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Rare earth element geochemistry of Middle Devonian reefal limestones of the Dianqiangui Basin, South China: implications for nutrient sources and expansion of the reef ecosystem

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The Givetian Period witnessed the greatest expansion of stromatoporoid-coral reefs from low to higher latitudes of the Phanerozoic. Multi-proxy seawater surface temperature reconstruction contradicts establishment of super-greenhouse climate as a major reason for reef expansion, yet many questions remain. This paper presents results of a rare earth element and Y (REY; rare earth elements and yttrium) geochemical study of two well-documented Middle Givetian reefal carbonate sections (Jiwozhai and Buzhai) of the Jiwozhai Formation of South China. The nearshore Jiwozhai patch reef succession displays greater biodiversity and more abundant coral than the marginal platform Upper Buzhai reef. Reef and micritic carbonate of the Jiwozhai section is characterized by shale-type post-Archean Australian Shale (PAAS)-normalized REY patterns, by very weak negative Ce anomaly values (Ce/Ce* 0.80 to 0.93; average = 0.89), slightly elevated Y/Ho values (28.9 to 39.1; average = 34.1), and near-unity values of $(Pr/Yb)_N$ (average = 0.87), $(Pr/Tb)_N$ (average = 0.80), and $(Tb/Yb)_N$ (average = 1.09). Moreover, REY patterns of deposits of the Jiwozhai section differ markedly from those of modern seawater. The described geochemical aspects of the Jiwozhai section and the positive correlation of REY and Th contents displayed by the section point to a terrestrial siliciclastic contribution contemporaneous with reef building. In contrast, REY patterns of the Upper Buzhai reef section samples are similar to those of modern seawater characterized by light rare earth element (LREE) depletion (average $(Pr/Yb)_N$ = 0.76), negative Ce anomalies (average Ce/Ce* = 0.77), and average super-chondrite Y/Ho ratios (average = 45.4)). Slightly positive Eu anomalies (Eu/Eu* = 1.15-1.73; average = 1.35) of the Upper Buzhai reef

section samples are attributed to the negligible effect of hydrothermal fluids. Middle REE (MREE) enrichment (average $(Tb/Yb)_N$ = 1.48) of Buzhai section carbonate samples and positive correlation of REY and Th suggest a riverine input. Thus, we suggest that terrestrial nutrients delivered by rivers far outweighed upwelling as a source of nutrients supplied to the Givetian reef ecosystem of South China. Coral and stromatoporoid adaption to turbid water containing abundant terrestrial sediment expanded reef-builder habitats thereby increasing reef distribution areas in the Givetian ocean.

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Abstract

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reef-builder habitats thereby increasing reef distribution areas in the Givetian ocean.

Keywords: Givetian Period; turbid water; REEs; Jiwozhai Formation; nutrients

1. Introduction

The Devonian Period experienced the greatest expansion of reefs of the Phanerozoic Eon, especially stromatoporoid-coral reefs during Givetian time (Copper, 2001). Reef development during the Devonian extended to latitudes higher than those attained by reefs during the Holocene climatic optimum (Copper, 2001; Jakubowicz et al., 2019). Indeed, the Devonian Laurentian, Russia-Siberia-Kazakhstan, and eastern Gondwana, Sino-Australo-centered reefs have been documented as extending for distances of 400 km to 3100 km (Copper and Scotese, 2003). Low latitude Middle Devonian reef-building metazoan was dominated by rugose and tabulate corals and stromatoporoids (Copper and Scotese, 2003). However, the cause(s) of global reef expansion during Middle Devonian time remains ambiguous.

The great expansion of metazoan reefs during Devonian time was initially attributed to the establishment of super-greenhouse climatic conditions during this period of Earth history (Berner, 1997; Copper and Scotese, 2003). However, later conodont apatite oxygen isotope studies of Devonian reef successions suggested that coral–stromatoporoid reefs flourished during cooler time intervals (Joachimski et al., 2003; Scotese et al., 2021). Climate and water quality affect coral reef growth and reef ecology in modern oceans (Pandolfi, 2015). Regardless of water temperature, nutrient and sediment abundances of sea water impact modern coral reef systems

(Erftemeijer et al., 2012; McCulloch et al., 2003; Rogers, 1990; Zaneveld et al., 2016).

Modern reef-building corals are known to flourish in oligotrophic waters. Moreover, the combination of increasing nutrient levels and rising seawater temperature is known to be responsible for the decline of coral ecology in recent years (Hughes et al., 2015; Rädecker et al., 2021; Wiedenmann et al., 2013). Some workers speculate that changing nutrient types and availabilities in Phanerozoic oceans exerted some degree of control on reef distribution (Wood, 1993; Kiessling, 2001). However, this concept suffered from a lack of robust evidence of nutrient levels (Copper and Scotese, 2003).

Rare earth elements and yttrium (REY), nitrate, phosphate, and silica abundances of modern seawater display similar vertical distribution profiles (Byrne and King, 1992; Shijft, 2015). Furthermore, REY, because of the similar ionic radii of REY^{3+} and Ca^{2+}, is quantitatively incorporated into inorganic and biogenic carbonate minerals (Swart, 2015). The large distribution coefficient of REY between carbonate minerals (e.g., calcite and aragonite) and seawater make REY concentration and distribution in carbonate rocks resistant to the effects of diagenesis and dolomitization (Banner and Hanson.1990; Liu et al.,2019; Webb et al.,2009). Consequently, REY is commonly applied to the analysis of trace marine nutrient levels and water mass transport in modern ocean and reef coral ecosystems (Hara et al.,2009; Grenier et al.,2018; Leonard et al., 2019; Pham et al.,2019; Saha et al., 2021). The fact that ancient limestone and modern coral can serve as seawater chemistry proxies (Northdurft et al., 2004) validates the use of carbonate REY geochemistry as a means of reconstructing changes in nutrient type and abundance in carbonate deposits.

The Middle Devonian Givetian reef tract of the Dianqiangui Basin of South China extends from slope to near-shore environments for more than 1700 km (Wu et al., 2010). The sedimentary succession, details of reef facies, and biodiversity of reef deposits of South China have been thoroughly studied in past decades (e.g., Wang et al., 1979; Liu et al., 2004; Wang 2001, Huang et al., 2020). The present paper considers REY geochemistry of Middle Devonian Givetian reefal carbonates of the Jiwozhai patch reef and Buzhai platform margin reef in Dushan County, South China. This study aims to decipher the sources of nutrients delivered to the Givetian reef complex of South China as well as the role that terrestrial nutrients played in the maintenance of reefs during Givetian reef expansion.

2. Geological Setting

The Dianqiangui Basin of the South China Block was located near the equator in the eastern part of the Palaeo-Tethys Ocean during the Givetian Period (Huang et al., 2020; Fig.1A. The Palaeo-Tethys, bordering the northern margin of Gondwana, formed ~400-385 Ma following Kwangsian Orogeny (Xian et al. 2019; Qiu et al. 2020). Marine transgression was associated with rift-related movement of the South China Block in Early Devonian time (Qie et al. 2019). The palaeo-geography of South China experienced significant change during Givetian time in association with syn-depositional rift faulting. The Givetian also was the acme of reef development during the Phanerozoic Era during which small multi-cycle reefs formed on the inner platform of South China (Wu et al., 2010).

The two studied reef sections expose the Jiwozhai Formation of Dushan County of the

Guizhou Province, China (Fig.1B, C). The Jiwozhai is overlain conformably by silty shale of the Hejiazhai Member of the Upper Devonian Wangchengpo Formation and is in conformable contact with underlying sandstone of the Songjiaqiao Member of the Middle Devonian Dushan Formation (Fig.2). The Brachiopod assemblage *Stringocephalus burtini*-*Undispirifer undiderus* and rugose coral assemblage *Endophyllum guizhouense*-*Sunophyllum elegantum* confirm a Givetian age of the Jiwozhai Formation (Liu et al.,2004, Qie et al.,2019; Huang et al.,2020).

Gray to dark-gray medium- to thick-bedded interlayered micritic limestone and marl comprise the primary lithology of the Jiwozhai Formation with occasional reef limestone deposits in the lower part of the unit. Variations in thickness and lithology of the Jiwozhai Formation between the studied sections likely reflect differences in paleo-geographic locations of deposition. Patch reefs (e.g., Jiwozhai patch reef) in the nearshore and abundant fringing reefs (e.g., Buzhai reef) on the platform margin comprise the dominant reef types of the Jiwozhai Formation. The enhanced biodiversity displayed by the Jiwozhai reef has been thoroughly described by Huang et al. (2020) and includes laminar stromatoporoids and tabulate corals as the prevailing reef builders. The upper reef deposits of the Jiwozhai Formation (hereafter referred to as the Upper Buzhai reef) and lower reef strata of the overlying Jipao Member of Dushan Formation comprise the Buzhai reef. The well- documented Buzhai reef is dominated by laminar stromatoporoids.

The Upper Buzhai reef section (GPS 25°50′56.12″N, 107°34′32.74″E) is located in Dongyao village along a country road (Fig.3a). The reef section comprises three alternating reef limestones and bioclastic limestones; the stratigraphically lowest bioclastic limestone separates the Jiwozhai Formation from the underlying Dushan Formation (Fig. 2). The lower reef interval of the Upper Buzhai reef section is about 2.9 m thick and made up largely of laminar stromatoporoids (Fig.3b) and subordinate sponge (Fig.3c), and tabulate and rugose corals (Fig.3d-e). Brachiopods (e.g., Stringocephalus, Fig.3f) appear to have been present as reef dwellers. The middle reef interval is about 6.1 m thick and dominated by laminar stromatoporoids, and is separated from the lower reef interval by about 2.0 m of bioclastic limestone. The upper part of the studied Jiwozhai Formation succession exposes approximately 8.7 m of reef limestone and 3.7 m of medium- to thick-bedded bioclastic limestone (Fig. 2), which is overlain by silty shale of the Wangchengpo Formation.

The Jiwozhai patch reef section (GPS 25°50′56.12″N, 107°34′32.74″E) is located in Dahekou Geopark in Dushan County and comprises three reef and bioclastic limestone intervals (Figs. 2). The Upper Buzhai reef section contains more reef limestone than is present in the Jiwozhai section whereas the latter contains more muddy limestone (Fig.4A) and a greater benthic fauna. Also, laminar stromatoporoids (Fig.4B-E), tabulate corals (Fig.4C,4F), and chaetetids (Fig.4G) appear to have been the dominate reef builders at the depositional location of the Jiwozhai section. Rugose corals (Fig.4B-4D) and brachiopods (Fig.4h) were also present but were present in subordinate numbers

3. Materials and methods

We measured the Upper Buzhai reef and Jiwozhai patch reef sections of the Jiwozhai Formation and collected 34 fresh rock samples for lithology and trace element analyses. One part of each specimen was used for preparation of thin sections for petrographic observation. The other part was micro-drilled for trace element analyses. Samples are numbered in order from bottom to top as BZ-1 to BZ-20 for Buzhai section and JWZ-1 to JWZ-14 for Jiwozhai section (Fig. 2). Powders of each sandstone, bioclastic limestone, and reef limestone sample were analyzed for rare earth and other trace elements. Thirty-four thin sections were produced for visual inspection under the polarized light microscope in Key Laboratory of Geological Resources and Environments, Guizhou University, Ministry of Education, China.

Approximately 50 mg of powder of each sample to be analyzed for trace element abundances were cleaned in ultra-pure water before acid dissolution. Samples were then dissolved in ultra-pure HNO_3 in a Teflon flask after which the solution was dried to remove the acid. The acid solution addition and solution drying procedure was repeated once again. A 4 ml 50% ultra-pure HNO_3 was used to dissolve the dried residue followed by spiking with Rh, In, Re, and Bi and dilution for analysis on a Thermal Fisher ICP-MS at Guizhou Tongwei Analytical Technology Co., Ltd. Details of the analytical procedures have been described by Liang et al. (2000). Two USGS standards (W-2a and BHVO-2) were used to monitor analytical error, instrument calibration, and drift. The analytical error for REE and other trace elements is less than 5%.

4. Results

Measured concentrations of rare earth and other trace elements of the Jiwozhai Formation samples are presented in Tables 1 and 2. Post-Archean Australian Shale (PAAS)- normalized element ratios $(Pr/Yb)_N$, $(Pr/Tb)_N$, and $(Tb/Yb)_N$ were calculated to define the degree of fractionation between light REE (LREE) and heavy REE (HREE), light REE and middle REE (MREE), and middle REE and heavy REE, respectively. Y/Ho ratios were calculated without normalization. Some rare earth element anomalies were calculated on a linear scale as per the following:

$$Ce/Ce^{*}=Ce/(0.5La+0.5Pr)$$

$$Eu/Eu^{*}=Eu/(0.5Sm+0.5Gd)$$

4.1. Jiwozhai reef section

Carbonates of Jiwozhai reef section have total REY (TREY) concentrations ranging from 2.31 to 82.38 ppm (average = 32.65 ppm). The average concentration of REY of analyzed reefal limestone samples is 37.28 ppm, greater than the 16.22 ppm average of analyzed bioclastic limestone samples. One sandstone sample (JWZ-1) contains the greatest TREY concentration of 155.2 ppm whereas the muddy limestone sample (JWZ-2) is characterized by a slightly greater TREY concentration of 82.38 ppm. All analyzed samples regardless of lithology display flat (shale-like) PAAS-normalized REY patterns defined by minor negative Ce anomalies and weak fractionation among LREE, MREE, and HREE (Fig. 5). Ce anomalies of carbonate samples vary from 0.80 to 0.93 (average = 0.89). Eu anomalies for all analyzed samples fall between 0.88 and 1.11 (average = 1.02) (Fig. 5). Average $(Pr/Yb)_N$, $(Pr/Tb)_N$, and $(Tb/Yb)_N$ ratios of analyzed carbonate samples is 0.87, 0.80, and 1.09, respectively, are similar to those of the siliciclastic rock sample (0.93, 0.87, and 1.07, respectively). Carbonate samples are characterized by Y/Ho ratios of 28.9 to 39.1 (average = 34.1), slightly greater than the 29.9 Y/Ho value of the siliciclastic rock sample. Mn/Sr values of analyzed carbonate samples range from 0.23 to 3.76 (average = 0.80).

Contents of Th and Zr of the analyzed siltstone sample are 12 ppm and 134 ppm, respectively. Thorium and Zr concentrations of carbonate samples are one to three orders magnitude less than those of the sandstone sample and display a significant positive correlation (r^2=0.964, N=13; Fig. 6a). TREY and Th also display a strong positive co-variance (Fig. 6b).

4.2. The Upper Buzhai reef section

PAAS-normalized REY patterns for the Upper Buzhai reef section sample suite is presented in Fig. 7. Four samples of sandstone and shale (BZ-1, BZ-2, BZ-19, and BZ-20) and one sample of muddy bioclastic limestone (BZ-3) display a typical shale-type REY pattern. Carbonate samples display an REY pattern similar to that of modern seawater characterized by LREE depletion (average $(Pr/Yb)_N$ = 0.76), negative Ce anomalies (average Ce/Ce* = 0.77), and super-chondrite Y/Ho ratios (average = 45.4). However, unlike the modern seawater REY pattern, 13 of 15 analyzed carbonate samples of the Upper Buzhai reef section display positive Eu anomalies (Eu/Eu* = 1.15-1.73; average = 1.35) and MREE enrichment ($(Tb/Yb)_N$ = 1.26-2.42; average = 1.48).

Four analyzed clastic sedimentary samples are characterized by Th and Zr concentrations (average = 6.63 ppm and 120 ppm, respectively) greater those of carbonate samples (average = 0.788 ppm and 8.20 ppm, respectively). Among carbonate samples, reefal limestone samples are characterized by less Zr, Th, REY and greater Y/Ho than are micritic limestone samples. Like the Jiwozhai reef section, samples of the Buzhai reef section display positive correlations of Th and Zr and TREY and Th (Fig. 8a,b). Total TREY of analyzed carbonate samples ranges from 2.96 ppm to 57.05 ppm (average = 10.89 ppm) compared with an average TREY value of detrital sedimentary samples of 78.80 ppm.

4.3. Comparison of the Upper Buzhai and Jiwozhai reef sections

The Upper Buzhai section carbonate sample suite is characterized by low immobile element (e.g., Th and Zr) and TREY concentrations and elevated Y/Ho ratios relative to the Jiwozhai section. Carbonate deposits of the Buzhai section display seawater-like PAAS-normalized REY patterns whereas carbonate samples of the Jiwozhai section are characterized by shale-type PAAS-normalized REY patterns. Reefal limestone samples of the Upper Buzhai and Jiwozhai sections are variably dissimilar to the PAAS-normalized modern seawater REY pattern.

5. Discussion

5.1. Assessment of diagenetic alteration

Given the very high partition coefficients of REY between calcite and seawater (Della Porta et al., 2015; Webb and Kamber, 2000; Zhao and Zheng, 2014; Zhong and Mucci, 1995), diagenetic models suggest that an unrealistically large water- carbonate ratio would be required to reset the REY pattern of carbonate deposits (Banner and Hanson, 1990). The Mn/Sr ratio has been widely used to identify the effects of meteoric diagenesis on primary carbonate. In general, Mn/Sr values > 1 suggest that carbonate has been affected by meteoric diagenesis (Derry et al., 2010). Mn/Sr of the Upper Buzhai section samples range from 0.27 to 1.15 and those of the Jiwozhai section range from 0.27 to 3.76 suggesting that carbonates of the studied sections experienced little meteoric alteration. Moreover, although aragonite is characterized by low partition coefficients of REY compared to calcite, it is likely that REY compositions and patterns are retained during aragonite transformation to calcite (Webb et al., 2009). Studies of modern marine limestones subjected to variable degrees of diagenesis support the survivability of REY distribution patterns in limestone deposits subjected to meteoric processes, marine burial diagenesis, and dolomitization (Della Porta et al.,2015; Liu et al.,2019; Luo et al.,2021; Webb et al.,2009). Therefore, it is likely that REY compositions and patterns of analyzed carbonate samples of the studied sections were minimally affected by diagenesis.

5.2. Evaluation of fresh water contribution

5.2.1. Jiwozhai section

The shale-like REY patterns illustrated by Jiwozhai carbonates deviate from those of modern oxic seawater characterized by HREE enrichment, super-chondrite Y/Ho ratios > 40, and negative Ce anomalies (Fig. 5). In contrast, these REY distributions are similar to those documented from continental or estuarine water characterized by Ce anomalies, weak HREE enrichment, variable MREE enrichment, and equal to or slightly greater than the chondrite Y/Ho ratio (Elderfield et al. 1990; Zhao et al. 2021). Such REY patterns could also have been produced by terrestrial contamination due to the elevated REY contents in shale relative to those of pure carbonate rocks. Indeed, approximately 2% siliciclastic contamination, which is enough to modify the REY composition and pattern of carbonate (Frimmel, 2009), corresponds to an upper threshold Th value of 0.28 ppm. Accordingly, carbonate samples containing < 0.28 ppm Th should display REY patterns similar to that of modern seawater. It is noteworthy, however, that the two samples (JWZ-8 and JWZ-13) having the lowest Th contents of 0.194 ppm and 0.059 ppm also display flat REY patterns (Fig.5) and equal Y/Ho ratios (34.4 and 35.3), neither of which cant be attributed to silicate contamination. However, a non-marine origin of the analyzed carbonate samples is at odds with the presence of coral, stromatopora, and Brachiopoda (Figs. 4B-H) as described in section 2. Therefore, riverine water input to coastal waters appears to have impacted the geochemistry of Jiwozhai section carbonates deposited during Givetian time.

5.2.2. The Upper Buzhai reef section

REY patterns of most reefal limestone samples of the Upper Buzhai reef section are similar to normal seawater, including LREE depletion, negative Ce anomalies, and elevated Y/Ho ratios (> 40). Three bioclastic limestone samples present slightly lower Y/Ho values (35.3 to 39.1; average = 35.6). Although terrestrial contamination cannot be ruled out, a Y/Ho ratio of 40 and Th content of 0.024 ppm of one reefal limestone sample (BZ-12) suggests some degree of freshwater contamination. Moreover, four samples (BZ-9, BZ-11, BZ-12, and BZ-18) contain < 0.1 ppm Th, low $(Pr/Tb)_N$ ratios (0.45 to 0.52; average = 0.49) and elevated $(Tb/Yb)_N$ ratios ranging from 1.26 to 1.72 (average = 1.47). Low Y/Ho ratios and MREE enrichment displayed by samples characterized by low Th content are attributed to mixing of riverine water with seawater.

5.3. Terrestrial contamination

The greater content of REY in shale than carbonate necessitates consideration of the possible role of terrestrial contamination of the studied Jiwozhai Formation carbonate samples. High field strength elements such as Th and Zr are rarely susceptible to chemical weathering and diagenesis (Frimmel, 2009). This supposition is supported by the positive correlation of Th and Zr concentrations of the studied samples (Figs. 6a and 8a). These elements are widely utilized to evaluate the extent of terrestrial sediment contamination of carbonate deposits (Frimmel, 2009; Zhao and Zheng, 2014; Zhao et al., 2021). Elevated contents of REY should be expected in carbonate samples that experienced greater degrees of terrestrial contamination as suggested by the positive correlation of TREY and Th (Figs. 6b and 8b). Terrestrial sediment contamination appears to have affected Jiwozhai carbonate samples as suggested by their shale-like REY patterns (Fig. 5). Therefore, both Jiwozhai and Buzhai reefs appear to have experienced terrestrial input during Givetian time.

Elevated Th contents (average = 1.97 ppm) and shale-like REY patterns of Jiwozhai section samples compared to those of the Buzhai section suggest that the depositional site of the Jiwozhai section experienced a greater terrestrial input than did the depositional site of the Upper Buzhai section, an argument supported by the paleo-geographic location and fossil assemblages of the Jiwozhai and the Upper Buzhai sections. That is, the Jiwozhai patch reef was located much closer to the Givetian shoreline than was the Buzhai platform margin reef (Figure 1). As described earlier (section 2), stromatoporoids appear to have been more abundant in the Upper Buzhai reef than in the Jiwozhai reef. Stromatopora is a calcified sponge (Kershaw, 1998) that favors clear seawater that received minimal terrestrial input (Kershaw, 1998; Konigshof and Kershaw, 2006). In contrast to stromatoporoid, coral can survive or even flourish in nearshore seawaters as evidenced by the Great Barrier Reef of Australia (Anthony, 1999; Saha et al., 2021). The 3.6 m to 6.8 m reef thickness of the Jiwozhai section is consistent with the view that coral reefs are restricted to the upper 4 m to 10 m of a turbid water column whereas these reefs can extend to depths in excess of 40 m depth in clear seawater (Yentsch et al.,2002).

5.4. Ce anomalies

Modern oxic seawater is characterized by negative Ce anomalies in PAAS- normalized REY patterns that reflect the lower solubility of tetravalent Ce than its neighboring La and Pr in seawater (Elderfield et al., 1990). However, negative Ce anomalies are absent from anoxic waters (Planavsky et al., 2010). Thus, the history of Ce anomalies recorded by carbonate rock successions can be used to trace ocean oxygenation histories (Wallace et al., 2017). Ce anomalies of carbonate samples of the Jiwozhai section average 0.89 and 0.77 in the Upper Buzhai carbonate sample suite, both values markedly greater than the 0.18 to 0.45 range of modern seawater values (Sholkovitz et al., 1994). The common presence of coral, stromatopora, and brachiopoda fossils in both studied sections excludes the possibility of sampling limestones deposited in a non-marine or anoxic environment. However, the nature of Ce anomalies in samples from both sections can be attributed to freshwater runoff. Terrestrial silicate detritus and freshwater lack Ce anomalies and are characterized by REY contents of one to several orders of magnitude greater than seawater (Tepe and Bau, 2016). Therefore, the introduction of a small amount of terrestrial detritus and freshwater into normal seawater will mask the latter's original negative Ce anomaly.

5.5. Eu anomalies

Positive Eu anomalies (denoted as Eu/Eu*) are commonly cited as evidence of hydrothermal input (Bau, 1991). However, enhanced plagioclase weathering induced by greenhouse conditions may also yield positive Eu anomalies (Verdel et al., 2018). Moreover, enriched Ba content is known to produce positive Eu anomalies because of Ba interference during ICP-MS analysis though this analytical artifact can be resolved by plotting Eu/Eu* vs. Ba/Eu (Jiang et al., 2007). The latter scenario is excluded as no significant linear correlation exists between Eu/Eu* and Ba/Eu (Figure 9a). The argument of plagioclase weathering is incompatible with the absence of an Eu anomaly in carbonate samples of the nearshore Jiwozhai reef section (0.88 - 1.11; average = 1.05) and the platform margin Upper Buzhai reef section (0.90 - 1.74; average = 1.25). Therefore, the introduction of high-temperature hydrothermal water into seawater the favored explanation of the positive Eu anomalies displayed by the carbonate sample suite of the Buzhai reefal section. This interpretation is buttressed by the occurrence of basalt layers in the Luofu Formation of Guangxi (Liu et al., 2012), an inferred deep-water (Nandan-type) equivalent of the Jiwozhai Formation (Qie et al., 2019).

The impact of hydrothermal fluids on ambient seawater can be estimated quantitatively by a simple two-member mixing model (Alexander et al., 2008). One member is modern seawater characterized by low Eu/Sm and Sm/Yb ratios and the other member is high-temperature hydrothermal fluids of much greater Eu/Sm and Sm/Yb ratios. The Sm/Yb versus Eu/Sm cross-plot (Fig. 9b) demonstrates that both ratios of Sm/Yb and Eu/Sm in the Buzhai carbonates can be explained by mixing small (less than 1%) fractions of high-temperature hydrothermal fluid with the seawater. It is likely that high-temperature fluid accounted for less than 1% of the seawater during accumulation of carbonates of the Upper Buzhai reef section.

5.6. Insights into nutrient sources and expansion of reef ecosystem

Coral is sensitive to the input of nutrients and sediment (Schlager, 1981; Hallock and Schlager, 1986). Indeed, the impact of increased nutrient supply on the coral reef ecosystem has become a focus of research in recent years. Upwelling nutrient (e.g., phosphorus and nitrogen)-laden modern deep seawater is known to be an important source of nutrients for some reef ecosystems (Andrews et al., 1982; Eidens et al., 2015; DeCarlo et al.2021). High-temperature hydrothermal fluids from the basalt altering in deep water of Dianqiangui Basin were characterized by remarkably positive Eu anomaly, which could be recorded in the chemical precipitates affected by upwelling deep water. However, the presence of weak positive Eu anomalies of carbonate samples of the Upper Buzhai reef section suggest that upwelling was not the dominant source of nutrients for the Buzhai and Jiwozhai reef ecosystems during the Givetian Stage. Indeed, as described above, the elevated content of Th in the analyzed Jiwozhai Formation samples point to runoff being the primary source of nutrients for both the Buzhai and Jiwozhai reef ecosystems. Moreover, the fact that the Jiwozhai reef deposits contain a considerable amount of marly limestone and a greater biodiversity than the Buzhai reef (Huang et al., 2020; Liu et al., 2004) suggests that reef building was sustained by continental runoff. It is noteworthy that a coral community dominated by tabulate and rugose coral described from the Fanning River area of Queensland, Australia, appears to have thrived in shallow turbid water during Givetian time (Zapalski et al., 2021). It appears that turbid-water reefs were not unusual during the Givetian.

Modern coral assemblages are tolerant of particulate organic matter (Sanders et al., 2005), yet dissolved nutrient loading exerts a critical impact on coral ecosystems as it appears to impede coral reproduction (Cox and Ward, 2002). Continental chemical weathering is the primary source of nutrients (e.g., phosphorus) of the marine ecosystem. The intensity of chemical weathering (and, therefore, the amount of dissolved nutrients delivered to the ocean) is recorded by the strontium isotopic composition of carbonate rocks. The strontium isotopic composition of the global ocean is homogenous over the residence time of Sr (~2.4 Ma) relative to the mixing time of the oceans (1.5 ka) (Krabbenhoft et al., 2010). Low $^{87}Sr/^{86}Sr$ values of Givetian carbonate relative to deposits of other Devonian time intervals implies weakened continental chemical weathering during this time (Qie et al., 2019). Therefore, the terrestrial nutrient supply that sustained the Givetian reefs and allowed them to flourish did not require enhanced chemical weathering.

6. Conclusions

(1) REE geochemistry of limestones of two Devonian reef sections of South China suggest that shale-type PAAS normalized REY patterns of near shore water in which the Givetian Jiwozhai Formation accumulated differed significantly different from marine water masses on the marginal platform of the Dianqiangui Basin. It reinforces the use of REE geochemistry of carbonate rocks to elucidate paleoceanography and paleogeography over geological time.

(2) The nutrient source that sustained the reef ecosystem that encompassed the studied Jiwozhai and Buzhai sections appears to have been dominated by terrestrial runoff. Upwelling of nutrient-rich deep water played a minimal role in maintaining the Givetian reef ecosystem.

Enhanced terrestrial sediment input associated with Givetian Jiwozhai coral-stromatoporoid reef development demonstrates that the coral ecosystem thrived in turbid waters.

(3) Results of the present study suggest that coral and stromatoporoid adaptation to turbid water played an important role in Middle Devonian (Givetian) expansion of coral-stromatoporoid reef complexes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figure 1

Fig.1. (A) Givetian paleogeography (B) palaeogeography of Dianqiangui Basin (C) map of the study area and its location in China.

(A) Givetian paleogeography (modified from Huang et al., 2020) showing the location of the Dianqiangui Basin (DB); (B) palaeogeography of Dianqiangui Basin during the Givetian Stage (modified from Huang et al., 2020); red stars indicate the locations of the studied Buzhai (BZ) and Jiwozhai (JWZ) reef sections; white rectangle shows the location of Fig. C; (C) map of the study area and its location in China; red stars show the locations of the Jiwozhai (JWZ) and Buzhai (BZ) reefs.

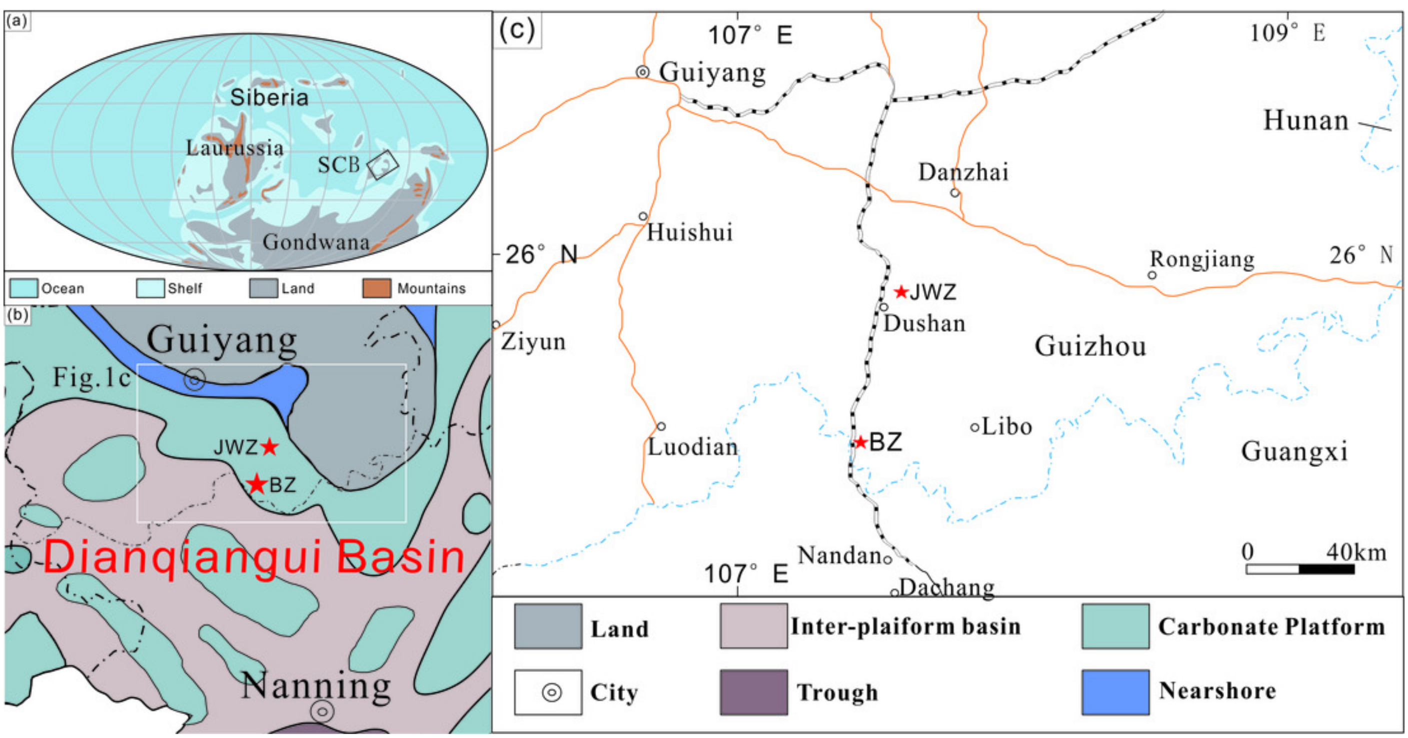

Figure 2

Stratigraphic columns of the Upper Buzhai and Jiwozhai reef sections.

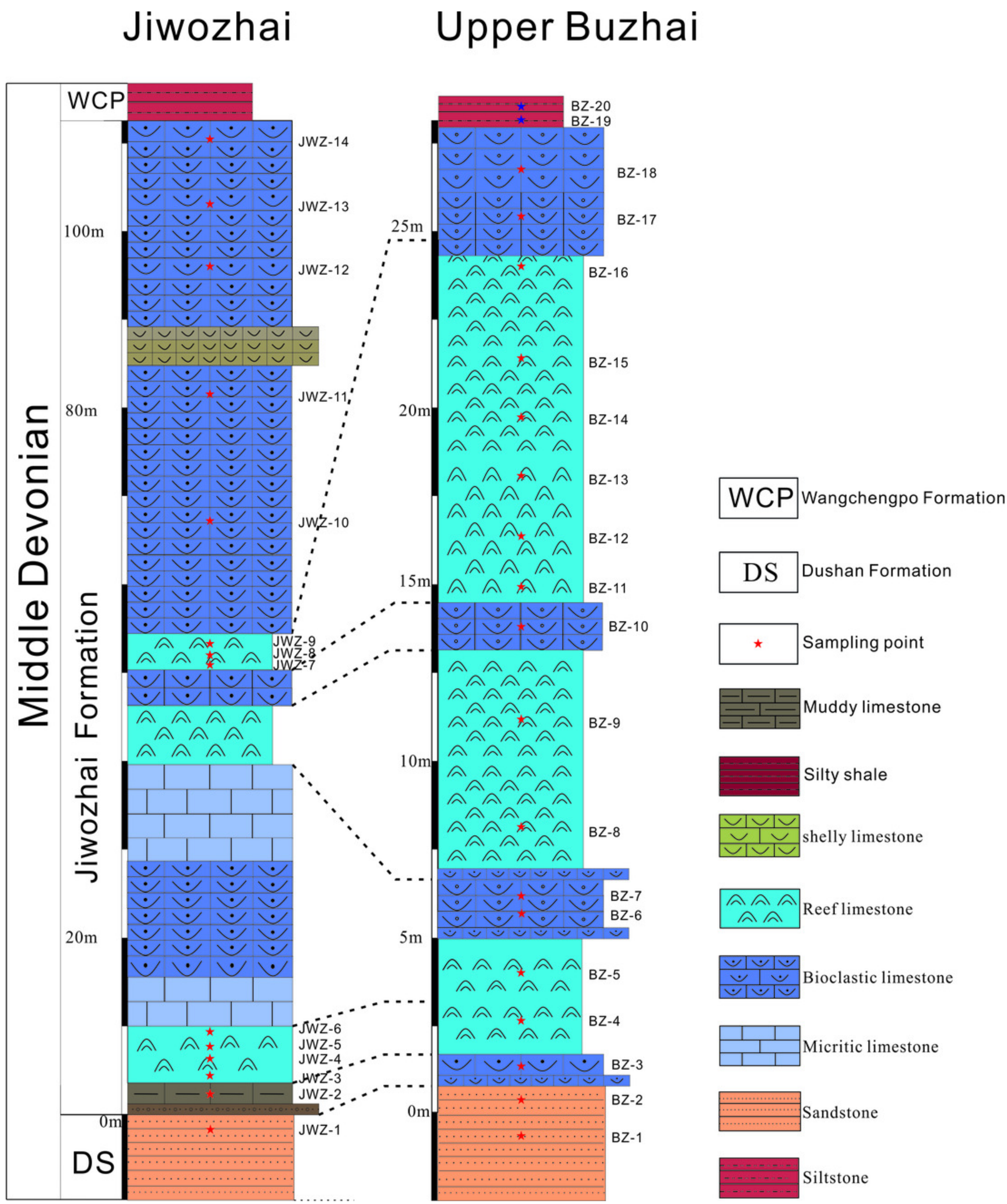
Jiwozhai
Upper Buzhai
Middle Devonian
Jiwozhai Formation
WCP
DS
100m
80m
20m
0m
25m
20m
15m
10m
5m
0m
JWZ-14
JWZ-13
JWZ-12
JWZ-11
JWZ-10
JWZ-9
JWZ-8
JWZ-7
JWZ-6
JWZ-5
JWZ-4
JWZ-3
JWZ-2
JWZ-1
BZ-20
BZ-19
BZ-18
BZ-17
BZ-16
BZ-15
BZ-14
BZ-13
BZ-12
BZ-11
BZ-10
BZ-9
BZ-8
BZ-7
BZ-6
BZ-5
BZ-4
BZ-3
BZ-2
BZ-1
WCP Wangchengpo Formation
DS Dushan Formation
Sampling point
Muddy limestone
Silty shale
shelly limestone
Reef limestone
Bioclastic limestone
Micritic limestone
Sandstone
Siltstone

Figure 3

Field photos and photomicrographs taken under polarized-light of Buzhai reef outcrops and samples

a. view of the Buzhai reef section; b. close-up of the reef-builder stromatopora; c. sponge fossil (center of photo); d. photomicrograph of tabulate coral ; e. photomicrograph of rugose coral f. close-up view of Stringocephalus sp;

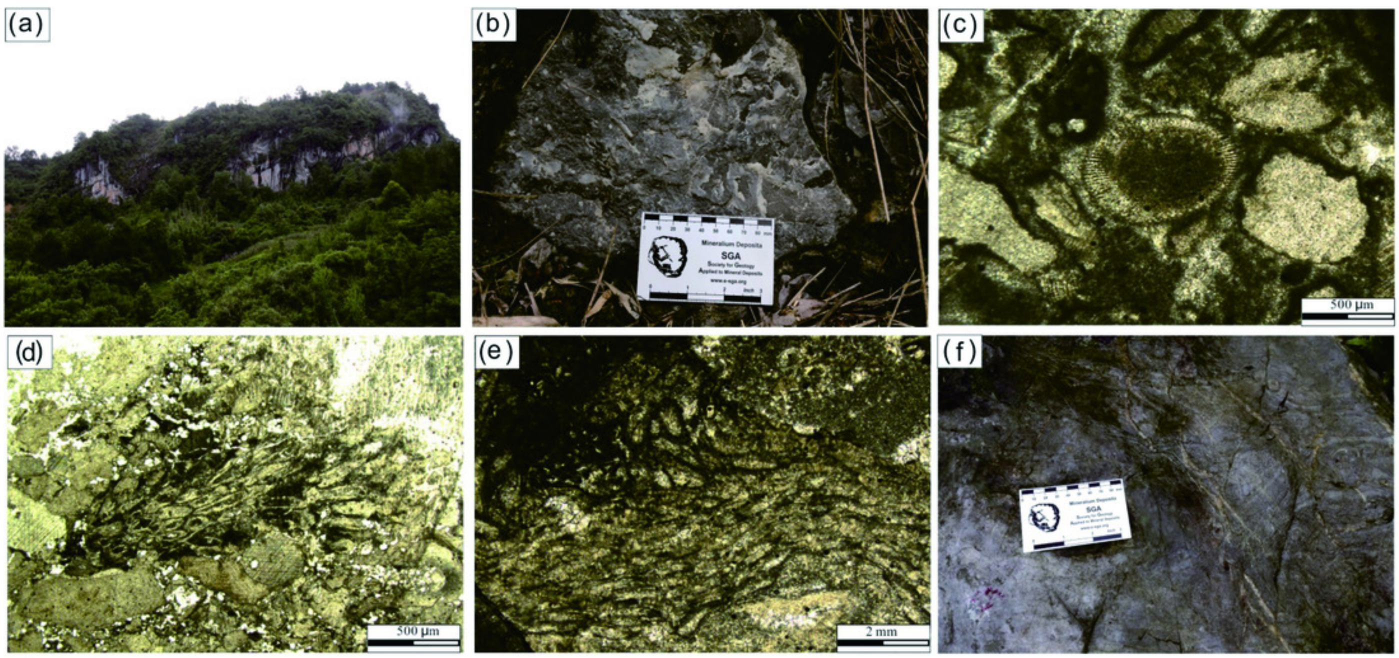

Figure 4

Field photos and photomicrographs taken under polarized-light of Jiwozhai reef section and outcrop samples

a. general view of the Jiwozhai patch reef; b. close-up of rugose coral (Ru) and stromatopora (St); c. close-up of rugose (Ru) and tabulate (Ta) corals; d. photomicrograph of rugose coral ; e. photomicrograph of laminar stromatopor ; f. photomicrograph of tabulate coral ; g. Chaetetid (Ch) encrusting tabulate (Ta) coral; h. photomicrograph of brachiopod

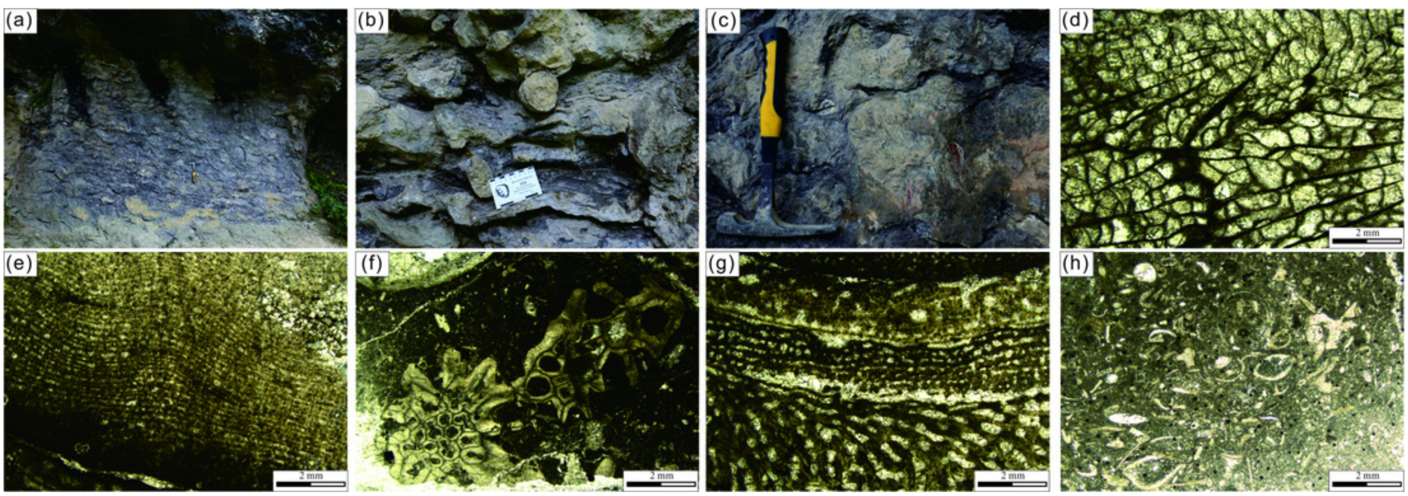

Figure 5

PAAS-normalized REY patterns for Jiwozhai reef section samples.

Modern seawater and river water REY patterns are from Wang et al.(2018). Refer to Fig. 2 for sample locations.

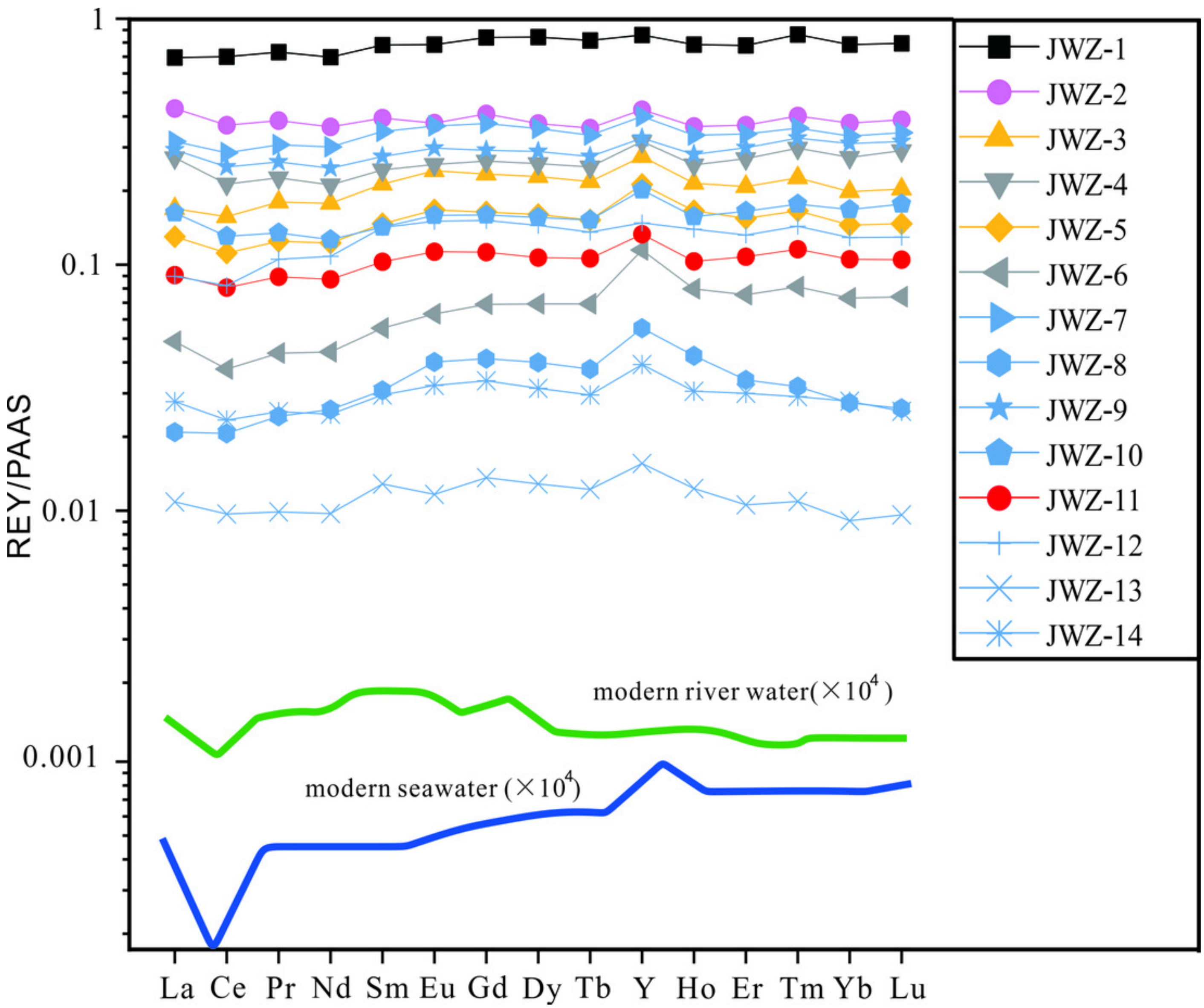

Figure 6

(a) Th vs. Zr cross-plot for Jiwozhai reef section samples; (b) Th vs. TREY cross- plot for Jiwozhai section samples

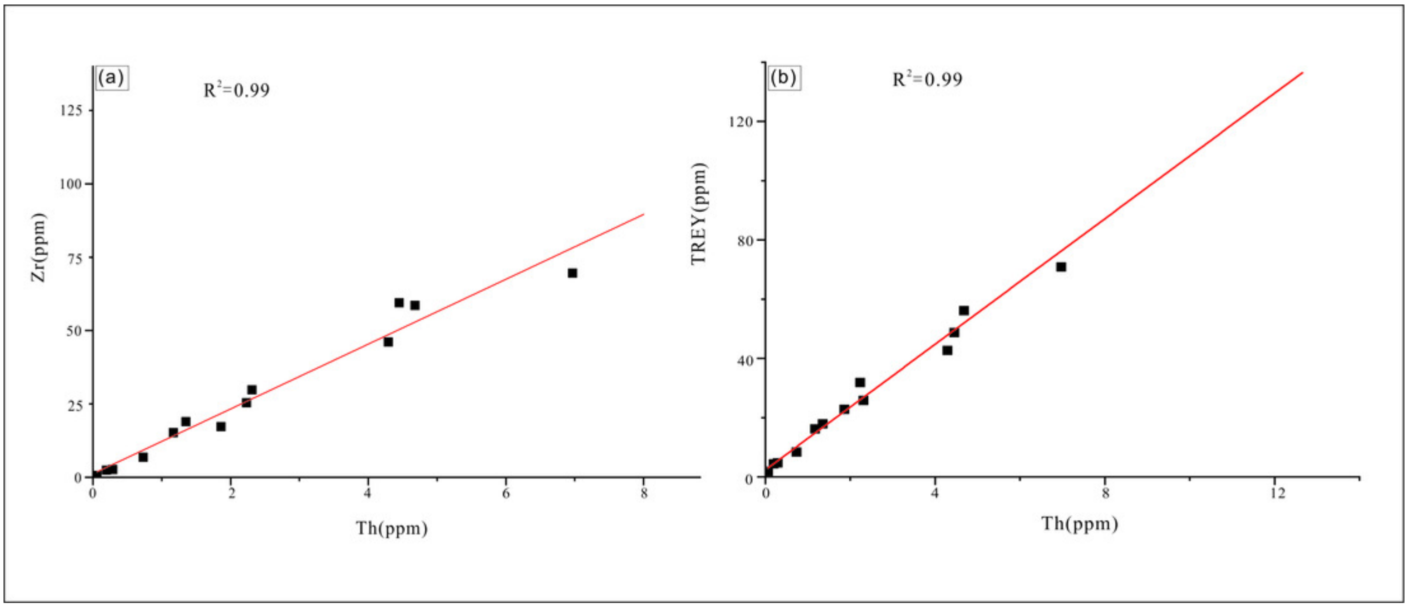

Figure 7

PAAS-normalized REY patterns for Buzhai reef section samples

Modern seawater and river water REY patterns are from Wang et al.(2018). Refer to Fig. 2 for sample locations

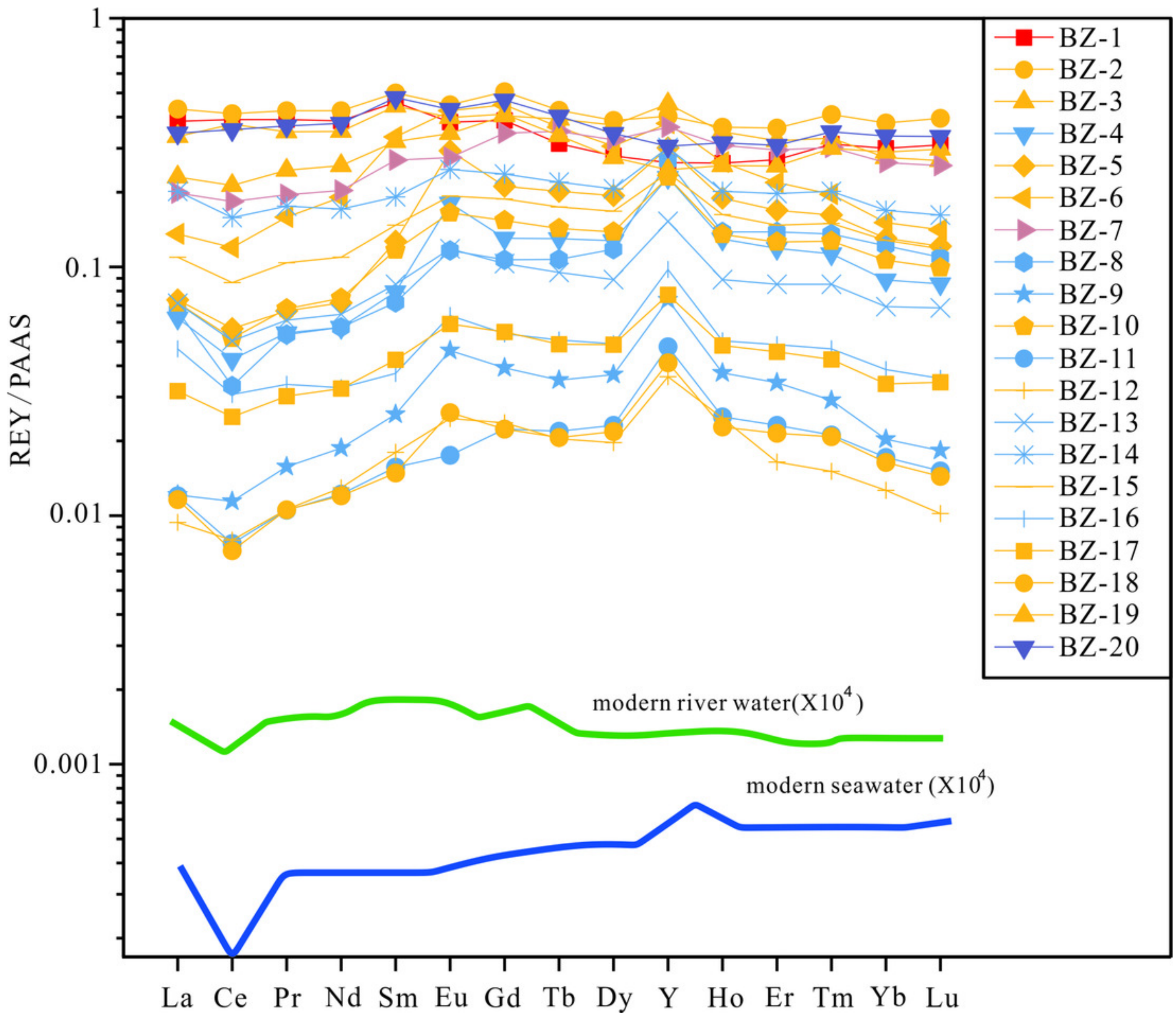

Figure 8

(a) Th vs. Zr cross-plot for Buzhai reef section samples; (b) Th vs. TREY cross-plot for Buzhai reef section samples.

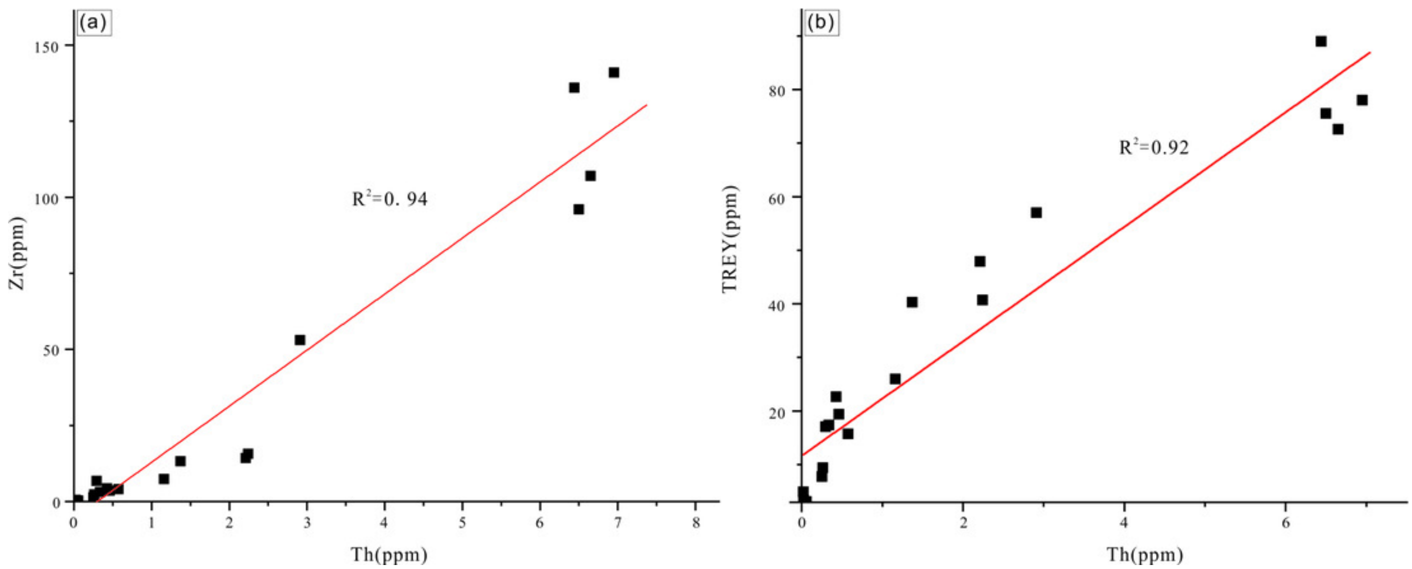

Figure 9

(a) Eu/Eu* vs. Ba/Eu cross-plot in for Buzhai reef section samples; (b) Eu/Sm vs. Sm/Yb cros- plot for Buzhai reef section samples.

Composition of two end members and the mixing line are from Alexander et al. (2008)

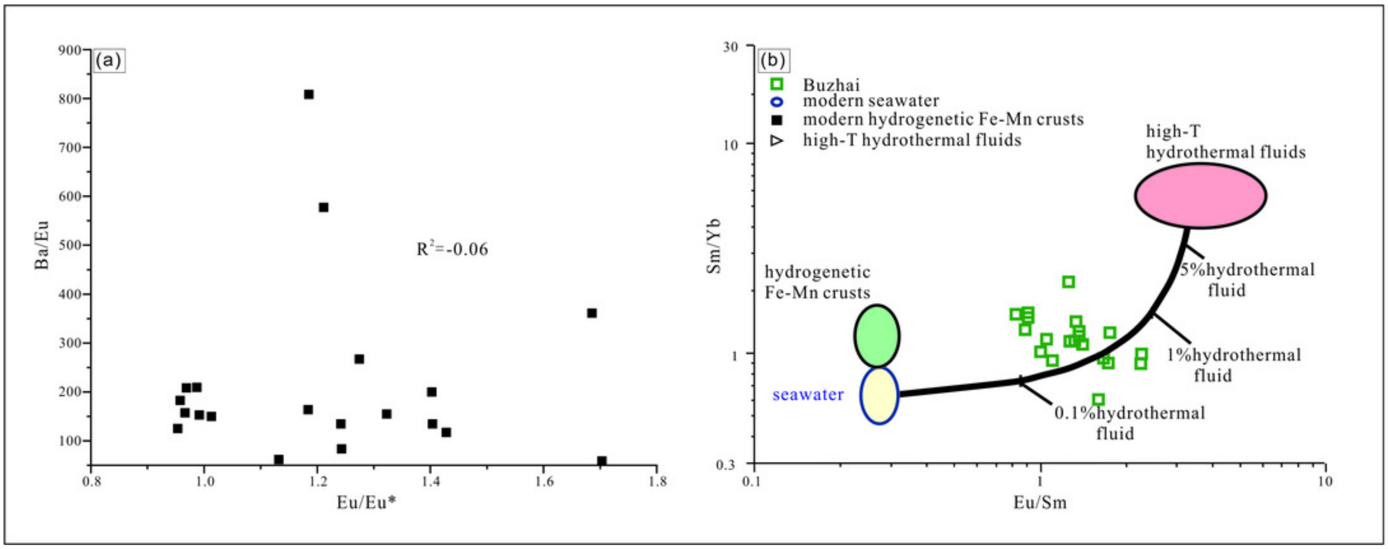

Table 1 (on next page)

Rare earth and other trace element concentrations of samples of the Jiwozhai reef section (mg/kg).

Sample JWZ-1 is sandstone from Dushan Formation; sample JWZ-2 is muddy limestone from the bottom of the Jiwozhai Formation; Samples from JWZ-3 to JWZ-9 are reefal limestone and the other samples are bioclastic limestone from Jiwozhai Formation.

Table 1. Rare earth and other trace element concentrations of samples of the Jiwozhai reef section (mg/kg).

	JWZ-1	JWZ-2	JWZ-3	JWZ-4	JWZ-5	JWZ-6	JWZ-7	JWZ-8	JWZ-9	JWZ-10	JWZ-11	JWZ-12	JWZ-13	JWZ-14
La	26.6	16.5	6.45	10.4	4.96	1.86	12.1	0.797	11.2	6.21	3.46	3.43	0.414	1.06
Ce	55.8	29.4	12.5	16.9	8.88	2.99	22.7	1.64	19.9	10.4	6.42	6.55	0.771	1.86
Pr	6.46	3.40	1.59	1.99	1.10	0.385	2.71	0.214	2.31	1.19	0.787	0.93	0.087	0.223
Nd	23.7	12.3	6.03	7.15	4.16	1.50	10.2	0.873	8.35	4.28	2.96	3.66	0.330	0.835
Sm	4.33	2.19	1.18	1.35	0.815	0.306	1.93	0.171	1.53	0.789	0.570	0.785	0.071	0.164
Eu	0.847	0.406	0.26	0.276	0.180	0.068	0.396	0.043	0.321	0.171	0.122	0.162	0.013	0.035
Gd	3.91	1.91	1.09	1.23	0.762	0.322	1.75	0.193	1.36	0.742	0.525	0.706	0.063	0.157
Tb	0.648	0.289	0.176	0.198	0.123	0.053	0.275	0.031	0.222	0.120	0.082	0.111	0.010	0.024
Dy	3.82	1.68	1.02	1.17	0.711	0.324	1.57	0.176	1.290	0.710	0.496	0.635	0.057	0.138
Ho	0.776	0.361	0.212	0.252	0.164	0.079	0.332	0.042	0.278	0.155	0.102	0.138	0.012	0.030
Er	2.22	1.05	0.593	0.768	0.439	0.215	0.968	0.097	0.850	0.470	0.307	0.376	0.030	0.086
Tm	0.353	0.165	0.092	0.122	0.068	0.033	0.147	0.013	0.134	0.072	0.047	0.059	0.004	0.012
Yb	2.21	1.06	0.56	0.771	0.409	0.206	0.939	0.077	0.876	0.473	0.297	0.363	0.026	0.078
Lu	0.341	0.167	0.087	0.125	0.063	0.031	0.148	0.0112	0.136	0.076	0.045	0.056	0.004	0.0119
Y	23.2	11.5	7.42	8.56	5.72	3.09	10.8	1.49	8.84	5.43	3.59	3.990	0.420	1.060
Ba	272	194	88.1	208	76.6	30.7	203	33.4	242	115	50.6	58.8	14.1	28.1
Mn	913	761	343	275	266	104	363	198	215	197	114	154	131	358
Sr	57.6	63.9	549	478	543	445	421	668	326	331	428	278	187	95.1
Zr	134	69.6	25.4	46.1	17.3	6.88	58.6	2.41	59.5	29.8	15.2	19.0	0.686	2.68
Th	12.0	6.97	2.23	4.29	1.86	0.729	4.68	0.194	4.45	2.31	1.17	1.35	0.0587	0.287

Note: Sample JWZ-1 is sandstone from Dushan Formation; sample JWZ-2 is muddy limestone from the bottom of the Jiwozhai Formation; Samples from JWZ-3 to JWZ-9 are reefal limestone and the other samples are bioclastic limestone from Jiwozhai Formation.

Table 2(on next page)

Rare earth and other trace element concentrations of samples of the Buzhai reef section (mg/kg).

BZ-1 and BZ-2 are sandstone samples from Dushan Formation; samples BZ-4, BZ-5, BZ-8, BZ-9, from BZ-11 to BZ-16 are reefal limestone, and the other samples are Bioclastic limestone from Jiwozhai Formation; BZ-19 and BZ-20 are siltstone samples from Wangchengpo Formation.

Table 2. Rare earth and other trace element concentrations of samples of the Buzhai reef section (mg/kg).

	BZ-1	BZ-2	BZ-3	BZ-4	BZ-5	BZ-6	BZ-7	BZ-8	JBZ-9	BZ-10	BZ-11	BZ-12	BZ-13	BZ-14	BZ-15	BZ-16	BZ-17	BZ-18	BZ-19	BZ-20
La	14.7	16.5	8.77	2.38	2.82	5.18	7.57	2.54	0.463	2.74	0.459	0.359	2.73	7.68	4.18	1.79	1.21	0.444	12.8	13.2
Ce	31.2	32.9	16.9	3.38	4.49	9.54	14.6	2.64	0.908	4.11	0.616	0.635	4.01	12.6	6.88	2.44	1.99	0.575	29.8	28.4
Pr	3.46	3.75	2.16	0.479	0.589	1.40	1.72	0.472	0.139	0.600	0.093	0.093	0.540	1.55	0.917	0.298	0.267	0.093	3.08	3.26
Nd	13.1	14.4	8.65	1.94	2.43	6.45	6.87	1.94	0.634	2.54	0.414	0.439	2.19	5.79	3.71	1.11	1.10	0.408	11.9	12.8
Sm	2.55	2.78	1.77	0.441	0.704	1.85	1.49	0.400	0.142	0.649	0.087	0.099	0.472	1.06	0.816	0.207	0.235	0.082	2.46	2.66
Eu	0.413	0.484	0.372	0.195	0.317	0.459	0.297	0.126	0.050	0.178	0.019	0.026	0.128	0.266	0.208	0.069	0.064	0.028	0.431	0.465
Gd	1.81	2.36	1.89	0.609	0.983	2.09	1.61	0.498	0.183	0.716	0.104	0.110	0.481	1.10	0.875	0.251	0.255	0.104	1.92	2.18
Tb	0.241	0.329	0.303	0.100	0.155	0.281	0.270	0.083	0.027	0.110	0.017	0.016	0.073	0.169	0.134	0.039	0.038	0.016	0.260	0.311
Dy	1.31	1.82	1.74	0.596	0.907	1.43	1.52	0.551	0.173	0.647	0.108	0.092	0.416	0.964	0.784	0.230	0.228	0.102	1.29	1.61
Ho	0.259	0.361	0.346	0.128	0.187	0.261	0.305	0.137	0.037	0.134	0.025	0.024	0.088	0.199	0.161	0.050	0.048	0.022	0.253	0.312
Er	0.769	1.03	0.918	0.338	0.481	0.624	0.843	0.394	0.098	0.359	0.066	0.047	0.243	0.563	0.419	0.139	0.130	0.061	0.725	0.877
Tm	0.128	0.168	0.135	0.046	0.066	0.080	0.124	0.056	0.012	0.052	0.008	0.006	0.035	0.082	0.061	0.019	0.017	0.008	0.123	0.143
Yb	0.847	1.07	0.777	0.250	0.368	0.425	0.740	0.343	0.057	0.300	0.048	0.036	0.195	0.476	0.361	0.109	0.095	0.046	0.816	0.946
Lu	0.133	0.170	0.115	0.037	0.052	0.061	0.110	0.047	0.008	0.043	0.006	0.004	0.029	0.069	0.051	0.015	0.015	0.006	0.128	0.144
Y	7.09	10.9	12.2	6.19	8.13	10.2	9.86	7.18	1.99	6.22	1.29	0.976	4.12	8.17	6.45	2.64	2.09	1.11	6.64	8.26
Ba	75.5	60.5	55.8	70.4	18.6	28.5	46.7	19.5	5.85	14.9	2.89	15.3	34.2	215	34.1	9.28	8.60	5.60	90.2	96.9
Mn	62.7	192	137	395	148	149	181	155	122	98.3	78.5	69.0	116	126	105	81.8	62.7	106	32.6	104
Sr	164	149	259	344	200	286	347	214	117	257	174	139	241	358	296	290	232	177	232	206
Zr	141	136	53.1	6.83	4.35	13.3	14.3	3.15	0.296	3.54	0.541	0.488	4.10	15.7	7.46	2.33	1.41	0.373	107	96.0
Th	6.95	6.44	2.91	0.293	0.425	1.37	2.21	0.335	0.018	0.458	0.020	0.024	0.573	2.24	1.16	0.259	0.251	0.055	6.65	6.50

Note: BZ-1 and BZ-2 are sandstone samples from Dushan Formation; samples BZ-4, BZ-5, BZ-8, BZ-9, from BZ-11 to BZ-16 are reefal limestone, and the other samples are Bioclastic limestone from Jiwozhai Formation; BZ-19 and BZ-20 are siltstone samples from Wangchengpo Formation.