Mid-Pliocene Asian monsoon intensification and the onset of Northern Hemisphere glaciation

Yi Ge Zhang1,2, Junfeng Ji1, William Balsam3, Lianwen Liu1, and Jun Chen1
1State Laboratory for Mineral Deposits Research, Institute of Surficial Geochemistry, Department of Earth Sciences, Nanjing University, Nanjing 210093, China
2Department of Marine Sciences, University of Georgia, Athens, Georgia 30602, USA
3Department of Earth and Environmental Sciences, University of Texas, Arlington, Texas 76019, USA

ABSTRACT
The late Pliocene onset of major Northern Hemisphere glaciation (NHG) is one of the most important steps in the Cenozoic global cooling. Although most attempts have been focused on high-latitude climate feedbacks, no consensus has been reached in explaining the forcing mechanism of this dramatic climate change. Here we present a key low-latitude climate record, the high-resolution Asian monsoon precipitation variability for the past five million years, reconstructed from South China Sea sediments. Our results, with supporting evidence from other records, indicate significant mid-Pliocene Asian monsoon intensification, preceding the initiation of NHG at ca. 2.7 Ma ago. This 1.4-million-year-long monsoon intensification probably enhanced monsoon-induced Asian continental erosion and chemical weathering and in the process left fingerprints in marine calcium isotopes. Furthermore, increased rock weathering and/or organic carbon burial probably lowered the contemporary atmospheric CO2 and may have triggered the NHG onset.

INTRODUCTION
Although ice sheet buildup in the Northern Hemisphere began ~11 million years ago, sustained major Northern Hemisphere glaciation (NHG) did not occur until ca. 2.7 Ma ago (Raymo, 1994; Shackleton et al., 1984). This was the final step in the Cenozoic global cooling trend, switching Earth from a greenhouse world to an icehouse world with periodical warming and waxing of ice sheets. To understand what drives this important climate change, a number of hypotheses have been proposed, most of which focused on the climatic influence of high latitudes, because high latitudes are the places where ice sheets occur. For example, enhanced North Atlantic Deep Water production driven by tectonic process (“Panama Hypothesis”; Haug and Tiedemann, 1998; Keigwin, 1982) and stratification in the subarctic Pacific (Haug et al., 2005) have been interpreted to increase precipitation, favoring ice sheet formation and accumulation in Northern Hemisphere high latitudes; favorable Milankovitch orbital parameters were also thought to facilitate the continental glacier buildup (Maslin et al., 1998). However, these scenarios are still being debated, and the ultimate driving force of NHG initiation is by no means resolved (Bartoli et al., 2005; Klocker et al., 2005; Lunt et al., 2008a, 2008b; Molnar, 2008).

Changes in low-latitude climate systems such as the Asian monsoon were generally thought unimportant when studying NHG onset. However, recent studies highlighted the key role of low-latitude climate dynamics in regulating global climate changes. For example, the Asian monsoon appears to be linked to El Niño Southern Oscillations in the equatorial Pacific and has a profound influence on extratropical climate (Zhang et al., 2007). The monsoon was also thought to be capable of affecting global biogeochemical cycling of carbon on geological timescales (Wang et al., 2003, 2004). Uncovering the history of the Asian monsoon and the role it played in the shift to an icehouse climate could be crucial to understanding global climate in general.

Here we present a high-resolution hematite to goethite ratio (Hm/Gt), an Asian monsoon precipitation proxy (Zhang et al., 2007), for the last five million years, reconstructed from southern South China Sea sediments. This record enabled us to reveal the details of the variability of key low-latitude climate systems over critical climate change intervals, and to explore its possible interplay with the NHG initiation.

MATERIALS AND METHODS
Samples were recovered at Ocean Drilling Program (ODP) Site 1143 (9°21.72′N, 113°17.11′E; 2777 m water depth), the same core we used in our previous study in which a transfer function was established (Zhang et al., 2007), enabling us to calculate hematite and goethite concentration in sediment samples from diffuse reflectance spectroscopy (DRS). We applied this technique to ODP 1143 samples covering the past 600 ka. Here we report on an additional 1807 samples measured using a Perkin Elmer Lambda 900 diffuse reflectance spectrophotometer, extending the Hm/Gt record back to 5 Ma ago. Sample preparation, analysis, and data processing were exactly the same as previously described (Zhang et al., 2007). DRS results and hematite and goethite concentration are listed in Table DR1 in the GSA Data Repository.

The benthic δ18O of samples from this site has been tuned to Earth’s orbit, and together with magnetostratigraphic and biostratigraphic age controls, yields an astronomically calibrated, high-resolution chronology for ODP 1143 (Tian et al., 2002). According to this chronology, the 2122 samples used in this study (including 315 from Zhang et al., 2007) encompass the past five million years with an average resolution of 2.4 ka between each sample.

PLIO-PLEISTOCENE MONSOON PRECIPITATION VARIATIONS
Hm/Gt is interpreted as a proxy for the variability of Asian monsoonal precipitation in SE Asia because during the soil formation process in the Mekong Basin, hematite and goethite formation are considered competitive; i.e., dry conditions are favorable for hematite formation, whereas humid conditions are favorable for goethite formation (Ji et al., 2004; Kampf and Schwertmann, 1983; Schwertmann, 1987; Schwertmann and Murad, 1983), and their ratio preserved in ODP 1143 via fluvial and marine transportation would be precipitation-dependent (Zhang et al., 2007). Our previous study reveals that in ODP 1143 sediments, Hm/Gt provides excellent recording of monsoonal precipitation variability because (1) iron oxide minerals in ODP 1143 are highly climate-sensitive, (2) monsoonal precipitation, rather than temperature, predominantly controls the Hm/Gt ratio, and (3) the Fe oxide signal is well preserved with little reduction/oxidation after deposition (Zhang et al., 2007). And our Hm/Gt record is comparable to stalagmite δ18O records from South China (see Zhang et al., 2007, their figure 4).

© 2009 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org.
Geology, July 2009; v. 37; no. 7; p. 599–602; doi: 10.1130/G25670A.1; 3 figures; Data Repository item 2009140. 599
As we extend the Hm/Gt record from late Pleistocene to early Pliocene, one may argue that the Mekong River northern headwaters extend up all the way into the tectonically active areas of SW China. Late Cenozoic uplift in this area was recorded, and the mountain building was explained by the lithospheric intrusion of the Tibetan Plateau (Burchfiel, 2004; Royden et al., 2008). The very recent tectonic events in the Mekong drainage area may alter the chemical runoff down the Mekong River by the balance between material eroded in the cooler/drier uplifted headwater regions versus the warmer/wetter more stable downstream regions in the Indochina peninsula, challenging the idea that the Hm/Gt record in the South China Sea is a monsoon proxy. However, we argue that the tectonic influence on Hm/Gt is limited because the lower reaches of the Mekong—Cambodia and Vietnam—that were relatively tectonically stable contribute most of the Fe oxides in ODP 1143. In addition, hematite and goethite, both of which are secondary minerals, are low in concentration in the unweathered rocks or weakly weathered soils that characterized the upper reaches of the Mekong (Liu et al., 2005). Instead, high annual temperature (~27 °C), precipitation (~3000 mm/a), and chemical weathering rate in the downstream Mekong suggest it very likely will produce the majority of Fe oxide minerals.

Hm/Gt variations indicate that Asian monsoon evolution for the past 5 Ma can be divided into three periods (Fig. 1): (1) early Pliocene (5.0–4.2 Ma ago) monsoon decline, (2) significant monsoon intensification during the mid-Pliocene (4.2–2.7 Ma ago), and (3) slow decline with higher variability after the onset of NHG (2.7 Ma ago to present). These observations are generally consistent with previous studies based on Chinese Loess (An et al., 2001). Among these three periods, the mid-Pliocene monsoon enhancement is highlighted here because it may have an impact on NHG initiation.

The Hm/Gt-revealed mid-Pliocene monsoon rainfall rise in SE Asia is supported by the differences between benthic and planktonic foraminifer δ18O (δ18O_p) from the same core (Fig. 1B). The significant increase in δ18O_p in ODP 1143 from 4.2 to 2.7 Ma ago was interpreted to result from an enhanced monsoon precipitation that diluted the surface seawater with relatively 18O-depleted rainwater (Fig. 1B) (Tian et al., 2004). Furthermore, this monsoon increase was indicated by other records from a variety of locations. In Figure 1 the Hm/Gt record from ODP 1143 (Fig. 1A) is compared to magnetic susceptibility of the Chinese Loess—Red Clay sequences from central China (Fig. 1C) (Sun et al., 2006), and Indian Ocean mean sediment flux (Fig. 1D) (Rea, 1992).

The Chinese Loess Plateau located in central China is covered by thick wind-deposited Chinese Loess—Red Clay sequences. These sequences provide a continuous continental climate record and have been used extensively for Asian monsoon reconstruction. After dust deposition, the monsoon precipitation-induced pedogenic processes that enhanced magnetic mineral (e.g., magnetite, maghemite) formation resulted in an increase in magnetic susceptibility (Zhou et al., 1990). Although soil magnetic susceptibility can be affected by a variety of factors, magnetic susceptibilities in Chinese Loess—Red Clay sequences (Fig. 1C) are generally interpreted as a summer monsoon proxy (Sun et al., 2006).

Indian Ocean mean sediment flux (Rea, 1992) is employed to monitor the erosion rate in South Asia and the transportation of terrigenous materials to the Bengal Fan, thought to be influenced by both the Asian monsoon and the tectonics of the Himalayan-Tibetan Plateau (Rea, 1992).

Although the four different records from diverse locations vary in detail as we expected, monsoon intensification during the mid-Pliocene (ca. 4.2–2.7 Ma ago) is clearly exhibited in each one of them (Fig. 1, highlighted with a shaded bar). These records confirm that mid-Pliocene monsoon intensification occurred in all major Asian monsoon areas, and consequently enhanced erosion of the Asian continent and increased terrigenous material production/transportation.

**GEOCHEMICAL IMPLICATIONS OF THE RISING MONSOON**

The Asian monsoon dominates in vast areas of East, South, and Southeast Asia. During the late Cenozoic, these regions were characterized by the highest suspended and dissolved load in river discharges to the ocean on Earth (Raymo and Ruddiman, 1992). Those suspended and dissolved loads were the product of rock erosion and chemical weathering. Thus, the evolution of the Asian monsoon would be critical in regulating both regional and global weathering and the geochemical cycling of important elements. For example, nine major rivers in the Asian monsoon area contribute more than one-third of the global riverine dissolved Ca flux to the ocean (data from Gaillardet et al., 1999) (Fig. 2). The Ca cycle is also an important player in global weathering, a player that is most sensitive to atmospheric CO2, because Ca-Mg silicate weathering is the largest sink for CO2 on geological time scales (Berner and Berner, 1997).

The global Ca cycle can be better constrained by Ca isotopes. For Ca the most commonly used isotope pairs are 44Ca and 40Ca, which are the stable isotopes with highest natural abundance, with the delta notation expressed as δ44Ca. Some workers also use 44Ca and 44Ca pairs (δ44Ca) because of the interference at mass 40 from argon in multicollector inductively coupled plasma-mass spectrometry (MC-ICP-MS) (e.g., Sime et al., 2007). δ44Ca records from both bulk marine calcite (e.g., De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005, 2007) and foraminiferal shells (e.g., Heuser et al., 2005; Sime et al., 2007) have been reconstructed for the late Cenozoic. Since the residence time of Ca in the ocean is ~10^6 years and the mixing time of the oceans is ~10^7 years, the oceans are likely to be homogeneous with respect to Ca, and the isotopic record at a particular site may be considered a global signal (Fantle and DePaolo, 2005). However, an interesting observation is that the δ44Ca records from bulk carbonates and foraminifera are apparently inconsistent. Although this discrepancy has not been successfully explained (Sime et al., 2007), existing carbonate δ44Ca records from dif-

![Figure 1. Comparison of Hm/Gt (A) and δ18O_p (B) from ODP 1143, South China Sea (Tian et al., 2004); magnetic susceptibility (C) from Zhaojiachuan Loess—Red Clay sequences, Chinese Loess Plateau (Sun et al., 2006); Indian Ocean Integrated mean sediment flux (D) (Rea, 1992). The mid-Pliocene (4.2–2.7 Ma) monsoon intensification is highlighted with a shaded bar; the dashed line indicates the onset of NHG at 2.7 Ma. ODP—Ocean Drilling Program; PDB—Pee Dee belemnite.](image-url)
fertent sediment cores around the world are generally consistent (De La Rocha and DePaolo, 2000; Fantle and DePaolo, 2005, 2007), corroborating the idea that bulk carbonate δ⁴⁴Ca might be a reasonable recorder of the Ca isotope signature of global seawater.

The bulk carbonate δ⁴⁴Ca record from Deep Sea Drilling Project (DSDP) Site 590 for the past 5 Ma (Fantle and DePaolo, 2005) is presented in Figure 3, and this record is compared to our monsoon precipitation proxy Hm/Gt (Fig. 3). Most strikingly, Asian monsoon precipitation recorded in South China Sea Hm/Gt records and marine carbonate δ⁴⁴Ca variations for the last 5 Ma seem to be correlated, although the two records differ significantly in time resolution. Particularly, the most remarkable increase of monsoon precipitation and δ⁴⁴Ca both occur during the mid-Pliocene, from ca. 4.2 to 2.7 Ma ago (Fig. 3).

To understand the general correlation between Asian monsoon precipitation and marine δ⁴⁴Ca over the last five million years, identifying the controlling factors of seawater Ca isotope composition variations would be helpful. Although the interpretation of marine Ca isotope records is an unsettled issue, and less well constrained hydrothermal Ca inputs complicate the problem even more, a recent model indicated that small changes in mean Ca isotope values of riverine Ca input could readily explain the observed δ⁴⁴Ca variations in the Neogene ocean (Sime et al., 2007). This study highlights the role of river discharge and hence the role of precipitation in the Ca cycle.

Rivers in the Asian monsoon region are characterized by high Ca²⁺ content, with nine of the major rivers in the area contributing more than one-third of the dissolved Ca²⁺ discharge of the 63 major global rivers to the ocean (2.56 Tmol Ca a⁻¹ divided by 7.64 Tmol Ca a⁻¹). The Yangtze River in China represents the largest worldwide annual riverine Ca²⁺ flux (0.903 Tmol a⁻¹; all data from Gaillardet et al., 1999). This could possibly be explained by the Cenozoic uplift of the Tibetan Plateau and the associated Asian monsoon development in this area (Raymo and Ruddiman, 1992).

Rivers in the Asian monsoon region also have distinct δ⁴⁴Ca signatures. Although a comprehensive Ca isotope study of all Earth’s major rivers has not yet been undertaken and riverine δ⁴⁴Ca may vary in the geological past, existing data suggest that rivers in East and South Asia such as the Yangtze, Ganges, and Huanghe are generally enriched in δ⁴⁴Ca, with the most positive δ⁴⁴Ca occurring in the Yangtze River (δ⁴⁴Ca = 0.27‰; Schmitt et al., 2003). On the other hand, rivers from the rest of the world, such as the Amazon, which has the second largest riverine Ca flux, seem to be ⁴⁴Ca-depleted (Fig. 2). Thus, if the Asian monsoon precipitation increases, river discharge in East Asia increases, and presumably the mean δ⁴⁴Ca of global riverine Ca increases. If changes in the riverine δ⁴⁴Ca lead δ⁴⁴Ca variations in seawater (Sime et al., 2007), then this provides a possible explanation to the general correlation between Hm/Gt in ODP 1143 and δ⁴⁴Ca in DSDP 590 as we observed. In other words, the Asian monsoon influences marine δ⁴⁴Ca via the Asian fluvial discharge of ⁴⁴Ca into the ocean.

Elevated riverine Ca discharge in Asian monsoon regions is also a likely indicator of enhanced chemical weathering, which is the largest sink of atmospheric CO₂ over geological time scales. In addition, increased detrital matter load and input to the ocean induced by monsoon intensification would facilitate organic carbon burial, which is the second largest CO₂ sink (Berner and Berner, 1997). As discussed above, we infer that the Asian monsoon and the corresponding chemical weathering and terrigenous material production/transportation in monsoon regions would have intensified during the mid-Pliocene, all of which will lead to a pCO₂ drop. Actually, a pronounced decline of pCO₂ has been observed from ca. 4 to 3 Ma ago, with pCO₂ decreasing from ~250 ppm to 180 ppm (Demicco et al., 2003; Pearson and Palmer, 2000) (Fig. 3). This 70 ppm CO₂ drop recently has been invoked to explain the late Pliocene NHG initiation in Greenland (Lunt et al., 2008a).

CONCLUSIONS

In this study we utilized an Asian monsoon precipitation variability proxy, the Hm/Gt ratio, from ODP 1143, southern South China Sea, to reveal low-latitude climate dynamics since the Pliocene. By comparison with other monsoon records, we confirmed that the mid-Pliocene (4.2–2.7 Ma ago) was characterized by a significant monsoon intensification. This intensifying monsoon probably left fingerprints in marine Ca isotopes. And monsoon-induced chemical weathering, continental erosion, and terrigenous inputs likely decreased atmospheric CO₂. Subsequently, this CO₂ drop could have triggered the onset of NHG as suggested by Lunt et al. (2008a).
ACKNOWLEDGMENTS
We thank Fengmei Li for the help with sample preparation and DRS measurement, Gaojun Li for stimulating discussion, Mian Liu for proofreading, and Li for sampling. William Ruddiman and Matthew Fantle offered constructive and thoughtful reviews. Samples used in this study were provided by the Ocean Drilling Program. This work was supported by the National Natural Science Foundation of China through grants 40573054, 40773056, and 40625012.

REFERENCES CITED
China through grants 40573054, 40773056, and 40625012. Program. This work was supported by the National Natural Science Foundation of Li for sampling. William Ruddiman and Matthew Fantle offered constructive and

urons. William Ruddiman and Matthew Fantle offered constructive and thoughtful reviews. Samples used in this study were provided by the Ocean Drilling Program. This work was supported by the National Natural Science Foundation of China through grants 40573054, 40773056, and 40625012.


MANUSCRIPT RECEIVED 23 NOVEMBER 2008
REVISED MANUSCRIPT RECEIVED 13 FEBRUARY 2009
MANUSCRIPT ACCEPTED 16 FEBRUARY 2009
PRINTED IN USA