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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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ABSTRACT

Detailed geochemical analyses ($\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, $\delta^{34}S_{sulfide}$, 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 $\delta^{34}S_{sulfide}$ 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 $\delta^{13}C_{carb}$ data show a sharp rise and peak in the *extraordinarius* zone, below the previously published $\delta^{13}C_{org}$ 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 $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$. The controversy over correlating Hirnantian graptolite zones with chitinozoan zones can also be addressed. The new $\delta^{13}C_{carb}$ data also allow direct comparison with Hirnantian $\delta^{13}C_{carb}$ data from Anticosti Island and the Baltic region, which are zoned by chitinozoan fossils. This comparison favors a correlation of the *taugourdeaui* and *scabra* chitinozoan zones with the *extraordinarius* graptolite zone.

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 ($\delta^{13}C$) 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 ($\delta^{18}O_{apatite}$) in Ordovician conodonts to show a global temperature fall in the late Ordovician. This conclusion was reinforced by clumped-isotope paleothermometry on Hirnantian 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 (Ghienne, 2003; Yan et al., 2010).

The Hirnantian extinction is recognized as the second most devastating extinction in the Phanerozoic, 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 paleontological 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 ^{13}C 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

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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, brachipods 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 (Soufiane 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 ($\delta^{13}C_{carb}$) 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 ($\delta^{13}C_{carb}$, $\delta^{13}C_{org}$, $\delta^{34}S_{sulfide}$) 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 $\delta^{13}C_{carb}$, 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 a 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 episode.

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 $\delta^{34}S_{sulfide}$ 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_2S, which then diffused to the zinc acetate solution to form solid ZnS. The ZnS was then centrifuged, rinsed and dried. The sulfide content (%S) was determined by boiling some powdered sample in acidified Cr(II) solution and collection of the evolved H_2S as Ag_2S in a silver nitrate solution. The dried Ag_2S 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.

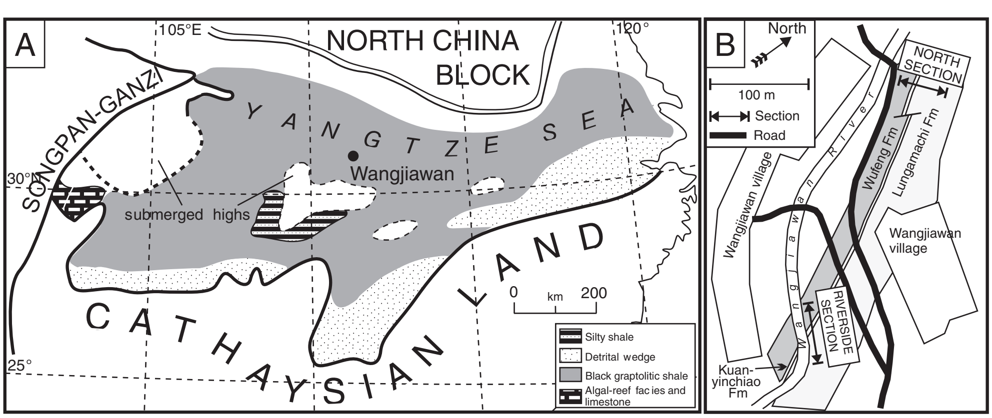

Fig. 1. (A) Paleogeographical map of the Hirnantian Yangtze Platform showing location of the Wangjiawan site and extent of the epeiric Yangtze Sea at Wufeng Formation time. (B) Map showing location of Wangjiawan (Riverside) and Wangjiawan (North) sections adjacent to the Wangjiawan village, Hubei, China. The Kuanyinchiao Formation is exposed between the Wufeng and Lungamachi Formations, and its thickness exaggerated to make it easily seen. Sampling was performed about a meter on either side of the Kuanyinchiao Formation. (A) is after Chen et al., 2004, (B) is adapted from Chen et al., 2006.