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Geoscience Frontiers

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## Research paper

# A high-resolution chemostratigraphy of post-Marinoan Cap Carbonate using drill core samples in the Three Gorges area, South China



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## ARTICLE INFO

## Article history:

Received 2 August 2014

Received in revised form

18 July 2015

Accepted 31 July 2015

Available online 28 August 2015

## Keywords:

Cap Carbonate

Ediacaran

Marinoan Snowball Earth

Carbon isotope chemostratigraphy

Methane hydrate

## ABSTRACT

Cap Carbonates overlie the Marinoan Snowball Earth-related glacial diamictite, and possibly record the drastic surface environmental change and biological evolution after the Snowball Earth. We conducted on-land drilling from the Liantuo Formation, through the Nantuo, to the lower Doushantuo Formation in the Three Gorges area of South China to collect fresh, continuous samples in the Three Gorges area. We obtained high-resolution chemostratigraphies of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of carbonates from the topmost part of the Nantuo Formation to the Cap Carbonate, in order to decode the detailed surface environmental change in the shallow marine setting. The  $\delta^{13}\text{C}$  chemostratigraphy possesses some unique characteristics: (1) stable  $\delta^{13}\text{C}$  values as a whole, but ubiquitous low  $\delta^{13}\text{C}$  anomalies through the Cap Carbonate, (2) increase of the  $\delta^{13}\text{C}$  values from  $-3$  to  $+5\%$  across the C2/C3 boundary, (3) no  $\delta^{13}\text{C}$  anomaly between the C1 and C2 boundary, and (4) presence of an anomalous high  $\delta^{13}\text{C}$  value ( $+2.3\%$ ) and a faint positive correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in the C1 unit.

Evidence of quite low  $\delta^{13}\text{C}$  anomalies (with a nadir of  $-41\%$ ), ubiquitous negative  $\delta^{13}\text{C}$  anomalies through the Cap Carbonate, and a high  $\delta^{13}\text{C}$  anomaly accompanied with a faint positive correlation between  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in the C1 unit supports decomposition and formation of methane hydrate during Cap Carbonate formation. The drastic increase of  $\delta^{13}\text{C}$  values from the upper C2 to C3 units indicates enhancement of primary productivity and organic carbon burial, possibly due to high continental fluxes after the Snowball Earth event, evidenced by high Sr isotope values. The increase is restricted to the proximal side of the inner shelf in South China, and the timing of the increase of  $\delta^{13}\text{C}$  values of carbonates is earlier at Three Gorges area than any other area, suggesting that the enhancement of primary productivity started in the proximal environment because of higher continental influxes. The increase in oxygen contents of seawater due to the enhanced primary productivity possibly resulted in the emergence of multicellular animals soon after Cap Carbonate deposition.

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## 1. Introduction

The Snowball Earth hypothesis describes one of the most interesting events of geologic time because of the drastic

environmental change and the subsequent dramatic biological evolution it implicated (Kirschvink, 1992; Hoffman et al., 1998). Although the causes that ended the Snowball Earth are still controversial, the worldwide occurrence of Cap Carbonate following the event indicates that seawater was supersaturated in carbonate (e.g. Hoffman et al., 1998; James et al., 2001; Hoffman and Schrag, 2002; Nogueira et al., 2003). It also suggests quite high atmospheric temperatures, an acidic terrestrial environment, and extensive continental weathering (e.g.

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Peer-review under responsibility of China University of Geosciences (Beijing).

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Hoffman and Schrag, 2002; Ohno et al., 2008; Sawaki et al., 2010).

The origin of the Cap Carbonate still remains controversial: cf. the Snowball Earth hypothesis (Hoffman et al., 1998; Hoffman and Schrag, 2002; Higgins and Schrag, 2003), the upwelling model, by which upwelling of deep water with high alkalinity and low  $\delta^{13}\text{C}_{\text{DIC}}$  values in a stratified ocean resulted in carbonate precipitation (Grotzinger and Knoll, 1995; Knoll et al., 1996; Kaufman et al., 1997; Ridgwell et al., 2003; Shields, 2005; Giddings and Wallace, 2009), the methane hypothesis (Kennedy et al., 2001; Jiang et al., 2003, 2008; Lin et al., 2011), and the low  $p(\text{O}_2)$  model (Sansjofre et al., 2011).

The Cap Carbonates contain enigmatic sedimentary structures, such as tepee-like structures (Aitken, 1991; James et al., 2001; Allen and Hoffman, 2005; Gammon et al., 2005; Jiang et al., 2006), sheet cracks (Kennedy, 1996; Jiang et al., 2006; Hoffman and Macdonald, 2010) and tube-like structures (Cloud et al., 1974; Hegenberger, 1993; Corsetti and Grotzinger, 2005). Framboidal pyrite, barite, and pseudomorphs of radial aragonite replaced by dolomite (Jiang et al., 2003, 2006) are also diagnostic. The lower part of the carbonate consists of microcrystalline dolostone and dolowackestone, and possesses stromatolite-like cavities, tepee-like structures, and sheet cracks (Jiang et al., 2003, 2006; Wang et al., 2008), whereas the upper part comprises laminated dolostone, shaly dolostone and limestone. Peloids are common, and faint microbial laminae and stromatolites are locally present (Jiang et al., 2010), although a depositional environment below fair-weather wave base is suggested by lack of grainstone and other shallow water features (Jiang et al., 2006, 2010).

The Cap Carbonates commonly have negative  $\delta^{13}\text{C}_{\text{carb}}$  values, referred to as the Cap Carbonate Negative Carbon Isotope Excursion, or CANCE (Zhu et al., 2007a), as reported in South China (e.g. Jiang et al., 2003, 2007, 2010; Condon et al., 2005; Zhu et al., 2007b; McFadden et al., 2008; Wang et al., 2008; Tahata et al., 2013), Australia (Walter et al., 2000), Oman (Fike et al., 2006; Le Guerroué et al., 2006), Canada (Narbonne et al., 1994; Kaufman et al., 1997), Namibia (summarized by Hoffman et al., 2007), Siberia (Melezhik et al., 2009), Mongolia (Macdonald et al., 2009) and India (Kaufman et al., 2006). In particular,  $\delta^{13}\text{C}_{\text{carb}}$  values down to  $-41\%$  in the middle part (Jiang et al., 2003, 2006),  $-44\%$  in the lower part, and  $-48\%$  in the upper part of the Cap Carbonate (Wang et al., 2008) are observed in South China, indicating the involvement of methane hydrate (Jiang et al., 2003, 2008; Kennedy et al., 2008; Wang et al., 2008). However, the timing of the formation of the low  $\delta^{13}\text{C}$  carbonates is controversial. Previous work considered the formation of the large negative  $\delta^{13}\text{C}$

anomalies to be simultaneous with deposition of the Cap Carbonate, implying that decomposition of methane hydrate terminated the Snowball Earth (Jiang et al., 2003, 2006; Wang et al., 2008). On the other hand, recent reappraisals have shown the formation of the carbonates with the low  $\delta^{13}\text{C}$  values to postdate the formation of the Cap Carbonate (Zhou et al., 2010; Bristow et al., 2011; Lin et al., 2011).

Although the Cap dolostones, generally speaking, have negative  $\delta^{13}\text{C}$  values, the absolute values and patterns of the  $\delta^{13}\text{C}$  value changes vary from place to place (Table 1, the summary in Jiang et al., 2003, 2010; Hoffman et al., 2007; Tahata et al., 2013). In Namibia, the different  $\delta^{13}\text{C}$  variations in the Cap Carbonate are well explained by a diachronous deposition model (Hoffman et al., 2007). However, the Cap Carbonates in South China are present from the proximal margin of the inner shelf, through the continental slope, to the basin (e.g. Jiang et al., 2011). Their  $\delta^{13}\text{C}$  values are different, and are related to the depositional environment; higher  $\delta^{13}\text{C}$  values occurring in the proximal environment compared to those in distal settings (Zhou et al., 2004; Shen et al., 2005; Jiang et al., 2010). Zhou et al. (2004) attributed the difference to ocean stratification or temporal diachroneity.

We conducted an on-land drilling program in South China to systematically collect continuous sequences from the Ediacaran to the Cambrian, from the proximal margin of the inner shelf, through the distal shelf margin, to the slope. The drilling enables us to collect relatively continuous, fresh samples for comprehensive geochemical studies (Ishikawa et al., 2008, 2013, 2014; Komiya et al., 2008; Ohno et al., 2008; Sawaki et al., 2008, 2010; Tahata et al., 2013). This work presents high-resolution  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from core samples drilled through the post-Marinoan Cap dolostones of the Doushantuo Formation in Three Gorges area of South China in order to show that higher primary productivity was recovered earlier in the proximal environment due to higher continental fluxes.

## 2. Geological outline

Neoproterozoic to Cambrian strata are widespread in South China. Paleogeographic reconstructions of the Yangtze area indicate a southeast-facing Ediacaran Yangtze platform, which comprises a shallow marine shelf to deep basin environment (Zhu et al., 2003, 2007b; Jiang et al., 2007, 2011). The strata were deposited in a rift basin between the Yangtze and Cathaysia blocks, which had formed by the break-up of Rodinia around 750 to

**Table 1**  
Summary of localities of Cap Carbonate and the  $\delta^{13}\text{C}$  values of the carbonate.

Localities	Cap Carbonate	Ranges of $\delta^{13}\text{C}$ values	$\delta^{13}\text{C}$ isotope trends	References
SW Brazil	Mirassol d'Oeste	-4 to -10	negative	Nogueira et al., 2003; Font et al., 2006
NE Oman	Hadash	0 to -1	negative	Fike et al., 2006; Le Guerroué et al., 2006
Central Australia	Moint Doreen	-2.5 to 5	negative	Kennedy, 1996
South Australia	Nuccaleena	-2 to -3	negative	Lemon and Gostin, 1990
Tasmania	Cumberland Creek	-2 to -5	negative	Calver and Walter, 2000
Western Australia	Lower Ranford	-2 to -3	negative	Kennedy, 1996
NW Namibia	Keilberg	-2 to -5	negative	Hoffman et al., 2007
Lesser Himalaya	Upper Blaini	-3 to 0	negative	Jiang et al., 2003; Kaufman et al., 2006
NW Canada	Ravernsthorat	-1 to -4	negative	James et al., 2001
California	Noonday	-2 to -3	negative	Corsetti and Kaufman, 2005
East Svalbard	Lower Dracosen	-3 to -5	negative	Halverson et al., 2004
Tuva-Mongolia Khongoryu	Tsagaan Oloom	-1 to -4	negative	Macdonald et al., 2009
Scotland-Ireland	Cranford	around -7	negative	McCay et al., 2006
South China (inner shelf facies)	Lower Doushantuo	-5 to 5 <sup>a</sup>	negative to positive	Jiang et al., 2003; Wang et al., 2008; This work
South China (outer shelf, slope and basin facies)	Lower Doushantuo	-10 to -3	negative	Jiang et al., 2003, 2010; Zhou et al., 2004; Shen et al., 2005
Tarim	Lower Zhamoketi	-8 to -4	negative	Shen et al., 2008
Burkina-Fasso	Middle Sud-Banboli	-1 to -4	negative	Porter et al., 2004

<sup>a</sup> Quite low  $\delta^{13}\text{C}$  values are eliminated.

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