

# Large-scale climatic fluctuations in the latest Ordovician on the Yangtze block, south China

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## ABSTRACT

The Ordovician-Silurian transition was a critical interval in Earth's history marked by dramatic climatic, oceanic, and biological turnovers. Here we present the chemical index of alteration (CIA) as a proxy of changes in intensity of chemical weathering, and its variations across the Ordovician-Silurian boundaries (Wufeng through Guanyinqiao, to Longmaxi Formations) from Wangjiawan and Nanbazi on the Yangtze block, south China, in order to explore the climatic changes. Our data show that the CIA values of sediments commonly range from 75 to 90 in the Wufeng and Longmaxi Formations, indicating a high degree of chemical weathering and thus a hot and humid climate during deposition. In contrast, a sharp drop in CIA values (most 60–70) in the Guanyinqiao Formation (or Hirnantian) suggests an overall cold and arid climate, interrupted by several intervals of warm climate when deposited. The temporal coincidence of two phases of massive biotic extinctions with the beginning and end of the cold climate epoch, respectively, suggests that the large climatic changes could be one of the main controls on the mass extinctions, although other factors may also have played a role.

## INTRODUCTION

During the Ordovician-Silurian transition, widespread drastic environmental changes took place; the most remarkable of these, in the context of a long-term greenhouse climate, was the abrupt glaciation in Gondwana (Brenchley et al., 1994, 2003; Saltzman and Young, 2005). The temporal coincidence of mass extinctions with the climate changes, particularly with the beginning and termination of glaciation, corroborates a cause and effect relationship between them; however, the intensity and extent of this glaciation and the effect upon the biotic crisis remain controversial (Sheehan, 2001). In the absence of direct glacial deposits on the Yangtze block of south China, evidence of climate changes during the latest Ordovician in this area remains elusive, and is mainly based on the occurrence of Hirnantian fauna (Chen, 1984; Rong, 1984).

Mineralogical and chemical compositions of siliciclastic deposits depend on the intensity of chemical weathering linked to the climate in provenance terrains (Nesbitt and Young, 1982; Fedo et al., 1997). Therefore changes in the mineralogical and chemical compositions of sedimentary rocks (particularly fine-grained siliciclastic rocks) can potentially be used as a proxy for climate changes. Accordingly, the chemical index of alteration (CIA) is proposed to evaluate the climate changes (Nesbitt and Young, 1982; Fedo et al., 1995, 1997; Young and Nesbitt, 1999; Feng et al., 2004; Rieu et al., 2007). High CIA values reflect the substantial removal of mobile cations (e.g., Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>) relative to stable residual constituents (Al<sup>3+</sup>, Ti<sup>4+</sup>) through intensive chemical weathering,

likely under warm and humid conditions. Low CIA values, however, indicate the near absence of chemical weathering, thereby reflecting cool and/or arid conditions. In this paper the paleoclimatic changes during the Ordovician-Silurian transition were reconstructed in the light of CIA values derived from the chemical composition of fine-grained siliciclastic rocks in the mid-upper Yangtze River region, China. The influences of paleoclimatic changes on biota are also discussed.

## GEOLOGICAL SETTING

From the Late Ordovician, the Yangtze carbonate platform gradually evolved into a siliciclastic-dominated deep shelf basin as a result

of amalgamation of the Yangtze block and the Cathaysia block to the east (Chen et al., 2004; Wang and Cai, 2007; Fig. 1A). Two sections, located at Wangjiawan, Yichang, Hubei province, and Nanbazi (~500 m away the classic Honghuayuan section), Tongzi, Guizhou province, ~500 km apart, were selected for the chemostratigraphic study. Paleogeographically, the Wangjiawan section was located on the deeper outer shelf, and the Nanbazi section was on the shallower inner shelf adjacent to the southern Dianqian uplift (Fig. 1A).

The Ordovician-Silurian boundary succession, in ascending order, includes the Wufeng, Guanyinqiao, and Longmaxi Formations (Fig. 1B), which are well constrained by graptolite biozonation (X. Chen et al., 2000, 2005). The Wufeng Formation, generally several meters to ~30 m thick, is mainly composed of black shales with more or less siliceous, carbonaceous, and silty materials; it is commonly overlain by the Guanyinqiao Formation, a thin horizon of argillaceous shelly limestones containing Hirnantian fauna (Rong et al., 2002). The overlying Longmaxi Formation, generally tens to several hundreds of meters thick, is mainly composed of black shales, silty shales, and locally siliceous mudstones. Details of the biostratigraphy and other relevant issues were provided previously (X. Chen et al., 2000, 2005; Rong et al., 2002; Su et al., 2003, for Nanbazi). Extensive studies

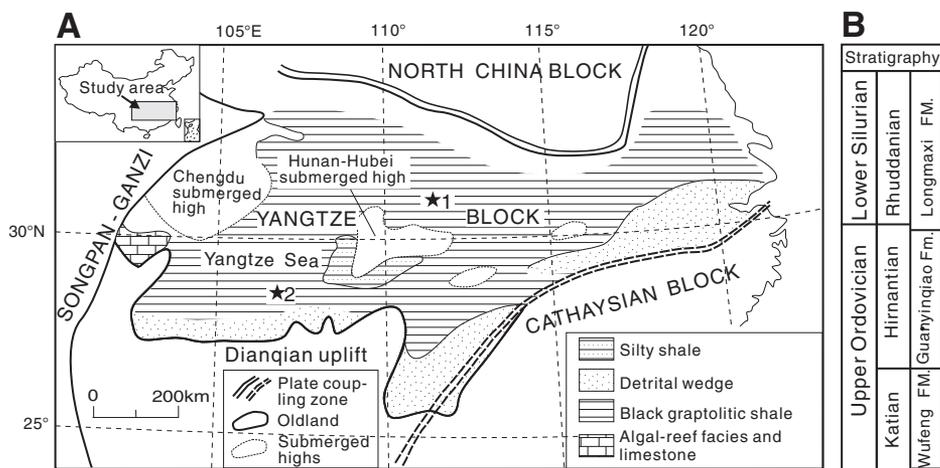


Figure 1. A: Lithofacies paleogeographic map of Yangtze block during the Late Ordovician Wufengian interval (modified from Chen et al., 2004). Studied sections: 1—Wangjiawan, Yichang, Hubei Province; 2—Nanbazi, Tongzi, Guizhou Province. B: Stratigraphic succession across Ordovician-Silurian boundary on Yangtze block, south China.

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indicate that mass biotic extinctions occurred in the latest Ordovician, and are mainly characterized by two pulses (X. Chen et al., 2005); the first pulse took place in the beginning of the Guanyinqiaoian interval, and the second in the end of the Guanyinqiaoian interval.

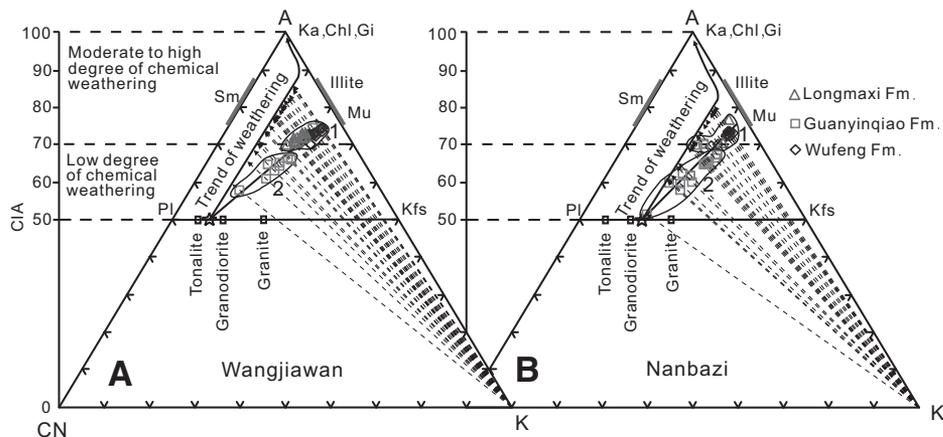
## METHODS

We collected 64 samples from the Wufeng, Guanyinqiao, and Longmaxi Formations from localities at Wangjiawan and Nanbazi (Fig. 1). Fine-grained siliciclastic components were powdered for geochemical analysis. Major elements were analyzed by an automatic X-ray fluorescence spectrometer (XRF-1500) using fusion glasses made from a mixture of sample powder and flux ( $\text{Li}_2\text{B}_4\text{O}_7$ ) in the proportion 1:5. Analytical precision for major element concentrations is generally better than 3% (Tables DR1 and DR2 in the GSA Data Repository<sup>1</sup>).

The chemical index of alteration (CIA) was applied to the paleoclimatic reconstruction of sediments, i.e., when deposited (Fedo et al., 1997; Young and Nesbitt, 1999; Feng et al., 2004). The CIA is expressed as:  $\text{CIA} = \text{molar} [(Al_2O_3)/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$ , where  $CaO^*$  represents the CaO in silicate minerals only (Nesbitt and Young, 1982, 1989). In such a case, it is necessary to make a correction to the measured CaO content for the presence of carbonates (calcite, dolomite) and apatite. In this study, the CaO was initially corrected for phosphate using available  $P_2O_5$  data ( $CaO^* = \text{mole } CaO - \text{mole } P_2O_5 \times 10/3$ ). If the remaining number of moles is less than that of  $Na_2O$ , the CaO value was adopted as the  $CaO^*$ . Otherwise, the  $CaO^*$  was assumed to be equivalent to  $Na_2O$  (McLennan, 1993).

When plotted in the A-CN-K ( $Al_2O_3$ - $CaO^*$  +  $Na_2O$ - $K_2O$ ) ternary diagram (Fig. 2), sediments produced by intense chemical weathering were plotted in positions commensurate with high CIA values (80–100), whereas incipiently weathered sediments were plotted near the feldspar join (CIA of 50–70) (Fig. 2). Theoretically, products of progressive weathering usually yield a series of CIA values distributed along a straight line (ideal weathering trend) parallel to the A-CN sideline (Nesbitt and Young, 1982; McLennan, 1993). However, most of our data points are on a line deviating from the theoretical trend, suggesting  $K_2O$  addition as a result of diagenetic K-metasomatism (conversion of kaolinite to illite) (Fedo et al., 1995, 1997; Rieu et al., 2007), so it is necessary to make corrections for the K-metasomatism (Fig. 2). For a

<sup>1</sup>GSA Data Repository item 2010164, supplementary information and additional chemical data, is available online at [www.geosociety.org/pubs/ft2010.htm](http://www.geosociety.org/pubs/ft2010.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.



**Figure 2.** Chemical compositional variations in Wufeng, Guanyinqiao, and Longmaxi Formations in A-CN-K ( $Al_2O_3$ - $CaO^*$  +  $Na_2O$ - $K_2O$ ) ternary diagrams and associated chemical index of alteration (CIA) variations. **A:** From Wangjiawan. **B:** From Nanbazi. In triangles, arrowed solid lines parallel to A-CN sidelines are ideal weathering trends of bedrocks. Trends may deviate and shift toward K-apex (K-metasomatism lines) due to K-metasomatism; their intersections (stars) with feldspar (P-K) join indicate feldspar proportion of unweathered source rocks. Correction for K-metasomatism is made by projecting data points back onto the ideal weathering pathway from K-apex (dashed arrows). Ka—kaolinite; Chl—chlorite; Gi—Gibbsite; Sm—smectite; Mu—muscovite; Pl—plagioclase; Kfs—K-feldspar.

comparison, both corrected ( $CIA_{corr}$ ) and uncorrected CIA values are illustrated in Figure 3.

## RESULTS AND DISCUSSION

### Results

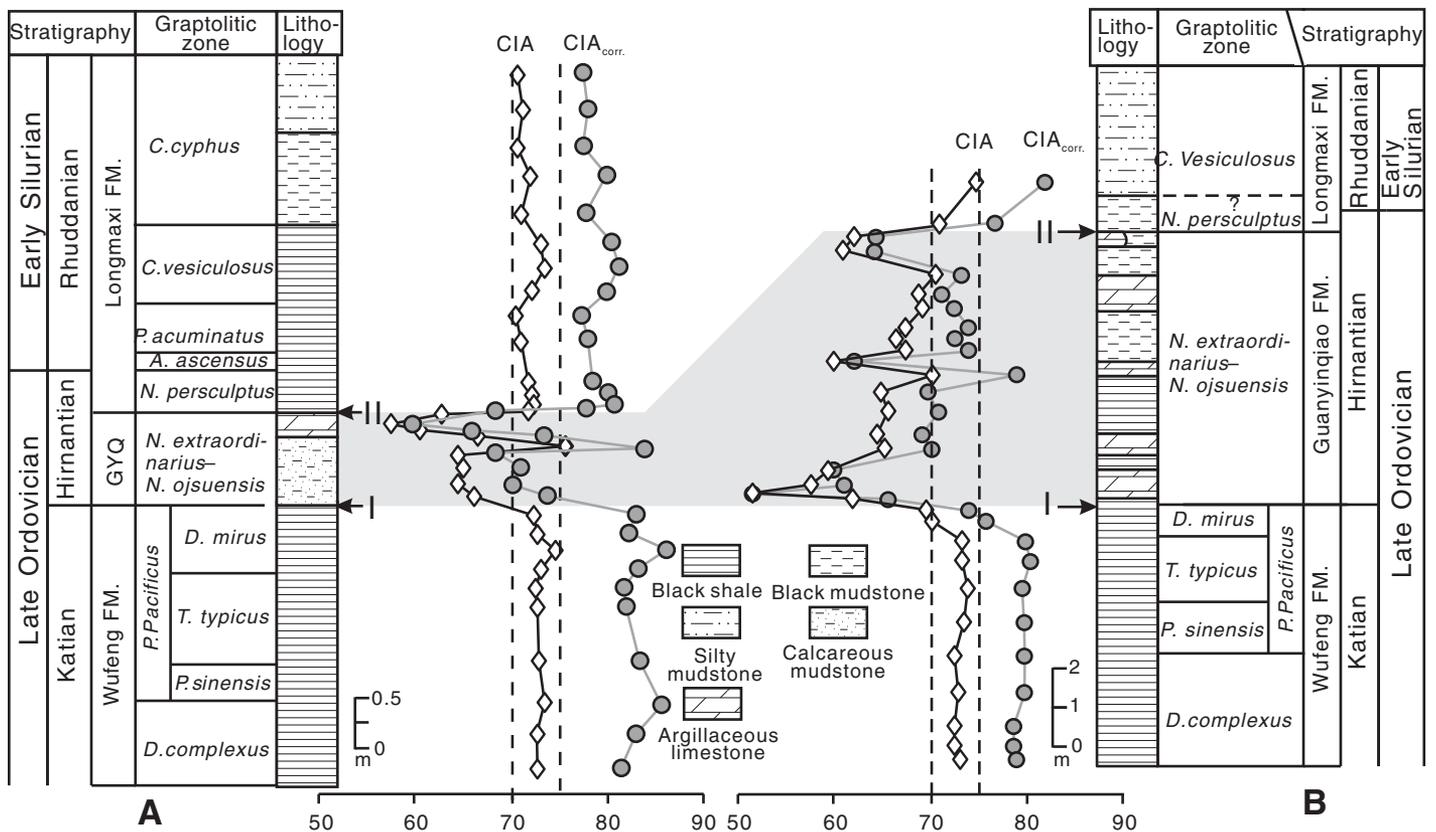
Across the Ordovician-Silurian boundary, there are significant compositional variations indicated by CIA values on the Yangtze platform (Figs. 2 and 3; Tables DR1 and DR2). At Wangjiawan,  $CIA_{corr}$  values of black shales from Wufeng Formation (from the *Dicellograptus complexus* through *Paraorthograptus pacificus* biozones) are relatively consistent (Fig. 3), ranging from 81.3 to 86.1 (average 83.1); they fall sharply to a trough between 59.7 and 73.7, except for one high value (83.8) (average 70.5) in the Guanyinqiao Formation (*Normalograptus extraordinarius*-*N. ojsuensis* biozones). Further upward, the  $CIA_{corr}$  values quickly return to persistently high values, although a little low compared to those in the Wufeng Formation, from 77.2 to 81.1 (average 78.9) immediately in the base of Longmaxi Formation (from *N. persculptus*), and upward. Therefore, the CIA values in the Wufeng and Longmaxi Formations are generally clustered in the same group (group 1), and are higher than those of average shales (70–75) (Nesbitt and Young, 1989, 1996). Those in the Guanyinqiao Formation are thus mainly clustered in group 2 (Fig. 2A). A similar trend of CIA changes was determined at Nanbazi, where the CIA values in the Wufeng and Longmaxi Formations, although a little low for  $CIA_{corr}$  are generally the same as those at Wangjiawan (Fig. 3A), and are clustered in group 1 (Fig. 2B). By comparison, in the Guanyinqiao Formation (Hirnantian) there,

$CIA_{corr}$  values, although apparently decreased, show a more fluctuating pattern, varying between 51.6 and 73.9 (average 67.7) (Fig. 3B), and mostly clustered in group 2 (Fig. 2B).

Our CIA values were corrected to the pre-metasomatic CIA values, minimizing the diagenetic influences which were resulted from  $K_2O$  addition during K-metasomatism (Fedo et al., 1995, 1997). Our samples are mostly fine-grained argillites with a very high fraction of clay minerals, deposited in a quiet hydrodynamic environment, thus greatly eliminating the influences of texture inhomogeneity on the chemical composition and CIA values (Nesbitt and Young, 1982). In our samples, those from the Guanyinqiao Formation commonly have a relatively high carbonate content; their influences on CIA values are seemingly minimal after CaO correction (McLennan, 1993), as evidenced by no apparent difference between carbonate-rich rocks and adjacent argillite interbeds (Fig. 3; Tables DR1 and DR2). Moreover, although the source rocks, as indicated by the intersection between the weathering trend line and feldspar join, might be a little different in composition at the two localities (Fig. 2), their influences on the CIA values may not be apparent, in view of overall acidic to intermediate igneous parent rocks yielding similar pristine CIA values in source terrains (Fedo et al., 1995).

### Climatic Changes and Denudation during the Ordovician-Silurian Transition

The compositions of most siliciclastic sediments are closely related to those of weathering profiles, rather than those of underlying bedrock (e.g., Nesbitt and Young, 1996). Therefore, the



**Figure 3.** Chemical index of alteration (CIA) variations across Ordovician-Silurian boundary at sections on Yangtze block. **A:** At Wangjiawan. **B:** At Nanbazi. CIA<sub>corr</sub> indicates corrected CIA values (solid circles) for K-metasomatism. Vertical dashed lines show CIA range of average shale. Shaded interval indicates Hirnantian climate cooling period. Arrows mark two major biotic crises (I, II) during the latest Ordovician.

composition, and subsequent CIA values, of sediments can serve as a proxy of intensity of chemical weathering and associated climate conditions (Nesbitt and Young, 1982; Fedo et al., 1997). Sediments (especially fine-grained argillites) deposited in a hot and humid tropic climate generally have CIA values from 80 to 100, those in a warm and humid climate have values from 70 to 80, and those in a cold and arid climate have values from 50 to 70 (Nesbitt and Young, 1982, 1989).

In this study, CIA<sub>corr</sub> values of fine-grained argillaceous sediments from the Wufeng and Longmaxi Formations, clustered between 75 and 85 (Figs. 2 and 3) and higher than those of average shales (70–75) (Nesbitt and Young, 1989, 1996), point to a hot and humid tropic climate under which the sediments could have undergone extreme weathering or recycling of antecedent sediments prior to deposition. This condition fully supports a greenhouse world, as attested to by other geochemical evidence (Qing and Veizer, 1994; Brenchley et al., 2003). By contrast, CIA<sub>corr</sub> values from the Guanyinqiao Formation, mainly clustered between 50 and 70 (Figs. 2 and 3), are very close to those of the Pleistocene glacial clays and/or tillites (Nesbitt

and Young, 1982, 1996), suggesting a predominantly cold and dry climate in which the sediments underwent weak to moderate weathering prior to deposition. Such a climatic condition generally reconciles the widespread presence of glaciations in Gondwana (e.g., Sheehan, 2001; Ghiene et al., 2007). However, some CIA<sub>corr</sub> values range between 70 and 75, indicating that short-term pulses of climate warming could have occurred; this scenario was better recorded at the Nanbazi section, where three pulses of relatively warm climate were apparent (Fig. 3B). In summary, during the Guanyinqiaoian interval (Hirnantian), the climate was fluctuating, rather than persistently cold and arid. This scenario is more complicated than the case documented in previous studies (Chen, 1984; Wang et al., 1997), as indicated typically by a single positive excursion in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values elsewhere (Brenchley et al., 1994, 2003; Saltzman and Young, 2005). In North Africa, a maximum of five glacial cycles, although commonly fewer, was reported during the Hirnantian glaciation (Ghiene et al., 2007), indicating that as many as five climate cycles might have occurred during this interval. It is interesting to note that five shale-limestone couplets were preserved at Nanbazi

(Fig. 3B), which may represent the products of five climate cycles and/or sea-level fluctuations, although they were not all equally transferred into the CIA signatures. The better preservation of climatic signatures at Nanbazi was probably attributable to the depositional setting, because it was located in the innermost shelf subdepression (or sag), with a relatively high rate of subsidence and/or less current erosion (Figs. 1 and 3), favorable for sediment storage.

Moreover, the distance to the provenance may also influence the weathering intensity; the shorter the distance (shorter transport and timing of weathering), the lower the CIA value, and vice versa. The differences in the longer-term CIA changes, i.e., decreasing upward at Wangjiawan (apparently from the Hirnantian) and relatively consistent, although initially slightly low, at Nanbazi (Fig. 3), may be related to the changes in their proximity to the sources. So Wangjiawan was probably more distal initially to the provenance, as indicated by the higher CIA values in the Wufeng Formation, but it was soon close to the source terrain, which was likely emerged rapidly on the east due to accelerated coupling and denudation of the orogen between the Yangtze and Cathaysia blocks (Chen et al.,

2004; Wang and Cai, 2007), i.e., from Hirnantian time. By comparison, Nabazi, although initially more proximal, generally remained in place relative to the southern source terrain in the course of northwestward thrusting of the Cathaysia block (Fig. 1A).

### Influences of Climate Changes on Organisms

The latest Ordovician crisis was characterized by two phases of mass extinctions (Brenchley et al., 1994, Sheehan, 2001), temporally coincident with the rapid climatic cooling in the beginning of the Guanyinqiaoian (terminal *D. mirus* subzone) and with the terminal cooling at the end of Guanyinqiaoian (terminal *N. extraordinarius*–*N. ojsuensis* zone) time (Fig. 3), suggesting a causal link between the extinctions and the rapid climatic changes. In general, marine organisms can adjust their physiology to adapt to slow temperature change, but they cannot adjust to frequent and extreme climatic changes that result in the suppression of the origination of new species, and lead to massive extinctions (Clarke, 1993; D. Chen et al., 2005). During the first pulse of climatic cooling, as typically represented by the Gondwana glaciation, the global temperature dropped significantly, ~8–10 °C (Brenchley et al. 1995); this could have been fatal to the fauna adaptive to the warm seawater, such as pelagic graptolites. In the meantime, the Gondwana glaciation and subsequent large sea-level fall (50–100 m or larger) (Chen, 1984; Brenchley et al., 1995) could have greatly decreased the living space of organisms, especially those in epicontinental seas (Sheehan, 2001). During the cold epoch, the fluctuating climates could have made ecologic environments more fragile (Clarke, 1993), even for those (i.e., Hirnantian fauna) adaptive to the cold climate.

The swift return to a warm climate in the beginning of Longmaxian time (or terminal Hirnantian) could have created detrimental stresses for those biota adaptive to the cold climate (Sheehan, 2001; Rong et al., 2002), leading to their massive decline. The subsequent rapid sea-level rise could also have resulted in extensive flooding over the antecedent colonization space, and subsequent oceanic anoxia (e.g., Yan et al., 2009), expelling the benthos from their previous ecologic niches, thereby leading to their significant decline.

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