

MULTI-PROXY ANALYSIS OF EDIACARAN SHALLOW- AND DEEP WATER CARBONATES, YANGTZE PLATFORM, SOUTH CHINA

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Dissertation submitted in partial fulfilment of the requirements for the degree of

Doktor der Naturwissenschaften (Dr. rer. nat.)

Fachbereich Geowissenschaften

Freie Universität Berlin

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September, 2015 - Berlin, Germany

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03.11.2015

ERKLÄRUNG

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Berlin, den 02.09.2015

SUMMARY

The Ediacaran era (635 to 542 Ma) has seen some of the largest geochemical fluctuations and biological innovations in Earth history. The change from icehouse to greenhouse climate resulted in melting of low latitude Marinoan ice sheets and presumably triggered the radiation of early animals at the Precambrian/Cambrian boundary. Contemporaneous oxygenation of the Earth's atmosphere and presumably the deeper oceanic realms further led to evolution of metazoans, predation and, as a result, extended bio-mineralisation.

The Doushantuo Formation on the Yangtze Platform, South China, is an ideal archive of temporal and spatial geochemical changes in the late Neoproterozoic oceans, as it spans 90 % of the Ediacaran (635 ± 0.6 to 551 ± 0.7 Ma) and was deposited under shallow- to deep water marine environmental conditions.

The major scope of this thesis is to understand the geochemical variations in Ediacaran marine carbonates and link them to environmental changes. Therefore carbonate rock leachates of the Doushantuo (and overlying Dengying) lithologies from the shallow water Xiaofenghe (Hubei Province) and deep water Yanwutan section (Hunan Province) have been sampled. These samples were investigated for their major- and trace element concentrations as well as for their $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{carb}}$ isotopic compositions. Radiogenic Sr and stable C and O isotopes were used to distinguish between pristine marine precipitates and those whose isotopic compositions have been modified by post depositional fluid flow. Paleo-seawater conditions, such as oxygenation of the water body and seawater-freshwater mixing were inferred from shale normalised REE+Y patterns of pristine carbonates. Redox-sensitive elements were used to assess pore-water redox conditions in the sediments. Furthermore, the Nd isotopic composition of shallow water carbonates was analysed to deduce the provenance of the lanthanide source of the Yangtze Platform sediments.

Finally this thesis aims to test whether Cd isotopes may be used to pinpoint the onset of bio-diversification and the appearance of early animals before the Cambrian explosion. Therefore Cd isotopes were analysed together with $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}$, TOC and N concentrations in carbonates and mudstones from the extreme shallow water section Xiaofenghe, Hubei Province.

This thesis provides deeper insight into carbonate diagenesis and focuses on the recognition of pristine, open marine seawater geochemical signatures from signatures modified by either mixing with freshwater or diagenetic overprint. Deep water carbonates at Yanwutan section show a distinct overprint by continental basin fluids, strongly modifying the isotope composition of the sediments. Despite this, marine REE+Y patterns are commonly still preserved in these lithologies. Shallow water carbonates at Xiaofenghe section reveal minor diagenetic overprint. However, the influence of terrestrial lanthanide input, presumably brought in by freshwater influx via estuarine mixing processes, strongly modified REE+Y patterns in the very shallow to lagoonal Xiaofenghe section.

N and Cd isotopic compositions of mudstones and carbonates in the same stratigraphic units reveal distinct fluctuations that cannot be explained by biological fractionation alone. Hence, $\delta^{15}\text{N}$ variations might be the result of isotope fractionation during diagenetic N-loss. The variation in

$\epsilon^{112/110}\text{Cd}$ may be caused by isotope fractionation during Cd incorporation in sulphides and likely modified by salinity-dependent fractionation during carbonate precipitation. The work suggests that the Cd isotope composition of Neoproterozoic carbonates, unlike modern marine precipitates, may not be used as proxy for biological Cd utilisation. It is likely that the modern enzyme responsible for the isotopically selective Cd utilisation in phytoplankton may not have been active in Precambrian organisms yet.

ZUSAMMENFASSUNG

Das Ediakarium (635 bis 542 Ma) war eine Periode gewaltiger geochemischer Umwälzungen und biologischer Innovationen. Der Wechsel von der marinoischen Eiszeit zum Treibhausklima ging einher mit massivem Abschmelzen der Eispanzer und mag durch den damit verbundenen Eintrag von Nährstoffen von den Kontinenten mit als Auslöser für die folgende Evolution von Metazoen gedient haben. Des Weiteren trug die zeitgleiche Sauerstoffanreicherung der Atmosphäre und der tieferen Schichten der Ozeane zur Evolution der Mehrzeller, sowie der Entwicklung von Jagdverhalten und daraus resultierend zur Entwicklung von Biomineralisation als Abwehrmechanismus bei.

Die Doushantuo Formation auf der Yangtse Plattform in Südchina gilt als perfekte Lokalität zur Erforschung von zeitlichen wie auch räumlichen geochemischen Veränderungen im ediakarischen Ozean. Die Formation wurde auf 635 ± 0.6 bis 551 ± 0.7 Millionen Jahre vor heute datiert und umfasst damit etwa 90 % des gesamten Ediakariums, des Weiteren finden sich in ihr unterschiedliche Ablagerungsräume vom Flach- bis hin zum Tiefwasser vereint.

Das Hauptanliegen dieser Arbeit besteht darin, die geochemischen Variationen in ediakarischen Karbonaten besser zu verstehen und durch diese auf die sich verändernden Umweltbedingungen im Ediakarium zurück zu schließen. Dafür wurden Karbonatauszüge von Doushantuo (und darüber anstehenden Dengying) Lithologien des Flachwasserprofils bei Xiaofenghe (Hubei Provinz) und des Tiefwasserprofils bei Yanwutan (Hunan Provinz) untersucht. Von den Proben wurden Haupt- und Spurenelementkonzentrationen sowie $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}_{\text{carb}}$ und $\delta^{13}\text{C}_{\text{carb}}$ Isotopenzusammensetzungen bestimmt. Radiogene Sr- und stabile O- und C-isotopenverhältnisse wurden als Indikator zur Abgrenzung von diagenetisch überprägten zu pristinen Karbonatproben genutzt. Paleo-Meerwasserbedingungen, wie die Sauerstoffsättigung oder der Einfluss von Frischwasser, wurden mittels PAAS normalisierter Seltener Erden Muster bestimmt. Die Analyse redox-sensitiver Elemente diente schließlich dazu Porenwasser Redoxbedingungen zu erfassen. Nd-Isotopenverhältnisse in den Flachwasserkarbonaten wurden zur Bestimmung der Herkunft der Lanthanidenquelle in den Karbonaten analysiert.

Abschließend wurde mit der Arbeit versucht Cd Isotope als Indikator für das Einsetzen verstärkter Biodiversität und dem Aufkommen der ersten Tierstämme im späten Ediakarium zu etablieren. Daher wurden neben Cd in Karbonaten auch N Isotopenverhältnisse in organikreichen Lithologien zusammen mit TOC und N Konzentrationen sowie $\delta^{13}\text{C}_{\text{org}}$ Werten im Xiaofenghe Flachwasserprofil bestimmt.

Die Arbeit gibt weitergehende Einblicke in die Karbonatdiagenese und versucht die Unterschiede zwischen pristinen und offenmarinen geochemischen Signaturen von überprägten Signaturen in Karbonatgesteinen (letztere durch Diagenese oder Mischung von Wassermassen) zu charakterisieren. Daraus resultierend, haben die Tiefwasserproben des Yanwutan Profils eine stärkere diagenetische Überprägung der Isotopensignaturen als die Flachwasserkarbonate erfahren. Diese Überprägung lässt sich vermutlich auf die Reaktion der Karbonate mit kontinentalen Beckenfluiden zurückführen. Diese Überprägung hat jedoch im allgemeinen die marinen seltenen

Erden Muster der Karbonate nicht verändert. Dahingegen zeigen die Flachwasserkarbonate von Xiaofenghe eine Veränderung der seltenen Erden Muster durch verstärkten Eintrag der Lanthaniden in Flussmündungsnähe.

N und Cd Isotopenzusammensetzungen in organikreichen Tonsteinen und Karbonaten der gleichen stratigraphischen Einheit zeigen starke Veränderungen durch das Ediakarium. Diese lassen sich nicht allein auf biologische Isotopenfraktionierung zurückführen. $\delta^{15}\text{N}$ Variationen könnten auch auf Isotopenfraktionierung bei diagenetischer Stickstoffabfuhr im Sediment zurückzuführen sein. Die Variationen in $\epsilon^{112/110}\text{Cd}$ werden möglicherweise durch Isotopenfraktionierung bei einem selektiven Einbau von Cd in Sulphide unter euxinischen Bedingungen, sowie salinitätsabhängiger Fraktionierung in Karbonate gesteuert. Als Resultat der Arbeit wird daher angenommen, dass die Cd Isotopenzusammensetzung von neoproterozoischen Karbonaten nicht von biologischer Fraktionierung gesteuert wurde. Anders als bei modernen marinen Sedimenten war damit das Enzym, das für die Cd Isotopenfraktionierung beim Einbau des Cd in phytoplanktonische Organismen verantwortlich ist, im Präkambrium vermutlich noch nicht aktiv.

摘要

在埃迪卡拉时期（635 至 542Ma），与生命大爆发有关的地球化学环境发生了剧烈波动。由于当时地球从冰窖环境转变为温室气候，低纬度地区的 Marinoan 冰盖开始融化，这一转变被认为是诱发前寒武纪/寒武纪生命大爆发的原因之一。与此同时，地球大气层以及深海中的氧气含量的增加，进一步加速了多细胞动物的演化和相关食物链的形成，以及由此而来的更为广泛的生物成矿作用。

中国南方扬子地台的陡山沱组，是研究新元古代末期海洋地球化学特征时空演化的理想对象，它跨越 90% 的埃迪卡拉期（ 635 ± 0.6 至 551 ± 0.7 Ma），记录了当时从浅海沉积环境到深海沉积环境。

本文主要研究目的是通过对埃迪卡拉时期海洋地球化学特征的变化，探讨当时的地球表层环境。本文的主要研究对象为陡山沱组的碳酸岩，样品采自湖北地区属于浅水相的小峰河段和湖南地区属于深水相九龙湾段。本文主要测定了所采样品的主微量元素的丰度、 $^{87}\text{Sr} / ^{86}\text{Sr}$ 、 $\delta^{18}\text{O}_{\text{carb}}$ 和 $\delta^{13}\text{C}_{\text{carb}}$ 同位素组成。放射铯同位素和稳定碳氧同位素可被用以指示后期成岩作用，而通过微量元素的页岩标准化可以研究古海洋环境下淡水/海水混合过程。对氧化还原过程敏感的微量元素还可以用来评估沉积孔隙水的氧化还原特征。此外，浅水碳酸盐岩的 Nd 同位素组成可以用来推断扬子地台沉积过程的镧系元素的来源。

最后，通过对铬同位素的研究，探讨是否能用铬同位素研究寒武纪早期的生命多样性。因此，通过对小峰河段极端浅水相样品中镉同位素、 $\delta^{13}\text{C}_{\text{org}}$ 、TOC、氮的丰度以及 $\delta^{15}\text{N}$ 的研究，探讨是否能用镉同位素来指示前寒武纪早期的生命多样性。

本文深入研究了碳酸盐成岩过程中海水和淡水的混合作用，并由此探讨原始海洋沉积的地球化学特征。与斜坡-深水相的盖帽碳酸岩不同，岩屋潭段的深水碳酸岩形成过程中，其同位素特征被陆相盆地流体强烈改造。尽管如此，岩屋潭段的 REE + Y 标准化配分模式依然保留海相特征。三峡地区小峰河段的浅水碳酸岩和盖帽碳酸岩的后期成岩作用非常微弱，然而由于海陆混合过程中陆源沉积物的输入，其 REE + Y 标准化配分模式受到了强烈改造。

生物分馏过程本身不足以解释泥岩和碳酸岩的氮-铬同位素变化。 $\delta^{15}\text{N}$ 变化可能由于成岩过程中的 N 的损失。 $\epsilon^{112/110}\text{Cd}$ 的变化可能是由于先期硫化物吸纳铬引起铬同位素分馏，后期又在不同盐度环境下的盐酸盐沉积过程中发生改造。本文研究表明，与现代海洋沉淀物不同，铬同位素不能指示新元古代碳酸岩中镉的生物作用。现代海洋环境中，浮游植物通过代谢铬而引起铬同位素分馏的作用可能在前寒武纪尚未出现。

ACKNOWLEDGEMENT OF FINANCIAL SUPPORT

The German Research Foundation, DFG:

DFG Research Group FOR 736 “The Precambrian-Cambrian Biosphere Revolution: Insights from Chinese Microcontinents”, subproject Be 1820/4-2 to H. Becker

The National Science Foundation of China, NSFC:

Grants (41230102, 41273009) and a 973 project (2013CB835000) to SY Jiang and JH Yang

Center for International Cooperation at Freie Universität Berlin:

Travel grant to Nanjing University for laboratory work, spring 2013 (to H. Becker)

Confucius Scholarship, China

Intensive language course grant at Nanjing University, spring 2015 (to S.V. Hohl)

ACKNOWLEDGEMENTS

I would like to thank Monika Feth and Konrad Hammerschmidt for their support in the lab and the Members of FOR 736 who helped in sampling the analysed rocks in the field in South China and other members for their helpful discussions, especially Christoph Heubeck and Xiaojuan Sun for providing sedimentology feedback and Michael Tatzel for invaluable input during daylong discussions.

I would like to thank Uwe Wiechert for his help analysing O and C isotopic compositions in carbonates, Frank Ohnemüller and the University of Bremen, Central Laboratory for Crystallography and Applied Material Sciences for XRD analysis and Antonia Gamper and the staff of Museum für Naturkunde for their contributions to stable isotope data.

Thanks also to the Chinese contributors of the Sino-German Research Group, in particular to Shao-Yong Jiang from the China University of Geosciences in Wuhan for his help in revising my work. From Nanjing University I would like to thank Jing-Hong Yang and Hai-Zhen Wei for their help analysing Nd isotopic compositions and Hong-Fei Ling, Da Li, and all members of their group for their heartily welcome in Nanjing.

Further I thank Steve Galer and Wafa Abouchami and the scientific staff at the Max Planck Institute für Chemie in Mainz for their help analysing Cd isotopes.

Finally I would like to thank my wonderful friends in Bonn, Berlin, Seoul, New York, Shanghai and Nanjing as well as my parents for their long lasting support.

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CHAPTER 1

INTRODUCTION

1.1 The Ediacaran period

The Ediacaran era represents the terminal period of the Neoproterozoic. It is characterised by fundamental global environmental changes, including the increasing oxygenation of the atmosphere and oceans (Knoll et al., 2004) as well as biological innovations such as the first appearance of acanthomorphic acritarchs (Zhou and Xiao, 2007), the evolution of multicellular life (e.g. Xiao et al., 1998; Yin et al., 2007; 2011), the Ediacaran biota (e.g. Waggoner, (2003) and references therein), and the first bio-mineralising animal *Cloudina* (Grant, 1989).

The Ediacaran starts with the deposition of a globally occurring characteristic cap carbonate stratum that overlies glacial deposits of the low-latitude Marinoan glaciation (Kirschvink, 1992). A GSSP point at the base of the Nuccaleena Formation cap carbonates (Flinders Range, South Australia) defines the beginning of the era (Knoll et al., 2006) and U-Pb zircon ages from ash beds within cap carbonates from the base of the Doushantuo Formation (Yangtze Gorges, South China) date their deposition 635.2 ± 0.6 Ma ago (Condon et al., 2005).

The melting of the presumably global Marinoan glaciation was most likely a result of elevated $p\text{CO}_2$ in the atmosphere, triggering super-greenhouse conditions (Hoffman, 1998). Coeval silicate weathering (Kennedy et al., 2006) along biological induced weathering by the emergence of fungi and lichen biota on land (e.g. Kump, 2014) may have increased the total nutrient flux into the oceans during the Ediacaran period. This flux presumably led to increased P/Fe ratios recorded in post Marinoan iron formations (Planavsky et al., 2010), may account for the rising $^{87}\text{Sr}/^{86}\text{Sr}$ record in marine carbonates during the Neoproterozoic and could have finally triggered the rise of animal life at the end of the Neoproterozoic (e.g. Kennedy, 2006).

Ediacaran marine sediments host major perturbations in the carbon cycle of the ocean. Following the globally occurring negative $\delta^{13}\text{C}_{\text{carb}}$ excursions in Marinoan cap carbonates, negative $\delta^{13}\text{C}_{\text{carb}}$ values occurring in some carbonate successions around the globe (e.g. Newfoundland) 580 Ma ago are believed to indicate the localised Gaskiers glaciation (Krogh et al., 1988). The middle Ediacaran further hosts the most pronounced negative $\delta^{13}\text{C}$ inorganic carbon anomaly in Earth's history with values in successions of Oman dropping down to a nadir of -12 ‰ (Le Guerroué et al., 2006). This so called Shuram-Wonoka anomaly has been identified in carbonate sections around the globe, yet its origin is highly debated. Hypotheses include oxidation of a huge dissolved carbon pool in the deep ocean during the rise of atmospheric and ocean $p\text{O}_2$ levels (Fike et al., 2006, McFadden et al., 2008), methane oxidation (Bjerrum and Canfield, 2011) and a burial diagenesis origin (Derry, 2010a; Swart and Kennedy 2011). Together with reasonable doubts that the Shuram-Wonoka anomaly reflects primary seawater compositions more and more publications challenge the role of carbon isotopes as reliable proxies for inter-platform or even global correlation of Ediacaran successions (e.g. Derry 2010b).

While early work on the Ediacaran mostly focused on the evolution and global correlation of the carbon isotopic composition in the Ediacaran ocean (Kaufman et al., 1997; M. Zhu et al., 2007), nowadays the tool box has been enlarged to include a range of geochemical proxies that have been applied to Ediacaran sediments around the world. To gather insights into paleo-weathering rates researchers are using Sr and Ca isotope compositions (Kasemann et al., 2005; Pokrovsky et al., 2011; Sawaki et al., 2008) and paleo-seawater pH may be inferred from boron isotope compositions (Ohnemüller et al., 2014). Other isotope systems such as Si, N, and Zn isotopes are used to study the effect of the biological fractionation of these stable isotope systems during the onset of complex multicellular life (Ader et al., 2014; Cremonese et al., 2013; Fan et al., 2014; Kunzmann et al., 2012). Sulphur, Fe, Mo and Cr isotopic compositions as well as iron speciation and redox-sensitive trace element analysis (Canfield et al., 2008; Fan et al., 2014; Frei et al., 2011; Wen et al., 2011) are used to gather information about ocean and atmosphere redox conditions and to test recent models of a redox stratified Ediacaran ocean developed on the Yangtze Platform (e.g. Li et al., 2010). Furthermore, numerous studies have shown that ratios and patterns of the rare earth elements (REE) and yttrium in carbonate rocks not only mirror the patterns of these elements in water from which they precipitated (Kamber and Webb, 2001; Nothdurft et al., 2004; Webb and Kamber, 2000) but also yield information about the paleo-seawater oxidation state (e.g. Ling et al., 2013).

1.2 OCEAN OXIDATION DURING THE TERMINAL PROTEROZOIC

The evolution of the modern oxygen-rich atmosphere and oceans apparently occurred in two major steps. The first major oxygenation step to levels higher than 10^{-5} present atmospheric level (PAL) was discovered by the diminishing of mass-independent fractionation (MIF) signals of sulphur isotopes in sediments younger than 2.45 Ga (e.g. Farquhar 2000). The second major oxygenation step took place in the late Neoproterozoic 0.8 - 0.6 Ma ago. It was until then, that deep ocean ventilation was not completely achieved and bio-essential but redox-sensitive metals bound in anoxic deep ocean sediments were not as available as in modern oceans. This restraint of bio-essential metals may also have restricted the evolution of animals before the late Neoproterozoic (e.g. Anbar and Knoll, 2002).

Some striking geochemical results from global occurring terminal Proterozoic marine sediment records suggest that the oceans of this period finally underwent a stepwise and protracted oxidation (e.g. Li et al., 2010). For example the fractionation of sulphur isotopes shifted from mass-independent fractionation before the GOE to mass dependent fractionation. The S isotope compositions of the Neoproterozoic were presumably influenced by the development of non-photosynthetic sulphide-oxidising organisms, leading to increasing $\Delta^{34}\text{S}$ values due to oxygenation of the atmosphere and the persistent ventilation of the deep ocean (e.g. Canfield and Teske, 1996; Canfield, 1998). Further arguments for the oxygenation of the oceans and atmosphere in the terminal Proterozoic are: long-living prolonged positive $\delta^{13}\text{C}_{\text{carb}}$ values with some (but extreme) negative $\delta^{13}\text{C}_{\text{carb}}$ excursions like the Shuram-Wonoka (which represents the largest relative change in $\delta^{13}\text{C}_{\text{carb}}$ in geologic time (e.g. Kaufman and Knoll, 1995)), authigenic accumulations of Mo and other redox-sensitive metals in sulfidic black shales towards the end of the Neoproterozoic (e.g. Scott et al., 2008), increasing negative Ce anomalies in carbonates at the Ediacaran/Cambrian boundary (Ling et al., 2013) and positive $\delta^{53}\text{Cr}$ excursions in Ediacaran carbonates (Frei et al., 2009).

The reasons for the oxygenation in the late Neoproterozoic are still debated. Canfield et al. (2007) and Planavsky et al. (2010) suggested that glacial melting increased nutrient influx and postglacial phosphate flux to the oceans, triggering primary productivity and subsequent burial of organic matter (OM). The publications by Derry (2006) and Kump (2014) point out that the weathering environment on the land surface changed from a solely physical to a biochemical weathering due to the evolution of fungi and lichen leading to the formation of fine grained soils and burial of OM after riverine transportation into the ocean. OM burial finally resulted in a net increase

in pO_2 as less oxygen is consumed for its oxidation. An alternative hypothesis by Lenton et al. (2014) is the establishment of a positive feedback system of evolution of complex eukaryotes, benthic filter feeding, phosphorous removal and deep ocean oxygenation.

However, while more and more geochemical studies point out that deep ocean basins could have been completely oxygenated by the end of the Neoproterozoic (Fike et al., 2006; Scott et al., 2008), Canfield et al. (2008) suggested a conflict with evidence for anoxic deep waters with ferruginous (Fe^{2+} enriched) or even euxinic (sulphides present) conditions persisting into the Cambrian. The redox stratified ocean model by Li et al. (2010) showed that a deep anoxic ocean might have maintained on the Yangtze Platform throughout the whole Ediacaran period. A recent publication by Sperling et al. (2015) even argues, on the base of a statistical evaluation of iron speciation data through Earth's history that the terminal Proterozoic oxygenation was limited and significant rise in ocean-atmosphere oxygen to present levels did not happen before the Palaeozoic era.

1.3 RESEARCH GOALS AND SCOPE OF THE THESIS

This dissertation is part of the larger framework of the Sino-German DFG Research Group FOR 736 "*The Precambrian-Cambrian Biosphere Revolution: Insights from Chinese Microcontinents*". The research project focused on marine sediments on the Yangtze Platform (South China) from the late early Ediacaran (above the glaciogenic sediments of the Marinoan glaciation) to the early Cambrian. The objective of the project was to understand the underlying processes of the Precambrian/Cambrian bio-radiation by constraining paleo-environmental conditions using a multidisciplinary (sedimentology, palaeontology, and geochemistry) approach.

The occurrence of shallow- and deep water sedimentary facies has established the Yangtze Platform in South China as a key area for the study of Neoproterozoic ocean oxidation and Ediacaran animal evolution following the Marinoan glaciation. The Doushantuo Formation directly overlies the tillites of the Marinoan Nantuo Formation. It has been precisely dated between 635.2 ± 0.6 and 551.1 ± 0.7 Ma and spans about 90 % of the Ediacaran (Condon et al., 2005) and due to its in most sections continuous marine sediment record it is ideal for high-resolution geochemical analysis of paleo-ocean chemistry. Furthermore the Doushantuo and overlying Dengying strata contain a vast fossil record, including animal embryos and macroscopic algae (Xiao et al., 1998).

The aim of this thesis is to understand the geochemical variations in Ediacaran marine carbonates from the Yangtze platform and link them to environmental changes. Therefore carbonate rock leachates of the Doushantuo and overlying Dengying lithologies from the shallow water Xiaofenghe (Hubei Province) and deep water Yanwutan section (Hunan Province) have been sampled. Together with my supervisor Harry Becker and several collaborators from Germany and China we investigated marine sediments for their major- and trace element concentrations as well as for their Sr, Nd, C, O, N and Cd isotopic compositions. Radiogenic Sr and stable C and O isotopes were used to distinguish between pristine marine precipitates and those whose isotopic compositions have been modified by post-depositional fluid flow. Paleo-seawater conditions, such as oxygenation of the water body and seawater-freshwater mixing were inferred from shale normalised REE+Y patterns of pristine carbonates. Redox-sensitive elements were used to assess pore-water redox conditions in the sediments. Nd isotopic composition of shallow water carbonates were analysed to deduce the provenance of the lanthanide source of the Yangtze Platform sediments. Additionally N and Cd stable isotope compositions from organic-rich lithologies and carbonates were obtained in the shallow water Xiaofenghe section to infer biological induced variations in these isotopic systems. Furthermore we tested whether Cd isotopes are a useful proxy to pinpoint the onset of biological diversification and the evolution of multi-cellular life short before the Precambrian/Cambrian boundary.

This dissertation aims to answer the following questions:

I How did alteration and post-diagenetic fluid flow affect the chemical compositions of Ediacaran carbonate rocks of the Yangtze Platform?

Before interpreting element concentrations and isotopic compositions in Proterozoic carbonates the role and amount of presumable diagenetic overprint of the studied lithologies has to be evaluated. In detail we try to test whether thorough petrographic pre-screening of the studied samples and modelling of mixtures of pristine marine precipitates (deduced from publications and modern analogues) with possible fluids overprinting the carbonate rocks can be used for distinguishing the impact of diagenetic alteration.

II Are there systematic differences in trace element signatures and isotopic compositions in shallow- and deep water sediments?

This is of particular interest to understand the temporal and lateral variations of the used

proxies in Ediacaran carbonates. In detail we want to assess the influences of continental input by weathering, riverine inflow and redox conditions on REE+Y, redox sensitive elements, Sr and Nd isotopes in marine carbonate precipitates.

III What processes control REE abundances, patterns and Ce anomalies in Ediacaran shallow water vs. deep water carbonates?

Shale normalised REE+Y patterns of marine carbonates are capable of recording secular changes in marine seawater compositions. Authigenic marine sediments may be used to infer paleo marine conditions in particular the influence on freshwater/seawater mixing as well as the redox state of the water body by comparing them with modern analogues.

IV What processes control the budget of redox sensitive trace elements in Ediacaran carbonate rocks from the deep and shallow Yangtze Platform?

Many researchers use redox-sensitive trace element enrichments in organic-rich shales to infer the redox state of the coexisting seawater. However the distribution of these elements in carbonate facies is poorly understood but it may help in our understanding of the syn- and post sedimentary processes linked to changes in the redox state of seawater and pore-water they precipitated out of.

V Can Cd isotope compositions be used as a new proxy for the onset of biological innovation and diversification?

Stable Cd isotopes are used in marine geochemistry to infer nutrient utilisation and bio-productivity in modern oceans. This geochemical proxy may further be used in Proterozoic carbonate rocks to assess whether biologic fractionation of stable Cd isotopes played a significant role at this crucial point in the history of the evolution of multicellular life.

The thesis is divided into six sub chapters. Three main chapters, each designed for individual publication, follow the introductory chapter. Chapter 5 is a conclusion chapter that summarises the obtained findings. Chapter 6 lists the scientific output generated by the author within the PhD project. Finally sections visited during fieldwork in South China are listed in Appendix (A I) and a brief analytical protocol is given for all measured trace- and major elements as well as the obtained isotopic compositions in Appendix (A II).

1.4 MAIN CHAPTERS OF THE THESIS

1.4.1 CHAPTER 2 (*PUBLISHED IN GEOCHIMICA ET COSMOCHIMICA ACTA 2015. 163, 262-278*)

The focus of the first manuscript is to gather insights in the processes of early diagenetic effects on carbonate sediments in order to be able to distinguish primary from altered geochemical signatures within the analysed rocks. Therefore the publication in GCA (Hohl et al., 2015) deals with the role of fluid-flow overprint on deep water Doushantuo carbonate rocks and early diagenetic effects on redox-sensitive element budgets. Qing-Jun Guo from the Centre for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing provided the sample powders, which were taken on a field campaign in South China in 2008. MSc student Stefan Herzlieb did chemical separation work and assisted in the analysis of the main- and trace elements and Sr isotope compositions using ICP-MS and TIMS. Some results of this work were described in his MSc thesis „Element- und Isotopenzusammensetzung von Karbonatgesteinen der Beckenfazies des Ediacariums der Yangtze Plattform (Südchina)“. Simon Hohl carried out sample analysis and data reduction, designed the modelling of fluid overprint on the carbonates, calculated the enrichment factors of redox sensitive elements relative to modern marine calcite standard CAL-S and wrote the final manuscript. Harry Becker obtained the funding for the project and helped in discussing the data and revising the manuscript.

1.4.2 CHAPTER 3 (*MANUSCRIPT SUBMITTED TO PRECAMBRIAN RESEARCH*)

The second manuscript deals with the influence of freshwater influx on a shallow water platform environment and the resulting trace element; Sr and Nd compositions in carbonate leachates. The main Collaborator in this project was Shao-Yong Jiang from the State Key Laboratory of Geological Processes and Mineral Resources, Faculty of Earth Resources, China University of Geosciences, Wuhan who organised the fieldwork and helped in the collection of the analysed carbonate samples. Further he and his team (Jing-Hong Yang and Hai-Zhen Wei) at the laboratory for Mineral Deposits Research, Department of Earth Sciences at Nanjing University helped in analysing the Nd isotopic compositions using MC ICP-MS. Antonia Gamper of Museum für Naturkunde Berlin, Leibniz Institute for Evolution and Biodiversity Science, Berlin helped in analysing the organic carbon isotope compositions and total organic carbon concentrations of the studied lithologies, while Uwe Wiechert provided carbon and oxygen isotope measurements in carbonates at his laboratory at the Institute for Geosciences at Freie Universität Berlin. Simon Hohl was responsible for sample

preparation, chemistry, data analysis and reduction and wrote the manuscript. Harry Becker organised the funding for the sample selection in South China, the trace- and major element analysis at Freie Universität Berlin as well as for the research stay at Nanjing University (spring 2013) for analysing Nd isotope compositions. Furthermore he helped in interpretation of the data and revised the manuscript.

1.4.3 CHAPTER 4 (UNPUBLISHED MANUSCRIPT)

The third manuscript tries to further enlarge the isotopic toolbox for pinning the onset of Ediacaran animal evolution. We used Cd stable isotopes, a new geochemical tracer and present the first Cd isotope dataset for Neoproterozoic carbonates. The purpose of this manuscript is to answer if modern biological fractionation of Cd isotopes (presumably controlled by biological uptake within the Cd anhydrase enzyme) was already present in the Ediacaran. Steven J. Galer helped in setting up a method for separation of Cd in carbonates and the analysis of spiked samples using TIMS at Max Planck Institut für Chemie, Mainz. Antonia Gamper of Museum für Naturkunde Berlin, Leibniz Institute for Evolution and Biodiversity Science, Berlin helped in analysing the organic carbon isotope compositions and total organic carbon concentrations as well as the N isotopic composition of the studied lithologies. Simon Hohl did the chemical separation and assisted during the measurement of Cd isotopes at Max Planck Institut für Chemie, Mainz. He interpreted the data and wrote the manuscript. Harry Becker provided funding for two trips to Mainz, helped discussing the obtained results and revised the manuscript.

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CHAPTER 2

MULTIPROXY CONSTRAINTS ON ALTERATION AND PRIMARY COMPOSITIONS OF EDIACARAN DEEP WATER CARBONATE ROCKS, YANGTZE PLATFORM, SOUTH CHINA

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2.1 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 ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70775$, $\delta^{18}\text{O} = -4$, $\delta^{13}\text{C}_{\text{carb}} = 1.1$), 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.

2.2 INTRODUCTION

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CHAPTER 3

Secular changes of water chemistry in shallow water Ediacaran ocean: Evidence from carbonates at Xiaofenghe, Three Gorges area, Yangtze Platform, South China

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3.1 ABSTRACT

Ediacaran carbonates from the shallow water section near Xiaofenghe (Three Gorges area, Hubei Province) on the Yangtze Platform, South China have been studied to understand post Marinoan changes in seawater chemistry. Major- and trace element abundances and Sr-Nd isotopic compositions were obtained on acetic acid leachates of carbonates from both the Doushantuo Formation (Members D1-4) and the overlying Dengying Formation. C and O isotopic compositions of these carbonate samples were also analysed using conventional phosphoric acid method. With the exception of the D1 cap carbonates ($^{87}\text{Sr}/^{86}\text{Sr}=0.7088$ to 0.713), most samples show low Mn/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ similar to seawater values (0.7078 in D2-D4 and 0.709 in Dengying) inferred from Ediacaran carbonates elsewhere. These data, together with the absence of a correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}_{\text{carb}}$, indicate minor diagenetic fluid overprinting. The initial ϵNd values of the carbonate leachates show a limited variation range from -4.3 to -7.5 with the highest values in D1, which overlap with the published data for Doushantuo sediments in South China, and possibly indicate an

isotopically homogenous Nd source in the source area during most of the Ediacaran. D1 samples of cap carbonates display negative $\delta^{13}\text{C}_{\text{carb}}$ values of -2.0 to -3.6 (VPDB) and $\delta^{18}\text{O}_{\text{carb}}$ values ranging from -6.5 to -7.3 (VPDB), whereas the overlying D2 strata show positive $\delta^{13}\text{C}_{\text{carb}}$ values around 6. Carbonate rocks from D3 and D4 show a large variation range of $\delta^{13}\text{C}_{\text{carb}}$ from -1.4 to 9.4, with some samples having unusually high $\delta^{13}\text{C}_{\text{carb}}$ values coupled to low TOC contents. Most carbonate leachates at the base of the Doushantuo display variable HREE enrichment ($\text{Pr}/\text{Yb} < 1$) similar to modern seawater signature and show superchondritic Y/Ho. This suggests evolution of seawater chemistry to modern open ocean conditions at the beginning of the Ediacaran, whereas lower Y/Ho in D3 correlate with flat REE+Y patterns, indicating a continuously change to freshwater-seawater mixing and suppression of HREE/LREE fractionation as in modern estuaries. Carbonate rock samples from D4 are rich in clay minerals (up to 15%), such as nontronite and saponite of possibly authigenic origin. A formation of these clay phases may only be possibly under extreme alkaline and saline conditions. The D4 carbonate leachates show the highest Y/Ho and lowest Ce/Ce* values and have unusually high $\delta^{13}\text{C}_{\text{carb}}$ values, which may also support the conditions of extreme shallowing and perhaps temporarily restricted basins that led to a rise in salinity due to high evaporation rates. Ce anomalies in carbonate leachates show strong variation throughout the profile and a secular increase of seawater oxygenation through the Ediacaran is not obvious. However the most pronounced Ce anomalies can be found in the upper Doushantuo (Ce/Ce* as low as 0.64).

3.2 INTRODUCTION

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Chapter 4

CADMIUM ISOTOPE VARIATIONS IN NEOPROTEROZOIC CARBONATES - A TRACER FOR REDOX PROCESSES AND WATER MASS MIXING?

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4.1 ABSTRACT

The use of Cd isotopes as proxy for modern ocean nutrient utilisation by phytoplankton has become an important tool in marine geochemistry. Of particular interest is the applicability of Cd isotopes as tracer of past marine bio-productivity. However, the detailed fractionation processes of Cd isotopes in the marine realm are still debated. Most studies favour substitution for Zn atoms in carbonic anhydrase of diatoms as the main driver for the fractionation. Cd isotopic compositions of leachates of Ediacaran shallow water carbonate sediments and N and C isotopic compositions from the Xiaofenghe section on the Yangtze Platform, S-China have been determined. The data, obtained by using double spike method and TIMS ($\epsilon^{112/110}\text{Cd}$ relative to NIST SRM 3108, external precision: $\pm 8\text{ppm}$) show ϵCd of +0.06 to +1.07 in the cap carbonates and in the lower Doushantuo, but significantly lighter values (-3.53 to -0.79) in the overlying Doushantuo and Dengying strata. Neither Cd concentrations, nor isotopic compositions correlate with P or Zn abundances. Given the experimentally derived $\alpha_{\text{CaCO}_3\text{-Seawater}}$ of 0.99955 for the fractionation of Cd into calcium carbonate, seawater in equilibrium with these carbonates should have ϵCd between 0.97 and 5.57, which is in the range of modern surface water. However the trend to lower values in the upper Ediacaran does not represent the signal expected for increased bio-productivity as proposed for the Ediacaran. The

upper Doushantuo displays substantial fluctuations of Y/Ho_{PAAS}, Pr/Sm_{PAAS}, N and C isotopic compositions, presumably caused by mixing of seawater with freshwater masses. Carbonates with negative ϵCd in this part of the section show negative Ce/Ce* anomalies and high $\delta^{13}\text{C}_{\text{carb}}$, which may indicate carbonate precipitation in shallow oxic water subjected to increased evaporation and variable salinity. Our data suggest that the variations in the Cd isotope composition of Ediacaran carbonates at Xiaofenghe are most likely a result of kinetic fractionation of Cd into inorganic carbonates. In the upper part of the Doushantuo, variations may be controlled by salinity whereas in post-Marinoan cap dolostones, sulfidic pore water conditions rather than bio-productivity may have produced heavy Cd isotopic compositions.

4.2 INTRODUCTION

The ocean at the end of the Proterozoic Era underwent some of the most remarkable chemical and biological transitions in Earth's history, such as the appearance of animal life (Knoll, 2015), major variations in sulphur and carbon isotope records (Kaufman and Knoll, 1995; Halverson and Hurtgen, 2007) and indications for the transition from an anoxic to a partial oxygenated deeper ocean (Planavsky et al., 2010).

The Yangtze Platform, South China is among the most promising areas in the world to study the bio-geochemical changes during the Ediacaran period at the end of the Neoproterozoic. Marine sediments of the Doushantuo and Dengying Formations cover the critical time span from the termination of the last Cryogenian ice age (the Marinoan glaciation) to the Precambrian/Cambrian boundary with the appearance of the first macroscopic fossils such as multicellular algae (Xiao et al., 2012) and the emergence of animals (Yin et al., 2007; Li et al., 2008).

In the past, nitrogen isotopic compositions in marine sediments provided insights into past ocean redox conditions and nitrogen biogeochemical cycling. Nitrogen is an essential macronutrient for the living biomass and the recycling of nitrogen species (e.g. NO_3^- , NH_4^+) in the water column is strongly dependent on reduction-oxidation reactions (Ader et al., 2014). However, a problem with the application of N isotopes in Precambrian sediments may be its post-depositional modification (e.g. by preferential volatilisation of ^{15}N fixed ammonium (Bebout and Fogel, 1992, Ader et al., 2014)). Therefore the use of another bio-available isotopic system is of great importance for ancient sediments.

Stable isotopic fractionations of Cd are another new, and not yet widely used, proxy for marine nutrient cycles in water (Lacan et al., 2006; Ripperger et al., 2007; Abouchami et al., 2011) and marine sediments (Schmitt, et al., 2009a; Horner et al., 2010). However, the oldest sediments analysed on their Cd isotopic compositions only date back to the Permian (Georgiev et al., 2015). Several authors have proposed that in the aftermath of the Neoproterozoic Marinoan glaciation, bio-productivity in the shallow Ediacaran ocean increased dramatically. The purpose of this work is to evaluate if Cd isotopes in shallow water carbonate sediments can be used as a paleo-productivity proxy during the Ediacaran and to extend the Cd isotope record back into the Neoproterozoic.

Cadmium concentrations in seawater show a nutrient like behaviour with surface depletion and deep water enrichment and mimic concentration patterns of the macro nutrient phosphorous (Boyle et al., 1976). The details of the processes leading to nutrient-like behaviour of Cd in modern seawater remain debated. Utilization of Cd in marine photosynthetic organisms is the most favoured explanation, because it leads to a depletion of the surface water Cd pool (Lacan et al., 2006). As the main driver for the Cd uptake Price and Morel (1990) described a variation of the enzyme carbonic anhydrase, which is active in the resorption of carbon dioxide during photosynthetic processes. The Cd incorporating carbonic anhydrase has so far only be described from diatoms (Xu et al., 2008).

Recent publications showed that Cd concentration patterns mirror major variations in their isotopic compositions (Ripperger et al., 2007; Schmitt, 2009a; Abouchami et al., 2011)). The data usually exhibit Cd depleted surface waters with isotopically heavy compositions and deep waters show higher Cd concentrations and lighter isotopic compositions, presumably reflecting surface removal of light isotopes by marine photosynthetic organisms and their decomposition and remineralisation in deep waters (Lacan et al., 2006; Ripperger et al., 2007).

4.3 GEOLOGIC BACKGROUND, SAMPLE SELECTION AND METHODS

The Xiaofenghe section (Hubei Province, South China) is situated 30 km NE of the Three Gorges Dam and developed on the S-SE facing passive margin of the Yangtze craton (Wang and Li, 2003). The section comprises of dolomite- and calcit bearing carbonate sediments and mudstones from the Doushantuo and overlying Dengying Formation and is described in literature to have been deposited under very shallow water or even lagoonal conditions (Vernhet and Reijmer, 2010; Xiao et al., 2012).

The section has been sampled in detail with the aim to determine in detail geochemical variations in carbonate sediment samples and to study the role of alteration and the preservation of primary compositions. The sampled rocks were pre-screened by microscope and SEM for alteration structures, such as calcitic veins or weathering fronts, cleaned and powdered. Major- and trace element compositions of acetic acid leachates and Sr-Nd-C_{carb}-O_{carb} isotopic compositions were reported in Hohl et al. (submitted).

Stable isotope ratios and concentration measurements of nitrogen and organic carbon were obtained using a Thermo-Finnigan MAT V isotope ratio mass spectrometer coupled to a Thermo Flash EA 1112 elemental analyser via a Thermo/Finnigan ConFlo III-interface at the Museum für Naturkunde Berlin. $\delta^{15}\text{N}$ analyses were performed on the bulk rock powder whereas for $\delta^{13}\text{C}_{\text{org}}$ measurements sample powders were decalcified using 2 M HCl. Isotopic ratios are expressed in the conventional delta notation relative to AIR and the V-PDB (Vienna PeeDee Belemnite) standard, respectively. The standard deviation for repeated measurements of a laboratory standard material (peptone) is generally better than 0.2 ‰ for both isotopic systems. After sample combustion a CO₂-trap was used to reduce interferences between bulk rock nitrogen and carbon isotope signals. $\delta^{13}\text{C}_{\text{carb}}$ of Xiaofenghe carbonates was obtained using standard methods at Freie Universität Berlin and were described by Hohl et al. (submitted).

For Cd isotope analysis we reacted 1 g of sample powder in pre-cleaned 50 ml centrifuge vials with 50 ml of 1 M acetic acid buffered to a pH of 5. Samples reacted under continuous rotation overnight, then were centrifuged and pipetted. A ¹⁰⁶Cd – ¹⁰⁸Cd spike was added to aliquots of the samples containing ~ 100 ng Cd, following the procedures described in Schmitt et al. (2009b). After equilibration with the spike, 0.6 ml of 8.5 M HBr/10ml sample were added to obtain a concentration of ~0.5 M HBr. The Cd separation and purification was achieved by using a two-step separation on Biorad Polyprep columns filled with 200 µl of Bio Rad AG1-X8, 100-200 mesh in nitric form and elution with 0.25 N HNO₃. The samples were then loaded onto single Re filaments and covered with 1 µl silica gel activator. Cd isotopic compositions were determined using a Thermo-Fisher Triton Thermal Ionisation Mass Spectrometer (TIMS) at the Max Planck Institut für Chemie in Mainz. The raw data was corrected offline for internal instrument mass fractionation using the exponential law. Following Abouchami et al. (2012) Cd isotope data were expressed as $\epsilon^{112/110}\text{Cd}$ values (deviations of ¹¹²Cd/¹¹⁰Cd in parts per 10,000 from a reference material):

$$\epsilon^{112/110}\text{Cd} = \left[\frac{{}^{110}\text{Cd}/{}^{112}\text{Cd}_{\text{RM}}}{{}^{110}\text{Cd}/{}^{112}\text{Cd}_{\text{Sample}}} - 1 \right] \times 10^4$$

As reference material (RM) we used the now widely accepted NIST SRM 3108 Cd standard (Abouchami et al., 2012). The Cd concentrations have been obtained by isotope dilution and have combined analytical uncertainties of less than 0.1 %.

4.4 RESULTS

$\epsilon^{112/110}\text{Cd}$ in three cap carbonates of Xiaofenghe ranges between -0.056 ± 0.62 and -0.455 ± 0.23 . The Cd concentrations in the same member vary between 0.2 and 0.62 $\mu\text{g/g}$ showing no correlation with the isotopic compositions. In contrast, $\epsilon^{112/110}\text{Cd}$ in the middle Doushantuo is $+1.069 \pm 0.35$ and -3.625 ± 0.11 close to the top of the Formation. The Cd isotopic data show a trend to lighter values up section. Cd concentrations range between 0.093 and 2.507 $\mu\text{g/g}$ and show no systematic variation with isotopic composition or stratigraphic position. $\epsilon^{112/110}\text{Cd}$ values of two analysed Dengying samples are -2.546 and -2.19 with 0.14 $\mu\text{g/g}$ and 0.1 $\mu\text{g/g}$ Cd respectively.

Cap carbonate strata show $\delta^{13}\text{C}_{\text{org}}$ data with an average value of -27 ‰. $\delta^{15}\text{N}$ compositions decrease upwards from 2.6 ‰ to 0.5 ‰. Throughout overlying strata of the lower Doushantuo Formation $\delta^{13}\text{C}_{\text{org}}$ values remain relative invariant ranging around ~ -28 ‰ before they decrease down to -33.8 ‰ in black shales of the middle Doushantuo Formation (~ 103.0 m). TOC values steadily increase from ~ 0.1 % strata overlying the cap carbonate to a maximum value of 1.105 % in strata comprising black shales (102.7 m). $\delta^{15}\text{N}$ compositions as well increase to an average value of ~ 4.5 ‰, however showing a wide range from 1.9 ‰ to 6.6 ‰. Thereby, the black shale shows constant ^{15}N -enriched isotope compositions of ~ 5 ‰.

Lime- and dolostones of the middle Doushantuo Formation are dominated by $\delta^{13}\text{C}_{\text{org}}$ values fluctuating around ~ 28 ‰ whereas TOC values decrease down to an average value of 0.09 % in strata comprising dolostones of the middle Doushantuo (~ 170 m). Strata overlying the black shale show $\delta^{15}\text{N}$ data stabilising around 4 ‰.

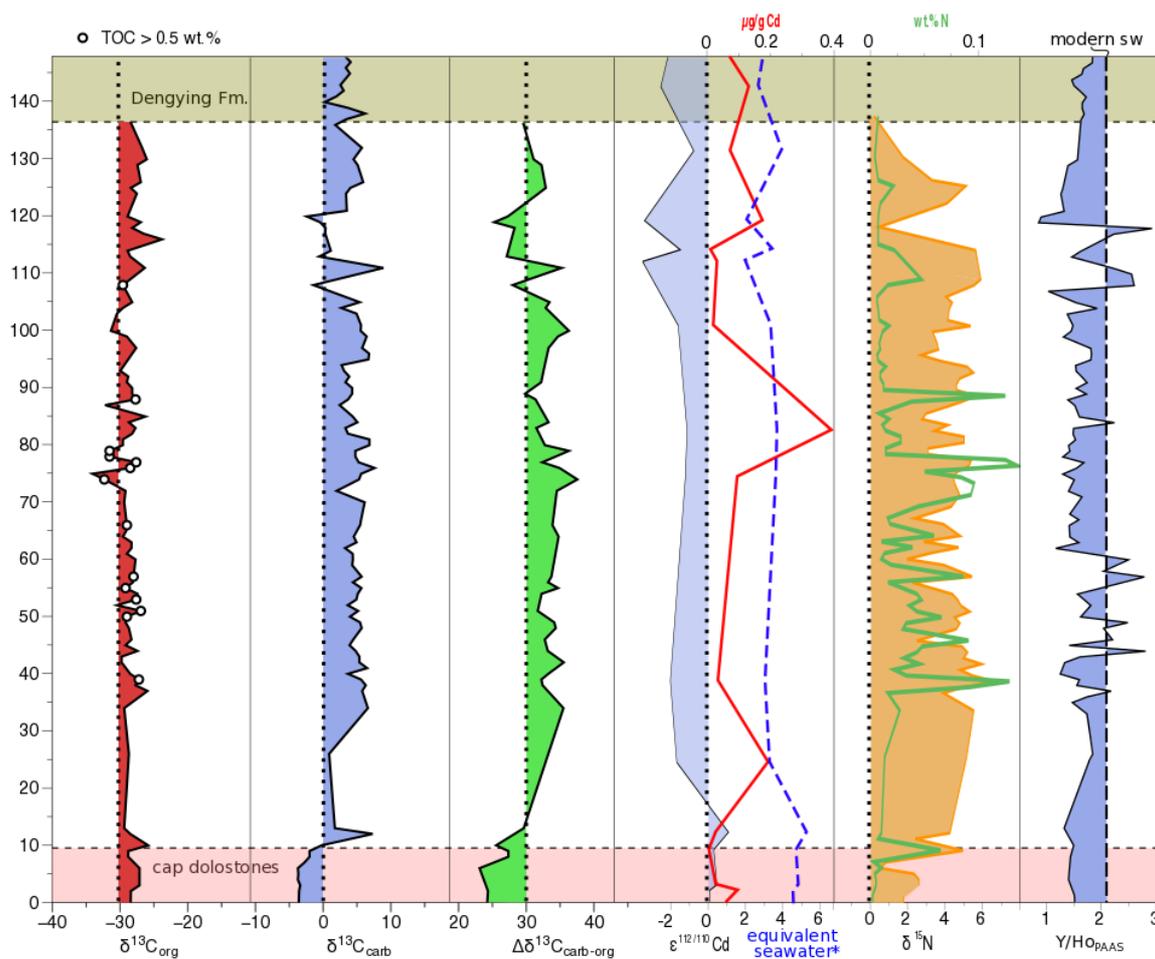


FIG. 4.1

a-c) Compiled organic and inorganic carbon isotope data from Hohl et al., (2015 in review). Instead of stratigraphic height, sample numbers are indicated on the y-axis for better resolution of the variations.

d) $\epsilon^{112/110}\text{Cd}$ of carbonate leachates (relative to NIST SRM 3108 Cd standard); red line represents Cd concentrations in $\mu\text{g/g}$; (*) dashed blue line represents the calculated isotopic composition of seawater for inorganic equilibrium precipitation of calcite following Horner et al. (2011).

e) Bulk rock $\delta^{15}\text{N}$ (relative to Air) and concentrations of Nitrogen in wt.% (green line).

f) Shale normalised Y/Ho ratios in carbonate leachates from Hohl et al. (2015 – in review); dashed line represents modern seawater after Bau et al. (1995).

$\Delta^{13}\text{C}_{\text{carb-org}}$ values range from 22.9 (in the basal Doushantuo Formation) up to 37.6 in the middle Doushantuo Formation (Fig. 4.1).

$\delta^{15}\text{N}$ values of Doushantuo cap carbonates vary between 0.5 and 2.6 whereas in middle Doushantuo they lie between 1.9 and 6.6 ‰. The data on the upper Doushantuo Formation show fluctuations in $\delta^{15}\text{N}$ compositions, where the respective light $\delta^{15}\text{N}$ values occur in samples with low

N concentrations in the bulk rock and may thus be an analytical artefact or the result of diagenetic modification of the primary isotopic signal (Fig. 4.1).

4.5 DISCUSSION

Phytoplankton utilisation of Cd may be the major process controlling the variations in modern seawater Cd budgets (Price and Morel, 1990; Lacan et al., 2006; Ripperger et al., 2007). As organically bound Cd is the major removal process of Cd in modern marine systems, ancient carbonate sediments could be an important archive for determining nutrient cycles in ancient seawater (Horner, Rickaby and Henderson, 2011). If this process was active in the late Neoproterozoic, it gives new insights into processes leading to the evolution of multicellular life at the Precambrian/Cambrian boundary. However a range of other processes may affect the variability of Cd concentrations and isotopic compositions in ancient marine sediments. Therefore when analysing Cd concentrations and isotopic compositions in ancient marine sediments, the influence of additional fractionation processes must be evaluated. The range of Cd isotope fractionations in carbonate leachates from Xiaofenghe section is larger than $4 \epsilon^{112/110}\text{Cd}$ units and cannot be explained by analytical artefacts as the observed variations change systematically throughout the profile (to lighter values at the top of the section).

4.5.1 INFLUENCE OF TERRESTRIAL INPUT

Fractionation of Cd isotopes in detrital minerals is reported to be at least one order of magnitude smaller than variations in seawater ($< 2 \epsilon^{112/110}\text{Cd}$ vs. $20 \epsilon^{112/110}\text{Cd}$ (Wombacher et al., 2003), hence the variation in Cd isotope data from Xiaofenghe section ($> 4 \epsilon^{112/110}\text{Cd}$) exceeds the isotopic variation in loess samples (Schmitt et al., 2009a). Data from Xiaofenghe show no correlation of Cd concentrations or isotope compositions with K and Al contents in acetic acid leachates or total clay contents in bulk rock assemblages, therefore the role of detrital Cd input may be negligible.

4.5.2 DIAGENESIS

Late fluid flow overprint is typical for Palaeozoic carbonates from South China and may have altered the Cd isotope compositions. Hohl et al. (submitted) have shown that, with the exception of the cap dolostones, carbonate rocks at Xiaofenghe were not affected much by late-stage fluid flow

(as indicated by their $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ data) and thus, their trace element budgets presumably reflect the partitioning and incorporation from Ediacaran seawater. $\epsilon^{112/110}\text{Cd}$ values > zero reference standard correlate with light carbon and oxygen isotopic compositions (Fig. 4.3). These “heavy” values are only abundant in the basal Doushantuo samples, which also have Mn/Sr ratios > 5, commonly used as denominator for meteoric fluid overprint (Brand and Veizer, 1980). Furthermore the samples have the lowest Cd and N concentrations, suggestive of preferential leaching of the elements from these samples. If Cd concentrations in the cap dolostones were modified by dissolution processes this could have led to removal of light Cd isotopes at the base of the Doushantuo.

4.5.3 POSSIBLE CD FRACTIONATION EFFECTS TO BE TESTED:

4.5.3.1 BIOLOGICAL FRACTIONATION

$\delta^{13}\text{C}_{\text{carb}}$ values at Xiaofenghe suggest a deposition under shallow water marine conditions fractionation of carbon isotopes by phytoplankton above the cap dolomites (Hohl et al., submitted). Several authors have favoured nutrient-like uptake of Cd into phytoplankton as the main driver for Cd isotope fractionation of more than 18 $\epsilon^{112/110}\text{Cd}$ units in modern oceans (Ripperger et al., 2007; Abouchami et al., 2014). However so far only one specific enzyme in diatoms (Cd carbonic anhydrase, (Xu et al., 2008)) has been identified as being capable of incorporating the toxic metal Cd into phytoplankton. Horner et al. (2013) suggested that nonspecific uptake of Cd into planktonic organisms may lead to subsequent storage of Cd in the cell membrane of planktonic organisms. Both uptake processes of Cd into organic matter will lead to a depletion of light Cd in the photic zone and heavy Cd isotope enrichment in the deeper parts of the water column. Under closed system conditions (e.g. a restricted basin) carbonates precipitating in an increasing productive environment towards the Cambrian should yield heavier isotopic compositions.

$\delta^{13}\text{C}_{\text{org}}$ values throughout the section agree with previously published data from the Doushantuo Formation (e.g. Ishikawa et al., 2013) and display values characteristic for marine phytoplankton. Although presumably deposited under very shallow- and photic conditions, the carbonate leachates reveal no trend to heavier $\epsilon^{112/110}\text{Cd}$ compositions up-section. $\epsilon^{112/110}\text{Cd}$ values drop above the basal Doushantuo cap dolomites, behaving opposite to increasing $\delta^{13}\text{C}_{\text{carb}}$ values.

$\epsilon^{112/110}\text{Cd}$ values show no correlation with $\delta^{15}\text{N}$. However, the curves of the two isotope systems match in some parts of the section. Whereas Cd isotopic compositions are higher in the

basal Doushantuo cap dolomites, corresponding nitrogen isotopic compositions show low but positive $\delta^{15}\text{N}$ values. The low nitrogen isotope composition of cap carbonate strata suggests strong N_2 -fixation by diazotrophs in the euphotic zone (Sachs and Repeta, 1999). Such scenarios (e.g. cyanobacterial blooms) are often documented from redox-stratified oceanic basins (e.g. in the modern Baltic Sea) (Struck et al., 2004; Ploug et al., 2010).

Elevated $\delta^{15}\text{N}$ values up to 6.6 ‰ of strata comprising the lower and middle Doushantuo Formation hint towards a shift in the nutrient regime to a NO_3^- dominated marine environment (Ader et al., 2014). Nitrogen isotope data imply, that NO_3^- became the predominantly utilised nutrient for primary producers while N_2 partly remained unused in surface waters. This can possibly be attributed to increased oxygen availability that is essential to allow remineralisation of organic matter via nitrification-denitrification interactions (Canfield et al., 2010, Ader 2014). Therefore, $\delta^{15}\text{N}$ data show that nitrate was stable in the shallow water during the early and middle Doushantuo and thus intermediate waters must have been at least mildly oxygenated (Ader et al., 2014). These oxic to suboxic conditions were further indicated by negative Ce anomalies recorded in carbonate leachates of the same member (table 4.1).

The upper Doushantuo shows fluctuations in the nitrogen isotope signature and a drop in $\delta^{15}\text{N}$ down to 0.2 ‰, which broadly mirrors fluctuations in the $\epsilon^{112/110}\text{Cd}$ and $\delta^{13}\text{C}$ (organic and carbonate) and may imply fluctuations with respect to the stability of nitrate due to changing oxygen levels.

4.5.3.2 REDOX CONTROLLED FRACTIONATION

Recent work by Gorgiev et al. (2015) highlighted aspects of redox controlled Cd concentrations and isotopic compositions in marine sediments. Cd is not a redox-sensitive element and only present in 2^+ state but Cd bound on organic matter (OM) will be enriched in anoxic sediments where OM oxidation is inhibited. Under euxinic conditions Cd may also have been bound into sulphides (CdS) contributing to sedimentary Cd enrichments in oxygen minimum zones (Janssen et al., 2014). OM and/or sulphide-rich sediments would show higher Cd concentrations and potentially lighter isotope composition than the remaining seawater as both OM and Cd-bearing sulphides preferentially incorporate lighter Cd isotopes (Schmitt, et al., 2009a).

Mn enrichment factors in the carbonate leachates (relative to the Mn concentration in the Phanerozoic calcite standard CAL-S) show a positive correlation with $\epsilon^{112/110}\text{Cd}$ (Fig. 4.3). As Mn in modern oxic surface waters is incorporated into Mn-oxides and hydroxides an enrichment of Mn in

the carbonate phases may reflect reduction to Mn^{2+} during anoxic pore-water-sediment interactions (Thomson et al., 1986). Whole rock organic matter contents vary strongly within the profile and neither correlate with Mn concentrations in the carbonate leachates nor with $\epsilon^{112/110}\text{Cd}$.

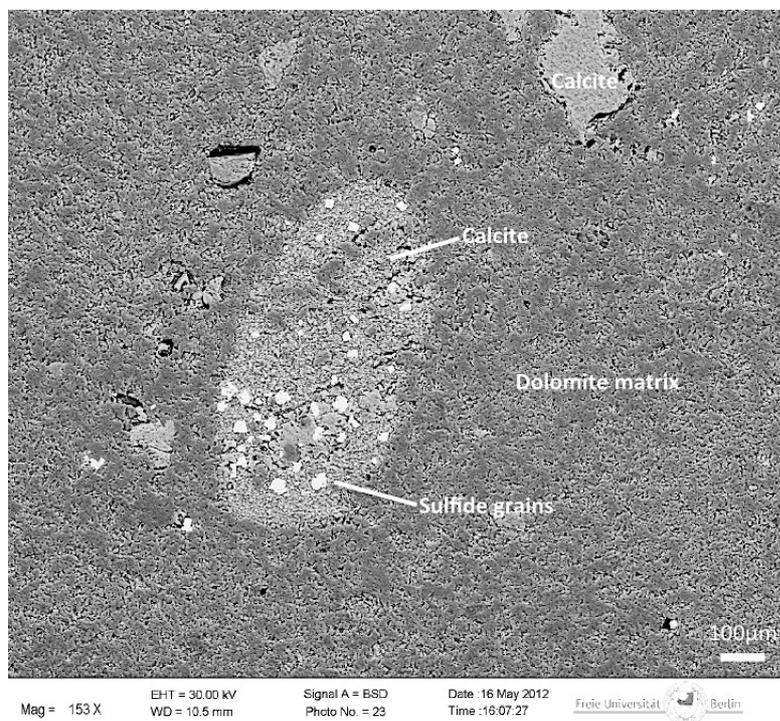


FIG. 4.2

BSD picture of a Xiaofenghe section cap dolostone at 2.36 m stratigraphic height. The sample shows calcitic fillings within a porous dolomitic matrix. Subhedral to euhedral (10 - 40 μm diameter) sulphide grains are abundant in samples of the basal Doushantuo cap carbonates.

The basal Doushantuo cap dolomites reveal Mn enrichments and positive fractionated $\epsilon^{112/110}\text{Cd}$ at low Cd concentrations. Furthermore subhedral 10 - 40 μm sulphide grains are abundant in these samples (Fig. 4.2). Although Ce/Ce^* ratios < 0.9 (Hohl et al., submitted) suggest that during cap dolomite precipitation surface waters on the Yangtze Platform were already suboxic to oxic. However, pore-water conditions may have been anoxic, leading to the precipitation of sulphides and Mn-rich carbonates. Framson and Leckie (1978) showed that under sulphidic conditions labile Cd co-precipitates with sulphides. The effect of authigenic sulphide formation on the fractionation of Cd isotopes within anoxic marine sediments is poorly understood. While Wombacher et al. (2003) found no evidence for fractionation of Cd isotopes in low temperature sulphide precipitation, the work done by Schmitt et al. (2009a) showed that hydrothermal sulphides had distinctively lower $\epsilon^{112/110}\text{Cd}$ values than marine sediments, indicating a substantial fractionation effect of up to 4 $\epsilon^{112/110}\text{Cd}$ units.

Preferential incorporation of light Cd isotopes into authigenic sulphides, leaving the carbonate phases isotopically heavy, may have only affected the basal Doushantuo at Xiaofenghe. Although middle and upper Doushantuo and Dengying carbonate leachates show co-variation of $\epsilon^{112/110}\text{Cd}$ with Mn enrichments, positive $\epsilon^{112/110}\text{Cd}$ values are only present in the lower Doushantuo. Pore-water conditions at Xiaofenghe were most likely more oxidised after the cap dolostone deposition as indicated by lower TOC contents and $S_{\text{pyrite}}/C_{\text{org}}$ ratios (Jiang et al., 2011; Xiao et al., 2012).

4.5.3.3 SALINITY CONTROLLED FRACTIONATION

Whereas inorganic carbonate precipitation in saline waters leads to a constant Cd fractionation factor of $\alpha_{\text{CaCO}_3\text{-Cd}_{\text{aq}}} = 0.99955 \pm 12$ (insensitive to temperature, Mg concentration and precipitation rate), inorganic freshwater carbonates are most likely incapable of fractionating Cd isotopes (Horner, Rickaby and Henderson, 2011b). Calculated $\epsilon^{112/110}\text{Cd}$ values for seawater in equilibrium with the carbonates analysed from Xiaofenghe section range between +0.975 and +5.569 (blue line Fig. 4.1). Cd uptake in freshwater calcites is much faster than in saline waters, where a decreased Cd uptake may be a result of ion blocking on the calcite mineral surface sites (Horner, Rickaby and Henderson, 2011b). Cd isotope compositional variations within carbonate leachates may therefore also be a result of variable salinity of the seawater at the Xiaofenghe depositional site. If correct, the Cd isotope signal may also have been influenced by freshwater-seawater mixing. Hohl et al., (2015 - submitted) show that the Xiaofenghe section might have been influenced by substantial freshwater inputs, which resulted in variable REE+Y ratios in the carbonate sediments.

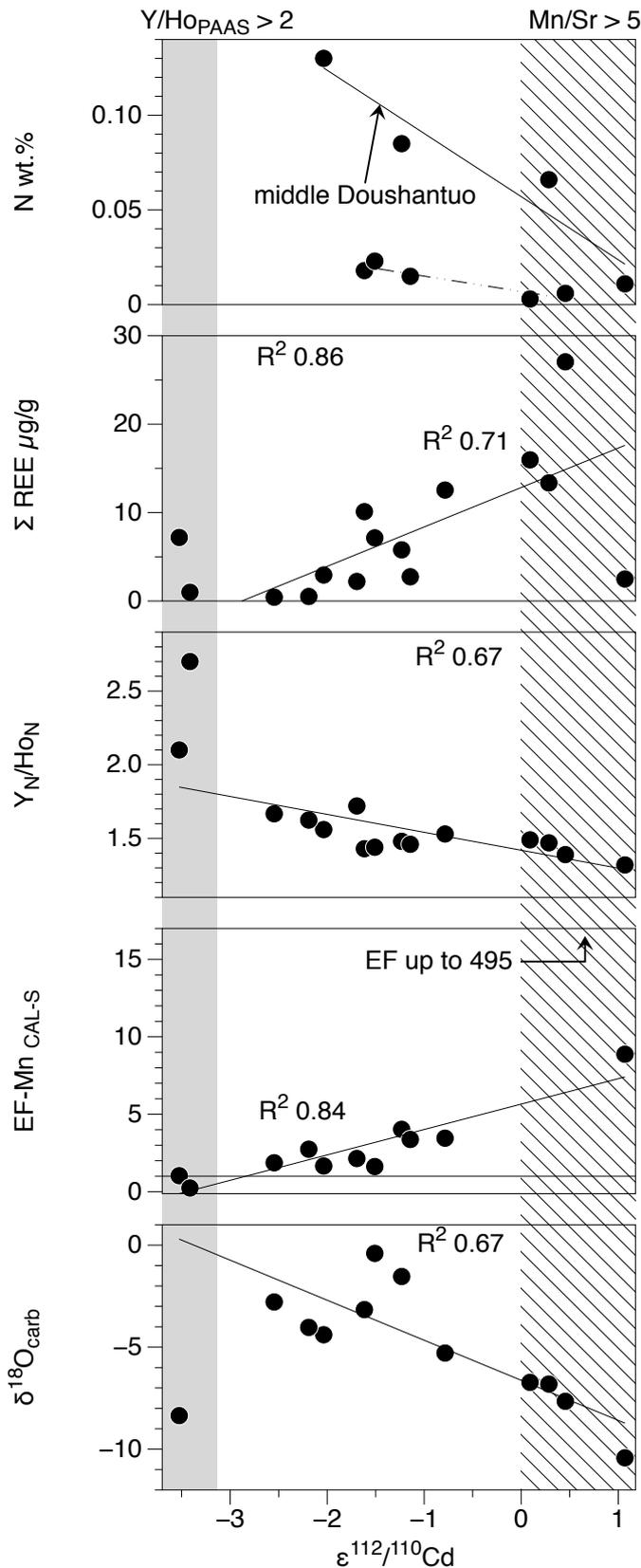


FIG. 4.3

Different proxies vs. $\epsilon^{112/110}\text{Cd}$ (relative to NIST SRM 3108 reference material). Positive correlations are given with R^2 value (excluding outliers in the shaded area ($Y_N/Ho_N > 2$) and the diagonal pattern area ($Mn/Sr > 5$)).

Positive $\epsilon^{112/110}\text{Cd}$ values correlate with high Mn/Sr ratios, very light oxygen isotopic compositions and low N concentrations.

Light $\epsilon^{112/110}\text{Cd}$ values are found in samples with low Σ REE concentrations, high fractionation of Y over Ho , no or minor Mn enrichment relative to Phanerozoic calcite standard CAL-S and less negative oxygen isotope compositions.

Shale normalised REE+Y patterns of modern oxidised surface waters are characterized by enrichment in HREE over LREE, negative Ce anomalies and superchondritic (>28) Y/Ho ratios (Elderfield and Greaves, 1982; Bau et al., 1996; Nozaki et al., 1997). It has been shown that marine carbonate minerals incorporate the REE+Y signatures of coeval seawater (Webb and Kamber, 2000; Kamber and Webb, 2001; Nothdurft et al., 2004). Thus REE concentrations in carbonates can be a useful tool for paleo-environmental reconstructions. Acetic acid leachates of carbonate rocks from Xiaofenghe section exhibit superchondritic Y/Ho ratios, however, Y/Ho ratios close to modern surface ocean values only occur in the middle Doushantuo and at the boundary to the Dengying Formation. Strong variations of Y/Ho_{PAAAS} from 1.5 to 2.5 in the upper Doushantuo correlate with the negative excursions of $\delta^{13}\text{C}_{\text{carb}}$, $\epsilon^{112/110}\text{Cd}$ and $\delta^{15}\text{N}$. These samples also display a reversal of the LREE/HREE fractionation from shale normalised Pr/Yb ratios of (down to 0.31 in middle Doushantuo and down to 0.23 in Dengying samples (table 4.1)) to shale normalised Pr/Yb ratios > 1 in some samples of the cap carbonates and upper Doushantuo, presumably as a consequence of a relative LREE enrichment.

Flat shale normalised REE+Y patterns occur at the boundary of middle to upper Doushantuo of the Xiaofenghe section and occur together with diminished yttrium anomalies. These signals are unusual for open marine sediments and are similar to conditions in estuarine mixing zones (Lawrence and Kamber, 2006). The Xiaofenghe samples show high Y_N/Ho_N ratios in samples with low $\epsilon^{112/110}\text{Cd}$ values and low total REE concentrations (Fig. 4.3). The match of these parameters suggests that temporally increased input of freshwater into a lagoonal environment increased the flux of light REE (therefore flattening the shale normalised carbonate leachate REE patterns, Hohl et al. (2015) submitted), decreased the salinity of the mixed water-mass and thus suppressing the Cd isotope fractionation during inorganic carbonate precipitation.

4.6 CONCLUSIONS

Ediacaran carbonate leachates at Xiaofenghe show Cadmium isotope fractionation with temporal evolution to light isotopic compositions. The variation of $\epsilon^{112/110}\text{Cd}$ signals overlaps with values reported for modern shallow seawater. However, the reasons for the fractionation of Cd isotopes may be diverse and are most likely controlled by inorganic processes rather than by substitution of Cd for Zn in phytoplankton. The Cd incorporating carbonic anhydrase is so far only

described for Diatoms and this enzyme might not have existed in the Precambrian (since the emergence of diatoms falls into the late Cretaceous).

The fractionation of Cd isotopes in Ediacaran carbonate leachates is most likely a result of inorganic processes such as precipitation of authigenic sulphides under anoxic pore-water conditions in cap dolostones at the base of the Doushantuo and changes in the fractionation rate due to variable salinity in carbonate sediments of the upper Doushantuo as a result of seawater-freshwater mixing in an estuarine-like environment.

4.7 ACKNOWLEDGEMENTS

This work was funded as a part of DFG Research Group FOR 736 “The Precambrian-Cambrian Biosphere Revolution: Insights from Chinese micro continents” (Subproject Be 1820/4-2). We thank Reimund Jotter and Wafa Abouchami at the Max-Planck-Institut für Chemie in Mainz for their support in the lab and members of FOR 736 who helped in sampling the analysed rocks in the field in South China. We would like to thank Uwe Wiechert for help with analysis of light stable isotopes at the Freie Universität Berlin. We acknowledge helpful comments and discussion on an early version of this manuscript by Michael Tatzel.

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Chapter 4: Cd isotope variations in Ediacaran carbonates

Table 4.1.: stable isotope data; N and C concentrations; assorted shale normalised REE ratios and Mn enrichments relative to Cal-S from Hohl et al. (2015b). D1-D4 = Doushantuo Fm., DG = Dengying Fm.

sample	Height [m]	Member	$\delta^{13}\text{C}_{\text{carb}}^1$	$\delta^{18}\text{O}_{\text{carb}}^1$	$\delta^{13}\text{C}_{\text{org}}$	$\Delta\delta^{13}$	$\varepsilon^{112/110}\text{Cd}^2$	2SE	Cd [$\mu\text{g/g}$]	$\delta^{15}\text{N}^3$	N [wt. %]	TOC [wt.%]	C/N	ΣREE [$\mu\text{g/g}$]	Ce/Ce ⁴	Y _N /Ho _N	Pr _N /Yb _N	EF Mn(Cal-S)
1	0.2	D1	-3.8	-6.7	-28	24.2	0.091	0.2	0.06	1.8	0.003	0.008	2.7	16	0.95	1.5	0.97	48
2	0.2	D1	-3.8	-6.7	-28	24.2				1.8	0.003	0.008						
3	0.75	D1			-26.7		0.056	0.62	0.1			0.11						
4	1.6	D1	-3.7	-7.7			0.46	0.23	0.028	2.6	0.006			27	0.83	1.4	1.1	30
5	1.6	D1	-3.7	-7.7						2.6	0.006							
6	2.3	D1	-3.8	-7.3	-26.7	22.9				2.3	0.005	0.0001	0.02					
7	3.85	D1	-3.2	-6.9						0.5	0.011							
8	4.8	D1	-1.2	-12.3	-28.4	27.2				0.8	0.004	0.06	15	2.1	0.71	1.4	0.97	1
9	4.8	D1	-1.2	-12.3	-28.4	27.2						0.06						
10	6.65	D2	0.0	-6.8	-25.4	25.4	0.29	2.51	0.006	4.9	0.066	0.016	0.2	13	1.2	1.5	1.05	496
12	12.1	D2			-28.1					2.4	0.008	0.25	32	4.9	0.84	1.4	0.85	7.8
13	22	D2	0.6	-10.4	-29	29.6	1.07	0.35	0.028	4.2	0.011	0.12	11	2.5	1.11	1.3	0.41	8.9
25	36	D2					-1.69	0.09	0.2					2.2	0.66	1.7	0.57	2.1
26	37.5	D2			-28.3					5.1	0.014	0.21	15	1.7	0.69	1.8	0.49	2.9
33	61.5	D2	6.4	-6.0										1	0.85	1.7	0.47	2.2
34	65	D2	6.5	-6.1	-29	35.5				5.5	0.028	0.12	4.4	0.33				0.71
35	70	D2	7.3	-3.5										2.1	0.76	1.5	0.47	1.4
36	72.5	D2													0.87	1.7	0.58	
37	73.7	D2			-25.5					3.9	0.017			3.8	0.9	2.1	0.77	6.4
38	75	D2	5.1	-4.8	-27.3	32.4				4.9	0.092			0.33	0.69	1.5	0.4	0.14
39	75.6	D2	5.4	-4.4	-26.8	32.2	-2.04	0.25	0.035	6.6	0.13	0.61	4.7	2.9	1.01	1.6	0.58	1.7
40	76	D2	5.2	-4.5	-28.1	33.3				5.4	0.034	0.22	6.6	2.9	1.15	1.3	0.62	5.2
41	76.5	D2								4.8	0.023							
42	77.5	D2	6.2	-4.1	-29.4	35.6				5.9	0.046	0.43	9.3	3.4	1.19	1.3	0.63	5.2
43	77.5	D2			-29.4					5.0	0.032	0.42	13	1.4	0.75	1.6	0.49	4.8
44	79.5	D2	6.2	-4.1	-27	33.2				5.2	0.044	0.41	9.4	1.7	0.69	2.6	0.37	1.7
45	80.5	D2			-28.8					4.9	0.049	0.38	7.7	13	0.86	1.4	1.31	3.8
46	81.5	D2	4.8	-5.0	-27.9	32.7				2.5	0.092	0.006	0.1	3.2	0.64	2.1	0.5	1.6
48	84.5	D2	6.1	-1.6	-28.3	34.4				4.6	0.031	0.45	14	3.6	0.76	1.9	0.65	2.2
49	85	D2	5.4	-4.4	-28.8	34.2				4.8	0.034	0.48	14	1.9	0.72	2.3	0.36	2.5
50	86	D2			-28.6					4.5	0.067	0.92	14	6.4	0.89	1.6	0.81	2.1
51	87.2	D2	5.2	-3.9	-26.5	31.7				5.3	0.044	0.71	16	6.9	0.76	1.7	0.89	2.5
52	88	D2			-30.1					4.8	0.037	0.36	10	7.3	0.97	1.7	0.7	2.2
53	88.7	D2			-27.2					4.6	0.048	0.71	15					
54	89	D2	5.2	-4.0	-27	32.2				4.4	0.044			6.7	0.8	1.5	0.91	1.1
55	90	D2	5.9	-2.5	-28.8	34.7						0.94						

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sample	Height [m]	Member	$\delta^{13}\text{C}_{\text{carb}}^1$	$\delta^{18}\text{O}_{\text{carb}}^1$	$\delta^{13}\text{C}_{\text{org}}$	$\Delta\delta^{13}$	$\epsilon^{112/110}\text{Cd}^2$	2SE	Cd [$\mu\text{g/g}$]	$\delta^{15}\text{N}^3$	N [wt. %]	TOC [wt.%]	C/N	ΣREE [$\mu\text{g/g}$]	Ce/Ce* ⁴	$\text{Y}_\text{N}/\text{Ho}_\text{N}$	$\text{Pr}_\text{N}/\text{Yb}_\text{N}$	EF Mn _(cal-s)
56	91.2	D2	5.5	-3.3	-27.7	33.2				2.3	0.017	0.29	17					
57	91.7	D2	6.1	-2.9	-27.6	33.7				5.4	0.087	0.77	8.9	1.3	0.69	2.58	0.49	2.3
58	92	D2	3.6	-1.2										3.2	1.2	1.94	0.33	2.5
59	92.5	D2								3.9	0.02							
60	93	D2			-27.3					1.9	0.011	0.26	23	2.4	0.72	2.3	0.57	1.4
61	96.2	D2			-28.6					3.2	0.014	0.35	25					
62	98	D2			-27.9					4.7	0.04	0.35	8.7	29	0.94	1.2	0.92	3.2
63	99	D2			-27.9					2.8	0.011	0.15	13	16	0.82	1.6	1.52	3.1
64	99.85	D2	5.6	-2.6	-29.2	34.8				4.8	0.06	0.32	5.3	10	0.92	1.4	1.36	2.9
65	100.95	D2			-28.7													
66	101.5	D2	5.3	-3.4	-28.6	33.9				3.9	0.019	0.65	34	3.5	0.95	1.4	0.82	3.6
67	101.85	D2	5.8	-2.4						2.4	0.017	0.28	16	6	0.8	1.6	1.22	4
68	102	D2	6.5	-1.7										12	0.88	1.4	0.96	3.2
69	102	D2	6.3	-1.3						4.3	0.045			9.4	0.92			2.5
70	102.1	D2			-29													
71	102.4	D2								4.8	0.094	0.95	10			1.6	0.8	
72	102.6	D2	5.7	-1.4	-28.8	34.5								4.5	1.1	1.4		4.9
73	102.6	D2								4.5	0.097	0.4	4.1				0.63	
74	102.7	D2	5.6	-1.5	-32	37.6	-1.23	0.35	0.1	4.4	0.085	1	12	5.8	1.19	1.5	0.73	4.0
75	103	D2			-33.8					4.6	0.051	0.21	4.1	8.8	1.4	1.3	0.83	2.9
76	103	D2	6.8	-1.1	-28.1	34.9				5.3	0.14	0.97	7.1	44	1.16	1.5	0.75	2.1
77	103	D2	5.1	-2.1	-27.2	32.3				5.4	0.13	0.89	7.1	11	0.98	1.6	0.7	2.4
78	103.5	D3			-31.2					3.1	0.015	0.59	39	3.9	0.98	1.3	1.07	1.2
79	103.5	D3	5.2	-3.4	-31.2	36.4				3.1	0.015	0.59	39	3.5	1.09	1.4	0.84	3.5
80	104	D3	3.5	-2.8	-29.2	32.7				5.0	0.029	0.11	3.9	14	1.33	1.4	1.32	
81	104	D3			-29.2					5.0	0.029	0.11	3.9	2.6	0.87	1.5	0.94	1.6
82	104.25	D3			-27.8		-1.14	0.12	0.4	3.4	0.015	0.17	11	2.7	1.09	1.5	1	3.4
83	104.5	D3	4.2	-2.2	-27.3	31.5				4.1	0.012	0.15	12	3.4	1.23	1.5	0.73	5.3
84	104.5	D3	5.0	-4.9	-28.3	33.3				2.7	0.018	0.23	13	2.9	0.76	2.1	0.31	2.3
85	105.5	D3			-25.8					3.0	0.009	0.43	48	2.9	0.71	1.6	0.75	1.5
87	108.15	D3			-31.9					4.9	0.039	0.21	5.5	5.7	1.08	1.5	1.2	9.5
88	108.7	D3	4.0	-1.0	-27.3	31.3				5.6	0.126	0.56	4.4	15	1.03	1.4	0.97	2.4
89	109.5	D3	2.0	-6.3	-27.8	29.8				4.6	0.013	0.13	10	8.6	1.06	1.7	1.39	34
90	109.5	D3			-27.8					4.6	0.013			11	0.86	1.5	1.29	4.4

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sample	Height [m]	Member	$\delta^{13}\text{C}_{\text{carb}}^1$	$\delta^{18}\text{O}_{\text{carb}}^1$	$\delta^{13}\text{C}_{\text{org}}$	$\Delta\delta^{13}$	$\epsilon^{112/110}\text{Cd}^2$	2SE	Cd [$\mu\text{g/g}$]	$\delta^{15}\text{N}^3$	N [wt. %]	TOC [wt.%]	C/N	ΣREE [$\mu\text{g/g}$]	Ce/Ce* ⁴	$\text{Y}_\text{N}/\text{Ho}_\text{N}$	$\text{Pr}_\text{N}/\text{Yb}_\text{N}$	EF Mn _(cal-s)
91	110	D3	3.6	-6.8	-28.6	32.2				4.8	0.01	0.096	9.6	14	0.94	1.7	2.59	116
92	110.5	D3			-28.4					5.5	0.01	0.087	8.7	16	0.86	1.6	3.24	257
93	111.1	D3	2.9	-6.8	-29.6	32.5				5.2	0.015	0.14	9.3	11	0.97	1.5	2.23	31
94	112.2	D3	2.8	-8.6						3.7	0.008			8.3	0.79	1.5	2.03	74
95	113.9	D3	6.6	-5.4						2.7	0.007	0.051	7.3	3.5	0.69	1.7	1.83	
96	116	D3	6.9	-4.6						3.6	0.01			3.0	0.7	1.8	1.23	
97	118.5	D3	6.1	-6.4	-27.2	33.3				3.6	0.009	0.072	8.0	6.7	0.87	1.7	1.37	162
99	123.8	D3	6.1	-2.3	-28.6	34.7				3.3	0.012	0.17	14.5	11	0.97	1.3	1.67	7
100	125	D3	5.4	-3.2	-31	36.4	-1.62	0.47	0.02	5.3	0.018	0.24	13.1	10	1.02	1.4	1.98	19
101	130	D3	5.7	-4.9						4.1	0.009			12	1.01	1.5	2.97	60
103	133.5	D3			-30.1					4.2	0.008	0.16	20	9.0	0.87	1.4	2.21	32
104	135	D3	3.7	-7.5	-29.2	32.9				4.4	0.007	0.31	44	16	0.99	1.8	1.17	2
105	136	D3	5.6	-6.7	-27.8	33.4				4.0	0.007	0.13	18	11	1.01	1.5	2.3	10
107	142	D4								5.5	0.017			12	0.86	1.1	1.04	2.1
108	142.4	D4	-1.3	-0.9	-29.2	27.9				5.9	0.048	1.6	34	1.9	0.77	2.4	0.38	0.1
110	152	D4												2.1	0.81	2.4	0.41	0.41
111	154	D4	9.4	-8.4	-25.9	35.3	-3.53	0.11	0.032			0.043		7.2	0.84	2.1	1.11	1
113	156.5	D4	-1.1	-0.4	-28.1	27.0	-1.51	0.59	0.011	5.6	0.023	0.13	5.5	7.1	1.2	1.4	0.42	1.6
114	158	D4			-28.5					4.3	0.008	0.065	8.1	7.4	1.1	1.6	0.54	3.5
116	160	D4			-23.3													
117	166	D4			-26.1					0.4	0.008	0.044	5.5	1.9	1.2	2.1	0.19	0.6
118	167	D4	0.4		-27.8	28.2	-3.41	0.1	0.18			0.022		0.99	0.7	2.7	0.23	0.2
119	168.5	D4	-1.4	-2.5	-26.5	25.1						0.032		0.96	1.1	0.92	0.34	0.6
120	168.6	D4	-1.3	-1.9	-28.5	27.2						0.035		1.2	0.99	0.96	0.43	0.8
121	172.2	D4	3.3	-1.8						4.1	0.01	0.18	18	9.1	0.69	1.3	0.87	2.7
124	174	D4	4.7	-3.0	-27.1	31.8				5.1	0.022	0.089	4	14.5	0.64	1.3	1.4	4.3
125	175.5	D4	4.9	-1.7	-28	32.9				3.3	0.008	0.026	3.3	11	0.67	1.3	1.7	2.6
126	177.3	D4			-26.5													
129	179.8	D4	5.2	-4.5	-27	32.2				1.7	0.005	0.14	29	13	0.75	1.4	2	1.9
130	180	D4	5.4	-5.3	-25.6	31.0	-0.79	0.12	0.074			0.086		13	0.7	1.5	2	3.5
132	182	D4			-26.3													
136	194	D4	1.8		-27.9	29.7				0.2	0.008	0.092	12					
137	200	DG	3.5	-0.6										0.99	1.1	1.6	0.29	3.3
138	200.1	DG	0.9	-2.8										2.1	0.83	1.6	0.54	1.2

sample	Height [m]	Member	$\delta^{13}\text{C}_{\text{carb}}^1$	$\delta^{18}\text{O}_{\text{carb}}^1$	$\delta^{13}\text{C}_{\text{org}}$	$\Delta\delta^{13}$	$\epsilon^{112/110}\text{Cd}^2$	2SE	Cd [$\mu\text{g/g}$]	$\delta^{15}\text{N}^3$	N [wt. %]	TOC [wt.%]	C/N	ΣREE [$\mu\text{g/g}$]	Ce/Ce ⁺⁴	Y _N /Ho _N	Pr _N /Yb _N	EF Mn _(cal-s)
139	200.5	DG												0.8	1	1.6	0.24	4.9
140	201.5	DG	4.3	-5.0										0.81	1	1.6	0.25	6.2
141	203	DG	0.9	-2.8			-2.55	0.14	0.13					0.43	0.76	1.7	0.15	1.9
142	205	DG	2.5	-2.2										0.69	1	1.6	0.21	2.8
143	205.5	DG	2.8	-1.0										1.4	1.1	1.5	0.31	3.3
144	207.5	DG												1.3	1.1	1.4	0.32	3.2
145	209	DG												0.56	0.86	1.6	0.2	5.7
146	213	DG	3.3	-4.0			-2.19	0.10	0.074					0.51	0.88	1.6	0.18	2.7
147	216	DG	3.1	-3.9										0.62	0.73	1.8	0.21	2.9
148	217	DG	3.2	-3.4										0.69	0.83	1.8	0.23	2.5

CHAPTER 5

CONCLUSIONS

This chapter is summarising the findings presented in the previous three chapters which are designed for individual publication. The eight main findings are:

1. The studied Ediacaran carbonates are affected by post-diagenetic alteration presumably caused by fluid-flow overprint. Fluids that overprinted the deep water and slope facies show a different composition than those overprinting the shallow water sections on the Yangtze Platform. In detail 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, a majority of carbonate rocks from the Yangtze Platform display primary shale normalised REE+Y patterns that preserved the composition of the coeval seawater.
2. Compared to shallow water samples, carbonates from the deep basin on the Yangtze Platform precipitated in waters, which were likely more enriched in ^{12}C . The decoupling of $\delta^{13}\text{C}_{\text{carb}}$ from $\delta^{13}\text{C}_{\text{org}}$ within those carbonates may be explained by the partial remineralisation of organic matter in the deep marine environment.
3. Secular changes in the seawater chemistry by evaporation and dilution with freshwater might influence the traditional carbon isotopes proxy used for inter-profile correlation. In particular, heavy $\delta^{13}\text{C}_{\text{carb}}$ values up to +9 ‰ at the top of the shallow water Xiaofenghe section may indicate temporarily high evaporation rates and high salinities. Given the fact that dilution by riverine inflow and evaporation under lagoonal conditions may have influenced Xiaofenghe section, negative excursions of $\delta^{13}\text{C}_{\text{carb}}$ in the middle Doushantuo cannot be linked to other profiles, neither on the Yangtze Platform, nor with globally occurring events like the Shuram-Wonoka excursion.
4. Shallow water carbonates at Xiaofenghe reveal $^{87}\text{Sr}/^{86}\text{Sr}$ values close to estimated global Ediacaran seawater. The carbonates also preserved their primary REE+Y patterns, and element

variations in the upper Doushantuo most likely reflect primary characteristics inherited from local mixing of freshwater and seawater in estuary-like conditions. In detail the mixing caused less pronounced Y/Ho anomalies and relatively flat shale normalised REE+Y patterns.

5. The $^{87}\text{Sr}/^{86}\text{Sr}$ compositions rise at the end of the Ediacaran presumably as a result of an increase of the ^{87}Sr flux into the ocean by increased continental weathering. Because of regionally enhanced weathering, Dengying samples at Xiaofenghe may be slightly more radiogenic (0.7090) compared to $^{87}\text{Sr}/^{86}\text{Sr}$ in basal samples from the Dengying Formation at other sections in the Three Gorges area.
6. The ϵNd_i values of shallow water carbonates at Xiaofenghe show a narrow range overlapping with literature data from phosphorite and black shale samples from nearby locations. This argues for a homogenous hinterland Nd isotopic composition of eroding material through most of the Ediacaran.
7. In the deep water carbonate samples redox-sensitive elements like Fe, Mo, U and V are depleted compared to Phanerozoic carbonates, whereas Mn and Ba are strongly enriched, suggesting anoxic and even sulfidic pore-water conditions in the deep Ediacaran ocean.
8. Ediacaran carbonate leachates at Xiaofenghe show Cadmium isotope fractionation with temporal evolution to light isotopic compositions. The variation of $\epsilon^{112/110}\text{Cd}$ signals overlaps with values reported for modern shallow seawater. However, the reasons for the fractionation of Cd isotopes is most likely a result of inorganic processes, such as precipitation of authigenic sulphides under anoxic pore-water conditions in the lower Doushantuo and changes in the fractionation rate due to variable salinity in the upper Doushantuo as a result of seawater-freshwater mixing in an estuarine-like environment.

CHAPTER 6

SCIENTIFIC OUTPUT

6.1 PEER REVIEWED PUBLICATIONS

Hohl, S.V., Becker, H., Herzlieb, S. and Guo, Q. (2015): Multiproxy constraints on alteration and primary compositions of Ediacaran deep water carbonate rocks, Yangtze Platform, South China
published in GCA, 2015

Gamper, A., Struck, A., Ohnemüller, F., Heubeck, C. and **Hohl, S.V.** (2015): Chemo- and biostratigraphy of the Gaojiashan section (Northern Yangtze Platform, South China): A new Pc-C boundary section.
published in Fossil Record, 2015

6.2 SUBMITTED MANUSCRIPTS

Hohl, S.V., Becker, H., Gamper, A., Jiang, S. Y., Wiechert, U., Yang, J.-Y. and Wei, H.Z.: Secular changes of water chemistry in shallow water Ediacaran ocean: Evidence from carbonates at Xiaofenghe, Three Gorges area, Yangtze Platform, South China.
Submitted to Precambrian Research, April 2015 (currently under review)

Sun, S., Heubeck, C., Hippler, D. and **Hohl, S.V.**: The nature of the Ediacaran-Cambrian contact at Meishuncun, Yunnan Province, China.
Submitted to Journal of the Geological Society of London, May 2015

6.3 UNPUBLISHED MANUSCRIPTS

Hohl, S.V., Galer, S.J., Gamper, A and Becker, H.: Cadmium isotope variations in Neoproterozoic carbonates - A tracer for redox processes and water mass mixing?

Hohl, S.V., Becker, H. Jiang S.Y and Guo, Q.: Geochemistry of Ediacaran cap dolostones of the Yangtze Platform, South China.

Rodler, A., **Hohl, S.V.**, Guo, Q. and Frei, R: Chromium isotope stratigraphy of Ediacaran cap carbonates, Doushantuo Formation, South China.

6.4 CONFERENCE ABSTRACTS AND PRESENTATIONS

Hohl, S.V., Galer, S.J. and Becker, H. (2015): Cd isotopic variations in Ediacaran carbonate rocks from South China; Biogenic or abiogenic isotope fractionation?

Oral presentation at Goldschmidt Conference 2015, Prague

Hohl, S.V., Becker, H., Gamper, A., Jiang, S.-Y., Wiechert, U. and Wei, H. (2014a): Multi-proxy study of shallow water Ediacaran carbonates (Xiaofenghe, Yangtze Platform, South China).

Poster presentation at the GSA Meeting 2014, Vancouver

Hohl, S.V., Galer, S.J. and Becker, H. (2014b): Cadmium isotopic fractionation in Ediacaran carbonates from the shallow water Xiaofenghe section, Yangtze Platform, South China.

Oral presentation at the GSA Meeting 2014, Vancouver

Hohl, S.V., Becker, H., Herzlieb, S., Guo, Q and Gamper, A. (2013): Multi-proxy study of shallow- and deep water Doushantuo carbonates, Yangtze Platform, South China.

Poster presentation at the Goldschmidt Conference 2013, Florence

Hohl, S.V., Becker, H., Hippler, D. and Bairo, W. (2012a): Trace element abundances in Doushantuo cap dolostones from platform and slope settings, Yangtze Platform, South China.

Poster presentation at the Goldschmidt Conference 2012, Montreal

Hohl, S.V., Becker, H., Hippler, D. and Bairo, W. (2012b): Trace element abundances in Doushantuo cap dolostones from platform and slope settings, Yangtze Platform, South China - Influence of calcification and postsedimentary fluid-flow.

Poster presentation at the Geological Society of London, Fermor meeting, 2012

6.5 GRADUATE THESIS SUPERVISION

Steffen Herzlieb (2013): Element- und Isotopenzusammensetzungen von Karbonatgesteinen der Beckenfazies des Ediacariums der Yangtze Plattform (Südchina), M.Sc. thesis, Freie Universität Berlin.

APPENDIX

A I: FIELD WORK

In order to obtain representative rock samples from shallow- and deep water marine facies from the Ediacaran we conducted field work on the Yangtze Platform, South China in spring 2012, sampling several sections in Hunan and Hubei Province. The visited sediment profiles were chosen based on various factors, such as existing detailed sedimentological descriptions and carbon isotope composition datasets. The fieldwork was performed with the help of the Chinese counterpart within the Sino-German joint Research Group FOR 736. Of particular interest were the shallow water Doushantuo Formation and overlying Dengying Formation in the Three Georges Region, Hubei Province and the deep water facies of Doushantuo, Hunan Province.

For this dissertation project, the Doushantuo Formation at Xiaofenghe section was sampled in high resolution from the base of the cap carbonates into the first meters of the overlying Dengying Formation. The northern part of the section, abbreviated as “NXF”, starts with about 4.8 m of cap dolomites with a clearly outcropping boundary to the diamictites of the Nantuo Formation below. Following an interval covered by vegetation, Member D2 begins with interlayered dolostones and shales with thin chert layers. At 23 m, a 6 m thick sequence of 10-20 cm thick phosphoritic layers in black shales crop out. The rest of D2 is dominated by alternating organic-rich carbonates and mudstones with pea-sized chert nodules. At 102 m, stratigraphic height a 1 m thick black shale layer occurs. The shale is overlain by a massive dolostone- and organic-rich limestone unit, which can be followed in the field until 136 m above the diamictites. We assume that the boundary between D2 and D3 should be within or a few meters above the black shale horizon at 102m. Further sampling of the section was continued on the southern flank of the valley at Xiaofenghe village. This part of the section is abbreviated as “SXF”. Following the description of (M. Zhu et al., 2013), using the prominent black shale layer at the top of D2 at NXF and SXF as a marker horizon, it is possible to follow the stratigraphy of the SXF profile up to 225 m above the diamictites, which includes the boundary between the Doushantuo and the overlying Dengying Formation. Member D4 consists of silty/sandy dolostones with decimetre-sized chert nodules interbedded with pure limestones (up to 99% calcite present). The upper Doushantuo Formation in the very shallow regimes like at Xiaofenghe section seems to be more influenced by clays, or in the case of the Hushan Dayukou section (Hubei, Province), sandy and silty dolostones (M. Zhu et al., 2013). Therefore it seems questionable if the upper Doushantuo deposited north of the Huangling anticline

can be correlated with the D4 of the depositional environment in the Yangtze Georges area where it consists of black shales and karst surfaces mark the transition to the overlying Dengying Formation (M. Zhu et al., 2007; Lin et al., 2011).

Samples from Yanwutan section used for geochemical analysis in the first Manuscript were taken on an earlier field campaign of FOR 736 Sino-German Research Group and results have been published in Guo et al. (2007).

We furthermore sampled cap carbonates at various sections in Hubei and Hunan Province throughout the Yangtze Platform from shallow water platform to deep water basin sedimentation environments. We also incorporated samples from previous field campaigns to Hunan and Guizhou Province into our composite study. The results of the analysed cap carbonates are subject of a manuscript that will be submitted in fall 2015 but is not incorporated into this dissertation.

Table A1. field work and analysed sections

<i>SECTION</i>	<i>FORMATIONS</i>	<i>COORDINATES</i>	<i>PROXIES</i>	<i>PUBLICATIONS</i>
<i>XIAOFENGHE</i> HUBEI	<i>CAPCARBS</i> <i>DS, DY</i>	<i>N30° 56' 29.5''</i> <i>E111° 13' 57.4''</i>	<i>REE,</i> <i>SR, ND, N, CD,</i> <i>C, O</i>	<i>HOHL ET AL.,</i> <i>PREC.RES. 2015</i> <i>(IN REVIEW)</i>
<i>JIJIWAN</i> HUBEI	<i>CAPCARBS</i>	<i>N30° 52' 59.9''</i> <i>E110° 52' 45.4''</i>	<i>REE,</i> <i>SR, C, O</i>	
<i>HUAJIPO</i> HUBEI	<i>CAPCARBS</i>	<i>N30° 46' 54.4''</i> <i>E111° 02' 02.1''</i>	<i>REE,</i> <i>SR, C, O</i>	<i>cap carbonate</i>
<i>HUANGLIANBA</i> Guizhou	<i>CAPCARBS</i>	<i>N28° 11' 34.3''</i> <i>E°109 15' 39.5''</i>	<i>REE,</i> <i>SR, C, O</i>	<i>data yet to</i> <i>publish</i>
<i>LONGBIZUI</i> Hunan	<i>CAPCARBS</i>	<i>N28° 29' 57.9''</i> <i>E109° 50' 28.0''</i>	<i>REE,</i> <i>SR, C, O</i>	
<i>YANWUTAN</i> Hunan	<i>CAPCARBS</i> <i>DS</i>	<i>N28° 25' 20.0''</i> <i>E110° 28' 42.1''</i>	<i>REE,</i> <i>SR, C, O</i>	<i>GUO ET AL.,</i> <i>2007; HOHL ET</i> <i>AL., GCA 2015</i>

DS = Doushantuo, DY = Dengying

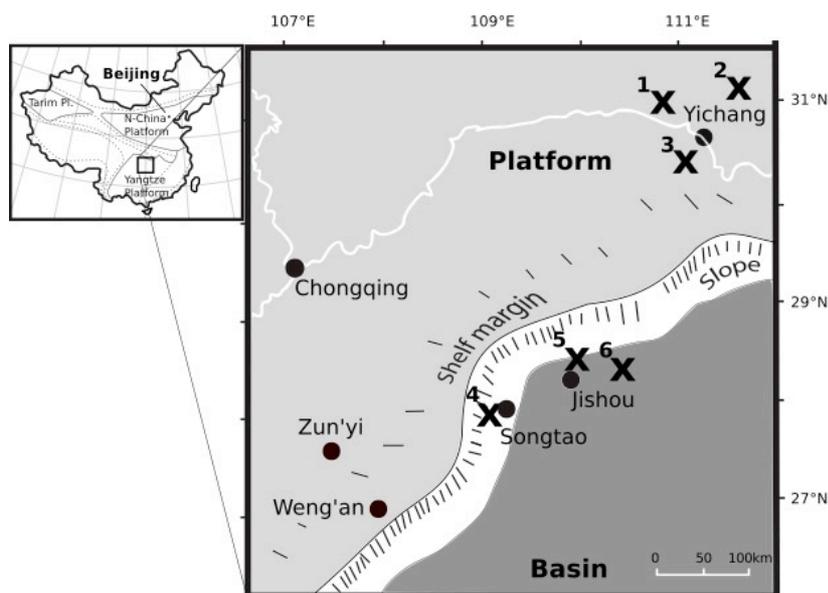


FIG. A I

Localities of sampled sections on the Yangtze Platform. Paleo depth inferred from the paleo-geographical map after Jiang et al. (2007). Shallow water sections: 1 = Jijiawan; 2 = Xiaofenghe; 3 = Huajipo (all Hubei Province); slope section: 4 = Huanglianba (Guizhou Province); basin sections: 5 = Longbizui; 6 = Yanwutan (both

Hunan Province).

A II: ANALYTICAL PROTOCOL

Prior to carbonate leaching chemistry we prepared polished thick sections of carbonate rock chips embedded in araldite resin and coated them with a thin gold layer. Following up we pre-screened the samples for possible alteration features, such as dedolomitisation or calcitic veins, using a Zeiss Supra 40 VP Ultra SEM coupled with an Oxford Instruments EDX analyser. As a result we were able to obtain sample powder by micro drilling into presumably unaltered areas. We further prepared thin sections of selected cap carbonate samples. Staining the thin sections using alizarin red calcite staining and Fe-dolomite staining methods helped in understanding their genesis.

For trace- and major element concentration analysis 20 to 50mg of finely grounded carbonate powder were commonly reacted with 1 ml 1 M acetic acid at 70°C over night and the solution centrifuged and filtered through 0.45 µm cellulose acetate filters. The elute was dried down, redissolved and diluted in 0.28 M HNO₃ for final measurement. 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 µl/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 HNO₃. The analytical precisions were usually better than 5 % (1SD) 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 % (1SD) for Cr and Mo. Procedural blanks on most trace elements and REE 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 50W-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 $^{87}\text{Sr}/^{86}\text{Sr} = 0.710246 (\pm 10, n=97)$. 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 according to the stratigraphic position of the samples, $^{87}\text{Rb}/^{86}\text{Sr}$ 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 below 0.5 ‰.

50 mg of sample powder were added to an adequate amount of ^{148}Nd and ^{147}Sm spike and then reacted with 2ml 0.5 M acetic acid over 12h, centrifuged and filtered through 0.45 µm PTFE syringe filters. After drying down the supernatant was redissolved in 2.5 M HCl and REE bulk separation was achieved by column separation using AG 50W-X8 (200-400 mesh) cation exchange resin. The REE were then further separated by dissolving the supernatant in 200 µl 0.15 M HCl followed by loading on ion exchange columns filled with Ln-Spec resin. Sm and Nd isotopic measurements were performed on a Thermo Finnigan Neptune Plus multicollector ICP-MS at the State Key Laboratory for Mineral Deposits Research at Nanjing University, Peoples Republic of China. A combined Scott and Cyclone quartz spray chamber and a PFA nebulizer with 100 µl/min were used with 5 runs and 10 passes for each sample, 300 s baseline and standard/sample bracketing performed to correct for instrumental drift.

The following cup configuration was applied:

L4	L3	L2	L1	C	H1	H2	H3	H4
^{141}Pr	^{142}Nd	^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{148}Nd	^{150}Nd

Raw Nd isotope ratios were normalised to a $^{146}\text{Nd}/^{144}\text{Nd}$ of 0.7219 (O'Nions et al., 1977). Repeated measurements ($n=5$) of a 50 ppb Ames Nd solution yielded $^{143}\text{Nd}/^{144}\text{Nd} = 0.511955 \pm 0.000013$ (2SD) and a 25 ppb Ames Nd solution yielded $^{143}\text{Nd}/^{144}\text{Nd} = 0.511944 \pm 0.000021$ (2SD) ($n=4$). The initial ratio of $^{143}\text{Nd}/^{144}\text{Nd}$ at a given time is expressed as deviation from CHUR at that time in the form of ϵ values, calculated with values for $^{147}\text{Sm}/^{144}\text{Nd}_{\text{CHUR}}$ of 0.196 and $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}$ of 0.51263 (Bouvier et al., 2008) and ages inferred from stratigraphy.

Stable isotopes of C and O in carbonate were determined in-house. The isotope ratio measurements were calibrated to Vienna-PeeDee Belemnite (V-PDB) with Carrara marble (CAM) and a calcite-carbonatite (KKS) as in-house standards. We report isotope ratios as per mill deviation from the international reference material V-PDB in the delta notation according to Coplen (2011). These in-house reference materials were previously calibrated using NBS-19 ($\delta^{18}\text{O} = -2.20$ ‰ and $\delta^{13}\text{C} = +1.95$ ‰) and NBS-18 ($\delta^{18}\text{O} = -23$ ‰ and $\delta^{13}\text{C} = -5.01$ ‰). The external errors of the measurements are ± 0.06 ‰ (1SD) for $\delta^{18}\text{O}$ and ± 0.03 ‰ (1SD) for $\delta^{13}\text{C}$, based on the reproducibility of an in-house limestone reference material (LM) and the NBS-19 standard.

Stable isotope ratios and concentration measurements of nitrogen and organic carbon were obtained using a Thermo-Finnigan MAT V isotope ratio mass spectrometer coupled to a Thermo Flash EA 1112 elemental analyser via a Thermo/Finnigan ConFlo III-interface at the Museum für Naturkunde Berlin. $\delta^{15}\text{N}$ analyses were performed on the bulk rock powder whereas for $\delta^{13}\text{C}_{\text{org}}$ measurements sample powders were decalcified using 2 M HCl. Isotopic ratios are expressed in the conventional delta notation relative to AIR and the V-PDB (Vienna PeeDee Belemnite) standard, respectively. The standard deviation for repeated measurements of a laboratory standard material (peptone) is generally better than 0.2 ‰. After sample combustion a CO_2 -trap was used to reduce interferences between bulk rock nitrogen and carbon isotope signals. $\delta^{15}\text{N}$ and $\delta^{13}\text{C}_{\text{org}}$ values of samples with analysed nitrogen and organic carbon contents < 0.01 mg and < 0.04 mg, respectively, are omitted from our interpretation due to low signal intensities and poor precision and accuracy.

Cd isotopic compositions were determined with the help of the Max Planck Institute for Chemistry, Mainz. For the separation we reacted 1 mg of sample powder with 50 ml of 1 M acetic acid buffered to a pH of 5. Samples were spiked with a $^{106}\text{Cd} - ^{108}\text{Cd}$ double spike following the procedures described in Schmitt et al. (2009). The Cd separation and purification was achieved by using two runs over Polyprep columns filled with 200 μl of Bio Rad AG1-X8, 100-200 mesh in nitric form and elution with 0.25 N HNO_3 . The samples were loaded onto single Re filaments analysed using a Thermal Ionisation Mass Spectrometer (TIMS) of type Thermo Finnigan Triton at the Max Planck institute for Chemistry in Mainz. The raw data was corrected offline for internal instrument

mass fractionation using the exponential law. The achieved data is expressed in epsilon (ϵ) notation relative to the reference standard material NIST SRM 3108. The Cd concentrations have been obtained by isotopic dilution, showing general analytical uncertainties of less than 0.1 %.

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A III: CURRICULUM VITAE

For reasons of data protection,
the curriculum vitae is not included in the online version

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