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Deciphering the impact of diagenesis overprint on negative δ^{13} C excursions using rock magnetism: Case study of Ediacaran carbonates, Yangjiaping section, South China

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ABSTRACT

Rock magnetism is used here to investigate the genesis of one of the puzzling negative carbon isotopic excursions of the Neoproterozoic in the Yangtze platform (South China). A detailed characterization of the magnetic mineralogy, which includes low-temperature and high-field magnetometry and classical magnetic measurement (ARM, IRM, susceptibility), was therefore performed along upper Doushantuo and lower Dengying Formations outcropping in the Yangjiaping section. The derived magnetic parameters show variations that can be interpreted as variations in magnetic grains size and in oxide contents. They show that the magnetic content is significantly reduced in samples presenting negative $\delta^{13}C_{calcite}$ values. We interpret this as a result of magnetite dissolution and secondary carbonate precipitation during early diagenesis bacterial sulfate reduction.

Combined with C and O isotopic data, paleomagnetic techniques thus show that the upper Doushantuo–lower Dengying negative excursion of the Yangjiaping section is largely due to diagenesis, although the preservation of a genuine δ^{13} C excursion of lower magnitude from +7% down to 0‰, instead of down to -9% as usually considered, cannot be ruled out. A corrected $\delta^{13}C_{carbonate}$ chemostratigraphic curve is therefore proposed. The unambiguous identification of a strong diagenetic component for this excursion casts doubts on the primary nature of other potentially time equivalent negative excursions of the Yangtze platform and thus to its correlation to negative excursions in other cratons (i.e. Shuram excursion). More generally, this study illustrates the potential of magnetic mineralogy characterization, a low cost, time efficient and non-destructive technique, as screening tool for diagenetic overprints of δ^{13} C and δ^{18} O.

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1. Introduction

Some puzzling negative Carbon isotopic excursions (reaching at least -5% and as much as -12%), that dwarf any Phanerozoic variations, occurred several times at the end of the Precambrian (Halverson et al., 2010, 2005; Hoffman and Schrag, 2002; Knoll, 2000). By analogy with the Phanerozoic, it has long been suggested that these negative excursions can be used as a global correlation tool. This assumption was justified by the fact that

most of the negative excursions are correlated to severe Neoproterozoic glaciations that punctuate this unique interval in Earth's history (e.g. Halverson et al., 2010, 2005; Knoll, 2000). This is of great importance for these periods since direct radiometric dating is generally hampered by the lack of suitable rocks and the fossil record is parse, rendering biostratigraphy of limited use (Knoll and Walter, 1992). Moreover, if true, this assumption also implies that δ^{13} C variations are a proxy for global carbon cycle perturbations, which would have been especially strong and frequent at this period. The causes for these putative carbon cycle perturbations are still under debate. Methane release (Bjerrum and Canfield, 2011; Jiang et al., 2003; Kennedy et al., 2001), snowball Earth (Hoffman and Schrag, 2002), overturn of a redox-stratified ocean (Grotzinger and Knoll, 1995; see also Shields, 2005) or advent

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of new species (Condon et al., 2005) have been advocated. However, major indeterminations remain concerning both the synchronism and the global extension of these negative excursions. Hence, the onshore–offshore negative δ^{13} C gradients in some Neoproterozoic basins have been interpreted as resulting from a redox stratification of the ocean (e.g. Ader et al., 2009; Giddings and Wallace, 2009a, 2009b; Jiang et al., 2007, 2011; Li et al., 1999; Shen et al., 2011). ¹³C-depleted carbonate would have essentially precipitated from deep anoxic water, which DIC was ¹²C-enriched by organic matter mineralization. Spatially restricted and not necessarily synchronous negative excursions would then indicate a transitional time interval during which the dissolved organic matter in the anoxic deep ocean inherited from the early Proterozoic would be progressively oxidized by an increasing sulfate flux to the oceans (Shen et al., 2011).

All these hypotheses, however, require that these excursions record a primary environmental signal rather than a diagenetic overprint. Recently, diagenetic overprinting has been reconsidered to explain the $\delta^{13}C/\delta^{18}O$ arrays often associated with Neoproterozoic negative δ^{13} C excursions (Derry, 2010a, 2010b; Knauth and Kennedy, 2009; Swart and Kennedy, 2011). $\delta^{13}C_{carbonate}$ is indeed liable to decrease during diagenetic processes if secondary carbonates precipitate from ¹²C-enriched pore fluids (see among others Ader and Javoy (1998), Coleman and Raiswell (1981), Irwin et al. (1977), Pierre and Rouchy (2004) and Rosales et al. (2001)). Knauth

and Kennedy (2009) argue in favor of a diagenetic overprint of the carbonate δ^{13} C (and δ^{18} O) signal due to large groundwater influx of dissolved carbon derived from terrestrial phytomass (i.e. meteoric diagenesis). Derry (2010b) argues in favor of fluid-rock interactions with high pCO₂ fluids during burial diagenesis for the largest-known carbon isotope excursion (i.e. the Shuram Excursion). But if, as envisaged by Grotzinger et al. (2011) in their review, the Shuram Excursion was a global diagenetic event, it must have been specific of this time period and remains to be identified. Indeed, none of the presently known diagenetic mechanisms seems liable to account for a globally distributed diagenetic isotope overprint event.

Given the implications of the interpretation of negative excursions in terms of changes in the global carbon cycle, ocean chemistry, or even diagenetic mechanisms during the Neoproterozoic, the issue of diagenesis is of paramount importance. Existing diagenetic tracers being too ambiguous to clearly identify all types of diagenetic overprints (Derry, 2010a, 2010b), new diagenetic proxies and different approaches are needed to evaluate the quality of the $\delta^{13}C_{carbonate}$ record.

We focus here on iron-bearing minerals with characteristic magnetic properties. They are ubiquitous in a sedimentary environment. Their mineralogy, concentration and grain size distribution are essentially controlled by the detrital input (i.e. by climatic factors) and by depositional and diagenetic redox conditions and can be investigated by standard magnetic methods (see for

635 Ma Nantuo

Fm

N3

N2

N1

-8 -4 0



magnesian dolomite

 δ^{18} O dolomite

example Evans and Heller (2003) and Verosub and Roberts (1995)). Several studies have already shown that the results obtained by these methods can be used as proxies for past climate conditions, water/sediments (bio)-geochemistry (Lascu et al., 2010) and diagenetic conditions (e.g. Garming et al., 2005; Riedinger et al., 2005; Rowan et al., 2009). Major magnetic changes are also sometimes related to fluids that were activated as a result of orogenesis (Weil and Van der Voo, 2002; O'Brien et al., 2007). So far however, only few studies have specifically considered the covariations between rock magnetic mineralogy and $\delta^{13}C_{carbonate}$ (Moreau and Ader, 2000).

Here we test this tracer in the Ediacaran upper Doushantuo and lower Dengving Formations of the Yangijaping section (South China) (Fig. 1A and B). This section presents two $\delta^{13}C_{carbonate}$ negative excursions (Macouin et al., 2004; Shen et al., 2005; Zhu et al., 2007). The upper one is usually correlated to the N3 excursion of the Doushantuo Formation at the Yangtze Gorge locality (Fig. 1C), itself correlated to the Shuram excursion essentially on the basis of its extremely negative δ^{13} C value (Condon et al., 2005; Jiang et al., 2011; Kimura et al., 2005; Zhu et al., 2007; Grotzinger et al., 2011). In the Yangjiaping section, this excursion has been partly attributed to a diagenetic overprint (Ader et al., 2009), to which a loss of primary paleomagnetic direction is associated (Macouin et al., 2004). Paleomagnetic directions being carried by magnetic Fe-bearing minerals, this diagenetic event must also have modified the magnetic mineralogy. We characterize here these magnetic mineralogy modifications and compare them to previously reported δ^{13} C values as well as δ^{18} O reported here for the first time. We show that rock magnetic parameters are sensitive tracers of diagenesis events and are promising tools to characterize their nature.

2. Geological setting

The Yangjiaping section outcrops along a road cut in the Hunan Province (Fig. 1A). The part of the section studied here corresponds to the upper Doushantuo Formation and lower Dengying Formation, which were deposited on the shelf margin of the large Yangtze platform (South China) (Jiang et al., 2011; Vernhet and Reijmer, 2010).

The Doushantuo Formation preserves an exceptional paleontological record of the Ediacaran fauna such as small bilaterian fossils (Chen et al., 2004), giant sulfur bacteria (Bailey et al., 2007) and possible animal embryo fossils (e.g. Hubert et al., 2005; Xiao et al., 1998, 2004). It records two or three negative δ^{13} C excursions (Condon et al., 2005; Jiang et al., 2003, 2011; Kimura et al., 2005; Lambert et al., 1987; Li et al., 1999; Macouin et al., 2004; Shen, 2002). The overlying Dengying Formation is mostly composed of dolomite in the shelf region and usually presents only positive $\delta^{13}C_{carbonate}$ values.

The $\delta^{13}C$ stratigraphic curve used as a reference for the Doushantuo and Dengying Formations has been compiled from various sections of the Yangtze Gorges area (e.g. liulongwan section), which corresponds to the inner platform (Lambert et al., 1987; Jiang et al., 2011). It contains three negative excursions. Recent U-Pb datings of two ash layers (Condon et al., 2005; Zhang et al., 2005) in sections of this area provide now wellbracketed ages for the duration of the Doushantuo Formation between 621 \pm 7 Ma/632.4 \pm 1.3 Ma and 555.2 \pm 6.1 Ma/ 551.07 ± 0.75 Ma. These datings also provide direct age determinations for its two major C-isotope negative excursions. The first one (N1, Jiang et al., 2011), at the base of Doushantuo Formation, is related to the cap carbonates (Jiang et al., 2003; Macouin et al., 2004; Shen, 2002). It corresponds to the deglaciation of the Marinoan glaciation at ca. 634 Ma. The upper one (N3, Jiang et al., 2011) occurs just below the Doushantuo/Dengying boundary, i.e. before or at 551 Ma.

The Yiangjiaping section studied here presents one negative excursion usually correlated to the N3 excursion (see review in Jiang et al. (2011)). We previously placed the Doushantuo–Denging boundary at the top of this negative excursion (Ader et al., 2009; Macouin et al., 2004), owing to the fact that the Dengying Formation normally presents only positive $\delta^{13}C_{carbonate}$ values in the shelf region. However, on the basis of sedimentological and stratigraphic studies, several authors place this limit just above the onset of the negative excursion (Jiang et al., 2011; Zhu et al., 2007). Here we adopt this position for the boundary. Note that this choice bears no consequence on the conclusions of the present study nor of those of our previous ones (Macouin et al., 2004; Ader et al., 2009).

3. Previous directional paleomagnetic and δ^{13} C results and new δ^{18} O results for the Yiangjiaping section

Since mechanical separation of calcite and dolomite is impossible for most samples, δ^{13} C and δ^{18} O from calcite or low magnesian dolomite ($\delta^{13}C_{calcite}$ and $\delta^{18}O_{calcite}$) and dolomite or high magnesian calcite ($\delta^{13}C_{dolomite}$ and $\delta^{18}O_{dolomite}$) were measured using different dissolution times by H₃PO₄ (4 h at room temperature and 2 h at 80 °C, respectively). A perfect chemical separation of calcite and dolomite being difficult (Al-Aasm et al., 1990; Yui and Gong, 2003; Baudrand et al., 2012) the so-called dolomite might be contaminated to some extent by calcite and vice-versa. The calcite and dolomite contents were roughly estimated during the isotope composition measurements with a precision of only \pm 10% of the measured value.

3.1. $\delta^{13}C$ data

The $\delta^{13}C_{carbonate}$ results for the studied part of the Yiangjiaping section have been previously described in Macouin et al. (2004) and Ader et al. (2009). In brief, two stratigraphic zones can be distinguished. The first part of the section (0 m and 90 m) corresponds to a positive $\delta^{13}C_{carbonate}$ excursion. Similar $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$ values comprised between 4.3‰ and 7.3‰ characterize it. This, together with the high carbonate content (> 50%) and the lack of recrystallization observed in thin sections, was previously taken as an evidence for a primary signature for the carbon isotopic signal in both calcite and dolomite (Ader et al., 2009; Macouin et al., 2004).

On the contrary, the upper part of the section (between 90 and 223 m) corresponds to a negative excursion. In this part, some samples display strong differences between $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$. $\delta^{13}C_{dolomite}$ decreases on average to 0‰ except for one very negative value of -22.5% obtained from a secondary carbonate vein-filling. $\delta^{13}C_{calcite}$ are similar to or more negative than $\delta^{13}C_{dolomite}$ and show erratic and large variations from +6.8% to -15.4%, with two extreme values down to -22.7%. The strongly negative $\delta^{13}C_{calcite}$ are best interpreted as resulting from secondary calcite crystallization from ^{12}C -enriched fluids. Although less erratic and negative, the $\delta^{13}C_{dolomite}$ could also have been modified. The negative excursion ends by a return to positive values (+5‰) of both $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$ ($\delta^{13}C_{carbonate}$).

3.2. δ^{18} O data

Because oxygen is a major component of sedimentary fluids, the likelihood that carbonate δ^{18} O values record a primary seawater signature is low (see among others Banner and Hanson (1990) and Kaufman and Knoll (1995)). Instead, they may record diagenetic events. Correlation arrays between δ^{18} O and δ^{13} C in particular, are usually considered as proxies for a diagenetic overprint of both δ^{18} O and δ^{13} C (see Derry (2010b) for a review).

Table 1

Summary of rock magnetic parameters and isotopic results. Carbon isotopic values are from Macouin et al. (2004) and Ader et al. (2009). δ^{18} O are from this study. Column headings indicate the following: sample number (sample), stratigraphic position in cm (*H*), δ^{13} C_{calcite}, δ^{18} O_{calcite}, δ^{18} O_{calcite}, approximate content in calcite or in low magnesian dolomite (%calcite), δ^{13} C_{dolomite}, δ^{18} O_{dolomite}, approximate content in dolomite (%dolomite), approximate content in carbonate (%carbonate), Anhysteretic Remanent Magnetization (ARM), Isothermal Remanent Magnetization (IRM) acquired at 0.15 T (IRM_{0.15 T}), IRM at 1.2 T (IRM_{1.2 T}), rock magnetic parameters ration (ARM/IRM and IRM_{1.2 T}/IRM_{0.15 T}), δ^{13} C_{org} and Total Organic Content (TOC).

Sample number	Н	$\delta^{13}C_{calcite}$	$\delta^{18}O_{calcite}$	%Calcite	$\delta^{13}C_{dolomite}$	$\delta^{18}O_{dolomite}$	%Dolomite	%Carbonates	ARM	IRM 0.15 T	IRM 1.2 T	ARM/IRM	IRM 1.2 T//IRM 0.15 T	$\delta^{13}C_{\text{org}}$	TOC
	(cm)	(‰ PDB)	(‰ PDB)	<u> </u>	(‰ PDB)	(‰ PDB)	<u> </u>	<u>+</u> 20% fer	(m ² /kg)	(m^2/kg)	(m ² /kg)		1///IRW 0.19 1	(‰ PDB)	
HU109	0	5.2	-7.4	31	5.4	-7.4	29	60	4.15E - 05	2.40E - 04	3.18E - 04	0.17	1.33	25.1	0.75
HU113	139	5.4 4.9	-7.8	62 72	5.3	-7.5	43 18	90	6.32E-05	4.37E-04	5.54E-04	0.14	1.27	-25.1	0.75
HU115	367	5.2	-7.4	13	5.9	-7.1	69	82							
D00501	496	5.4	-6	15	5.5	-6.1	29	44	4.84E – 05	2.25E - 04	2.75E - 04	0.22	1.22		
D00505	498	4.0	0	20	47	0.7	22	60	2.56E - 05	1.26E - 04	1.03E - 04	0.2	1.3	25.1	0.52
D00500	191	4.8	-8	30 20	4.7	- 8.2	14	42	4.87E-05	2.95E - 04	5.82E - 04	0.10	1.29	-25.1	0.55
D00510	2601	2.0	- 7.2	29 73	4.5	- 7.9	14	45 02	0.93E-03	J.20E-04	7.22E-04	0.17	1.59	_ 23 4	0 17
HU119	3093	66	-7.8	105	7.1	-74	< 0.5	105	5 32E - 06	2.73E - 05	3 24E – 05	019	1 19	-25.4	0.17
HU120	3393	6.8	-75	102	73	-8	13	115	5.522 00	2.752 05	5.212 05	0.15	1.15		
HU122	4171	6.7	-7.6	76	6.4	-8.3	29	105	1.11E-05	5.75E-05	7.05E-05	0.19	1.23		
D00615	4750	6.7	-7.1	69	6.9	-7.9	21	90	8.62E-06	5.07E-05	6.10E-05	0.17	1.2		
HU124	4930	6.5	-7.6	82	6.2	-8	2	84	5.52E-06	2.80E-05	3.41E-05	0.2	1.22		
HU125	5230	6.9	-7.8	69	6.4	-8.3	31	100	1.19E - 05	6.78E-05	8.15E-05	0.18	1.2	-21.1	0.16
HU126	5506	6.6	-8	67	6.6	-7.6	28	95	7.66E-06	3.92E-05	4.92E - 05	0.2	1.26		
D00625*	5544	7		85	7.2	-7.4	5	90						-22.4	0.24
HU128	5675	6.5	-6.5	30	6.5	-6.5	47	77							
HU131	6889	7.3	-7.2	100			< 0.5	100	7.43E-07	3.43E-06	3.99E-06	0.22	1.16		
D00635*	7389	6.8		75	7.3		25	100						-20.9	0.28
HU133*	7509								3.22E - 06	1.74E - 05	1.99E - 05	0.19	1.15		
HUI35	8228	7.5	- /./	88	7.1	-8.8	11	99							
DO0301	9386	5.5		45	5.7		47	92						-25.3	0.61
DO0305	9720	3.7	-7	40	2.5	-7.2	30	70							
DO0309	11,531	-2.9		43	4.1		72	115						-28.1	0.02
DO0311	11,680	-5.1	-8.6	20	2	-7	80	100						-24.8	0.03
DO0319	13,047	1.1	-6.2	15	1.8	-5	39	54						-26.9	0.9
D00323	13,625	0.2	-5	12	0.6	-5.1	52	64	3.74E - 06	2.41E - 05	7.56E – 05	0.16	3.13		
DO0327	14,068	-1.1	-6.4	16	0.2	-5.5	69	85	7.34E – 06	3.65E – 05	8.12E-05	0.2	2.22		
D00327a	14,068								3.43E-06	1.80E – 05	5.15E-05	0.19	2.85		
D00327b	14,068	0.0		10	2.2	4.6	50	C 2	2.50E-07	7.30E-06	1.84E-05	0.03	2.52	26.5	0.44
D00329	15,151	0.8	7	12	2.2	-4.6	50 47	62						-20.5	0.44
D00337 *	16,239	-1	-7	47	0.4	-4.0	47	54	133E 07	2.47E 06	2 86E 06	0.05	1 16	-27.5	0.56
D00337	16,459								3.03E - 07	2.471 = 00 8.741 = 06	9.52E - 06	0.03	1.10		
D00343	17,008	-72	_93	24	25	-77	67	91	1.67E - 07	1.99F - 06	2.13E - 06	0.05	1.05		
D00347	17,637	-12	-101	22	-04	-96	68	90	8.07E - 06	4.65E - 05	5.12E - 05	0.17	11		
D00349	17.638	1.2	1011	22	0.11	510	00	50	8.54E – 08	1.48E-06	6.27E-06	0.06	4.25		
D00351 *	18,274	-15.4	- 10.3	63	3	-8.2	24	87						-24	0.02
D00353	18,437	-3.2	-11.5	6			< 0.5	6	7.80E-08	3.23E-06	3.64E-06	0.02	1.13		
HU172	18,657	-6.4	-9.5	33	2.5	-8.5	74	107							
HU174	18,847	-14.1	-9.3	32			< 0.5	32							
HU175	18,929	-11.7	-10	21	3.6	-7.5	90	111							
HU176	19,037	-7.2	-8.5	49	-0.5	-7.1	45	94						-25.9	0.02
HU177	19,092	-4.9	-8.2	27	3.6	-7	61	88	8.15E-08	1.71E - 06	1.87E - 06	0.05	1.09		
HU180	19,545	-2.8	-7	45	-1.4	-5.7	58	103	1.04E - 05	6.03E-05	6.49E-05	0.17	1.08	-29.5	0.83
HU181	19,626	-0.5	-7.6	15	0.2	-7.7	86	101							
HU182	19,627	-2.5	-5.7	10	-0.8	7.0	70	80	5.08E - 07	1.72E - 05	1.73E - 05	0.03	1.01		
HUI83	19,907	2.6	-6.9	27	3.5	- 1.2	54	81 02	0.015 00	E 74E 05	0.605 05	0.15	1 5 1		
	20,437	4.0	-0.5	48 25	0.3 6.6	-5.9	44 61	92	0.01E-06	5./4E-05	0.08E-05	0.15	1.51		
DO1101	20,580	4.9	-0	23	0.0	-0 112	26	00	104E 09	2 5 2 E 0 7	2.055 07	0.04	10		
DO1101	20,009	- 22.7	- 10.0	70	5.9	- 11.5	20 41	91 111	1.04£ - 08 5.01F 07	2.33E-07 3.92E 06	432F 06	0.04	1.2	- 27 3	0.06
HI1192	21,347	6	-67	15	6.8	-74	64	79	4.89F - 08	1.81E - 06	1.91F - 06	0.03	1.06	-27.5	0.00
110152	22,234	5	-0.7	15	0.0	- /		, ,	1.031-00	1.011-00	1.511-00	0.05	1.00		

We report here the available δ^{18} O values obtained simultaneously to the previously published δ^{13} C values (Table 1) but not reported so far. They are comprised between -12% and -4% and are typical for Neoproterozoic sedimentary rocks (Knauth and Kennedy, 2009; Jacobsen and Kaufman, 1999).

In the $\delta^{13}C_{dolomite}$ versus $\delta^{18}O_{dolomite}$ diagram (Fig. 2A), samples from the positive and negative excursions plot in two distinct zones. No correlation array can be identified for dolomite within and between each sample group. In the $\delta^{13}C_{calcite}$ versus $\delta^{18}O_{calcite}$ diagram (Fig. 2B), samples from the positive excursion plot in the same area as in the Fig. 2A without correlation array. Samples from the negative excursion either plot with samples from the positive excursion or define a negative $\delta^{13}C_{calcite}$ and $\delta^{18}O_{calcite}$ array. This array can also be suspected but is much less obvious in the data obtained on bulk carbonates by Zhu et al. (2007) (Fig. 2C). It suggests a diagenetic overprint, in agreement with the strong differences between $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$ and with thin sections and the SEM observations (Fig. 3A) showing secondary carbonate crystallizations.

section that probably indicated a low latitude position of South China at these times. They had also highlighted a relationship between C-isotope, directional data and natural remanent magnetization (NRM) intensity (see Fig. 4 of Macouin et al. (2004)). Samples from the negative excursion are associated with remagnetization, have the weakest NRMs or have unstable magnetizations (Fig. 1B). Mechanisms explaining the acquisition of low $\delta^{13}C_{calcite}$ and a contemporaneous loss of magnetization require new data to be further understood, in particular to determine which magnetic mineralogy is associated.

We further explore this diagenetic event, with the objective to characterize how it is recorded by rock magnetic parameters.

4. Magnetic study

4.1. Acquisition of rock magnetic properties

3.3. Directional paleomagnetic data

Macouin et al. (2004) had obtained directional paleomagnetic results from the upper Doushantuo Formation in the Yangjiaping Magnetic susceptibility (χ) was measured with a kappabridge KLY3-CS3 (Agico©) magnetic susceptibility meter at the IPGP paleomagnetic laboratory (France). The anhysteretic remanent magnetization (ARM) and the isothermal remanent magnetization (IRM) have been obtained in same laboratory with a 2G cryogenic magnetometer. The ARM was determined using a continuous field



Fig. 2. Distribution of δ^{13} C against δ^{18} O. C are data from Zhu et al. (2007) (see text).

Fig. 3. Back scattered electron images of the Upper Doushantuo beds samples (A) calcite (in light gray) and dolomite (gray) with pyrite (white) at the fringe of calcite. (B) Cubic pyrite in dolomitic matrix. (C) Phosphatized (P) spherical microfossil (Embryo or acritarch?) in the dolomitic matrix. Pyrites (Py) are visible inside the fossil. (D) Pyritized (Py) possible fossil membrane.

of 0.1 mT and application of a parallel alternating field (AF) with peak field of 90 mT. Hysteresis cycles at room temperature up to maximum field of 1 T were measured with a Princeton Vibrating Sample Magnetometer (VSM) at both the IPGP paleomagnetic laboratory (Paris, France) and the IRM laboratory (Minneapolis, USA) to determine the hysteresis parameters, coercivity of remanence (Hcr), coercive force (Hc), saturation remanence (Mrs), and saturation magnetization (Ms).

Measurements of the remanence at low temperatures have been obtained at the IRM laboratory (Minneapolis, USA) using the Magnetic Properties Measurement system (Ouantum Design©). The loss of remanence on warming from 10 K to 300 K was measured for two different initial states: zero field cooled (ZFC). where the sample is cooled to 10 K in the absence of magnetic field prior to the application of a 2.5 T field and field cooled (FC), where the sample is cooled to 10 K in a 2.5 T magnetic field. Saturation isothermal remanent magnetization (SIRM) experiments have been obtained by applying a 2.5 T field at room temperature (RT-SIRM) and then cooling the sample to low temperature and reheating to room temperature in a zero field. Finally, scanning electron microscope observations were performed with a JEOL instrument (JSM-6360LV) at the GET laboratory (Toulouse, France) operating at 15 kV with an Electron Dispersive System (EDS) that allows a punctual qualitative characterization of the chemical composition.

4.2. Identification of magnetic minerals

Applying these various magnetic measurements to a selection of samples we can identify the different magnetic phases present in the upper Doushantuo and lower Dengying carbonates.

4.2.1. Magnetic susceptibility as a function of temperature: χ -T curves

The χ -*T* curves (magnetic susceptibility as a function of the temperature) obtained for 13 samples show Curie points between 500 and 600 °C (Fig. 4A, B, and D). This indicates that the main Fe-oxides is a ferrimagnetic phase that can be magnetite, oxidized magnetite or maghemite. A Hopkinson peak for the magnetite

(Fig. 4B) appears sometimes both in non-altered (DO0635: $\delta^{13}C_{calcite}=6,8\%$) and in altered samples (sample DO0351: $\delta^{13}C_{calcite}=-15,4\%$). The Hopkinson effect is best detected in samples with single-domain (SD) pure magnetite grains presenting a narrow size grain range.

Some curves are almost reversible (Fig. 4A and B) but others (Fig. 4C and D) are not. The latter reveal important mineralogical transformations above 400 or 600 °C, which prevent the identification of the magnetic phases. Heating under an inert atmosphere (argon) to avoid oxidation reduced the changes (Fig. 4C) but did not completely prevent them.

4.2.2. Low-temperature experiments

Goethite is revealed in the sample DO0319B by a large difference between the ZFC and FC curves (Fig. 5B) and a large increase in SIRM (factor \sim 3) on cooling (Fig. 5E). Goethite seems to be absent in the samples DO0351 and DO0635, since the increase in the RT-SIRM curves is weak.

Hematite seems to be rarely present in the samples, a clear Morin transition of hematite (see Ozdemir et al., 2008) being detected only in the SIRM curves of the sample DO0301. A weak evidence of a Morin transition can also be detected in the FC curve of sample DO0319 (Fig. 5B). But, if it was related to the presence of hematite, one would have also expected a clear Morin transition on the RT-SIRM curve, which is not the case (Fig. 5E), ruling out the likelihood that hematite is present in this sample.

The characterization of the ferrimagnetic phase revealed by the χ -*T* experiments is not trivial here, mainly because of the weak magnetization of these carbonates. A Verwey transition of magnetite at around 120 K (see Ozdemir et al., 2002) can be suspected in the ZFC–FC curves of the sample DO0319 (Fig. 5B) that could indicate the presence of a small amount of magnetite in this sample. In the sample DO0635, the grain size distribution of the ferrimagnetic phase extends down to the superparamagnetic size range as indicated by the 1/*T* like dependence in FC and ZFC curves (Fig. 5A). The associated RT-SIRM curve is noisy. The hump-shaped SIRM cooling curve between 300 K and Tv (temperature of the Verwey transition) and the matching humped curve during warming in the same temperature range are, according to Ozdemir and Dunlop (2010), a hallmark



Fig. 4. Susceptibility as a function of temperature (χ –*T*). (A, B) Reversible curves denoting the presence of magnetite, (C) curve showing mineralogical transformations, (D) curve obtained under Argon; the mineralogical modifications occur later during cooling and the signature of magnetite is visible on the heating curve.



of maghemitization. Since both the very weak Verwey transition in the ZFC–FC curves (Fig. 5A) and the Hopkinson peak in χ –*T* experiments indicate the presence of magnetite in this sample, it is likely that magnetite presents a superficial layer of maghemite due to grain surface oxidation or that both maghemite and magnetite coexist (Channell and Xuan, 2009; Ozdemir and Dunlop, 2010). Finally, low-temperature experiments for the sample DO0351 seem to reflect a small size for the ferrimagnetic phase, in the single domain to pseudo single-domain range. This ferrimagnetic phase is likely also composed of oxidized magnetite since neither the ZFC/FC nor the RT-SIRM curves display the signature of the Verwey transition of pure magnetite and the SIRM curves present a hump shape.

In conclusion, these temperature-dependant experiments at low temperature have revealed the presence of a ferrimagnetic phase composed of magnetite more or less oxidized and sometimes also of goethite and hematite.

4.2.3. Other experiments

ARM and IRM acquisition curves on eleven samples (Fig. 6A–D) also display the presence of a ferrimagnetic phase since 60–95% of the IRM acquisition have been obtained before 150 mT. In some

samples, they also exhibit (Fig. 6B and D) the presence of a high coercivity phase. This phase probably corresponds to goethite or to hematite as shown by the low-temperature measurements (Fig. 5B and E).

SEM observations and energy-dispersive spectroscopic (EDS) spectrum analysis of iron-bearing minerals were made on fresh fractures of whole rocks and on thin-sections. Both dolomitic and calcitic zones were observed (Fig. 3A). Pyrites (Fig. 3A–D) are present in both zones. Greigite has also been recognized. The largest pyrites are sometimes visible at the fringe of large calcitic zones (Fig. 3A). The main magnetic phases (magnetite and goethite) identified here by the magnetic method, have not been observed and are therefore probably too small to be visible, i.e. smaller than 1 μ m.

To conclude, the different magnetic measurements presented and the SEM observations have allowed the identification of magnetite (probably oxidized), maghemite, goethite, hematite, pyrite and probably a small amount of other types of iron sulfides, such a greigite.

However, in order to relate changes in the ferrimagnetic phase composition to carbon or oxygen isotope evidence for a diagenetic event a more systematic investigation is necessary.



Fig. 6. Curves of acquisition of IRM. *M* is the remanent magnetization as a function of the applied field (*H*). (A, B) are representative of most of the measured samples. The saturation is obtained before 400 mT. (C, D) Curves showing the presence of hematite and/or goethite.



4.3. Size and amount of magnetic minerals

4.3.1. Hysteresis parameters

The rock hysteresis loops measured in the Doushantuo carbonates display varying degrees of wasp-waisting (Fig. 7), indicating different populations of magnetic grains with distinct coercivities (Tauxe et al., 1996). The presence of mixture prevents a clear interpretation of hysteresis parameters in terms of grain size. After correction for the combined effects of paramagnetic and diamagnetic contributions (i.e., the matrix contribution), parameters extracted from the total hysteresis loop data set are reported on the Day plot (Day et al., 1977; Fig. 7) range between $1.69 \le \text{Hcr/Hc} \le 5.6$ and $0.16 \le \text{Mrs/Ms} \le 0.29$.

4.3.2. ARM and IRM

In order to evaluate the stratigraphic variations of concentration and size of the magnetic phases, we systematically acquired on 31 samples, IRM at 150 mT ($IRM_{0.15 T}$) and at 1.2 T ($IRM_{1.2 T}$) and the ARM at saturation (100 mT). Results are reported in the Table 1 and in Fig. 1B.

The IRM_{1.2 T}/IRM_{0.15 T} ratio is a good indicator of the proportion of low coercivity phases versus high coercivity phases. When it is higher than 1, it denotes the presence of high coercivity phases (here goethite). When it is close to 1, it indicates that only the ferrimagnetic phase (probably magnetite) is present, as it is the case in most of our samples (Fig. 1B). We can therefore consider that the main magnetic carrier in the Doushuantuo carbonates is the ferrimagnetic phase (probably magnetite), except for 3 samples (DO0323, DO0327 and DO0349) containing high coercivity iron oxides (probably goethite). Thus, except for these three samples, the IRMs can be interpreted as indicators for the concentration of magnetite.

The ARM/IRM ratio is sensitive to magnetite grain size (Moreau and Ader, 2000; King et al., 1982), small grains acquiring the strongest anhysteretic remanent magnetizations (Banerjee et al., 1981). One can note that greigite revealed by SEM and EDS observations can contribute to the low/middle coercivity signal attributed to magnetite but this does not change our conclusions.

5. Correspondence between rock magnetic parameters and $\delta^{13}\text{C}_{carb}$

The positive excursion is characterized by relatively stable rock magnetic parameters (e.g. IRM and ARM and their ratio) (Fig. 2B) as well as isotopic parameters, while the negative excursion displays very large and erratic variations for both types of signals (Fig. 2B).

Within the positive excursion, an abrupt $\delta^{13}C_{carb}$ increase from 3–5‰ to 7‰ occurs at 320 m. It is synchronous with a carbonate content increase from values lower than 60% to values higher than 60% (Table 1) and with a diminution of one order of magnitude of ARM and IRM_(1.2 T and 0.15 T) (Fig. 8). This reflects a decrease of magnetic content. ARM/IRM ratio remains unchanged indicating that grain size probably remains similar.

Within the negative excursion, erratic and large variations of the IRM and ARM/IRM values and of $\delta^{13}C_{calcite}$ are observed while $\delta^{13}C_{dolomite}$ remains relatively constant (Fig. 1B). When plotting $\delta^{13}C_{calcite}$ as a function of the ratio ARM/IRM (Fig. 9), two groups can be clearly distinguished. The first group of samples displays ARM/IRM > 0.12 and mostly positive $\delta^{13}C_{calcite}$ while the second one displays ARM/IRM < 0.12 and mostly negative $\delta^{13}C_{calcite}$. The contrasted ARM/IRM between the two groups indicates significant grain-size differences. ARM/IRM values < 0.12 correspond to large (multidomain) or very small (superparamagnetic) grains. They are associated to lower IRM values (Fig. 1B), which reflect a lower content in magnetic oxides (i.e. in magnetite, see Section 4.3). ARM/IRM



Fig. 8. $\delta^{13}C$ as a function of IRM and ARM data for the samples of the positive $\delta^{13}C$ excursion between 0 and 90 m.



Fig. 9. $\delta^{13}C_{\text{calcite}}$ as a function of ARM/IRM and definition of groups. Zone P and N correspond respectively to samples from the positive $\delta^{13}C$ excursion (0–90 m) and from the negative excursion (above 90 m).

values > 0.12 correspond to a different grain size range. The two groups cannot be distinguished by their hysteretic parameters.

These two groups do not present differences in carbonate content but in organic carbon contents (TOC). Samples with the lowest TOC content (<0.1%) correspond to the most negative $\delta^{13}C_{calcite}$ and to ARM/IRM <0.12 (Table 1).

6. Discussion

6.1. Detecting a diagenetic event using the magnetic record

The magnetic mineralogy is initially controlled by depositional features (terrigenic input or authigenesis) and may afterward be modified by the different phases of diagenesis. For the positive excursion, the magnetite is probably primary because magnetite grains carry a primary magnetization (Macouin et al., 2004) and present no significant grain-size changes. The sharp magnetic content decrease and carbonate content increase at 25 m suggests changes in the relative contribution of detrital input to the sediment. The sharp $\delta^{13}C_{carbonate}$ increase from 5% to 7% associated with these changes, therefore, most probably reflects the variability of the surface water inorganic carbon isotope composition ($\delta^{13}C_{DIC}$) at the platform scale (Patterson and Walter, 1994; Panchuk et al., 2005; Swart and Eberli, 2005; Swart, 2008). Both types of variations (magnetite content and $\delta^{13}C$) could therefore simply result from a sea level change.

For the negative excursion, samples were separated into two groups (independent of the stratigraphy), which present striking differences in terms of magnetite grain-size, magnetite content, $\delta^{13}C_{calcite}$ and probably TOC, but neither in carbonates content nor in $\delta^{13}C_{dolomite}$. Samples presenting high ARM/IRM (> 0.12) do not show any sign of $\delta^{13}C$ and $\delta^{18}O$ diagenetic overprint (they present similar $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$ and no $\delta^{13}C/\delta^{18}O$ array). They also preserved the primary paleomagnetic direction (Macouin et al., 2004), and present similar amount and grain size of magnetite as samples from the positive excursion. There are no clear differences in hysteretic parameters between altered samples and non-altered samples. These samples therefore do not show any obvious evidence for a diagenetic alteration of the magnetic mineralogy nor of the isotope signals.

In contrast, samples presenting ARM/IRM < 0.12 mostly present different $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$ and/or low $\delta^{18}O_{calcite}$, indicating a diagenetic overprint. The Ediacaran paleomagnetic direction is erased in these samples, pointing towards primary magnetite dissolution. This is corroborated by the low magnetite content and its specific grain-size distribution (multidomain and/or superparamagnetic grains) deduced from our rock magnetic study. Because these diagenetically altered samples present the most negative $\delta^{13}C_{calcite}$, the present study demonstrates that, at the Yangjiaping section, the negative excursion is largely due to some diagenesis process.

However, the absence of significant differences in $\delta^{13}C_{dolomite}$ between the two groups suggests that even in the samples strongly altered by diagenesis, the dolomitic phase may have preserved its original isotopic composition, although a minor diagenetic overprint cannot be completely ruled out. We therefore propose a corrected chemostratigraphic curve based on $\delta^{13}C_{dolomite}$ data (Fig. 10), keeping in mind that it might still overestimate the amplitude of the negative excursion if dolomite underwent a still unidentified diagenetic overprint. This curve is very similar to that of the other sections from the shelf margin (Zongling and Tianping) (Fig. 10) and should replace in ulterior chemostratigraphic reconstructions the one established on bulk carbonates by Zhu et al. (2007) and reproduced in Jiang et al. (2011). It is not possible to unambiguously identify such a diagenetic



overprint (and therefore correct for it) in δ^{13} C chemostratigraphic curves established using bulk carbonate δ^{13} C and for which neither separate calcite and dolomite δ^{13} C analyses nor rock magnetic data are available. It is worth noting that some geochemical diagenetic indicators (Mn/Sr < 1 and H/C < 2), recently reported by Kunimitsu et al. (2011), for the part of the Yianjiaping section studied here, have failed to identify this diagenetic event.

However, as shown by the chemostratigraphic curve established on bulk carbonate δ^{13} C analyses for the same section by Zhu et al. (2007), this diagenetic alteration produces a typical noisy pattern. It is therefore tempting to imagine that the noisy δ^{13} C patterns documented in several other sections of the Doushantuo Formation throughout the Yangtze platform (Weng'an, Zonglin, Jiulongwan see review in Jiang et al. (2011)) reflect similar diagenetic events. Some of the inconsistencies identified between chemostratigraphic curves across the Yangtze platform (Fig. 10 and Ader et al., 2009; Jiang et al., 2011) could be explained by diagenetic overprints. In particular, if the N3 excursion, which is clearly identified only in the reference locality of the Yangtze Gorges was also largely diagenetic, its correlation to the Shuram/Wonoka excursion would be very questionable.

6.2. Nature of diagenetic event

The diagenetic event identified above leads to (i) magnetite dissolution and loss of primary magnetization; (ii) modification of δ^{13} C and δ^{18} O of calcite at least, and perhaps to a lesser extent of dolomite; and (iii) a noisy δ^{13} C and δ^{18} O pattern. In order to constrain the mechanism for this diagenetic event, we discuss below the likelihood that the three types of diagenetic events known to decrease the δ^{13} C and δ^{18} O of carbonates (meteoric diagenesis, burial diagenesis and organic diagenesis) might also dissolve magnetite while irregularly overprinting the sedimentary sequences thus leaving behind a noisy pattern.

6.2.1. Meteoric diagenesis

Meteoric diagenesis of carbonates occurs when they are infiltrated by and reequilibrated with meteoric water. This invariably leads to $\delta^{18}O_{carb}$ modifications. Significant $\delta^{13}C_{carb}$ modifications can also occur in regions proximal to vadose water recharge (da Silva and Boulvain, 2008; Armstrong-Altrin et al., 2009), provided that the meteoric water was enriched in low- δ^{13} C dissolved inorganic carbon by interaction with soils where active mineralization of organic matter takes place. Meteoric diagenesis may thus result in a positive correlation between bulk $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$. This led Knauth and Kennedy (2009) to interpret most Neoproterozoic negative $\delta^{13}C_{carb}$ excursions as resulting from meteoric alteration. This interpretation requires the presence of terrestrial phytomass and organic-rich soils in the Neoproterozoic, for which no definitive evidence has been found so far in the fossil record. Regardless, the hypothesis of meteoric alteration can be tested by the $\delta^{13}C_{carb}$ variations along onshore offshore transects. As the meteoric water flow becomes more distal, $\delta^{13}C_{carb}$ should increase reflecting the progressive meteoric fluid DIC buffering by C isotope exchange with the carbonates in proximal areas (e.g. Fouke et al.; 2005; da Silva and Boulvain, 2008). In the case of Doushantuo Formation, $\delta^{13}C_{carb}$ values vary widely along the platform with a mixture of both positive and negative values for the inner-shelf section, dominantly positive values for the shelf-margin sections and dominantly negative values for the basin sections (Fig. 10 and see also Fig. 4 of Jiang et al. (2007) and Ader et al. (2009) for a complete discussion). Even if the negative $\delta^{13}C_{carb}$ values in the inner-shelf and shelf-margin sections present some degree of $\delta^{18}O_{carb}$ and $\delta^{13}C_{carb}$ covariations, which could be individually explained by meteoric alteration, the whole platform pattern cannot be explained solely by meteoric alteration, in the absence of an identifiable increasing $\delta^{13}C_{carb}$ trend towards the basin.

Moreover, although few studies have specifically focused on the effect of meteoric diagenesis on the preservation of the magnetic signal in carbonated platform, they have shown either almost no effect on the primary magnetization (Lu et al., 1996), or an enhanced preservation potential in the case of dolomitization (McNeill and Kirschvink, 1993). The diagenetic event identified in this study is therefore very unlikely to be of the meteoric alteration type.

6.2.2. Burial diagenesis with high pCO₂ fluids

Fluid-rock interactions during burial diagenesis are known to lead to secondary chemical remanant magnetization (CRM) via magnetite neoformation (e.g. Elmore et al., 2006; Aubourg and Pozzi, 2010). The mechanism responsible for these magnetite neoformation are still debated, circulation of orogenic fluids (see among others Jackson (1990), McCabe and Channell (1994) and O'Brien et al. (2007)) or temperature increasing during burial without external supply of long-range fluid flow (Elmore et al., 2006; Moreau et al., 2005; Aubourg et al., 2008). The lack of secondary magnetite and marked secondary CRM in the present section excludes this type of remagnetization.

Moreover this type of secondary chemical remagnetization is not known to be associated with carbon isotope changes. One study even demonstrates the opposite (Evans and Battles, 1999). Changes in $\delta^{13}C_{carb}$ would require circulation of high-pCO₂ fluids generated during burial diagenesis. This has been proposed by Derry (2010b) to explain the late Neoproterozoic negative $\delta^{13}C$ anomalies (as low as -12%) with correlation arrays between $\delta^{18}O$ and $\delta^{13}C$ found in Oman (Shuram), Australia (Wonoka), SE Siberia and South China (N3 anomaly of Doushantuo Formation).

In such a scenario, iron oxides (including magnetite) would have reacted with the high pCO_2 fluids to form siderite as predicted by the stability diagram of minerals in the Fe–S–C–O system (Rosing et al., 2010; Sverjensky and Lee, 2010) and by experimental hematite– CO_2 reactions (Murphy et al., 2011). Siderite is a paramagnetic mineral at room temperature. In the frame of this study both MEB observations and MPMS measurements at low temperature should have allowed its detection at least in the diagenetically altered samples, which is not the case. The typical low-temperature FC and ZFC curves for siderite show a large difference in induced magnetization (SIRM) below 35 K and a sharp drop at 35 K that is not observed in any of our samples.

In addition, the diagenetic alteration shows a very irregular stratigraphic distribution at the meter scale as opposed to what would be expected for basin scale fluid migration. Fluid–rock interaction with a high-pCO₂ fluid is thus unlikely to be responsible for pattern of isotopic and paleomagnetic diagenetic overprint in the Yangjiaping section.

6.2.3. Thermochemical sulfate reduction

Thermochemical sulfate reduction (TSR) takes place during burial diagenesis between hydrocarbon and dissolved sulfate when they are buried to depths that correspond to temperatures of about 100–140 °C (Machel et al., 1995). It liberates hydrogen sulfide in the interstitial porosity, which might lead to magnetite dissolution and formation of pyrite. This would be compatible with the magnetite dissolution identified here in the diagenetically altered samples.

TSR was reported in several hydrocarbon reservoir settings spatially associated with anhydrite (see reviews by Machel et al. (1995) and Machel (2001)). However, no anhydrite and hydrocarbon have been identified so far in the Doushantuo and Dengying Formations and the sulfate content of seawater at the time was probably low (McFadden et al., 2008) and insufficient to allow anhydrite deposition. Moreover, the diagenetic overprint identified here does not affect homogeneously thick portions of the sedimentary column (at least 10 m) as expected in the case of TSR (Machel et al., 1995; Machel, 2001).

6.2.4. Bacterial sulfate reduction

Bacterial sulfate reduction (BSR) is a common anaerobic respiratory process during early diagenesis (see review by Canfield and Berner (1987)). It occurs when oxygen, nitrate, Mn and Fe oxihydroxides have been used up, leaving sulfate as the sole electron acceptor (Canfield, 2009). Sulfate reducing bacteria then oxidize either sedimentary labile organic matter or methane by reducing pore-water sulfate, (Eqs. (1) and (2)), liberating hydrogen sulfide in the pore water.

$$2CHOH + SO_4^2 \rightarrow 2HCO_3^- + HS^- + H^+$$
(1)

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^{-} + H_2O + HS^{-}$$
 (2)

 $\rm HS^-$ first reacts with the Fe²⁺ previously produced by dissimilatory iron reduction of iron oxi-hydroxides to produce metastable iron monosulphides or greigite (Eq. (4)) that readily transform to pyrite (see review in Rickard and Luther (2007)) (Eq. (5)).

$$Fe^{2+} + HS^{-} \rightarrow FeS(s) + H^{+}$$
 (4)

$$FeS(s) + HS^{-} + H^{+} \rightarrow FeS_{2} + H_{2}$$
(5)

If BSR keeps going, HS^- after having titrated the available Fe^{2+} will build up in the pore-water resulting in the dissolution of magnetite (see Eq. (3)) (Haese et al., 1998; Canfield and Berner, 1987; Froelich et al., 1979).

$$Fe_3O_4 + HS^- + H^+ \rightarrow 3Fe^{2+} + S^0 + 4H_2O$$
 (3)

This leads to important modifications in magnetite grain size distribution, a decrease in magnetite content and thus a potential loss of the primary magnetization (Garming et al., 2005; Riedinger et al., 2005; Moreau and Ader, 2000; Housen and Musgrave, 1996), as observed here. Hysteretic parameters obtained here are in the same area as the one corresponding to magnetite dissolution due to gas hydrates (Musgrave et al., 2006; Fig. 7).

The HCO₃⁻ released by organic matter or methane oxidation during BSR is characterized by a δ^{13} C of about -26% for organic matter oxidation (Peterson and Fry, 1989) and comprised between -110% and -20% for methane oxidation (Barker and Fritz, 1981; Kvenvolden, 2000; see also summary in Pierre and Rouchy (2004)). Its crystallization as authigenic carbonates results in lower bulk carbonate δ^{13} C and most of the time lower δ^{18} O as well (e.g. Ader and Javoy, 1998; Coleman and Raiswell, 1981; Irwin et al., 1977; Pierre and Rouchy, 2004; Sass et al., 1991).

Both H₂S and ¹²C-rich DIC build up are restricted to the bacterial sulfate reduction zone. When this zone is located within the sediment, it is restricted to a relatively narrow zone limited upward by onset of BSR and downward by the exhaustion of either sulfate or available labile organic matter. This results in local alterations of the rocks magnetic and $\delta^{13}C_{carb}$ signals, inducing diagnostic irregularities in their stratigraphic patterns.

This scenario has already been proposed to account for the combined $\delta^{13}C_{carb}$ negative values and loss of primary magnetization occurring irregularly in a Jurassic claystone-limestone succession of the Paris basin (Moreau and Ader, 2000). We propose here that it also best explains the erratic isotopic and rock magnetic signals as well as the occasional very negative $\delta^{13}C_{calcite}$ (< -15‰) observed in the Yiangjiaping section. The not so negative δ^{13} C values by themselves do not permit to distinguish between methane and organic matter oxidation by BSR. However, given the very low TOC in altered samples, AOM is probably more likely to have generated sufficient amount of HS⁻ to dissolve most of the magnetic carriers (Rowan et al., 2009; Garming et al., 2005; Riedinger et al., 2005; Housen and Musgrave, 1996) and sufficient amount of ¹³C depleted CO₂ to induce such negative $\delta^{13}C_{calcite}$ values (Irwin et al., 1977; Pierre and Rouchy, 2004). Methane could have been produced by bacterial methanogenesis in the black shales levels present either above the cap carbonate or at the top of the Doushantuo Formation in most shelf, slope and basinal sections.

The timing of this alteration depends on the depth of AOM zones within the sediment itself controlled by downward sulfate and upward methane diffusion rates. The availability of methane depends on the biogenic or thermogenic source of methane. The sulfate diffusion rate is limited by its content in the overlying waters and by the thickness and permeability of the sediment through which it must diffuse before reaching the BSR zone. The rate of sulfate diffusion is thus greatly enhanced when the seawater is sulfate-rich and the BSR zone is located close to the water/sediment interface. The combination of these factors yield highly variable depth for the AOM, ranging from a few centimeters to hundreds of meters (see review in Regnier et al. (2011)).

This type of early diagenesis may also explain the noisy $\delta^{13}C_{carb}$ signal documented in several other carbonate-rich intervals (e.g. Weng'an; Zonglin, Jiulongwan) and the pronounced $\delta^{13}C_{carb}$ negative excursions recorded in the carbonate beds of organic-rich shale dominated intervals of the Doushantuo Formation throughout the Yangtze platform (Jiang et al., 2011). In these intervals, anomalously low $\Delta^{13}C_{carb-org}$ mirror the low $\delta^{13}C_{carb}$ (Ader et al., 2009 and references therein), which constitutes an additional feature compatible with (although not diagnostic of) this type of diagenesis.

All Ediacaran negative excursions may not result from this type of diagenesis. If it was to prove the case however, it is legitimate to investigate the reasons why this type of diagenesis would have been more frequent in the Neoproterozoic than in other time periods. For such a diagenetic process to occur, the seawater sulfate content must have been high enough to sustain a H₂S production locally exceeding the iron oxide content in the sediment, while underlying sediments generated enough methane via methanogenesis. This second condition requires that enough labile organic matter has escaped aerobic and anaerobic (including BSR) organic matter degradation, i.e. either that the organic matter primary productivity was extremely high, or that the water column was oxygen and possibly sulfate-poor (McFadden et al., 2008; Li et al., 2010) at the time of these underlying sediments deposition. If this diagenetic process proved to be responsible for most of the negative δ^{13} C excursions in the Ediacaran, it may thus simply reflect the transition from sulfate-poor to sulfate-rich oceans.

7. Conclusion

The new rock magnetic data presented here (ARM, IRM, low temperature magnetometry) and combined with C and O isotopic data demonstrate that the Upper Doushantuo-lower Dengying negative excursion of the Yangjiaping section is largely due to diagenesis. A new chemostratigraphic δ^{13} C-curve is proposed by discarding the unambiguously identified diagenetic data. In the present state of knowledge, our data do not rule out a possible primary δ^{13} C excursion of low magnitude (down to -0.5%) as recorded by $\delta^{13}C_{dolomite}$. Based on the rock magnetic mineralogy, we interpret the diagenetic event to have dissolved magnetite grains. Given the erratic occurrence of the diagenetically altered samples, we suggest that magnetite dissolution resulted from the build up of hydrogen sulfide during early diagenetic bacterial sulfate reduction probably by methane rather than by organic matter oxidation. This identification of a diagenetic event questions the primary nature of other potentially time equivalent negative excursions in other cratons (i.e. Shuram and Wonoka excursions). Further rock magnetism investigations of existing C-isotopic profiles associated with precise dating are required to identify if such a diagenetic overprint is also present in negative excursions from other sections before interpreting them in terms of primary environmental signatures.

In this case study, paleomagnetism techniques (paleodirections and magnetic mineralogy) and the difference in $\delta^{13}C_{calcite}$ and $\delta^{13}C_{dolomite}$ virrat04w**f3**24locessam3(guess)1851.3(to)2366.8(identif-)] constraints on the type of diagenetic event from the point of view of iron redistribution among diagenetic phases. This could be very useful in identifying and characterizing diagenetic overprints not only on carbonate δ^{13} C and δ^{18} O but also on iron speciation data, which are increasingly used to reconstruct ocean redox stratification in the Neoproterozoic. Moreover, measurements allowing magnetic mineralogy characterization (as opposed to paleodirections determination) are low cost, time efficient and non-destructive, and thus ideal screening tools to use.

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References

- Ader, M., Javoy, M., 1998. Diagenèse précoce en milieu sulfuré réducteur: une étude isotopique dans le Jurassique basal du basin de Paris. C. R. Acad. Sci. Ser. IIA 327, 803–809.
- Ader, M., Macouin, M., Trindade, R.I.F., Hadrien, M.H., Yang, Z., Sun, Z., Besse, J., 2009. A multilayered water column in the Ediacaran Yangtze platform? Insights from carbonate and organic matter paired delta(13)C. Earth Planet. Sci. Lett. 288, 213–227.
- Al-Aasm, I.S., Taylor, B.E., South, B., 1990. Stable isotope analysis of multiple carbonate samples using selective acid extraction. Chem. Geol.: Isot. Geosci. Sect. 80, 119-125.
- Armstrong-Altrin, J.S., Lee, Y.I., Verma, S.P., Worden, R.H., 2009. Carbon, oxygen, and strontium isotope geochemistry of carbonate rocks of the upper Miocene Kudankulam Formation, southern India: implications for paleoenvironment and diagenesis. Chem. Erde—Geochem. 69, 45–60.
- Aubourg, C., Pozzi, J.P., 2010. Toward a new < 250 degrees C pyrrhotite-magnetite geothermometer for claystones. Earth Planet. Sci. Lett. 294, 47–57.
- Aubourg, C., Pozzi, J.P., Janots, D., Sahraoui, L., 2008. Imprinting chemical remanent magnetization in claystones at 95 degrees C. Earth Planet. Sci. Lett. 272, 172–180.
- Banerjee, S.K., King, J., Marvin, J., 1981. A rapid method of magnetic granulometry with applications to environmental studies. Geophys. Res. Lett. 8, 333–336.
- Banner, J.L., Hanson, G.N., 1990. Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. Geochim. Cosmochim. Acta 54, 3123–3137.
- Barker, J.F., Fritz, P., 1981. Carbon isotope fractionation during microbial methane oxidation. Nature 293, 289–291.
- Bailey, J.V.Joye, Kalanetra, K.M., Flood, B.E, Corsetti, F.A., 2007. Evidence of giant sulphur bacteria in Neoproterozoic phosphorites. Nature 445, 198–201.
- Baudrand, M., Aloisi, G., Lecuyer, C., Martineau, F., Fourel, F., Escarguel, G., Blanc-Valleron, M.M., Rouchy, J.M., Grossi, V., 2012. Semi-automatic determination of the carbon and oxygen stable isotope compositions of calcite and dolomite in natural mixtures. Appl. Geochem. 27, 257–265.
- Bjerrum, C.J.B., Canfield, D.E., 2011. Towards a quantitative understanding of the late Neoproterozoic carbon cycle. Proc. Natl. Acad. Sci. USA 108, 5542–5547.
- Canfield, D.E., Berner, R.A., 1987. Dissolution and pyritization of magnetite in anoxic marine sediments. Geochim. Cosmochim. Acta 51, 645–659.
- Channell, J.E.T., Xuan, C., 2009. Self-reversal and apparent magnetic excursions in Arctic sediments. Earth Planet. Sci. Lett. 284, 124–131.
- Chen, J.Y., Bottjer, D.J., Oliveri, P., Dornbos, S.Q., Gao, F., Ruffins, S., Chi, H.M., Li, C.W., Davidson, E.H., 2004. Small bilaterian fossils from 40 to 55 million years before the Cambrian. Science 305, 218–222.
- Coleman, M.L., Raiswell, R., 1981. Carbon, oxygen and sulfur isotope variations in concretions from the Upper Lias of N.E. England. Geochim. Cosmochim. Acta 45, 329–340.
- Condon, D., et al., 2005. U–Pb ages from the neoproterozoic Doushantuo Formation, China. Science 308 (5718), 95–98.
- da Silva, A.C., Boulvain, F., 2008. Carbon isotope lateral variability in a Middle Frasnian carbonate platform (Belgium): significance of facies, diagenesis and sea-level history. Palaeogeogr. Palaeoclimatol. Palaeoecol. 269, 189–204.

- Day, R., Fuller, M., Schmidt, V.A., 1977. Hysteresis properties of titanomagnetites grain-size and compositional dependence. Phys. Earth Planet. Inter. 13, 260–267.
- Derry, L.A., 2010a. A burial diagenesis origin for the Ediacaran Shuram–Wonoka carbon isotope anomaly. Earth Planet. Sci. Lett. 294, 152–162.
- Derry, L.A., 2010b. On the significance of delta(13)C correlations in ancient sediments. Earth Planet. Sci. Lett. 296, 497–501.
- Dobrzinski, N., Bahlburg, H., 2007. Sedimentology and environmental significance of the Cryogenian successions of the Yangtze Platform, South China block. Palaeogeogr. Palaeoclimatol. Palaeoecol. 254, 100–122, http://dx.doi.org/10. 1016/j.palaeo.2007.03.043.
- Elmore, R.D., Foucher, J.L.E., Evans, M., Lewchuk, M., Cox, E., 2006. Remagnetization of the Tonoloway Formation and the Helderberg Group in the Central Appalachians: testing the origin of syntiliting magnetizations. Geophys. J. Int. 166, 1062–1076.
- Evans, M.A., Battles, D.A., 1999. Fluid inclusion and stable isotope analyses of veins from the central Appalachian Valley and Ridge province: implications for regional synorogenic hydrologic structure and fluid migration. Geol. Soc. Am. Bull. 111, 1841–1860.
- Evans, M., Heller, F., 2003. Environmental Magnetism: Principles and Applications of Enviromagnetics. Academic Press, ISBN: 0-12-243851-5.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43, 1075–1090.
- Fouke, B.W., Schlager, W., Vandamme, M.G.M., Henderiks, J., Van Hilten, B., 2005. Basin-to-platform chemostratigraphy and diagenesis of the Early Cretaceous Vercors Carbonate Platform, SE France. Sediment. Geol. 175, 297–314.
- Garming, J.F.L., Bleil, U., Riedinger, N., 2005. Alteration of magnetic mineralogy at the sulfate-methane transition: analysis of sediments from the Argentine continental slope. Phys. Earth Planet. Inter. 151 (3–4), 290–308.
- Giddings, J.A., Wallace, M.W., 2009a. Facies-dependent delta(13)C variation from a Cryogenian platform margin, South Australia: evidence for stratified Neoproterozoic oceans? Palaeogeogr. Palaeoclimatol. Palaeoecol. 271, 196–214.
- Giddings, J.A., Wallace, M.W., 2009b. Sedimentology and C-isotope geochemistry of the 'Sturtian' cap carbonate, South Australia. Sediment. Geol. 216, 1–14.
- Grotzinger, J.P., Fike, D.A., Fischer, W.W., 2011. Enigmatic origin of the largestknown carbon isotope excursion in Earth's history. Nat. Geosci. 4, 285–292.
- Grotzinger, J.-P., Knoll, A.-H., 1995. Anomalous carbonate precipitates: is the Precambrian the key to the Permian? Palaios 10 (6), 578–596.
- Haese, R.R., Petermann, H., Dittert, L., Schulz, H.D., 1998. The early diagenesis of iron in pelagic sediments: a multidisciplinary approach. Earth Planet. Sci. Lett. 157 (3-4), 233-248.
- Halverson, G.P., Hoffman, P.F., Schrag, D.P., Maloof, A.C., Rice, A.H.N., 2005. Toward a Neoproterozoic composite carbon-isotope record. Geol. Soc. Am. Bull. 117 (9–10), 1181–1207.
- Halverson, G.P., Wade, B.P., Hurtgen, M.T., Barovich, K.M., 2010. Neoproterozoic chemostratigraphy. Precambrian Res. 182, 337–350.
- Hoffman, P.F., Schrag, D.P., 2002. The snowball Earth hypothesis: testing the limits of global change. Terra Nova 14, 129–155.
- Housen, B.A., Musgrave, R.J., 1996. Rock-magnetic signature of gas hydrates in accretionary prism sediments. Earth Planet. Sci. Lett. 139, 509-519.
- Hubert, B., Alvaro, J.J., Chen, J.Y., 2005. Microbially mediated phosphatization in the Neoproterozoic Doushantuo Lagerstatte, South China. Bull. Soc. Geol. Fr. 176 (4), 355–361.
- Irwin, H., Curtis, C., Coleman, M.L., 1977. Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. Nature 269, 209–213.
- Jackson, M., 1990. Diagenetic sources of stable remanence in remagnetized paleozoic cratonic carbonates—a rock magnetic study. J. Geophys. Res.—Solid Earth Planets 95, 2753–2761.
- Jacobsen, S.B., Kaufman, A.J., 1999. The Sr, C and O isotopic evolution of Neoproterozoic seawater. Chem. Geol. 161, 37–57.
- Jiang, G.Q., Kaufman, A.J., Christie-Blick, N., Zhang, S.H., Wu, H.C., 2007. Carbon isotope variability across the Ediacaran Yangtze platform in South China: implications for a large surface-to-deep ocean delta C-13 gradient. Earth Planet. Sci. Lett. 261, 303–320.
- Jiang, G.Q., Kennedy, M.J., Christie-Blick, N., 2003. Stable isotopic evidence for methane seeps in Neoproterozoic postglacial cap carbonates. Nature 426 (6968), 822–826.
- Jiang, G.Q., Shi, X.Y., Zhang, S.H., Wang, Y., Xiao, S.H., 2011. Stratigraphy and paleogeography of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in South China. Gondwana Res. 19, 831–849.
- Kaufman, A.J., Knoll, A.H., 1995. Neoproterozoic variations in the C-isotopic composition of seawater—stratigraphic and biogeochemical implications. Precambrian Res. 73, 27–49.
- Kennedy, M.J., Christie-Blick, N., Sohl, L.E., 2001. Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals? Geology 29 (5), 443–446.
- Kimura, H., Azmy, K., Yamamuro, M., Jiang, Z.W., Cizdziel, J.V., 2005. Integrated stratigraphy of the upper Neoproterozoic succession in Yunnan Province of South China: re-evaluation of global correlation and carbon cycle. Precambrian Res. 138 (1–2), 1–36.
- King, J., Banerjee, S.K., Marvin, J., Ozdemir, O., 1982. A comparison of different magnetic methods for determining the relative grain-size of magnetite in

natural materials—some results from lake-sediments. Earth Planet. Sci. Lett. 59, 404–419.

- Knauth, L.P., Kennedy, M.J., 2009. The late Precambrian greening of the Earth. Nature 460, 728–732.
- Knoll, A.H., 2000. Learning to tell Neoproterozoic time. Precambrian Res. 100 (1–3), 3–20.
- Knoll, A.H., Walter, M.R., 1992. Latest Proterozoic stratigraphy and earth history. Nature 356, 673–678.
- Kunimitsu, Y., Setsuda, Y., Furuyama, S., Wang, W., Kano, A., 2011. Ediacaran chemostratigraphy and paleoceanography at a shallow marine setting in northwestern Hunan Province, South China. Precambrian Res. 191, 194–208.
- Kvenvolden, K.A., 2000. Natural gas hydrate: introduction and history of discovery. In: Max, M.D.E. (Ed.), Natural Gas Hydrate in Oceanic and Permafrost Environments. Kluwer Academic Publishing, Netherlands, pp. 9–16.
- Lambert, I.B., Walter, M.R., Wenlong, Z., Songnian, L., Guogan, M., 1987. Palaeoenvironment and carbon isotope stratigraphy of upper Proterozoic carbonates of the Yangtze Platform. Nature (London) 325 (6101), 140–142.
- Lascu, I., Banerjee, S.K., Berquo, T.S., 2010. Quantifying the concentration of ferrimagnetic particles in sediments using rock magnetic methods. Geochem. Geophys. Geosyst. 11, http://dx.doi.org/10.1029/2010GC003182.
- Li, R., Chen, J., Zhang, S., Lei, J., Shen, Y., Chen, X., 1999. Spatial and temporal variations in carbon and sulfur isotopic compositions of Sinian sedimentary rocks in the Yangtze Platform, South China. Precambrian Res. 97 (1–2), 59–75.
- Li, C., Love, G.D., Lyons, T.W., Fike, D.A., Sessions, A.L., Chu, X.L., 2010. A stratified redox model for the Ediacaran Ocean. Science 328, 80–83.
- Lu, G., Aharon, P., Wheeler, C.W., McCabe, C., 1996. Magnetostratigraphy of the uplifted former atoll of Niue, South Pacific: implications for accretion history and carbonate diagenesis. Sediment. Geol. 105, 259–274.
- Machel, H.G., Krouse, H.R., Sassen, R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. Appl. Geochem. 10, 373–389.
- Machel, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings—old and new insights. Sediment. Geol. 140, 143–175.
- Macouin, M., Besse, J., Ader, M., Gilder, S., Yang, Z., Sun, Z., Agrinier, P., 2004. Combined paleomagnetic and isotopic data from the Doushantuo carbonates, South China: implications for the "snowball Earth" hypothesis. Earth Planet. Sci. Lett. 224, 387–398.
- McCabe, C., Channell, J.E.T., 1994. Late Paleozoic remagnetization in limestones of the Craven basin (northern England) and the rock magnetic fingerprint of remagnetized sedimentary carbonates. J. Geophys. Res.—Solid Earth 99, 4603–4612.
- McFadden, K.A., Huang, J., Chu, X.L., Jiang, G.Q., Kaufman, A.J., Zhou, C.M., Yuan, X.L., Xiao, S.H., 2008. Pulsed oxidation and biological evolution in the Ediacaran Doushantuo Formation. Proc. Natl. Acad. Sci. USA 105, 3197–3202.
- McNeill, D.F., Kirschvink, J.L., 1993. Early dolomitization of platform carbonates and the preservation of magnetic polarity. J. Geophys. Res.—Solid Earth 98, 7977–7986.
- Moreau, M.G., Ader, M., 2000. Effects of diagenesis on magnetic mineralogy in a Jurassic claystone–limestone succession from the Paris Basin. J. Geophys. Res B: Solid Earth Planets 105 (2), 2797–2804.
- Moreau, M.G., Ader, M., Enkin, R.J., 2005. The magnetization of clay-rich rocks in sedimentary basins: low-temperature experimental formation of magnetic carriers in natural samples. Earth Planet. Sci. Lett. 230, 193–210.
- Murphy, R., Lammers, K., Smirnov, A., Schoonen, M.A.A., Strongin, D.R., 2011. Hematite reactivity with supercritical CO(2) and aqueous sulfide. Chem. Geol. 283, 210–217.
- Musgrave, R.J., Bangs, N.L., Larrasoana, J.C., Gracia, E., Hollamby, J.A., Vega, M.E., 2006. Rise of the base of the gas hydrate zone since the last glacial recorded by rock magnetism. Geology 34, 117–120.
- O'Brien, V.J., Moreland, K.M., Elmore, R.D., Engel, M.H., Evans, M.A., 2007. Origin of orogenic remagnetizations in Mississippian carbonates, Sawtooth Range, Montana. J. Geophys. Res.—Solid Earth 112, http://dx.doi.org/10.1029/ 2006JB004699.
- Ozdemir, O., Dunlop, D.J., 2010. Hallmarks of maghemitization in low-temperature remanence cycling of partially oxidized magnetite nanoparticles. J. Geophys. Res.—Solid Earth 115, http://dx.doi.org/10.1029/2009JB006756.
- Ozdemir, O., Dunlop, D.J., Berquo, T.S., 2008. Morin transition in hematite: size dependence and thermal hysteresis. Geochem. Geophys. Geosyst. 9, http://dx. doi.org/10.1029/2008GC002110.
- Ozdemir, O., Dunlop, D.J., Moskowitz, B.M., 2002. Changes in remanence, coercivity and domain state at low temperature in magnetite. Earth Planet. Sci. Lett. 194, 343–358.
- Panchuk, K.M., Holmden, C., Kump, L.R., 2005. Sensitivity of the epeiric sea carbon isotope record to local-scale carbon cycle processes: tales from the Mohawkian Sea. Palaeogeogr. Palaeoclimatol. Palaeoecol. 228, 320–337.
- Patterson, W.P., Walter, L.M., 1994. Depletion of 13C in seawater ΣCO_2 on modern carbonate platforms: significance for the carbon isotopic record of carbonates. Geology 22, 885–888.
- Peterson, B.J., Fry, B., 1989. Stable isotopes in ecosystem studies. Annu. Rev. Ecol. Syst. 18, 293–320.

- Pierre, C., Rouchy, J.M., 2004. Isotopic compositions of diagenetic dolomites in the Tortonian marls of the western Mediterranean margins: evidence of past gas hydrate formation and dissociation. Chem. Geol. 205, 469–484.
- Regnier, P., Dale, A.W., Arndt, S., LaRowe, D.E., Mogollon, J., Van Cappellen, P., 2011. Quantitative analysis of anaerobic oxidation of methane (AOM) in marine sediments: a modeling perspective. Earth-Sci. Rev. 106, 105–130.
- Rickard, D., Luther, G.W., 2007. Chemistry of iron sulfides. Chem. Rev. 107, 514–562.
- Riedinger, N., Pfeifer, K., Kasten, S., Garming, J.F.L., Vogt, C., Hensen, C., 2005. Diagenetic alteration of magnetic signals by anaerobic oxidation of methane related to a change in sedimentation rate. Geochim. Cosmochim. Acta 69, 4117–4126.
- Rosales, I, Quesada, S., Robles, S., 2001. Primary and diagenetic isotopic signals in fossils and hemipelagic carbonates: the Lower Jurassic of northern Spain. Sedimentology 48 (5), 1149–1169.
- Rosing, M.T., Bird, D.K., Sleep, N.H., Bjerrum, C.J., 2010. No climate paradox under the faint early Sun. Nature 464, 744–747, http://dx.doi.org/10.1038/ nature08955.
- Rowan, C.J., Roberts, A.P., Broadbent, T., 2009. Reductive diagenesis, magnetite dissolution, greigite growth and paleomagnetic smoothing in marine sediments: a new view. Earth Planet. Sci. Lett. 277, 223–235.
- Sass, E., Bein, A., Almogi-Labin, A., 1991. Oxygen-isotope composition of diagenetic calcite in organic rich rocks: evidence for ¹⁸O depletion in marine anaerobic pore water. Geology 19, 839–842.
- Shen, Y., 2002. C-isotope variations and paleoceanographic changes during the late Neoproterozoic on the Yangtze Platform, China. Precambrian Res. 113 (1-2), 121-133.
- Shen, B., Xiao, S.H., Bao, H.M., Kaufman, A.J., Zhou, C.M., Yuan, X.L., 2011. Carbon, sulfur, and oxygen isotope evidence for a strong depth gradient and oceanic oxidation after the Ediacaran Hankalchough glaciation. Geochim. Cosmochim. Acta 75, 1357–1373.
- Shen, Y., Zhang, T.G., Chu, X.L., 2005. C-isotopic stratification in a Neoproterozoic postglacial ocean. Precambrian Res. 137 (3–4), 243–251.
- Shields, G.A., 2005. Neoproterozoic cap carbonates: a critical appraisal of existing models and the plumeworld hypothesis. Terra Nova 17 (4), 299–310.
- Steiner, M., Wallis, E., Erdtmann, B.D., Zhao, Y.L., Yang, R.D., 2001. Submarinehydrothermal exhalative ore layers in black shales from South China and associated fossils—insights into a Lower Cambrian facies and bio-evolution. Palaeogeogr. Palaeoclimatol. Palaeoecol. 169 (3-4), 165–191.
- Sverjensky, D.A., Lee, N., 2010. The great oxidation event and mineral diversification. Elements 6, 31–36.
- Swart, P.K., 2008. Global synchronous changes in the carbon isotopic composition of carbonate sediments unrelated to changes in the global carbon cycle. PNAS 105, 13741–13745.
- Swart, P.K., Eberli, G., 2005. The nature of the δ^{13} C of periplatform sediments: implications for stratigraphy and the global carbon cycle. Sediment. Geol. 175, 115–129.
- Swart, P.K., Kennedy, M.J., 2012. Does the global stratigraphic reproducibility of δ^{13} C in neoproterozoic carbonates require a marine origin? A pliocenepleistocene comparison. Geology 40, 87–90.
- Tauxe, L., Mullender, T.A.T., Pick, T., 1996. Potbellies, wasp-waists, and superparamagnetism in magnetic hysteresis. Journal Geophys. Res.—Solid Earth 101, 571–583.
- Vernhet, E., Reijmer, J.J.G., 2010. Sedimentary evolution of the Ediacaran Yangtze platform shelf (Hubei and Hunan provinces, Central China). Sediment. Geol. 225, 99–115.
- Verosub, K.L., Roberts, A.P., 1995. Environmental magnetism—past, present, and future. J. Geophys. Res.—Solid Earth 100, 2175–2192.
- Weil, A.B., Van der Voo, R., 2002. Insights into the mechanism for orogen-related carbonate remagnetization from growth of authigenic Fe-oxide: a scanning electron microscopy and rock magnetic study of Devonian carbonates from northern Spain. J. Geophys. Res.—Solid Earth 107, http://dx.doi.org/10.1029/ 20011B000200.
- Xiao, S.H., Knoll, A.H., Yuan, X.L., Pueschel, C.M., 2004. Phosphatized multicellular algae in the Neoproterozoic Doushantuo Formation, China, and the early evolution of florideophyte red algae. Am. J. Bot. 91 (2), 214–227.
- Xiao, S.H., Zhang, Y., Knoll, A.H., 1998. Three-dimensional preservation of algae and animal embryos in a Neoproterozoic phos phorite. Nature 391 (6667), 553–558.
- Yui, T.F., Gong, S.Y., 2003. Stoichiometry effect on stable isotope analysis of dolomite. Chem. Geol. 201 (3–4), 359–368.
- Zhang, S.H., Jiang, G.Q., Zhang, J.M., Song, B., Kennedy, M.J., Christie-Blick, N., 2005. U-Pb sensitive high-resolution ion microprobe ages from the Doushantuo Formation in south China: constraints on late Neoproterozoic glaciations. Geology 33, 473–476.
- Zhu, M.Y., Zhang, J.M., Yang, A.H., 2007. Integrated Ediacaran (Sinian) chronostratigraphy of South China. Palaeogeogr. Palaeoclimatol. Palaeoecol. 254, 7–61.