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Chromium isotope stratigraphy of Ediacaran cap dolostones, Doushantuo Formation, South China

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ABSTRACT

The Yangtze Platform in South China is considered a key site for studying Neoproterozoic ocean oxygenation. Comprehensive Cr concentration and isotopic signatures are presented from cap dolostones of the Doushantuo Formation from a deep water and a shallow marine carbonate section, that have previously been used to constrain the redox evolution of Ediacaran seawater in space and time employing major and trace element abundances as well as Sr-, O- and C-isotope compositions. The majority of the studied samples yield elevated Cr concentrations and negatively fractionated δ^{53}Cr signals due to (i) detrital contamination consistent with Cr signatures of other post-Marinoan cap dolostones, (ii) diagenetic carbonate alteration and post-depositional remobilization of Cr. Al concentrations were used as indicator of detrital contamination and to calculate authigenic Cr concentration and isotope signatures when the detrital contribution of Cr was $<$40%, which generally resulted in slightly lower Cr concentrations and slightly higher Cr isotopic signals in these samples. Diagenetic alteration of a majority of the studied cap dolostones is evident from low Sr concentrations and light $\delta^{18}O_{carb}$ signals that correlate with low Cr concentrations and negatively fractionated δ^{53}Cr values. Post-depositional remobilization of Cr results in the loss of heavy Cr isotopes and consequently light Cr isotopes are retained during precipitation of secondary carbonates. However, some samples might still show pristine Ediacaran seawater signals. Two samples pertaining to the deep water cap dolostone section at Yanwutan and one sample pertaining to the shallow water section at Jijiawan yield slightly positively fractionated δ^{53}Cr signals, particularly when corrected to presumably authigenic signals ($\delta^{53}Cr_{auth}$). These values are consistent with those from other Neoproterozoic carbonate sections deposited in an oxygenated environment. This short sequence of positively fractionated $\delta^{53}Cr_{auth}$ is concurrent with a cap dolostone $^{87}Sr/^{86}Sr$ signal close to Ediacaran seawater values with relatively high Sr and Cr concentrations, with decreased detrital contamination and with a pronounced negative Ce anomaly. They indicate either light pulses of enhanced oxidative weathering or, inferred from a few least-altered samples, prevailing oxic conditions during cap dolostone deposition. The Cr isotopic composition of Ediacaran cap dolostones pertaining to the Doushantuo Formation reveals fine-scale fluctuations in post-glacial detrital contamination and diagenesis balanced against a clear signal of oxidative weathering. Cr isotopes have the potential to further enhance our understanding of Neoproterozoic weathering regimes and past ocean oxygenation, however, before the Cr isotope system can be faithfully applied to delineate changes in redox conditions recorded in ancient marine carbonates, possible diagenetic alteration of the Cr signal as well as Cr contribution from detrital contamination need to be taken into consideration.

1. Introduction

The Neoproterozoic shows the most significant increase in atmospheric O_2 concentration in Earth's history (Holland, 2006) accompanied by significant changes in ocean redox conditions from anoxic (maybe ferruginous) to oxic conditions in the deep and shallow seawater (Canfield *et al.*, 2008; Johnston *et al.*, 2010; Li *et al.*, 2010); various models have been proposed to understand the climate evolution during the Neoproterozoic (Fairchild and Kennedy, 2007). However, remarkable environmental changes characteristic for the Neoproterozoic eventually facilitated the development of complex, aerobic life (e.g. Zhu *et al.*, 2007; Knoll, 2011; Sahoo *et al.*, 2012).

The progression of oxidative continental weathering and redox conditions in the marine realm throughout Earth's past can be inferred from concentrations and isotope signatures of redox sensitive trace elements recorded in chemically precipitated sediments (e.g. Anbar *et al.*, 2007; Asael *et al.*, 2013; Bekker *et al.*, 2004; Rouxel *et al.*, 2005). Ancient marine

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sediments potentially yield information about the chromium (Cr) isotopic variation of seawater in the geological past, which possibly allow to infer the oxygenation history of the oceans and atmosphere (e.g. Frei *et al.*, 2009; Crowe *et al.*, 2013; Planavsky *et al.*, 2014). Cr has a relatively simple speciation chemistry (Ellis *et al.*, 2002). Of the environmentally stable Cr(III)–Cr(VI) redox pair, Cr(VI) is highly soluble whereas Cr(III) is highly particle-reactive and forms insoluble Cr-hydroxide complexes (Rai *et al.*, 1987). The oxidation of Cr(III) to Cr(VI), catalyzed by Mn-oxyhydroxides (Eary and Rai, 1987; Fendorf and Zasoski, 1992), is accompanied by an isotopic fractionation where the mobilized Cr(VI) is enriched in the heavier isotope ^{53}Cr (Ellis *et al.*, 2004, 2002; Zink *et al.*, 2010) while no significant isotope effect was observed during adsorption of Cr(VI) onto particles (Ellis *et al.*, 2004). This means, that the weathered soil remains isotopically lighter in respect to Cr while oxidative atmospheric weathering enriches the run-off in ^{53}Cr (Izbicki *et al.*, 2008; Crowe *et al.*, 2013; Frei and Polat, 2013; Berger and Frei, 2014). The isotopically heavy, mobilized Cr(VI) is then transported by rivers (Farkaš *et al.*, 2013; Frei *et al.*, 2014; Paulukat *et al.*, 2015) – possibly affected by signals derived from regional variable Cr isotopic compositions of geologically different drainage systems (Scheiderich *et al.*, 2015) – to the open ocean, where oxygenated water bodies stabilize it. This is perhaps indicated by a comparison of the surface seawater δ^{53}Cr signature of the Argentinian Basin (Bonnand *et al.*, 2013), and water samples of the Paraná River estuary and of the Paraná river (Frei *et al.*, 2014). Results of these studies allow postulating that isotope effects during riverine transport of Cr to the oceans are not significant, and that the point sources of Cr have a dominant effect on the local Cr isotope signal recorded in seawater. This is consistent with findings for another locality recently reported by Paulukat *et al.* (2015). Ocean Cr isotope signals were also found to correlate strongly with Cr concentration (Scheiderich *et al.*, 2015) and Cr incorporation into synthetic calcite indicated marginal to no effects on Cr isotope fractionation between ambient seawater and marine abiogenic carbonates (Dixon *et al.*, 2013; Rodler *et al.*, 2015). However, a possibly more complex internal redox cycling of Cr in the ocean can be assumed based on the variability of Cr isotope signatures in river water (Farkaš *et al.*, 2013; Frei *et al.*, 2014; Paulukat *et al.*, 2015) and the heterogeneity of δ^{53}Cr in modern ocean seemingly dependent on water depth, water-mass sources and mixing of water masses (Scheiderich *et al.*, 2015).

Here, we investigate the Cr isotope signature of a deep water and a shallow marine cap dolostone section pertaining to the Doushantuo Formation (635–551 Ma; Condon *et al.*, 2005) on the Yangtze Platform, and their use as redox archives of ancient seawater conditions. The Doushantuo Formation is considered one of the key formations for studying ocean oxidation and animal evolution in the aftermath of the Marinoan glaciation. We investigate the Cr isotope stratigraphy in the context of a previous study that included cap dolostones from the Doushantuo Formation to delineate paleo-redox conditions from detailed isotope, major and trace element variations (Hohl *et al.*, 2015).

2. Geological setting

The Yangtze Platform in South China is certainly one of the best geological archives for studying the Ediacaran Ocean. It was established on the SE flank of the Yangtze Block continental margin creating a continuous marine sedimentary record of shallow- and deep water facies (e.g. Jiang *et al.*, 2011). In the last two decades, the Doushantuo Formation on the Yangtze Platform became the most promising spot for studying temporal and lateral ocean oxygenation and nutrient influx in the Neoproterozoic as marine sediments cover the critical time span following the low latitude Marinoan glaciation. U/Pb geochronology in various ash beds throughout the Doushantuo Formation have been used to infer the age of 635.2 ± 0.6 Ma at the beginning of the cap dolostone deposition to 551.1 ± 0.7 Ma shortly before the Precambrian/Cambrian boundary spanning almost 90% of the Ediacaran (Condon *et al.*, 2005) and covering the emergence of early animal life (Xiao *et al.*, 1998; Zhu *et al.*, 2007).

The cap dolostones building up the lower part of the Doushantuo Formation overlie tillites of the Nantuo Formation and are predominantly composed of massive dolostones with unusual light $\delta^{13}C_{carb}$ isotope anomalies and unique sedimentological structures such as tepees, rip up clasts, veins and crossbedding, presumably as a result of deposition during the change from icehouse to greenhouse conditions (Font *et al.*, 2010).

The Yanwutan section (YAW) is situated E of the city of Jishou, Hunan province (N28°25′20.0″ E110°28′42.1″; Fig. 1). The cap dolostones and overlying mudstones of the lower Doushantuo at Yanwutan were deposited in deep waters of the Nantuo Basin (Guo *et al.*, 2007; Zhu *et al.*, 2007; Ader *et al.*, 2009) whereas the middle and upper Doushantuo are considered to be composed of a massive slide sheet from a more shallow water environment (Vernhet *et al.*, 2006). However, Guo *et al.* (2007) and Hohl *et al.* (2015) have shown that negative $\delta^{13}C_{carb}$ values and trace element enrichments occur throughout the Yanwutan section, which therefore correlate with other deep water sections throughout the platform (Jiang *et al.*, 2007; Ader *et al.*, 2009).

The Jijiawan section (JJW), Hubei province (N30°52′59.9″ E110°52′45.4″; Fig. 1) is located on the southern flank of the Yangtze River, 17 km west of Maoping (Zhu *et al.*, 2007). It is described to have been deposited under shallow marine conditions in a large intra shelf basin, separated by over 100 km from the south-facing slope of the Yangtze Platform (Vernhet, 2007). The basal part of cap dolostones of the JJW section consists of brecciated dolostones with several calcitic veins. The middle part contains fine-laminated micritic dolostones and chert layers. The top of the cap dolostone member is a massive dolomite with slump-fold structures (Hohl *et al.*, under review). The cap dolostones are overlain by a black shale horizon with an ash layer that has been precisely dated by Condon *et al.* (2005) to 632.5 ± 0.5 Ma using U–Pb chronology.

3. Analytical procedures

3.1. Sample preparation, elemental and C, O and Sr isotope analyses

We used rock powders of 5 cap dolomite rocks pertaining to the Doushantuo Formation at the Yanwutan section, which have been described in detail by Guo *et al.* (2007) and Hohl *et al.* (2015) and rock chips of 7 cap dolostones pertaining to the Doushantuo Formation at the Jijiawan section that were crushed and subsequently milled in an automatic agate mortar (Fritsch pulverisette, type 02.102) to prepare rock powders. The cap dolostones pertaining to the Jijiawan section are described in detail by Hohl *et al.* (under review). Only ultrapure acids (double distilled or Seastar™) and ultrapure water from a Milli-Rho–Milli-Q system (18 MΩ MilliQ™) were used to treat the samples, which were processed and stored using previously cleaned Teflon™ beakers (cleaned with 6 mol L^{-1} HCl at 130 °C for 24 h). Sample preparation and ion chromatographic separation were all performed in Class 1000 clean rooms. Sample leachates were prepared by dissolving ~20 mg rock powder in 2 mol L^{-1} HCl for ~10 min. Elemental concentrations of these sample leachates were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer, Optima 7000 DV) and calibrated against a series of synthetic solutions prepared from certified single element solutions (Perkin Elmer). The external reproducibility was assessed by multiple analyses of the international reference materials JDo-1 (Permian dolostone, $n = 22$) and JLs-1 (Triassic limestone, $n = 3$), which were within the range of the certified values (Imai *et al.*, 1996); the results for Al and Sr concentrations (μg g^{-1}) show a relative standard deviation (1RSD) of <5%.

Major and trace element concentrations of the cap dolostone samples were analyzed in acetic acid leachates as outlined by Hohl *et al.* (2015). In