Carbon- and sulfur-isotope geochemistry of the Hirnantian (Late Ordovician) Wangjiawan (Riverside) section, South China: Global correlation and environmental event interpretation

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Detailed geochemical analyses (δ13Ccarb, δ13Corg, δ34Ssulfide, and abundance of sulfide, carbonate and organic carbon) were performed on samples from the Wangjiawan (Riverside) section, close to the GSSP (Global Stratotype Section and Point) for the Hirnantian stage of the Ordovician. New data show two increases in carbonate content coincident with two glacial pulses that reduced detrital input. The new δ34Ssulfide data show distinct changes in this section, with relatively high values in the Kuanyinchiao Formation, a pattern observed throughout the Yangtze Platform. However, there is no consensus on the cause of these changes. The new δ13Ccarb data show a sharp rise and peak in the extraordinarius zone, below the previously published δ13Ccarb peak in the persculptus zone. A compilation of the new results with other sections indicates the Hirnantian carbon-isotope excursion starts near the pacificus–extraordinarius boundary and elevated values remain until the end of the excursion in the persculptus zone for both δ13Corg and δ13Ccarb. The controversy over correlating Hirnantian graptolite zones with chitinozoan zones can also be addressed. The new δ13Ccarb data also allow direct comparison with Hirnantian δ13Ccarb data from Anticosti Island and the Baltic region, which are zoned by chitinozoan fossils. This comparison favors a correlation of the taugourdeau and scabra chitinozoan zones with the extraordinarius graptolite zone.

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1. Introduction

The Hirnantian stage of the Late Ordovician hosts a confluence of several significant events, including a glaciation, sea level changes, a severe mass extinction, and a global positive carbon-isotope (δ13C) excursion (e.g., Finney et al., 1999; Melchin and Holmden, 2006; Fan et al., 2009; LaPorte et al., 2009; Young et al., 2010; Jones et al., 2011). The relationship between these events is only partially understood and the initial cause of the glaciation and its relationship to the carbon cycle perturbation remain unknown.

The Hirnantian glaciation was recognized from glacial sediments in north Gondwana (Saharan Africa, South Africa and Arabia) (Deynoux and Trompette, 1981; Deynoux, 1985; Ghienne, 2003; Ghienne et al., 2007; Le Heron et al., 2007). Trotter et al. (2008) used temperature-dependent oxygen isotopes (δ18Oapatite) in Ordovician conodonts to show a global temperature fall in the late Ordovician. This conclusion was reinforced by clumped-isotope paleothermometry on Ordovician calcites (Finnegan et al., 2011) that shows cooling and rapid ice accumulation at this time — perhaps twice the ice volume as the Last Glacial Maximum. Detailed geochemical and sedimentological work has identified more than one episode of glacial advance and retreat (Ghi enne, 2003; Yan et al., 2010).

The Hirnantian extinction is recognized as the second most devastating extinction in the Phanerzoic, after the Permian–Triassic extinction, with the elimination of about 86% of species (Sheehan, 2001; Bambach et al., 2004). Although a gradual decline in biodiversity is recognized during the Katian (Kaljo et al., 2011), fine-scaled palaeontological work demonstrates that the greatest loss was across the Katian–Hirnantian boundary (Brenchley et al., 1994; Sheehan, 2001; Rong et al., 2002; Chen et al., 2005a; Fan et al., 2009), thought to coincide with the onset of a severe cooling (Finnegan et al., 2011). This coincidence has provided a solid case for linking the extinction with decreased temperature and a drop in sea level, the latter, in turn, eliminating vast epeiric sea habitats (Brenchley et al., 1994; Sheehan, 2001). Further graptolite and brachiopod extinctions also occur later in the Hirnantian (Rong et al., 2002; Chen et al., 2005a; Fan et al., 2009).

The Hirnantian stage also records a sharp perturbation in the carbon cycle, seen in the enrichment of 13C in both sedimentary carbonate and organic matter. Some have attributed this to an increased burial of organic matter (e.g., Brenchley et al., 2003). An alternative hypothesis
is that a global regression exposed carbonate platforms that were then preferentially weathered, resulting in an increase in riverine $\delta^{13}$C (Kump et al., 1999; Melchin and Holmden, 2006). This would then drive a corresponding increase in oceanic $\delta^{13}$C composition.

The uncertainty in correlating sections from different continents has hampered the study of the glaciation, the mass extinction, and the changes in carbon cycling that mark the Hirnantian (Delabroye and Vecoli, 2010). There is no one correlative fossil group (graptolites, chitinozoans, brachiopods or conodonts) present in all sections worldwide. Graptolites are common in the shaly deposits of South China, where the GSSP at Wangjiawan (North) is established, but the carbonate-dominated successions of Anticosti Island and Estonia are dominated by conodont and chitinozoan fossils (Souflane and Achab, 2000; Copper, 2001; Brenchley et al., 2003; Kaljo et al., 2008; Achab et al., 2011); graptolites from these areas are only tenuously related to Chinese graptolites (Riva, 1988; Melchin, 2008; Young et al., 2010). It is similarly challenging to correlate Gondwanan glacial sediments with tropical sections that often have the best fossil and isotope records. Thus, precisely comparing the timing of the glacial onset with other (biological and geochemical) events is difficult.

Furthermore, the use of carbon isotopes to correlate sections has not been straightforward (Chen et al., 2006; Delabroye and Vecoli, 2010). To date no Chinese section – including the GSSP section for the Hirnantian stage (Wangjiawan North) – has any published carbonate-carbon isotope ($\delta^{13}$C$_{\text{carb}}$) data, which is the most commonly used chemostratigraphic tool (e.g., Gradstein et al., 2004).

This study presents high-resolution (cm-scale) characterization of carbon- and sulfur-cycling, including isotopic ($\delta^{13}$C$_{\text{carb}}$, $\delta^{13}$C$_{\text{org}}$, $\delta^{34}$S$_{\text{sulfide}}$) and abundance (sulfide, or %S, and total organic carbon, or TOC) data, across the Hirnantian interval of the Wangjiawan (Riverside) section in order to constrain changes in the local geochemistry as well as linking these to global trends in $\delta^{13}$C$_{\text{carb}}$ organic deposition (TOC), and the glaciation.

2. Geology, stratigraphy and the extinction boundary

Numerous studies have been published on the Late Ordovician of the Yangtze platform, including biostratigraphic (e.g., Chen et al., 2000; Vandenbroucke et al., 2005), paleogeographic (Zhang et al., 2000; Chen et al., 2004), chemostratigraphic (Chen et al., 2005b; Fan et al., 2009), as well as carbon and sulfur isotope-event studies (Yan et al., 2008, 2009; Zhang et al., 2009).

The Wangjiawan site was an outer shelf location on the South China craton during the Ordovician–Silurian transition (Chen et al., 2004; Fig. 1A). The Wufeng, Kuanyinchiao and Lungamachi Formations span the uppermost Ordovician and Lower Silurian, in ascending order. The Wufeng and Lungamachi Formations are comprised of dark shales and occasional chert with abundant graptolite fossils (Chen et al., 2000; Chen et al., 2006). The Kuanyinchiao Formation is thin (less than 50-cm thick) argillaceous limestone that contains abundant shelly fossils (Hirnantian fauna) (Chen et al., 2000). The Kuanyinchiao Formation marks a drop in eustatic sea level (Fan et al., 2009) and the associated Hirnantian fauna are recognized as cool/cold water fauna (Rong et al., 2002). This is consistent with global cooling and sequestration of water into Gondwanan ice caps during the Hirnantian glacial epoch.

The Wangjiawan (Riverside) section is found on the banks of the Wangjiawan River by the southeastern end of Wangjiawan village, located about 42 km north of Yichang city. The Wangjiawan (North) section, located ~180 m northwest of the Riverside section, hosts the Global Stratotype Section and Point (GSSP) for the Hirnantian (Late Ordovician) (Fig. 1B). The Riverside section is less weathered than the North section and thus provides better material for geochemical analysis.

3. Methods

An almost continuous section of approximately 2.5 m of sedimentary rock was sampled across the Hirnantian interval at the Wangjiawan (Riverside) section (Fig. 1B). Samples were chipped and pieces without weathering or veining were selected for powdering.

Sedimentary sulfide was extracted from 0.1 to 0.3 g of powdered sample for $\delta^{34}$S$_{\text{sulfide}}$ analysis. The sulfide extraction procedure is based on the method presented by Burton et al. (2008). The sample was placed in a tube along with an inner vial of zinc acetate solution. The tube was sealed with a cap and the air removed under vacuum. Acidified 6 M chromium(II) chloride solution was then injected into the tube through an opening. The mixture was shaken for 48 h. The Cr(II) ions reacted with any sulfide to form H$_2$S, which then diffused to the zinc acetate solution to form solid ZnS. The ZnS was then centrifuged, rinsed and dried. The sulfide content (%) was determined by boiling some powdered sample in acidified Cr(II) solution and collection of the evolved H$_2$S as Ag$_2$S in a silver nitrate solution. The dried Ag$_2$S was then weighed and the %S calculated (Canfield et al., 1986).

Total organic carbon (TOC) was determined by treating powdered samples with 6 M HCl to remove carbonate. The sample was then rinsed to remove the acid. The mass difference between the original sample and acid-treated residue was used to determine carbonate content. The dried sample was then combusted and the evolved CO$_2$ analyzed on the mass spectrometer. During the mass spectrometric analysis the sample peak height was calibrated against organic carbon standards to estimate the organic carbon content.

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Isotopic determinations for sulfide ($\delta^{34}\text{S}_{\text{sulfide}}$) were carried out using a Costech ECS 4010 Elemental Analyzer coupled to a Thermo-Finnigan Delta V Plus mass spectrometer. Approximately 300 µg of ZnS was combusted in a tin cup at 1000 °C, and the evolved SO₂ gas is then sampled by the mass spectrometer. Sulfur-isotope compositions ($\delta^{34}\text{S}$) were calibrated against NBS-127, IAEA-S1, and IAEA-S3 and are expressed as a permil ($\sigma$) deviation, relative to the V-CDT (Vienna Canyon Diablo Troilite) scale. Reproducibility, based on replicate analyses is better than 0.4‰ ($1\sigma$).

Isotopic determinations for organic carbon ($\delta^{13}\text{C}_{\text{org}}$) were carried out using the above elemental analyzer–mass spectrometer system. Approximately 300 µg of acidified sample was combusted at 1000 °C, and the evolved CO₂ gas was then sampled by the gas bench–mass spectrometer. Carbon-isotope compositions were calibrated against IAEA-NBS-21 graphite, IAEA-C6 sucrose and in-house acetanilide standards and are expressed as a permil ($\sigma$) deviation, relative to the V-PDB (Vienna Pee Dee Belemnite) scale. Duplicate samples were reproducible within 0.25‰ ($1\sigma$).

Carbonate carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) were carried out using a Thermo-Finnigan Gas Bench II coupled to a Delta V Plus mass spectrometer. Approximately 150 µg of bulk-powdered sample was reacted for 4 h at 72 °C with excess 100% phosphoric acid in a helium-sealed tube. The evolved CO₂ was then sampled by the gas bench–mass spectrometer. Isotopic measurements were calibrated against NBS-19, NBS-20, and two in-house standards, with analytical errors of 0.2‰ ($1\sigma$) for $\delta^{13}\text{C}_{\text{carb}}$ and 0.4‰ ($1\sigma$) for $\delta^{18}\text{O}_{\text{carb}}$ and are expressed as a permil ($\sigma$) deviation relative to the V-PDB (Vienna Pee Dee Belemnite) scale.

4. Results

The $\delta^{13}\text{C}_{\text{carb}}$ profile shows a positive excursion from about −4 to −1‰ in the Kuanyinchiao Formation. A return to pre-break-up values occurs in the persculptus zone of the Lungamachi Formation. Carbonate content is less than 5% for the Pacific zone except in the uppermost 2 cm where it begins to rise, peaking at −60% in the basal extraodinarius zone. Carbonate then declines to 10–30% until a second peak at −85% in the Kuanyinchiao Formation (Hirnantian Fauna zone). Values drop abruptly to under 10% at the start of the Lungamachi Formation.

The $\delta^{13}\text{C}_{\text{org}}$ generated in this study is broadly consistent with previously published $\delta^{13}\text{C}_{\text{org}}$ data for the Wangjiawan (Riverside) section (Chen et al., 2005b; Fan et al., 2009). However, the new data show a higher peak and steeper decline in the upper Kuanyinchiao Formation (Hirnantian Fauna zone), probably due to the greater sampling density of this study. This sharp decline in $\delta^{13}\text{C}_{\text{org}}$ within the Hirnantian Fauna zone is also seen at the Wangjiawan (North) (Wang et al., 1997; Fan et al., 2009), Huanghuachang (Wang et al., 1997), Nanbazi (Yan et al., 2009), and Fenxiang (Wang et al., 1997) sections within China. In the Lungamachi Formation some $\delta^{13}\text{C}_{\text{org}}$ values vary by 1 to 1.5‰ from previously published values (Fig. 2). The reason for this is uncertain.

Total organic carbon (TOC) is generally above 5% in the Lungamachi Formation, but dips sharply in the Kuanyinchiao Formation and remains low (~1%) until the Lungamachi Formation. Peak $\delta^{13}\text{C}_{\text{org}}$ values occur in the low TOC interval. However, $\delta^{13}\text{C}_{\text{org}}$ appears to move independently of TOC. Even the transitions from low to high (or high to low) TOC in the Wufeng and Lungamachi Formations (2–10%) do not affect the $\delta^{13}\text{C}_{\text{org}}$ signals.

The new $\delta^{34}\text{S}_{\text{sulfide}}$ results produced a smooth profile between −20‰ and −10‰ in the pacificus and lower extraodinarius zones. The upper extraodinarius zone exhibits a large range of values, but then the smooth profile resumes in the Kuanyinchiao Formation (Hirnantian Fauna zone), although values are about 20‰ heavier than in the pacificus zone. In the overlying Lungamachi Formation values return to the pre-break-up baseline of around −20‰. These $\delta^{34}\text{S}_{\text{sulfide}}$ profiles are consistent with previously published results from the Wangjiawan (North), Nanbazi (Yan et al., 2009) and Honghuayuan (Zhang et al., 2009) sections, all of which document an ~20‰ enrichment in $\delta^{34}\text{S}_{\text{sulfide}}$. Further upsection into the Silurian (ascensus zone and above) $\delta^{34}\text{S}_{\text{sulfide}}$ values are highly variable, between −30‰ and +22‰.

5. Discussion

5.1. Sulfur geochemistry

Sulfide in the sediment comes mainly in the form of pyrite. It is produced by sulfide reducing bacteria, which metabolize sulfate (SO₄²⁻) to sulfide (S²⁻). The sulfide then reacts with any available iron in the sediment to form pyrite (FeS₂), a stable mineral that is preserved in sediments (Goldhaber and Kaplan, 1974). The metabolic activity of the sulfide reducing bacteria generally depletes (or fractionates) the resulting sulfide in 34S, by up to 70‰ (Goldhaber and Kaplan, 1974; Canfield, 2001; Sim et al., 2011a). The final isotopic composition of sulfide is determined by the isotopic composition of the source sulfate, and the magnitude of fractionation, which depends on various factors. Firstly, metabolic activity generally results in minimal fractionation under sulfate-limited conditions where most of the sulfide will be metabolized. Secondly, increasing the rate of bacterial sulfate reduction, by increasing the amount and reactivity of organic matter (Berner, 1984), will reduce the amount of fractionation (Habicht and Canfield, 1997; Canfield, 2001; Habicht and Canfield, 2001; Sim et al., 2011b). Thirdly, increasing the presence of additional sulfur cycles (i.e., partial sulfide oxidation to elemental sulfur (S⁰) followed by disproportionation, forming sulfide and sulfate from S⁰), will increase the fractionation (Habicht and Canfield, 1997; Canfield, 2001; Habicht and Canfield, 2001). Sedimentation rate has also been cited in affecting $\delta^{34}\text{S}_{\text{sulfide}}$ (Goldhaber and Kaplan, 1974), although this is probably because of the way it affects the supply of organic matter (Berner, 1978) and sulfate (Chambers, 1982).

The new $\delta^{34}\text{S}_{\text{sulfide}}$ data show values from −20‰ and −14‰ in the pacificus zone but form a very tight cluster around −10‰ across the pacificus-extraodinarius boundary and through much of the extraodinarius zone, despite other major geochemical changes at this time, including sharp changes in sulfide content. The fact that $\delta^{34}\text{S}_{\text{sulfide}}$ is little changed would indicate that those factors most responsible for the fractionation of sulfur isotopes (i.e., the sulfate $\delta^{34}\text{S}$ and availability, reduction rate, and disproportionation) were surprisingly stable. Yan et al. (2008) suggested this boundary hosted a change from euxinic to oxic conditions from iron, carbon and sulfur studies from the Wangjiawan (North) section. However, the constant $\delta^{34}\text{S}_{\text{sulfide}}$ values suggest this did not occur, as a change in sulfide source would generally bring a change in $\delta^{34}\text{S}_{\text{sulfide}}$. Alternatively, the redox change may have occurred 10–20 cm below the pacificus-extraodinarius boundary, where the $\delta^{34}\text{S}_{\text{sulfide}}$ pattern changes slightly.

In the upper extraodinarius zone, just before the Kuanyinchiao Formation, $\delta^{34}\text{S}_{\text{sulfide}}$ fluctuates between about −20‰ and +15‰. There is little change in TOC or carbonate deposition and redox indicators from the Wangjiawan (North) section (reactive iron and degree of pyritization; Fig 2) suggests the water column was still oxygenated (Yan et al., 2008). Yan et al. (2010) determined a chemical alteration index (CAI) – a compilation of cation ratios that indicate weathering rates – that shows a coincident shift to greater weathering, i.e., a less arid interglacial episode (Fig 2). However, the cause of the $\delta^{34}\text{S}_{\text{sulfide}}$ variability is uncertain. It could be due to changes in sulfate $\delta^{34}\text{S}$, sulfate availability or disproportionation as the relevant factors. Although distinguishing between these requires other data.
values as a change from anoxic to oxic waters that forced the sulfate reducing bacteria further into the sediment, where sulfate can become limited because the supply of water, and therefore sulfate, from the overlying water column is limited. However, Zhang et al. (2009) suggest that the increase in δ34Ssulfide, was caused by a proportional increase in seawater sulfate δ34S on the Yangtze Platform, the sulfate δ34S rise being caused by the rapid burial of sulfate, and organic carbon, in local anoxic deep-water sub-basins, although such a situation has not yet been demonstrated in modern or ancient settings. It is also possible that bacterial reduction rate increased through the delivery of a more reactive type of organic matter, albeit less of it. Alternatively, it is possible that the new environment of the Kuanyinchiao Formation had hosted a different mix of sulfur cycling bacteria that may not have had a different sulfate reduction rate, which in turn increases the δ34Ssulfide. But TOC has no apparent effect in this section (in fact the intervals with lowest TOC have the highest δ34Ssulfide). Likewise, changing sedimentation conditions, as recorded by carbonate content, also has no effect. Availability of sulfate is consistent with controlling δ34Ssulfide in some portions of this section, but not all. Changing sulfate δ34S is also a possibility but further work, perhaps on carbonate-associated sulfate, is required to test this. Changing of organic matter reactivity, thereby encouraging or discouraging higher bacterial metabolic rates, could be the cause but organic geochemical work is required to investigate this. Alternatively, changes in the bacterial communities may be a solution but this cannot be tested in ancient strata.

In short, there is no simple and consistent explanation for the δ34Ssulfide values in this section. Increased TOC can increase bacterial reduction rate, which in turn increases the δ34Ssulfide. But TOC has no apparent effect in this section (in fact the intervals with lowest TOC have the highest δ34Ssulfide). Likewise, changing sedimentation conditions, as recorded by carbonate content, also has no effect. Availability of sulfate is consistent with controlling δ34Ssulfide in some portions of this section, but not all. Changing sulfate δ34S is also a possibility but further work, perhaps on carbonate-associated sulfate, is required to test this. Changing of organic matter reactivity, thereby encouraging or discouraging higher bacterial metabolic rates, could be the cause but organic geochemical work is required to investigate this. Alternatively, changes in the bacterial communities may be a solution but this cannot be tested in ancient strata.

5.2. Reliability of δ13Ccarb as a primary signal

The new δ13Ccarb results show a positive excursion in the extraordina
tarius zone. This excursion matches the timing and magnitude of other known Hirnantian δ13Ccarb excursions from sections around the world where graptolite biostratigraphic analysis has been done (Fig. 3). This is strong evidence that this signal is derived from Hirnantian seawater. However, the absolute values are shifted to the negative by about 3–4‰ compared to the δ13Ccarb of most other sections where the base-line is about 0‰ (Fig. 3).

Differences in δ13Ccarb values between open ocean and platform settings, and even different parts of platforms, have been demonstrated in modern and ancient settings (Patterson and Walter, 1994; Immemhauser et al., 2002, 2003; Panchuk et al., 2005, 2006; LaPorte et al., 2009; Cramer et al., 2010). The more proximal platform sites can have either more negative or more positive δ13Ccarb values. In some modern settings δ13Ccarb is more negative compared to the open ocean due to 13C-depleted organic matter being oxidized but not adequately mixed with the open ocean (Patterson and Walter, 1994), commonly referred to as ‘aging’ of waters. However,
cases from the Silurian (Cramer et al., 2010) and Ordovician (LaPorte et al., 2009) show the more proximal sediments having more positive δ¹³C_carb values. The causes for these δ¹³C_carb offsets are still debated, e.g., varying meteoric water influence (Immenhauser et al., 2003), water aging (Patterson and Walter, 1994), increased weathered carbonate input (Melchin and Holmden, 2006), or varying photosynthetic activity (LaPorte et al., 2009). But most importantly, correlation of these offset excursions has been documented in sections with tight biostratigraphic constraints, such as the Aptian (Di Lucia et al., 2012), Cenomanian (Jarvis et al., 2006), Carboniferous (Immenhauser et al., 2003), Silurian (Cramer et al., 2010), and Ordovician (LaPorte et al., 2009). Furthermore, these δ¹³C_carb excursions and offsets appear unaffected by changing lithology.

There are diagenetic processes known to alter δ¹³C_carb, from the original seawater values. These include meteoric diagenesis, burial diagenesis, argonite versus calcite precipitation, and the oxidation or production of organic matter (Algeo et al., 1992; Immenhauser et al., 2002; Swart et al., 2009; Colombie et al., 2011). However, none of these appears to explain the positive δ¹³C_carb excursion of the extraordinary zon

Early meteoric diagenesis is related to sea level drop and the exposure of sediments to freshwater and sometimes soil zone CO₂ (Allan and Matthews, 1982; Immenhauser et al., 2002). This causes a negative shift in both δ¹⁸O_carb and δ¹⁸O_water. As such, a correlation between δ¹⁸O_carb and δ¹³C_carb is traditionally viewed as an indicator of meteoric diagenesis (Banner and Hanson, 1990; Algeo et al., 1992) (Fig. A4A for the data from this study). Since meteoric diagenesis drives δ¹³C_carb to more negative values, the positive extraordinary δ¹³C_carb excursion cannot be explained by this process. However, the negative δ¹³C_carb excursion (δ¹³C_carb almost −8‰) is seen at the peak of the second, more intense, glacial pulse in the Kuanyinchiao Formation (Fig. 2). This coincidence of glacioeustatic shallowing and very negative δ¹³C_carb values suggests early meteoric diagenesis (Immenhauser et al., 2002). However, δ¹⁸O_water shows no negative excursion. Two explanations are possible. Firstly, the δ¹³C_carb signal was preserved while the depleted δ¹⁸O_water values were reset through deep burial diagenesis, wherein oxygen in pore waters re-equilibrated with carbonate oxygen under heat and pressure (Algeo et al., 1992; Immenhauser et al., 2002). Alternatively, this negative δ¹³C_carb spike reflects the primary global seawater signal, which is also seen in the persculptus zone of the Blackstone Range (Yukon) (Fig. 3) but is not identified in other sections because of insufficient sampling detail. Detailed sampling of geographically widespread sections would be required to confirm this.

Another diagenetic possibility is that arising from local organic matter oxidation, providing ¹³C-depleted carbonate, which could alter δ¹³C_carb within the sediment (Joachimski, 1994). Evidence for this possibility is seen by plotting %TOC against δ¹³C_carb. For the sediments where there is significant carbonate (>10%) there is no correlation (Fig. 4B). However, the weak correlation (R² = 0.28) is exhibited in sediments where carbonate content is under 10% (pacificus, upper persculptus and lower ascensus zones). This result is expected as a high carbonate content would buffer against any contamination from organic matter. Also, this result does not affect the integrity of the positive δ¹³C_carb excursion as it occurs within the sediments where carbonate content is >10%.
the cause of the excursion was δ13C changes in the overlying water and that the data were not significantly altered during diagenesis.

Another source of δ13C variation arises from differences in mineralogy. Laboratory experiments have shown that argonite is enriched in 13C by about 1.7‰ compared to calcite precipitated from the same water (Romanek et al., 1992). Observations from natural environments have shown an even greater difference, up to 4–5‰ (e.g., Swart, 2008). As aragonite is not easily preserved in the sedimentary record, it is not easy to determine what role variable mineralogy had in the Wangjiawan Formation (Riverside) δ13C_carb values. However, as the Hirnantian δ13C_carb excursion is global, and recognized in sections from varying water depths and lithologies, it cannot be attributed to local aragonite formation. Alternatively, it is possible that an increase in global seawater Mg2+ could have led to widespread aragonite formation (de Choudens-Sanchez and Gonzalez, 2009). However, a rapid global Mg2+ increase and subsequent decrease within about a million years (the duration of the δ13C_carb excursion) would be unlikely as the residence time of magnesium in the oceans is currently about 13 million years (Broecker and Peng, 1982).

Thus, the positive δ13C_carb excursion in the extraordinarius zone is most probably a reliable chemostatigraphic tool. It is unlikely that diagenetic factors created a positive excursion, where there was not one, and that such an excursion would be of the same timing and magnitude as is recorded in other sections worldwide. However, the negative spike in the Kuanyinchiao Formation is probably the result of diagenetic influences. Also, where the carbonate content is less than 10%, there may be some diagenetic alteration due to organic matter oxidation, but this does not include the positive or negative δ13C_carb excursions.

5.3. δ13C_carb, δ13C_org and stratigraphic correlations

The Wangjiawan data show that the δ13C_carb excursion begins at the base of, or just below, the extraordinarius zone (see Fig. 2) and peaks within the extraordinarius zone. The δ13C_org curve also begins to rise in parallel with the δ13C_carb but peaks in the Hirnantian Fauna zone, coincident with a negative spike in δ13C_carb values. As Chen et al. (2005b, 2006) have identified the upper half of the Kuanyinchiao Formation to be the basal persculptus graptolite zone, it places the δ13C_org peak in the lower persculptus zone. Thus, the δ13C_carb and δ13C_org data reach their peak values in different biozones.

This pattern of δ13C_carb and δ13C_org starting to rise near the pacificus-extraordinarius boundary is evident in other sections where graptolite stratigraphy is available (Fig. 3). δ13C_carb also peaks in the extraordinarius zone (Fig. 3), with the exception of the Vinici Creek section, Nevada (Fig. 3; LaPorte et al., 2009). δ13C_org is not as consistent, peaking in either the extraordinarius (e.g., Monitor Range, Nevada; LaPorte et al., 2009) or the persculptus (e.g., Dob’s Linn, Scotland; Underwood et al., 1997) zones, or plateauing throughout (e.g., Vinici Creek, Nevada; LaPorte et al., 2009). But δ13C_carb and δ13C_org all return to baseline values in the persculptus zone (Fig. 3), marking the end of the Hirnantian carbon-isotope excursion. The rise in δ13C_carb and δ13C_org in the late pacificus–early extraordinarius zones and the return to baseline values in the persculptus zone appear to be the most significant chemostatigraphic features.

At Anticosti Island and Estonia, where graptolite stratigraphy is poorly constrained (Delabroye and Vecoli, 2010), chitinozoans are used (Fig. 3). However, debate arises in the correlation of chitinozoan with graptolite biozones. Some workers (e.g., Melchin and Holmden, 2006; Fan et al., 2009; Achab et al., 2011) correlate the chitinozoans taugourdeaui and scabra with the graptolite persculptus zone. However, Baltic stratigraphers (e.g., Brenchley et al., 2003; Kaljo et al., 2007, 2008) place taugourdeaui and scabra within the extraordinarius zone (see Delabroye and Vecoli (2010) and Young et al. (2010) for reviews of the biostratigraphic debate).

Workers preferring the former correlation scheme (taugourdeaui + scabra = persculptus) have based this on the correlation of Anticosti/Estonian δ13C_carb profiles with the δ13C_org profiles of Wangjiawan and Dob’s Linn (e.g., Achab et al., 2011). This scheme matches the shallow rises in the extraordinarius zone and strong rises in the persculptus zone. However, comparison of the Anticosti/Estonian δ13C_carb Curves with other profiles shows that the taugourdeaui + scabra = persculptus scheme is ill fitting (see dashed lines in Fig. 3). All δ13C_carb Curves show the strongest rise near the pacificus–extraordinarius zone. Furthermore, in the graptolite-zoned sections once the Hirnantian carbon-isotope excursion begins, both δ13C_carb and δ13C_org Values remain elevated until returning to baseline in the persculptus zone (Jones et al., 2011). This condition is broken in the Anticosti δ13C_carb profile if the taugourdeaui + scabra = persculptus scheme is adopted (Fig. 3).

By correlating the taugourdeaui and scabra chitinozoan zones with the extraordinarius zone, the Anticosti/Estonian δ13C_carb and δ13C_org curves produce a much more comfortable fit with the graptolite-zoned sections, and conform to the pattern of beginning in the extraordinarius zone and ending in the persculptus zone (Fig. 3).

Thus, the Baltic stratigraphers appear correct in correlating the taugourdeaui and scabra chitinozoan zones with the extraordinarius zone. This scheme would also predict that a δ13C_org analysis of the Dob’s Linn section, Scotland, the GSSP for the base of the Silurian “extraordinarius” zone at Anticosti Island and Estonia, where graptolite stratigraphy is poorly constrained, may not be reliable.
also tie in with the sulfur isotope results, where it is possible that the 
 elevated δ^{34}S_{sulfide} of the Kuanyinchiao Formation was the result of a 
 more reactive organic matter supply that increased sulfate reduction 
 rates (Section 5.1).

The consistent pattern of δ^{13}C_{org} profiles across the Yangtze Platform 
 at Wangjiawan (Wang et al., 1997; Fan et al., 2009), Huanghuachang 
 (Wang et al., 1997), Nanbazi (Yan et al., 2009), and Fenxiang (Wang 
 et al., 1997) indicates that whatever factors caused the δ^{13}C_{org} shifts, 
 these have to be basin-wide mechanisms.

5.4. δ^{13}C rise and Hirnantian environmental events

Explanations for the Hirnantian δ^{13}C excursion have fallen into two 
 camps. According to the first, the rise of δ^{13}C is attributed to an increase 
 in primary productivity and organic burial which sequesters δ^{12}C, leaving 
 the inorganic carbon pool enriched in δ^{13}C (e.g., Marshall and Middleton, 
 1990; Brenchley et al., 1994; Marshall et al., 1997; Brenchley et al., 
 2003). This is known as the “productivity” hypothesis. On the other 
 hand, the second explanation invokes an alteration of weathering pat-
 terns due to ice sheets covering high-latitude land, but lowered sea 
 levels exposing more carbonate platforms in lower latitudes (e.g., 
 Kump et al., 1999; Melchin and Holmden, 2006). This is known as the 
 “weathering” hypothesis. Workers suggest that carbonate platforms 
 were preferentially exposed during the glacial sea level fall, providing 
 more carbonate and less organic matter for weathering. Silicate weath-
 ering was also reduced as ice sheets covered continental Gondwana, 
 leading to a build up of CO₂ in the atmosphere (Kump et al., 1999) until 
 sufficient greenhouse warming caused the deglaciation.

The available TOC data (Fig. 3) argues against the productivity hy-
 pothesis. If increased organic matter burial was responsible for the posi-
 tive δ^{13}C_{carb} and δ^{13}C_{org} excursions, then a coincident increase in TOC 
 would be expected. But TOC actually declines in most sections coinci-
 dent with the elevated δ^{13}C values. Although one could argue for organ-
 ic matter deposition in some yet to be analyzed basin, or even the deep 
 sea, the available evidence is not favorable to this hypothesis. Other 
 sections, not shown in Fig. 3, that also show low TOC at this interval 
 include Nanbazi (China; Yan et al., 2009), Cape Manning and Truro 
 Lake (Arctic Canada; Melchin and Holmden, 2006).

The weathering hypothesis could be bolstered by examples of posi-
 tive δ^{13}C_{carb} excursions coincident with sea level falls. Comparable 
 events could be the Carboniferous–Permian glaciations, which occa-
 sionally show coincident δ^{13}C shifts, although they are not as consistent 
 as the Hirnantian (Mili et al., 2001; Grossman et al., 2008; Birgenheier 
 et al., 2010; Buggisch et al., 2011). On the other hand, the Pleistocene 
 glacial cycles show δ^{13}C_{carb} falling during glacial maxima (i.e., sea 
 level minima) (e.g., Curry and Oppo, 2005), indicating that an increased 
 weathering of carbonate is not significant. However, one could argue 
 that carbonate platforms were much more extensive during the Paleo-
 zoic compared with the Pleistocene (Kump et al., 1999).

The lack of consensus on the interpretation of the δ^{13}C shifts (during 
 the Hirnantian, as well as other time periods) hampers our ability to ro-
 bustly interpret the events causing this geochemical signal. Under-
 standing the causal relationships between the Hirnantian glaciation 
 and carbon-cycle perturbation may await a more fundamental under-
 standing of the mechanisms behind the δ^{13}C signal.

6. Conclusions

New geochemical data provide a record of changing environmental 
 conditions associated with the Hirnantian of South China. Two glacial 
 pulses coincide with increases in sediment carbonate content. δ^{34}S_{sulfide} 
 data shows elevated values in the Kuanyinchiao Formation, consistent 
 with other sections throughout the Yangtze Platform. However, there 
 is no consensus on the cause of these changes. New δ^{13}C_{carb} data shows a peak in the extraordinary zone, before 
 the well-established δ^{13}C_{org} peak in the persculptus zone. Previous global 
 Hirnantian correlations have matched δ^{13}C_{carb} peaks with the Wangjia-
 wan δ^{13}C_{carb} peak, making correlative sections comparatively too young 
 and promoting a correlation of taugourdeaui and scabra chitinozoans 
 with the persculptus graptolite zone. Instead, the new data suggests 
 that the taugourdeaui and scabra zones correlate with the extraordinari-
 ous zone. Although the ultimate cause of the Hirnantian glaciation and its re-
 lationship to the δ^{13}C_{carb} perturbation remain elusive, the new data and 
 refined correlation framework presented here provide another step to-
 ward addressing these issues.

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