Precambrian Research 216–219 (2012) 152–161

Contents lists available at SciVerse ScienceDirect

Precambrian Research

journal homepage: www.elsevier.com/locate/precamres

An ^{17}O record of late Neoproterozoic glaciation in the Kimberley region, Western Australia

Huiming Bao[a,*], Zhong-Qiang Chen[b], Chuanming Zhou[c]

[a] Department of Geology and Geophysics, Louisiana State University, Baton Rouge, LA 70803, United States
[b] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan), Wuhan 430074, China
[c] State Key Laboratory of Palaeobiology and Stratigraphy, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, China

ARTICLE INFO

Article history:
Received 20 February 2012
Received in revised form 29 June 2012
Accepted 29 June 2012
Available online 10 July 2012

Keywords:
^{17}O depletion
Carbonate-associated sulfate
Kimberley
Neoproterozoic
Glaciation
Cap dolostones

ABSTRACT

We have recently reported non-mass-dependent ^{17}O depletion in sulfate deposited after the Marinoan glacial meltdown at ca. 635 million years ago. Further investigation linking the $\Delta^{17}O$ of barite to its sedimentological–geological context in Marinoan South China reveals that the ^{17}O depletion in sulfate is most pronounced at sites near paleo-continents, supporting the hypothesis that atmospheric O_2 was the source of the depletion which was transferred to sulfate via oxidative weathering of sulfides. Host minerals or rocks for the Marinoan ^{17}O depletion have been limited to barite (southern China and western Africa) and carbonate-associated sulfate (CAS) in limestone lenses within a diamictite (Svalbard). If the Marinoan ^{17}O depletion event is indeed related to an extraordinary atmospheric condition, the signal should be global in its distribution. The Kimberley region of Western Australia was close to a continent in the late Neoproterozoic and will serve as a test of our hypothesis that the anomalous ^{17}O depletion may be widely recorded in the rock records of this time period.

We report here that the CAS in the Moonlight Valley (MV) cap dolostones, Texas/Mabel Downs (TMD), the eastern Kimberley region, Western Australia is anomalously depleted in ^{17}O ($\Delta^{17}O$ value as low as −0.68‰). The magnitude of the anomaly decreases gradually toward the overlying Ranford mud-silt-sandstones. This finding not only expands the geographic distribution of the depleted ^{17}O signal, but also the type of host rocks or minerals that the anomalous sulfate resides. The CAS in the MV cap dolostones in Palm Spring (PS) section, ~150 km south of TMD, however, does not bear a ^{17}O depletion. Neither does the CAS in the Egan cap dolostones. The presence and absence of pronounced ^{17}O anomalies in the two time-equivalent yet spatially different MV cap dolostones are consistent with the paleogeography that indicates TMD was close to the continent while PS was at an open-ocean environment. While sharing some of the same sedimentological features with that of the MV cap dolostones at TMD, the Egan cap has distinct $\delta^{13}C$ and $\delta^{18}O$ values for dolostones and distinct $\Delta^{17}O$, $\delta^{34}S$ and $\delta^{18}O$ values for CAS, supporting an earlier assignment of the Egan glaciation to be younger than Marinoan in the late Neoproterozoic.

1. Introduction

Glacigenic deposits of late Neoproterozoic age have been studied since the 1960s in the Kimberley region of Western Australia (Coats and Preiss, 1980; Dow and Gemuts, 1969; Li, 2000; Plumb, 1981). Recent work by Corkeron and her colleagues (Corkeron, 2007, 2008; Corkeron and George, 2001; Grey and Corkeron, 1998) added further sedimentological, geochemical, and paleontological insights into the stratigraphic correlation, paleogeography, and ages of the many glacial events. The most widely occurring glacial deposits in the Kimberley region are the Moonlight Valley (MV) diamictite and cap dolostones. There has been no geochronological data on the age of the MV diamictite, but a Marinoan age was inferred based on sedimentary and stable carbon isotope similarities to other Marinoan glacial packages in central and South Australia (Corkeron, 2007; Grey and Blake, 1999).

Signals of non-mass-dependent ^{17}O depletion have recently been found in sulfate deposited after the Marinoan glacial meltdown at ca. 635 million years ago (Bao et al., 2008, 2009). An extremely high pCO_2 atmosphere could result in a large magnitude of ^{17}O depletion or anomaly in atmospheric O_2 and in turn transfer the anomaly to sulfate oxygen via oxidative weathering. The finding has become one of the strongest lines of evidence supporting the "snowball" Earth hypothesis (Hoffman et al., 1998; Kirschvink, 1992). Further studies linking the $\Delta^{17}O$ of barite to its sedimentological–geological context in Marinoan South China (Peng et al., 2011; Zhou et al., 2010) support that the ^{17}O-depleted sulfate was derived from oxidative weathering and the anomalous

* Corresponding author.
E-mail address: bao@lsu.edu (H. Bao).

0301-9268/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.precamres.2012.06.019

^{17}O signal was recorded at sites close to paleo-continental runoff while the signal was diluted or undetectable in the open oceans. If the ^{17}O depletion is indeed closely related to an extraordinary atmospheric condition, the signal should be global in its spatial distribution. The Kimberley region of Western Australia experienced continental glaciations in the late Neoproterozoic (Corkeron, 2008; Dow and Gemuts, 1969), within the context of Rodinian continental configurations at that time (Hoffman and Li, 2009; Li et al., 2008). A positive identification of this anomalous signal in Australia would support our hypothesis. However, a negative finding does not necessarily negate our hypothesis due to factors such as dilution by mixing, elimination by microbial activities, or lack of preservation, as we will demonstrate later in this paper.

Host minerals or rocks for the Marinoan sulfate ^{17}O anomalies have been limited to barite (South China and western Africa) (Bao et al., 2008; Peng et al., 2011; Zhou et al., 2010) and carbonate-associated sulfate (CAS) in limestone lenses within the diamictite (Svalbard) (Bao et al., 2009). In the Kimberley region, neither limestone lenses nor barite have been reported from the MV diamictite or cap dolostones. That leaves us the option of examining the triple oxygen isotope composition of CAS in the MV cap dolostones. A confirmation of sulfate ^{17}O depletion in a new host rock would add to our understanding of the origin and preservation of the anomalous ^{17}O signal. In addition, two MV cap dolostone sections, the Texas/Mabel Downs (TMD) and Palm Spring (PS), in the eastern Kimberley region exhibit different sedimentary features and represent different depositional settings. Thus, we expect to see some variation in the magnitude of the sulfate ^{17}O anomaly between the two sections.

In addition, the Egan diamictite and cap dolostones are well exposed in Mt. Ramsay area of the Kimberley region (Fig. 1), and its age has been assigned to be younger than the MV (Corkeron, 2007; Corkeron and George, 2001) (see Coats and Preiss, 1980 for a different view), largely based on occurrence of the stromatolite *Tungussia julia* (Grey and Corkeron, 1998). The morphology of stromatolites is strongly affected by facies/environmental settings and its utility in stratigraphic correlation is often problematic. Lacking radiometric dating, the current age assignment of the Egan, as well as other Neoproterozoic diamictites in the Kimberley region, is tentative. Since anomalously ^{17}O-depleted sulfate has been so far exclusively associated with Marinoan glaciation around the world, the presence or absence of the signal, together with CAS's $\delta^{34}S$ and $\delta^{18}O$ values will help to test if the Egan is indeed a glaciation event younger than Marinoan.

In this study, we present the first sulfate ^{17}O data for two MV and one Egan cap dolostones in the Kimberley region. These data are accompanied by the $\delta^{18}O$ and $\delta^{34}S$ of CAS and the corresponding $\delta^{13}C$ and $\delta^{18}O$ data of the host dolostones and by sedimentological and petrographic context. The results confirm the presence of anomalously depleted sulfate ^{17}O signals in the Kimberley Neoproterozoic and support a Marinoan age for the MV and a younger age for the Egan.

2. Sedimentological and petrographic context

In the eastern Kimberley region, the Neoproterozoic sequences include the Duerdin and Albert Edward Groups. The former comprises the Fargoo Formation, Frank River Sandstone, Moonlight Valley Formation, and Ranford Formation. The latter consists of the Mount Foster Sandstone, Elvire Formation, Boonall Dolomite, Timperley Shale, Nyuless Sandstone, and Flat Rock Formation (Table 1). Of these, the Fargoo and Moonlight Valley formations are considered as equivalents of the Elatina glaciation (Corkeron, 2007), whereas the Boonall Dolomite is correlated with the Egan Formation of the neighboring Mount Ramsay area based on a common occurrence of domical stromatolites. The Egan Formation can be correlated with the Wonoka Formation of South Australia based on a common occurrence of stromatolite *Tungussia julia* and both units were referred to as possible equivalents to the Gaskiers glaciation of Newfoundland, but more likely local events (Grey and Corkeron, 1998; Table 1).

The three cap-dolostone sections in the Kimberley region (Fig. 1) have been described by Corkeron and her colleagues (Corkeron, 2007, 2008; Corkeron and George, 2001). Sedimentological and stable carbon and oxygen isotope analysis of the two MV cap dolostones have also been conducted by others (Kennedy, 1996; Williams, 1979). The TMD cap dolostones (Fig. 2) were mostly deposited in a low-energy, below storm wave-base environment as indicated by laterally continuous and thin beddings bearing wavy algal laminae (Figs. 2 and 3). On the other hand, the PS dolostones (Fig. 2), now ~150 km south of TMD, were probably deposited in an open, high-energy environment as suggested by disrupted beddings, flat-pebble-like breccia, more and bigger detrital grains, and lack of fine algal laminae (Figs. 2 and 3). Our observation and conclusion are consistent with an earlier paleogeographic reconstruction for these MV deposits, which suggests that the two time-equivalent MV cap dolostones at TMD and PS were deposited at a near-continent and a distal or open-ocean location, respectively, on the basis of paleocurrent data and facies relationship (Corkeron, 2008; Williams, 1979). Being not disrupted by wave action, the TMD MV capstones could be supratidal as suggested (Williams, 1979) or deeper-water (below storm wave base) as suggested (Corkeron, 2007; Kennedy, 1996).

The Egan cap dolostones (Fig. 4) are rich in fine but often deformed algal laminae, tepee structures, and are more abundant in detrital quartz grains than the two MV dolostones, indicating a shallower depositional environment. These visually different sedimentological and petrographic features, however, are not sufficient to exclude the possibility that the Egan is not of the same age as that of the MV cap dolostones. The evidence supporting Egan's younger age came from the occurrence of one characteristic stromatolite (Grey and Corkeron, 1998), basinal stratigraphic sequence and facies analysis (Corkeron and George, 2001), and carbon isotope data ($\delta^{13}C$) of the dolostones (Corkeron, 2007). In this study, the lower ~4 m purple-reddish cap dolostones, below a 1.2-m thick distinct yellow dolostone bed, were analyzed for CAS (Table 2).

3. Analytical methods

Dolostone sections were sampled in 0.2–1 m interval. Thin-sections were prepared and examined, and carbonate samples were analyzed for the $\delta^{13}C$ and $\delta^{18}O$ at Nanjing Institute of Geology and Palaeontology. For carbon and oxygen isotope analyses, powders were obtained using dental drills from dolostones and an aliquot of 80–100 μg was reacted with orthophosphoric acid for 150–200 s at 72 °C in a Kiel IV carbonate device automatically connected to a MAT 253. Isotopic data are reported in per mil (‰) versus VPDB. Standard deviation (1σ) for multiple runs of a reference sample is better than 0.05‰ for $\delta^{13}C$ and 0.1‰ for $\delta^{18}O$.

Laboratory procedures for extracting, purifying, and measuring the triple oxygen ($\delta^{18}O$ and $\Delta^{17}O$) and sulfur ($\delta^{34}S$) isotope composition of CAS in bulk carbonates are detailed in an earlier paper (Bao et al., 2009). In brief, fresh dolostone chips were crushed into smaller grains using mortar and pestle. Approximately 100 g carbonates were slowly digested in 1–3 M HCl solutions and multiple supernatants were collected until no further fizzing in acid. The solution was then centrifuged, filtered through a 0.2 μm filter, and acidified before saturated $BaCl_2$ droplets were added. Precipitates were collected after >12 h and treated with DDARP method (Bao, 2006), a step critical for accurate oxygen isotope measurement for sulfate. The cleaned and dried $BaSO_4$ was then run for three different isotope parameters: (1) $\Delta^{17}O$, by converting

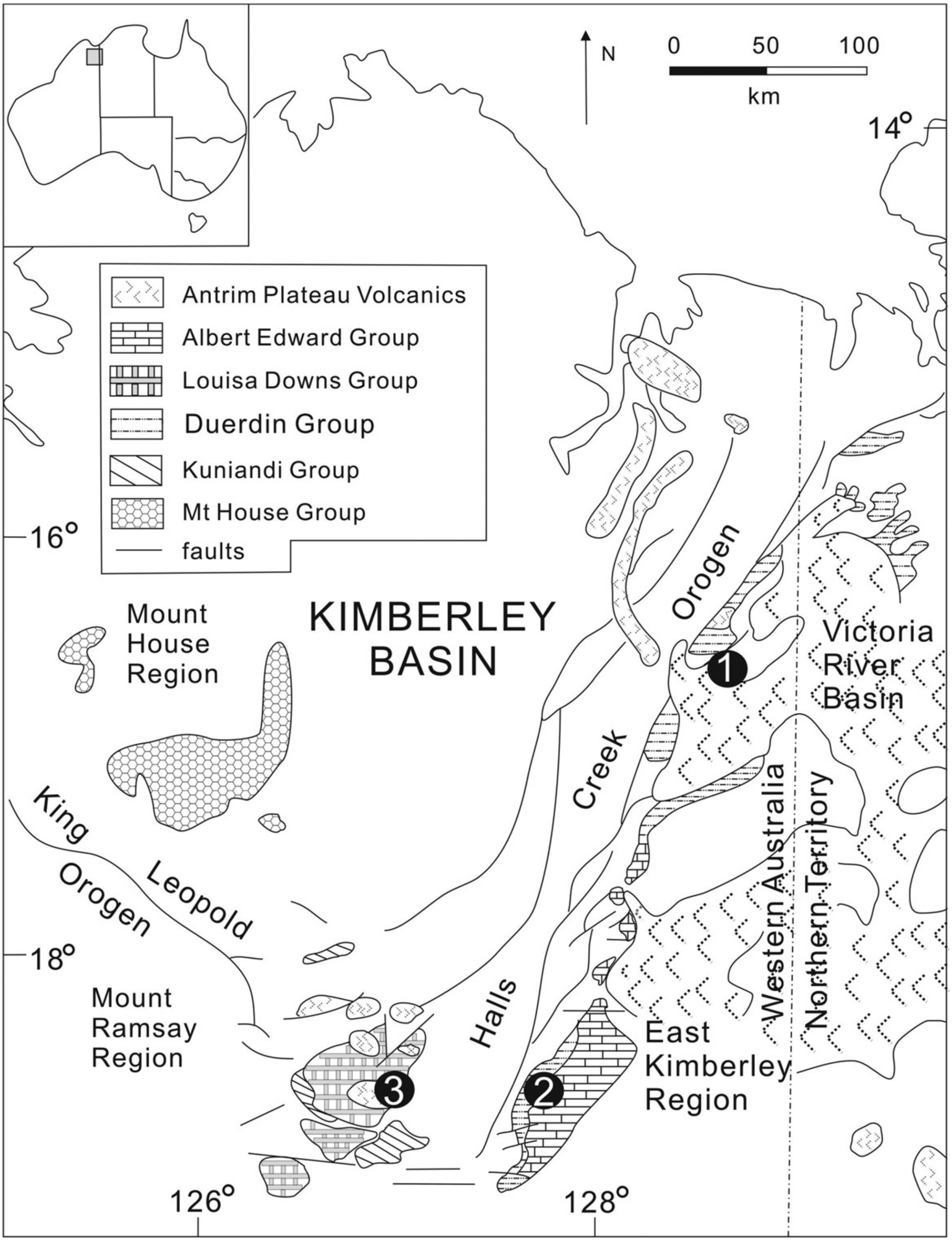

Fig. 1. A geographic map showing the distribution of Neoproterozoic rocks in the Kimberley region of NW Australia (modified from Corkeron, 2007). The studied sections: 1, Texas/Mabel Downs, the type section of the Moonlight Valley (MV) Formation; 2, Palm Spring, where the MV Formation is also exposed; 3, the type section for the Egan Formation at Mt. Ramsay. Stratigraphic units are listed in Table 1.

to O_2 using a CO_2-laser fluorination method (Bao and Thiemens, 2000); (2) $\delta^{18}O$, by converting to CO through a Thermal Conversion Elemental Analyzer (TCEA) at 1450 °C; (3) $\delta^{34}S$, by converting to SO_2 through an Elemental Analyzer at 1050 °C. The $\Delta^{17}O$ was run in dual-inlet mode while the $\delta^{18}O$ and $\delta^{34}S$ in continuous-flow mode. Both the $\Delta^{17}O$ and $\delta^{18}O$ were run on a MAT 253 while the $\delta^{34}S$ on a Micromass Isoprime. The $\Delta^{17}O$ was calculated using the definition of $\Delta^{17}O \equiv \delta'^{17}O - 0.52 \times \delta'^{18}O$ in which $\delta' \equiv 1000 \ln(R_{sample}/R_{standard})$ and R is the molar ratio of $^{18}O/^{16}O$ or $^{17}O/^{16}O$. All δ values are in VSMOW and VCDT for sulfate oxygen and sulfur, respectively. The analytical standard deviation (1σ) for replicate analysis associated with the $\Delta^{17}O$, $\delta^{18}O$, and $\delta^{34}S$ are ±0.05‰, ±0.5‰, and ±0.2‰, respectively. All sulfate related analyses were conducted at Louisiana State University except for the $\delta^{34}S$ measurement which was done at University of Maryland.

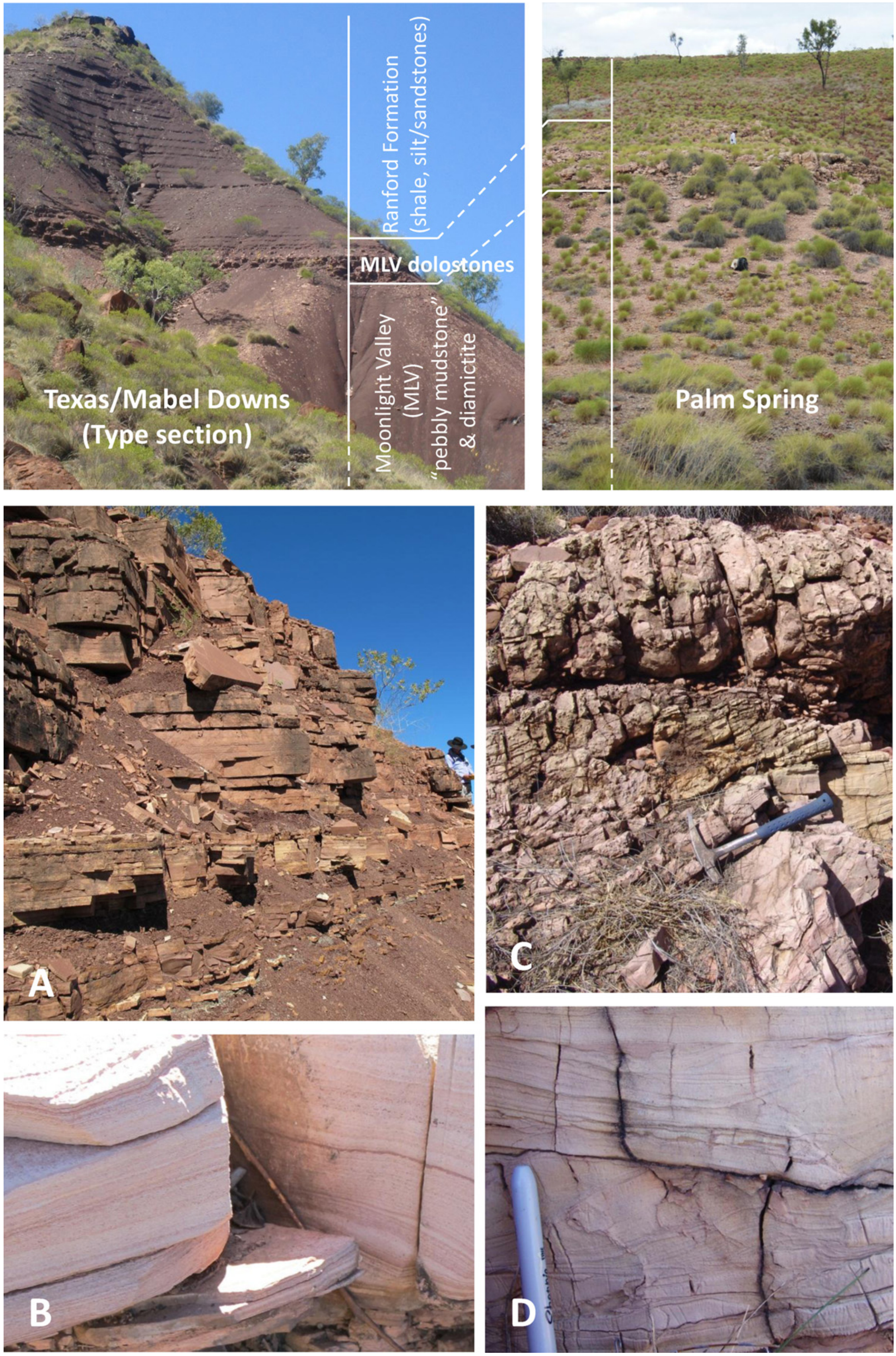

Fig. 2. (Upper panel) Field views of two Moonlight-Valley diamictite and cap dolostone sections and their underlain and overlain deposits in the Kimberley region, Western Australia: Texas/Mabel Downs (TMD) (17°4.9′S, 128°21.0′E) and Palm Spring (PS) (18°26.1′S, 127°49.7′E). (Lower panel) Outcrop comparison between the two Moonlight Valley cap dolostone sections: (A) Texas/Mabel Downs (TMD): thinly bedded and laterally continuous; (B) TMD: fine and occasionally wavy laminae (15 cm in cross view); (C) Palm Spring (PS): thinly bedded and laterally disrupted (hammer length 40 cm); (D) PS: cross-beddings and erosional surfaces (15 cm in cross view).

Table 1
Neoproterozoic stratigraphic correlations between the Kimberley region and South Australia (modified from Grey and Calver, 2007; Grey and Corkeron, 1998; Lan and Chen, 2012; Preiss et al., 2011). Gray fill indicates glacigenic deposits or the equivalents.

MOUNTRAMSAY		EAST KIMBERLEY		ADELAIDE RIFT COMPLEX			
Louisa Downs Group	Lubbock Formation	Albert Edward Group	Flat Rock Formation	Pound Subgroup	Rawnsley Quartzite	Gaskiersor localglaciations	Ediacaran
	Tean Formation		Nyuless Sandstone		Ediacaran Member		
	McAlly Shale		Timperley Shale		ChaceQuatzite Member		
	Yurabi Formation				Bonney Sandstone		
	Egan Formation		Boonall Dolomite	Wilpena Group	Wonoka Formation		
			Elvire Formation		Bunyeroo Formation		
			Mt Forster Sandstone		ABCRange Quartzite		
Kuniandi Group	Mt Bertram Sandstone	Duerdin Group	Ranford Formation		Brachina Formation		
	Wirara Formation						
	Stein Formation						
				Umberatana Group	Nuccaleena Formation		
	Landrigan Formation		MoonlightValley Formation FrankRiver Sandstone Fargoo Formation		Elatina Formation	Marinoan glaciation	Cryogenian
					Tapley Hill Formation		
					SturtianTilllite	Sturt glaciation	

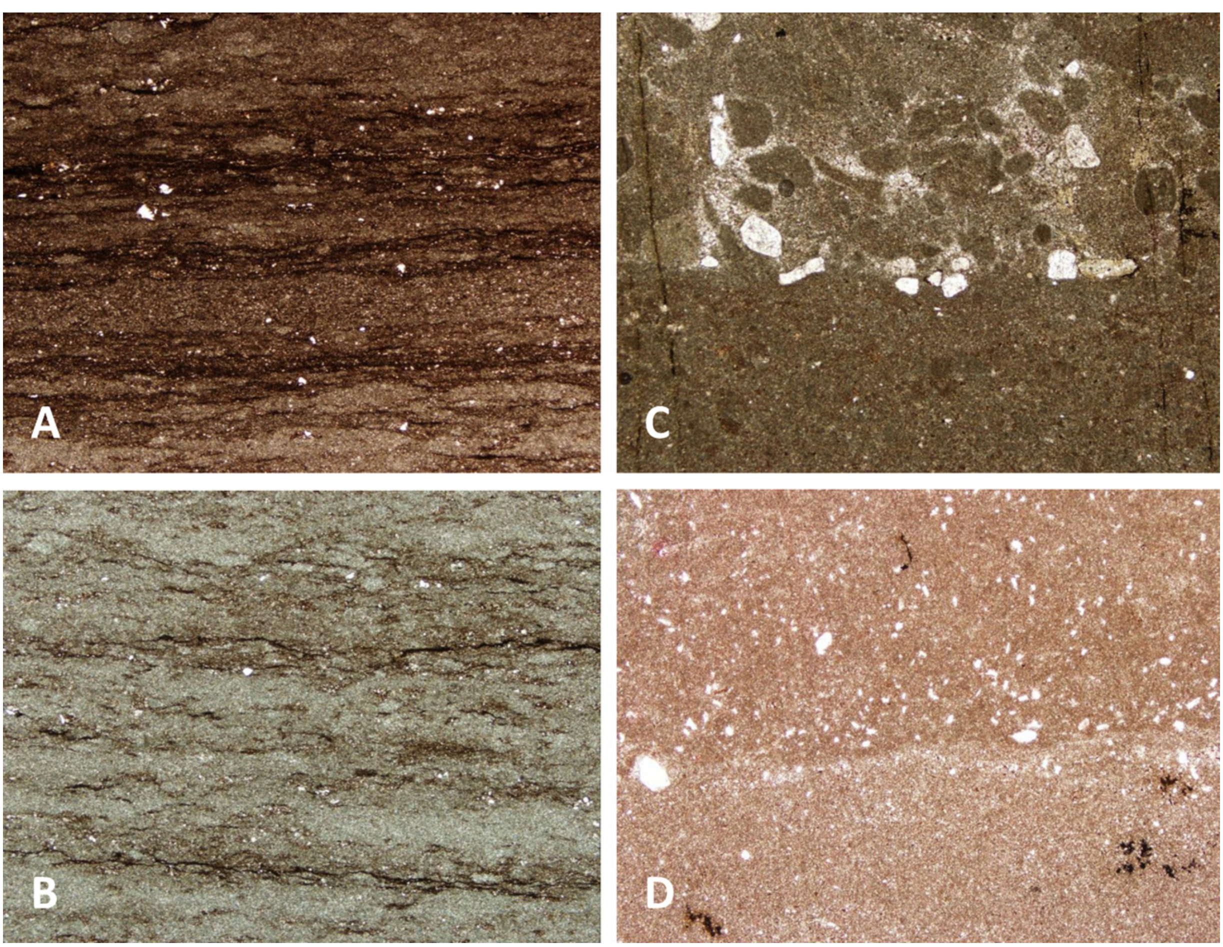

Fig. 3. Photomicrographs of thin-sections in transmitted lights; 3.5 mm in cross view for all: (A) (ZCB10-8) and (B) (ZCB10-14) are from Texas/Mabel Downs, both displaying wavy laminae with fewer quartz clasts; (C) (ZCB10-38) and (D) (ZCB10-36) from Palm Spring, showing erosional surface and internal clasts, with more quartz clasts and no or poorer lamination.

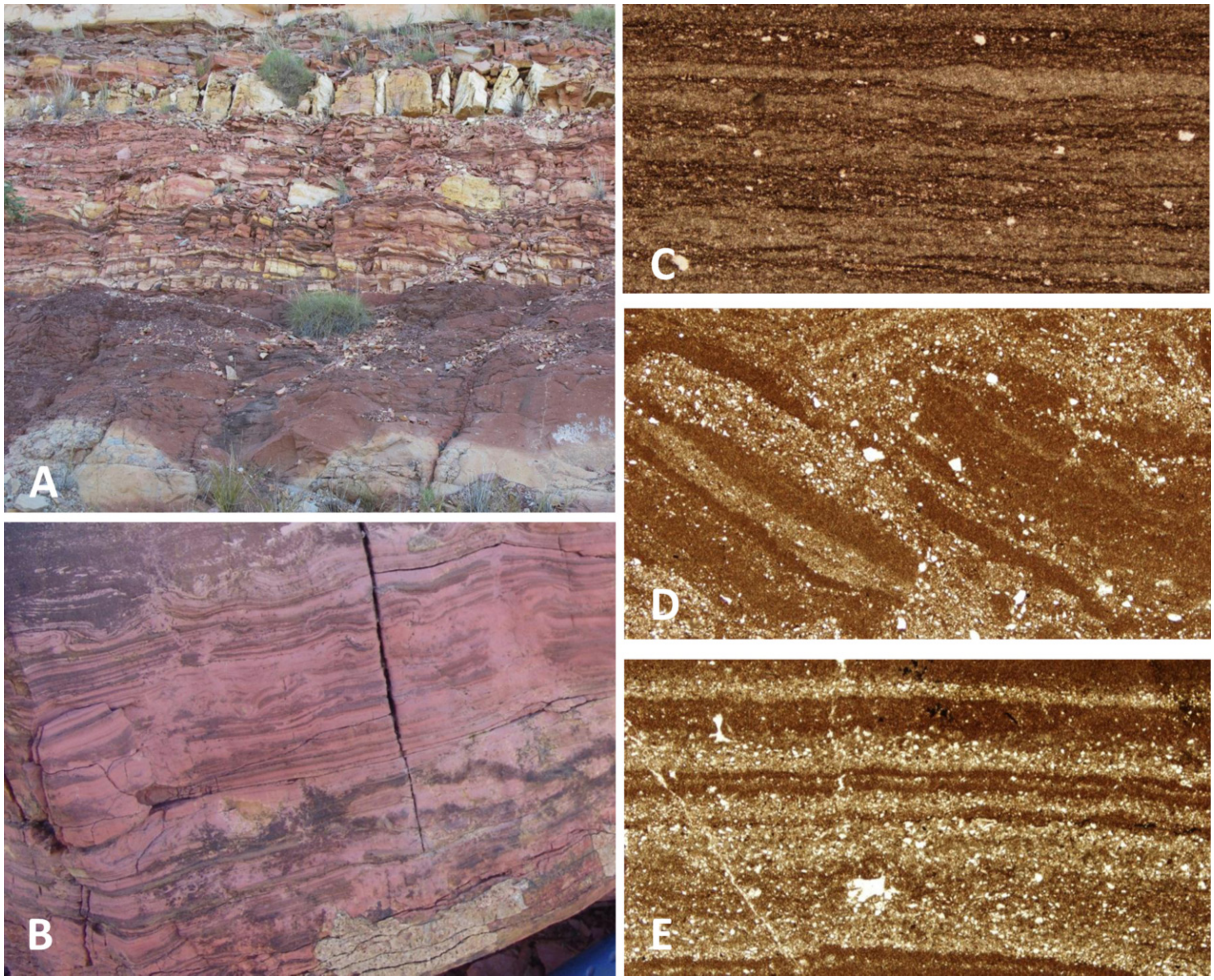

Fig. 4. (A) Field outcrop view of the type section of the Egan diamictite and cap dolostone at Mt. Ramsay (6 m in cross view) (18°34.2′S, 127°6.3′E); (B) close-up view of a cap-dolostone outcrop with fine and occasionally disrupted laminae (30 cm in cross view); (C) fine, horizontal algal laminae with fewer quartz clasts (ZCB10-97); (D) disrupted algal laminae with abundant quartz clasts (ZCB10-101); (E) horizontal algal laminae with abundant quartz clasts (ZCB10-104). Photomicrographs of (C), (D), and (E) are in transmitted light with 3.5 mm in cross view.

4. Results

CAS content ranges from 150 to 500 ppm in the cap dolostones as estimated from the weights of extracted sulfate as barite and that of the initial dolostone chips. The weathering resistant lenses sporadically occurring in the MV diamictite in TMD are found to be poor in carbonate and contain little sulfate. Thin-section examination revealed that disseminated pyrite grains in all the three cap dolostones are rare or absent. This minimizes the chance of the extracted CAS being contaminated by post-depositional oxidation or by extraction procedures. We analyzed but are not reporting the CAS data from the Walsh cap dolostones at Mt. House area, which represents a glacial event possibly of Marinoan (Corkeron, 2007) or an older age (Li, 2000) in the Kimberley region, because there are abundant disseminated pyrite grains in the sheet-crack-rich dolostones. Stable isotope data and their corresponding stratigraphic levels in cap dolostones are reported in Table 2.

4.1. *Pronounced ^{17}O depletion in CAS from the MV cap dolostones at Texas/Mabel Downs section while absent at Palm Spring section*

The CAS from the MV cap dolostones at the type section TMD displays non-mass-dependent ^{17}O depletion throughout the entire ~8 m thick dolostone sequence, ranging from −0.35 to −0.68‰ (Fig. 5). The magnitude of the ^{17}O anomaly generally decreases with increasing stratigraphic heights. The accompanied δ^{34}S value increases slightly from the 21–22‰ in the lower 4 m to 22–23‰ in the upper 4 m, while the δ^{18}O remains largely unchanged at 19–20‰ except for the highest two samples which are 1–2‰ more positive (Fig. 5).

While exhibiting a pronounced ^{17}O anomaly at the TMD section, the CAS at PS section is largely normal with Δ^{17}O values ranging from −0.01 to −0.26‰. The δ^{34}S for both sections are nearly identical, although the δ^{18}O at PS section are 0–2‰ lower than those at TMD. Note that the sampled MV cap dolostone sequence at PS section is less than 4 m in thickness, thinner than the TMD section.

The δ^{13}C and δ^{18}O of the MV cap dolostones at TMD decrease slightly (from −2.1 to −2.7‰ and from −6.4 to −7.4‰, respectively) with increasing stratigraphic heights, although the trend is not strictly monotonic. The PS section displays similar values and trends with a notably 0–0.7‰ lower value in the δ^{13}C and 1–2‰ higher value in the δ^{18}O than those at the TMD section (Fig. 6).

4.2. *The Egan cap dolostones are different from the MV ones*

The Egan cap dolostones are very different from those of the MV ones in the δ^{13}C and δ^{18}O of the host dolostones (Fig. 7) as well as the Δ^{17}O, δ^{34}S, and δ^{18}O of the CAS (Fig. 8). The Egan cap has the δ^{13}C and δ^{18}O of dolostones at ~+1‰ and ~−1‰, respectively,

Table 2
Stratigraphic levels and stable isotope composition of carbonate-associated sulfate and their late Neoproterozoic host cap dolostones (the Moonlight Valley at Texas/Mabel Downs and at Palm Spring and the Egan at Mt. Ramsay) in the Kimberley region, Western Australia.

Sample	$\delta^{34}S_{CAS}$ (VCDT)	$\delta^{18}O_{CAS}$ (VSMOW)	$\Delta^{17}O_{CAS}$	$\delta^{13}C_{dolostone}$ (VPDB)	$\delta^{18}O_{dolostone}$ (VPDB)	Height (m) from the base of the cap
Egan cap dolostones (the lower ~4 m)						
ZCB10-106	26.3	23.1	−0.07	−0.1	−1.5	3.85
ZCB10-105	25.3	22.3	−0.09	0.0	−1.0	2.85
ZCB10-104	24.5	22.3	−0.10	0.1	−0.7	1.85
ZCB10-103	24.1	23.5	−0.07	0.3	0.0	1.70
ZCB10-102	23.9	23.5	n.a.	0.1	−1.1	1.30
ZCB10-101	23.5	22.4	−0.05	0.4	−0.6	0.90
ZCB10-100	24.3	22.6	−0.09	0.6	−1.1	0.50
ZCB10-99	24.0	22.7	−0.14	0.5	−1.7	0.36
ZCB10-98	23.7	22.0	−0.16	0.7	−0.8	0.18
ZCB10-97	23.9	23.2	−0.15	0.9	−0.5	0.12
ZCB10-96	23.3	22.4	−0.15	1.0	0.5	0.08
ZCB10-95	26.7	23.6	−0.07	1.8	−1.2	Diamictite
Moonlight Valley cap dolostones at Texas/Mabel Downs (type section)						
ZCB11-4	*22.7*	18.5	−0.46	n.a.	n.a.	8.1
ZCB11-3	*22.1*	18.2	−0.44	n.a.	n.a.	7.7
ZCB11-2	*22.4*	19.3	−0.37	n.a.	n.a.	7.1
ZCB11-1	*21.6*	18.0	−0.52	n.a.	n.a.	6.3
ZCB10-6	22.1	20.7	−0.44	−2.7	−6.9	7.7
ZCB10-7	21.9	19.6	−0.35	−2.6	−7.1	7.1
ZCB10-8	22.5	19.5	−0.47	−2.6	−7.2	6.3
ZCB10-9	21.9	18.0	−0.47	−2.7	−7.0	5.5
ZCB10-10	21.9	19.5	−0.46	−2.5	−7.4	5.0
ZCB10-11	22.0	19.8	−0.51	−2.4	−7.0	4.4
ZCB10-12	22.6	19.8	−0.49	−2.4	−7.1	4.0
ZCB10-13	n.a.	n.a.	n.a.	−2.4	−7.2	3.5
ZCB10-14	21.5	19.7	−0.61	−2.4	−7.0	3.0
ZCB10-15	21.2	19.0	−0.58	−2.3	−6.9	2.5
ZCB10-16	22.2	18.6	−0.62	−2.2	−6.8	2.0
ZCB10-17	21.2	18.6	−0.63	−2.2	−6.8	1.6
ZCB10-18	n.a.	n.a.	n.a.	−2.2	−6.6	1.2
ZCB10-19	21.9	19.5	−0.68	−2.2	−6.8	0.9
ZCB10-20	21.8	19.5	−0.56	−2.2	−6.8	0.6
ZCB10-21	20.9	19.9	−0.66	−2.3	−6.7	0.4
ZCB10-22	21.3	19.3	−0.62	−2.1	−6.4	0.2
ZCB10-23	21.8	19.3	−0.57	−2.2	−6.4	0.0
Moonlight Valley cap dolostones at Palm Spring						
ZCB10-41	21.1	17.0	−0.09	−3.0	−5.1	3.3
ZCB10-40	21.4	18.1	−0.12	−3.1	−5.7	2.3
ZCB10-39	22.0	17.8	−0.26	−2.9	−5.3	1.5
ZCB10-38	19.7	17.5	−0.05	−2.9	−5.0	1.1
ZCB10-37	20.8	16.9	−0.01	−2.5	−4.2	0.9
ZCB10-36	20.9	17.1	−0.18	−2.5	−4.5	0.5
ZCB10-35	21.5	19.6	−0.15	−2.3	−4.6	0.2

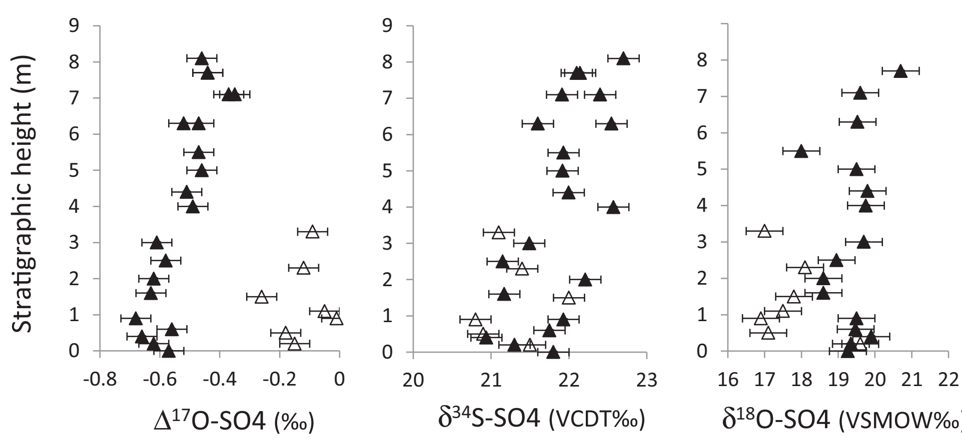

Fig. 5. The magnitude of anomalous ^{17}O depletion ($\Delta^{17}O$), the $\delta^{34}S$, and the $\delta^{18}O$ of carbonate-associated sulfate (CAS) in two Moonlight-Valley cap dolostones and their changes with stratigraphic level from the base of the cap in the Kimberley region, Western Australia: Texas/Mabel Downs (solid triangles) and Palm Spring (hollow ones).

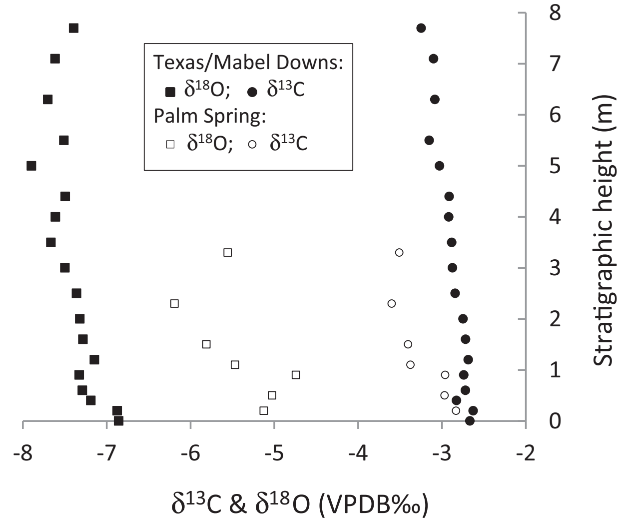

Fig. 6. The $\delta^{13}C$ and $\delta^{18}O$ of cap dolostones from two MV sections (Texas/Mabel Downs and Palm Spring) and their changes with stratigraphic height starting from the base of the dolostones. Analytical error bars are smaller than the symbols.

average of ~3‰ and ~5‰ more positive than those of the two MV cap dolostones. Also, the Egan cap's CAS has $\delta^{34}S$ values ranging from 23.3‰ to 26.7‰ and $\delta^{18}O$ values from 22.3‰ to 23.6‰, average of ~3‰ and ~4‰ more positive than those in the two MV caps, respectively.

5. Discussion

5.1. A new host rock for non-mass-dependent ^{17}O depletion in sulfate

This is the first report of non-mass-dependently depleted CAS ^{17}O signals from a dolostones sequence capping a late Neoproterozoic diamictite. So far, pronounced sulfate ^{17}O depletion is only known in barite crystal fans at an erosional surface of the cap carbonates in several locations in southern China and in western Africa (Bao et al., 2008; Peng et al., 2011), or in the CAS from limestone lenses within a diamictite in Svalbard (Bao et al., 2009), all of which have been regarded as Marinoan in age. No CAS from cap carbonates or dolostone facies was known to bear ^{17}O depletion before this study. Therefore, this finding extends the depleted sulfate ^{17}O signal to a new type of host rock and mineral, which is consistent with what is expected for a global atmosphere-related event.

Three mutually non-exclusive scenarios can explain the decreasing magnitude of ^{17}O anomaly during the course of cap dolostone deposition at TMD. (1) There should be a window of time during which the magnitude of the ^{17}O depletion in atmospheric O_2 reached the highest after the glacial meltdown. After that window, magnitude of the ^{17}O depletion in atmospheric O_2 and therefore the anomaly for sulfate initially derived from oxidative weathering would decrease. This decrease could occur over the course of the cap dolostone deposition. (2) The ratio of sulfate from oxidative weathering over sulfate of preexisting or ocean source may be decreasing over time at this particular site. The latter source of sulfate should bear no or little ^{17}O anomaly. (3) The intensity of microbial sulfur recycling at this site could have increased over the course of the cap dolostone deposition and thus shortened the time needed to erase an anomalous ^{17}O signal in dissolved sulfate. Although there is no conclusive sedimentological or geochemical evidence to rule out any of the scenarios, the small increase in the $\delta^{34}S$ in the upper 4 m dolostone sequence supports scenario 2 and/or 3, that is, a lesser amount of influx of sulfate from oxidative weathering and/or increasing intensity of microbial sulfur cycling over time at TMD. The slightly positive correlation between $\Delta^{17}O$ and $\delta^{34}S$ as seen here at MV cap dolostones are also present in Marinoan South China and Svalbard, possibly implying a common cause.

It is logical to wonder why this is the first finding of CAS ^{17}O anomaly in the cap carbonates while Marinoan cap carbonates are global in distribution. We do have CAS analysis for a few other Marinoan cap carbonates, for example, the Svalbard cap dolostones (the lower Dracoisen Formation) and the basal Doushantuo cap carbonates from South China Block. Neither of the CAS in them displays any ^{17}O depletion. The common occurrence of disseminated pyrite grains in these cap carbonates renders the extracted CAS suspicious and therefore this data is not reported. This brings us the preservation issue of the sulfate ^{17}O anomaly in minerals or rocks. As clearly demonstrated in the Svalbard case, CAS with pronounced ^{17}O depletion is found in limestone facies while not found in dolostone facies (Bao et al., 2009). The suggested cause is the effective microbial sulfur recycling that resulted in the resetting of sulfate oxygen isotope composition to that of the ambient, more evaporative, water that favored dolomite precipitation. It is not known why the CAS has ^{17}O anomalies in the TMD cap dolostones in the Kimberley region but not in the dolostone lenses in Svalbard. Further insight may be obtained by examining the sedimentological context of the limestone versus dolostone facies in Svalbard.

The preservation of ^{17}O anomaly in the rock record is also determined by the degree of dilution from preexisting sulfate in the oceans, as implied by the highly variable $\Delta^{17}O$ values of the

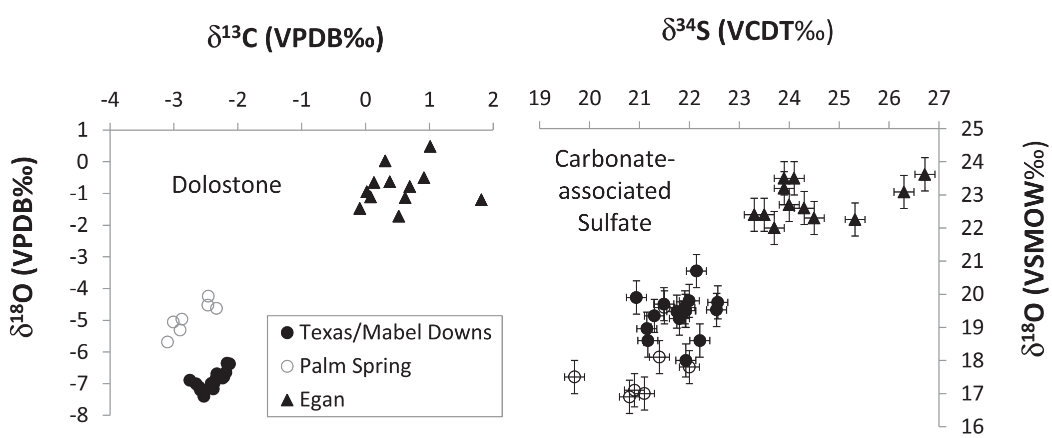

Fig. 7. The $\delta^{13}C$ and $\delta^{18}O$ for dolostones (left) and the $\delta^{34}S$ and $\delta^{18}O$ for dolostone-associated sulfate (right) in the three Neoproterozoic cap dolostones in the Kimberley region, Western Australia.

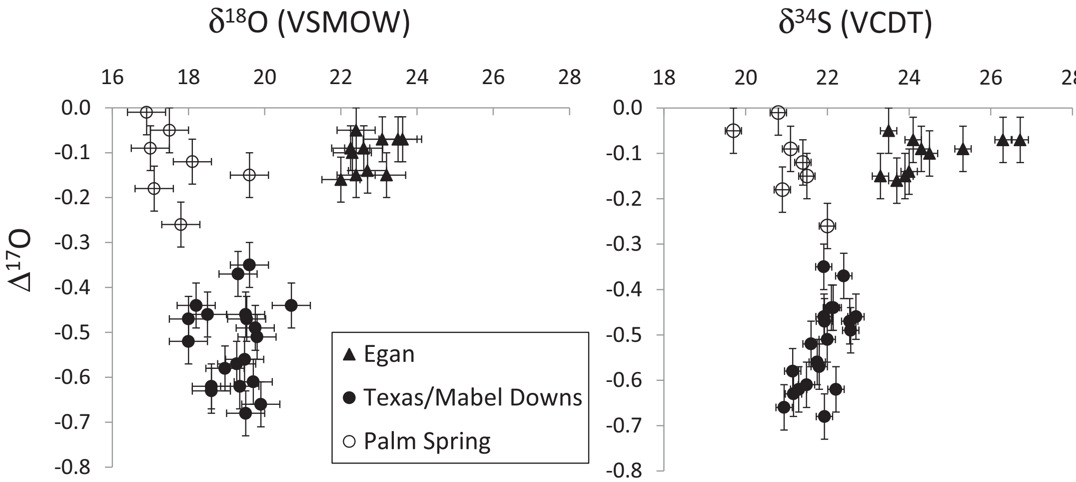

Fig. 8. The $\Delta^{17}O$–$\delta^{18}O$ (left) and $\Delta^{17}O$–$\delta^{34}S$ (right) spaces of carbonate-associated sulfate (CAS) in three Neoproterozoic cap dolostones in the Kimberley region, Western Australia. The ^{17}O anomaly in CAS is pronounced at Texas/Mabel Downs but undetectable at the time-equivalent Palm Spring section. Another probably younger Neoproterozoic glaciation can easily be distinguished by sulfur and triple oxygen isotope data of the CAS.

multiple barite growth fans in southern China (Peng et al., 2011). The preservation issue is further manifested in the time-equivalent MV cap dolostone section at PS.

5.2. *Geographical heterogeneity in sulfate ^{17}O signal distribution*

In a sharp contrast to those in TMD, the CAS ^{17}O signals are normal in the time-equivalent MV cap dolostones at PS. A few scenarios can result in the observed geographic $\Delta^{17}O$ heterogeneity. First, there were similar initial sulfate pools in the two sites but had different levels of microbial sulfur recycling in the two water bodies as was the case proposed for the Svalbard dolostone and limestone difference. However, both TMD and PS sections are dolostone, have similar $\delta^{13}C$ and $\delta^{18}O$ values for the dolomite, and have even similar $\delta^{34}S$ and $\delta^{18}O$ for their CAS (Figs. 5–7). In fact, it is the TMD section, where algal laminae are prevalent, that has the anomalous sulfate ^{17}O signals. That leaves us with the second scenario: influx of ^{17}O anomalous sulfate was much higher at TMD site than at PS site. This scenario is consistent with the paleogeographic reconstruction detailing that TMD site was close to ice out-wash discharge or river runoff whereas PS site was more distal (Corkeron, 2008). Riverine sulfate normally has a higher proportion of sulfate that is derived from sulfide oxidation involving atmospheric O_2, the ultimate source of the sulfate ^{17}O depletion. The $\Delta^{17}O$ heterogeneity probably reflects the complex geometry of the sedimentary basin.

The $\delta^{13}C$ values in PS are slightly lower than those in TMD, which is different from what is characterized in an earlier study (Williams, 1979), whereas the $\delta^{18}O$ values are higher in PS than in TMD. Our $\delta^{13}C$ and $\delta^{18}O$ pattern between the two MV sections are similar to those reported by Corkeron (2007) but with slightly different absolute values, probably reflecting lateral stable isotope variations among different profiles in the same location.

5.3. *The Egan cap dolostones is probably associated with a different late Neoproterozoic glaciation*

We have seen that one MV cap dolostone sequence has a pronounced sulfate ^{17}O anomaly while a time-equivalent MV dolostone sequence ~150 km away bears none. There are many reasons that a ^{17}O-depletion signal is not preserved in the rock records even there was one initially as we pointed out earlier. Thus, the lack of ^{17}O anomaly in the Egan cap dolostones cannot be sufficient evidence to exclude the possibility that the Egan is of the same age as that of the MV, i.e., the Marinoan. However, we favor the view that the Egan glaciation is temporally different from the MV one for the following additional arguments. In terms of the occurrence of algal laminae and perhaps the proximity to a continent, the TMD cap dolostones are similar to the Egan cap. However, not only we do not see an ^{17}O-depetion signal (Fig. 8) in the Egan cap, but also the $\delta^{13}C$–$\delta^{18}O$ space (Figs. 6 and 7) and CAS′ $\delta^{34}S$–$\delta^{18}O$ space (Figs. 7 and 8) of the Egan cap are distinctively different from those of the TMD cap dolostones. Specifically, the $\delta^{13}C$ and $\delta^{18}O$ of the Egan cap are in average of ~3‰ and ~5‰ more positive than those of the TMD ones, respectively, as were also reported in earlier studies (Corkeron, 2007; Williams, 1979). The $\delta^{34}S$ and $\delta^{18}O$ of the CAS are also in average of ~3‰ and ~4‰ more positive, respectively, in the Egan cap. While the presence of the Lower Carbonate Unit under the Egan diamictite may explain the abundance of dolostone clasts in the Egan diamictite which perhaps affected the C, O, and S stable isotope compositions in its cap, it cannot explain why the PS cap, whose diamictite is also overlying a carbonate unit, the Eliot Range dolomites, has a rather similar stable isotope signatures as those from the TMD.

6. Conclusion

The Moonlight Valley cap dolostones at its type section site Texas/Mabel Downs, the Kimberley region, Western Australia bear carbonate-associated sulfate that is non-mass-dependently depleted in ^{17}O. This occurrence represents a new set of host rock and mineral for the anomalous sulfate ^{17}O signal. The anomaly reaches −0.68‰ and its magnitude generally decreases (toward zero) with stratigraphic level of the cap dolostones and slightly with the increasing of the corresponding $\delta^{34}S$ value of the CAS, a phenomenon consistent with what we have seen in the Marinoan (~635 Ma) deposits in southern China and in Svalbard. A coeval MV cap dolostone sequence at Palm Spring, the Kimberley region, however, does not possess a pronounced ^{17}O anomaly in their CAS, due probably to its location distal to ice sheet or in an open ocean environment. The spatial heterogeneity in CAS $\Delta^{17}O$ value in the Marinoan Kimberley and the lack of anomaly in another dolostone facies in Svalbard reveal that mixing (dilution) and microbial sulfur cycling may have played roles in the preservation of the anomalous ^{17}O signal in the rock record, although the details of these discrepancies remain elusive. In addition, the newly found negative $\Delta^{17}O$ signal serves as an independent line of evidence supporting a Marinoan age for the MV diamictite and a younger age for the Egan diamictite. These conclusions are corroborated by sedimentological evidence and by the corresponding $\delta^{34}S$ and $\delta^{18}O$ values of the CAS and the $\delta^{13}C$ and $\delta^{18}O$ values of the dolostones.

Acknowledgments

Financial and field support is provided by a visiting scholar fund to Bao from State Key laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences (2010), Gledden Visiting Senior Fellow (to HB) from the University of Western Australia (2010), and NASA Astrobiology grant (10-EXO10-0115 to HB). Additional funding came from National Natural Science Foundation of China, Chinese Academy of Sciences, and Ministry of Science and Technology of China (to CMZ). We thank Yongbo Peng, Changjie Liu, Bryan Killingworth, and Dustin Boyd for laboratory assistance and two reviewers for their comments.

References

Bao, H., Fairchild, I.J., Wynn, P.M., Spötl, C., 2009. Stretching the envelope of past surface environments: Neoproterozoic Glacial Lakes from Svalbard. Science 323, 119–122.

Bao, H.M., 2006. Purifying synthetic barite for oxygen isotope measurement by dissolution and reprecipitation in a chelating solution. Analytical Chemistry 78, 304–309.

Bao, H.M., Lyons, J.R., Zhou, C.M., 2008. Triple oxygen isotope evidence for elevated CO_2 levels after a Neoproterozoic glaciation. Nature 453, 504–506.

Bao, H.M., Thiemens, M.H., 2000. Generation of O_2 from $BaSO_4$ using a CO_2-laser fluorination system for simultaneous analysis of $\delta^{18}O$ and $\delta^{17}O$. Analytical Chemistry 72, 4029–4032.

Coats, R.P., Preiss, W.V., 1980. Stratigraphic and geochronological reinterpretation of late Proterozoic glaciogenic sequences in the Kimberley region, Western-Australia. Precambrian Research 13, 181–208.

Corkeron, M., 2007. 'Cap carbonates' and Neoproterozoic glacigenic successions from the Kimberley region, north-west Australia. Sedimentology 54, 871–903.

Corkeron, M., 2008. Deposition and palaeogeography of a glacigenic Neoproterozoic succession in the east Kimberley, Australia. Sedimentary Geology 204, 61–82.

Corkeron, M.L., George, A.D., 2001. Glacial incursion on a Neoproterozoic carbonate platform in the Kimberley region, Australia. Geological Society of America Bulletin 113, 1121–1132.

Dow, D.B., Gemuts, I., 1969. Geology of the Kimberley Region, Western Australia: The East Kimberley. Western Australia Geological Survey, Western Australia.

Grey, K., Blake, D.H., 1999. Neoproterozoic (Cryogenian) stromatolites from the Wolfe Basin, east Kimberley, Western Australia: correlation with the Centralian Superbasin. Australian Journal of Earth Sciences 46, 329–341.

Grey, K., Calver, C.R., 2007. Correlating the Ediacaran of Australia. In: Vickers-Rich, P., Komarower, P. (Eds.), The Rise and Fall of the Ediacaran Biota. The Geological Society of London Special Publication, pp. 115–135.

Grey, K., Corkeron, M., 1998. Late Neoproterozoic stromatolites in glacigenic successions of the Kimberley region, Western Australia: evidence for a younger Marinoan glaciation. Precambrian Research 92, 65–87.

Hoffman, P.F., Kaufman, A.J., Halverson, G.P., Schrag, D.P., 1998. A Neoproterozoic snowball earth. Science 281, 1342–1346.

Hoffman, P.F., Li, Z.X., 2009. A palaeogeographic context for Neoproterozoic glaciation. Palaeogeography Palaeoclimatology Palaeoecology 277, 158–172.

Kennedy, M.J., 1996. Stratigraphy, sedimentology, and isotopic geochemistry of Australian Neoproterozoic postglacial cap dolostones: deglaciation, $\delta^{13}C$ excursions, and carbonate precipitation. Journal of Sedimentary Research 66, 1050–1064.

Kirschvink, J.L., 1992. Late Proterozoic low-latitude glaciation: the snowball Earth. In: Schopf, J.W., Klein, C. (Eds.), The Proterozoic Biosphere. Cambridge University Press, Cambridge, pp. 51–52.

Lan, Z.W., Chen, Z.Q., 2012. Possible animal body fossils from the Late Neoproterozoic interglacial successions in the Kimberley region, northwestern Australia. Gondwana Research 21, 293–301.

Li, Z.X., 2000. New palaeomagnetic results from the 'cap dolomite' of the Neoproterozoic Walsh Tillite, northwestern Australia. Precambrian Research 100, 359–370.

Li, Z.X., Bogdanova, S.V., Collins, A.S., Davidson, A., De Waele, B., Ernst, R.E., Fitzsimons, I.C.W., Fuck, R.A., Gladkochub, D.P., Jacobs, J., Karlstrom, K.E., Lu, S., Natapov, L.M., Pease, V., Pisarevsky, S.A., Thrane, K., Vernikovsky, V., 2008. Assembly, configuration, and break-up history of Rodinia: a synthesis. Precambrian Research 160, 179–210.

Peng, Y.B., Bao, H.M., Zhou, C.M., Yuan, X.L., 2011. ^{17}O-depleted barite from two Marinoan cap dolostone sections, South China. Earth and Planetary Science Letters 305, 21–31.

Plumb, K.A., 1981. Late Proterozoic (Adelaidean) tillites of the Kimberley–Victoria River region, Western Australia and Northern Territory. In: Hambrey, M.J., Harland, W.B. (Eds.), Earth's Pre-Pleistocene Glacial Record. Cambridge University Press, Cambridge, pp. 504–514.

Preiss, W.V., Gostin, V.A., McKirdy, D.M., Ashley, P.M., Williams, G.E., Schmidt, P.W., 2011. The glacial succession of Sturtian age in South Australia: the Yudnamutana Subgroup. In: Arnaud, E., Halverson, G.P., Shields-Zhou, G. (Eds.), The Geological Record of Neoproterozoic Glaciations, vol. 36. Geological Society, London, Memoirs, pp. 701–712.

Williams, G.E., 1979. Sedimentology, stable-isotope geochemistry and palaeoenvironment of dolostones capping late Precambrian glacial sequences in Australia. Journal of Geological Society of Australia 26, 377–386.

Zhou, C., Bao, H., Peng, Y., Yuan, X., 2010. Timing the deposition of ^{17}O-depleted barite at the aftermath of Nantuo glacial meltdown in South China. Geology 38, 903–906.