sub>T</sub>	AI	10C	OCAR	11C	Mo (nnm)	M0 <sub>EF</sub>	$\delta^{3}S_{py}$	Fe <sub>carb</sub>	Fe <sub>ox</sub>	Fe <sub>mag</sub>	Fe <sub>Py</sub>	Fe <sub>HR</sub>	Fe <sub>T</sub>	Fe <sub>py</sub> /Fe <sub>HR</sub>	Fe <sub>HR</sub> /Fe <sub>T</sub>	Fe <sub>carb</sub> /Fe <sub>T</sub>	Fe <sub>py</sub> /Fe <sub>T</sub>	Fe <sub>OX</sub> /Fe <sub>T</sub>	Fe <sub>mag</sub> /Fe <sub>T</sub>
		(111)	(WL%)	(WL%)	(WL%)	(mgcm - kyr -)	(WL%)	(ppm)		(‰)	(WL%)	(WL%)	(WL%)	(WL%)	(WL%)	(WL%)						
VI	GX248-2	18.78	4.2							-24.3	1.25	0.10	0.07	0.04	1.45	4.17	0.03	0.35	0.30	0.01	0.02	0.02
VI	GX248-1	18.60																				
VI	GX247-1	18.49	3.8		0.3	1.1	2.6				0.69	0.06	0.07	0.20	1.02	3.81	0.20	0.27	0.18	0.05	0.02	0.02
VI	GX246-5	18.40	4.1		0.3	0.9	3.1			-38.1	1.24	0.13	0.09	0.10	1.55	4.15	0.06	0.37	0.30	0.02	0.03	0.02
VI	GX246-4	18.28																				
VI	GX246-3	18.16																				
VI	GX246-2	18.07																				
VI	GX246-1	17.97																				
VI	GX245-7-2	17.89																				
VI	GX245-5	17.81																				
VI	GX245-3	17.68	5.1		0.1	0.5	6.6				2.15	0.26	0.24	0.03	2.68	5.12	0.01	0.52	0.42	0.01	0.05	0.05
VI	GX245-2	17.61																				
VI	GX245-1	17.55																				
VI	GX244	17.45																				
VI	GX243-3	17.34	4.5		0.2	0.6	6.7			-28.1	1.73	0.25	0.20	0.08	2.25	4.53	0.03	0.50	0.38	0.02	0.05	0.04
VI	GX243-2	17.25																				
VI	GX243-1	17.16																				
VI	GX242-5	17.11																				
VI	GX242-3	17.00																				
VI	GX242-2	16.94			0.5	1.7																
VI	GX242-1	16.89	4.0				1.3			-33.8	0.33	0.06	0.04	1.60	2.03	4.02	0.78	0.51	0.08	0.40	0.02	0.01
VI	GX241-2	16.79	3.5							-26.0	0.70	0.06	0.04	0.73	1.53	3.48	0.48	0.44	0.20	0.21	0.02	0.01
VI	GX240-7	16.71																				
VI	GX240-6	16.65	4.1		0.2	0.5	4.3															
VI	GX-240-4-2	16.51																				
VI	GX-240-3-2	16.45	4.1		0.2	0.8	4.4			-25.7	1.59	0.15	0.11	0.51	2.36	4.07	0.21	0.58	0.39	0.12	0.04	0.03
VI	GX-240-3-1	16.39																				
VI	GX-240-2	16.35																				
VI	GX-240-1	16.34																				
VI	GX-239-8	16.30	3.6	8.9	0.3	1.0	1.3	0.9	1	-34.3	0.53	0.06	0.03	1.40	2.02	3.62	0.69	0.56	0.15	0.39	0.02	0.01
VI	GX-239-7	16.26	4.3	8.7	0.4	1.5	1.2	1.0	1	-37.9	0.39	0.07	0.04	2.07	2.56	4.28	0.81	0.60	0.09	0.48	0.02	0.01
VI	GX-239-6	16.22	3.3	8.1	0.3	1.0	1.9	0.5	0													
VI	GX-239-5	16.18	3.3	8.8	0.3	0.9	1.2	1.1	1	-29.3	0.36	0.07	0.03	0.86	1.32	3.28	0.65	0.40	0.11	0.26	0.02	0.01
VI	GX-239-4	16.12	3.2	8.9	0.3	1.1	0.5	0.8	0		0.44	0.06	0.04	0.80	1.33	3.19	0.60	0.42	0.14	0.25	0.02	0.01
VI	GX-239-3	16.04	4.0	6.5	0.2	0.6	3.6	1.2	1													
VI	GX-239-2	15.97	4.3	6.0	0.2	0.8	4.2	1.2	1	-36.2	1.61	0.11	0.06	1.55	3.33	4.31	0.47	0.77	0.37	0.36	0.02	0.01
VI	GX-239-1	15.92	3.6	8.6	0.3	1.0	1.4	0.9	1		0.59	0.07	0.03	1.47	2.16	3.61	0.68	0.60	0.16	0.41	0.02	0.01
V	GX-237-Top	15.77	3.9	6.7	0.2	0.2	3.2	0.6	0													
V	GX237-16	15.65	1.5		0.5	0.5				- 33.3	0.50	0.04	0.02	0.39	0.95	1.54	0.41	0.62	0.32	0.25	0.03	0.01
V	GX237-15	15.64																				
V	GX237-14	15.62	0.0		0.4	0.4				20.2	0.50	0.02	0.01	0.24	0.00	0.02	0.20	0.00	0.50	0.00	0.02	0.01
V	GX237-13	15.61	0.9		0.4	0.4				- 28.2	0.53	0.02	0.01	0.24	0.80	0.92	0.30	0.86	0.58	0.26	0.02	0.01
V	GX237-12	15.59	0.6		0.2	0.2				-26.7												
V	GX237-11	15.58	4.4		0.2	0.2				27.0	0.50	0.02	0.01	0.22	0.00	1 10	0.20	0.70	0.40	0.20	0.02	0.01
V	GX237-10	15.56	1.1		0.3	0.3				-27.9	0.53	0.03	0.01	0.22	0.80	1.10	0.28	0.73	0.48	0.20	0.03	0.01
V	GX237-9	15.55	1.5		0.4	0.4				- 32.0	0.92	0.07	0.03	0.39	1.41	1.52	0.28	0.93	0.61	0.26	0.04	0.02
V	GA237-8 CV227-7	15.55	1.ŏ		0.5	0.0				- 34.3	0.71	0.04	0.01	0.49	1.25	1.//	0.39	0.71	0.40	0.27	0.02	0.01
v	GA23/-/	15.52	16							250	0.86	0.07	0.02	0.40	1 / /	1.60	0.24	0.80	0.52	0.20	0.04	0.02
v	GA237-0	15.50	1.0							- 55.0	0.00	0.07	0.03	0.49	1.44	1.02	0.54	0.09	0.55	0.50	0.04	0.02
v	GA237-3 CV227-4	15.49	16		0.6	0.5				26.2	0.55	0.05	0.02	0.47	1.00	1.65	0.42	0.66	0.24	0.20	0.02	0.01
v	GA237-4 CV227-2	15.47	1.0		0.0	0.0				- 30.2	0.00	0.05	0.02	0.47	1.09	1.05	0.45	0.00	0.54	0.29	0.05	0.01
v	GA237-3 CV327-3	15.40	10		1.4	12				12.2	0.50	0.10	0.04	0.70	1 / 2	1 02	0.55	0.74	0.26	0.41	0.05	0.02
v	GA237-2 CY227-1	15.44	1.9 2.1	46	0.2	1.5	5.2	1	1	- 42.2	0.00	0.10	0.04	0.79	1,45	1.35	0.55	0.74	0.20	0.41	0.03	0.02
v	GA237-1 CX235H	15.45	2.1 1.8	-1.0	0.2	0.2	J.2 17	1 2	1 2	- 37.0	0.42	0.07	0.02	0.97	1.47	2.14	0.00	0.09	0.15	0.45	0.03	0.01
v	JAZJJII	10.04	1.0	5.5	0.5	0.7	1./	4	4	57.0	0.20	0.05	0.02	0.00	1.00	1.01	5.75	0.74	0.10	0.54	0.00	0.01

**Table 2**Geochemical data for Ganxi section.

V         CC233-1         15.00         L		V	GX233-2	15.23		4.3	1.4	18.4	2.7	5	8	-37.5	0.34	0.11	0.02	0.63	1.09	1.76	0.58	0.62	0.19	0.36	0.06	0.01
V         CC2122         15.0         CC212         15.0         CC213         CC21         CC213         CC213 <thc213< th=""> <thc213< th=""> <thc213< th=""></thc213<></thc213<></thc213<>		V	GX233-1	15.11																				
V         CX321         L48         C         L4         L3         L4         L3         L4         L3         L4         L3         L4         L3         L3         L4         L3         L		V	GX232-2	15.00	0.8							-35.8	0.31	0.02	0.01	0.28	0.62	0.77	0.45	0.81	0.41	0.36	0.03	0.01
V         CC231         L4         Z         S4.3         O.8         S4<8         O         -14.8         O.20         O.56         L10         L58         O.10         O.28         O.13         O.15         O.11           V         CC230-1         1453         16         1         1         1.0         0.28         0.31         0.13         0.55         0.01         0.28         0.31         0.13         0.55         0.21         0.13         0.51         0.12         0.13         0.51         0.12         0.13         0.51         0.12         0.13         0.13         0.14         0		V	GX232-1	14.90		1.7	0.3	4.4	7.3	4	17													
V         CAURANCE         HAUB         LAURANCE         LAURANCE <thlaurance< th="">         LAURANCE         L</thlaurance<>		V	GX231	14.75	2.0	6.4	4.2	54.3	0.8	58	80	-41.8	0.20	0.29	0.06	0.56	1.11	1.98	0.51	0.56	0.10	0.28	0.15	0.03
V         CCCCCCC         CCCCCCCC         CCCCCCC         CCCCCCCC         CCCCCCC         CCCCCCCC         CCCCCCC         CCCCCCC         C		V	GX230-3	14.61		2.0	0.7	0.5	4.0	~	14	27.2	0.50	0.05	0.02	0.50	1 1 2	1.55	0.50	0.72	0.22	0.20	0.02	0.01
i         cocose         i         cocose         i <th< td=""><td></td><td>V</td><td>GA230-2</td><td>14.55</td><td>16</td><td>2.9</td><td>0.7</td><td>9.5</td><td>4.9</td><td>Э</td><td>14</td><td>-37.3</td><td>0.50</td><td>0.05</td><td>0.02</td><td>0.56</td><td>1.12</td><td>1.55</td><td>0.50</td><td>0.72</td><td>0.32</td><td>0.36</td><td>0.03</td><td>0.01</td></th<>		V	GA230-2	14.55	16	2.9	0.7	9.5	4.9	Э	14	-37.3	0.50	0.05	0.02	0.56	1.12	1.55	0.50	0.72	0.32	0.36	0.03	0.01
V         CXZ29         H4B         H2B         H2B <td></td> <td>v</td> <td>GX230-1 GX229_4</td> <td>14.45</td> <td>1.0</td> <td></td>		v	GX230-1 GX229_4	14.45	1.0																			
v         CX23-2         14.8         0.8         5.0         1.7         2.1         1.5         1.1         1.6         -3.2         0.1         0.02         0.83         0.81         0.51         0.12         0.32         0.03         0.01           W         CX23-3         133         10         -30         0.3         0.3         0.03         0.03         0.04         0.04         0.05         0.05         0.05         0.05         0.05         0.05         0.05         0.05         0.05         0.02         0.01         0.01           W         CX23-1         133         26         67         10         12         16         17         17         0.45         0.01         0.01         0.01         0.01         0.01         0.05         0.05         0.05         0.02         0.01     <		v	GX229-3	14.29																				
V         CX228-1         147         0.7 </td <td></td> <td>v</td> <td>GX229-2</td> <td>14.18</td> <td>1.8</td> <td>5.0</td> <td>1.7</td> <td>22.1</td> <td>1.5</td> <td>11</td> <td>16</td> <td>-36.2</td> <td>0.21</td> <td>0.11</td> <td>0.02</td> <td>0.58</td> <td>0.92</td> <td>1.81</td> <td>0.63</td> <td>0.51</td> <td>0.12</td> <td>0.32</td> <td>0.06</td> <td>0.01</td>		v	GX229-2	14.18	1.8	5.0	1.7	22.1	1.5	11	16	-36.2	0.21	0.11	0.02	0.58	0.92	1.81	0.63	0.51	0.12	0.32	0.06	0.01
N         CK228-3         139         16           N         CK228-3         139         5         4         4         -361         0.30     <		v	GX229-1	14.07																				
I         CX228         1.51         V.         V.        V.       V.        V.<		IV	GX228-3	13.99	1.6																			
IV       CX22       13       V       V       CX22       137       20       51       01       24       25       0.5       0.2       0.55 <t< td=""><td></td><td>IV</td><td>GX228-2</td><td>13.91</td><td></td><td>3.9</td><td>0.4</td><td>4.9</td><td>3.7</td><td>3</td><td>6</td><td>-30.3</td><td>0.39</td><td>0.03</td><td>0.02</td><td>0.40</td><td>0.84</td><td>1.63</td><td>0.48</td><td>0.52</td><td>0.24</td><td>0.25</td><td>0.02</td><td>0.01</td></t<>		IV	GX228-2	13.91		3.9	0.4	4.9	3.7	3	6	-30.3	0.39	0.03	0.02	0.40	0.84	1.63	0.48	0.52	0.24	0.25	0.02	0.01
IV       CX227       1.37       2.6       6.7       1.0       1.28       1.6       4       4       -3.7       0.20       0.02       0.43       1.70       2.44       0.84       0.65       0.28       0.82       0.21       0.31       0.02       0.01         IV       CX224       13.81       0.03       1.50       2.0       1.51       2.0       1.51       2.0       0.55		IV	GX228-1	13.84																				
IV       CX225       13.4       2.0       5.1       0.4       4.6       2.5       8       12       -37.5       0.44       0.02       0.61       1.0       2.00       0.55       0.22       0.20       0.02       0.01         IV       CC221       13.31       2.0       5.0       0.8       101       2.0       1.4       2       -38.4       0.30       0.02       0.75       1.8       2.44       0.30       0.58       0.19       0.37       0.01       0.00       0.01         V       CX216       1.21       1.4       2.0       0.8       8.8       -38.0       1.02       0.06       0.02       0.55       1.83       2.14       0.30       0.87       0.27       0.26       0.03       0.00       0.01       0.00       0.01       0.00       0.07       1.83       2.14       0.30       0.87       0.27       0.26       0.03       0.01       0.01       0.02       0.55       1.21       0.44       0.02       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.01       0.		IV	GX227	13.79	2.6	6.7	1.0	12.8	1.6	4	4	-36.1	0.20	0.05	0.02	1.43	1.70	2.64	0.84	0.65	0.08	0.54	0.02	0.01
IV         CX224         13.34         0.8         1.5         0.2         2.4         8.9         1         7           VV         CX221         13.32         2.2         6.8         0.11         1.9         4         5           VV         CX21         13.32         2.2         6.8         0.3         0.3         0.01         1.00         0.01 <td></td> <td>IV</td> <td>GX225</td> <td>13.74</td> <td>2.0</td> <td>5.1</td> <td>0.4</td> <td>4.6</td> <td>2.5</td> <td>8</td> <td>12</td> <td>-37.5</td> <td>0.44</td> <td>0.04</td> <td>0.02</td> <td>0.61</td> <td>1.10</td> <td>2.00</td> <td>0.55</td> <td>0.55</td> <td>0.22</td> <td>0.30</td> <td>0.02</td> <td>0.01</td>		IV	GX225	13.74	2.0	5.1	0.4	4.6	2.5	8	12	-37.5	0.44	0.04	0.02	0.61	1.10	2.00	0.55	0.55	0.22	0.30	0.02	0.01
IV       CX221       131       2.0       5.2       0.8       0.11       2.0       1       2       -38.4       0.39       0.02       0.75       1.18       2.04       0.63       0.55       0.91       0.27       0.01       0.01         IV       CC219       1315       2.6       7.8       1.5       1.57       0.51       0.53       0.57       0.53       0.57       0.53       0.57       0.56       0.01       0.00       0.01         IV       CX216       1.27       2.2       2.0       0.5       0.53       0.57       0.53       0.57       0.56       0.01       0.00         IV       CX217       1.21       1.7       3.7       0.4       0.64       3.2       4       -75.3       0.45       0.61       0.65       0.74       0.64       0.38       0.27       0.01       0.07         IV       CX210-1       1.15       1.5       1.6       0.3       0.44       8.4       1       4       -75.3       0.45       0.97       0.11       0.46       0.3       0.47       0.46       0.3       0.47       0.40       0.33       0.47       0.40       0.41       0.41       0.42		IV	GX224	13.64	0.8	1.5	0.2	2.4	8.9	1	7													
IV         CA220         13.0         2.1         2.0         0.3         5.3         1.1         4         5         -41.1         0.24         0.01         1.00         1.00         1.00         0.35         0.37         0.25         0.03         0.05         0.03         0.05         0.03         0.05		IV	GX221	13.31	2.0	5.2	0.8	10.1	2.0	1	2	-38.4	0.39	0.03	0.02	0.75	1.18	2.04	0.63	0.58	0.19	0.37	0.01	0.01
IV         CX.19         I.13         2.0         1.4         0.13         0.14         0.13         0.14         0.13         0.15         0.13         0.15         0.13         0.15         0.13         0.15         0.13         0.15         0.13         0.15         0.15         0.13         0.15         0.		IV	GX220	13.20	2.2	6.9	0.5	5.9	1.9	4	5	41.1	0.24	0.04	0.01	1 10	1 20	2.64	0.70	0.52	0.00	0.42	0.01	0.00
In       Corr       <			GX219 CV216	13.15	2.0	7.8 4.2	1.5	19.7	1.1	4	4	-41.1	0.24	0.04	0.01	0.55	1.39	2.04	0.79	0.53	0.09	0.42	0.01	0.00
IP         CXC13         12.2         12.2         12         10         0.5         0.14         5         6         -41.3         0.26         0.01         0.96         1.27         2.20         0.76         0.58         0.12         0.44         0.02         0.01           IV         CX121         113         17         37         0.4         0.6         43         2         4         <		IV	GA210 CY215	12.71	2.1	4.Z 3.5	0.3	0.5	4.5	3	5	- 38.0	1.20	0.00	0.02	0.55	1.65	2.11	0.50	0.87	0.57	0.20	0.05	0.01
IV         CX211-2         213         1.1         2.1         0.2         0.3<		IV	GX213	12.34	22	7.0	0.5	0.9	14	5	6	-413	0.26	0.04	0.01	0.96	1 27	2 20	0.76	0.58	0.12	0 44	0.02	0.01
IN         CX212         12.13         1.7         3.7         0.4         0.6         1.3         2         4           NG         CX211-1         11.87         1.9         5.2         0.5         0.8         1.1         3         4         -35.3         0.43         0.03         0.66         1.5         1.86         0.59         0.62         0.23         0.36         0.02         0.01           N         CX210-3         1.146         1.8         2.6         0.3         0.44         2.5         5.6         5.6         0.27         0.07         0.01         0.97         1.31         2.06         0.74         0.64         0.13         0.47         0.03         0.00           N         CX206-1         1.19         2.1         5.6         1.8         3.1         3.4         7         10         -352         0.36         0.01         0.97         1.40         2.09         0.69         0.67         0.17         0.47         0.03         0.00           N         CX206-1         1.056         2.4         3.05         2.6         0.65         0.67         0.17         0.47         0.03         0.00           N         CX206-1 </td <td></td> <td>IV</td> <td>GX213</td> <td>12.13</td> <td>1.1</td> <td>2.1</td> <td>0.2</td> <td>0.3</td> <td>8.7</td> <td>2</td> <td>7</td> <td>11.5</td> <td>0.20</td> <td>0.01</td> <td>0.01</td> <td>0.50</td> <td>1.27</td> <td>2.20</td> <td>0.70</td> <td>0.50</td> <td>0.12</td> <td>0.11</td> <td>0.02</td> <td>0.01</td>		IV	GX213	12.13	1.1	2.1	0.2	0.3	8.7	2	7	11.5	0.20	0.01	0.01	0.50	1.27	2.20	0.70	0.50	0.12	0.11	0.02	0.01
I         N         CX211-1         1187         9.9         5.2         0.5         0.4         0.1         0.1         0.01         0.05         1.15         1.86         0.52         0.23         0.36         0.02         0.31           N         GX210-1         11.56         2.1         6.8         0.4         0.7         2.6         5         6        365         0.7         0.01         0.97         1.31         2.06         0.74         0.64         0.31         0.47         0.03         0.00           N         GX209-1         11.30         1.8         4.6         0.4         0.4         7         10         -352         0.45         0.60         0.17         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.47         0.44         0.44         0.44         1.4		IV	GX212	12.13	1.7	3.7	0.4	0.6	4.3	2	4													
I         V         CX210-3         11.76         0.9         1.1         0.2         0.3         10.8         1         7           V         CX208-2         11.44         1.8         2.6         0.3         0.4         8.4         1         4           V         CX208-1         11.30         1.8         4.6         0.4         0.4         8.4         1         4         -         5.6         -         5.6         -         6.6         0.01         0.97         1.40         2.06         0.67         0.17         0.47         0.03         0.00           V         CX208         11.19         2.1         5.6         1.8         3.1         3.4         7         1.0         -         3.5         0.65         0.01         0.97         1.40         2.9         0.69         0.67         0.17         0.47         0.03         0.01           V         CX205-1         10.65         2.4         3.0         0.6         5.4         4         6         7         7         1.0         2.7         0.21         0.31         1.3         1.40         0.44         0.3         0.60         0.1         0.33         1.40         0.		IV	GX211-1	11.87	1.9	5.2	0.5	0.8	4.1	3	4	-35.3	0.43	0.03	0.01	0.68	1.15	1.86	0.59	0.62	0.23	0.36	0.02	0.01
IV         CX210-1         11.56         21         6.8         0.4         0.7         2.6         5         6         -36.5         0.27         0.07         0.01         0.97         1.31         2.06         0.74         0.64         0.13         0.47         0.03         0.00           IV         CX209-1         11.41         18         46         0.4         0.8         42         3         5           IV         CX207         11.11         2.3         3.8         0.4         0.7         7.7         1.0         -35.2         0.36         0.01         0.97         1.40         2.09         0.69         0.67         0.17         0.47         0.03         0.00           IV         CX206-1         10.06         0.7         0.8         0.1         1.27         1.40         2.09         0.69         0.67         0.17         0.47         0.03         0.00           IV         CX206-1         10.06         0.7         0.9         0.14         1         1         2         1         1         2         1         1         2         1         1         2         1         1         2         1         1		IV	GX210-3	11.76	0.9	1.1	0.2	0.3	10.8	1	7													
IV       CX209-1       11.40       1.8       2.6       0.3       0.4       8.4       1       4         IV       CX208-1       11.13       1.8       4.6       0.4       3.4       7       10       -35.2       0.36       0.06       0.01       0.97       1.40       2.09       0.69       0.67       0.17       0.47       0.03       0.00         IV       CX206-1       11.9       2.1       5.6       1.8       3.1       3.4       7       10       -35.2       0.36       0.06       0.01       0.97       1.40       2.09       0.69       0.67       0.17       0.47       0.03       0.00         IV       CX206-1       10.50       2.2       3.3       0.6       5.4       4       6       -		IV	GX210-1	11.56	2.1	6.8	0.4	0.7	2.6	5	6	-36.5	0.27	0.07	0.01	0.97	1.31	2.06	0.74	0.64	0.13	0.47	0.03	0.00
IN       CX209-1       11.30       1.8       4.6       0.4       0.8       4.2       3       5         IV       CX207       11.11       2.3       3.6       1.8       0.4       0.7       5.7       7       10       -35.2       0.6       0.01       0.37       1.40       2.09       0.69       0.67       0.17       0.47       0.03       0.00         IV       CX207-1       10.17       2.4       0.5       1.4       0.8       0.69       0.67       0.17       0.47       0.03       0.00         IV       CX206-1       10.6       2.2       4.3       0.5       0.6       1.4       4.8       6       7       7       1		IV	GX209-2	11.44	1.8	2.6	0.3	0.4	8.4	1	4													
IV       CX208       11.19       2.1       5.6       1.8       3.1       3.4       7       10       -35.2       0.36       0.01       0.97       1.40       2.09       0.69       0.67       0.17       0.47       0.03       0.00         IV       CX2061       11.12       2.3       3.8       0.4       0.7       5.7       7.7       12       7       10       7       10       7       10       7       10       7       10       7       10       10       7       10       10       7       10		IV	GX209-1	11.30	1.8	4.6	0.4	0.8	4.2	3	5													
IV       G.220 <sup>-1</sup> 11.11       2.3       3.8       0.4       0.7       5.7       7       1       2         IV       G.2205-1       10.65       2.2       4.3       0.5       0.8       5.6       9       15       5.6       9       15         IV       G.2205-1       10.76       2.4       4.8       0.3       0.6       5.4       4       6       5.6       9       15       5.6       9       15       5.6       9.7       7.4       1.4       4.8       6       7.7       7.8       5.7       7.4       1.4       4.8       6       7.7       7.8		IV	GX208	11.19	2.1	5.6	1.8	3.1	3.4	7	10	-35.2	0.36	0.06	0.01	0.97	1.40	2.09	0.69	0.67	0.17	0.47	0.03	0.00
IV       GZQ0-1       10.90       2.2       4.3       0.5       0.8       5.0       9       15         IV       GZQ05-1       10.76       2.4       4.8       0.3       0.6       5.4       4       6       7         IV       GZQ05-1       10.76       2.4       4.8       0.3       0.6       5.4       4       6       7         IV       GZQ04-2       10.66       0.7       0.9       0.2       0.3       10.4       1       12       7<		IV	GX207	11.11	2.3	3.8	0.4	0.7	5.7	7	12													
IV       GA202-2       10.37       2.4       3.3       0.3       1.4       4.6       0       7         IV       GX205-1       10.76       2.4       4.8       0.3       10.4       1       12         IV       GX204-2       10.56       0.8       10.9       0.2       0.3       10.4       1       12         IV       GX204-1       10.58       0.8       10.9       2.0       11       16       -27.2       0.21       0.03       0.01       1.33       1.58       2.16       0.84       0.73       0.10       0.62       0.01       0.00         IV       GX201       10.57       2.4       4.6       0.3       0.6       5.3       1       2       -       -       -       -       -       -       -       0.30       0.04       0.00       1.45       1.79       1.72       0.81       1.00       0.18       0.84       0.02       0.00         V       GX196-197       9.44       1.7       1.10       0.81       1.00       0.18       0.86       0.02       0.00         V       GX196-195       9.25       1.1       1.0       0.2       0.3       0.16 <t< td=""><td></td><td>IV</td><td>GX206-1</td><td>10.96</td><td>2.2</td><td>4.3</td><td>0.5</td><td>0.8</td><td>5.6</td><td>9</td><td>15</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></t<>		IV	GX206-1	10.96	2.2	4.3	0.5	0.8	5.6	9	15													
IV       GX204-2       10.70       2.4       4.6       0.3       0.0       3.4       4       0         IV       GX204-2       10.66       0.7       9       0.2       0.3       10.4       1       12         IV       GX204-1       10.58       0.8       1.0       0.2       0.3       10.9       2       11       16       -27.2       0.21       0.3       0.01       1.33       1.58       2.16       0.84       0.73       0.10       0.62       0.01       0.00         IV       GX201       10.27       2.4       4.6       0.3       0.6       5.3       1       2       7       0.3       0.1       1.33       1.58       2.16       0.84       0.73       0.10       0.62       0.01       0.00         IV       GX201       10.27       2.4       4.6       0.3       0.6       5.3       1       2       7       7       0.21       0.61       0.02       0.01       0.06       0.84       0.73       0.10       0.62       0.01       0.00       0.01       0.54       1.7       1.0       0.81       1.00       0.18       0.62       0.01       0.01       0.01       0			GA205-2 CV205-1	10.67	2.2	0.5 4 9	0.8	1.4	4.0 5.4	4	6													
IN       GX204-1       10.05       0.0.       0.0.       0.0.       0.0.       0.0.       10.0.       10.0.       0.0.0.       0.0.0.       0.0.0.<		IV	GX203-1 CX204-2	10.70	2.4	4.0	0.3	0.0	10.4	1	12													
IV       GX203       10.51       2.2       7.4       0.3       0.5       2.0       11       16       -27.2       0.21       0.3       0.1       1.33       1.58       2.16       0.84       0.73       0.10       0.62       0.01       0.00         IV       GX200       10.27       2.4       4.6       0.3       0.6       5.3       1       2       0.30       0.04       0.00       1.45       1.79       1.72       0.81       1.00       0.18       0.84       0.02       0.00         IV       GX200       9.971       3.0       2.5       0.2       0.4       8.0       3       8       0.01       1.45       1.79       1.72       0.81       1.00       0.18       0.84       0.02       0.00         IV       GX194-195       9.44       1.7       4.1       0.3       0.5       6.4       5       10       0.4       1.45       1.65       0.87       0.88       0.09       0.77       0.01       0.01         IV       GX194-195       9.11       1.3       3.3       0.6       7.3       4       9       0.17       0.05       0.01       1.16       1.45       1.65       0.87 </td <td></td> <td>IV</td> <td>GX204-2 GX204-1</td> <td>10.00</td> <td>0.7</td> <td>1.0</td> <td>0.2</td> <td>0.3</td> <td>10.4</td> <td>2</td> <td>11</td> <td></td>		IV	GX204-2 GX204-1	10.00	0.7	1.0	0.2	0.3	10.4	2	11													
IV       GX201       10.27       2.4       4.6       0.3       0.6       5.3       1       2         IV       GX200       9.98       1.7       1.8       0.2       0.4       9.7       2       8       0.30       0.44       0.00       1.45       1.79       1.72       0.81       1.00       0.18       0.84       0.02       0.00         IV       GX196-197       9.44       1.7       4.1       0.3       0.5       6.4       5       10       0.5       0.61       5.7       0.61       0.01       0.81       1.00       0.18       0.84       0.02       0.00         IV       GX194-195       9.25       1.1       1.0       0.2       0.3       1.13       1       7       -262       0.20       0.01       1.17       1.10       0.81       1.00       0.18       0.86       0.02       0.00         IV       GX192       9.01       1.3       3.3       0.3       0.6       7.3       4       9       1.17       1.15       1.38       1.55       0.83       0.89       0.11       0.74       0.03       0.00       1.45       1.5       1.38       1.55       0.83       0.89		IV	GX203	10.51	2.2	7.4	0.3	0.5	2.0	11	16	-27.2	0.21	0.03	0.01	1.33	1.58	2.16	0.84	0.73	0.10	0.62	0.01	0.00
IV       GX200       9.98       1.7       1.8       0.2       0.4       9.7       2       8       0.30       0.4       1.70       1.72       0.81       1.00       0.18       0.84       0.02       0.00         IV       GX196-197       9.44       1.7       4.1       0.3       0.5       6.4       5       10       - <td></td> <td>IV</td> <td>GX201</td> <td>10.27</td> <td>2.4</td> <td>4.6</td> <td>0.3</td> <td>0.6</td> <td>5.3</td> <td>1</td> <td>2</td> <td></td>		IV	GX201	10.27	2.4	4.6	0.3	0.6	5.3	1	2													
IV       GX 199       9.71       3.0       2.5       0.2       0.4       8.0       3       8         IV       GX 196-197       9.44       1.7       4.1       0.3       0.5       6.4       5       10         IV       GX 196-197       9.44       1.7       4.1       0.3       0.5       6.4       5       10         IV       GX 194-195       9.25       1.6       5.7       0.5       0.9       3.9       1.1       1       7       -262       0.20       0.01       1.26       1.45       1.65       0.87       0.88       0.09       0.77       0.01       0.01         IV       GX 192       9.01       1.3       3.3       0.3       0.6       7.3       4       9		IV	GX200	9.98	1.7	1.8	0.2	0.4	9.7	2	8		0.30	0.04	0.00	1.45	1.79	1.72	0.81	1.00	0.18	0.84	0.02	0.00
IV       GX196-197       9.44       1.7       4.1       0.3       0.5       6.4       5       10         IV       GX194-195       9.25       1.1       1.0       0.2       0.3       1.1       1       7       -26.2       0.20       0.03       0.00       0.94       1.17       1.10       0.81       1.00       0.18       0.86       0.02       0.00         IV       GX192       9.01       1.3       3.3       0.3       0.6       7.3       4       9       9         IV       GX191       8.93       1.6       5.4       0.8       1.5       3.3       7       9       0.17       0.05       0.01       1.15       1.38       1.55       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX190       8.13       2.2       1.3       0.2       0.4       1.0       2		IV	GX199	9.71	3.0	2.5	0.2	0.4	8.0	3	8													
IV       GX194-195       9.25       1.1       1.0       0.2       0.3       11.3       1       7       -26.2       0.20       0.03       0.00       0.94       1.17       1.10       0.81       1.00       0.18       0.86       0.02       0.00         IV       GX193       9.12       1.6       5.7       0.5       0.9       3.9       8       9       -32.6       0.16       0.02       0.01       1.26       1.45       1.65       0.87       0.88       0.09       0.77       0.01       0.01         IV       GX191       8.93       1.6       5.4       0.8       1.5       3.3       7       9       0.17       0.05       0.01       1.15       1.38       1.55       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX190       8.81       2.2       1.3       0.2       0.4       10.2       2       12       1.5       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX187       8.52       1.2       4.7       0.8       1.3       3.4       10       17       10.2       3.5       14       25       -27.6		IV	GX196-197	9.44	1.7	4.1	0.3	0.5	6.4	5	10													
IV       GX193       9.12       1.6       5.7       0.5       0.9       3.9       8       9       -32.6       0.16       0.02       0.01       1.26       1.45       1.65       0.87       0.88       0.09       0.77       0.01       0.01         IV       GX192       9.01       1.3       3.3       0.3       0.6       7.3       4       9       0.17       0.05       0.01       1.26       1.45       1.65       0.87       0.88       0.09       0.77       0.01       0.01         IV       GX190       8.81       2.2       1.3       0.2       0.4       10.2       2       12       1.15       1.38       1.55       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX187       8.52       1.2       4.7       0.8       1.3       3.4       10       17       7       0.7       0.02       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01         IV       GX186       8.46       1.0 <td></td> <td>IV</td> <td>GX194-195</td> <td>9.25</td> <td>1.1</td> <td>1.0</td> <td>0.2</td> <td>0.3</td> <td>11.3</td> <td>1</td> <td>7</td> <td>-26.2</td> <td>0.20</td> <td>0.03</td> <td>0.00</td> <td>0.94</td> <td>1.17</td> <td>1.10</td> <td>0.81</td> <td>1.00</td> <td>0.18</td> <td>0.86</td> <td>0.02</td> <td>0.00</td>		IV	GX194-195	9.25	1.1	1.0	0.2	0.3	11.3	1	7	-26.2	0.20	0.03	0.00	0.94	1.17	1.10	0.81	1.00	0.18	0.86	0.02	0.00
IV       GX192       9.01       1.3       3.3       0.3       0.6       7.3       4       9         IV       GX191       8.93       1.6       5.4       0.8       1.5       3.3       7       9       0.17       0.05       0.01       1.15       1.38       1.55       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX191       8.93       1.6       5.4       0.8       1.2       1.3       0.3       0.6       5.4       6       15         IV       GX187       8.52       1.2       4.7       0.8       1.3       3.4       10       17       0.05       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01         IV       GX186       8.46       1.0       5.9       0.5       0.9       3.5       14       25       -27.6       0.07       0.02       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01         IV       GX184       8.39       0.9       3.0       3.5       14       25       -27.7       0.99       0.03		IV	GX193	9.12	1.6	5.7	0.5	0.9	3.9	8	9	-32.6	0.16	0.02	0.01	1.26	1.45	1.65	0.87	0.88	0.09	0.77	0.01	0.01
IV       CX191       8.93       1.6       5.4       0.8       1.5       3.3       7       9       0.17       0.05       0.01       1.15       1.38       1.55       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX190       8.81       2.2       1.3       0.2       0.4       102       2       12       13       1.35       0.83       0.89       0.11       0.74       0.03       0.00         IV       GX189H       8.65       0.9       3.3       0.3       0.6       5.4       6       15       .		IV	GX192	9.01	1.3	3.3	0.3	0.6	7.3	4	9		0.45	0.05	0.01	4.45	1.00	4.55	0.00	0.00	0.14	0.74	0.00	0.00
IV       GX190       8.81       2.2       1.3       0.2       0.4       10.2       2       12         IV       GX.189H       8.65       0.9       3.3       0.6       5.4       6       15         IV       GX.187       8.52       1.2       4.7       0.8       1.3       3.4       10       17         IV       GX186       8.46       1.0       5.9       0.5       0.9       3.5       14       25       -27.6       0.07       0.02       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01         IV       GX184       8.39       0.9       3.0       0.4       0.8       5.8       14       38       28       29       0.91       0.07       0.82       0.02       0.01         III       GX182       8.28       1.2       1.5       2.4       4.2       8.1       101       462         IIII       GX179       8.12       1.2       0.9       1.0       1.7       10.2       33       234       -27.7       0.09       0.03       0.00       1.01       1.13       1.24       0.90       0.91       0.0		IV	GX191	8.93	1.6	5.4	0.8	1.5	3.3	/	9		0.17	0.05	0.01	1.15	1.38	1.55	0.83	0.89	0.11	0.74	0.03	0.00
IV       GX187       8.03       6.03       6.03       6.03       6.03       6.04       6       13         IV       GX187       8.52       1.2       4.7       0.8       1.3       3.4       10       17         IV       GX186       8.46       1.0       5.9       0.5       0.9       3.5       14       25       -27.6       0.07       0.02       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01         IV       GX184       8.39       0.9       3.0       0.4       0.8       5.8       14       38       25       1.2       0.07       0.82       0.02       0.01         IV       GX184       8.39       0.9       3.0       0.4       0.8       5.8       14       38       38       39       0.93       0.07       0.91       0.07       0.82       0.02       0.01         III       GX180       8.17       1.0       1.4       3.4       5.9       7.2       177       877       111       6X178       8.04       1.2       2.4       4.64       194       102       33       2.4       64       194		IV	GX 190	8.81	2.2	1.3	0.2	0.4	10.2 5.4	2	12													
IV       GX167       5.52       1.2       4.7       6.5       1.5       1.6       1.7         IV       GX186       8.46       1.0       5.5       0.9       3.5       14       25       -27.6       0.07       0.02       0.01       0.83       0.93       1.02       0.90       0.91       0.07       0.82       0.02       0.01         IV       GX184       8.39       0.9       3.0       0.4       0.8       5.8       14       38         III       GX180       8.17       1.0       1.4       3.4       5.9       7.2       177       877         III       GX179       8.12       1.2       0.9       1.0       1.7       10.2       33       234       -27.7       0.09       0.01       1.01       1.13       1.24       0.90       0.91       0.07       0.82       0.02       0.00         III       GX179       8.12       1.2       0.9       1.0       1.7       10.2       33       234       -27.7       0.09       0.01       1.01       1.13       1.24       0.90       0.91       0.07       0.82       0.02       0.00         IIII       GX177       7.95		IV	GX-18911 CX187	8.05	1.2	3.3 4.7	0.5	13	3.4	10	17													
IV       GA186       6.10       6.10       6.01		IV	GX186	8.46	1.2	59	0.5	0.9	3.5	14	25	-276	0.07	0.02	0.01	0.83	0.93	1.02	0.90	0.91	0.07	0.82	0.02	0.01
III       GX182       8.28       1.2       1.5       1.1 <t< td=""><td></td><td>IV</td><td>GX184</td><td>8.39</td><td>0.9</td><td>3.0</td><td>0.4</td><td>0.8</td><td>5.8</td><td>14</td><td>38</td><td>27.0</td><td>0.07</td><td>0.02</td><td>0.01</td><td>0.00</td><td>0.55</td><td>1,02</td><td>0.50</td><td>0.51</td><td>0.07</td><td>0.02</td><td>0.02</td><td>0.01</td></t<>		IV	GX184	8.39	0.9	3.0	0.4	0.8	5.8	14	38	27.0	0.07	0.02	0.01	0.00	0.55	1,02	0.50	0.51	0.07	0.02	0.02	0.01
III       GX180       8.17       1.0       1.4       3.4       5.9       7.2       177       877         III       GX179       8.12       1.2       0.9       1.0       1.7       10.2       33       234       -27.7       0.09       0.03       0.00       1.01       1.13       1.24       0.90       0.91       0.07       0.82       0.02       0.00         III       GX178       8.04       1.2       2.4       1.9       3.3       7.4       64       194       94       93       94       93       96       96       96       97.0		III	GX182	8.28	1.2	1.5	2.4	4.2	8.1	101	462													
III       GX179       8.12       1.2       0.9       1.0       1.7       10.2       33       234       -27.7       0.09       0.03       0.00       1.13       1.24       0.90       0.91       0.07       0.82       0.02       0.00         III       GX178       8.04       1.2       2.4       1.9       3.3       7.4       64       194       -       -       -       -       0.01       1.13       1.24       0.90       0.91       0.07       0.82       0.02       0.00         III       GX177       7.95       1.4       2.9       2.0       3.4       7.0       66       158       0.12       0.08       0.01       1.10       1.30       1.40       0.84       0.93       0.08       0.78       0.06       0.00         III       GX176       7.89       1.1       2.5       2.8       4.8       7.7       64       183       -       0.01       1.10       1.30       1.40       0.84 </td <td></td> <td>III</td> <td>GX180</td> <td>8.17</td> <td>1.0</td> <td>1.4</td> <td>3.4</td> <td>5.9</td> <td>7.2</td> <td>177</td> <td>877</td> <td></td>		III	GX180	8.17	1.0	1.4	3.4	5.9	7.2	177	877													
III       GX178       8.04       1.2       2.4       1.9       3.3       7.4       64       194         III       GX177       7.95       1.4       2.9       2.0       3.4       7.0       66       158       0.12       0.08       0.01       1.10       1.30       1.40       0.84       0.93       0.08       0.78       0.06       0.00         III       GX175       7.80       1.4       2.6       2.4       4.1       6.5       80       191       -32.6		III	GX179	8.12	1.2	0.9	1.0	1.7	10.2	33	234	-27.7	0.09	0.03	0.00	1.01	1.13	1.24	0.90	0.91	0.07	0.82	0.02	0.00
III       GX177       7.95       1.4       2.9       2.0       3.4       7.0       66       158       0.12       0.08       0.01       1.10       1.30       1.40       0.84       0.93       0.08       0.78       0.06       0.00         III       GX176       7.89       1.1       2.5       2.8       4.8       7.7       64       183         III       GX175       7.80       1.4       2.6       2.4       4.1       6.5       80       191       -32.6		III	GX178	8.04	1.2	2.4	1.9	3.3	7.4	64	194													
III       GX176       7.89       1.1       2.5       2.8       4.8       7.7       64       183         III       GX175       7.80       1.4       2.6       2.4       4.1       6.5       80       191       -32.6		III	GX177	7.95	1.4	2.9	2.0	3.4	7.0	66	158		0.12	0.08	0.01	1.10	1.30	1.40	0.84	0.93	0.08	0.78	0.06	0.00
III GX175 7.80 1.4 2.6 2.4 4.1 6.5 80 191 - 32.6		III	GX176	7.89	1.1	2.5	2.8	4.8	7.7	64	183													
	_	III	GX175	7.80	1.4	2.6	2.4	4.1	6.5	80	191	- 32.6												

(continued on next page)  $\qquad \overset{\text{$\Sigma$}}{\overset{\text{$\Im$}}{\overset{\text{$\Im$}}{\overset{\text{$Y$}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}}{\overset{{Y}}{\overset{{Y}}}}{\overset{{Y}}}{\overset$ 

Table 2 (continued)

Unit	Sample	Height	Fe <sub>T</sub>	Al	TOC	OCAR (mgcm <sup>-2</sup> kyr <sup>-</sup>	TIC	Mo (nnm)	Mo <sub>EF</sub>	$\delta^{34}S_{py}$	Fe <sub>carb</sub>	Fe <sub>ox</sub>	Fe <sub>mag</sub>	Fe <sub>Py</sub>	Fe <sub>HR</sub>	Fe <sub>T</sub>	Fe <sub>py</sub> /Fe <sub>HR</sub>	Fe <sub>HR</sub> /Fe <sub>T</sub>	$Fe_{carb}/Fe_{T}$	$Fe_{py}/Fe_{T}$	$Fe_{OX}/Fe_{T}$	$Fe_{mag}/Fe_{T}$
		(111)	(100)	(10)	(101/0)	(Ingeni Kyi	) (100)	(ppiii)		(700)	(1110)	(100)	(110)	(110)	(1110)	(110.0)						
III	GX174	7.70	0.8	1.2	2.2	3.8	9.5	84	396	26.4	0.07	0.00	0.00	0.04	0 70	0.67	0.00	1.00	0.10	0.05	0.00	0.00
	GX173	7.58	0.7	0.4	0.4	0.7	11.5	21	172	-26.4	0.07	0.02	0.00	0.64	0.73	0.67	0.88	1.00	0.10	0.95	0.02	0.00
	GX172	7.47	0.7	0.9	0.5	0.8	11.1	22	1/3													
	GX171	7.38	0.9	0.5	0.5	0.8	11.0	23	246													
	GX170	7.23	1.5	2.5	3.8	6.6 5.C	6.0	202	438													
	GX169	7.10	0.6	1.0	3.2	5.6	9.3	/1	383	20.0												
	GX108 CV160 167	6.93	0.5	0.5	0.7	1.1	7.4	22	218	-26.0												
	GX100-107	6.51	1.1	1.9	1.0	0.2	6.2	223	740													
	GX159 CX158	6.38	1.1	2.8	4.0 Q Q	15.2	5.0	154	300													
Ш	GX150 GX157	6.25	1.5	2.0	3.0	6.8	7.2	164	574													
Ш	GX157	6.14	0.3	0.4	14	24	10.0	71	855													
Ш	GX155	6.00	0.5	0.4	1.4	2.4	93	87	585													
Ш	GX153	5.88	0.8	16	73	93	7.2	705	2296	-330	0.09	0.18	0.01	0.81	1.08	0.80	0.75	1.00	0.12	1.00	0.22	0.01
Ш	GX152	5.80	0.9	1.8	4.8	6.0	6.7	210	799	5510	0.00	0110	0.01	0101	1100	0.00	017.0	1100	0112	1100	0.22	0101
Ш	GX151	5.70	0.9	1.5	6.9	8.7	7.7	469	1944													
III	GX150	5.63	0.9	1.3	5.1	6.5	6.6	205	936													
III	GX149	5.58	0.5	1.1	2.9	3.6	8.0	90	538													
III	GX148	5.53	0.3	0.6	2.1	2.7	8.1	69	616													
III	GX147	5.37	0.2	0.4	0.8	1.0	11.1	42	603													
III	GX146	5.19	1.0	1.3	5.8	7.3	1.4	287	1351	-33.4	0.08	0.13	0.00	0.69	0.90	0.96	0.77	0.93	0.08	0.72	0.13	0.00
III	GX-144	5.11	0.9	1.5	4.8	6.1	4.9	258	981													
III	GX143	5.07	0.7	1.7	3.8	4.8	3.7	232	962	-28.7	0.01	0.01	0.00	0.67	0.69	0.74	0.97	0.93	0.01	0.91	0.01	0.00
III	GX142	5.02	0.5	2.6	0.4	0.5	9.9	9	44													
III	GX141	4.97	1.2	2.1	3.8	4.8	6.1	168	547													
III	GX140	4.91	0.7	0.8	6.1	7.8	6.6	441	3096													
III	GX139	4.78	0.2	0.2	1.4	1.8	9.6	51	1219													
III	GX138	4.66	0.7	1.3	5.6	7.1	7.1	339	1406													
III	GX136	4.57	0.6	0.9	1.8	2.2	9.5	84	653													
III	GX132	4.10	1.1	1.6	6.5	8.3	7.3	145	661													
III	GX130	3.85	1.0	1.5	4.1	5.2	7.5	81	307													
III	GX127	3.60	0.3	0.1	0.8	1.0	10.8	25	811													
III	GX125	3.46	1.1	1.5	5.3	6.7	6.2	81	335													
III	GX124	3.41	2.0	3.6	9.1	11.5	5.0	82	150													
III	GX123	3.35	1.0	1.3	6.5	8.2	5.5	334	1088													
III	GX122	3.27	0.9	1.2	6.3	8.0	6.8	313	951	-32.4	0.09	0.11	0.00	0.78	0.98	0.89	0.79	1.00	0.10	0.87	0.12	0.00
II	GX120	3.11	0.3	0.5	0.3	0.3	11.4	3	47													
II	GX119	2.97	0.5	0.8	0.3	0.4	10.0	2	14													
II	GX117	2.71	0.4	0.6	0.2	0.3	10.6	1	9	22.0	0.00	0.45	0.01	0.70		0.04	0.00	1.00	0.00	0.00	0.4.0	0.01
II	GX115	2.44	0.9	1.5	0.4	0.6	9.3	5	21	-33.8	0.20	0.15	0.01	0.78	1.14	0.94	0.68	1.00	0.22	0.83	0.16	0.01
11	GX113	2.29	0.3	0.6	0.2	0.2	11.4	/	105													
11	GX112 CV110	2.20	2.3	6.1	0.7	0.8	2.3	13	17													
11	GXIIU CV109	2.00	1.0	5.0	0.6	0.7	2.2	20	26	25.2	0.00	0.05	0.01	1 5 0	1 71	1.96	0.02	0.02	0.04	0.95	0.02	0.00
11	GX108	1.82	1.9	5.9	0.6	0.7	2.3	20	20	- 35.3	0.08	0.05	0.01	1.58	1./1	1.80	0.92	0.92	0.04	0.85	0.03	0.00
11	GX107	1.//	1.0	0.5	0.5	0.7	2.7	23	29 49													
п	GX100	1.72	0.4	0.0	0.0	0.8	2.4	30 7	40 96	226												
п	GX-104 CV102	1.30	1.2	4.2	0.2	0.3	10.7	10	22	- 52.0												
II I	GA103	1.40	1.2	4.5 7.5	28	3.5	4.1	10	24	_ 38 5	0.06	0.68	0.05	0.65	1 /3	1 74	0.45	0.82	0.03	0.37	0.30	0.03
I	GX102 GX-101	1.41	0.9	3.4	2.0 15	19	5.0	15	24 30	- 50.5	0.00	0.00	0.05	0.05	1,45	1./4	0.45	0.02	0.05	0.57	0.35	0.05
I	GX-101	1 31	13	2.8	1.5	24	4.4	20	45													
I	CX99	1.51	1.5	2.0	1.9	2.7	4.0	17	40													
I	GX98-2	1.17	24	8.4	5.6	71	4.0	47	52													
I	GX97	0.99	0.7	19	21	26	53	15	58													
ī	GX-96-2	0.89	2.5	7.4	42	5.4	0.0	92	102	- 35 7	0.03	1 28	0.11	0.78	2.21	2.49	0 35	0.89	0.01	0.31	0.52	0.04
i	GX95	0.78	1.7	3.8	4.6	5.9	1.4	43	64	55.7	5,55		0,11	0.70	2.21	2,15	0.00	5.00	5.01	0.01	5.52	510 1

0.02 0.01 0.01 0.49 0.76 0.33 0.60 0.19 0.60 0.10 0.13 0.0G 1.00 0.1 8 0.19 0.49 0.55 1.39 1.03 2.07 2.10 1.68 1.11 0.39 0.83 0.61 0.02 0.02 0.02 0.69 0.34 1.57 0.15 0.13 0.12 33.5 34.9 35.1 67 111 671 1222 388 304 748 927 587 28 44 324 402 196 229 394 203 362 4.0 3.8 8.8 8.2 8.2 11.6 8.1 8.1 11.6 7.6 3.1 3.0 3.0 9.1 6.5 6.4 9.1 8.8 8.8 8.8 1.0 2.1 1.8 1.4 1.1 1.1 1.0 2.2 2.2 2.1 2.1 0.65 0.47 0.36 0.31 0.31 0.31 0.31 0.25 0.15 0.15 0.11 0.06 GX93 GX-91 GX90 GX89 GX89 GX87 GX85-2 GX85-2 GX85-1 GX85-1 GX83-2 GX83-2 GX83-2

-----

values at 8.65–15.65 m 0.7–3.0%, mean 1.7%, and maximum values at 15.65–18.78 m (3.2–5.1%, mean 3.9%).

Fe<sub>ox</sub> constitutes a small proportion of the total Fe budget (Fe<sub>ox</sub>/Fe<sub>T</sub>, mean 0.08), although relatively high levels of Fe<sub>ox</sub> are found at 0–1.41 m in the lower part of the Dalong Formation (mean 0.91%). Similarly, Fe<sub>mag</sub> is also low, generally representing only ~0.01 of Fe<sub>T</sub> (i.e., Fe<sub>mag</sub>/Fe<sub>T</sub>). The most important reactive iron components are Fe<sub>carb</sub> and Fe<sub>py</sub> (Fig. 3). Fe<sub>carb</sub>/Fe<sub>T</sub> contents are relatively low and stable at 0–9.98 m (0.01–0.22), whereas Fe<sub>py</sub> concentrations show uniformly high values (mean Fe<sub>py</sub>/Fe<sub>T</sub> 0.84; mean Fe<sub>py</sub>/Fe<sub>HR</sub> 0.84) except for the basal 5 samples. From 9.98 to 18.78 m, Fe ratios are variable, with Fe<sub>py</sub>/Fe<sub>T</sub> ranging from 0.01 to 0.62 (mean 0.31), Fe<sub>py</sub>/Fe<sub>HR</sub> ranging from 0.01 to 0.84 (mean 0.5), and Fe<sub>carb</sub>/Fe<sub>T</sub> ranging from 0.08 to 0.61 (mean 0.26).

Pyrite sulfur isotope compositions ( $\delta^{34}S_{py}$ ) range widely within the study section, from -42.0 to -24.3% (mean -33.5%). From 0 to 10.5 m,  $\delta^{34}S_{py}$  increases from <-33% to -26%, after which it decreases upsection to -42.2% at the LPME (~15.3 m). Above the LPME,  $\delta^{34}S_{py}$  values show a general increase to -25.7% but with large sample-to-sample variation (Fig. 3).

# 6. Discussion

#### 6.1. Secular marine redox variation at Ganxi

In order to better interpret our chemostratigraphic data, we subdivided the Ganxi section into six units (I–VI; Fig. 3) based on variations in redox conditions and geochemical controls, as discussed below. Unit I comprises the uppermost Wuchiapingian (0 to 1.41 m), Unit II the lower *C. wangi* Zone of the lowermost Changhsingian (1.41–3.11 m), Unit III the upper *C. wangi* and lower *C. changxingensis* zones of the lower Changhsingian (3.11–8.28 m), Unit IV the upper *C. changxingensis* and lower *C. yini* zones of the upper Changhsingian (8.28–13.99 m), Unit V the upper *C. yini* and *C. meishanensis* zones of the uppermost Changhsingian (13.99–15.77 m), and Unit VI the lowermost Induan (15.77–18.78 m).

In Unit I, ferruginous bottomwater conditions are suggested by high  $Fe_{HR}/Fe_T$  (0.82–1.0) and low  $Fe_{pv}/Fe_{HR}$  (0.19–0.45) in most samples. However, persistently euxinic conditions are indicated by high Mo concentrations (mean 301 ppm, maximum 402 ppm) and Mo<sub>FF</sub> (mean 821, maximum 1222) for the basal 0.4 m of Unit I, and intermittently euxinic conditions are indicated by intermediate Mo concentrations (mean 34 ppm, maximum 92 ppm) and Mo<sub>FF</sub> (mean 60, maximum 111) for the rest of Unit I. The generally euxinic conditions of Unit I are consistent with high OCAR (mean 9.7 mg/cm<sup>2</sup>/kyr for 0–0.4 m, 3.9 mg/cm<sup>2</sup>/kyr for 0.4–1.41 m) (Fig. 3). As suggested by Li et al. (2012), the low  $Fe_{py}/Fe_{HR}$ values of Unit I most likely reflect pyrite weathering in the original samples, an inference supported by elevated Fe<sub>ox</sub>/Fe<sub>HR</sub> (0.31-0.75) in these carbonate-lean shales (mean TIC = 2.8%), a lithology that is easily affected by localized oxidative weathering. We note that elevated Fe<sub>ox</sub>/ Fe<sub>HR</sub> values are found only within Units I to III and not in the remainder of the study section, suggesting that near-surface weathering has influenced only the lower part of the section to a measurable degree. This inference is supported by a strong negative correlation between Fe<sub>pv</sub>/Fe<sub>T</sub> and  $Fe_{ox}/Fe_T$  ( $R^2 = 0.78$ , p < 0.01) for Units I–III and non-correlation for Units IV–V ( $R^2 = 0.05$ , p = 0.15). Given probable post-depositional alteration of some samples, we therefore infer dominantly euxinic depositional conditions for Unit I.

In Unit II, many samples have Fe<sub>T</sub> of <0.5% (Table 2), making them unsuitable for redox interpretation based on Fe-speciation data. Two samples (GX108 and GX115) with Fe<sub>T</sub> > 0.5% show high Fe<sub>HR</sub>/Fe<sub>T</sub> values (0.92, 1.0) and high Fe<sub>py</sub>/Fe<sub>HR</sub> values (0.68, 0.92), suggesting euxinic bottomwater conditions (Fig. 3). In contrast, Mo is only weakly enriched (mean Mo = 12 ppm, Mo<sub>EF</sub> = 23), suggesting suboxic to weakly euxinic conditions. This interpretation is consistent with low OCAR (0.24–0.92 mg/cm<sup>2</sup>/kyr). However, low Mo<sub>EF</sub> values in Unit II may have been



Fig. 4. Expanded view on the variation of Fe-S-C systematics around the Permian-Triassic boundary at Ganxi. Abbreviations, figure and explanations as in Fig. 3. The yellow bands correspond to volcanic ash layers.

due to a reduced ocean Mo reservoir (e.g., caused by the marine euxinia of Unit I), an insufficient supply of organic matter during sedimentary Mo uptake, or both (see Section 3, and Cheng et al., 2015). Therefore, based on current data, we cannot determine the redox conditions of Unit II with certainty.

Although several samples in Unit III have  $Fe_T < 0.5\%$  (Table 2), most samples having  $Fe_T > 0.5\%$  exhibit high  $Fe_{HR}/Fe_T$  (0.93–1.0) and high  $Fe_{py}/Fe_{HR}$  (0.75–0.97), indicating strongly and persistently euxinic bottomwater conditions (Fig. 3). Mo concentrations are variable but mostly high (9–705 ppm, mean 155 ppm), and  $Mo_{EF}$  values are significantly elevated (43–3100, mean 710), which are consistent with redox interpretations based on Fe speciation data as well as high OCAR (mean 5.1 mg/cm<sup>2</sup>/kyr). The agreement of redox interpretations for Unit III based on Fe speciation and Mo abundance data indicates that oxidative weathering of pyrite was not important, in contrast to Unit I, possibly owing to greater resistance to weathering by these more carbonate-rich samples (mean TIC = 7.8%).

In Unit IV, all samples have Fe<sub>T</sub> > 0.5% and are characterized by moderate to high Fe<sub>HR</sub>/Fe<sub>T</sub> (0.53–1.0), suggesting anoxic conditions. Fe<sub>py</sub>/Fe<sub>HR</sub> shows persistently high values (0.81–0.90) at 8.46–10.51 m but variable values (0.30–0.84) at 10.51–13.84 m, suggesting persistently euxinic water conditions during deposition of lower Unit IV, switching to fluctuating euxinic conditions that were punctuated by ferruginous episodes during deposition of upper Unit IV (Fig. 3). However, low Mo concentrations (1–14 ppm, mean 5 ppm) and Mo<sub>EF</sub> (2–38, mean 9) suggest suboxic to anoxic conditions. We interpret the low Mo enrichments in Unit IV as a possible result of low aqueous Mo availability (see Section 3) rather than low organic matter availability in view of significantly elevated OCAR at 13–15.3 m (mean 14.1 mg/cm<sup>2</sup>/kyr; Fig. 3).

In Unit V, all samples have  $Fe_T > 0.5\%$  and show moderate to high  $Fe_{HR}/Fe_T$  (0.51–0.93, mean 0.72) and variable  $Fe_{pv}/Fe_{HR}$  (0.28–0.73,

mean 0.47) (Figs. 3 and 4), reflecting dominantly ferruginous conditions punctuated by euxinic episodes. Mo abundances (1–58 ppm, mean 11 ppm) and  $Mo_{EF}$  (0.5–80, mean 17) are consistent with a generally ferruginous system, in which H<sub>2</sub>S did not build up sufficiently to enhance Mo uptake strongly (Cheng et al., 2015).

In Unit VI, all samples have Fe<sub>T</sub> > 3% and exhibit highly variable Fe<sub>HR</sub>/Fe<sub>T</sub> (0.27–0.77, mean 0.54) and Fe<sub>py</sub>/Fe<sub>HR</sub> (0.01–0.81, mean 0.47) (Figs. 3 and 4), indicating dominantly ferruginous conditions punctuated by euxinic episodes. Fluctuating redox conditions may have shifted to dominantly oxic conditions in the uppermost part of this unit, as suggested by Fe<sub>HR</sub>/Fe<sub>T</sub> of <0.38 (Fig. 3).

The euxinic-to-ferruginous transition inferred within Unit IV is further confirmed by secular variation in the  $\delta^{34}S_{pv}$  record at Ganxi (Fig. 3). Petrographic observations demonstrate that sedimentary pyrite crystals at Ganxi consist mainly of small framboids (<10 µm; Fig. 6), consistent with their formation in an anoxic water column (Wilkin et al., 1996). For this reason, the  $\delta^{34}S_{py}$  record at Ganxi can be used to proxy oceanic sulfur cycling during the study interval. The gradual increase of  $\delta^{34}S_{pv}$  from Unit I to lower Unit IV (<-33% to -26%) is consistent with pervasive <sup>34</sup>S-depleted pyrite burial in sediments deposited under large-scale anoxic and euxinic conditions during this interval, which may have gradually shifted the  $\delta^{34}S$  of residual seawater sulfate to higher values. In contrast, the gradual decrease of  $\delta^{34}S_{py}$  from lower Unit IV to Unit V (from -26% to -42.2%) can be explained as the effect of reduced burial of <sup>34</sup>S-depleted pyrite under increasing ferruginous conditions. Similar patterns of secular variation in  $\delta^{34}S_{pv}$  have been reported from other PTB sections, e.g., Nhi Tao (Vietnam) and Meishan (South China) (Algeo et al., 2008; Shen et al., 2011), suggesting that these isotopic records preserve a global signature of oceanic sulfur cycling. Similar patterns of oceanic sulfur cycling have been reported for the late Cambrian SPICE (Gill et al., 2011) and the Botoman Sinsk



Fig. 5. Stratigraphic and redox chemistry correlation of the Shangsi (A), Ganxi (B), and Xiakou sections (C). Data sources: Xiakou (Shen et al., 2016); Ganxi (this study); Shangsi (Xiang et al., 2015). Abbreviations, figure legend and explanation as in Fig. 3.

event (Zhuravlev and Wood, 1996). We note that the upsection increase of  $\delta^{34}S_{py}$  in Unit VI with large variability (from -42.2% to -24.3%) is consistent with increasing water-column oxygenation, as indicated by Fe-speciation data (see Section 6.1). This process may have shifted pyrite formation to the sediment, where limited porewater sulfate supply would have reduced isotopic fractionations during microbial sulfate reduction (MSR) (Zaback et al., 1993).

# 6.2. Geochemical controls on marine redox conditions at Ganxi

# 6.2.1. Watermass euxinia related to elevated marine productivity, low $Fe_{HR}$ fluxes and ample sulfate availability (Units I–III)

Water-column redox chemistry is generally controlled by the relative fluxes of C, S and Fe in marine systems, which is related to oceanic productivity, organic matter decay, and detrital/hydrothermal iron supply (Poulton and Canfield, 2011; Raiswell and Canfield, 2012; Feng et al., 2014). In the modern ocean, oxygen-poor conditions in open (unrestricted) settings are generally associated with high marine productivity linked to upwelling of nutrient-rich thermoclinal waters, which occurs intensely at subtropical latitudes on the western and, especially, eastern margins of ocean basins (Meyer and Kump, 2008; Ducklow and McCallister, 2004; Schunck et al., 2013).

Paleogeographic reconstructions indicate that the South China Craton was located in a peri-equatorial setting with long western and eastern coastlines during the Permian (Fig. 1A; Erwin, 2006; Yin et al., 2014; Wei et al., 2015). The Ganxi section was located on the paleo-western margin of South China, facing into the Qinling (or eastern Paleo-Tethys) Sea (Fig. 1B). The high OCAR values observed in Units I and III (mean = 6.5 mg/cm<sup>2</sup>/kyr and 5.1 mg/cm<sup>2</sup>/kyr, respectively; Fig. 3) are consistent with elevated productivity (cf. Algeo et al., 2013 and Fig. 7A). Lower



Fig. 6. Back-scattered electron (BSE) images of pyrite framboids from Ganxi: (A) a typical sample deposited under euxinic seawater conditions (GX148), and (B) a typical sample deposited under ferruginous seawater conditions (GX233).



Fig. 7. Schematic representation of Fe-S-C dynamical controls on marine redox conditions during deposition of Units I and III (A), Unit IV (B), and Units V–VI with (C) and without volcanic inputs (D). See text for detailed explanation.

mean OCAR in Unit II (0.54 mg/cm<sup>2</sup>/kyr; Fig. 3) suggests a transient decline of marine productivity. Other nearby sections (e.g., Shangsi, Zhoujiaba, and Chaotian) show similarly elevated TOC values in correlative strata (Xiang et al., 2015; Wei et al., 2015; Saitoh et al., 2014), consistent with generally high but somewhat variable productivity on the paleo-western margin of the South China Craton during the Late Permian.

Controls on secular variation in marine productivity at Ganxi are uncertain, but some tentative inferences can be drawn. Lithofacies changes are not closely correlated with TOC and OCAR variation at Ganxi, suggesting that marine productivity was not noticeably modulated by terrigenous inputs and/or eustatic changes (see Section 2). The lack of a relationship to terrigenous proxies specifically implies that marine productivity did not depend on riverine nutrient fluxes. An alternative source of nutrients was upwelling on the western margin of the South China Craton (Fig. 1), which may have been driven by offshore Ekman transport (Wei et al., 2015). Other sections from the same (paleo-western) margin of the South China Craton provide some evidence in support of upwelling, e.g., radiolarian cherts or radiolarian-bearing siliceous limestones containing moderately high TOC values in the lower Changhsingian at Shangsi and Xiajiaba (Wei et al., 2015; Xiang et al., 2015). On the eastern Panthalassic Ocean margin, strong upwelling linked to vigorous global-ocean circulation produced abundant chert deposits in western Canada during a 30-Myr-long depositional phase (from the Early Permian to the mid-Changhsingian) so distinctive that it has been termed the 'Permian Chert Event' (Beauchamp and Baud, 2002). We hypothesize that the western margin of the South China Craton was influenced by secular variation in upwelling intensity (ultimately linked to the vigor of global-ocean circulation) during the Late Permian, although further work will be needed to rigorously test this idea.

If marine productivity is sufficiently high, it can lead to development of euxinia at intermediate water depths. Two prerequisites must be met: (1) relatively low Fe<sub>HR</sub> fluxes, and (2) ample sulfate availability. Fe<sub>HR</sub> ranges from 0.69 to 2.21% (mean = 1.30%) for Units I to III, suggesting generally low Fe<sub>HR</sub> fluxes to the study site. Fe<sub>T</sub> shows a strong positive correlation with Al ( $R^2 = 0.68$ , p < 0.001) and Fe<sub>HR</sub> ( $R^2 = 0.56$ , p < 0.001), suggesting that Fe<sub>T</sub> was mainly from terrestrial sources instead of hydrothermal vents (Li et al., 2012). Therefore, the low Fe<sub>T</sub> values (mean = 1.3%) in Units I to III are consistent with low terrigenous Fe fluxes during the early Changhsingian.

Sulfate availability in a marine system can be investigated by using  $\delta^{34}S_{py}$  if sedimentary pyrite was formed mainly in the water column (Feng et al., 2014; Poulton et al., 2015). The S-isotopic composition of sedimentary pyrite is influenced by the availabilities of sulfate and organic matter, because they are limiting reactants controlling first-order reaction rates during microbial sulfate reduction (MSR). Increased productivity rates may deplete sulfate supply, in turn decreasing isotopic fractionation during MSR ( $\varepsilon_{py} = \delta^{34}S_{SO4} - \delta^{34}S_{py}$ ) and generating heavier  $\delta^{34}S_{py}$  (Leavitt et al., 2013). As indicated by petrographic observations of abundant small pyrite framboids (Fig. 6), sedimentary pyrite was formed mainly in the water column at Ganxi. The lack of correlation between TOC and  $\delta^{34}S_{py}$  (R<sup>2</sup> = 0.14; *p* = 0.144) is consistent with ample sulfate supply during MSR in Units I-III. Therefore, both low Fe<sub>HR</sub> fluxes and ample sulfate availability at Ganxi probably contributed to the development of euxina, at least in Units I and III (see Section 6.1).

6.2.2. Ferruginous conditions related to low marine sulfate and excess Fe<sub>HR</sub> (Units IV–VI)

In anoxic marine systems characterized by low marine sulfate, low productivity, high  $Fe_{HR}$  fluxes, or combinations thereof, ferruginous conditions can potentially develop (Feng et al., 2014). Because of wide-spread development of euxinia in Late Permian oceans (Isozaki, 1997; Kaiho et al., 2012; Takahashi et al., 2014; Chen et al., 2015), contemporaneous seawater sulfate concentrations are thought to have been much lower (~4 mM) than in the modern ocean (~28 mM) (Luo et al., 2010; Song et al., 2014; Algeo et al., 2015). This conclusion is consistent with results from Units I and III at Ganxi, which display evidence for persistent euxinia (see Section 6.1). If seawater sulfate were locally drawn down below a critical level, then ferrous Fe would build up in the water column, yielding ferruginous conditions.

Our Fe speciation results for Ganxi indicate dominantly ferruginous conditions during deposition of Units IV to VI (Fig. 3; see Section 6.1). This shift away from the euxinic conditions of Units I and III must have been caused by reductions in either sulfate or organic carbon supply, an increase in Fe<sub>HR</sub> supply, or some combination thereof (cf. Feng et al., 2014). Our OCAR data show large variations within Units IV–VI, which suggests that reduced organic matter supply was not the main factor controlling development of ferruginous conditions. Specifically, OCAR exhibits low values at 8.4–13 m (mean 0.73 mg/cm<sup>2</sup>/kyr) and 15.3–18.8 m (mean 0.72 mg/cm<sup>2</sup>/kyr) but high values at 13–15.3 m (mean 14.1 mg/cm<sup>2</sup>/kyr). Significantly, these values are both lower and higher than those seen in Units I (6.5 mg/cm<sup>2</sup>/kyr) and III (5.1 mg/cm<sup>2</sup>/kyr).

On the other hand,  $Fe_T$  exhibits a general increase upsection at Ganxi, from 1.3% in Units I–III to 1.7% in Units IV–V and 3.9% in Unit VI (Fig. 3), signifying an increasing flux of terrigenous iron (see Section 6.2.1). Higher fluxes of Fe may have played an important role in drawing H<sub>2</sub>S down to near-zero through pyrite formation, thereafter allowing ferrous Fe to build up in the water column (cf. Li et al., 2012). A similar phenomenon has been reported from modern restricted-marine settings with greatly enhanced Fe<sub>HR</sub> fluxes (e.g., Meyers, 2007). The cause of enhanced Fe fluxes to Ganxi during the Permian-Triassic transition may have been intensified weathering and erosion of continents during and following the end-Permian crisis (see Section 6.3).

# 6.2.3. Control of high-frequency redox fluctuations by sulfate availability (Units V–VI)

Although characterized by dominantly ferruginous conditions, Units V and VI at Ganxi exhibit frequent, transient shifts to euxinic or oxic watermass conditions (Fig. 3; see Section 6.1). In general, development of watermass euxinia is favored by higher marine productivity and sulfate concentrations (see Section 6.2.1). The euxinic samples in Units V and VI have low OCAR values (mean ~ 1.0 mg/cm<sup>2</sup>/kyr) (Table 2), suggesting that elevated marine productivity was probably not the main cause of these euxinic episodes. Rather, we infer that these episodes were triggered by transient increases in sulfate supply (Fig. 7C-D) above the generally low background values (~4 mM) present in Late Permian oceans (see Section 6.2.2). Although riverine sulfate supply may have fluctuated in response to the vagaries of continental weathering, we suggest that episodically enhanced sulfate fluxes on the South China Craton were related to volcanic activity. Frequent inputs of volcanic sulfate aerosols can increase production of H<sub>2</sub>S by MSR and, in turn, pyrite formation as well as isotopic fractionation during BSR, which will yield isotopically lighter  $\delta^{34}S_{py}$  in a euxinic water column (Habicht et al., 2002, Bradley et al., 2016). Indeed, in Units V and VI, most samples with locally elevated Fepv/FeHR ratios are associated with ash layers (Fig. 4), offering direct evidence of a volcanic source of sulfate. This mechanism is further supported by the observation that most ash layers are associated with a small negative  $\delta^{34}S_{py}$  excursion (Fig. 4), consistent with episodic inputs of sulfate to the ocean via volcanic activity. The link between volcanic eruptions and both sulfate inputs and euxinia development is supported by a moderate negative correlation between  $\delta^{34}S_{py}$  and  $Fe_{py}/Fe_{HR}$  in Units V–VI ( $R^2 = 0.38$ , p < 0.01; Fig. 4); the imperfectness of this correlation is due to a combination of low sampling resolution and partial derivation of pyrite sulfur from sources other than ash layers.

#### 6.3. Redox variation at Ganxi in a regional context

The significance of secular redox variation at Ganxi can be best understood in the context of regional redox patterns during the Late Permian to Early Triassic. The western continental slope of the South China Craton was an environmentally sensitive area owing to possible eastern-boundary upwelling (Wei et al., 2015). Detailed redox studies based on Fe speciation data undertaken on two correlative sections on the same margin (Xiakou and Shangsi) can help to elucidate regional patterns of redox variation. Shen et al. (2016) recently reconstructed redox conditions at Xiakou (Fig. 5C), which was located downramp from Ganxi in the same embayment (i.e., Xiakou-Lichuan Bay; Fig. 1B) at water depths of ~200-300 m. Xiang et al. (2015) reconstructed redox conditions at Shangsi (Fig. 5A), which was located in a different deepwater coastal embayment (i.e., Guangyuan-Liangping Bay; Fig. 1B) located several hundred kilometers to the south, closer to the Kangdian Oldland. Both the Xiakou and Shangsi sections consist of siliceous limestone and mudstone with numerous ash interbeds, consistent with accumulation in a deep-shelf setting (~200-300 m; Xiang et al., 2015; Shen et al., 2016).

Ganxi, Xiakou, and Shangsi are among the most well-studied PTB sections in South China, all having well-established conodont zonation schemes, on the basis of which the stratigraphic completeness of these sections (i.e., an absence of significant hiatuses) has been inferred. These sections can be intercorrelated on the basis of conodont biostratigraphy and marker horizons, e.g., the LPME and PTB (Shen et al., 2013; Xiang et al., 2015; Shen et al., 2016). Ganxi and Shangsi have nearly identical biozonation schemes: in both sections, Unit III spans the upper C. wangi to lower C. changxingensis zones, Unit IV the lower C. changxingensis to mid-C. yini zones, Unit V the mid-C. yini thru C. meishanensis zones, and Unit VI the I. isarcica Zone (Fig. 5; note: the Unit V/VI contact falls within the H. parvus Zone at Shangsi, but this zone has not been recognized yet at Ganxi). The uppermost Permian at Xiakou is zoned slightly differently, with Units III-IV corresponding to the middle and upper C. changxingensis changxingensis-C. deflecta Zone. Unit V at Xiakou, which begins in the uppermost ~1.3 m of this biozone, extends to the mid-H. parvus Zone, and Unit VI extends upward into the I. isarcica Zone, matching the unit subdivisions at Shangsi.

This correlation framework provides a basis for evaluation of regional patterns of marine redox variation on the western margin of the South China Craton during the Permian-Triassic transition (Fig. 5). The most salient redox pattern in all three sections is an upsection transition from euxinic conditions to mainly ferruginous conditions. Whereas the euxinic lower part of each section shows little redox variation, the ferruginous upper part shows frequent, brief transitions to euxinic or oxic conditions (although ferruginous conditions prevailed >70% of the time). Significantly, the transition from euxinic to ferruginous conditions differs in timing among the three sections, occurring in the uppermost part of Unit III at Shangsi, in the mid to upper part of Unit IV at Ganxi, and in the upper part of Unit V at Xiakou. These differences in timing of the euxinic-to-ferruginous transition are sufficiently large that there is effectively no possibility that they were actually synchronous, and that the differences are due to a few anomalous samples.

The pattern of regional redox variation described above provides insights regarding the causes of redox changes during the Late Permian. Recent studies have inferred that euxinia developed mainly within the oceanic thermocline region (~200–1000 m depth) (Algeo et al., 2011a; Winguth and Winguth, 2012; Clarkson et al., 2016), and that the tops of these oxygen-minimum zones (OMZs) expanded upward during the latest Changhsingian (Feng and Algeo, 2014), leading to eruption of hydrogen sulfide into the ocean-surface layer at and following the LPME (Kump et al., 2005; Algeo et al., 2007, 2008). The water depth estimates for all three sections (~200-300 m) are consistent with accumulation in the upper oceanic thermocline region. In this context, the transition from euxinic to ferruginous conditions in the three study sections (Fig. 5) might be interpreted as a shift from the core of the OMZ to its upper margin, where suboxic (i.e., ferruginous) conditions existed. The problems with this interpretation are that the observed redox pattern (1) implies contraction rather than expansion of the OMZ, which is unlikely given widespread evidence of enhanced euxinia during the latest Permian (e.g., Brennecka et al., 2011; Shen et al., 2011; Shen et al., 2016; Lau et al., 2016), and (2) is inconsistent with a eustatic mechanism because bathymetric relationships among the study sections show no relationship to the sequence of onset of redox changes (which occurred first and last in the deeper sections, Shangsi and Xiakou, with the relatively shallower section, Ganxi, between them).

Instead of a eustatic mechanism, we infer that paleogeographic factors (specifically, proximity to land areas) were the main control on the timing of the euxinic-to-ferruginous transition in the three study sections. The Shangsi section, within the Guangyuan-Liangping Bay, was located much closer to a paleo-landmass (the Kangdian Oldland) than the other two sections (Ganxi and Xiakou), which were located hundreds of kilometers more distally in the Xiakou-Lichuan Bay, a deepwater area surrounded only by the carbonate Yangtze Platform and not in proximity to any paleo-landmass (Fig. 1B). If terrigenous (e.g., Fe) fluxes were an important control on redox changes in the study sections, then the proximal Shangsi section would have been affected first, followed by the more distal sections, progressing from shallower (Ganxi) to deeper ones (Xiakou). This is, in fact, the sequence in which the euxinic-to-ferruginous transition developed in the three study sections (Fig. 5), implicitly supporting our hypothesis that terrigenous (e.g., Fe) fluxes were a critical control on redox conditions on the South China Craton during the Permian-Triassic transition.

In view of these considerations, we hypothesize that an increased flux of river-borne Fe during the latest Permian was responsible for the broad regional transition from euxinic to ferruginous marine redox conditions. This hypothesis is consonant with evidence of elevated weathering fluxes through the PTB interval. Such evidence has been provided in many forms by earlier studies (reviewed in Algeo et al., 2011b): (1) a shift from fine-grained meandering to conglomeratic braided facies in fluvial systems (Ward et al., 2000; López-Gómez et al., 2005), (2) transported soil clasts (pedoliths) and elevated accumulation rates in terrestrial successions (Retallack, 1999, 2005), (3) freshwater algal blooms (Afonin et al., 2001), (4) an abrupt influx of terrigenous siliciclastics to carbonate platforms and elevated accumulation rates in marine successions (Tong et al., 2007; Algeo and Twitchett, 2010; Weidlich and Bernecker, 2011), and (5) appearance of soil-derived biomarkers in shallow-marine successions (Sephton et al., 2005; Xie et al., 2005, 2007). These features suggest a massive disturbance of terrestrial ecosystems, including large-scale soil erosion, in conjunction with the LPME (Algeo et al., 2011b). Enhanced subaerial weathering during the Late Permian was probably due to climatic warming (Korte et al., 2005; Joachimski et al., 2012) leading to faster soil reaction rates, acid rainfall (Wignall, 2007), and the vulnerability of ecologically disturbed landscapes to erosion (Looy et al., 1999, 2001). All of these environmental changes were likely triggered by early stages of eruption of the Siberian Traps Large Igneous Province (Reichow et al., 2009; Burgess et al., 2014; Burgess and Bowring, 2015).

The timing of appearance of features related to weathering intensification is always close to the LPME/PTB, although exact dating is generally impossible in terrestrial successions. The two last-named features (i.e., fluxes of siliciclastics and soil-derived biomarkers) are more securely dated owing to their observation in marine sections. At Meishan, the influx of soil-derived biomarkers is correlative with the upper part of Bed 23, corresponding to the lower or mid-C. *yini* Zone (Wang and Visscher, 2007). Although the euxinic-to-ferruginous transition at Ganxi began somewhat earlier (i.e., in the upper *C. changxingensis* Zone; Fig. 4), the transition was not completed until the mid-*C. yini* Zone, i.e., correlative with the influx of soil-derived biomarkers at Meishan. The observation that the euxinic-to-ferruginous transition can be both older (e.g., at Shangsi) and younger than this (e.g., at Xiakou; Fig. 5) is consistent with the hypothesis that terrigenous fluxes controlled marine redox changes during the latest Permian (since such fluxes are inherently spatially heterogeneous). The present study demonstrates the value of high-resolution chemostratigraphic analyses undertaken on multiple sections in a regional paleogeographic framework.

### 7. Conclusions

Our study of the Fe-Mo-S-C systematics of the Ganxi section documents long-term redox changes during the Late Permian and earliest Triassic at a carbonate-ramp locale on the paleo-western margin of the Yangtze Platform, South China. Iron speciation and Mo concentrations indicate that water-column redox conditions were euxinic during the late Wuchiapingian (Unit I) and early-mid Changhsingian (Unit III) and then gradually evolved to ferruginous by the late Changhsingian (Unit IV). This euxinic-ferruginous transition is also supported by secular  $\delta^{34}S_{py}$  records at Ganxi, which suggest pervasive oceanic pyrite burial under widespread euxinic conditions in Units I-III followed by a significant reduction related to development of ferruginous conditions in Units IV-VI. The euxinic conditions of Units I and III can be attributed to high primary productivity possibly linked to upwelling. The shift to mainly ferruginous conditions in Unit IV was most likely caused by increased terrigenous Fe fluxes to marine systems as a consequence of enhanced subaerial weathering. Enhanced weathering was likely a response to disruption of terrestrial ecosystems associated with early eruptive stages of the Siberian Traps Large Igneous Province. The euxinic-to-ferruginous transition may have been promoted also by lowered seawater sulfate concentrations related to earlier massive pyrite burial. In Units V and VI, dominantly ferruginous conditions were punctuated by euxinic episodes that were probably the result of volcanic sulfate inputs (associated with ash layers) into a low-sulfate ocean

Comparison of redox patterns at Ganxi with those from the nearby Shangsi and Xiakou sections shows similar euxinic-to-ferruginous transitions in all three sections, although with differences in timing: the transition is in the uppermost part of Unit III at Shangsi, in the mid to upper part of Unit IV at Ganxi, and in the upper part of Unit V at Xiakou. The most likely explanation for the diachroneity of redox changes is that marine sections more proximal to paleo-landmasses (i.e., Shangsi) were the first to receive a pulse of Fe-bearing terrigenous detritus, followed by progressively more distal and deeper sections (i.e., Ganxi and then Xiakou). This hypothesis is supported by evidence of intensified weathering fluxes and destruction of terrestrial ecosystems from Permian-Triassic boundary strata in many earlier studies. The present study demonstrates that enhanced terrigenous weathering fluxes were most likely the key factor controlling marine redox changes during the latest Permian in a regional paleogeographic framework.

#### Acknowledgments

This research was supported by National Key Basic Research Program of China (Grant 2013CB955704), National Natural Science Foundation of China (Grant Nos. 41172311, 41602022, 41402001), 111 Project (B08030) and the MOST Special Fund from the State Key Laboratory of Geological Processes and Mineral Resources (MSFGPMR10). The authors greatly appreciate valuable discussions with Profs. Shucheng Xie and Genming Luo. We also thank Qing Hu and Sha Wu for helps during sampling in field and Zihu Zhang, Yifei Zhu, Shida Tang for laboratory assistance.

#### References

- Afonin, S.A., Barinova, S.S., Krassilov, V.A., 2001. A bloom of zygnematalean green algae *Tympanicysta* at the Permian-Triassic boundary. Geodiversitas 23, 481–487.
- Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: implications for analysis of paleoredox and paleohydrographic conditions. Paleoceanography 21, PA1016 (23 pp.).
- Algeo, T.J., Twitchett, R.J., 2010. Anomalous Early Triassic sediment fluxes due to elevated weathering rates and their biological consequences. Geology 38, 1023–1026.
- Algeo, T.J., Ellwood, B., Nguyen, T.K.T., Rowe, H., Maynard, J.B., 2007. The Permian–Triassic boundary at Nhi Tao, Vietnam: evidence for recurrent influx of sulfidic watermasses to a shallow-marine carbonate platform. Palaeogeogr. Palaeoclimatol. Palaeoecol. 252, 304–327.
- Algeo, T.J., Shen, Y.N., Zhang, T.G., Lyons, T.W., Bates, S., Rowe, H., Nguyen, T.K.T., 2008. Association of <sup>34</sup>S-depleted pyrite layers with negative carbonate δ<sup>13</sup>C excursions at the Permian-Triassic boundary: evidence for upwelling of sulfidic deep-ocean water masses. Geochem. Geophys. Geosyst. 9, Q04025 (10 pp.).
  Algeo, T.J., Kuwahara, K., Sano, H., Bates, S., Lyons, T.W., Elswick, E., Hinnov, L., Ellwood, B.,
- Algeo, T.J., Kuwahara, K., Sano, H., Bates, S., Lyons, T.W., Elswick, E., Hinnov, L., Ellwood, B., Moser, J., Maynard, J.B., 2011a. Spatial variation in sediment fluxes, redox conditions, and productivity in the Permian-Triassic Panthalassic Ocean. Palaeogeogr. Palaeoclimatol. Palaeoecol. 308, 65–83.
- Algeo, T.J., Chen, Z.Q., Fraiser, M.L., Twitchett, R.J., 2011b. Terrestrial-marine teleconnections in the collapse and rebuilding of Early Triassic marine ecosystems. Palaeogeogr. Palaeoclimatol. Palaeoecol. 308, 1–11.
- Algeo, T.J., Henderson, C.M., Tong, J., Feng, Q., Yin, H., Tyson, R.V., 2013. Plankton and productivity during the Permian–Triassic boundary crisis: an analysis of organic carbon fluxes. Glob. Planet. Chang. 105, 52–67.
- Algeo, T.J., Luo, G.M., Song, H.Y., Lyons, T.W., Canfield, D.E., 2015. Reconstruction of secular variation in seawater sulfate concentrations. Biogeosciences 12, 2131–2151.
- Beauchamp, B., Baud, A., 2002. Growth and demise of Permian biogenic chert along northwest Pangea: evidence for end-Permian collapse of thermohaline circulation. Palaeogeogr. Palaeoclimatol. Palaeoecol. 184, 37–63.
- Bradley, A.S., Leavitt, W.D., Schmidt, M., Knoll, A.H., Girguis, P.R., Johnston, D.T., 2016. Patterns of sulfur isotope fractionation during microbial sulfate reduction. Geobiology 14, 91–101.
- Brennecka, G.A., Herrmann, A.D., Algeo, T.J., Anbar, A.D., 2011. Rapid expansion of oceanic anoxia immediately before the end-Permian mass extinction. Proc. Natl. Acad. Sci. U. S. A. 108, 17631–17634.
- Burgess, S.D., Bowring, S.A., 2015. High-precision geochronolology confirms voluminous magmatism before, during, and after Earth's most severe extinction. Sci. Adv. 1, e1500470.
- Burgess, S.D., Bowring, S., Shen, S.Z., 2014. High-precision timeline for Earth's most severe extinction. Proc. Natl. Acad. Sci. U. S. A. 111, 3316–3321.
- Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chem. Geol. 54, 149–155.
- Canfield, D.E., Poulton, S.W., Knoll, A.H., Narbonne, G.M., Ross, G., Goldberg, T., Strauss, H., 2008. Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. Science 321, 949–952.
- Cao, C.Q., Love, G.D., Hays, L.E., Wang, W., Shen, S.Z., Summons, R.E., 2009. Biogeochemical evidence for euxinic oceans and ecological disturbance presaging the end-Permian mass extinction event. Earth Planet. Sci. Lett. 281, 188–201.
- Chen, Z.Q., Yang, H., Luo, M., Benton, M.J., Kaiho, K., Zhao, L.S., Huang, Y.G., Zhang, K.X., Fang, Y.H., Jiang, H.S., Qiu, H., Li, Y., Tu, C.Y., Shi, L., Zhang, L., Feng, X.Q., Chen, L., 2015. Complete biotic and sedimentary records of the Permian–Triassic transition from Meishan section, South China: ecologically assessing mass extinction and its aftermath. Earth–Sci. Rev. 149, 67–107.
- Cheng, M., Li, C., Zhou, L., Xie, S.C., 2015. Mo marine geochemistry and reconstruction of ancient ocean redox states. Sci. China D Earth Sci. 58, 2123–2133.
- Clarkson, M.O., Poulton, S.W., Guilbaud, R., Wood, R.A., 2014. Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments. Chem. Geol. 382, 111–122.
- Clarkson, M.O., Wood, R.A., Poulton, S.W., Richoz, S., Newton, R.J., Kasemann, S.A., Bowyer, F., Krystyn, L., 2016. Dynamic anoxic ferruginous conditions during the end-Permian mass extinction and recovery. Nat. Commun. 7. http://dx.doi.org/10.1038/ ncomms12236.
- Ducklow, H., McCallister, S.L., 2004. The biogeochemistry of carbon dioxide in the coastal oceans. In: Robinson, A.R., Brink, K. (Eds.), The Global Coastal Ocean-Multiscale Interdisciplinary Processes: The Sea. Harvard University Press, Cambridge, Massachusetts, pp. 269–315.
- Erwin, D.H., 2006. Extinction: How Life on Earth Nearly Ended 250 Million Years Ago. Princeton University Press, Princeton, New Jersey (320 pp.).
- Feng, LJ., Li, C., Huang, J., Chang, H.J., Chu, X.L., 2014. A sulfate control on marine middepth euxinia on the early Cambrian (ca. 529–521 Ma) Yangtze platform, South China. Precambrian Res. 246, 123–133.
- Feng, Q.L., Algeo, T.J., 2014. Evolution of oceanic redox conditions during the Permo-Triassic transition: evidence from deepwater radiolarian facies. Earth-Sci. Rev. 137, 34–51.
- Feng, Z.Z., Yang, Y.Q., Jin, Z.K., Li, S.W., Bao, Z.D., 1997. Lithofacies Palaeogeography of Permian of South China. Petroleum University Press, Beijing (242 pp. (in Chinese)).
- Gill, B.C., Lyons, T.W., Young, S.A., Kump, L.R., Knoll, A.H., Saltzman, M.R., 2011. Geochemical evidence for widespread euxinia in the later Cambrian ocean. Nature 469 (7328), 80–83.
- Grice, K., Cao, C.Q., Love, G.D., Böttcher, M.E., Twitchett, R.J., Grosjean, E., Summons, R.E., Turgeon, S.C., Dunning, W., Jin, Y.G., 2005. Photic zone euxinia during the Permian-Triassic superanoxic event. Science 307, 706–709.

- Habicht, K.S., Gade, M., Thamdrup, B., Berg, P., Canfield, D.E., 2002. Calibration of sulfate levels in the Archean ocean. Science 298, 2372–2374.
- Helz, G.R., Miller, C.V., Charnock, J.M., Mosselmans, J.F.W., Pattrick, R.A.D., Garner, C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. Geochim. Cosmochim. Acta 60, 3631–3642.
- Helz, G.R., Bura-Nakić, E., Mikac, N., Ciglenečki, I., 2011. New model for molybdenum behavior in euxinic waters. Chem. Geol. 284, 323–332.
- Isozaki, Y., 1997. Permo-Triassic boundary superanoxia and stratified superocean: records from lost deep sea. Science 276, 235–238.
- Jin, C.S., Li, C., Algeo, T.J., Planavsky, N.J., Cui, H., Yang, X.L., Zhao, Y.L., Zhang, X.L., Xie, S.C., 2016. A highly redox-heterogeneous ocean in South China during the early Cambrian (~529–514 Ma): implications for biota-environment co-evolution. Earth Planet. Sci. Lett. 441, 38–51.
- Joachimski, M.M., Lai, X.L., Shen, S.Z., Jiang, H.S., Luo, G.M., Chen, B., Chen, J., Sun, Y.D., 2012. Climate warming in the latest Permian and the Permian-Triassic mass extinction. Geology 40, 195–198.
- Kaiho, K., Oba, M., Fukuda, Y., Ito, K., Ariyoshi, S., Gorjan, P., Riu, Y., Takahashi, S., Chen, Z.Q., Tong, J.N., Yamakita, S., 2012. Changes in depth-transect redox conditions spanning the end-Permian mass extinction and their impact on the marine extinction: evidence from biomarkers and sulfur isotopes. Glob. Planet. Chang, 94–95, 20–32.
- Korte, C., Kozur, H.W., Veizer, J., 2005. δ<sup>13</sup>C and δ<sup>13</sup>O values of Triassic brachiopods and carbonate rocks as proxies for coeval seawater and palaeotemperature. Palaeogeogr. Palaeoclimatol. Palaeoecol. 226, 287–306.
- Kump, LR, Pavlov, A., Arthur, M.A., 2005. Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia. Geology 33, 397–400.
- Lau, K.V., Maher, K., Altiner, D., Kelley, B.M., Kump, L.R., Lehrmann, D.J., Silva-Tamayo, J.C., Weaver, K.L., Yu, M.Y., Payne, J.L., 2016. Marine anoxia and delayed Earth system recovery after the end-Permian extinction. Proc. Natl. Acad. Sci. U. S. A. 113, 2360–2365.
- Leavitt, W.D., Halevy, I., Bradley, A.S., Johnston, D.T., 2013. Influence of sulfate reduction rates on the Phanerozoic sulfur isotope record. Proc. Natl. Acad. Sci. U. S. A. 110, 11244–11249.
- Lenniger, M., Nøhr-Hansen, H., Hills, L.V., Bjerrum, C.J., 2014. Arctic black shale formation during cretaceous oceanic anoxic event 2. Geology 42, 799–802.
- Li, C., Love, G.D., Lyons, T.W., Fike, D.A., Sessions, A.L., Chu, X.L., 2010. A stratified redox model for the Ediacaran ocean. Science 328, 80–83.
- Li, C., Love, G.D., Lyons, T.W., Scott, C.T., Feng, L.J., Huang, J., Chang, H.J., Zhang, Q., Chu, X.L., 2012. Evidence for a redox stratified Cryogenian marine basin, Datangpo Formation, South China. Earth Planet. Sci. Lett. 331-332, 246–256.
- Li, C., Planavsky, N.J., Shi, W., Zhang, Z.H., Zhou, C.M., Cheng, M., Tarhan, L.G., Luo, G.M., Xie, S.C., 2015. Ediacaran marine redox heterogeneity and early animal ecosystems. Sci. Rep. 5, 1–8.
- Looy, C.V., Brugman, W.A., Dilcher, D.L., Visscher, H., 1999. The delayed resurgence of equatorial forests after the Permian-Triassic ecological crisis. Proc. Natl. Acad. Sci. U. S. A. 96, 13857–13862.
- Looy, C.V., Twitchett, R.J., Dilcher, D.L., van Konijnenburg-van Cittert, J.H.A., Visscher, H., 2001. Life in the end-Permian dead zone. Proc. Natl. Acad. Sci. U. S. A. 98, 7879–7883.
- Loope, G.R., Kump, L.R., Arthur, M.A., 2013. Shallow water redox conditions from the Permian-Triassic boundary microbialite: the rare earth element and iodine geochemistry of carbonates from Turkey and South China. Chem. Geol. 351, 195–208.
- López-Gómez, J., Arche, A., Marzo, M., Durand, M., 2005. Stratigraphical and palaeogeographical significance of the continental sedimentary transition across the Permian-Triassic boundary in Spain. Palaeogeogr. Palaeoclimatol. Palaeoecol. 229, 3–23.
- Luo, G., Kump, L.R., Wang, Y.B., Tong, J.N., Arthur, M.A., Yang, H., Huang, J.H., Yin, H.F., Xie, S.C., 2010. Isotopic evidence for an anomalously low oceanic sulfate concentration following end-Permian mass extinction. Earth Planet. Sci. Lett. 300, 101–111.
- McLennan, S., 2001. Relationships between the trace element composition of sedimentary rocks and upper continental crust. Geochem. Geophys. Geosyst. 2, 1525–2027.
- Meyer, K.M., Kump, L.R., 2008. Oceanic euxinia in Earth history: causes and consequences. Annu. Rev. Earth Planet. Sci. 36, 251–288.
- Meyers, S.R., 2007. Production and preservation of organic matter: the significance of iron. Paleoceanography 22, 1–16.
- Mutwakil, N., Xia, W.C., Zhang, N., 2006. Late Permian (Changhsingian) conodont biozonation and the basal boundary, Ganxi section, western Hubei Province, South China. Can. J. Earth Sci. 43, 121–133.
- Nielsen, J.K., Shen, Y., 2004. Evidence for sulfidic deep water during the Late Permian in the East Greenland Basin. Geology 32, 1037–1040.
- Payne, J.L., Clapham, M.E., 2012. End-Permian mass extinction in the oceans: an ancient analog for the twenty-first century? Annu. Rev. Earth Planet. Sci. 40, 89–111.
- Peng, Y.Q., Tong, J.N., Shi, G.R., Hansen, H.J., 2001. The Permian–Triassic boundary set: characteristics and correlation. Newsl. Stratigr. 39, 55–71.
- Poulton, S.W., Canfield, D.E., 2005. Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. Chem. Geol. 214, 209–221.
- Poulton, S.W., Canfield, D.E., 2011. Ferruginous conditions: a dominant feature of the ocean through Earth's history. Elements 7, 107–112.
- Poulton, S.W., Fralick, P.W., Canfield, D.E., 2010. Spatial variability in oceanic redox structure 1.8 billion years ago. Nat. Geosci. 3, 486–490.
- Poulton, S.W., Henkel, S., März, C., Urquhart, H., Flögel, S., Kasten, S., Sinninghe Damsté, J.S., Wagner, T., 2015. A continental-weathering control on orbitally driven redox-nutrient cycling during cretaceous oceanic anoxic event 2. Geology 43, 963–966.
- Proemse, B.C., Grasby, S.E., Wieser, M.E., Mayer, B., Beauchamp, B., 2013. Molybdenum isotopic evidence for oxic marine conditions during the latest Permian extinction. Geology 41, 967–970.

Raiswell, R., Canfield, D.E., 1998. Sources of iron for pyrite formation in marine sediments. Am. J. Sci. 298, 219–245.

Raiswell, R., Canfield, D.E., 2012. The iron biogeochemical cycle past and present. Geochim. Perspect. 1, 1–220.

- Reichow, M.K., Pringle, M.S., Al' Mukhamedov, A.I., Allen, M.B., Andreichev, V.L., Buslov, M.M., Davies, C.E., Fedoseev, G.S., Fitton, J.G., Inger, S., Medvedev, A.Y., Mitchell, C., Puchkov, V.N., Safanova, I.Y., Scott, R.A., Saunders, A.D., 2009. The timing and extent of the eruption of the Siberian Traps large igneous province; implications for the end-Permian environmental crisis. Earth Planet. Sci. Lett. 277, 9–20.
- Retallack, G.J., 1999. Postapocalyptic greenhouse paleoclimate revealed by earliest Triassic paleosols in the Sydney Basin, Australia. Geol. Soc. Am. Bull. 111, 52–70.
- Retallack, G.J., 2005. Earliest Triassic claystone breccias and soil-erosion crisis. J. Sediment. Res. 75, 679-695.
- Saitoh, M., Ueno, Y., Nishizawa, M., Isozaki, Y., Takai, K., Yao, J.X., Ji, Z.S., 2014. Nitrogen isotope chemostratigraphy across the Permian-Triassic boundary at Chaotian, Sichuan, South China. J. Asian Earth Sci. 93, 113–128.
- Schoepfer, S.D., Shen, J., Wei, H., Tyson, R.V., Ingall, E., Algeo, T.J., 2015. Total organic carbon, organic phosphorus, and biogenic barium fluxes as proxies for paleomarine productivity. Earth-Sci. Rev. 149, 23–52.
- Schunck, H., Lavik, G., Desai, D.K., Grosskopf, T., Kalvelage, T., Loscher, C.R., Paulmier, A., Contreras, S., Siegel, H., Holtappels, M., Rosenstiel, P., Schilhabel, M.B., Graco, M., Schmitz, R.A., Kuypers, M.M., Laroche, J., 2013. Giant hydrogen sulfide plume in the oxygen minimum zone off Peru supports chemolithoautotrophy. PLoS ONE 8, e68661.
- Scott, C.T., Lyons, T.W., 2012. Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: refining the paleoproxies. Chem. Geol. 324, 19–27.
- Scott, C.T., Lyons, T.W., Bekker, A., Shen, Y.N., Poulton, S.W., Chu, X.L., Anbar, A.D., 2008. Tracing the stepwise oxygenation of the Proterozoic ocean. Nature 452, 456–459.
- Scott, C.T., Bekker, A., Reinhard, C.T., Schnetger, B., Krapež, B., Rumble, D., Lyons, T.W., 2011. Late Archean euxinic conditions before the rise of atmospheric oxygen. Geology 39, 119–122.
- Sephton, M.A., Looy, C.V., Brinkhuis, H., Wignall, P.B., De Leeuw, J.W., Visscher, H., 2005. Catastrophic soil erosion during the end-Permian biotic crisis. Geology 33, 941–944.
- Shen, J., Algeo, T.J., Feng, Q., Zhou, L., Feng, L., Zhang, N., Huang, J., 2013. Volcanically induced environmental change at the Permian–Triassic boundary (Xiakou, Hubei Province, South China): related to West Siberian coal-field methane releases? J. Asian Earth Sci. 75, 95–109.
- Shen, J., Schoepfer, S.D., Feng, Q.L., Zhou, L., Yu, J.X., Song, H.Y., Wei, H.Y., Algeo, T.J., 2015. Marine productivity changes during the end-Permian crisis and Early Triassic recovery. Earth-Sci. Rev. 149, 136–162.
- Shen, J., Feng, Q.L., Algeo, T.J., Li, C., Planavsky, N.J., Zhou, L., Zhang, M.L., 2016. Two pulses of oceanic environmental disturbance during the Permian–Triassic boundary crisis. Earth Planet. Sci. Lett. 443, 139–152.
- Shen, Y.A., Farquhar, J., Zhang, H., Masterson, A., Zhang, T.G., Wing, B.A., 2011. Multiple Sisotopic evidence for episodic shoaling of anoxic water during Late Permian mass extinction. Nat. Commun. 2, 210–214.
- Song, H.Y., Tong, J.N., Algeo, T.J., Song, H.J., Qiu, H.O., Zhu, Y.Y., Tian, L., Bates, S., Lyons, T.W., Luo, G.M., Kump, L.R., 2014. Early Triassic seawater sulfate drawdown. Geochim. Cosmochim. Acta 128, 95–113.
- Takahashi, S., Yamasaki, S.I., Ogawa, Y., Kimura, K., Kaiho, K., Yoshida, T., Tsuchiya, N., 2014. Bioessential element-depleted ocean following the euxinic maximum of the end-Permian mass extinction. Earth Planet. Sci. Lett. 393, 94–104.

- Tong, J.N., Zhang, S.X., Zou, J.X., Xiong, X.Q., 2007. Events during Early Triassic recovery from the end-Permian mass extinction. Glob. Planet. Chang. 55, 66–80.
- Wang, C.J., Visscher, H., 2007. Abundance anomalies of aromatic biomarkers in the Permian-Triassic boundary section at Meishan, China-evidence of end-Permian terrestrial ecosystem collapse. Palaeogeogr. Palaeoclimatolol. Palaeoecol. 252, 291–303.
- Ward, P.D., Montgomery, D.R., Smith, R., 2000. Altered river morphology in South Africa related to the Permian-Triassic extinction. Science 289, 1740–1743.
- Weidlich, O., Bernecker, M., 2011. Biotic carbonate precipitation inhibited during the Early Triassic at the rim of the Arabian platform (Oman). Palaeogeogr. Palaeoclimatol. Palaeoecol. 308, 129–150.
- Wei, H.Y., Algeo, T.J., Yu, H., Wang, J.G., Guo, C., Shi, G., 2015. Episodic euxinia in the Changhsingian (late Permian) of South China: evidence from framboidal pyrite and geochemical data. Sediment. Geol. 319, 78–97.
- Wignall, P.B., 2007. The end-Permian mass extinction-how bad did it get? Geobiology 5, 303–309.
- Wignall, P.B., Twitchett, R.J., 1996. Oceanic anoxia and the end-Permian mass extinction. Science 272, 1155–1158.
- Wignall, P.B., Twitchett, R.J., 2002. Extent, duration, and nature of the Permian-Triassic superanoxic event. In: Koeberl, C., MacLeod, K.C. (Eds.), Catastrophic Events and Mass Extinctions: Impacts and Beyond. Geol. Soc. Am. Spec. Pap 356, pp. 395–413.
- Wilkin, R.T., Barnes, H.L., Brantley, S.L., 1996. The size distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. Geochim. Cosmochim. Acta 60, 3897–3912.
- Winguth, C., Winguth, A.M., 2012. Simulating Permian–Triassic oceanic anoxia distribution: implications for species extinction and recovery. Geology 40, 127–130.
- Xiang, L., Schoepfer, S.D., Zhang, H., Yuan, D.X., Cao, C.Q., Zheng, Q.F., Henderson, C.M., Shen, S.Z., 2015. Oceanic redox evolution across the end-Permian mass extinction at Shangsi, South China. Palaeogeogr. Palaeoclimatol. Palaeoecol. 448, 59–71.
- Xie, S.C., Pancost, R.D., Yin, H.F., Wang, H.M., Evershed, R.P., 2005. Two episodes of microbial change coupled with Permian/Triassic faunal mass extinction. Nature 434, 494–497.
- Xie, S.C., Pancost, R.D., Huang, J.H., Wignall, P.B., Yu, J.X., Tang, X.Y., Chen, L., Huang, X.Y., Lai, X.L., 2007. Changes in the global carbon cycle occurred as two episodes during the Permian–Triassic crisis. Geology 35, 1083–1086.
- Yin, H.F., Feng, Q.L., Lai, X.L., Baud, A., Tong, J.N., 2007. The protracted Permo-Triassic crisis and multi-episode extinction around the Permian–Triassic boundary. Glob. Planet. Chang. 55, 1–20.
- Yin, H.F., Xie, S.C., Luo, G.M., Algeo, T.J., Zhang, K.X., 2012. Two episodes of environmental change at the Permian-Triassic boundary of the GSSP section Meishan. Earth-Sci. Rev. 115, 163–172.
- Yin, H.F., Jiang, H.S., Xia, W.C., Feng, Q.L., Zhang, N., Shen, J., 2014. The end-Permian regression in South China and its implication on mass extinction. Earth-Sci. Rev. 137, 19–33.
- Zaback, D.A., Pratt, L.M., Hayes, J.M., 1993. Transport and reduction of suflate and immobilization of sulfide in marine black shales. Geology 21, 141–144.
- Zheng, Q.F., Cao, C.Q., Zhang, M.Y., 2013. Sedimentary features of the Permian-Triassic boundary sequence of the Meishan section in Changxing County, Zhejiang Province. Sci. China D Earth Sci. 56, 956–969.
- Ziegler, P.A., 1998. Evolution of the Arctic-North Atlantic and the Western Tethys. Am. Assoc. Petr. Geol. Mem. 43 (198 pp.).
- Zhuravlev, A., Wood, R., 1996. Anoxia as the cause of the mid-Early Cambrian (Botomian) extinction event. Geology 24, 311–314.