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The intensity of chemical weathering: Geochemical constraints from marine detrital sediments of Triassic age in South China

Ming-Yu Zhao, Yong-Fei Zheng *

CAS Key Laboratory of Crust-Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei 230026, China

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ABSTRACT

A geochemical study of major-trace elements in detrital sediment and carbon–oxygen isotopes in carbonate was carried out for a marine stratigraphic profile of Early Triassic that is composed of argillaceous limestone and calcareous mudstone in the Lower Yangtze basin, South China. The results place constraints on the geochemical behaviors of various elements in the detrital sediment that was deposited in the residual Paleotethyan seawater. This leads to establishment of new geochemical proxies for chemical weathering of continental crust. In terms of the correlations between element concentrations and their variations in the profile, the elements are categorized into four groups with respect to the difference in their geochemical behaviors. The first group is composed of Al, Th, Sc, Be, In, Ga, K, Rb and Cs that are tightly correlated due to their immobility during chemical weathering. The second group is composed of Ca and Na that show opposite variation trends with Th and Sc, on account of their mobile behavior in the weathering profile. The third group is composed of high field strength elements such as Ti, Nb, Ta, Zr and Hf that are closely correlated with each other because they were primarily taken up by heavy minerals from sedimentary provenance. The fourth group is composed of redox sensitive elements such as Co, Cu, Fe, Mn and Ni that are correlated with S and thus mainly hosted by sulfides. Th, Sc, Ca and Na were not amenable to changes in sedimentary provenance, and thus are selected to establish the new proxies for chemical weathering. These are composed of logarithmic parameters such as log(Th/Ca), log(Sc/Ca), log[Th/(Na/5 + Ca)] and log[Sc/(Na/5 + Ca)]. They exhibit synchronous increases at the Permian–Triassic boundary, the middle Griesbachian and the early Smithian, indicating the enhancements of chemical weathering. High proxy values approaching the values for the extremely weathered product of granodiorite occurred in the middle to late Griesbachian and early Smithian, demonstrating the occurrences of extreme chemical weathering and very warm paleoclimate in those periods. These paleoclimatic changes are concordant with results from geochemical studies elsewhere in the world. Therefore, the intensity of chemical weathering can be indicated by the new geochemical proxies for the different properties of elements in marine detrital sediments.

1. Introduction

Marine sedimentary rocks record the overall information on the evolution of the Earth's surface in the geological history. Chemical precipitates (e.g., carbonate, sulfate, phosphate, organic material and pyrite) record the geochemistry of seawater, including temperature, composition, productivity and redox status. On the other hand, detrital sediments record the composition of provenance rocks from the continental crust due to chemical weathering. In fact, the chemical weathering is a process that converts atmospheric CO_2 and silicate rocks to alkalinity and divalent cations, which are then buried on the seafloor as chemical precipitates (e.g., Berner et al., 1983; Kump et al., 2000). As such, the chemical weathering has played an important role in regulating the stability of Earth's climate (e.g., Kump and Arthur, 1997; Molnar, 2004). While much attention has been paid to the chemical precipitates from the seawater, rare studies have been devoted to the geochemistry of terrigenous detritus linked to the chemical weathering.

The chemical weathering is a major mechanism that partitions elements between crustal rocks and natural water (e.g., Taylor and McLennan, 1985). It is primarily controlled by the climate in the source region, but its effects on the composition of weathered products are also dictated by the property of crustal rocks. Elements with different mobility are differentiated during chemical weathering, and the degree of chemical differentiation is determined by the intensity of chemical weathering. If some elements in weathered terrigenous detritus suffer minor effect from further differentiation during fluvial transport, the ratios between them in ultimate marine sediments can be used to gain information about the intensity of chemical weathering. After removing chemical precipitates such as carbonate, element ratios of detrital materials such as Al/Ti, Al/K, Al/Na, Ca/Ti, K/Ti, Na/Ti, Sc/Ti, Rb/Sr, La/Lu and La/Sm in mixed carbonate and detrital sediments have been used to decipher the intensity of chemical weathering (Li et al., 2003;

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* Corresponding author.
E-mail address: yfzheng@ustc.edu.cn (Y.-F. Zheng).

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Wei et al., 2003, 2006). In addition, element X/Al ratios such as K/Al, Mg/Al, Rb/Al and Ti/Al for untreated mixed carbonate and detrital sediments also have been used to trace the intensity of chemical weathering (Zabel et al., 2001; Clift et al., 2008; Sun et al., 2008; Tian et al., 2011). However, no such kinds of geochemical studies were performed on ancient marine sediments before the Quaternary.

A number of studies have utilized the Chemical Index of Alteration (CIA) of ancient detrital sediments to trace the change in chemical weathering (Nesbitt and Young, 1982; Scheffler et al., 2003; Rieu et al., 2007; Yan et al., 2010). Because CIA is calculated by the relation of molar $[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$ where CaO^* only represents the CaO in silicate minerals (Nesbitt and Young, 1982), individual variables may have impact on the calculated CIA values. For instance, K_2O concentrations may be complicated by secondary enrichment (Nesbitt and Young, 1989; Fedo et al., 1996), and Al_2O_3 concentrations may be affected by chemical precipitates (Murray and Leinen, 1996; Kryc et al., 2003). As a consequence, the CIA index is unlikely applicable to all sedimentary environments.

Because of the difference in the mobility of various elements during the chemical weathering of crustal rocks (Zhao and Zheng, 2014), the intensity of chemical weathering in the source region may be quantified by measuring the difference. The abundances and ratios of elements in marine detrital sediments, if properly organized, can be used for this purpose. Due to the complexity of geological processes, however, a single index for chemical weathering may be subjected to a lot of interferences, and thus not applicable to all sedimentary environments. Therefore, a comprehensive understanding of the general behaviors and interferential factors of various elements in marine detrital sediments is necessary in order to establish geochemical proxies for the intensity of chemical weathering.

In this paper, we present a combined study of geochemical approaches to understand the behaviors of major and trace elements in marine detrital sediments from the Lower Yangtze basin of Early Triassic in South China. The target region was a residual Paleotethyan sea between two converging continental blocks at that time, with the seawater of euxinic property for marine deposition. On the other hand, a geochemical study of paleosols indicates enhanced chemical weathering in the Early Triassic (Sheldon, 2006). In order to quantify the intensity of chemical weathering, we select the appropriate elements that are sensitive to chemical weathering and only have suffered minor influence from the other factors. In doing so, the carbon and oxygen isotope compositions of impure carbonates in the sequence were also analyzed for stratigraphic comparison. As such, the records of chemical weathering are used to investigate their implications for the paleoclimatic change in the Early Triassic. Consequently, the results provide insights into the relationship between tectonism, chemical weathering and paleoclimate in this period.

2. Geological setting and samples

The South China Block is composed of three landmasses of the Cathaysian terrane, the Jiangnan orogen and the Yangtze Craton (Zheng et al., 2013). It was located in the eastern edge of the Paleotethyan Ocean during the Late Paleozoic (e.g., Luo et al., 2010). There were two large basins of the Lower Yangtze and Qian-Gui-Xiang, and a connected platform with carbonates and detrital sediments at that time (Fig. 1A). Due to the progressive convergence between the South China Block and the North China Block during the Late Paleozoic, continental collision took place in the Triassic to result in the Qinling-Tongbai-Hong'an-Dabie-Sulu orogenic belt (Wu and Zheng, 2013). As a consequence, sedimentary environments in the Middle-Lower Yangtze basins would be evolved from a broad Paleotethyan ocean to a narrow Paleotethyan sea during the Paleozoic (Zheng et al., 2013). Stratigraphic sequences may vary from deposition of deep water to deposition of shallow water in this period, with a residual Paleotethyan sea in the Early Triassic prior to the final collision between the two continental blocks. Marine deposition in these basins exhibits the fluctuation between transgression and retrogression phases due to variable rates of the continental convergence in the Late Permian to Early Triassic. Consequently, euxinic seawater is expected for the marine deposition prior to the continental collision in the Middle-Lower Yangtze basins.

This study deals with sedimentary rocks of Early Triassic from the suburb of Chaohu city in Anhui province (Fig. 1B). It is about 180 km away from the Meishan section in the Zhejiang province (Fig. 1A), which is known as the Global Stratotype Section and Point of the Permian–Triassic boundary (PTB). The Chaohu area was located in the central part of the Lower Yangtze basin in the Late Paleozoic (Feng et al., 1997). The West Pingdingshan section was selected for this study because it has received extensive studies of chemostratigraphy, magnetostratigraphy and biostratigraphy of conodonts, ammonoids and bivalves (Tong et al., 2002, 2007; Zhao et al., 2007; Sun et al., 2009). The results from biostratigraphic studies indicate that this section was entirely deposited in a marine environment.

The West Pingdingshan section contains four sedimentary formations, which are named as Dalong, Yinkeng, Helongshan and Nanlinghu in ascending order (Fig. 2). The Dalong Formation is characterized by siliceous shale, with a depositional age of the latest Permian (Fig. 2). The key index fossil for the lowermost Triassic, *Hindeodus parvus*, has not yet been found in the West Pingdingshan section. However, the PTB in this section can still be defined based on the "boundary sequence set" (Peng et al., 2001; Sun et al., 2009). The contact between the Dalong Formation and the overlying Yinkeng Formation consists of "boundary clay beds", "boundary limestone" and mudstone in ascending order. The "boundary clay beds" in the uppermost part of the Dalong Formation can be correlated with beds 25 and 26 of the Meishan section, whereas the 25-cm-thick "boundary limestone" in the lowermost part of the Yinkeng Formation accords with bed 27 of the Meishan section. The Yinkeng Formation is dominated by alternations of thin- to medium-bedded argillaceous limestone and mudstone in the lower part and mudstone intercalated with thin-bedded calcareous mudstone in the upper part (Fig. 2). The overlaying Helongshan Formation is covered by a landslip in the lower part, and consists of alternations of thin-bedded argillaceous limestone and mudstone in the upper part (Fig. 2). In the top of the section, the Nanlinghu Formation is represented by thick-bedded limestone, intercalated by thin- to medium-bedded limestone (Fig. 2). The Griesbachian–Dienerian boundary and the Dienerian–Smithian boundary are within the Yinkeng Formation and are defined by the ammonoid *Prionolobus* and the conodont *Neospathodus waageni*, respectively (Tong et al., 2002; Zhao et al., 2007; Sun et al., 2009), whereas the Smithian–Spathian boundary situated in the Helongshan Formation is defined by the conodont *Neospathodus triangularis* (Tong et al., 2002).

A total of 92 samples were collected along the West Pingdingshan section in an interval of about 1 m. It started from a GPS position of 31°38'03''N and 117°49'41''E from the Dalong Formation upwards. In order to fulfill the analyses of carbonate C-O isotopes and detrital element concentrations simultaneously, argillaceous limestone and calcareous mudstone were collected preferentially. For the intervals containing no calcareous component, mudstone was collected. Samples 11CH133 and 11CH134 came from levels below the "boundary sequence set", followed by samples 11CH135 and 11CH136 collected from the "boundary clay beds" and the "boundary limestone", respectively.

3. Methods

All the limestone and argillaceous limestone samples were examined under a microscope to ensure that they are free of visible recrystallization or metamorphism. The limestone, argillaceous limestone, calcareous mudstone and mudstone samples were crushed into small chips, and the fresh chips containing no veins were picked out and ground into powder for geochemical analyses.