Multiproxy constraints on alteration and primary compositions of Ediacaran deep-water carbonate rocks, Yangtze Platform, South China

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Abstract

The occurrence of shallow and deep-water sedimentary facies has established the Yangtze Platform in South China as a key site for the study of Neoproterozoic ocean oxidation and Ediacaran animal evolution following the Marinoan glaciation. The Yanwutan section in Hunan Province is one of the few coherent sections on the Yangtze Platform where Ediacaran deep-water carbonate sediments (predominantly dolostones) are preserved together with organic carbon-rich shales. Here we present new major and trace element abundance data as well as Sr-, O- and C-isotope compositions of leachates from carbonates of the Doushantuo Formation. We evaluate the role of diagenetic modification of the carbonate rocks and constrain the redox evolution of Ediacaran seawater in space and time. $^{87}\text{Sr}/^{86}\text{Sr}$ systematically varies with $\delta^{18}\text{O}_{\text{carb}}$, Sr- and Ba abundances, indicating variable but mostly strong modification of fluid-mobile elements by continental basin fluids. In contrast, REE+Y patterns have preserved seawater-like compositions. Cap dolostones (unit I) on top of the Nantuo diamictites differ from cap dolostones at shallow-water sections on the Yangtze Platform in that they show no Ce-anomalies, and little alteration near the top ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7078$, $\delta^{18}\text{O} = -4.0$, $\delta^{13}\text{C}_{\text{carb}} = 1.1$), suggesting that $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}$ of cap dolostones at many other sections were compromised by hydrothermal alteration. The overlying organic carbon poor micritic dolostone (unit II) shows negative Ce-anomalies that disappear towards the top of the unit. No Ce-anomalies occur in subsequent organic carbon-rich muddy dolostone units (units III to IV). These observations, enrichments in TOC that correlate with variations in redox-sensitive metals in the carbonates, negative $\delta^{13}\text{C}_{\text{carb}}$ in units II to IV and the decoupling of $\delta^{13}\text{C}_{\text{carb}}$ from $\delta^{13}\text{C}_{\text{org}}$ argue for the existence of mostly anoxic deep-water at the Yangtze passive continental margin during the Ediacaran. The negative Ce-anomalies at the base of unit II (with negative $\delta^{13}\text{C}_{\text{carb}}$) may reflect fluctuations towards suboxic or oxic conditions or an allochthonous origin of this unit. However, trace metal enrichments in carbonates of the same unit argue for reducing conditions in pore-water, whereas the carbonates may have preserved the REE+Y signatures inherited from suboxic- to oxic seawater. The trace element and negative $\delta^{13}\text{C}_{\text{carb}}$ values in units II to IV are consistent with a stratified basin model with a large partially remineralised organic matter reservoir in anoxic bottom and pore-waters.

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1. INTRODUCTION

The terminal Neoproterozoic, also known as the Ediacaran period, was characterized by important global biological and environmental changes: The geological

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record of Ediacaran sediments reveals large variations in carbon isotope compositions (Kaufman et al., 1997; Hoffman et al., 1998; Halverson et al., 2005; Jiang et al., 2007; Guo et al., 2007; Ader et al., 2009) as well as fossil evidence of the appearance of the first animals on Earth (Xiao et al., 2012). The Marinoan glaciation, a major glaciation event of global distribution marks the end of the Cryogenian and the beginning of the Ediacaran with the deposition of cap carbonates on top of glacial sediments at 635 Ma (Le Hir et al., 2009). However the timespan of the global post Marinoan cap carbonate deposition is still a matter of debate (Font et al., 2010; Trindade et al., 2003). The Marinoan glaciation has been evoked by some as a possible cause for some of the subsequent chemical perturbations of the Ediacaran ocean–atmosphere system (Hoffman et al., 1998; Hyde et al., 2000). Several processes have been discussed as triggers for the transition from global glaciation to a greenhouse-like climate that would have been necessary to melt a global (or nearly global) ice sheet. Among these methane clathrate destabilisation by flooding of permafrost meadows (Kennedy et al., 2008) or a proposed elevation in atmospheric CO₂ concentrations, producing super-greenhouse warming to melt the ice sheets (Hoffman et al., 1998) are the most promising explanations. Rapid glacial meltdown would lead to a global transgression and super-greenhouse warming would result in intense continental weathering, producing an enormous alkalinity and nutrient flux into the oceans and a lowering in ocean pH (Hoffman et al., 1998; Kasemann et al., 2005). Recent work by Sansjofre et al. (2011) postulated much lower pCO₂ levels for the Ediacaran, challenging the super greenhouse rapid meltdown hypothesis of previous authors. Evidence from trace metal data (Lyons et al., 2014 and references therein) indicates anoxic (and locally euxinic) conditions in most parts of the middle to late Neoproterozoic ocean. This hypothesis has been supported by various datasets that show enrichments in redox-sensitive trace elements like U, Mo and V in euxinic black shales (Scott et al., 2008; Sahoo et al., 2012). The input of these elements is largely controlled by the oxidative weathering of crustal minerals and more modest enrichments of these elements occur together with the first geological evidence for increases in atmospheric oxygen (GOE see (Holland, 2006)) or even slightly before (Anbar et al., 2007). A further increase in the abundances of redox sensitive elements in black shales during the late Neoproterozoic is coeval with a second rise in atmospheric and ocean oxygen (Och and Shields-Zhou, 2012). However, the development and vertical extend of the oxygenated surface layer of the oceans during this time remains controversial, as is the timing of large-scale oxygenation of deeper water masses in the oceans.

The Doushantuo Formation (635–551 Ma (Condon et al., 2005)) on the Yangtze Platform, South China, turned out to be one of the key formations for studying ocean oxidation and animal evolution in the aftermath of the Marinoan glaciation. The Doushantuo Formation is comprised of shales, dolomites, limestones and cherts, which are overlying the Nantuo diamictites, deposited at the end of the Marinoan glaciation. It contains a well preserved fossil record (Yuan et al., 2002; Chen and Chi, 2005) and many

datasets on carbon, sulphur and strontium isotopes, iron speciation and trace element concentrations were published (Jiang et al., 2006, 2007; Guo et al., 2007; Zhao et al., 2009; Ader et al., 2009; Sawaki et al., 2010; Li et al., 2010, 2013; Huang et al., 2011; Ling et al., 2013). Most previous geochemical studies have focussed on shallow-water facies on the platform margin, especially around the Three Gorges area in Hubei province. To further test a postulated stratified redox model for the Ediacaran oceans (Li et al., 2010; Lyons et al., 2014) and the inferred links to animal evolution (Canfield et al., 2007; McFadden et al., 2008; Xiao et al., 2012) multiproxy studies of carbonate rocks may add valuable information (e.g. Huang et al., 2011; Ling et al., 2013). In the present contribution we evaluate evidence for the vertical extent of oxygenated water masses in the Yangtze basin by study and comparison of major and trace elements and Sr, C and O isotopic compositions of carbonates from the deep-water Yanwutan section, Hunan Province.

Organic or inorganic carbonates precipitated from seawater incorporate the trace element and isotopic compositions of the latter, sometimes with minor, in other cases with significant fractionation (Brand and Veizer, 1980, 1981). During solidification and burial, marine carbonates may be exposed to diagenetic fluids of variable composition and origin, e.g. pore-waters, meteoric or hydrothermal fluids. As ambient conditions and the composition of these fluids are different from seawater, carbonate minerals may partially dissolve in these fluids and reprecipitate as early diagenetic dolomite or late diagenetic low Mg-calcite (Brand and Veizer, 1980). The identification of primary chemical signals of marine precipitates (reflecting seawater chemistry) requires assessing the influence of diagenesis and effects of later fluid-rock interaction on the chemical and isotopic composition of the carbonates.

Trace elements in leachates of carbonate rocks are useful tools for constraining redox conditions in ancient marine environments, in particular if they are combined with isotopic data on the same samples. A detailed analysis of the alteration history of marine carbonates using different elements and isotopic tracers is crucial for interpretation of such data.

The aims of the present study were to distinguish diagenetic overprinting of carbonate rocks from primary, seawater-derived signatures and to constrain compositional variations of Ediacaran seawater in space and time. Our data suggests that in spite of variable diagenetic alteration, one sample at the top of the cap carbonates has ⁸⁷Sr/⁸⁶Sr = 0.70775 and is close to early Ediacaran seawater values given in Jacobsen and Kaufman (1999) and, compared to other cap carbonates, heavier but not completely unusual stable isotope compositions of −4.0 for δ¹⁸O and +1.1 for δ¹³C respectively (Brazilian cap carbonates from the Araras platform show similar values (Nogueira et al., 2007). Despite one more sample above the cap carbonates analysed by Guo et al. (2007), the Yanwutan section has been overprinted by a fluid with light oxygen isotopic composition and radiogenic Sr. Since these samples still retain marine seawater REE+Y patterns, the lanthanides must have been less susceptible to overprinting by diagenetic

fluid-flow. A further conclusion from the data is that the deep-water of the Yangtze basin may have been anoxic well into the upper Doushantuo.

2. GEOLOGICAL SETTING

The Doushantuo Formation is comprised of marine sediments deposited in a passive margin setting along the south-eastern side of the Yangtze Block (Jiang et al., 2011). The deposits are mainly carbonates and carbonate mudstones with interbedded shales and minor phosphorite and chert layers (Zhao, 1985). U–Pb geochronology on zircons of ash beds occurring at the base and top of the Doushantuo Formation have been used to define its duration from 635.2 ± 0.6 Ma to 551.1 ± 0.7 Ma, spanning almost 90% of the Ediacaran in South China (Condon et al., 2005).

The lowermost unit of the Doushantuo Formation is a cap carbonate layer of 1–5 m thickness overlying the Nantuo diamictites of the Marinoan glaciation associated with a significant (but variable) negative carbon isotope excursion (Jiang et al., 2003; Huang et al., 2009), followed by interbedded organic carbon-rich mudstones and dolostones. On shallow-water platform sections the subdivision of the Doushantuo into four general sedimentological facies: DI (cap carbonates), DII (alternating organic carbon rich shales and dolostones topped by a phosphorite layer, DIII (massive banked limestones) and DIV – (organic-rich black shales with carbonate concretions and cherts) is now widely used and accepted (McFadden et al., 2008; Zhu et al., 2007). In the deep-water basin

sections this subdivision may not be useful because the different depositional environment has led to more shale- and chert-dominated sediment accumulations. The Doushantuo Formation is overlain by massive dolomites of the Dengying Formation on the platform and shales and cherts of the time equivalent Liuchapo Formation in the basin.

The Yanwutan section near the city of Jishou, Hunan province (Fig. 1), is predominantly composed of mudstones and dolostones deposited under slope margin to basin environments (Guo et al., 2007; Zhu et al., 2007) of the Nanhua Basin. This basin was developed along the Yangtze block as a result of the breakup of Rodinia (Wang and Li, 2003) and might have been restricted in its connection to the open ocean.

The Yanwutan section begins with ca. 8 m of cap dolomites on top of the Nantuo diamictites at the base, followed by 12 m of organic carbon-rich shale with interbedded mud- and dolostones (Fig. 2). A 35 m thick unit, starting with a poorly developed basal phosphorite hard ground, followed by organic-poor dolomite pack- and grainstones and organic-rich muddy dolostones, overlies these strata. This unit also includes micritic phosphorites, biolaminations and possibly current related sedimentary structures and was interpreted as a massive submarine slide block of shallow-water origin (Vernhet et al., 2006; Vernhet, 2007). The carbonate unit is overlain by partly brecciated dolostones and mudstones, containing chert layers and nodules (5 m). According to their stratigraphic position, petrologic description and TOC concentrations we have divided the samples used for this study into four subgroups (see Fig. 2):

Fig. 1. Location of study area and paleogeographically reconstruction of the platform margin shortly after deposition of the post Marinoan cap carbonates (635 Ma) modified after (Jiang et al., 2011). The cross indicates location of Yanwutan at N28 25.333 E110 28.701.

Fig. 2. Stratigraphic profile of the Doushantuo Formation at Yanwutan section. (a–c) $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ normalised to VPDB and % TOC (Guo et al., 2007). The filled symbols represent samples studied in this work, the crosses represent the full dataset, one cap dolomite sample plots at -30‰ . (d, e) Mn/Sr ratios and $^{87}\text{Sr}/^{86}\text{Sr}$. The grey bar marks the Ediacaran seawater composition inferred from least altered marine carbonate rocks (Jacobsen and Kaufman, 1999). (f) Ce/Ce* normalised to PAAS, micritic dolostones reveal distinct negative Ce-anomalies. The grey bar indicates the analytical uncertainty. (g) Y/Ho normalised to PAAS indicates strong fractionation in all carbonates except the lowermost cap carbonate (see text).

- (I) Cap dolomites
 - Massive light grey fine grained dolomitized grainstones with abundant “tepee” structures
- (II) Organic carbon-poor dolostone unit
 - Fine-sand-grained dolomitized grainstones and packstones with crossbedding structures
- (III) Muddy dolostones and organic-rich dolostones
 - Dark coloured dolomite with crossbedding interbedded with thinly laminated marls
- (IV) Dolostone sample with chert nodules
 - Dolomitic breccia with chert bands and chert nodules

The section contains smaller allochthonous slide blocks and olistoliths with a variety of sedimentological facies, such as tepees and ripples which has been used to argue for a shallow-water origin of unit II and III lithologies and mass flow transport of parts of the section into deeper environments (Vernhet et al., 2006, 2007). We note, however, that $\delta^{13}\text{C}_{\text{carb}}$ values are negative at about -4 to -9 throughout the Yanwutan section (Guo et al., 2007) as for other slope or deep-water sections on the Yangtze Platform (Ader et al., 2009). This observation does not support a shallow-water origin of parts of the section, as shallow-platform carbonates of DII to DIV mostly display positive $\delta^{13}\text{C}_{\text{carb}}$ (Ader et al., 2009).

3. MATERIAL AND METHODS

We analysed 14 carbonate rocks of the Doushantuo Formation of the Yanwutan section which have been described in detail by (Guo et al., 2007). Carbon and

oxygen isotopic compositions of the carbonates were reported by (Guo et al., 2007).

For chemical analysis 20 mg of sample powder were treated with 3 M acetic acid for 12 h at 70°C following Huang et al. (2009). Insoluble residues were separated by centrifugation and filtration through $0.45\ \mu\text{m}$ cellulose acetate syringe filters, testing the residues using XRD have shown that the residues are free of any remaining carbonate phases. The supernatant was dried, redissolved in 0.5 ml 3 M HNO_3 , and dried again to remove the remaining acetic acid. Finally the precipitate was redissolved in 1 ml 0.28 M HNO_3 , weighed and diluted with 0.28 M HNO_3 to 1:20,000 for trace element and to 1:40,000 for major element analysis. All measurements were performed on a Thermo Finnigan Element XR sector-field ICP mass spectrometer at Freie Universität Berlin using a Scott type quartz spray chamber and a $100\ \mu\text{l}/\text{min}$ nebulizer. Sample time was 120 s with 20 samples/peak and 60 total scans. With this analytical setup tuning generally yielded low oxide rates of 2–5% CeO^+ and less than 1% BaO^+ . We determined element concentrations by external calibration to the matrix-matching CAL-S carbonate standard (Yeghicheyan et al., 2003). For drift correction the diluted samples were doped with solutions of 2 ppb In and 1 ppb Tl for elements analysed in low resolution mode (REE, Y, Rb, Pb, Sr, Mo, Cd, In, Tl, P, Th, U), and 12.5 ppb Co for elements analysed in medium resolution mode (Mg, Al, Ca, Mn, Cr, Fe, Co, K, V, Zn, Ti). Background corrections were performed by subtraction of the raw intensities of aspirated 0.28 M HNO_3 . The analytical precisions were usually better than 5% RSD for most REE, Y, Rb, Cd, Ti, Zn, Ba, Pb, Mg, Al, Ca, Mn, K, Th, 10% for Sr, U, V, Fe and La and above 10% RSD for Cr and Mo.

The limit of detection on LREE was 100–620 pg/g and 16–240 pg/g on HREE. Procedural blanks on most trace elements and REE were negligible. Limit of detection for redox sensitive elements U, V and Mo was 1.4–4.5 ng, for Ba, Mg, Mn and Fe 12–26 ng, and for Sr 200 ng. Procedural blanks of major and trace elements were generally below the acid background signal intensities.

Aliquots of the acetic acid leachates were used for Sr isotopic composition measurements. Approximately 1 µg Sr was loaded in 2.5 M HCl on 1 ml AG 50 W-X8 (200–400 mesh) cation-exchange resin for separation of Sr from the matrix.

The Strontium isotopic composition was determined using a Thermo-Finnigan Triton TIMS at FU Berlin. Repeated measurements of SRM 987 yielded $^{87}\text{Sr}/^{86}\text{Sr} = 0.710266$ (± 15 , $n = 6$). Mass fractionation was corrected assuming a $^{86}\text{Sr}/^{88}\text{Sr}$ ratio = 0.1194 (Nier, 1938) and the exponential law. Minor interferences of ^{87}Rb on ^{87}Sr were corrected using $^{85}\text{Rb}/^{87}\text{Rb} = 2.59265$. Initial $^{87}\text{Sr}/^{86}\text{Sr}$ were calculated assuming depositional ages (600 Ma), $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (calculated from ICP-MS data) and a half-life of ^{87}Rb of 4.88×10^{10} years. Corrections of radiogenic ingrowth were usually between 0.01 and 0.5‰ except YAW505 where the correction due to the ingrowth of Rb decay is on the order of 2‰. In general corrections are minor and do not change the interpretation of the carbonate data.

4. RESULTS

4.1. Sr isotopic compositions

The $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions of the cap dolomites (Table 1) range from 0.72170 at the base of the micritic cap dolomite unit to 0.70775 at the top at 6.4 m. The organic carbon-poor dolostone unit (from 20.8 to 27 m stratigraphic height) shows $^{87}\text{Sr}/^{86}\text{Sr}$ between 0.70964 and 0.71547. The third unit, comprised of dolostones, muddy dolostones, or organic-rich dolostones also shows high $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.71071–0.71281. The cherty dolostone at the top of the Yanwutan section has $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.71547.

4.2. Major and trace element concentrations

Major and trace element concentrations in acetic acid leachates of Yanwutan section display considerable variations (Table 1) making them the perfect samples to describe not only Precambrian seawater chemistry but also effects of early and late rock diagenesis. Major element concentrations of Ca, Mg, Mn and Fe were used to calculate hypothetical dolomite mass fractions (Table 1), assuming that during dolomitisation, Mg^{2+} , Fe^{2+} and Mn^{2+} will substitute for Ca^{2+} in CaCO_3 , forming stoichiometric dolomite $\text{Ca}(\text{Mg}, \text{Mn}, \text{Fe})(\text{CO}_3)_2$. Typically samples show 18–21 wt.% Ca and 9–12 wt.% Mg, whereas the lowermost cap carbonate in unit I (YAW 500) contains only 3.8 wt.% Ca and 0.9 wt.% Mg, and unit IV sample YAW 535 having only 2.6 wt.% Ca. All analysed carbonate rocks are dolostones with just minor proportions of calcite in the matrix. Samples with very low bulk Ca and Mg contents are

siliciclastic rocks rather than carbonates. The carbonate samples have very low Al contents (< 1200 µg/g) with only the lowermost cap carbonate YAW 500 exceeding 3000 µg/g Al and low Rb contents (< 1.1 µg/g) with 2.3 µg/g in YAW 500, this together with elevated K content (3600 µg/g) argues for partial leaching of alkali bearing silicates in this sample.

Manganese displays large variations throughout the profile. Concentrations of Mn of around 670 µg/g at the base increase to 2800 µg/g in overlying cap dolomites and return to values between 290–650 µg/g in the carbonates of units II and III. The sample of unit IV shows a slight increase again to 960 µg/g. Fe contents in cap dolomites are generally high (350–440 µg/g) but show non-systematic variations, with unit IV showing the highest value with 689 µg/g Fe.

Sr and Ba concentrations display large variations throughout the profile (Sr 37–880 µg/g, Ba 24–690 µg/g) and carbonates also show high variability in their Pb concentrations (5.9–238 µg/g) with the highest concentrations in the cap dolomites and a gradual decrease throughout the profile.

The Yanwutan cap dolomites (like elsewhere on the Yangtze Platform) have undergone carbonate diagenesis. They yield high Mn/Sr ratios of 17–23 with the uppermost sample YAW 505 showing a lower value of 8.7. The cap dolomites show increasing concentrations of Sr from 38 to 319 µg/g and increasing $\delta^{18}\text{O}$ values from -10 to -4 from base to top. Mn/Sr shows a positive correlation with $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.72170 at the base to 0.70775 at the top) and a negative correlation with $\delta^{18}\text{O}$ (Fig. 2). Unit II and III show no correlations of isotopic tracers with Mn/Sr, which tend to be lower than data for the cap dolomites (< 10). The Mn/Sr ratios in unit II are decreasing with stratigraphic height from 4 to 0.8, with variable Sr contents from 138 to 832 µg/g and relatively constant concentrations in Mn (400–650 µg/g). $\delta^{18}\text{O}$ values range between -9.4 and -6.9 . Mn/Sr ratios in unit III range from 3 to 7, having low Sr (60–108 µg/g) and variable Mn concentrations (293–649 µg/g) and decreasing $\delta^{18}\text{O}$ values down to -2.7 . The chert-rich dolomitic sample of unit IV has elevated Mn/Sr of 25 with very low Sr abundances of 38 µg/g, $\delta^{18}\text{O}$ of -11.3 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71547 and seems to be the most altered sample. The sample with the lowest $^{87}\text{Sr}/^{86}\text{Sr}$, a cap dolomite with the heaviest $\delta^{13}\text{C}_{\text{carb}}$ in the section, plots close to the inferred $^{87}\text{Sr}/^{86}\text{Sr}$ of Ediacaran seawater derived from little altered carbonate rocks from other Ediacaran profiles around the world (Jacobsen and Kaufman, 1999; Halverson et al., 2010) and has a Mn/Sr below 10.

There is no correlated decrease of $\delta^{18}\text{O}$ with $\delta^{13}\text{C}$ nor a correlation of Mn/Sr with light stable isotopic data (Guo et al., 2007) or $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios. We note a correlation of increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and decreasing Sr concentration and $\delta^{18}\text{O}$ for the two lower units II and I.

Before discussing the results of the rare earth elements and Y, analytical limitations and normalization procedures for the calculation and evaluation of Eu and Ce-anomalies are warranted. It has been shown that Eu concentration measurements on the ICP-MS are strongly affected by

Table 1
Major and trace elemental data Yanwutan.

	YAW500 cap dolost.unit I	YAW503A cap dolost unit I	YAW503B cap dolost unit I	YAW505 cap dolost unit I	YAW518 dolost.unit II	YAW519 dolost.unit II	YAW521 org-rich dst unit II	YAW522 dolost unit II	YAW524 muddy dst unit III	YAW526 muddy dst unit III	YAW528 dolost unit III	YAW529 muddy dst unit III	YAW530 muddy dst unit III	YAW532 muddy dst unit III	YAW535 muddy dst unit IV
Stratigraphic position [m]	0–0.3	3.9	3.9	6.4	20.8	22.5	24.9	27	32.3	35.6	40.4	43	45.2	50.3	56.7
Rb µg/g	2.3	0.56	0.53	0.74	0.53	0.35	0.29	0.08	0.71	0.65	0.56	1.08	1.04	0.48	0.06
Sr µg/g	37	155	118	319	137	187	141	833	88	60	118	90	108	123	39
Ba µg/g	75.8	24.1	24.4	691.9	243.8	236.8	56.8	14.5	30.2	67	75.2	60.1	42.4	29.2	32.8
Y µg/g	2.68	6.71	4.49	13.42	2.44	1.35	2.86	5.72	5.06	4.41	4.04	3.27	4.07	3.16	0.87
Cd µg/g	1.96	0.8	0.62	2.98	2.41	16.7	0.77	1.06	3.51	7.36	0.91	1.46	2.37	1.09	0.88
La µg/g	0.79	2.56	1.81	3.5	0.89	0.48	2.02	1.4	2.83	2.4	1.72	2.13	2.54	2.02	0.16
Ce µg/g	2.12	5.43	3.83	8.32	1.33	0.9	3.06	2.64	4.77	3.64	3.28	3.8	4.87	3.53	0.45
Pr µg/g	0.3	0.69	0.48	1.13	0.26	0.15	0.4	0.38	0.6	0.46	0.42	0.44	0.57	0.41	0.08
Nd µg/g	1.39	2.85	2.01	5	1.13	0.63	1.45	1.66	2.34	1.71	1.71	1.61	2.08	1.49	0.4
Sm µg/g	0.45	0.73	0.54	1.52	0.29	0.16	0.29	0.53	0.58	0.38	0.44	0.34	0.44	0.34	0.11
Eu µg/g ¹	0.102	0.213	0.149	0.386	0.052	0.038	0.073	0.233	0.119	0.077	0.092	0.075	0.104	0.069	0.026
Gd µg/g	0.51	0.87	0.61	1.77	0.31	0.18	0.33	0.64	0.64	0.44	0.48	0.39	0.48	0.36	0.12
Tb µg/g	0.09	0.146	0.1	0.316	0.055	0.032	0.058	0.114	0.107	0.079	0.087	0.063	0.084	0.061	0.019
Dy µg/g	0.55	0.89	0.6	1.97	0.35	0.19	0.37	0.71	0.67	0.54	0.55	0.41	0.55	0.4	0.12
Ho µg/g	0.099	0.183	0.122	0.382	0.076	0.041	0.082	0.137	0.141	0.124	0.114	0.085	0.116	0.084	0.023
Er µg/g	0.27	0.55	0.36	1.07	0.24	0.13	0.26	0.38	0.41	0.4	0.34	0.26	0.34	0.26	0.07
Tm µg/g	0.037	0.076	0.051	0.149	0.036	0.02	0.04	0.05	0.058	0.062	0.049	0.037	0.05	0.038	0.01
Yb µg/g	0.25	0.52	0.34	1.01	0.26	0.14	0.27	0.3	0.38	0.44	0.32	0.25	0.34	0.26	0.06
Lu µg/g	0.037	0.085	0.056	0.151	0.039	0.022	0.042	0.041	0.053	0.067	0.049	0.038	0.051	0.039	0.009
Zn µg/g	167	246	136	286	63	116	46	80	50	122	104	116	101	40	18
Pb µg/g	238	35	33	53	44	21	8	6	23	16	20	21	30	28	11
P µg/g	139	142	180	327	519	288	95	66	196	184	236	231	249	238	405
U µg/g	0.33	0.37	0.37	2.91	0.35	0.07	0.29	0.53	0.41	0.63	2.83	0.59	30.03	1.24	1.71
Th µg/g	0.57	0.36	0.4	0.74	0.17	0.19	0.15	0.08	0.41	0.29	0.37	0.39	0.66	0.35	0.03
Mo µg/g	0.45	0.49	0.28	0.58	0.1	0.06	0.07	0.26	0.04	0.05	0.39	0.11	0.52	0.12	4.55
V µg/g	2.52	10.3	10.1	21.9	24.7	15.7	11.6	22.7	38.9	88.8	52.8	56.9	45.8	52.6	3.2
Cr µg/g	4.95	4.68	4.52	5.4	16.68	5.31	4.06	4.23	19.4	24.4	11	11.9	9.2	3.9	28.2
Ti µg/g	b.d.l.	35	19	217	25	41	19	31	b.d.l.	b.d.l.	18	30	79	33	b.d.l.
Mn µg/g	669	2809	2716	2774	575	639	405	630	294	403	532	591	627	649	961
Fe µg/g	436	395	410	347	157	88.6	156	439	79.1	112	184	121	134	123	687
K µg/g	3668	998	1032	1859	884	521	454	106	1221	1204	821	1264	1491	690	715
Mg wt. %	0.90	12	11.7	10.6	11.1	12.1	9.8	12	10.6	11.6	9	12	11.4	12	0.3
Al wt. %	0.32	0.12	0.12	0.2	0.1	0.08	0.05	0.03	0.12	0.11	0.07	0.12	0.13	0.07	0.01
Ca wt. %	3.79	21.3	20.6	18.9	19.7	21.4	17.8	21.4	18.4	20.5	16.3	20.6	19.9	21	2.63
Mn/Fe	1.53	7.11	6.62	8	3.66	7.21	2.59	1.44	3.71	3.59	2.88	4.88	4.7	5.27	1.4
Mn/Sr	17.9	18.1	23	8.7	4.1	3.4	2.9	0.8	3.3	6.7	4.5	6.6	5.8	5.3	24.8
Dolomite wt. % ¹	59	97	97	97	96	96	95	96	97	97	95	98	97	97	38
Ce/Ce ⁺²	0.94	0.94	0.96	0.94	0.66	0.69	0.82	0.88	0.89	0.85	0.94	0.9	0.92	0.92	0.81
Eu/Eu ⁺³	1.03	1.32	1.29	1.14	0.84	1.07	1.15	1.97	0.96	0.97	0.96	1.03	1.09	0.96	1.11
Y _N /Ho _N	1	1.34	1.35	1.29	1.18	1.21	1.27	1.54	1.32	1.31	1.3	1.41	1.29	1.38	1.39
Dy _N /Sm _N	1.43	1.44	1.32	1.53	1.42	1.41	1.52	1.61	1.37	1.68	1.48	1.43	1.48	1.41	1.24
Nd _N /Yb _N	0.46	0.45	0.49	0.51	0.36	0.38	0.45	0.46	0.52	0.32	0.44	0.53	0.51	0.48	0.58
⁸⁷ Sr/ ⁸⁶ Sr _(meas.) ⁴	0.721704	0.713924	0.713884	0.707754	0.71066	0.709644	0.711894	0.715467	0.71281	0.71071	0.712518	0.711268	0.711906	0.71225	0.715472
	−18	−8	−10	−41	−16	−10	−16	−70	−13	−13	−130	−15	−15	−25	−19

(continued on next page)

Table 1 (continued)

	YAW500	YAW503A	YAW503B	YAW505	YAW518	YAW519	YAW521	YAW522	YAW524	YAW526	YAW528	YAW529	YAW530	YAW532	YAW535
	cap dolomite unit I	cap dolomite unit I	cap dolomite unit I	cap dolomite unit I	dolomite unit II	dolomite unit II	org-rich dolomite unit II	dolomite unit II	muddy dolomite unit III	muddy dolomite unit III	dolomite unit III	muddy dolomite unit III	muddy dolomite unit III	muddy dolomite unit III	muddy dolomite unit IV
$^{87}\text{Sr}/^{86}\text{Sr}_{(600\text{Ma})}$	0.720186	0.713834	0.713772	0.707696	0.710564	0.709597	0.711842	0.715464	0.712608	0.710437	0.712399	0.710967	0.711665	0.712153	0.715435
$^{87}\text{Rb}/^{86}\text{Sr}$	0.177	0.0106	0.0131	0.00679	0.0112	0.00549	0.0061	0.0003	0.0236	0.0319	0.0139	0.0352	0.0282	0.0113	0.00434
$\delta^{18}\text{O}_{\text{carb}}$	-10	-9.2	-9.2	-4	-5.8	-6.6	-7.6	-9.4	-5.2	-4	-5.6	-3.5	-4.2	-3.1	-11.3
$[\text{‰ VPDB}]^5$															
$\delta^{13}\text{C}_{\text{carb}}$	-4.1	-3.6	-3.6	1.1	-4.3	-8.9	-7.4	-6.9	-8.7	-8	-7.2	-7	-7.3	-6.3	-6.3
$[\text{‰ VPDB}]^5$															
TOC wt. % ⁴	0.1	0.6	0.6	0.4	0.1	0.2	1.2	0.8	2.2	1.9	1	0.5	0.7	0.6	0.1

¹ Dolomite fraction calculated using ICP-MS data and ratio of Ca to dolomite incorporated elements Fe, Mn, Mg.

² Ce-anomalies calculated following (Lawrence and Kamber, 2006).

³ Eu/Eu* anomalies corrected for BaO interferences using Ba concentrations following (Dulski, 1994).

⁴ Measured and initial $^{87}\text{Sr}/^{86}\text{Sr}$ data with 2SE in-run precision (assuming a depositional age of 600 Ma).

⁵ Stable isotope and TOC data from Guo et al., 2007 with standard deviation better than $\pm 0.1\text{‰}$.

interfering BaO^+ molecules (Dulski, 1994). If these molecular interferences are not corrected for, a diagram of Ba/Nd vs. Eu/Eu^* (calculated according to $\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/(\text{Sm}_\text{N}^2 * \text{Tb}_\text{N})^{1/3}$, see below) will show a positive correlation, indicating analytical artefacts on Eu abundance measurements (Electronic Supplement Fig. A). Our Eu data therefore was corrected by using the measured Ba concentration and oxide formation rates following the equations given by Dulski (1994). After correction of these artefacts, most samples have no Eu-anomalies within the range of analytical uncertainty. The REE + Y patterns were normalised relative to PAAS (McLennan, 1989) and are shown in Fig. 3. Values for Ce/Ce^* and Eu/Eu^* were calculated following the equations given in Lawrence and Kamber (2006): $\text{Ce}/\text{Ce}^* = \text{Ce}_\text{N}/(\text{Pr}_\text{N} * \text{Pr}_\text{N}/\text{Nd}_\text{N})$ and $\text{Eu}/\text{Eu}^* = \text{Eu}_\text{N}/(\text{Sm}_\text{N}^2 * \text{Tb}_\text{N})^{1/3}$.

These equations avoid using La and Gd for the calculation of Ce/Ce^* and Eu/Eu^* , because these elements may be enriched by natural processes, and thus may cause apparent depletions in Ce and Eu anomalies, respectively (Ling et al., 2013). In unit II the most negative Ce-anomalies appear ($\text{Ce}/\text{Ce}^* \approx 0.7$, Fig. 2) where increasing Mn/Fe is anti-correlated with Ce/Ce^* . All other units show no or only slightly negative Ce/Ce^* (0.9–1.0). All analysed carbonate leachates have seawater-like REE + Y patterns (Fig. 3) with relative enrichment of HREE over LREE. Furthermore, positive Y anomalies are prevalent, with normalised $\text{Y}/\text{Ho}_{\text{PAAS}}$ varying between 1.2 and 1.5 (except YAW 500 for which no Y anomaly was found).

5. DISCUSSION

5.1. Post-depositional diagenesis of carbonates

In this section we discuss possible influences of late fluid-flow interaction on fluid-mobile trace elements and C, O and Sr isotopic compositions of the Yanwutan carbonate rocks following approaches in the literature (Derry, 2010; Brand and Veizer, 1981; Derry et al., 1989; Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). Studies of carbonate diagenesis in Phanerozoic rocks (Brand and Veizer, 1980) generally observed elevated contents of Mn^{2+} , Fe^{2+} and Zn^{2+} and decreasing contents of Sr^{2+} , Na^{2+} and Mg^{2+} due to dissolution of primary CaCO_3 and precipitation of carbonate cements under the influence of meteoric diagenesis. In the presence of meteoric fluids, the partition coefficient of Sr^{2+} between calcite and water $K_{\text{calcite/water}}$ is <1 and $K_{\text{calcite/water}}$ for Mn^{2+} is >1 (Banner and Hanson, 1990). Therefore when discussing the influence of diagenesis on ancient carbonates, Mn/Sr ratios are commonly used to estimate the influence of diagenetic overprinting. Kaufman and Knoll (1995) proposed that Proterozoic carbonate samples with Mn/Sr ratio <10 might still retain their primary $\delta^{13}\text{C}$ signatures. Yanwutan carbonate leachates from different units reveal a broad variation in Mn/Sr ratios but also in their Sr concentrations. Despite the cap dolomites and unit IV cherty dolomite, all Yanwutan Mn/Sr ratios are below 10. In some cases however, Mn may behave more conservatively, whereas Sr is preferentially leached during the exchange with late

Fig. 3. REE+Y patterns of leachates of carbonate rocks from Yanwutan units I to IV, normalised to PAAS (McLennan, 1989). Units correspond to their positions in the section from base to top. Grey field in unit I shows data from Jiulongwan cap carbonates (Huang et al., 2009), revealing a much broader REE+Y variation. All samples throughout the Yanwutan section show fractionation of HREE over LREE with Y anomalies being present in most of the samples (except the lowermost cap carbonate), indicating their marine origin. Negative Ce-anomalies can be seen in unit II, whereas an apparent anomaly in unit I is due to enrichment in La which can be assessed by calculating the real anomalies following (Lawrence and Kamber, 2006) (see Fig. 3). Note that Eu has been corrected for interferences from BaO following (Dulski, 1994) and shows no resolvable anomalies.

fluids, leading to an increase of the Mn/Sr ratios as it can be seen at the base of unit I. Therefore reliance on Mn/Sr ratios alone may sometimes be misleading in rocks with large variations in their Sr concentration.

Late fluid flow and diagenesis can significantly change the stable isotope composition of carbonate rocks (Brand and Veizer, 1981). The isotopic exchange between pore fluids and the carbonate minerals will generally shift $\delta^{18}\text{O}$ in carbonates towards lower values than those of seawater because oxygen is abundant in aqueous fluids and the latter often contain oxygen originally derived from isotopically light meteoric precipitation (Brand and Veizer, 1981; Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). Knauth and Kennedy (2009) proposed that lithification processes lead to a conjugate decrease in both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, however, in detail, correlations are rarely clear and both isotopic systems are often decoupled (Electronic Supplement Fig. B). In many studies it has been argued that both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ changed during post depositional diagenesis (e.g. Derry, 2010), but in some cases, primary compositions may still be preserved in carbonate rocks (Stoll and Schrag, 2000; Tahata et al., 2013). The Yanwutan samples show significant variation in $\delta^{13}\text{C}$ (+2 to −9) and $\delta^{18}\text{O}$ (−3 to −12) (Guo et al., 2007), however no co-variation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ exists (Electronic Supplement Fig. B). The range and magnitude of the negative $\delta^{13}\text{C}_{\text{carb}}$ is not unusual in Ediacaran deep-water dolomites (e. g., Ader et al., 2009) and extreme light values have been explained by either primary carbonate precipitation during bacterial sulphate reduction processes (Van Lith et al., 2003), the presence of methanotrophic biomass (Ader et al., 2009) or the vicinity of methane seeps and the reaction with $\delta^{13}\text{C}$ -depleted hydrocarbon fluids (e.g. Jiang et al., 2003). Furthermore the Yanwutan section presumably comprises the time range of the Shuram–Wonoka anomaly, which represents the largest relative change in $\delta^{13}\text{C}_{\text{carb}}$ in geologic time (e.g. Kaufman and Knoll, 1995 and references therein). This worldwide occurring anomaly has been explained as a large-scale perturbation and upwelling event of a large pool of dissolved organic carbon in deep-water of the Ediacaran ocean (Fike et al., 2006; Grotzinger et al., 2011), or, alternatively, as a secondary diagenetic signal in the sedimentary record (Derry, 2010; Macouin et al., 2012).

Alteration of the Sr isotopic system could either be due to *in situ* mobilization of radiogenic Sr from silicate phases by pore-water or by externally derived fluids. Alternatively, external fluids percolating through clastic sediments or continental basement may have increased the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the sediments by precipitation of secondary carbonate minerals. Because Sr is a fluid-mobile element, its concentrations may decrease in secondary carbonates that formed after reaction with fluids in open systems (Brand and Veizer, 1981).

The Yanwutan dataset seem to have at least two samples in the cap dolostones and at the base of unit II that are presumably close to pristine Ediacaran compositions ($\delta^{13}\text{C} = 1.1$, $\delta^{18}\text{O} = -4$) (see Fig. 2) and Sr isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70775$ in the cap dolostone). Those values can be compared to datasets published for the relatively undisturbed Brazilian Marinoan cap carbonates of

Fig. 4. (a–d) Open system fluid-carbonate mixing model for Ediacaran carbonate rocks from units I to IV from the Yanwutan section following [Jacobsen and Kaufman, 1999](#). Variable fluid-rock ratios (crosses on the line) with a distinct fluid composition of $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7074 and a presumed original carbonate composition of $\delta^{18}\text{O}$ of 0, $\delta^{13}\text{C}$ of 1.5, 330 $\mu\text{g/g}$ Sr and 700 $\mu\text{g/g}$ Ba was used in the model. (Circles: cap dolomites – unit I; squares: micritic dolostones – unit II; triangles: carbon rich dolostones – unit III; star: cherty dolostone – unit IV). Note that variations of unit I and II in $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ concentrations match for an open system fluid mixing (b), whereas unit III plots above the curve, indicating either a different fluid source or variable enrichments of the fluid in radiogenic Sr. Variations of increasing Sr and Ba concentrations with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ for all samples (c + d). Variations in $\delta^{13}\text{C}$ do not match for most of the units (except the cap dolomites) with the proposed model mixing curve (a).

the Mirassol d'Oeste and Guia formations ($\delta^{13}\text{C} = -5.2$ to -1.5 , $\delta^{18}\text{O} =$ up to -5.3 and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7074$ to 0.7080) ([Nogueira et al., 2007](#); [Sansjofre et al., 2011](#)).

In order to assess the influence of fluid overprint on Sr and oxygen isotopes of the pristine carbonates, we have fitted an open system fluid-rock mixing model ([Jacobsen and Kaufman, 1999](#)) to our isotopic and mobile element concentration data (Fig. 5). As a starting point for the model, the pristine marine carbonate composition, the following values were used: $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7074, $\delta^{13}\text{C}$ of 1.1 and 700 $\mu\text{g/g}$ Ba (inferred from the most pristine sample of our dataset). Values for $\delta^{18}\text{O}$ (0), Sr (330 $\mu\text{g/g}$) and C (1200 $\mu\text{g/g}$) ([Jacobsen and Kaufman, 1999](#)) were taken as values for Neoproterozoic marine carbonate compositions. For the model we use variable fluid/rock ratios (0.01–10) and a 'continental' fluid composition with 80 $\mu\text{g/g}$ Ba, 50 $\mu\text{g/g}$ Sr and 1000 $\mu\text{g/g}$ C, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7240$, $\delta^{18}\text{O}_{\text{carb}} = -13.5\text{‰}$ and $\delta^{13}\text{C}_{\text{carb}} = -12\text{‰}$ ([Jacobsen and Kaufman, 1999](#)). The mixing model provides a good fit to most of the Yanwutan carbonate rocks (unit I and II and possibly III) and is consistent with other evidence for post-depositional hydrothermal overprinting ([Huang et al., 2011](#)). Data of unit III do not match the model well in that they show relative higher $^{87}\text{Sr}/^{86}\text{Sr}$ values for given $\delta^{18}\text{O}$ and slightly lower Sr concentrations. This may be explained by lower Sr concentrations and higher $^{87}\text{Sr}/^{86}\text{Sr}$ in the fluid that affected unit III. Unit IV sample overlaps in its $^{87}\text{Sr}/^{86}\text{Sr}$ composition with the model but has a lower $\delta^{18}\text{O}$ value, a low Sr content and the highest Mn/Sr ratio, which might be explained by subsequent meteoric fluid overprint with a different composition. In order to model

variations in the Ba content of the samples, concentrations of Ba much higher than in Phanerozoic carbonates (>700 $\mu\text{g/g}$) must be assumed for the precursor rocks. This may be explained by early diagenetic Ba enrichments in pore-waters due to anoxic conditions near the seafloor and bacterial sulphate reduction. Assuming such higher initial Ba concentrations in carbonates, later post-diagenetic fluid flow will then lead to similar trends of mobile element leaching as for Sr (Fig. 4 c, d). Modelling the variations in $\delta^{13}\text{C}$ is only successful for the cap carbonate samples all other units are offset from the model curve and plot in a cluster rather than a curved trend. Clearly, the $\delta^{13}\text{C}$ signature in most Yanwutan carbonates is decoupled from fluid-mobile elements. Furthermore $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ do not reveal any correlations with any of the seawater REE+Y proxies such as Y/Ho or Pr/Yb (see [Electronic Supplement Fig. C](#)).

5.2. Origin of abundance variations in REE+Y

Here we discuss the potential use of REE+Y in carbonates as paleo-environment proxies and possible influences on them by leaching or dissolution of silicates and other detrital phases.

The rare earth elements and Y substitute for Ca^{2+} in carbonate lattices. It has been shown that REE+Y signals in non-skeletal marine carbonates of modern and ancient seawater can preserve the composition of coeval seawater ([Banner, 1988](#); [Webb and Kamber, 2000](#)). Although REE can be susceptible to diagenetic alteration ([Palmer, 1985](#); [Sholkovitz and Shen, 1995](#)) solid state diffusion is minimal

Fig. 5. With the exception of a cap dolomite all Y/Ho ratios are superchondritic. A Negative correlation of Al concentrations with Y/Ho ratios occurs in the cap dolomites (dots) and in rocks from unit II (squares).

even under metamorphic conditions (Cherniak, 1998). Because of the low concentrations of these elements in fresh water, meteoric alteration should not influence the REE+Y patterns in carbonate rocks significantly and consequently many ancient dolomite rocks may record REE+Y patterns of coeval seawater (Webb et al., 2009).

The REE+Y patterns obtained by acetic acid leaching of carbonates from Yanwutan reveal typical seawater-like patterns with significant relative enrichment of the HREE over the LREE and negative Ce-anomalies (Fig. 3). The concentrations of the REE and Y in these leachates seem not to be influenced by leaching of silicate phases since no correlation of these proxies with Al or Ti concentrations can be found in the samples. We note that the isotopically most pristine cap dolomite shows the highest total REE concentration of all carbonate rocks analysed here. We also found a weak positive correlation ($R^2 = 0.85$) between total REE and Al concentrations in the muddy dolostone and cherty dolostone samples of units III and IV. This may be explained by limited acetic acid leaching of aluminosilicate minerals such as clays. Furthermore we use Nd/Yb_{PAAS} ratios to monitor any MREE enrichment that is typical for apatite leaching (Nothdurft et al., 2004). Nd/Yb_{PAAS} ratios are generally low (<0.6) and display no correlation with P concentrations, arguing against phosphate leaching (Shields and Stille, 2001).

Throughout the profile Y/Ho ratios are superchondritic but do not reach values typical for modern marine carbonates of about 60–90 (Nozaki et al., 1997). The highest Y/Ho ratio in Yanwutan carbonates is 42.3 in unit III. However these values are close to previously published maximum values for Y/Ho in Doushantuo carbonates (e.g. Huang et al., 2009, 2011; Ling et al., 2013). Superchondritic, but relatively low Y/Ho ratios may be a result of seawater/freshwater mixing (Lawrence and Kamber, 2006). Y/Ho ratios within the cap dolomites at Yanwutan (unit I) and in unit II show negative correlations with

Al concentrations, presumably resulting from dilution of seawater with freshwater maybe caused by slow melting of icebergs along with increased continental REE input (Fig. 5).

To test for hydrothermal input, Eu-anomalies (PAAS normalised) were calculated following Lawrence and Kamber (2006). A positive Eu-anomaly could denote an enrichment of Eu²⁺ in the water column, due to the reduction of the element in reducing high-temperature fluids (e.g. Derry and Jacobsen, 1990). With the possible exception of the uppermost sample of unit II, interference-corrected Eu data of Yanwutan section show no resolvable Eu-anomalies, suggesting no or negligible mixing of seawater with ocean-ridge derived hydrothermal fluids or subsequent alteration by such fluids (Electronic Supplement Fig. A). In sections of the Three Gorges area the impact of high temperature reducing fluids on the cap carbonates was inferred from positive Eu-anomalies (Huang et al., 2009) and clumped isotope data (Bristow et al., 2012). Temperatures of up to 200 °C in the D2 units of the Doushantuo Formation have been determined from illite crystallinity (Derkowski et al., 2013). The fluid source is unclear, however a reducing hydrothermal MORB fluid can be ruled out given the geologic position of the Neoproterozoic Yangtze Platform on a passive continental margin and the absence of basalts within the sedimentary rocks (Wang and Li, 2003).

In order to test the robustness of our Ce data and the inferred Ce-anomalies we use two different approaches. Following (Shields and Stille, 2001) we use Dy_N/Sm_N ratios to test if Ce-anomalies are influenced by MREE enrichment. Dy_N/Sm_N ratios at Yanwutan are all >1 and show no correlation with Ce/Ce*, arguing for the robustness of the cerium data in this section. To test if an anomalous La-anomaly may be affecting the Ce/Ce* ratios, Bau et al. (1996) proposed a method which is additionally checking for Pr anomalies using $Pr/Pr^* = 2Pr_N / (Ce_N + Nd_N)$. $Pr/Pr^* \geq 1$ can only be caused by a real negative Ce-anomaly since there are no natural ways to produce an Nd anomaly and thus the Ce deficiency is not due to an anomalous behaviour of neighbouring La. With the exception of the cap carbonates, all other samples plot in the field of Ce/Ce* < 0.95 and Pr/Pr* < 1.05 (5% error on the REE analysis), i.e. they have a negative Ce-anomaly (Fig. 6).

Modern oxalic aquatic systems show strong negative Ce-anomalies (PAAS-normalised) in their dissolved load. The Ce deficiency in the water results from the preferential scavenging of Ce^{IV}O₂ by Mn- and Fe-rich oxides and hydroxides (Elderfield et al., 1988; Byrne and Kim, 1990; Alibo and Nozaki, 1999). In deeper suboxic to anoxic waters Ce-anomalies diminish due to the dissolution of settling oxides (German et al., 1991). Areas of preferred Mn²⁺ oxidation like at the oxic/suboxic boundary in the Black Sea therefore show strong association of REE and Mn. In contrast, the uptake of REE by Fe³⁺ oxides is typically associated with submarine hydrothermal plume activity (German et al., 1991; Ling et al., 2013). Ling et al. (2013) showed that Ediacaran carbonates throughout the Doushantuo formation of shallow-water sections record

Fig. 6. Ce/Ce^* vs. Pr/Pr^* . Field I, neither Ce nor La-anomaly, field IIa positive La-anomaly, no Ce-anomaly, field IIb negative La-anomaly, no Ce-anomaly, field IIIa: positive Ce-anomaly, field IIIb: negative Ce-anomaly. Except the cap carbonates (unit I: dots) most samples clearly plot in the field of negative Ce-anomalies.

negative Ce-anomalies with Ce/Ce^* between 0.71 and 0.92 for Doushantuo, and as low as 0.4 for carbonates from the overlying Dengying formation (551–543 Ma). Because modern oxidised seawater has a Ce/Ce^* ratio < 0.55 , Ling et al. (2013) interpreted the Ediacaran data to indicate the existence of fully oxidized surface waters since the middle Dengying.

Using $Ce/Ce^* < 0.9$ as indicator for real negative Ce-anomalies, we infer anoxic conditions (0.94–0.96) in unit I carbonate rocks, suboxic to oxic conditions in unit II (0.66–0.88) and suboxic to anoxic conditions in units III and IV (0.85–0.92 and 0.81 respectively) (Fig. 2). The only unit that might indicate oxic conditions is therefore unit II, which begins above a phosphoritic hardground at 21 m and which has been discussed as being part of a allochthonous slide sheet which may have originated at shallower slope or platform edge conditions (Vernhet et al., 2006, 2007).

5.3. Origin of abundance variations of redox-sensitive elements

In this section we highlight the role of redox sensitive trace elements (other than Ce) and their enrichment in carbonates due to anoxic and presumably sulfidic pore-water conditions in the sediments.

Abundances of redox-sensitive metals in organic carbon rich shales and iron speciation in sediments have provided the main arguments in support of redox-stratified oceans during most of the Proterozoic (Li et al., 2010; Lyons et al. 2014). According to previous work late Proterozoic oceans may have had very different abundances of redox-sensitive trace elements compared to modern

oxygenated seawater (e.g. Anbar and Knoll, 2002). It is debatable if carbonate rocks may reflect these compositional changes in seawater composition over time, as the influence of secondary diagenetic overprint and redistribution of redox sensitive elements by pore-waters have not been evaluated in detail so far.

Trace element variations in carbonates that formed in different environments are usually discussed in the reference frame of the trace element composition in known sediment compositions. For shales methods have been proposed for trace metals, by calculating the enrichment factor (EF) of an element relative to abundances in an average shale composite (Tribouillard et al., 2006). Here, we will use a similar approach but for the first time by comparison of the element enrichment in analysed samples to element abundances in a modern marine carbonate.

For shales, the enrichment factor of an element is usually calculated as following: $EF_{El} = (X_{El}/Al_{avg. shale})/(X_{El}/Al_{sample})$, where X is the concentration of the trace metal in the bulk rock and $Al_{avg. shale}$ and Al_{sample} are the concentrations of Al in the reference and the sample respectively. Due to acetic acid leaching of Yanwutan samples we are able to only calculate the enrichment factor of the trace elements in the carbonate phase. Relative to average shale all redox-sensitive elements (Mn, Mo, U, V) in the analysed carbonates show strong enrichment up to two to three orders of magnitude for most of the elements in unit I–III and up to four orders of magnitude for Cd and Mo in unit IV (Electronic Supplement Fig. D). Average shale represents an inappropriate normalisation standard for carbonates. This approach produces large uncertainties since carbonate rocks are characterized by very low siliciclastic input and acetic acid leachates of the carbonate fraction will underestimate concentrations of Al, K, Th and Ti in the bulk rock and thus distorts the ratios of elements with different chemical behaviour.

In this work we used a different approach by evaluating the enrichment of Fe, Mn, Mo, U and V and the productivity tracers Ba, Zn and Cd relative to the marine calcium carbonate standard Cal-S for which a broad range of trace element data is available (Yeghicheyan et al., 2003). The carbonate standard Cal-S is a micritic marine limestone, deposited on a shallow water platform at the Eastern border of the Parisian basin during the Tithonian. Cal-S has REE+Y patterns comparable to modern oxidised seawater, showing negative Ce-anomalies and enrichment of HREE relative to LREE. This composition makes it a good material for comparison and evaluation of trace element enrichments in ancient carbonates. Enrichment factors are defined as follows: $EF_{El(CAL-S)} = (X_{El(HAsc)}/Al_{(HAsc)})/(X_{El(CAL-S)}/Al_{(CAL-S)})$. $X_{El(HAsc)}/X_{El(CAL-S)}$ = concentration of redox sensitive element in leachate/reference material CAL-S;

$Al_{(HAsc)}/Al_{(CAL-S)}$ = Al concentration in leachate/reference material CAL-S. $EF_{El(CAL-S)} > 1$ indicates enrichment of element X relative to modern seawater carbonate precipitates, values < 1 indicate depletions (Fig. 7).

To test the influence of silicate phase input on redox sensitive element budgets in carbonate rocks we calculated Al/Ti ratios. The modern shallow water carbonate standard Cal-S used for normalization has 84 $\mu\text{g/g}$ Al and 12 $\mu\text{g/g}$ Ti

Fig. 7. TOC concentration Ce/Ce^* ratios and enrichment factors (EF) of redox-sensitive elements Mn, Fe, Mo, U, V and productivity tracer elements (Ba, Zn, Cd) relative to Jurassic marine limestone CAL-S (=1, dotted line). EF scales are logarithmic. Most redox sensitive elements show no or minor enrichments such as for V from unit II upsection. Ba and Mn are strongly enriched in the samples relative to CAL-S reference material. Sample YAW 535 near the top of the section is strongly enriched in all elements but is also the sample with the lowest carbonate content of all samples. For definition of enrichment factors, see text.

and an Al/Ti ratio of 7. Carbonate leachates from Yanwutan yielded Al/Ti ratios around 50 and show therefore a relative excess of aluminium, possibly due to the dissolution of detrital material, such as clay minerals and subsequent carbonate precipitation (Krye et al., 2003). However the range of variations in the Al concentrations do not exceed those of other trace elements, hence, normalisation relative to the standard does not blur correlations of trace element abundances (Van Der Weijden, 2002). Furthermore there are no correlations of the redox sensitive elements with total Al concentrations nor with the variability in Sr, Ba or oxygen isotope compositions, indicating that the redox sensitive elements have neither been influenced by leaching of silicates nor by late stage post-depositional fluid flow.

Enrichment factors of the redox-sensitive elements (Ba, Mn, Fe, Mo, U, V, Cd and Zn) show strong variability. In comparison to the carbonate standard Cal-S Ba and Mn are strongly enriched throughout the profile whereas the redox sensitive trace metals V, Mo, U, Fe and the bioavailable metals Zn and Cd are significantly depleted within the carbonates of Yanwutan profile (with exception to the upper most unit IV). For Mo, V and U, enrichments in seawater precipitates such as carbonate rocks may indicate oxic to suboxic conditions in the waterbody or near the water/sediment interface since they behave soluble under reducing conditions and get trapped in

non-carbonatic phases like black shales or black cherts (Emerson and Huested, 1991; Calvert and Pedersen, 1993; Tribouillard et al., 2006; Chang et al., 2009).

Depletion of Mo and Fe in carbonates may therefore be indicative for anoxic and even sulfidic conditions in the sediment body since accumulation of Fe in sediments usually occurs as iron sulphides, whereas under ferruginous conditions, Fe^{2+} may also be incorporated into carbonates (Canfield et al., 1993). Enrichment in Fe can only be seen on top of unit II and unit IV respectively. Fe and furthermore Mo depletion relative to modern carbonates ($EF_{(Cal-S)} < 1$) in Yanwutan samples would therefore argue for anoxic or even sulfidic pore-water conditions as Fe and Mo may have been incorporated into non-carbonatic phases such as sulphides.

U and V are depleted throughout the lower units of Yanwutan, with V being slightly enriched at the top from unit II up section. The depletion of U may again be due to incorporation of the redox sensitive element in non-carbonatic phases, whereas V may be less susceptible to reducing pore-waters and therefore show enrichment factors above 1 V may therefore act as the first indicator for a shift to more oxic conditions in basinal bottom waters and slight oxygenation of the pore-water at the end of the Ediacaran, however Mo and Fe depletion at the same time still argue for the presence of H_2S in these units.

Fig. 8. (A) $\delta^{13}C_{org}$ vs. TOC showing negative correlation. (B) Enrichment of Mn concentrations in acetic acid carbonate leachates relative to a pure carbonate standard vs. TOC in bulk rock. Note the weak positive correlation in units I and II (dots and squares, despite one outlier $R^2 = 0.93$) – a possible preserved signal of organic carbon rich Mn compounds getting dissolved and reprecipitated under reducing bottom/pore-water conditions.

Our observations match with recently published datasets from Brazilian Ediacaran sections, revealing generally low trace metal concentrations in marine sediments of the Araras platform at the same time of pyrite formation in presumably anoxic intervals (Sansjofre et al., 2014).

In Yanwutan carbonates the bioproductivity tracers Ba, Cd and Zn yield enrichments towards the top of units I, II and IV for Zn and in some samples of unit II, III and IV for Cd. Barium concentrations in the carbonate rocks are high, which may reflect the release of Ba into early pore-water during bacterial sulphide reduction under reducing conditions (Torres et al., 1996). It should be noted that Ba concentrations originally might have been even higher because they were at least partially affected by the fluid-mobile behaviour of Ba (Fig. 4 and discussion in Section 5.1).

Manganese as Mn^{2+} is thermodynamically unstable and precipitates under oxic conditions as Mn II or Mn IV oxide or hydroxide particulate matter (Bruland, 1983), scavenging other trace elements like REE, especially tetravalent

Cerium (Elderfield et al., 1988; Byrne and Kim, 1990; Alibo and Nozaki, 1999). Therefore modern stratified basins like the Black Sea or the Cariaco Trench show a decrease in Mn^{2+} concentrations in the oxygen rich surface layer and negative Ce-anomalies but under anoxic deep-water environments Mn oxides will redissolve and dissolved Mn concentrations in seawater increase, (de Baar et al., 1988; Lewis and Landing, 1991). Consequently, enrichment factors of Mn in carbonate leachates <1 should indicate Mn depletion in an oxic waterbody. In contrast, $EF-Mn_{(CAL-S)} > 1$ would indicate an excess in dissolved Mn^{2+} due to the dissolution Mn bearing particles leading to local enrichments of Mn in carbonate sediments. Precipitation-dissolution processes of Mn species are prevalent in the water/sediment interface (Thomson et al., 1986). In the Yanwutan carbonate samples the Mn enrichment $EF-Mn_{(CAL-S)}$ of units I and II correlate with an increase in TOC (Fig. 8b), which may indicate dissolution of organic matter associated Mn particulates under early diagenetic anoxic and maybe even sulfidic pore-water conditions. Unit III shows a decrease in $EF-Mn_{(CAL-S)}$ by an order of magnitude with gradually decreasing TOC values. While $EF-V_{(CAL-S)}$ increases at the end of unit II above 1, $EF-Mo_{(CAL-S)}$ and $EF-Fe_{(CAL-S)}$ drop by almost one order of magnitude, indicating a decoupling of these elements and suggesting continued sulfidic conditions within the sediments. Lower enrichments in Mn in unit III argue for less reducing pore-water compositions during the deposition of unit III.

In contrast to the trace metal record arguing for reducing pore-water conditions at least the carbonates of unit II have preserved negative Ce-anomalies as a record of oxic to suboxic conditions in the water column. As all carbonates preserve marine REE+Y patterns, the Ce-anomalies were most likely not lost by contact with reducing bottom or pore-waters.

Given the fact that unit II carbonates record negative $\delta^{13}C_{carb}$ values (−4 to −9) we believe that they were deposited in deeper realms of the Yangtze Platform and not under shallow marine conditions as Vernhet et al. (2006) postulated. The negative Ce-anomalies of unit II would therefore argue for short intervals of suboxic to oxic conditions in the basin at still anoxic to sulfidic pore-water conditions in the sediments.

5.4. Modell for the trace elemental budget in Yanwutan carbonates and effects of reducing pore-waters

1. Development of seawater like REE+Y patterns
REE+Y incorporation onto Fe and Mn oxides/hydroxides and organic compounds respectively. PAAS normalized REE+Y patterns of seawater will show HREE over LREE enrichment and if seawater was partially oxidised a negative Ce anomaly ($Ce/Ce^* < 0.9$) will be visible.
2. The precipitation of carbonates incorporates the REE+Y signatures of the seawater.
3. Remobilization of trace elements under reducing pore-water conditions and incorporation in secondary non-carbonatic phases:

Fe and Mo:

Under the presence of free H_2S (sulfidic pore-water conditions) Fe and Mo may be incorporated into sulfides.

Ba and Mn:

Reducing conditions (presumably with the help of bacterial sulfate reduction) can liberate labile Ba and Mn phases. Due to their fluid-mobile behaviour they will redistribute within the profile, eventually reprecipitating as Barite or Ba- and Mn-rich carbonates along the redoxfront.

V, U and the bioavailable redox metals like Zn and Cd:

The redox sensitive metals are soluble under reducing conditions. In consequence they get relatively depleted in the carbonate phases and commonly enrich in black-shales.

REE+Y:

The lanthanides concentrations within the carbonates may not be susceptible to reducing pore-water overprint as all acetic acid leachates show no correlated enrichment in redox sensitive elements and total REE concentrations. Furthermore all carbonates still preserve seawater-like REE+Y signatures and (most prominent in unit II) negative Ce anomalies, indicating oxidising conditions in the water column at the time of their precipitation.

On the basis of Ce/Ce^* , the water column of the basin sampled by carbonate sediments of the Yanwutan section was probably oxic (part of unit II) to suboxic/anoxic (unit III) during the Ediacaran, providing further arguments for anoxic conditions in deeper marine realms of the Yangtze basin between 635 and 551 Ma.

Throughout this time interval, sediments deposited in the basin were anoxic and even sulfidic, leading to a release of redox sensitive trace metals into the pore-waters and presumably capture of some Fe and Mo into sulfides.

The $\delta^{13}\text{C}_{\text{carb}}$ data are decoupled from other tracers. We note that the negative and variable $\delta^{13}\text{C}_{\text{carb}}$ in the cap dolomites may reflect alteration processes, however, the consistently negative values in units II to IV offer no indication for an origin by diagenetic alteration and fluid flow (in contrast to fluid-mobile elements such as O, Sr and Ba). Our data may support the ideas of a large DOC pool in the deep basin areas, which was oxidised as a result of bacterial activity (Ader et al., 2009). According to Ader et al., 2009 high TOC values and correspondingly low $\delta^{13}\text{C}_{\text{org}}$ in the lower Doushantuo of Yanwutan and Fengtan (Yuanling) sections might be explained by secondary productivity (e.g. activity of methanotrophs (Gong and Hollander, 1997; Hinrichs et al., 2000)) and limited organic matter mineralisation under anoxic conditions, and thus increasing the TOC and trace metal contents in sediments. The decoupling of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ is most prominent in unit II of Yanwutan section (Ader et al., 2009), perhaps due to the partial oxidation of a large DOC pool as proposed for the Mid-Ediacaran Shuram-Woonoka anomaly (Fike et al., 2006). Unit III shows a slow return of $\delta^{13}\text{C}_{\text{carb}}$ to less negative values (−7) and the lowest $\delta^{13}\text{C}_{\text{org}}$ of −34.

Presumably, this reflects a higher oxidation potential, however, the absence of negative Ce-anomalies indicates that the formation conditions of the carbonates at that time remained anoxic.

6. CONCLUSION

Dolomitic rocks from the Doushantuo Formation at Yanwutan (Hunan, China) provide the rare opportunity to study a relatively coherent deep-water section of the Ediacaran on the Yangtze Platform. Compared to surface water carbonates all Yanwutan samples were precipitated from deep waters which were likely more enriched in ^{12}C , in stark contrast to data from shallow water sections on the Yangtze Platform (e.g. Xiao et al., 2012). In most samples of the present work, diagenetic fluid-flow led to a substantial redistribution of fluid-mobile elements, notably, losses of Sr and Ba, and addition of radiogenic Sr and light oxygen from typical continental basin fluids. In spite of the alteration of fluid-mobile elements, some samples, including the uppermost cap carbonate, display primary carbon isotope signatures that appear to reflect marine water compositions and processes in their original depositional environments and their evolution. As in shallow-water environments on the platform, cap dolomites were initially precipitated after the Marinoan glaciation. However, in contrast to platform settings Yanwutan cap dolomites show no negative Ce-anomalies, indicating anoxic depositional conditions and thus a chemically stratified water mass in the basin (Canfield, 1998; Li et al., 2010). A presumably partially allochthonous dolostone unit shows negative Ce-anomalies which disappear towards the top consistent with carbonate precipitation under oxic to suboxic conditions.

Redox sensitive elements like Fe, Mo, U and V are depleted compared to Phanerozoic platform carbonates, whereas Mn and Ba are strongly enriched, suggesting anoxic and even sulfidic pore-water conditions, which may not have overprinted the partly negative Ce anomalies inherited from a precipitation in an suboxic to oxic seawaterbody. An increase in the abundances of redox sensitive elements towards the top of the Yanwutan section (especially in V concentrations) may indicate a change to less reducing conditions in the later Ediacaran. The trace element data and the decoupling of $\delta^{13}\text{C}_{\text{carb}}$ from $\delta^{13}\text{C}_{\text{org}}$ may be explained by the partial remineralisation of organic matter in the deep marine environment (Ader et al., 2009).

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2015.04.037>.

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